Identification of PAH Discharging into Eyak Lake from Stormwater Drains

By

Jeffrey W. Short, Larry G. Holland, Marie L. Larsen, Adam Moles, Stanley D. Rice

Auke Bay Laboratory
Alaska Fisheries Science Center
National Marine Fisheries Service, NOAA
11305 Glacier Highway
Juneau, Alaska 99801-8626

Final Report for Copper River Watershed Project

Kristin Smith, Director

December, 2006

Executive Summary

Passive sampling devices were deployed in the fall, late spring, and early summer in Eyak Lake to measure the relative levels of various non-point sources of polycyclic aromatic hydrcarbons (PAH) in runoff draining into the lake. Passive samplers consisting of polyethylene membrane devices (PEMDs) were deployed for 30 days at 5 sites within the lake, which provide a time-integrated metric of PAH contamination. Concentration of total PAH (TPAH) in the PEMDs ranged from 685 – 6,910 ng g^{-1} polyethylene at the three contaminated deployment sites along the western end of the lake, but were less than 95 ng g^{-1} elsewhere, including the effluent of the Cordova water treatment facility. PAH Composition patterns were heavily petrogenic, indicating that uncombusted oil such as spills or urban runoff was the source. Concentrations of PAH were greatest during fall, presumably associated with stormwater runoff from fall precipitation. The concentrations found at the western sites correspond with estimated aqueous concentrations of ~86 – 1,160 ng L^{-1}. Although well below the Alaska Water Quality Criteria of 15,000 ng L^{-1} for total PAH, the highest of these concentrations are near the threshold for toxicity to salmon embryos, but any such impacts are likely to be sporadic and localized because incubation in upwelling habitats would protect embryos from exposure.

Introduction

Eyak Lake provides economically significant nursery habitat supporting commercial fisheries near the Copper River delta, and some of this habitat is vulnerable to pollution discharges from the city of Cordova. Nursery habitat within the lake supports production of coho and sockeye salmon (*Oncorhynchus keta* and *O. nerka*) that contribute nearly $1M to local fishery ex-vessel income (Moffett 2006), as well as habitat for 8 other fish species (HRD Alaska 2001). Both species spawn in shallow water upwelling zones within the lake, many of which are adjacent to developed uplands within Cordova. In particular, one of Cordova's storm-water runoff outfalls discharges directly into the western end of the lake (see Fig. 1), near the city's diesel-powered electric generation facility, which has been the site of oil discharges into the lake (ADEC 2006). The impact of pollutants from these and other non-point sources on the early life stages of fish remains a concern that has not been adequately addressed by previous monitoring efforts.

Previous hydrocarbon monitoring in Eyak Lake has focused mainly on monocyclic aromatic hydrocarbons, including benzene, toluene, ethyl-benzene and xylenes (i.e. "BTEX") (e.g. Williams 1992). While these compounds can be acutely toxic to fish, the concentrations required to elicit toxic effects (in the parts per million, or mg/L), are rarely attained in field settings (Short and Springman 2006). Hence, obvious fish kills caused by exposure to petroleum products only occur following catastrophic releases of the more volatile refined products such as gasoline and diesel fuel (e.g. Ho et

al. 1999). Juvenile life stages are most vulnerable to BTEX poisoning, followed by adults (Rice et al, 1977).

Recent research shows that the embryonic life stages of fish are especially sensitive to oil pollution through a different toxicity mechanism than that associated with BTEX exposure. Crude and refined oils contain suites of polycyclic aromatic hydrocarbons (PAH) that can impair the development of fish embryos following relatively brief exposures to concentrations in the low parts per billion ($\mu g\ L^{-1}$) (Marty et al. 1997, Heintz et al. 1999, Carls et al. 1999). Toxic responses to such exposures can be insidious, in that most of the mortality is delayed, occurring throughout the lifespan of the exposed cohort, and hence may not be immediately apparent. Results from one study suggest that continuous embryonic exposure to PAH at the State of Alaska water quality standard of 15 $\mu g\ L^{-1}$ would eventually kill nearly half the exposed individuals (Heintz et al. 2000).

Three- and 4-ring PAH are thought to be most toxic to fish embryos, including those bearing alkyl-substituents which are more abundant than the un-substituted PAH in petroleum and most refined products. Waste petroleum products such as small spills of crankcase oils in internal combustion engines are readily transported to receiving waters by storm water runoff (HDR Alaska, 2001), which has the potential to result in PAH concentrations that are toxic to fish embryos.

Monitoring based on analysis of traditional grab samples is not well suited to

episodic pollutant discharges. Such conventional water sampling is often inadequate because run-off pollutants can be seasonal and sporadic. Dilution and scale can camouflage large discharges if the samples are taken at the wrong location or time of year. However, organisms present in these waterbodies are capable of bio-accumulating hydrocarbons, making low-level chronic contaminants a potentially serious problem for any waterbody dependent on a healthy ecosystem.

