

Polycyclic aromatic hydrocarbons in San Francisco Estuary sediments

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Received 4 August 2003; received in revised form 5 January 2004; accepted 12 January 2004

Abstract

The objectives of this study were to examine surface sediments in the San Francisco Estuary for PAH composition over a range of spatial and temporal scales to determine distributions, trends, and possible sources. Surface sediments (top 5 cm) were collected at 26 sites from 1993 to 2001. The mean total PAH (Σ PAH) concentration in sediments was spatially distributed as Central Bay (230 mg/kg TOC), South Bay (217 mg/kg TOC), North Estuary (96 mg/kg TOC), Extreme South Bay (87 mg/kg TOC), and Delta (31 mg/kg TOC). Overall, the mean Σ PAH concentrations were significantly higher in the Central Bay and South Bay segments compared to the North Estuary, Extreme South Bay and Delta segments, and the Delta was significantly lower than all other segments (Kruskal–Wallis, $H=156.94$, $df=4$, $p=0.000$). In addition, no significant difference in Σ PAH concentration was found between the Central Bay and South Bay. This distribution reflects the large amount of urbanized and industrialized areas that surround the Central Bay and South Bay compared to the less urbanized and rural areas surrounding the Delta. Temporal trend analysis showed a statistically significant temporal trend in Σ PAH concentration at only 1 of the 26 sampling sites located throughout the estuary (San Pablo Bay, significant decrease, $p=0.024$, $r^2=0.314$, $n=16$), which suggests that Σ PAH concentrations in the estuary generally remained constant from 1993 to 2001. Source analysis using PAH isomer pair ratios as indicators showed that PAH are derived primarily from combustion of fossil fuels/petroleum (gasoline, crude oil, and coal) and biomass (wood and grasses), with minor amounts of PAH derived from direct petroleum input.

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Keywords: Biomass; Combustion; PAH; Petroleum

1. Introduction

The San Francisco Estuary is the largest urbanized estuary on the west coast of the U.S. and the primary receiving water body of the Bay Area. Freshwater flows in primarily through the Delta in the northeast, which discharges 37% of California's runoff into the

San Francisco Estuary (McKee et al., 2002). Because the estuary is situated in a highly populated (6.8 million, U.S. Census Bureau, 2000) and urbanized area, it is subject to chemical contamination from a variety of sources and pathways. The immediate area surrounding the estuary is highly industrialized and includes petroleum refineries, chemical manufacturers, and steel producers, among other high energy demanding industries. The estuary receives stormwater and wastewater effluents from 40 municipal wastewater treatment plants, 30 municipalities, and 30 industrial

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dischargers (SFBRWQCB, 2003). It receives as much as 40,000 tons total of at least 65 contaminants each year (Cloern et al., 1995). There are power generation plants (e.g., Hunter's Point and Potrero power plants) with combustion turbines that operate on petroleum distillate fuel and natural gas. Commercial vessels such as oil tankers, container ships, and freighters use the estuary to transport manufactured goods and raw materials. In addition, the Bay Area was recently cited as having the second highest amount of vehicular traffic congestion in the United States (TTI, 2003).

One particularly ubiquitous category of pollutants is polycyclic aromatic hydrocarbons (PAH). The San Francisco Estuary Regional Monitoring Program (RMP) has routinely monitored for PAH in the estuary since 1993. PAH can originate from a variety of anthropogenic sources in urban areas by thermal combustion processes (e.g., cooking and heating oils and coal burning), vehicular emissions (e.g., automobiles and trucks), and biomass burning (e.g., fireplaces and controlled burning, etc.) (Simoneit, 1984). High-temperature combustion, as previously described for urban areas, emits the high molecular weight PAH (four rings or more) (Neff, 1979). PAH generally occur as complex mixtures and not as single compounds in urban area environmental samples. Some PAH such as benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, chrysene, dibenz[*a,h*]anthracene, and indeno[1,2,3-*c,d*]pyrene have mutagenic and genotoxic potential (Arcos and Argus, 1975; WHO, 1989).

Both unburned and combusted fossil fuels impart their PAH signature in the marine environment (Hites et al., 1980; Boehm and Farrington, 1984; Prah et al., 1984; Voudrias and Smith, 1986; Bidleman et al., 1990; Bouloubassi and Salot, 1993; Bieger et al., 1996; Maruya et al., 1996; Simcik et al., 1996; Wakeham, 1996; Bixian et al., 2001; Mazeas and Budzinski, 2001; Countway et al., 2003). Unburned fossil fuel (petroleum)-derived PAH are preferentially biodegraded compared to combustion-derived PAH (Jones et al., 1986). PAH in the atmosphere can enter the water column by gas exchange across the air–water interface, dry deposition of airborne particulate matter, or wet deposition by rainfall (McVeety and Hites, 1988; Dickhut and Gustafson, 1995; Simcik et al., 1996; Gustafson and Dickhut, 1997; Dickhut et al., 2000; Tsai et al., 2002).

The volatile PAH (two to three rings), which occur in relatively high amounts as alkylated congeners, are derived mainly from combustion emissions of vehicles that use petroleum-derived fuels and lubricants (Marcus et al., 1988; Rogge et al., 1993; Schauer et al., 1999, 2002). They are transported into the estuary water column mainly by gas exchange at the air–water interface. Once in the water column, these dissolved PAH bind to suspended particulate matter and can be transported to the surface sediments. The four to six ring non-volatile or soot PAH derive from high-temperature combustion processes and are transported into the water column primarily by atmospheric deposition of soot particles. It has been previously suggested that soot formed from combustion processes plays a major role in PAH cycling in the estuary (Maruya et al., 1996; Pereira et al., 1999). Because PAH are minor components in petroleum, boats and other watercraft can introduce refined petroleum and combustion-derived PAH to the water column through their engine emissions (Wachs et al., 1992; Mastran et al., 1994). Additionally, PAH can enter the water column through urban runoff (Hoffman et al., 1984, 1985).

PAH isomer pairs have similar physical–chemical properties, thus they have similar dilution and distribution with particulate matter and other environmental phases even though the individual isomers may be characteristic of different sources (Dickhut et al., 2000). Ratios of certain specific PAH isomer pairs can therefore be applied as distinct chemical tracers to infer possible sources of PAH in environmental samples. For example, PAH isomer pair ratios were applied to identify automobile emissions as the major source of PAH in the Chesapeake Bay (Dickhut et al., 2000). Yunker et al. (2002) applied PAH isomer pair ratios to show that PAH in the Fraser River Basin and Estuary (British Columbia, Canada) were derived from biomass, coal, and petroleum combustion. In the York River Estuary, PAH isomer pair ratios showed that particulate samples from surface waters were compositionally more similar to coal than to automotive exhaust (Countway et al., 2003).

