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Marine Chemistry 64 (1999) 99–113

MARINE CHEMISTRY

Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California

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Received 31 July 1997; revised 23 June 1998; accepted 27 July 1998

Abstract

Dated sediment cores collected from Richardson and San Pablo Bays in San Francisco Bay were used to reconstruct a history of polycyclic aromatic hydrocarbon (PAH) contamination. The sedimentary record of PAHs in Richardson Bay shows that anthropogenic inputs have increased since the turn of the century, presumably as a result of increasing urbanization and industrialization around the Bay Area. Concentrations range from about 0.04–6.3 $\mu g\ g^{-1}$. The dominant origin of the PAHs contributing to this modern contamination is from combustion processes. Depth profiles in San Pablo Bay indicate higher concentrations of PAHs since the 1950s than during the late 1800s, also presumably resulting from an increase in urbanization and industrialization. Total PAHs in San Pablo Bay range from about 0.04–1.3 $\mu g\ g^{-1}$. The ratios of methylphenanthrenes/phenanthrene and (methylfluoranthenes + methylpyrenes)/fluoranthene were sensitive indicators of anthropogenic influences in the estuary. Variations in the ratio of 1,7-dimethylphenanthrene/2,6-dimethylphenanthrene indicate a gradual replacement of wood by fossil-fuel as the main combustion source of PAHs in San Francisco Bay sediments. The profile of perylene may be an indicator of eroding peat from marshlands. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: sediment cores; polycyclic aromatic hydrocarbon; anthropogenic

1. Introduction

The polycyclic aromatic hydrocarbons (PAHs) are an important class of compounds that are prevalent in sediments in modern estuaries. PAHs are derived from natural or anthropogenic sources. Natural sources include (a) forest and prairie fires (Blumer and Youngblood, 1975); (b) natural petroleum seeps; and (c) post-depositional transformations of biogenic precursors over relatively short periods of time (Wakeham et al., 1980). Anthropogenic sources include (a) combustion of fossil-fuel (Hites et al., 1977), and long-range atmospheric transport of PAHs adsorbed onto soot or airborne particulate matter (Lunde and Bjorseth, 1977; Laflamme and Hites, 1978); (b) urban runoff containing PAHs derived from abrasion of street asphalt and automobile tires, and vehicular emissions (Wakeham et al., 1980); and (c) spillage of petroleum and its refined products which contain complex assemblages of PAHs (Boehm et al., 1991).

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PII: S0304-4203(98)00087-5

Several studies have described the cycling of PAHs in marine environments (Lipiatou and Saliot, 1991; Broman et al., 1991; Naf et al., 1992; Bouloubassi and Saliot, 1993a,b, 1994; Wakeham, 1996). The source and physicochemical properties of the individual PAHs determine their biogeochemical fate in estuarine systems. Differential water solubilities (Boehm and Quinn, 1973; Eganhouse and Calder, 1976), preferential biodegradation of low molecular weight oil-derived PAHs with respect to higher molecular weight pyrogenic ones (Jones et al., 1986), and different particle associations of PAHs depending on their sources (Prahl and Carpenter, 1983; Readman et al., 1984; Jones et al., 1986; Bouloubassi and Saliot, 1993a,b), control the speciation of PAHs in marine systems. In addition, recent studies (Farrington et al., 1983; McGroddy and Farrington, 1995; Gustafson et al., 1997; Gustafson and Gschwend, 1997) indicate that the soot phase in estuarine sediments may significantly affect the environmental speciation of PAHs. Pyrogenic PAHs associated with soot particles may be sequestered in a physical–chemical form that is unavailable for equilibrium partitioning. These strong associations of PAHs with soot particles in sediments probably make them less bioavailable than liquid sources of PAHs such as petroleum or creosote.

San Francisco Bay is the largest urbanized estuary on the west coast of the United States. Organic contaminants derived from urban, industrial and agricultural activities have contaminated the Bay (Spies et al., 1985; National Oceanic and Atmospheric Administration, 1987; Long et al., 1988; Hostettler et al., 1989; Davis et al., 1990; Boehm et al., 1991). However, there are no reports on concentrations of individual PAHs in sediments from San Francisco Bay prior to 1983. Geographic and temporal trends in PAH contamination of surficial sediments in San Francisco Bay between 1983 and 1988 have been reported (Long et al., 1988, and references therein), but little information is known about historical inputs of PAHs before that time.

A history of PAH input into San Francisco Bay can best be understood from a history of industrialization of the Bay area. An excellent account of early industrialization and energy production around the Bay is presented by Coleman (1952). Industrialization started after the Gold Rush in 1849, when the population of San Francisco was about 1000 people. Major sources of PAH input were in place shortly thereafter. In 1852, the San Francisco Gas generated gas for street lights by retorting coal. Pacific Gas and Electric began operation of a coal–gas plant in Oakland in 1865. The first oil refinery went into production at Alameda in 1880. By 1887, ferry steamers on the Bay were powered by fuel oil. Bilge pumping and flushing of oil storage tanks led to oil slicks on the Bay. The Richmond oil refinery started operations in 1902. With the introduction of the gasoline-powered automobile in 1907, streets and roads were paved with asphalt. By 1900, human and factory wastes were being pumped into the Bay. The year 1910 ushered in a decade of rapid growth and change. There was a great demand for petroleum and its refined products towards the end of World War I, between 1917–1919. In 1929, natural gas was introduced for the first time in San Francisco. Although industrialization of the Bay area slowed down during the Great Depression of 1929, it gained significant momentum during World War II (1941–1945) when the greatest increase in industrialization took place. Today, the population of the Bay area is about 6.5 million. Major contemporary inputs of PAHs in San Francisco Bay include storm drains carrying urban runoff, industries, waste water treatment plants, and oil refineries.