A more efficient sampling method that integrates temporal variation in the concentrations of freely dissolved organic pollutants in water is through the use of passive samplers. These devices mimic absorption of contaminants by living organisms but without the metabolic alteration of compounds or other complicating factors inherent in the use of biological organisms as water quality indicators. These samplers are placed in the waterbody for one month and then removed for lab analysis. Polyethylene membrane devices (PEMDs) are one of the most cost-effective passive samplers for monitoring low concentrations of contaminants in receiving waters. They consist of a strip of polyethylene plastic from which the plasticizers added to ordinary commercial polyethylene are absent, leaving molecular-scale cavities in which pollutants such as PAH can become trapped. These samplers are extraordinarily sensitive: PAH concentrations accumulated in PEMDs during placement in receiving waters may exceed ambient concentrations by factors above 10^5 (Carls et al. 2004), permitting detection of individual PAH in receiving waters below 1 part per trillion (ng L^{-1}).

The objectives of this pilot study are to evaluate seasonal variability of PAH

contamination in Eyak Lake. The approach is based on seasonal deployment of PEMD samplers near suspected pollution sources in comparison with deployments at more remote locations. The high sensitivity of these samples permits detection of inputs and distribution patterns that would escape detection by monitoring based on grab samples. The semi-quantitative response of PEMDs permits estimation of the approximate time-averaged PAH concentrations in the sampled waters, which may be compared with concentrations known to be toxic to fish embryos. Also, because the distribution pattern of PAH accumulated by PEMDs reflects concentrations in the ambient water during deployment (Carls et al. 2004), these patterns can provide an indication of the sources that contribute to the PAH accumulated.

Study Region

Eyak Lake covers ~ 970 ha within a total catchment basin of ~10,500 ha (HDR Alaska 2001), with primarily residential development associated with city of Cordova (pop. ~2,400) along its western and southern shores (Fig. 1). The mean lake depth is 2.44 m (HRD Alaska, 2001), implying a lake volume of 2.37×10^7 m^3. Precipitation totaling ~4 m yr^{-1} implies a mean turnover time of about 2.5 weeks. Precipitation is greatest during fall and least during late winter and early spring. The lake consists of three main arms: the north, west and southeast arms (Fig. 1).

Study Sites

Eleven PEMD samplers were deployed at 5 sites in Eyak Lake (Figure 1) during three sampling events. Three sites are located on the western end of the lake adjacent to the Cordova residential area. Two of these sites, denoted Nirvana Park 1 and 2 (hereafter NP1 and NP2) were deployed within 10 m of each other directly in front of a stormwater discharge outfall into the lake to serve as field replicates, and the third is adjacent to the Cordova Electric Cooperative power generation station (hereafter CEC). The remaining two sites are located near Power Creek at the end of the northeast arm of the lake (hereafter PC), and on the lake side of the weir across Eyak River (hereafter EW), the lake's effluent stream. The samplers were deployed at a depth of 1 m within 10 m of the shoreline for 30 days beginning on September 18, 2005, May 1, 2006, and June 4, 2006. Samplers were deployed during all three periods at the NP1 and EW sites only. At the NP2 site, samplers were deployed during the first and third deployment period, while at the PC site, they were deployed during the first and third periods. Samplers were deployed at the PC site during the third period only. Also, a sample was deployed in the Cordova water treatment facility effluent stream during the third sampling period. During each of the three sample deployments, one sampler was retained in the laboratory (lab blank). Field blank PEMDs were exposed to air for one minute at the beginning of the first and third sampling periods.

Materials and Methods

Polyethylene Membrane Devices

The passive samplers were membranes of low density polyethylene (Brentwood Plastics, St. Louis, MO, USA) each measuring 4.9 cm x 50 cm x ~98 µm (total mass = 2.2 g, Carls et al. 2004) wound around posts in an aluminum pipe canister (11 cm outside diameter x 6 cm depth) with perforated end caps that allowed the water to flow freely past the strips. Samplers were prepared prior to assembly to ensure that the membranes had not previously accumulated hydrocarbons from air (Huckins et al. 1996). Preparation was by sonic extraction in pentane followed by a rinse with pentane during removal from the sonic bath, stored in hydrocarbon-free glass jar with a dichloromethane-rinsed aluminum foil lid and frozen (-20°C) until assembly of deployment canisters.

All canisters, screens, tools, and associated hardware were washed with soap and water and rinsed with chromatography grade dichloromethane prior to use. The whole device was wrapped in two separate layers of hydrocarbon-free aluminum foil and placed in two Ziplock bags following assembly. This double wrapping procedure was also utilized during transport and retrieval to and from the field to prevent passive sampling of air. All sampler assemblies were stored at -20º C except during transport.

Hydrocarbon Analysis

Following retrieval, each membrane was wiped to remove gross surface contamination, placed in a centrifuge tube, and spiked with six deuterated PAH standards (Table 1). After evaporation of the hexane spike solvent, the tube was placed in a sonic bath and extracted in 100 ml pentane:dichloromethane (80:20 v/v) for 130 min. The sonicator was on for the first 20 min of each 50-min period. The membrane was rinsed with pentane following removal, and the combined rinsate and extract was concentrated to 20 to 30 ml, dried with 2 to 4 g of sodium sulfate, concentrated to 1 to 2 ml in hexane, and applied to 1.5 g silica gel columns and eluted with 19 ml of pentane:dichloromethane (50:50). The eluent was concentrated to ~1 ml and the internal standard (hexamethylbenzene) was added prior to analysis.

Extracts were analyzed by gas chromatography equipped with a mass selective detector (GC/MS), and PAH concentrations were determined by the internal standard method (Short et al. 1996). Concentrations of total PAH were calculated by summing the concentration of 44 analytes listed in Table 1. Total PAH extracted from the device was converted to ng/g values based on an average weight of 10 membranes determined previously (Carls et al. 2004). Relative PAH concentrations were calculated as a ratio of the concentration of the individual analyte to the total PAH concentration for the sample.