PAH are generally major components of the total extractable organic matter present in sediments and are minor components in water. This study focused on PAH in San Francisco Estuary sediments. Its objectives were to examine sediments for PAH composition

over a range of spatial and temporal scales to determine distributions, trends, and possible sources.

2. Materials and methods

2.1. Sediment collection and extraction

Sediments analyzed in this study were collected during the wet (January–March) and dry (July–

September) seasons of 1993 to 2001 (Fig. 1). Sediment samples were collected at 26 sites in the estuary using a modified Van Veen grab with a surface area of 0.1 m². The grab was made of stainless steel, and the jaws and doors were coated with Dykon[®] to improve chemical inertness. All scoops, buckets, and stirrers used to collect and composite sediments were constructed of Teflon[®] or stainless steel coated with Dykon[®]. When the sampler was on deck, the top 5 cm of sediment was scooped from each of two

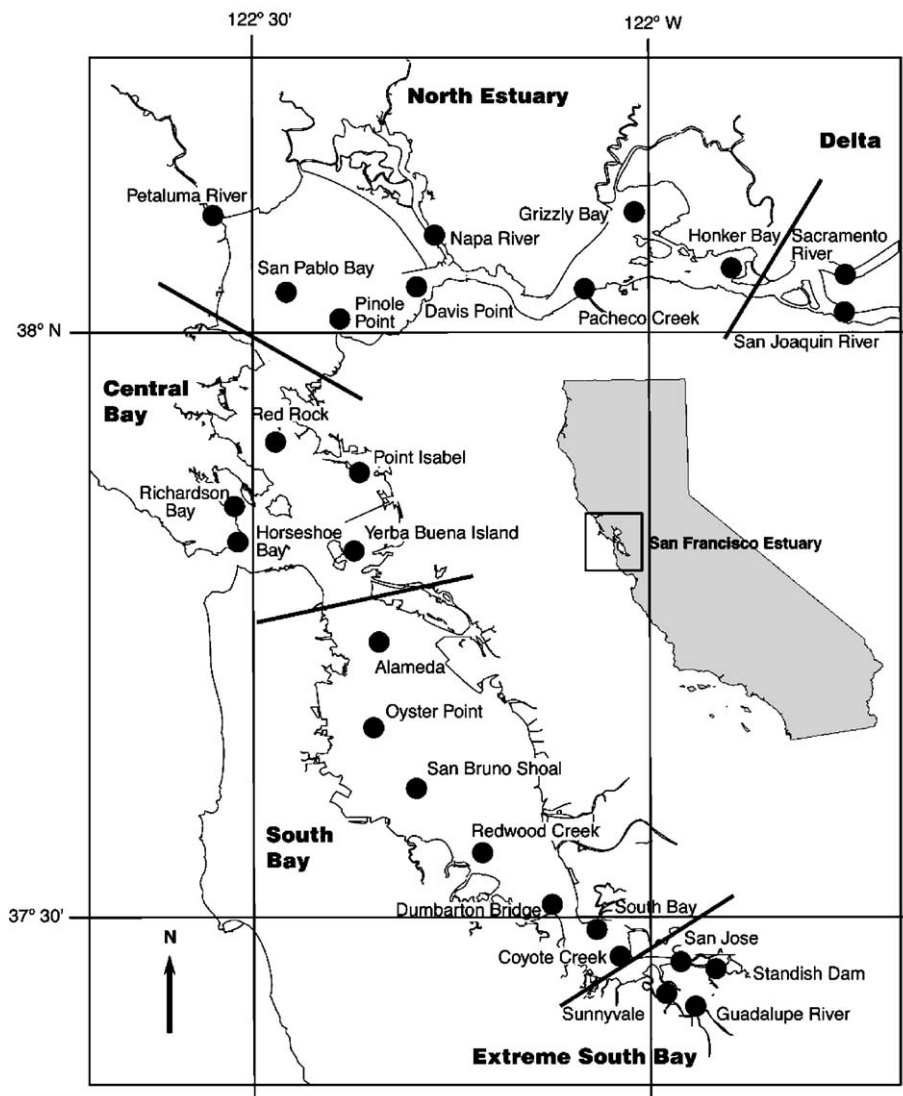


Fig. 1. Map of sediment sampling sites in the San Francisco Estuary.

replicate grabs and homogenized in a bucket to provide a single composite sample for each station. Homogenized samples were placed into precleaned 250-ml wide mouth jars with Teflon[®] lined lids and stored in a cooler (4 °C) until shipment to the laboratory. At the laboratory, any standing water in the samples was drained and discarded. The sample was then further homogenized and a 10-g subsample was weighed for extraction. Surrogate recovery standards were added to the 10-g sample aliquot, and the sample was mixed with pelletized diatomaceous earth, until a dry, free-flowing mixture was obtained. This mixture was placed into the Dionex Accelerated Solvent Extraction (ASE) System and extracted with dichloromethane (DCM) at elevated temperature and pressure for 30 min (EPA Method 3545). The sample extracts were dried with granular Na₂SO₄, and a Labconco Rapid Vap was used to reduce the extract volume to approximately 3 ml in DCM. Extracts were cleaned up with an alumina/copper column and then concentrated by evaporation to 1 ml in DCM.

2.2. Total organic carbon

Sediment samples were thawed, homogenized at room temperature, and then dried at 60 °C overnight. An aliquot (15–20 mg) was weighed and placed in a glass vial. To remove inorganic carbon 6 N hydrochloric acid was added to the sample (Nieuwenhuize et al., 1994), which was then heated gradually to 120 °C on a hot plate for 10 min. The sample was removed, cooled, treated again with acid, and reheated to 120 °C for 30 min. The treated samples were then crimped in a tin boat. The total organic carbon (TOC) content of sediments was measured using a Carlo Erba 2500 Elemental Analyzer. Sediments were combusted at 1030 °C in a quartz tube containing layers of chromium oxide and silver cobaltous-cobaltic oxide with oxygen acting as the oxidizing agent. The reaction products (CO₂ and nitrogen oxides) were swept by a continuous He flow into a second quartz tube filled with active copper granules where nitrogen oxides were reduced into elemental nitrogen at 650 °C. The gas mixture (CO₂, N₂, and H₂O) was separated with a stainless steel column (2 m length, 6 mm o.d., 4 mm i.d.) packed with Poropack QS and detected by a thermal conductivity detector. Accuracy

of carbon measurements was evaluated by the analysis of MESS-2, Beaufort Sea marine sediment reference material (National Research Council of Canada). A minimum of three blanks and three certified reference material samples were analyzed and acceptable precision and accuracy values were $\pm 3\%$ and $\pm 1\%$, respectively.