Because of the refractory nature of PAHs and their affinity for fine-grained sediments rich in organic carbon, sediment cores from protected embayments where accumulation of fine-grained sediments are high, have been used to reconstruct PAH chronologies (Hites et al., 1980; Venkatesan et al., 1980; Gschwend and Hites, 1981; Latimer and Quinn, 1996; Gustafson et al., 1997). Determination of the history of accumulation of PAHs in sediments may be useful for assessing PAH sources, distributions, and trends in San Francisco Bay. This information is important to better understand the speciation of PAHs in marine systems and develop strategies for protection and environmental management of San Francisco Bay. In 1990 and 1993 sediment cores were collected from two embayments in San Francisco Bay. In this study, we construct the depositional history of combustion and fossil-fuel derived PAHs in these cores in order to assess possible sources, distributions, and trends of these compounds in San

Francisco Bay, and to enhance our understanding of PAH speciation in the marine environment.

2. Materials and methods

2.1. Sample collection

Sample collection sites for the sediment cores are shown in Fig. 1. Three cores were collected at site RB92-3 in Richardson Bay. Gravity core SFB082092-3 (abbreviated hereon as RB92-3) was used for all analyses described by Fuller et al. (1999); Hornberger et al. (1999); van Geen et al. (1999); Ritson et al. (1999). The other gravity core SFB082092-3 (abbreviated hereon as RB92-3org) was used for analyses of all organic constituents in this paper, by Hostettler et al. (1999) and Venkatesan et al. (1999). A box core was also collected at this site and subcored for dating (RB92-3 box core, Fuller et al., 1999), analysis of organic contaminants (RB92-3org box core, Pereira et al. (1999); Hostettler et al. (1999); Venkatesan et al. (1999)), and foraminiferal Cd/Ca determinations (RB92-3 box core, van Geen et al. (1999)). In addition, one gravity core SFB020790-8 (hereon abbreviated as SP90-8) was collected from San Pablo Bay (Fuller, personal communication).

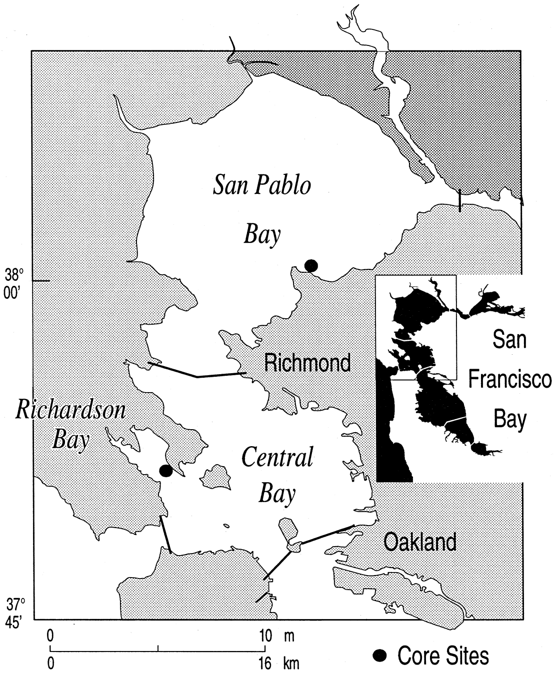

Fig. 1. Sample collection sites for surficial and bed sediments and sediment cores in San Francisco Bay.

Before splitting the butyrate liners of cores RB92-3 and RB92-3org, variations in density and magnetic susceptibility were measured at 1 cm intervals on a core logger manufactured by Geotech, UK. A ^{137}Cs source was used for the gamma-ray porosity estimator (GRAPE) system. The GRAPE system was calibrated by adjusting the Compton scattering coefficient to match the densities of a core liner filled with water (density 1 g cm^{-3}) and an aluminum rod (2.7 g cm^{-3}) of the same diameter, respectively (Kayen and Phi, 1995). The magnetic susceptibility coil was calibrated with a standard provided by Bartington Inc., the manufacturer of the coil. The sediment cores from Richardson Bay (RB92-3org and RB92-3 box core) were stored at -15°C for 1–2 weeks prior to analysis. The sediment core from San Pablo Bay (SP90-8) which was collected as part of a geological study by another research group was refrigerated at 2–5°C for a period of about 3 years prior to analysis. The effect of sample holding time on the degradation of PAHs probably is minimal, but unknown at this time.

2.2. Sample preparation

The cores were allowed to come to ambient temperature and sectioned into different horizons using a core-cutting device. The box core from Richardson Bay (RB92-3org box core) was sectioned into 5 cm horizons, and the gravity core (RB92-3org) into 10 cm horizons. The gravity core from San Pablo Bay (SP90-8) was split lengthwise, and sub-samples were taken for analysis from various horizons. The samples were placed in clean aluminium pans (previously washed and baked at 450°C), covered with aluminium foil, and allowed to dry at room temperature for 4–5 days. The samples were ground and uniformly mixed in a porcelain mortar and pestle, and passed through a 32 mesh stainless steel sieve. The samples were stored in a freezer in pre-cleaned glass jars provided with teflon-lined lids.

