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**Partitioning and Bioavailability of Polynuclear Aromatic Hydrocarbons in an
Intertidal Marsh**

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TABLE OF CONTENTS

Table of Contents	ii
List of Tables & Figures	ii
Abstract	1
Key words	1
Problem & research objectives	2
Review of methodology use	3
Discussion of results & their significance	4
Principal findings, conclusions & recommendations	9
Summary	9
Acknowledgments	9
References	10

LIST OF FIGURES & TABLES

Figure 1. Figure 1. Relationship of total PAHs to the percentage of silt in sediments in Hoffman Marsh in 1993-94.	6
Figure 2. Overall relationship of the biota-sediment accumulation factor (BSAF) for PAHs to the octanol-water partition coefficient ($\log K_{OW}$) for three common groups of intertidal estuarine organisms in Hoffman Marsh in 1993-94.	8
Table 1. Table 1. Polycyclic Aromatic Hydrocarbons (PAHs) in the sediments at the high and low intertidal zone sites at Hoffman Marsh.	5

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are trace organic pollutants now so ubiquitous in aquatic ecosystems that the major organic signature in urban storm runoff is that of weathered PAHs. PAHs are formed by combustion of organic matter including petroleum and wood but anthropogenically produced PAHs have increased greatly over the last century. PAHs are a problem in the environment since some are potent carcinogens to humans and wildlife alike. PAHs include the most toxic fraction of tobacco smoke, benzo(a)pyrene, naphthalene, and phenanthrene and are often found in association with other organic pollutants such as chlorinated biphenyls (PCBs), and organochlorine compounds such as DDT. The persistence of PAHs in the environment and their concentration in the fat of living organisms increases the toxicity of PAHs and current regulatory standards are based on the bulk concentration of PAHs in the sediments and the amount of organic carbon in the sediments. Our research was intended to improve the understanding of PAHs in sediments, particularly the spatial and temporal variations in the bioavailability and bioaccumulation in shellfish and polychaete worms in the sediments of the San Francisco Bay Estuary.

We concentrated on 18 individual PAH compounds and measured their seasonal and spatial variations in the intertidal sediments and biota. We found that the sediment pore water concentration of PAHs may be more important in determining the bioconcentration of PAHs in living tissue than the simple bulk concentrations in the sediments. Similarly, we found that the kind of organic carbon present is more important in determining the bioconcentration of PAHs in shellfish and polychaete worms than the simple total amount of carbon present. The explanation is probably that silt and small organic fragments, especially soot, may be mostly composed of PAHs while other organic carbon such as decaying leaves is not. Soot contains a lot of PAHs but they are strongly bound to the carbon matrix and are paradoxically less bioavailable than lower amounts of PAH bound to naturally-occurring carbon. Winter storms carrying accumulated sooty fallout and auto crankcase drippings from the watershed and depositing them preferentially in the upper intertidal of the estuary explains the observed PAH speciation and distribution as well as the observed bioconcentration patterns in the sediment-dwelling biota. We recommend that attention be paid to the kind of organic carbon and its site in the pore-waters in the setting of future regulatory standards.

Key words. Polyaromatic hydrocarbons, PAH, estuaries, sediments, shellfish, polychaetes, San Francisco Bay, environmental regulations, sediment-water partitioning, bioconcentration of pollutants.