Samples were extracted and analyzed in batches of 12 along with two reference samples, a method blank and a spiked method blank for quality control. Method

detection limits (MDLs) are summarized in Short et al. (1996). Most of these MDLs are less than 2 ng g^{-1} PEMD. Sample precision is generally better than ± 20% based on the combined results of the reference samples, and accuracy is generally better than ± 15% based on comparison with National Institute of Standards and Technology standards used for the spiked blanks.

Data Analysis

Concentrations of PAH in the PEMDs are presented as ng/g PEMD, with three figures significant. To facilitate comparison among samples, individual PAH concentrations are normalized to the total PAH (TPAH) concentration of the sample.

Relating PAH concentrations measured in PEMDs to corresponding concentrations in the medium sampled, it is necessary to either measure or make assumptions regarding the PAH sampling rate of the PEMD (Huckins et al. 1999, Luellen 1999). The sampling rate is the equivalent volume of sampled medium from which all the PAH are extracted per unit time, and is a sensitive function of the flow rate of the ambient medium across the PEMD surface. Under quiescent conditions the flow rate and hence sampling rate may be slow and difficult to estimate. For prolonged exposures, a lower limit on the aqueous concentration corresponding with a PAH concentration measured in a PEMD may be estimated from the equilibrium concentration factor. This factor is simply the ratio of the PAH concentrations in the PEMD and in the sampled water at equilibrium. Approximate values for concentration factors for PAH in PEMDs

are summarized as a regression line relating concentration factor to molecular mass in Carls et al. (2004), and are listed in Table 1. These values are used here to estimate the minimum aqueous PAH concentration corresponding with concentrations measured in deployed PEMDs. The aqueous concentration is estimated as the ratio of the PEMD concentration and the concentration factor. The total estimated aqueous PAH concentration is reported as the sum of the estimated individual PAH.

Results and Discussion

Concentrations of PAH were significantly greater than those of field blanks only at the three sites at the western end of Eyak Lake. Total PAH (TPAH) concentrations in the PEMD samplers deployed at these sites ranged from 685 – 6,910 ng g^{-1}. These correspond with ambient mean aqueous concentrations of ~ 86 – 1,160 ng L^{-1}. Concentrations in PEMDs deployed at that other stations in the lake were lower by factors of at least ten, ranging from 33.7 – 60.1 ng g^{-1}, corresponding with mean ambient aqueous concentrations of 3.52 – 11.2 ng L^{-1} and comparable with concentrations found in the field blanks. The TPAH concentration in the PEMD deployed at the Cordova water treatment facility was also quite low, at 94.6 ng g^{-1}. This implies a mean aqueous concentration of 11.2 ng L^{-1} in the effluent stream, also comparable with the field blank concentrations. No PAH were detected in the laboratory blanks.

The agreement of the deployments at the field replicate sites (NP1 and NP2) was within a factor of ~ 4. The ratio of the TPAH in PEMDs deployed at the two sites was

2.34 for the first deployment period and 4.42 for the second.

The concentrations of TPAH accumulated by the PEMDs were consistently greater during the first deployment during fall compared with the subsequent late-spring and early-summer deployments, by factors of 2 – 3 (Fig. 2). Although this variation range is similar to that of the replicates, the fact that similar declines are evident at all three sites suggests that the greatest concentrations of aqueous PAH occur during fall at these sites.

The composition of the PAH accumulated by the PEMDs varied slightly among sites and seasons. The compositions of the replicate deployments at the NP sites during fall 2005 were nearly identical, and included substantial contributions from naphthalene, fluorene, dibenzothiophene and phenanthrene/anthracene homologues (Fig. 3). The preponderance of alkyl-substituted homologues clearly indicates inputs related to refined petroleum products (Youngblood and Blumer 1975), which have undergone weathering losses of the most volatile homologues, especially the less-substituted naphthalenes. The minor but detectable contributions 4-ring PAH homologues, including pyrene/fluoranthenes and chrysenes indicate contributions from less volatile sources such as lubricating oils. Overall, the PAH distribution is consistent with automotive petroleum products contaminating stormwater runoff.

Comparison of the PEMDs deployed during fall 2005 and late-spring 2006 at the NP sites reveals subtle differences in the distributions of accumulated PAH. Whereas the

fall and late-spring PAH distributions evident from the NP2 site are nearly identical, those from the NP1 site are slightly different, mainly in the abundance of un- and less-substituted phenanthrenes/anthracenes (compare Figs. 3 and 4). The decline in the relative abundance of the more alkyl-substituted PAH within the phenanthrenes/anthracenes, fluroanthenes/pyrenes and chrysene homologues implies contributions from another combustion-related PAH source, perturbing the pattern evident from the fall deployments. Relative PAH abundances that decline with greater alkyl substitution within a homologous series is a hallmark of combustion-related PAH sources (Lake et al. 1979). This discrepancy among late-spring deployments at the two NP sites suggests that these replicates were in fact sampling slightly different contaminant mixtures despite their close proximity, and corroborates the lower reproducibility observed among late-spring deployments compared with the fall deployments at the NP sites. The early-summer deployment (at the NP1 site only) had a PAH distribution pattern that closely resembled the patterns found at this site from the earlier deployments (compare Figs. 3, 4 and 5), except for somewhat lower proportions of naphthalene homologues and greater proportions of chrysene homologues during the early-summer deployment (Fig. 5).