2.3. Isolation of PAHs

Ten to fourteen grams of dry sediment were placed in a 50 ml centrifuge tube provided with a screw cap and Teflon-lined silicone rubber septum. After addition of a surrogate standard solution containing d8-naphthalene, d10-acenaphthene, d12-chrysene, and d12-perylene (Ultra Scientific, RI, USA), the sample was extracted with 20 ml of methylene chloride (Burdick and Jackson, MI, USA) for 2 h on a wrist-action shaker. The sample was centrifuged and the solvent decanted into a Zymark Turbovap 500 concentrator (All brand names are for identification purposes only and do not constitute endorsement by the U.S. Geological Survey). The extraction procedure was repeated two more times with 20 ml of methylene chloride for 2 h. The combined methylene chloride extracts were evaporated to a volume of about 1 ml. The solvent was exchanged with 3 ml of hexane and evaporated down to 1 ml. The hexane exchange was repeated two more times. Freshly activated copper powder was added to the sample extract to remove elemental sulfur. The extract was then chromatographed on a column of 5 g and 2.5 g activated silica gel (Davison #923 and #62, respectively) and 2.5 g deactivated (5% water) alumina. The column was eluted with hexane and 30% benzene in hexane. The 30% benzene in hexane fraction containing the PAHs was concentrated and analyzed by gas chromatography-ion trap mass spectrometry using d10-phenanthrene as an internal standard. Analyte recoveries were determined from a seven replicate spike sample from Richardson Bay. All reported sample analyte concentrations were corrected based on recoveries of PAHs from the spiked sediment.

2.4. Gas chromatography-mass spectrometry

Samples were analyzed on a Finnigan-Mat Magnum gas chromatograph ion-trap mass spectrometer (Finnigan Mat, San Jose, CA, USA) equipped with a SPI injector (septum programmable injector). The gas chromatograph was maintained at 60°C for 5 min and programmed at 6°C min^{-1} to 300°C immediately following sample injection. The capillary column (30 m, 0.25-mm i.d., containing a 0.25 μm bonded phase of DB-5MS) was interfaced directly to the ion source of the mass spectrometer. Five point calibration curves for all the analytes under investigation were constructed and were linear over the calibration range investigated.

2.5. Quality assurance procedures

Laboratory reagent and glassware blanks were processed with each set of core samples. Two sets of duplicate samples from each core were also analyzed. A mid-level analytical standard solution of pahs was analyzed daily with each batch of six to eight samples. A NIST standard reference material (SRM 1941, organics in marine sediment) was analyzed in triplicate along with the core samples from Richardson and San Pablo Bays. The mean percentage recovery of PAHs in marine sediment NIST SRM 1941 are as follows: naphthalene, 41; 2-methylnaphthalene, 61; 1-methylnaphthalene, 54; acenaphthylene, 50; acenaphthene, 52; 9[*H*]fluorene, 71; 2-methylphenanthrene, 81; 1-methylphenanthrene, 99; chrysene/triphenylene, 118; phenanthrene, 95; anthracene, 79; fluoranthene, 113; pyrene; 112; benz[*a*]anthracene, 71; benzo[*b*]fluoranthene, 96; benzo[*k*]fluoranthene, 69; benz[*a*]pyrene, 54; perylene, 66; benzo[*g.h.i*]perylene, 69; indeno[1,2,3-*cd*]pyrene, 83.

2.6. Elemental analyses

Organic carbon and nitrogen determinations in sediments from Richardson Bay were made by MSI Analytical Laboratories, Santa Barbara, CA. Organic carbon and nitrogen determinations in sediments from San Pablo Bay were made by Huffman Laboratories, Golden, CO.

2.7. Age dating of sediment cores

A suite of radionuclides was measured in a gravity core and a box core from Richardson Bay, and in a gravity core from San Pablo Bay, to constrain the age of different sediment horizons. An age model for Richardson Bay constrained by ^{210}Pb and ^{234}Th indicates that the sedimentation rate was on the order of 0.8 cm year^{-1} over the past 70 years and that bioturbation mixes surface sediment down to about

~ 30 cm depth in about a decade (Fuller et al., 1999). Profiles of bomb-produced ^{137}Cs and ^{239,240}Pu in Richardson Bay sediment are consistent with this age model (Fuller et al., 1999). Prior to erosional disturbance of the watershed around the turn of the century, the sedimentation rate at the Richardson Bay site was lower by about an order of magnitude (van Geen et al., 1999). The gravity core from Richardson Bay used for the present study, RB92-3org, was collected within ~ 10 m of the dated core (RB92-3). Profiles of ^{210}Pb, ^{137}Cs, and ^{239,240}Pu in the San Pablo Bay core indicate considerably higher, albeit sporadic, sedimentation than in Richardson Bay over the past several decades (Fuller et al., 1999). A hiatus in the core suggested by the radionuclides and other properties is consistent with historical bathymetry data indicating a prolonged period of erosion in the area at the turn of the century. The San Pablo Bay core does not extend to sediment deposited before erosional disturbance of the watershed (van Geen et al., 1999).