PROBLEM AND RESEACH OBJECTIVES

Problem: Polycyclic aromatic hydrocarbons (PAHs) are usually common trace organic compounds in the sediments and water column of many streams, lakes, and estuaries. The name PAH derives from a molecular structure consisting of multiple, fused aromatic hydrocarbon rings. PAHs are present in petroleum products, and are also produced by combustion of petroleum-based fuels but also from organic matter including wood. Due to human population and living standard increases the amounts of anthropogenically produced PAHs has increased greatly over the last century. PAHs are now such ubiquitous pollutants in aquatic ecosystems in urban areas that the major organic signature in urban storm runoff is that of weathered PAHs (Eganhouse & Kaplan, 1982; Eganhouse et al., 1982) Hoffman et al. 1984). The oil drops from everyone's car crankcase that produce a black spot on the driveway or highway contain considerable amounts of PAHs as does the soot from the household fire, power station smoke stack, or forest fire. PAHs are a problem since some are potent carcinogens to humans and wildlife alike. For example, the most toxic fraction of tobacco smoke, benzo(a)pyrene is a large 5-ring PAH, and more common PAHs include small molecules such as benzene, a major component of gasoline, naphthalene, a major component of mothballs, and large multi-benzene ring compounds such as benzo(a)pyrene and phenanthrene, the most common PAH in many sediments. They are hydrophobic (water hating) and are thus associated with organic matter in the same way as other pollutants such as chlorinated biphenyls (PCBs), and organochlorine compounds such as DDT.

The long half-life and ability to concentrate in fatty tissue increases the toxicity of PAHs and regulatory agencies such as the US Environmental Protection Agency have long sought to improve the science behind its present standard for PAHs in bulk sediments since this would provide a simple and measurable degree of protection for wildlife and human consumers of fish and shellfish. Unfortunately, the uptake and bioaccumulation of PAHs is not a simple process since it is affected at least by the amount of carbon in the sediments and the kind of organisms present (Pereira et al., 1992). The direct measurement of each type of PAH in sediments, pore-waters, or biota is prohibitively expensive since complex extraction and analytical procedures are needed, especially at low concentrations that still are harmful to health.

Research objectives: Our research was intended to improve the understanding of the fate and transport of PAHs in urban environment. We intended to track the spatial and temporal variations of PAHs in the sediments and pore-water and correlate these findings with the variations in the bioavailability and bioaccumulation of PAHs in shellfish and polychaete worms that live in the sediments of the San Francisco Bay Estuary. The ultimate objective was to provide data to improve the standard for PAHs in sediments and further protect human and wildlife.

REVIEW OF METHODOLOGY USED

PAHs are difficult to measure quantitatively since they comprise many different compounds that are often present in trace amounts, require extensive sample preparation and costly devices for analysis. It took about three weeks to prepare each batch of a dozen or so samples and much more time to analyze the large set of sample peaks generated by each sample. We took the approach that spatial and temporal patterns of PAHs were important and that there should also be measurements of the major biota in the estuarine sediments. We thus chose to cover the seasons with the minimum of three measurements made in 1993-94, included three intertidal zones, and three kinds of common sediment-dwelling organisms.

Site description. Samples were taken in the Hoffman Marsh site, an approximately 25 ha (60 acre) intertidal wetland that is situated along the eastern shore of San Francisco Bay, adjacent to the University of California, Berkeley's Richmond Field Station in the City of Richmond, California. It was close to the Environmental Engineering and Health Science Laboratory where samples were processed. It is presumably the remnant of a much larger marsh that existed prior to the construction of Highway 80 and the Southern Pacific railroad tracks. In its present form the wetland consists of 50% brackish salt marsh, 30% mudflats, and 20% open water channels. The vegetation in the inner part of the wetland has been mapped but the present study also includes the outer portion of the wetland beyond the railroad tracks and more exposed to the wind and tides. The site was chosen partially for its convenience but primarily because it close to Meeker Ditch and Potrero Creek that drain one of the more polluted areas in San Francisco Bay (SFEI, 1994). Several early studies on PAHs and other organic contaminants were made in the parking lots and streets that drain to Hoffman Marsh (Stenstrom, et al., 1982, 1984; Pitt & Boseman 1982). The mudflat area that is the focus of this study and is important since it is fertile and supports feeding by flocks of shorebirds.