2.3. GC-MS analysis

The method of PAH analysis was based on EPA Method 8270 which was modified to provide sufficient sensitivity for PAH in San Francisco Estuary sediments. The target method detection limit for determining an individual compound was approximately 5- $\mu\text{g/kg}$ dry weight of sediment. A 1- μl splitless injection was analyzed on a Fisons GC 8000 Series II capillary gas chromatograph equipped with a Fisons MD800 mass spectral detector (GC-MS) using electron impact (70 eV) and operating in selected ion monitoring mode. The GC was equipped with a deactivated fused silica guard column (6 m \times 320 μm i.d.) and a fused silica capillary column coated with DB-5MS (30 m \times 250 μm i.d.; 0.25 μm film thickness, J&W Scientific). The temperature program of the GC oven was as follows: isothermal at 40 °C for 1 min, 10 °C/min to 340 °C, held isothermal at 340 °C for 20 min. Helium was used as the carrier gas at 1.0 ml/min constant flow.

2.4. Quality assurance

The 25 target PAH analyzed in the sediment samples were biphenyl, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, acenaphthene, acenaphthylene, anthracene, dibenzothiophene, fluorene, phenanthrene, 1-methylphenanthrene, benz[*a*]anthracene, chrysene, fluoranthene, pyrene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene, perylene, benzo[*g,h,i*]perylene, and indeno[1,2,3-*c,d*]pyrene. Total PAH (ΣPAH) was the sum of the 25 target PAH. Compound concentrations below detection limits were assumed to be zero for the summation of ΣPAH in each sample.

The cleaned sample extracts and blanks were spiked with a deuterated surrogate recovery standard mixture (Ultra Scientific) consisting of naphthalene-

d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂, prior to solvent extraction. Recoveries of surrogates generally ranged from 50% to 120% of the spiked concentration. Concentrations of all analytes were corrected for surrogate recoveries. A deuterated internal standard was used to calculate all concentrations. Just prior to GC-MS analysis, the extracts were spiked with a deuterated internal standard mixture consisting of fluorene-d₁₀ and benzo[*a*]pyrene-d₁₂. All solvents used were of analytical grade.

To evaluate the accuracy of the analysis a National Institute of Standards (NIST) standard reference sediment SRM 1941a (Organics in Marine Sediment) was analyzed (1 per 20 field samples). The concentrations averaged within 22% of the certified concentrations. To evaluate the precision of the analysis, two replicates of field samples were analyzed. The relative standard deviation (RSD) of the replicates was 17%.

Five calibration standard mixtures consisting of the PAH target analytes were prepared. One calibration standard was at a concentration near, but above, the method detection limit. The others corresponded to the range of concentrations found in the environmental samples but did not exceed the working range for the GC-MS system.

Method detection limits (MDLs) for parent PAH analytes in sediments ranged between 0.2 and 18 µg/kg dry weight over the sampling period. A clean matrix sample (Ottawa Sand, National Research Council of Canada) spiked with PAH was used to determine the MDL, which was calculated as the Student's *t*-value (3.143 for seven replicates) times the standard deviation of seven replicate extractions. Operation detection limits were set at three times the mean concentration of method blanks for each PAH.

2.5. Statistical analyses

Comparisons between estuary segments, sampling seasons, and seasonal variation at individual sampling stations were conducted for sediment ΣPAH concentrations using the nonparametric Kruskal–Wallis test for multiple comparisons (Zar, 1984). The Kruskal–Wallis test was used because the results of Levene's test showed that the variances

were not equal ($p < 0.05$). If the null hypothesis stating that the sample distributions were from the same population was rejected ($p < 0.05$), then a nonparametric multiple comparison for unequal sample sizes was performed in a manner paralleling the Tukey test, with rank sums being used instead of means (Zar, 1984).

Linear regression analysis showed that ΣPAH had significant positive relationships ($p < 0.05$) with both TOC and percent fines (grain size < 63 µm). Therefore, sediment contaminant concentrations at each station were normalized for percent fines and TOC using multiple linear regression analysis. Percent fines and TOC were the independent variables and sediment ΣPAH concentration the dependent variable. Residuals from this analysis represent the variation in contaminant concentration that remains after the effect of TOC and percent fines has been removed. Values falling above or below the regression line have positive or negative residuals, respectively. Adding the mean station ΣPAH concentration to each residual rescaled the residuals. First-order kinetic processes are natural log (ln)-linear with respect to time. Therefore, temporal trends were examined for each station by performing a linear regression analysis using the ln (rescaled residual) as the dependent variable, and sampling date as the independent variable. A significantly positive slope ($p < 0.05$) was assumed to indicate an increase in the concentration of the contaminant at the station over time. Similarly, a significant negative slope assumes a decrease over time, while a lack of significance indicates no change in sediment concentration. The environmental half-life was calculated when significant decreases were found.

Principal component analysis (PCA) was used to identify any meaningful patterns and associations of individual compounds in the PAH data. PAH compositions of sediments were used as input parameters (25 PAH or variables were analyzed for each sampling station and calculated as fractions of ΣPAH in that sediment). For the PCA data matrix, PAH were the columns and sampling sites were the rows. Individual PAH in the data that were previously assigned as not detected were reassigned concentration values of one-half the method detection limit for the PCA analysis. The PCA statistical program used was Minitab 10 Xtra (Minitab, 1995).

3. Results and discussion

3.1. Spatial distributions

The Σ PAH concentrations in the sediment samples collected from 1993 to 2001 are shown in Table 1. The Σ PAH concentrations are normalized to the TOC content in the sediment samples. In order to determine Σ PAH spatial distributions, the RMP samples were grouped into five segments: the Extreme South Bay (four stations), South Bay (seven stations), Central Bay (five stations), North Estuary (eight stations), and Delta (two stations) (RMP, 2003). Segments were selected based on hydrographical information with boundaries defined by several major bridges.

The mean Σ PAH concentrations in sediments was spatially distributed as Central Bay (230 mg/kg TOC), South Bay (217 mg/kg TOC), North Estuary (96 mg/kg TOC), Extreme South Bay (87 mg/kg TOC), and Delta (31 mg/kg TOC). Overall, the mean Σ PAH concentrations were significantly higher in the Central Bay and South Bay segments compared to the North Estuary, Extreme South Bay and Delta segments, and the Delta was significantly lower than all other segments (Kruskal–Wallis, $H=156.94$, $df=4$, $p=0.000$). This significantly higher Σ PAH concentrations in Central Bay and South Bay segments are likely due to their location in a more heavily populated, urbanized, and industrialized region of the estuary, hence the greater potential for PAH loading from urban runoff (stormwater), municipal and industrial wastewater effluents, and atmospheric deposition of vehicular emissions. In addition, no significant difference in mean Σ PAH concentration was found between the Central Bay and South Bay and between the Extreme South Bay and North Estuary segments.