3. Results and discussion

The magnetic susceptibility and density records of core RB92-3 and RB92-3org show a number of common features albeit with a systematic offset in the depth of these features (Fig. 2). The sharpest feature is the transition from a minimum to a maximum in both properties taking place over a depth interval of about 10 cm. The transition is centered at about 60 cm and 70 cm depth in cores RB92-3 and RB92-3org, respectively. The offset between common features increases deeper in the cores. For instance, a local maximum in magnetic susceptibility and GRAPE density located at 105 cm depth in core RB92-3 appears to correlate to the same feature at 120 cm depth in core RB92-3org. We attribute these systematic offsets to a slightly higher sedimentation rate at the site used for reconstructing the input history of organic contaminants. Because there is no indication of a systematic offset in the upper 40 cm of the two cores, the following simple formulation was determined to correlate sediment horizons in the two cores by visual trial and error:

$$\mathrm{Depth}_{\mathrm{RB92-3}} = 40\,\mathrm{cm} + 0.8\left(\mathrm{Depth}_{\mathrm{RB92-3org}} - 40\,\mathrm{cm}\right)$$

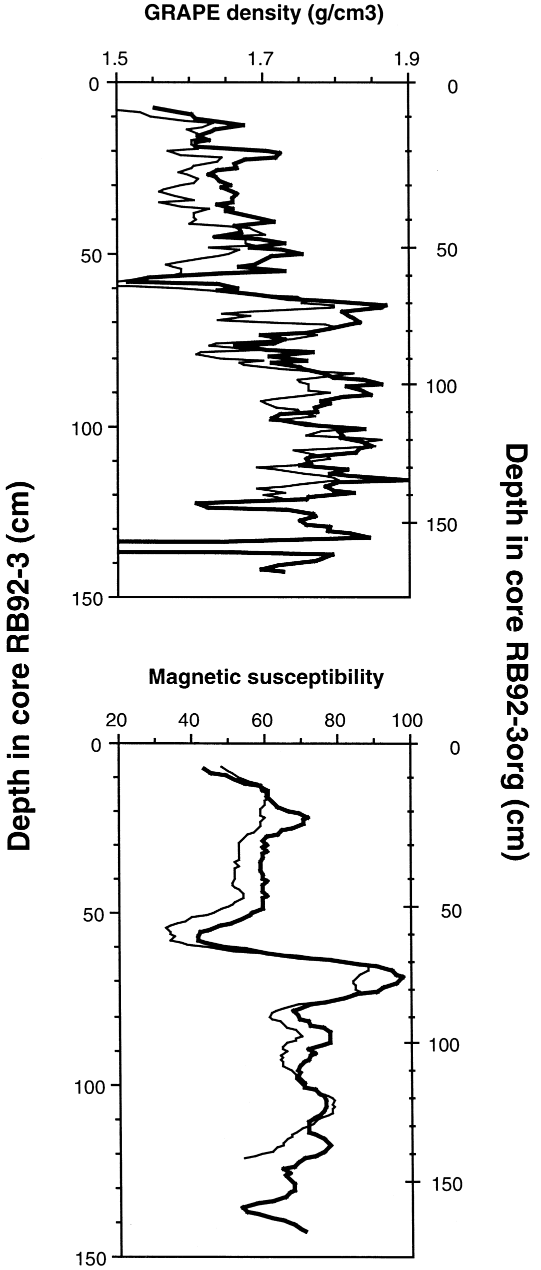

Fig. 2. Comparison of magnetic susceptibility and GRAPE records in cores RB92-3 (heavy line) and RB92-3org (thin line). The depth scales of the two cores are shown on the opposite side of the figure. The formula described in the text indicates the conversion between the two depth scales.

where $\mathrm{Depth}_{\mathrm{RB92\text{-}3}}$ and $\mathrm{Depth}_{\mathrm{RB92\text{-}3org}}$ refer to depths in centimeters in the two cores. This is the formula that relates the two depth scales shown in Fig. 2. Because dating information is limited to core RB92-3 (Fuller et al., 1999; van Geen et al., 1999), this formulation must be used to translate depths in RB92-3org to equivalent depths in core RB92-3. A difference in sedimentation rate for the two cores is not implausible given the significantly larger variations documented for other parts of the mouth of Richardson Bay (Fuller et al., 1999; van Geen et al., 1999). No depth adjustment appears to be required for the box core.

3.1. Total organic carbon

TOC concentration profiles in cores from Richardson and San Pablo Bays are shown in Fig. 3a_1 and a_2, respectively. Concentrations of organic carbon ranged from 7.4 to 11.2 mg g^{-1} dry sediment in Richardson Bay, and from 5.9 to 17 mg g^{-1} in San Pablo Bay. The TOC profile in Richardson Bay probably indicates a relatively uniform input of organic carbon over the last century. Atomic C/N ratios ranged from 7.8–8.9, which is characteristic of a mixture of both marine and terrigenous inputs of organic matter.