Three major mudflat habitats were selected for sampling of PAHs and associated factors in sediments, pore waters, and biota; upper, middle and lower tidal zones since these correspond approximately with the conventional tide high-based classification system of Rickets et al. (1968). Samples were taken in a random array in July and October 1993 and April 1994. Three groups of organisms that were both common and present in sufficient numbers were collected in for PAH analysis. They were the Asian clam, *Potamocorbula amurensis*, the Japanese littleneck clam, *Tapes japonica*, and polychaetes of the families Capitellidae, Neptyidae, Neridae, Phyllocidae, and Sponidae. In addition sediment samples were assayed for particle size and pore water and sediment organic carbon and the lipid content of the biota was also measured.

PAHs were obtained from duplicate of triplicate samples of cleaned organisms following gut evacuation, freezing, drying, homogenization, extraction with a dichloromethane and reduction with rotary evaporation. A known amount of perdeuterated PAH was added prior to extraction to act as a recovery efficiency surrogate. Sediment sediments were treated similarly and pore water was separated from sediments using vacuum extraction

(Winger & Lesier, 1991). Samples were cleaned up from the solvent extraction using two kinds of packed column chromatography (Aceves et al., 1988) and analyzed for 18 individual 2-6 ring PAHs using a Varian 3400 gas chromatogram coupled to a Saturn II ion trap mass spectrometer system (GC-MS). The PAHs were identified using recorded mass spectra and retention times and were quantified using the peak area method based on injections of serial dilutions of a 16 compound PAH mixture (see Risebrough, 1994). Final PAH concentrations were computed from a PC spreadsheet software after correction for percentage recovery and relative instrument sensitivity. Dissolved organic carbon was analyzed after combustion from its infra-red spectra using a Beckman 915B TOC analyzer (APHA, 1985).

DISCUSSION OF RESULTS AND THEIR SIGNIFICANCE

The PAHs measured in detail in this study show good correspondence with those collected in a recent but more general survey (Table 1). For example the range of TPAH (39 congeners) reported by the State study (SFBERMP, 1993) for the 16 stations monitored in fall 1993 was 0.188-3.27 mg/kg dry weight compared with a range of 0.03 to 1.4 mg/kg for this study (Table 1). To determine the similarity of sediment PAH profiles, ratios of specific isomers are used (for example, phenanthrene to anthracene = PHEN/ANTH). The agreement for these ratios between this study and the State study was not good and may be due to photooxidation in the upper intertidal zone or differences in PAH metabolism or transformation in the two habitats. An alternative explanation is the greater physical stirring in the intertidal that exchanges pore waters with the overlying water more rapidly.

TPAHs normalized to either sediment dry weight or sediment organic carbon were significantly associated with the silt fraction (Fig. 1). Thus TPAHs increases with the percent organic carbon and intertidal height. This is a similar finding to other workers but has importance in understanding the seasonal and spatial patterns of PAHs discussed later. In the sediments, the 18 total PAHs (TPAH) assayed were highest in July, intermediate in spring and winter and lowest in October. In the pore-water, lower molecular weight PAHs, primarily naphthalene and phenanthrene were detectable at the ng/L range but most of the larger PAHs were not detected.

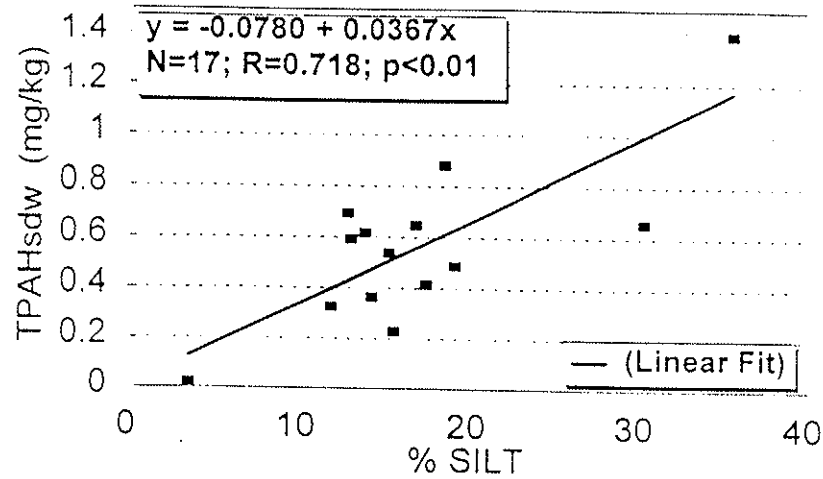
Table 1. Polycyclic Aromatic Hydrocarbons (PAHs) in the sediments at the high and low intertidal of the WRC-supported study at Hoffman Marsh compared with those collected sub-tidally by the State at nearby Point Isabel (tidal location not specified).