The PAH distributions characterizing the CEC deployments show less seasonal variability than do the NP deployments (Fig. 6). The CEC patterns are dominated by the naphthlene and fluorene homologues that suggest a diesel fuel source, consistent with the contamination history of this site. Diesel fuel is indicated by the scant contribution from higher-boiling 4-ring PAH homologues. Gasoline spills are usually too ephemeral to

contribute substantially to persistent PAH signatures, although some contribution from gasoline discharges cannot be ruled out on the basis of the PAH results alone.

The generally low aqueous PAH concentrations implied by the PEMD results indicate that associated adverse effects on fish embryos is probably rare and localized to the western extreme of Eyak Lake. Total PAH concentrations near 400 ng L^{-1} may cause adverse effects to exposed embryos (Carls et al. 1999), provided the PAH distribution is dominated by 3-ring PAH. Our estimates of aqueous PAH concentrations approach this level at the NP sites, more so during fall than during late spring/early summer. Given that our estimation of aqueous PAH concentrations is prone to underestimation, the possibility that stormwater-related PAH discharges occasionally result in adverse effects to fish embryos incubating nearby cannot be eliminated. But if they occur, these adverse exposures are likely sporadic, and given the close proximity to the shoreline of the NP and CEC deployment sites, such effects are almost certainly limited spatially to within a few ten's of meters of the shoreline, along a few hundreds of meters alongshore at most. Deposition of salmon embryos appears to be limited to portions of the lake bed that is flushed by groundwater upwelling, and this flushing action would serve to protect the embryos from exposure to PAH dissolved in the overlying surface waters (Professional Fisheries Consultants 1985). Moreover, the salmon spawning area closest to the NP and CEC sites within the lake is ~ 200 m distant, and most of the spawning habitat is further away (Professional Fisheries Consultants 1985).

The very low PAH concentrations associated with the Cordova water treatment

facility strongly suggest that treated effluent water does not contribute materially to the PAH detected at the NP or CEC sites, which further implicates stormwater runoff as a major source of PAH at these sites. The persistent chronic discharge of refined petroleum products from the historical legacy of multiple spills associated with operation of the CEC power generation facility is another major PAH source, contributing to the PAH burden of nearshore waters at the western end of the lake. However, the very low concentrations when detected elsewhere in the lake indicate these PAH inputs are rapidly diluted by surface runoff water. This is not surprising, given that the proportion of the lake's catchment basin of 10,500 ha that consists of roads is probably well under 100 ha.

Literature Cited

Alaska Department of Environmental Conservation. 2006. Public notice draft of Alaska's 2006 integrated water quality monitoring and assessment report. Alaska Department of Environmental Conservation, Juneau, Alaska.

Carls, M.G., S.D. Rice and J. E. Hose. 1999. Sensitivity of fish embryos to weathered crude oil: Part II. Low-level exposure during incubation causes malformations, genetic damage, and mortality in larval pacific herring (*Clupea pallasi*). Environ. Toxicol. Chem. 18: 481-493

Carls, M. G., Holland, L. G., Short, J. W., Heintz, R. A., and Rice, S. D. 2004. Monitoring polynuclear aromatic hydrocarbons in aqueous environments with passive low-density polyethylene membrane devices. Environ. Toxicol. Chem. 23:1416-1424

Heintz, R.A., J.W. Short, and S.D. Rice. 1999. Sensitivity of fish embryos to weathered crude oil: Part II. Incubating downstream from weathered Exxon Valdez crude oil caused increased mortality of pink salmon (*Oncorhynchus gorbuscha*) embryos. Environ. Toxicol. Chem. 18:494-503.

HDR Alaska. 2001. Eyak Lake waterbody assessment final report. HDR Alaska, Inc., 2525 C St., Suite 305, Anchorage, Alaska, 99503.

Heintz, R. A., S. D. Rice, A. C. Wertheimer, R. F. Bradshaw, F. P. Thrower, J. E. Joyce, and J. W. Short. 2000. Delayed effects on growth and marine survival of pink salmon *Oncorhynchus gorbuscha* after exposure to crude oil during embryonic development. Mar. Ecol. Prog. Ser. 208:205-216.

Ho, K., Patton, L., Latimer, J.S., Pruell, R.J., Pelletier, M., Mckinney, R., Jayaraman, S. 1999. The chemistry and toxicity of sediment affected by oil from the North Cape spilled into Rhode Island Sound. Mar. Pollut. Bull. 38:314-328.

Huckins, J. N., Petty, J. D., Orazio C. E., Lebo, J. A., Clark, R. C., Gibson, V. L., Gala, W. R., and Echols, K. R. 1999. Determination of uptake kinetics (sampling rages) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. Environ. Sci. Technol. 33:3918-3923.

Lake, J.L., Norwood, C., Dimock, C., Bowen, R. 1979. Origins of polycyclic aromatic hydrocarbons in estuarine sediments. Geochimica Cosmochimica Acta 43:1847-1854.

Luellen, D. R. 1999. Accumulation of PAHs and petroleum biomarkers in SMPDs and fish to discriminate petroleum sources. Doctoral dissertation. North Carolina State University.