In San Pablo Bay, bathymetric reconstructions (Fuller et al., 1999) indicated that this Bay was eroding and not depositing sediment before 1950. Sediments deposited between ∼ 1860 and 1890 appear to occupy the horizons between 125 cm and 240 cm in the core. These sediments probably are domi-

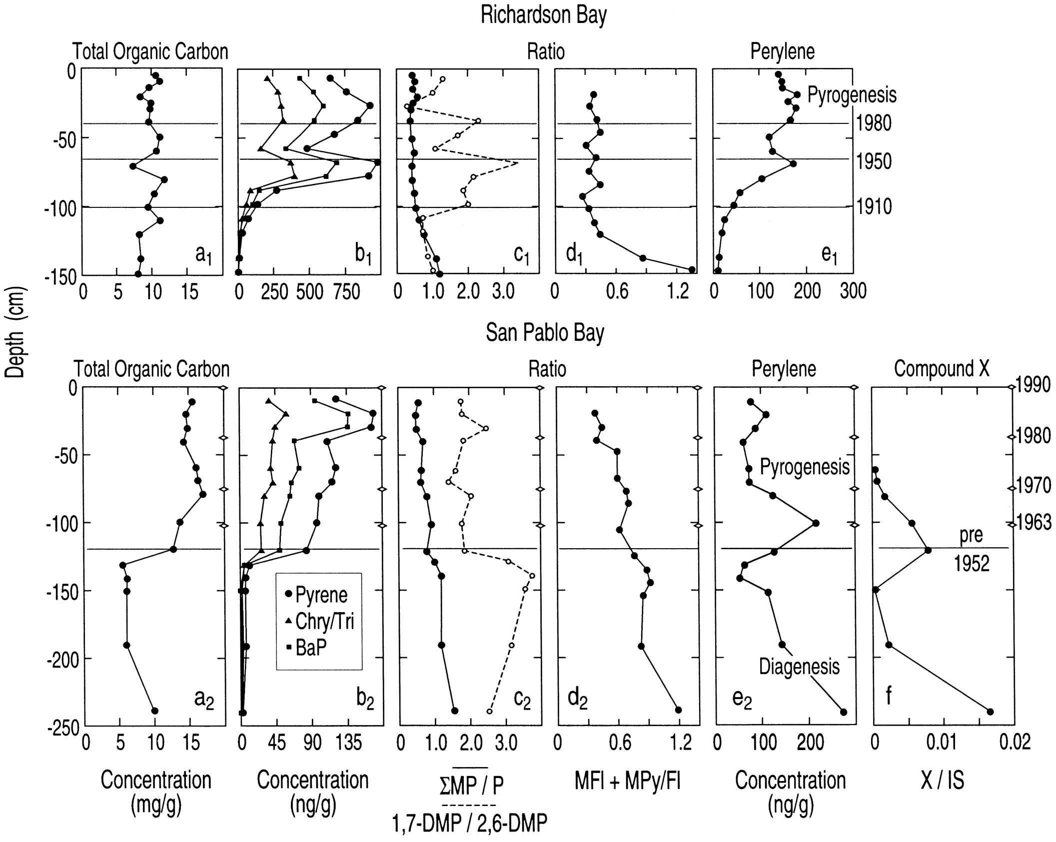

Fig. 3. Sediment cores from Richardson and San Pablo Bays. (a_1 and a_2) Distributions of total organic carbon (TOC). (b_1 and b_2) Concentration vs. depth profiles of pyrene, chrysene/triphenylene, and benz[*a*]pyrene. (c_1 and c_2) Ratios of methylphenanthrenes to phenanthrene (MP/P, solid line), and 1,7-dimethylphenanthrene to 2,6-dimethylphenanthrene (1,7-DMP/2,6-DMP, dashed line). (d_1 and d_2) Ratios of (methylfluoranthenes + methylpyrenes) to fluoranthene (MFl + MPy)/Fl. (e_1 and e_2) Concentration vs. depth profiles of perylene. (f) Ratio of Compound X to Internal standard (X/IS) in a sediment core from San Pablo Bay. Dates are adjusted for differences in sedimentation rate between RB92-3 and RB92-3org.

nated by debris mobilized by hydraulic mining in the Sierra Nevada. Sediments upcore from 125 cm were deposited after 1950 (based upon ^{137}Cs, ^{239,240}Pu, and ^{210}Pb dating). San Pablo Bay shows higher TOC concentrations than found in Richardson Bay in the horizons deposited in the last 40 years (upcore from 125 cm). Deeper horizons show lower TOC concentrations, comparable to those observed in Richardson Bay. Atomic C/N ratios in sediments from San Pablo Bay range from 9.5–13.6 with no apparent difference between the older and more recent sediments. Thus, in both periods represented in the core, the carbon was more characteristic of terrigenous inputs (Prahl et al., 1980; C/N 12–14) than marine inputs (Muller, 1977; C/N ∼6). However, the ranges of C/N values for both cores also may result from diagenetic fractionation processes in the sediments.

Use of agricultural technologies such as mechanization, water manipulation, fertilization, and weed and pest control increased significantly after World War II in the Central Valley in response to increasing worldwide demand for crops (Preston, 1981). These increased agricultural activities could have contributed to increased soil erosion and agricultural runoff, resulting in the observed greater TOC inputs in modern times evident in the San Pablo Bay core. The reduced TOC between 190 and 130 cm may also be due to dilution of TOC by inorganic sediment input from hydraulic mining.

3.2. Polycyclic aromatic hydrocarbons (PAHs)

The PAH fractions in different horizons of the sediment cores from Richardson and San Pablo Bays contain a complex assemblage of more than 21 different compounds. Concentrations of these compounds are shown in Tables 1 and 2. PAHs ranged from two ring naphthalene to six ring benzo[*g.h.i*]perylene. Trends were similar among all compounds. Concentrations of all compounds were greater in Richardson Bay than in San Pablo Bay.