PAH (mg/Kg dry wt.)	Hoffman Marsh		Pt. Isabel
	Lower intertidal	Upper intertidal	sub-tidal
Total PAHs	1.4	0.62	2.13
Naphthalene	n.a.	0.0069	0.021
Acenaphthene	0.0023	0.0004	0.009
Acenaphthylene	nd	0.0005	0.015
Fluorine	0.0047	0.0027	0.009
Phenanthrene	0.093	0.038	0.114
Anthracene	0.012	0.0071	0.0042
Fluoranthene	0.27	0.13	0.27
Pyrene	0.15	0.058	0.35
Benz[a]anthracene	0.072	0.039	0.13
Crysene	0.17	0.06	0.11
Benzo[b]fluoranthene	0.11	0.075	0.10
Benzo[k]fluoranthene	0.055	0.029	0.11
Benzo[e]pyrene	0.099	0.047	0.11
Benzo[a]pyrene	0.074	0.029	0.2
Perylene	0.032	0.014	0.052
Indono[1.2.3.c.d]pyrene	0.11	0.03	0.14
Dibenz[a,h]anthracene	0.022	0.008	0.012
Benzo[g,h,i]perylene	0.11	0.04	0.16
PHEN/ANTH	7.7	5.4	2.7
FLUA/PYR	1.8	2.2	0.8
BA/CHRY	0.4	0.7	1.1
BBFL/BKFL	2.1	2.6	0.9
BEP/BAP	1.3	1.3	0.6

na = not available; nd = not detected.

The apparent organic carbon normalized sediment-pore-water partition coefficient (K_{oc}') mirrored the literature octanol-water (K_{ow}) values in October but were an order of magnitude in January. $\log(K_{oc}')$ was positively correlated with $\log(K_{ow})$ showing a linear dependence of partitioning behavior with the hydrophobicity of a given PAH. The regression slopes of the regressions were significantly different with season indicating a relative enrichment of PAHs in October relative to January. The (K_{oc}') values indicated that fluorene and phenanthrene were more available in coarser sediments with less organic carbon.

(a) TPAHsdw vs. %SILT
All sediments (N=17)



(b) TPAHsoc vs. %SILT
All sediments (N=17)