Marty, G. D., J. W. Short, D.M. Dambach, N.H. Willits, R.A. Heintz, S.D. Rice, J.J. Stegeman, and D.E. Hinton. 1997. Ascites, premature emergence, increased gonadal cell apoptosis, and cytochrome P4501A induction in pink salmon larvae continuously exposed to oil-contaminated gravel during development. Can. J. Zoo. 75: 989-1007.

Moffett, S. 2006. Personal communication. Alaska Department of Fish and Game, (Cordova).

Professional Fishery Consultant. 1985. Eyak Lake AMSA Cooperative Management Plan. Prepared for the Eyak Lake AMSA Study Team. Cordova, AK. Professional Fishery Consultants, Cordova, Alaska.

Rice, S.D., Short, J.W., Karinen, J.F. 1977. Comparative oil toxicity and comparative animal sensitivity. *In* Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems (Edited by D.A. Wolfe), pp. 78-94. Proceedings of a symposium. New York, Pergamon Press.

Short, J.W. and Springman, K.R. 2006. Identification of hydrocarbons in biological samples for source determination. *In* Oil Spill Environmental Forensics - Fingerprinting and Source Identification. *Edited by* Z.Wang and S.A.Stout. Elsevier Science, London.

Williams, R. March 1992. Eyak Lake Water Quality Monitoring, Cordova, Alaska. A Report of Field Work Conducted from July 1991 Through May 1992. Alaska Department of Environmental Conservation Monitoring and Laboratories Operations, Juneau, AK.

Youngblood, W.W., Blumer, M. 1975. P:olycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. Geochimica Cosmochimica Acta 39:1303-1314.

Tables

Table 1. Hydrocarbon analytes, abbreviations, and concentration factors.

Figures

Figure 1. Map of the study area. Numbers identify PEMD deployment sites (1 = NP1, 2 = NP2, 3 = CEC, 4 = PC, 5 = EW; see Study Sites in text).

Figure 2. Seasonal variation of total PAH accumulated by polyethlyene membrane devices (PEMDs) deployed in the western end of Eyak Lake, September 2005 – July 2006. NP1 = Nirvana Park 1, NP2 = Nirvana Park 2, CEC = Cordova Electric Cooperative. Black bars: fall 2005, grey bars: late spring 2006, white bars: early summer 2006.

Figure 3. Distribution of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed at the replicate NP sites during fall 2005. Site NP1 = black bars, NP2 = grey bars. See Table 1 for PAH abbreviations.

Figure 4. Distribution of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed at the replicate NP sites during late spring 2006. Site NP1 = black bars, NP2 = grey bars. See Table 1 for PAH abbreviations.

Figure 5. Distribution of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed site NP1 during early summer 2006. See Table 1 for PAH abbreviations.

Figure 6. Comparison of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed at the CEC sites during fall 2005 and early summer 2006. Fall = black bars, early summer = grey bars. See Table 1 for PAH abbreviations.

Table 1. Hydrocarbon analytes, abbreviations, and concentration factors.

PAH		Concentration Factor*
Naphthalene	**N0**	288
C1-Naphthalenes	**N1**	682
C2-Naphthalenes	**N2**	1615
C3-Naphthalenes	**N3**	3822
C4-Naphthalenes	**N4**	9046
Biphenyl	**bip**	1428
Acenaphthene	**ace**	1262
Acenaphthylene	**acn**	1428
Fluorene	**F0**	2988
C1-Fluorenes	**F1**	7072
C2-Fluorenes	**F2**	16741
C3-Fluorenes	**F3**	39628
C4-Fluorenes	**F4**	93804
Dibenzothiophene	**D0**	9046
C1-Dibenzothiophenes	**D1**	21414
C2-Dibenzothiophene	**D2**	50690
C3-Dibenzothiophene	**D3**	119989
C4-Dibenzothiophene	**D4**	284027
Phenanthrene	**P0**	6253
C1-Phenanthrenes/Anthracenes	**P1**	14802
C2-Phenanthrenes/Anthracenes	**P2**	35038
C3-Phenanthrenes/Anthracenes	**P3**	82939
C4-Phenanthrenes/Anthracenes	**P4**	196327
Anthracene	**A0**	6253
Fluoranthene	**flu**	27392
Pyrene	**pyr**	27392
C1-Fluoranthenes/Pyrenes	**FP1**	64840
C1-Fluoranthenes/Pyrenes	**FP2**	153483
C1-Fluoranthenes/Pyrenes	**FP3**	363312
C1-Fluoranthenes/Pyrenes	**FP4**	860003
Benz-*a*-anthracene	**baa**	135706
Chrysene	**C0**	321233
C1-Chrysenes	**C1**	760396
C2-Chrysenes	**C2**	1799948
C3-Chrysenes	**C3**	4260691
C4-Chrysenes	**C4**	10085560
Benzo-*b*-fluoranthene	**bbf**	
Benzo-*k*-fluoranthene	**bkf**	
benzo-*e*-pyrene	**bep**	
benzo-*a* -pyrene	**bap**	
Perylene	**per**	

Table 1 (Continued)

Indeno-[*c,d*]-pyrene	**icp**
Dibenz-[*a,h*]-anthracene	**dba**
Benzo-[*g,h,i*]-perylene	**bgp**

*Concentration factors calculated from data in Carls et al. 2004.