The mean Σ PAH distribution in the estuary showed a trend from lower to higher sediment concentrations between segments and also within a segment (Table 1). For example, from the Delta to the Central Bay the mean Σ PAH concentrations increased (Delta = 31 mg/kg OC, North Estuary = 96 mg/kg OC, Central Bay = 230 mg/kg OC). Within the North Estuary, Σ PAH concentrations also increased from east to the west. The Central Bay accumulates 2.4 times more Σ PAH than the North Estuary and 7.4 times more than the Delta.

During the dry season, the mean Σ PAH concentration in sediments was spatially distributed as Central Bay (224 mg/kg TOC), South Bay (184 mg/kg TOC), Extreme South Bay (90 mg/kg TOC), North Estuary (84 mg/kg TOC), and Delta (17 mg/kg TOC). Mean Σ PAH concentrations were significantly higher in the Central Bay and South Bay segments compared to the Extreme South Bay, North Estuary, and Delta (Kruskal–Wallis, $H=105.23$, $df=4$, $p=0.000$). The Delta was significantly lower than all other segments. No significant difference was found between the Central Bay and South Bay segments and between the Extreme South Bay and North Estuary segments. Again, higher concentrations of Σ PAH were found in the Central Bay and South Bay segments that are more urbanized and industrialized, while lower PAH concentrations were found in the Delta, which has a rural setting. During the dry season, there is a decrease in freshwater inflow from surrounding rivers and creeks, hence Σ PAH loading via freshwater inflow is also decreased. However, there are also strong afternoon and evening westerly winds that result from the temperature and pressure differences between the Pacific Ocean and the interior of California. These winds can suspend, transport, and deposit road dust, soot, and other PAH containing particles directly to the water column, especially into the Central Bay and South Bay segments that are directly downwind of the Bay Area Peninsula.

During the wet season, the mean Σ PAH concentration in sediments changed somewhat and was spatially distributed as South Bay (259 mg/kg TOC), Central Bay (237 mg/kg TOC), North Estuary (111 mg/kg TOC), Extreme South Bay (83 mg/kg TOC), and Delta (51 mg/kg TOC). Mean Σ PAH concentrations were significantly higher in the South and Central Bay segments compared to the North Estuary, Extreme South Bay, and Delta segments (Kruskal–Wallis, $H=56.51$, $df=4$, $p=0.000$). No significant difference was found between the South Bay and Central Bay segments and between the North Estuary, Extreme South Bay, and Delta segments.

Although the mean Σ PAH concentrations were greater in the wet season than in the dry season for 6 of the 9 years that surface sediments were collected, for the estuary as a whole no significant difference was observed in sediment Σ PAH concen-

Table 1
PAH total concentrations (mg/kg TOC) and distributions in San Francisco Estuary sediments

Segment	Station	93-03	93-09	94-02	94-08	95-02	95-08	96-02	96-07	97-01	97-08	98-02	98-07	99-02	99-07	00-02	00-07	01-02	01-08	Total mean	Wet mean	Dry mean
Delta	Sacramento River	4	10	43	36	34	8	86	11	119	3	42	3				21		9	31	55	13
Delta	San Joaquin River	17	12	31	12	11	15	41	14	162	9	22	36		36		38		16	31	47	21
NE	Honker Bay			111	27	54	36	31	39	38	45	35	48	64	39		47		34	46	56	39
NE	Grizzly Bay	17	20	211	55	43	41	66	39	49	4	31	51	71	65		41		39	53	70	39
NE	Pacheco Creek	36	14	216	46	12	48	64	26	18	48	28	136		81		48		42	58	63	54
NE	Napa River	34	32	142	54	80	65	42	52	66	45	103	96	205	65	77	75	43	54	74	88	60
NE	Davis Point	17	49	89	72	23	30	56	17	4	155	20	55	60	41	42	42	37	38	47	39	55
NE	Pinole Point	33	29	82	68	29	43	37	67	55	89	49	92	102	94		63		52	61	55	66
NE	San Pablo Bay	368	206	607	414	203	178	242	420	570	312	304	482		151	269	122	130	136	301	337	269
NE	Petaluma River					108	124	127	63	44	53	43	113		73	201	90	499	48	122	170	80
CB	Red Rock				0.3	11		223		40	42	27	71	30	25		21		41	48	66	33
CB	Point Isabel	224	183	537	171	284	197	181	200	140	215	138	186	255	141		216		318	224	251	203
CB	Richardson Bay	349	559	637	235	301	252	319	427	198	217	152	218	225	249		338		378	316	312	319
CB	Horseshoe Bay	125	293	481	316	213	223	150	361	608	122	337	482	610	502		445		288	347	361	337
CB	Yerba Buena Island	71	162	280	220	101	68	149	143	92	142	140	309	198	123		141		180	157	147	165
SB	Alameda			571	246	368	103	141	181	111	303	232	386	353	355		440		321	294	296	292
SB	Oyster Point	124	211	559	120	225	130	329	179	240	101	240	160	174			135		172	207	270	151
SB	San Bruno Shoal			917	363	208	198	165	245	204	160	123	124	232	117		136		229	244	308	197
SB	Redwood Creek	158	104	652	248	149	156	221	255	145	171	126	212	210			179		167	210	237	186
SB	Dumbarton Bridge	199	142	632	203	234	201	304	181	168	258	107	182	240			195		209	230	269	196
SB	South Bay	193	89	914	209	244	147	262	213	117	145	100	112	131	177		133		161	209	280	154
SB	Coyote Creek					232	116	145	177	128	93	43	94	88	67		123		68	114	127	105
ESB	San Jose							96	103	46	124	148	228	144	84		59		125	116	108	121
ESB	Sunnyvale							73		39		77	109	186	112		100			99	94	107
ESB	Standish Dam							67		31	73	16	39	74	63		50		55	52	47	56
ESB	Guadalupe River										103	62	53	110	69		80		76	79	86	76
	Mean	123	132	406	156	144	113	145	155	137	121	106	157	179	124	147	130	177	130	145	163	131
		Mean	Mean	Mean	Mean	Mean																
	Segment	Total	Wet	Dry	OC	% Fines																
	CB	230	237	224	0.9	58																
	SB	217	259	184	1.2	79																
	NE	96	111	84	1.2	72																
	ESB	87	83	90	1.4	71																
	Delta	31	51	17	0.6	33																
	Total	662	742	599																		

PAH listed in text.

Data are shown as sampling year and month (YY-MM).

Data are normalized to total organic (TOC) content.

CB=Central Bay, ESB=Extreme South Bay, NE=Northern Estuary, and SB=South Bay.