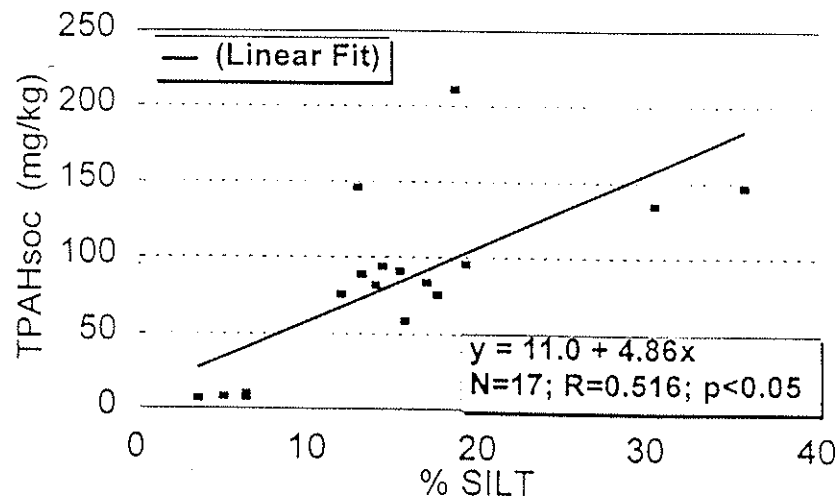
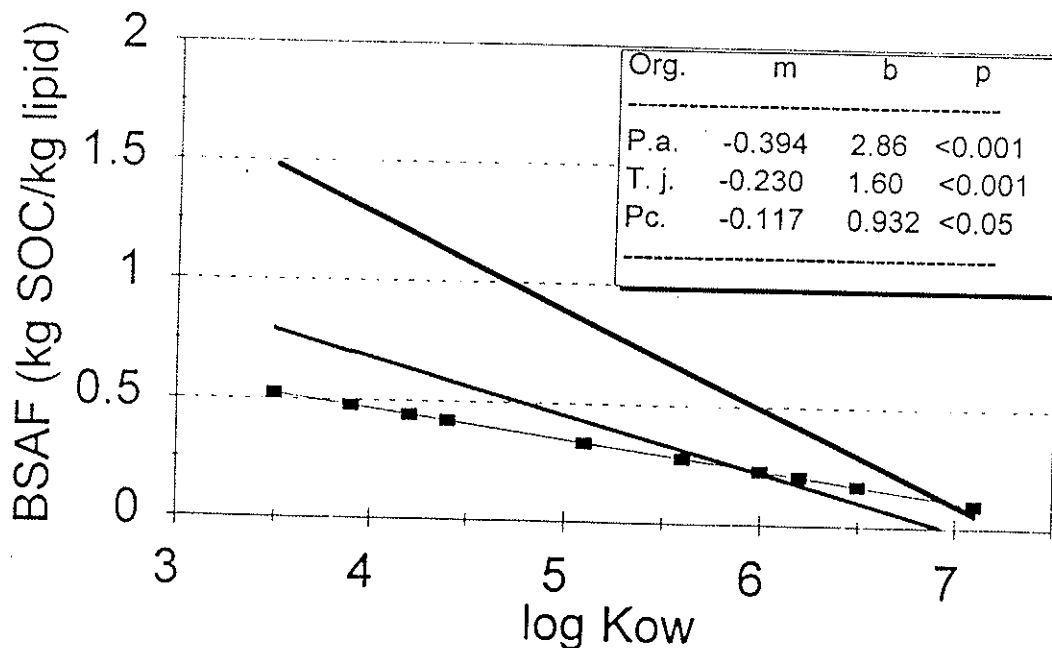


Figure 1. Relationship of total PAHs normalized to dry weight (TPAHsdw) or to sediment organic carbon (TPAHsoc) to the percentage of silt in sediments in Hoffman Marsh in 1993-94. Note the linear and statistically significant relationship of the PAHs to silt and that the most silty (small particle) sediments contained the most PAHs.

In the estuarine biota the ratio of PAHs in the organisms to sediment organic carbon constitute a biota-sediment accumulation factor (BSAF). These BSAFs spanned nearly three orders of magnitude (0.007 to 5.4) for two species of bivalve and the polychaete assemblage. BSAFs were significantly negatively associated with $\log K_{ow}$ for all organisms and followed the general pattern *P. amurensis* > *Tapes japonica* > polychaetes (Fig. 2). The San Francisco intertidal sediments showed distinct spatial and temporal patterns for and in BSAFs for all organisms. The intertidal zone variations of BSAFs followed the general pattern of low intertidal > middle intertidal > high intertidal (Fig. 3) while the seasonal changes were October > summer > spring > winter.