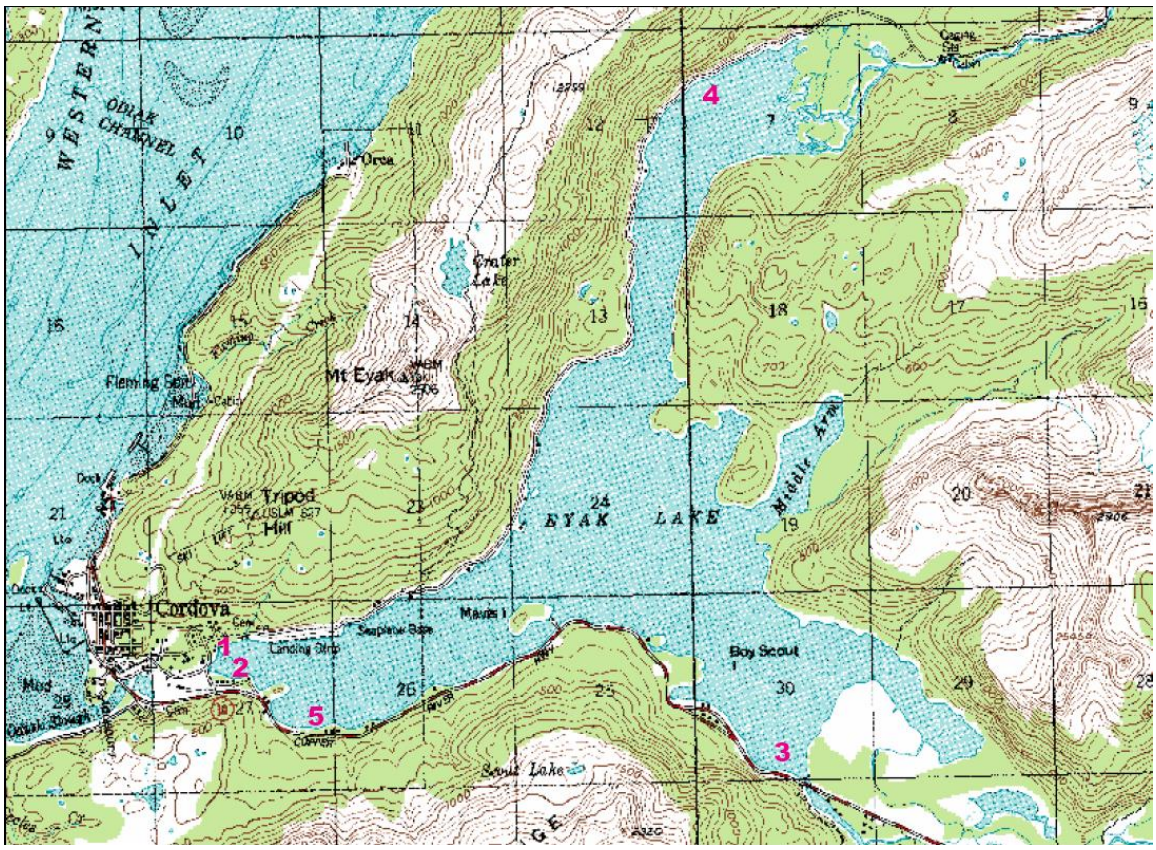

Figure 1. Map of the study area. Numbers identify PEMD deployment sites (1 = NP1, 2 = NP2, 3 = EW, 4 = PC, 5 = CEC; see Study Sites in text).