Concentrations vs. depth profiles of three pyrogenic PAHs, pyrene, chrysene/triphenylene, and benz[*a*]pyrene in Richardson and San Pablo Bays are shown in Fig. 3b_1 and b_2, respectively. The profile for total PAHs was similar to that of the pyrogenic PAHs. Based on the dating model of the Richardson Bay core, it appears that prior to 1900, pre-industrialization levels of the pyrogenic PAHs were very low (∼5 ng g^{-1}). The dominant source of these pyrogenic PAHs probably was from the burning of wood or coal, or from natural forest fires. Concentrations of the three pyrogenic PAHs started to increase around the turn of the century in response to increasing urbanization and industrialization around the Bay area. The sharpest increase in the concentrations of PAHs occurred after about 1910, when rapid growth in industrialization and associated fossil-fuel combustion took place in the Bay area (Coleman, 1952). Concentrations of the three pyrogenic PAHs in recent anthropogenically contaminated surficial sediment horizons are ∼1.3 μg g^{-1}, more than two orders of magnitude greater than concentrations in pre-industrialization horizons. The decline in the concentrations of the pyrogenic PAHs between about 1950–1960 may be due to a switch from coal to oil and gas as home heating fuels (Hottle and Howard, 1971; Gustafson et al., 1997). Between 1944–1961, the use of coal in the United States declined by 40%, while the use of oil and gas increased by 200% (Hites et al., 1980).

Concentrations of the three pyrogenic PAHs in recent surficial sediments of San Pablo Bay are, in general, significantly lower (about five times) than those in Richardson Bay. The PAHs in San Pablo Bay are higher in sediments deposited since 1950 than deeper in the core. Although it is possible that sources of PAHs are greater in Richardson Bay than in San Pablo Bay, the latter core is nearer to at least some important sources of PAHs (for example, all oil refineries are located in this region). However, it is known that oil-derived PAHs undergo preferential biodegradation more so than combustion-derived PAHs (Jones et al., 1986). Also, higher sedimentation rates occur in San Pablo Bay (4 cm $year^{-1}$) than in Richardson Bay (0.9 cm $year^{-1}$); if PAHs are locally derived, then higher sedimentation could dilute PAH concentrations. Greater inputs of organic carbon could also dilute the PAH vs. TOC relationship. The integrated concentrations (mass/area) of total PAHs at the two sites were determined by the method of Fuller et al. (1999) for each core. It was determined that total PAHs deposited at Richardson Bay from a depth of about 138 cm to the surface was

Table 1
Concentrations of polycyclic aromatic hydrocarbons in Richardson Bay gravity core RB92-3org (ng g^{-1} dry weight)

Compounds	Depth (cm)													
	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100	100–110	110–120	120–138	138–148
Naphthalene	33	25	34	36	32	24	24	26	7.1	6.5	4.7	3.2	3.2	2.1
2-Methylnaphthalene	13	11	17	16	16	9.5	7.9	9.2	3.2	3.2	2.4	2.1	2.4	1.6
1-Methylnaphthalene	8.1	7.2	11	10	8.3	6.7	5.0	6.1	1.7	1.7	1.1	1.1	1.1	0.6
Acenaphthylene	15	14	18	18	15	10	12	7.8	1.5	1.0	< 0.5	< 0.5	< 0.5	< 0.5
Acenaphthene	20	18	41	30	25	16	14	14	2.9	1.6	0.7	< 0.5	< 0.5	< 0.5
9[*H*] fluorene	22	22	41	35	27	18	25	17	3.5	2.9	1.6	1.4	1.0	0.8
Phenanthrene	236	336	430	405	332	200	418	311	62	48	20	12	5.3	4.3
Anthracene	75	103	133	144	90	71	117	71	11	9.2	3.6	1.6	< 0.5	< 0.5
2-Methylphenanthrene	35	55	65	62	46	32	59	39	11	9.3	5.3	3.9	3.0	2.5
1-Methylphenanthrene	27	42	48	49	36	22	49	30	7.3	6.6	3.3	2.2	1.2	1.1
Fluoranthene	537	693	773	691	604	392	873	740	228	121	57	25	6.4	2.1
Pyrene	648	761	926	840	675	484	980	915	269	136	70	29	7.0	2.2
Benz[*a*]anthracene	175	264	280	257	218	125	316	233	69	43	18	7.6	2.1	0.7
Chrysene	208	285	304	316	238	158	370	396	86	57	23	11	3.5	2.0
Benzo[*b*]fluoranthene	323	462	475	473	383	261	580	555	168	106	42	14	4.8	2.1
Benzo[*k*]fluoranthene	163	121	143	159	94	99	195	194	46	25	13	4.9	1.6	< 0.5
Benz[*a*]pyrene	432	525	600	531	442	332	692	617	144	100	33	12	1.9	< 0.5
Perylene	137	106	92	136	119	126	171	105	56	43	24	17	10	8.9
Indeno[1,2,3-*cd*]pyrene	380	446	450	333	333	266	583	550	151	98	36	14	4.8	1.7
Dibenz[*a.h*]anthracene	30	35	33	31	36	24	43	42	8.4	6.4	3.9	1.3	0.7	< 0.5
Benzo[*g.h.i*]perylene	368	381	529	379	345	291	737	666	181	104	37	13	5.3	1.8
Total PAH	3884	4674	5440	5951	4115	2968	6273	5444	1518	931	401	175	66	36