The relationship between BSAF and K_{ow} was dependent on the kind of organisms and covarying parameters such as sediment organic carbon, TPAHs, and the percent of fine sediments. Stepwise multiple regression was used to explain much of the variation in BSAF for all organisms. For *P. amurensis*, the Asian clam sediment organic carbon was most important (32%) and the PAHs fat-loving potential ($\log K_{ow}$) was also important (18%) while other factors such as TPAHs concentration, and the percent of fine sediments contributed lesser amounts in the regression that explained 57% of total variation. For *T. japonica*, the Japanese littleneck clam the regression showed TPAHs normalized to sediment organic carbon (30%), $\log K_{ow}$ (15%) and the percent of fine sediments (7%). For polychaetes, the regression indicated $\log K_{ow}$ (9.2%), and TPAH normalized to lipids (8%). The only variable that appears in all regression equations was $\log K_{ow}$. The differences in $\log K_{ow}$ and PAH bioaccumulation are not surprising. The amount of lipid in estuarine benthic organisms varies considerably with their diet and state of sexual development. For example, clams increase their lipid content when they are ready to spawn since eggs contain a lipid reserve. Spawning time varies with the kind of clam as well as how well the food supply satisfied their requirements.

BSAF vs. log K_{ow} by organism



— *P. amurensis* — *T. japonica* ■ *Polychaetes*

Figure 2. Overall relationship of the biota-sediment accumulation factor (BSAF) for PAHs to the octanol-water partition coefficient (log K_{ow}) for three common groups of intertidal estuarine organisms in Hoffman Marsh in 1993-94. *P. amurensis* = Asian clam, *T. japonica* = Japanese littleneck clam, polychaetes = an assemblage of at least three families. Log K_{ow} is a measure of the hydrophobicity or "water hating/fat loving" potential of a substance and is correlated with the molecular weight of the PAH with large molecules being most fat loving and inclined to accumulate in living organisms if all other factors are equal. This figure indicates that the kind of organism modifies the bioaccumulation of PAHs in intertidal sediments.

PRINCIPAL FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

This technical completion report presents the results of a multi-year study of the mechanisms that control the uptake and bioaccumulation of PAHs in an estuarine sediment in San Francisco Bay. The importance of our findings is that PAHs are more strongly associated with silt particles (small organic carbon fragments) or that the silt particles themselves were composed of PAHs. This finding would be true if the silt particles were soot or fly ash. Further bioavailability of PAHs in the estuarine environment was strongly mediated by the sediment pore-water phase, rather than the bulk sediment concentration as is currently used in environmental regulation. The decreased bioavailability of PAHs to sediment organisms in winter could be most easily related to seasonal variation in sediment input and composition, since a years supply of soot would be carried into San Francisco Bay in the few storms that characterize the wet season in California. The larger amount of fly ash in the upper intertidal could also explain the spatial variations in PAHs in sediment pore-waters and BSAFs. The differences in BSAFs between bivalves and polychaetes was probably due to differences in their ability to metabolize and excrete PAHs rather than differences in uptake rates.

Currently the regulations for PAHs are based on an equation that takes into account only the bulk sediment concentration and the amount of soluble organic carbon in the sediment. Our findings indicate that a better standard would take into account the kind of organic carbon since some carbon fractions such as soot bind PAHs more tightly, and make them less bioavailable, than other sediment organic carbon fractions such as decaying leaves.

SUMMARY

Studies were carried out on the concentration of polycyclic hydrocarbons (PAHs) and their bioaccumulation in sediment-dwelling organisms in Hoffman Marsh, an intertidal mudflat in east San Francisco Bay. The area is polluted by local runoff containing PAHs from airborne soot as well as liquid PAHs deposited from leaking automobile crankcases. We determined that the bioaccumulation of PAHs in common clams and worms were only partially explicable using the conventional fat-loving potential ($\log K_{ow}$), the amount of PAHs in the bulk sediments, and amounts of total organic carbon in the sediments. The kind of benthic animal, the season of year, the animal's position in the intertidal zone, the amount of PAHs in the pore-water in between sediment particles, and the kind of organic carbon considerably modified the bioaccumulation of these toxic, cancer-causing PAH pollutants. Additional research results are given in Maruya (1995) and Maruya et al., 1996

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