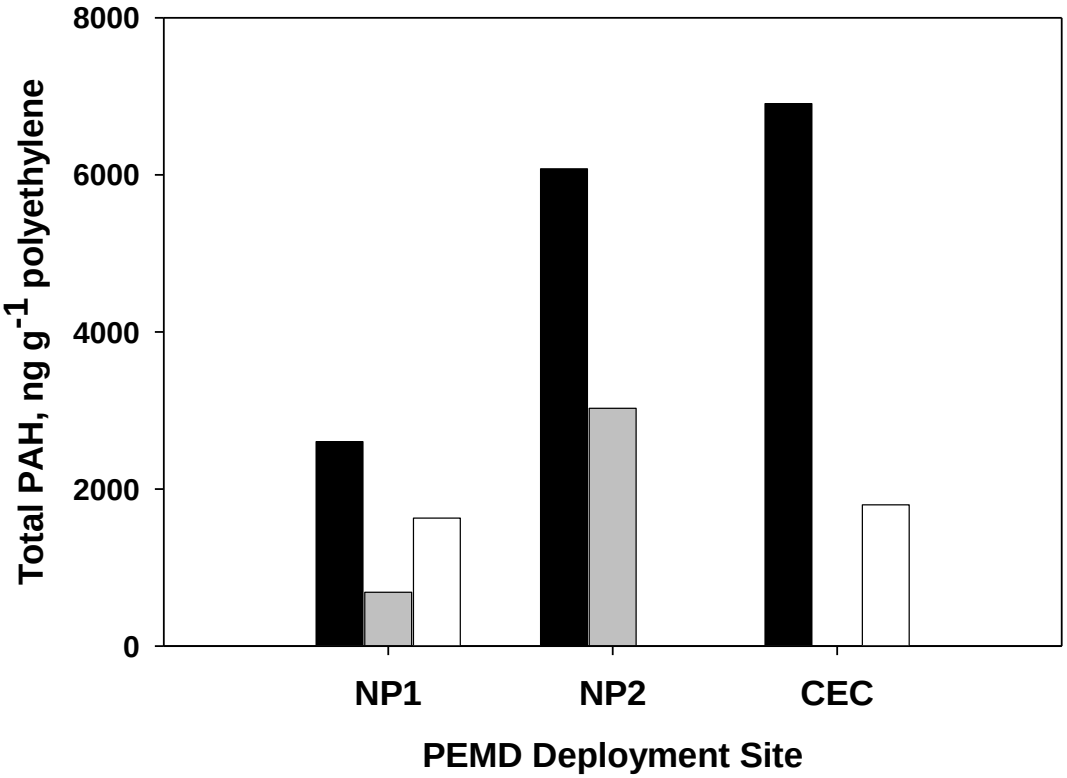

Figure 2. Seasonal variation of total PAH accumulated by polyethlyene membrane devices (PEMDs) deployed in the western end of Eyak Lake, September 2005 – July 2006. NP1 = Nirvana Park 1, NP2 = Nirvana Park 2, CEC = Cordova Electric Cooperative. Black bars: fall 2005, grey bars: late spring 2006, white bars: early summer 2006.

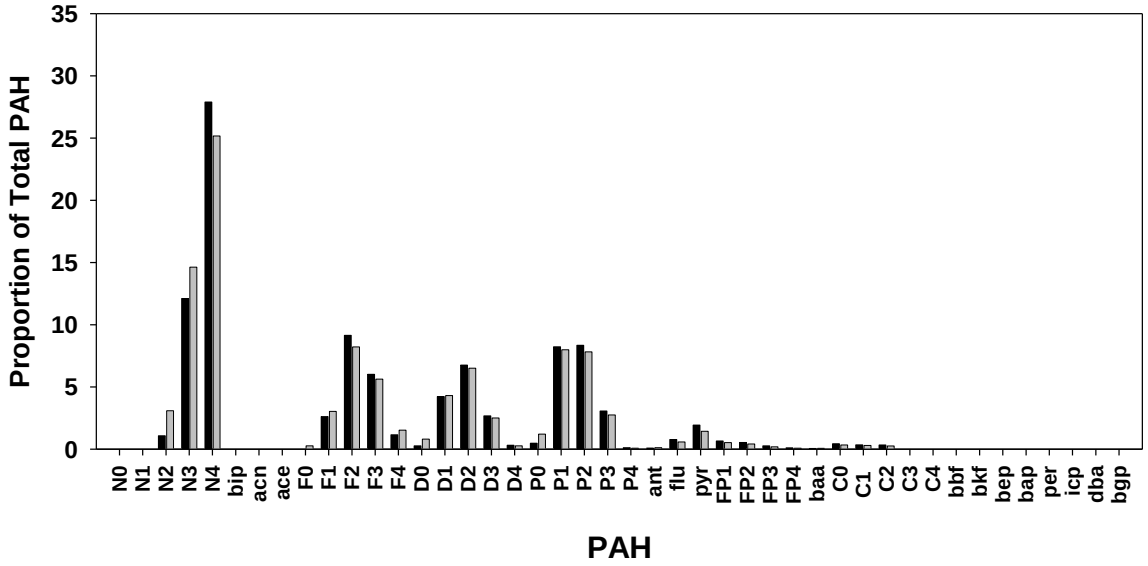

Figure 3. Distribution of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed at the replicate NP sites during fall 2005. Site NP1 = black bars, NP2 = grey bars. See Table 1 for PAH abbreviations.

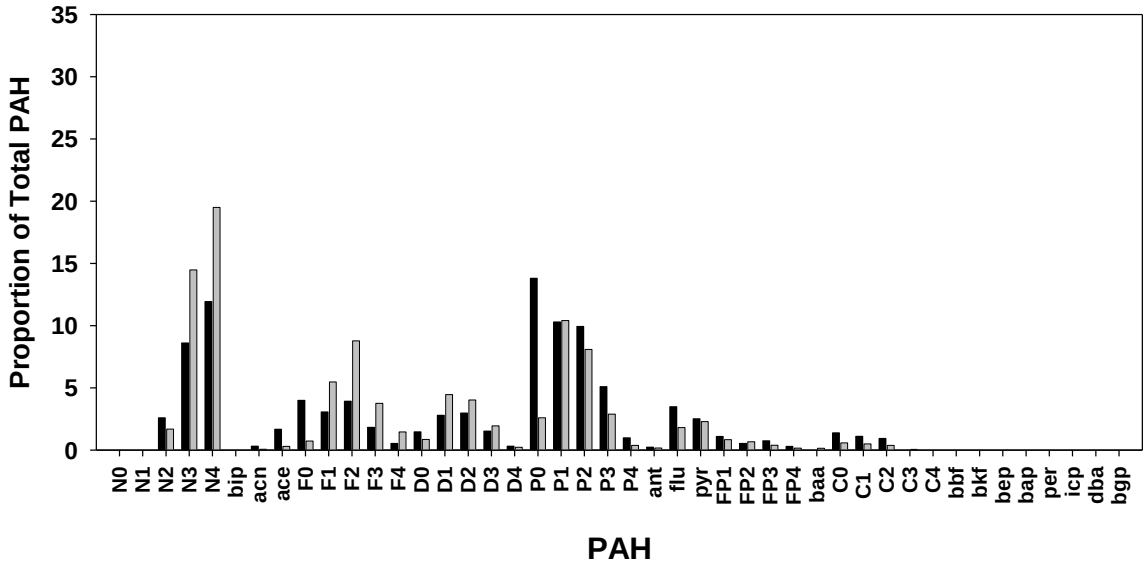

Figure 4. Distribution of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed at the replicate NP sites during late spring 2006. Site NP1 = black bars, NP2 = grey bars. See Table 1 for PAH abbreviations.