Table 2
Concentrations of polycyclic aromatic hydrocarbons in San Pablo Bay gravity core SP90-8 (ng g^{-1} dry weight)

Compounds	Depth (cm)													
	0–10	10–20	20–30	30–40	50–60	60–70	70–80	90–100	110–120	120–130	130–140	140–150	180–190	228–239
Naphthalene	18	20	20	15	14	15	11.8	13	13	7.4	5.9	4.1	5.0	4.1
2-Methylnaphthalene	13	11	12	10	11	13	11.6	14	14	5.5	4.2	2.1	2.9	3.7
1-Methylnaphthalene	6.4	5.8	6.1	5.3	5.0	5.6	5.0	5.0	5.3	6.1	4.4	1.1	1.4	1.7
Acenaphthylene	2.4	4.4	3.7	1.7	2.4	3.4	1.7	1.5	2.4	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Acenaphthene	3.9	5.9	5.9	3.2	2.3	2.3	1.6	2.5	1.6	0.7	< 0.5	< 0.5	0.7	< 0.5
9[*H*]fluorene	7.8	7.6	6.7	7.2	5.7	6.9	6.5	7.1	5.1	3.5	3.3	2.2	2.7	2.7
Phenanthrene	47	54	56	37	38	36	30	27	23	7.1	4.5	3.2	4.1	5.1
Anthracene	10	13	13	11	8.9	11	8.7	6.8	6.5	1.7	1.3	0.8	0.9	0.8
2-Methylphenanthrene	10	9.7	10	9.3	9.1	8	8.6	9.0	7.0	2.2	1.8	1.4	1.8	2.9
1-Methylphenanthrene	5.7	6.3	7.0	6.0	6.0	5.5	6.0	6.6	4.2	2.3	1.9	1.4	1.5	1.5
Fluoranthene	108	124	128	80	83	72	69	65	53	14	7.9	7.2	8.0	3.2
Pyrene	122	169	166	111	121	116	100	97	84	12	6.4	6.5	6.5	2.6
Benz[*a*]anthracene	38	51	49	35	39	34	30	23	21	5.3	3.3	2.7	3.0	1.1
Chrysene	37	59	45	42	39	42	31	26	27	5.0	3.9	2.6	3.5	2.1
Benzo[*b*]fluoranthene	98	139	124	81	90	77	64	61	49	9	5.5	3.6	4.8	2.7
Benzo[*k*]fluoranthene	30	40	35	28	27	22	19	14	17	2.6	1.4	1.2	1.4	0.7
Benz[*a*]pyrene	95	137	136	69	75	65	63	52	50	5.4	3.0	< 0.5	2.6	0.8
Perylene	76	108	87	59	71	70	124	214	123	59	52	111	138	269
Indeno[1,2,3-*cd*]pyrene	106	160	146	76	84	69	76	62	64	3.9	2.2	1.8	1.9	0.9
Dibenz[*a.h*]anthracene	6.9	14	15	8.9	7.7	8.6	6.6	6.9	6.5	0.8	0.5	< 0.5	< 0.5	< 0.5
Benzo[*g.h.i*]perylene	111	158	144	74	88	69	53	46	45	2.7	2.0	1.2	1.4	1.5
Total PAH	955	1298	1217	770	829	753	728	762	622	157	116	154	193	308

400 μg cm^{-2}. Most of this PAH was deposited between 1930 and 1992 at an average rate of 6.4 μg cm^{-2} $year^{-1}$. The amount deposited in San Pablo Bay from a depth of 228 cm to the surface was 119 μg cm^{-2}. This PAH was deposited between 1952 and 1990 at an average rate of 3.1 μg cm^{-2} $year^{-1}$. In comparison, Christensen and Zhang (1993) and Simcik et al. (1996) observed that maximum PAH fluxes to Lake Michigan were 0.1–0.28 μg cm^{-2} $year^{-1}$. From sediment traps, Sanders et al. (1996) cited PAH fluxes in the Mediterranean of 0.01–0.03 μg cm^{-2} $year^{-1}$, and cited a flux of 0.24 μg cm^{-2} $year^{-1}$ in Puget Sound. They found a flux of 1.17 μg cm^{-2} $year^{-1}$ into Esthwaite Water. To top it all, Smith and Levy (1990) found a PAH flux of 40–200 μg cm^{-2} $year^{-1}$ into sediments in Saguenay Fjord, which received a heavy load of industrial effluent and had very high PAH concentrations in sediments. Higher contaminant burdens in Richardson Bay probably are due to inputs of combustion-generated PAHs from the highly industrialized south and central bays. Riverine inputs of PAHs to San Pablo Bay generally are low, and PAHs in San Pablo Bay probably represent localized inputs.

There was a significant correlation between TPAH and organic carbon content of sediments in San Pablo Bay ($R = 0.86$). However, TPAH did not show any significant correlation with the organic carbon content in sediments from Richardson Bay. Lack of correlation of these parameters in Richardson Bay is probably indicative of polluted sediments (Bouloubassi and Saliot, 1993a,b). In addition, whereas partitioning of PAHs into the organic coatings on sediment may be an important process in San Pablo Bay, the PAHs in sediments of Richardson Bay may be bound or occluded in soot particles that are generated during combustion of organic materials including fossil-fuels, and as such they are less available to partition into the organic carbon of sediments. These bound combustion PAHs may be less available for biological uptake than PAHs derived from petroleum spills (Farrington et al., 1983; Gustafson et al., 1997). In any event, factors more complex than simple partitioning of PAHs into sediment-associated organic carbon control PAH concentrations in San Francisco Bay sediments. At least some appreciation of estuarine processes is necessary to understand concentrations in this system.