PAH data available on SFEI website at www.sfei.org.

trations between the wet and dry seasons (Kruskal–Wallis, $H=1.80$, $df=1$, $p=0.181$). To determine if location near estuary margins and freshwater discharges (mouths of urban creeks and rivers) is an important determinant of Σ PAH sediment concentration, seasonal variation at individual stations was investigated. The Sacramento River in the Delta (Kruskal–Wallis, $H=4.82$, $df=1$, $p=0.028$) and Oyster Point in the South Bay (Kruskal–Wallis, $H=5.36$, $df=1$, $p=0.021$) showed significantly higher mean Σ PAH sediment concentrations in the wet season compared to the dry season. No significant seasonal differences were found at other sampling sites.

3.2. Temporal trends

Variation in long-term sediment Σ PAH concentration trends may be influenced by sediment characteristics. For instance, sediments with more fines (silt and clay) and high TOC generally have higher contaminant concentrations than sandy and low TOC sediments (Luoma, 1990; Horowitz, 1991). Sediments that contain soot particles, which are formed from combustion of coal, refined fossil fuels (e.g., diesel and fuel oils), and vegetation (biomass burning), can bind or occlude PAH, thus making them less available to partition with TOC in sediments (Gustafsson and Gschwend, 1997). Trends can also be influenced by sediment proximity to sources, and the complex sediment transport dynamics that occur within the San Francisco Estuary (Krone, 1979).

Linear regression analysis showed a statistically significant trend for Σ PAH sediment concentrations at only 1 of the 26 sampling sites throughout the estuary. The San Pablo Bay station sediments showed a significant decrease in Σ PAH concentration over the sampling period ($p=0.024$, $r^2=0.314$, $n=16$). The environmental half-life for Σ PAH in the San Pablo Bay station sediments was estimated to be 230 days (33 weeks). This decrease in Σ PAH concentration in San Pablo Bay may be the result of local watershed management efforts to control non-point source contaminant (sediments, surface runoff) input from local tributaries, since the Delta, as shown here, is not a major source of PAH to San Pablo Bay and the North Estuary.

3.3. Sources

The following four PAH isomer pair ratios were applied as distinct tracers to identify possible sources of PAH in sediments: anthracene/anthracene+phenanthrene (An/178); benz[a]anthracene/benz[a]anthracene+chrysene (BaA/228); fluoranthene/fluoranthene+pyrene (Fl/Fl+Py); and indeno[1,2,3-*c,d*]pyrene/indeno[1,2,3-*c,d*]pyrene+benzo[*g,h,i*]perylene (IP/IP+BghiP). The PAH isomer pair ratios determined from estuary sediment samples (means and ranges given in Table 2) were compared to PAH isomer pair ratios determined from several major PAH sources (environmental samples, petroleum, and single-source combustion), which were compiled previously by Yunker et al. (2002). These possible sources of PAH in the estuary sediments are listed in Table 2. Additionally, for each sediment sample PAH isomer pair ratios, An/178, BaA/228 and IP/IP+BghiP were plotted against Fl/Fl+Py to show how PAH distribute relative to their possible sources (Fig. 2, based on Yunker et al., 2002). Based on the PAH isomer pair ratio measurements compiled by Yunker et al. (2002): An/178 ratio <0.10 indicates dominance of petroleum and >0.10 indicates dominance of combustion; Fl/Fl+Py ratio <0.40 petroleum, 0.40 – 0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood; BaA/228 ratio <0.20 petroleum, 0.20 – 0.35 petroleum and combustion, and >0.35 combustion; and IP/IP+BghiP <0.20 petroleum, 0.20 – 0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood.

Table 2 shows that the mean values of the PAH isomer pair ratios for the sediment samples are consistently close and fall into narrow ranges. Thus, these values are useful for identifying possible PAH sources. The PAH isomer pair ratios show that PAH in estuary sediments are derived primarily from combustion sources (Table 2 and Figs. 2 and 3), which is consistent with a previous finding that fossil fuel combustion was a major source of PAH in San Francisco Estuary sediment cores (Pereira et al., 1999). The possible major sources of combustion derived PAH include fossil fuels/petroleum (gasoline, crude oil, and coal) and biomass (wood and grasses). In addition, there are minor amounts of PAH that are possibly derived from direct input of unburned fossil fuels/petroleum (kero-

Table 2

Possible PAH sources as determined from PAH isomer pair ratios

Estuary segment	An/178 ^a	Fl/Fl + Py ^a	BaA/228 ^a	IP/IP + BghiP ^a
Delta	0.19 (0.11–0.26)	0.43 (0.30–0.51)	0.42 (0.27–0.60)	0.43 (0.23–0.90)
North Estuary	0.23 (0.08–0.54)	0.44 (0.35–0.61)	0.45 (0.21–0.59)	0.45 (0.06–0.79)
Central Bay	0.25 (0.09–0.41)	0.45 (0.42–0.63)	0.47 (0.28–0.57)	0.46 (0.33–0.65)
South Bay	0.24 (0.17–0.48)	0.43 (0.35–0.63)	0.47 (0.32–0.57)	0.47 (0.37–0.64)
Extreme South Bay	0.21 (0.10–0.53)	0.44 (0.01–0.58)	0.42 (0.24–0.51)	0.48 (0.36–0.93)
Mean range	0.19–0.25	0.43–0.45	0.42–0.47	0.43–0.48
PAH sources	An/178 ^b	Fl/Fl + Py ^b	BaA/228 ^b	IP/IP + BghiP ^b
<i>Petroleum/fossil fuels</i>				
Kerosene		0.46	0.35	0.48
Diesel oil	0.09 (0.03–0.17)	0.26 (0.01–0.47)	0.35 (0.12–0.71)	0.40 (0.25–0.65)
Crude oil		0.22 (0.14–0.26)		0.09
Shale oil	0.26	0.34	0.45	0.39
Lubricating oil		0.29		0.12 (0.00–0.13)
Coal	0.20 (0.00–0.41)			
Asphalt			0.50	0.52–0.54
<i>Combustion</i>				
Lignite and brown coal	0.08 (0.00–0.16)		0.44 (0.39–0.49)	0.57
Bituminous coal	0.33 (0.31–0.36)	0.53 (0.48–0.58)	0.34 (0.18–0.50)	0.48 (0.35–0.62)
Hard coal briquettes		0.57 (0.52–0.62)	0.43 (0.36–0.49)	0.52 (0.44–0.57)
Coal tar (SRM 1597)	0.18	0.58	0.54	0.53
Wood soot	0.26	0.50	0.43–0.49	0.55
Wood	0.19 (0.14–0.29)	0.51 (0.41–0.67)	0.46 (0.30–0.54)	0.54 (0.49–0.77)
Grasses	0.17 (0.13–0.23)	0.58 (0.53–0.63)	0.46 (0.44–0.49)	0.58 (0.52–0.69)
Gasoline	0.11	0.44	0.33–0.38	0.09–0.22
Kerosene	0.14 (0.12–0.16)	0.50	0.37 (0.30–0.44)	0.37
Diesel	0.11 (0.01–0.27)	0.39 (0.20–0.58)	0.38 (0.18–0.69)	0.35 (0.19–0.50)
No. 2 fuel oil		0.51 (0.47–0.55)		
Crude oil	0.22	0.44 (0.42–0.46)	0.49 (0.47–0.50)	0.47 (0.46–0.48)
<i>Environmental samples</i>				
Bush fire		0.61	0.23	0.70
Savanna fire particulate		0.59 (0.58–0.60)		0.39 (0.31–0.44)
Road dust	0.18	0.42		0.51
Lubricating oil, rerefined				0.36
Used engine oil, gasoline passenger car	0.22	0.30	0.50	0.18
Used engine oil, diesel car, truck and bus		0.37		0.29
Tunnel with light duty gasoline vehicles		0.45 (0.42–0.49)	0.46 (0.39–0.51)	0.30 (0.26–0.35)
Tunnel with heavy duty diesel trucks and gasoline vehicles		0.42 (0.41–0.44)	0.57 (0.53–0.60)	0.30 (0.24–0.40)
Roadway tunnels	0.13 (0.13–0.14)	0.43	0.42 (0.39–0.46)	0.30 (0.23–0.37)
Urban air (including SRM 1648 and 1649a)	0.08 (0.06–0.09)	0.56 (0.55–0.57)	0.30 (0.24–0.33)	0.40 (0.27–0.48)
Creosote treated wood piling	0.20 (0.16–0.26)	0.62 (0.61–0.64)	0.50 (0.46–0.53)	0.64 (0.59–0.68)