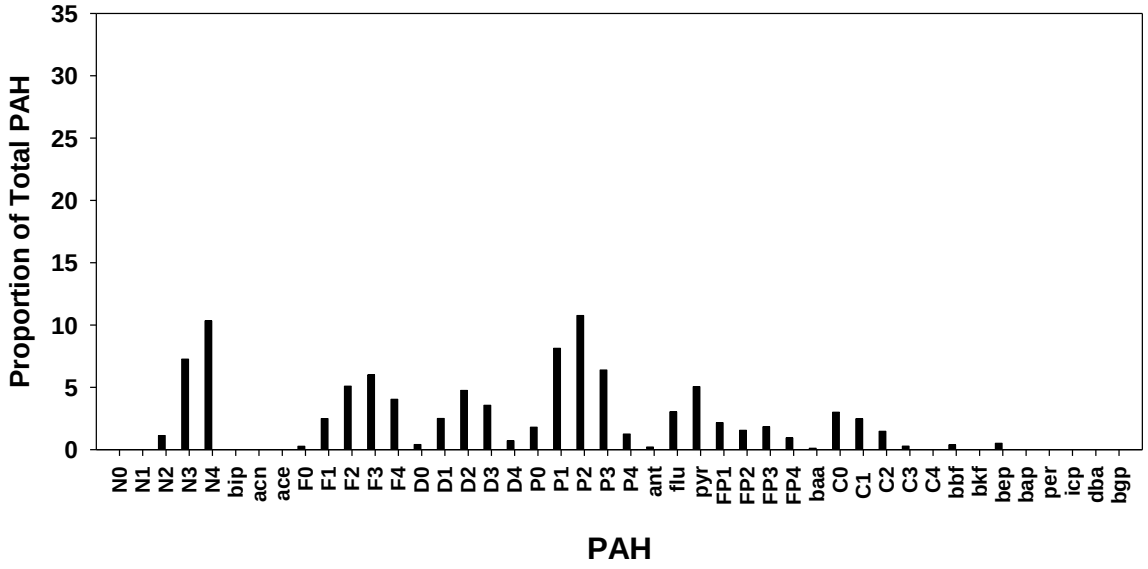

Figure 5. Distribution of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed site NP1 during early summer 2006. See Table 1 for PAH abbreviations.

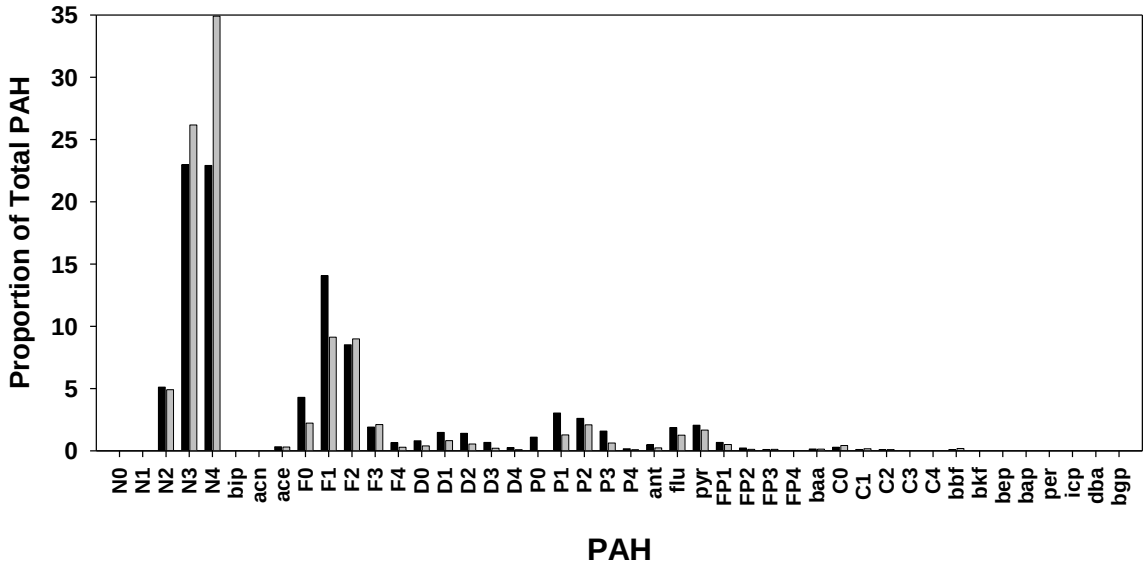

Figure 6. Comparison of PAH accumulated by polyethlyene membrane devices (PEMDs) deployed at the CEC sites during fall 2005 and early summer 2006. Fall = black bars, early summer = grey bars. See Table 1 for PAH abbreviations.