^a PAH isomer pair ratios are the means and ranges (in parenthesis) for all the 1993–2001 sediment samples.^b Means and/or ranges (in parenthesis) of PAH sources identified from Yunker et al. (2002).

sene, shale oil, and coal). Several environmental samples that are also possible sources of PAH in sediments include used engine oil from gasoline passenger cars, air emissions collected from roadway tunnels with vehicular traffic, and creosote-treated wood pilings.

The An/178 isomer pair ratios show that PAH are derived primarily from combustion (98–100% frequency) with lower occurrence of PAH from petro-

leum (1–2% frequency) (Fig. 3). Combustion of crude oil (all segments) and wood (all segments, primarily Delta) are possible major sources of PAH in sediments. Crude oil is a possible source for PAH because the North Estuary is home to several large crude oil refineries that could contribute PAH from the refining process through their air emissions and wastewater effluents. Atmospheric deposition of

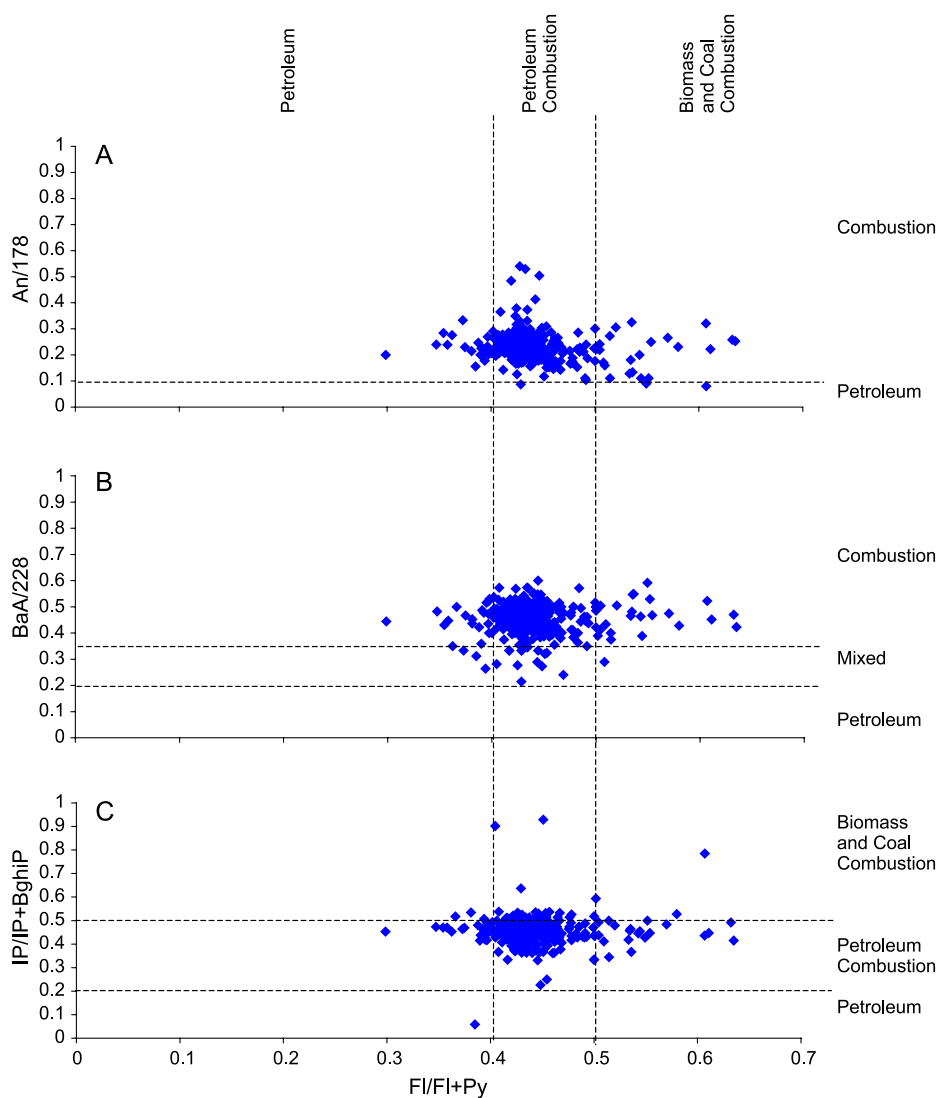


Fig. 2. Plots of PAH isomer pair ratios for source identification: (A) $An/178$ versus $FI/FI+Py$, (B) $BaA/228$ versus $FI/FI+Py$, and (C) $IP/IP+BghiP$ versus $FI/FI+Py$. Isomer pair ratios were calculated for all individual stations where possible. Source boundary lines are based on Yunker et al. (2002).

PAH from wood combustion has been previously implicated as a transport pathway into the San Francisco Estuary, especially during winter months (Tsai et al., 2002). This observation was also supported by biomarker tracer evidence where retene, a tracer compound of conifer wood combustion (Ramdahl, 1983), was identified in air and estuary water samples (Oros and David, 2002; Tsai et al., 2002). Used engine oil, creosote, and shale oil (primarily

North Estuary and Central Bay) are possible minor (1–2% frequency) sources of PAH to sediments. The shale oil signature in sediments could possibly derive from weathered Miocene Monterey Formation source rock that is broadly distributed throughout the San Francisco Bay Area or from Monterey oil. This is supported by identification of the C_{28} hopane biomarker, $17\alpha(H)$, $18\alpha(H)$, $21\beta(H)$ -28,30-bisnorhopane, which is a tracer compound for Monterey oil

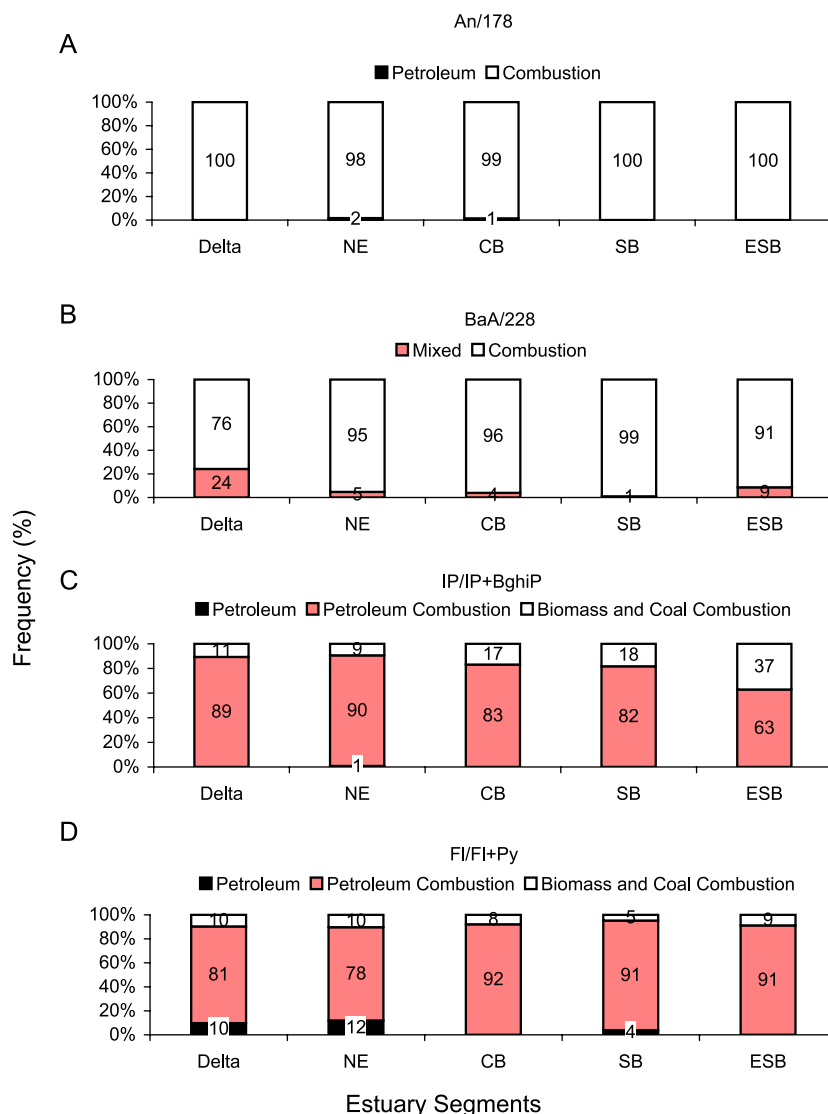


Fig. 3. Bar plots of PAH isomer pair ratios showing frequency (%) of PAH derived from various sources in Estuary segments: (A) An/178 ratio showing % of PAH from petroleum and combustion sources, (B) BaA/228 showing % of PAH from mixed and combustion sources, (C) IP/IP+BghiP ratio showing % of PAH from petroleum, petroleum combustion, and biomass and coal combustion sources, and (D) Fl/Fl+Py ratio showing % of PAH from petroleum, petroleum combustion, and biomass and coal combustion. Abbreviations: NE=North Estuary, CB=Central Bay, SB=South Bay, and ESB=Extreme South Bay. Bar plots were generated for all individual stations within each segment where possible by determining frequency (%) of samples between source boundary lines based on Yunker et al. (2002) (see Fig. 2 for source boundaries).

(Kvenvolden et al., 1995). The C_{28} hopane biomarker was first identified in estuary mussels (Risebrough et al., 1980) and more recently in the particulate fraction of water samples (unpublished data, 2003). The An/178 isomer pair ratios closely match those

determined from two environmental sources (Grimmer et al., 1981; Goyette and Brooks, 1998) that include creosote-treated wood pilings and used engine oil from gasoline passenger cars, which likely contribute PAH to sediments primarily by weather-

92% frequency) with lower occurrences of PAH from unburned petroleum (0–12% frequency), and biomass and coal combustion (5–10% frequency) (Fig. 3). Combustion of crude oil and gasoline (all segments, primarily North Estuary and Extreme South Bay) are possible major sources of PAH, while combustion of wood is a possible minor contributor. Unburned petroleum, specifically kerosene and diesel oil, are also possible sources of PAH, but also only minor contributors. Kerosene is used as a fuel (Jet A) for commercial turboprop and turbojet aircraft engines. Hence, the likely possible sources for kerosene in the estuary are regional airports. The Fl/Fl+Py isomer pair ratios closely match those determined from two (Benner et al., 1989; Fraser et al., 1998) environmental sources, which include roadway tunnels (all segments, primarily Delta and South Bay), and a tunnel with light duty gasoline vehicles (all segments, primarily Central Bay).

The BaA/228 isomer pair ratios show that PAH are derived primarily from combustion (76–99% frequency) with lower occurrences of PAH from mixed (combustion and petroleum) sources (1–24% frequency) (Fig. 3). Combustion of coal (all segments) and biomass (wood and grasses) are possible major sources of PAH in sediments. The BaA/228 isomer ratios for the samples closely match those determined from environmental samples that include roadway tunnels (all segments, primarily Delta and Extreme South Bay) and a tunnel with light duty gasoline vehicles (all segments).

The IP/IP+BghiP isomer pair ratios show that PAH are derived primarily from petroleum combustion (63–90% frequency) with a lower occurrence of PAH derived from biomass and coal combustion (9–37% frequency), and petroleum (0–1% frequency) (Fig. 3). Combustion of crude oil (all segments, primarily South Bay) and coal (all segments, primarily Extreme South Bay) are possible major sources of PAH. Coal is no longer used as a major fuel and is no longer mined in the Bay Area (i.e., Mount Diablo Coal Mining District), however, soil erosion and tidal action could transport historically deposited coal and coal soot to the surface sediments. Unburned petroleum (1% frequency) in the diesel oil range is found in the North Estuary (Table 2). Diesel can enter the estuary primarily through stormwater runoff following release from diesel-powered vehicles and machinery.

Although distinct sources can be inferred from PAH isomer pair ratios, it is well documented that in

urban areas PAH can originate from a variety of sources and be transported by different pathways. The wide ranges of the PAH isomer pair ratios found in estuary sediments show that a unique source's PAH signature could be altered by biological (e.g., bacterial degradation), chemical (e.g., oxidation and reduction), and physical (e.g., air mass mixing and sediment resuspension) processes during transport and after deposition into sediments.

3.4. Principal component analysis

PCA was used to identify any meaningful patterns and associations of individual PAH compounds in the data. Two groups, the two to three ring volatiles and the four to six ring non-volatile or soot-derived PAH, were identified within the first principal component (PC1) which accounted for 31% of the variability. The second principal component (PC2) accounted for an additional 16% of the variability. The two PAH groups are enclosed in ovals shown in Fig. 4A. In general, sediment samples had similar PAH fingerprints with no obvious spatial or temporal clustering (Fig. 4B). Sites Sacramento River (1995-02, year-month), Red Rock (1994-08), Guadalupe River (1997-08), and Pacheco Creek (1994-02) were characterized by relatively high concentrations of the two to three ring volatile PAH (e.g., biphenyl, naphthalene, and alkyl-substituted naphthalenes), while the remaining sampling sites were characterized more by the four to six ring non-volatile or soot-derived PAH (e.g., benzo[a]pyrene and indeno[1,2,3-c,d]pyrene).

4. Summary and conclusions

San Francisco Estuary surface sediments were examined for PAH composition over a range of spatial and temporal scales to determine distributions, trends, and possible sources. Overall, the mean Σ PAH concentrations were significantly higher in the Central Bay and South Bay segments compared to the North Estuary, Extreme South Bay, and Delta segments, the Delta was significantly lower than all other segments. The Central Bay and South Bay showed significantly higher concentrations of Σ PAH than other estuary segments probably due to their location in highly urbanized and industrialized areas, while the Delta

segment showed significantly lower sediment Σ PAH concentrations due to its location in a less urbanized and rural area. Additional important factors that could influence the distribution of Σ PAH concentrations in sediments include sedimentation (deposition rates, historical deposition), degradation, sources, and proximity to sources.

A statistically significant temporal trend for Σ PAH was found at only 1 of 26 sampling stations during the sampling period (San Pablo Bay, with a significant decrease). This suggests that the Σ PAH concentrations in San Francisco Estuary sediments were relatively constant over the sampling period. The lack of any significant trends in Σ PAH concentration in sediments, except San Pablo Bay (decreasing trend), is consistent with results from a study by [Schneider et al. \(2001\)](#), which reported that Σ PAH concentrations in Lake Michigan sediment cores have remained constant since the 1980s. In contrast, [Van Metre et al. \(2000\)](#) reported that Σ PAH concentrations in sediment cores from 10 U.S. lakes and reservoirs have increased during the past 20–40 years. Overall, the general trend for Σ PAH concentration in marine and freshwater sediments does not appear to be a decreasing one.

Because occasional increases in Σ PAH loading could occur, especially during rainfall (first flush) events, sediments that are located near estuary margins and freshwater discharges (mouths of urban creeks and rivers) could show a significant seasonal difference in Σ PAH concentration. This was the case for 2 of 26 sampling sites (Sacramento River and Oyster Point) in the estuary. Physical processes such as tidal influenced mixing and resuspension of sediments are likely masking any seasonal differences. Furthermore, the majority of sampling sites were located along the spine of the estuary at mid-bay areas (deep channels) away from shorelines. This sampling approach, established in 1993 and used through 2001, would have eliminated all the shallow water depth near-shore sites that are more heavily influenced by stormwater runoff, soil erosion, and tidal mixing.

Sediment sampling sites had similar PAH signatures over the sampling period. However, during a few sampling events some sampling sites were characterized by relatively high concentrations of the two to three ring volatile PAH including alkylated members, while the majority of the sampling sites contained a dominance of four to six ring non-volatile or soot-

derived PAH. This suggested that combustion and combustion-related activities were contributing the bulk of PAH found in estuary sediments.

PAH isomer pair ratio analysis showed that the possible major sources of combustion derived PAH are fossil fuels/petroleum (gasoline, crude oil, and coal) and biomass (wood and grasses). In addition, there are minor amounts of PAH that are possibly derived from direct input of unburned fossil fuels/petroleum (kerosene, shale oil, and coal). Several environmental samples that are also possible major sources of PAH in sediments include used engine oil from gasoline passenger cars, emissions collected from roadway tunnels with vehicular traffic, and creosote-treated wood pilings. Coal, unburned and combusted, could also contribute minor amounts of PAH to sediments, however, because coal is no longer used as a major fuel or mined in the Bay Area, its chemical signature in sediments is likely due to soil erosion and tidal resuspension of historically deposited coal and coal soot.

Although the possible sources of PAH in sediments can be inferred based on PAH isomer pair ratio analysis, like most organic compounds PAH could also undergo chemical and biological alteration beginning immediately upon their release into the environment (e.g., atmospheric photolysis and oxidation), during their transport, and after deposition in marine sediments (e.g., aerobic and anaerobic biodegradation). The extent of alteration, mild or severe, could determine if a unique source's PAH isomer pair ratio signature is retained. In addition, physical mixing between two or more sources could also alter the ratios found in environmental samples. Thus, PAH isomer pair ratio analysis is not a definitive tool for source determination and should be used in conjunction with other source identification methods such as biomarker profiling, and carbon stable and radioisotope analyses, to confirm the sources of PAH found in marine sediments.

Acknowledgements

We would like to thank the East Bay Municipal Utility District (Oakland, CA), the Geochemical and Environmental Research Group (Texas A&M), Genine Scelfo (University of California, Santa Cruz), and Dr. Robert Risebrough (Bodega Bay Institute, Berkeley,

CA) for sediment chemical analysis. Capt. Gordon Smith of the *R/V David Johnston* (U.C. Santa Cruz), Sarah Lowe (San Francisco Estuary Institute), and Applied Marine Sciences (Livermore, CA) are acknowledged for their assistance with field sample collecting. The authors would also like to thank the reviewers for their comments and suggestions, which improved the quality of this manuscript. This project was funded by the San Francisco Estuary Regional Monitoring Program, which is managed by the San Francisco Estuary Institute (Oakland, CA).

Associate editor: Dr. Stuart Wakeham.

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