3.3. Sources of PAHs

Combustion of organic materials such as fossil-fuels, refuse, etc., gives rise to PAHs by step-wise free radical mechanisms. Combustion derived PAHs are dominated by the unsubstituted moieties, whereas PAHs in petroleum are dominated by the alkylated homologs (Laflamme and Hites, 1978). Lower formation temperatures, such as in the formation of petroleum, preserve a higher degree of alkylation (Youngblood and Blumer, 1975).

The ratios of methylphenanthrenes to phenanthrene (MP/P) were examined as an indication of anthropogenic influences such as combustion of organic materials around the bay. These ratios are reported to be in the range of 0.5–1 in sediments dominated by phenanthrenes arising from combustion processes, and from 2–6 in sediments dominated by fossil-fuel phenanthrenes (Prahl and Carpenter, 1983). The ratio of MP/P is reported to be 4.0 for used crankcase oil (Pruel and Quinn, 1988), close to 1.0 for street and urban dust samples (Takada et al., 1990, 1991), and about 0.5 for atmospheric fallout (Takada et al., 1991).

Ratios of MP/P in the cores from Richardson and San Pablo Bays are shown in Fig. $3c_1$ and c_2, respectively. Prior to 1900, the MP/P ratios in preindustrial horizons of both cores ranged from 1–1.5. These ratios in the deeper sediment horizons probably represent natural inputs in the older sediment horizons. The MP/P ratios gradually decreased upcore, presumably in response to increasing urbanization and industrialization around the Bay, with concomitant increase in the combustion of biomass and fossil-fuels such as coal and petroleum, and combustion of natural gas. The MP/P ratios are about 0.5–0.7 in the uppermost sediments, indicating that the dominant recent sources of PAHs in San Francisco Bay are from combustion processes and not from recent petroleum spills. Similar findings have been reported in sediments from Chesapeake Bay, MD (Schantz et al., 1990), and from Narragansett Bay, RI (Lake et al., 1979). It is interesting to note that the MP/P ratios in both sediment cores are in good agreement, in contrast to the concentration levels of PAHs and other molecular marker compounds. It is especially noteworthy that the MP/P ratio begins to change before PAH concentrations increase noticeably. Therefore, the MP/P ratio appears to be a more sensitive indicator of anthropogenic influences on sediment character around the bay over the past century. Because the MP/P ratio may be sensitive to environmental fractionation, a more robust parameter such as the ratio of (methylfluoranthenes + methylpyrenes)/fluoranthene (Youngblood and Blumer, 1975; Laflamme and Hites, 1978; Gustafson et al., 1997) was investigated as shown in Fig. 3d_1 and d_2 for Richardson and San Pablo Bays, respectively. Generally, this ratio is above unity if the source is petroleum. The ratios in both sediment cores follow the same trend as the MP/P ratios, thus confirming that the dominant sources of these compounds are from combustion processes.

The ratios of 1,7-dimethylphenanthrene/2,6-dimethylphenanthrene in sediment cores from Richardson and San Pablo Bays (Fig. 3c_1 and c_2, respectively) were examined as an indicator of the relative contribution to pyrogenic PAHs from biomass (woody) vs. fossil-fuel combustion (Benner et al., 1995; Gustafson et al., 1997). 1,7-Dimethylphenanthrene is a PAH emitted primarily by burning soft woods such as pine. 2,6-Dimethylphenanthrene is a PAH that is emitted in modest concentrations by both fossil-fuel combustion and residential wood combustion. The trend in this ratio in the San Pablo Bay core clearly indicates an increase in soft wood combustion prior to ~ 1950, followed by an increase in fossil-fuel combustion from ~ 1950 to the present. The trend in this ratio in Richardson Bay is not as apparent, but still seems to indicate an increase in soft wood burning from ~ 1900 to ~ 1950, followed by an increase in fossil-fuel combustion from ~ 1950 to the present.

3.4. Inputs of perylene

Distributions of perylene in sediment cores from Richardson and San Pablo Bays are shown in Fig. 3e_1 and e_2. Sources of perylene may be anthropogenic or biogenic. The sedimentary record of perylene in Richardson Bay is similar to the PAH profiles shown in Fig. 3b_1, indicating that during the pre-industrial period prior to 1900, levels of perylene were low and gradually increased upcore around the turn of the century in response to increasing anthropogenic activities around the Bay. The dominant source of this perylene is probably from pyrogenic processes.

In contrast, in San Pablo Bay, the concentration of perylene increased with increasing depth in the sediment column, especially below a depth of 150 cm. The increase in concentrations of perylene in the deeper and older sediments suggests in situ formation of perylene from biogenic precursors under anaerobic conditions during early diagenesis (Orr and Grady, 1967; Aizenshtat, 1973; Wakeham et al., 1980; Venkatesan, 1988 and references therein). As stated above, however, a similar increase in the concentration of perylene with increasing depth was not observed in Richardson Bay. It is conceivable that perylene in San Pablo Bay is derived from a terrigenous precursor that is transported to San Pablo Bay via the Sacramento and San Joaquin Rivers. Perylene has been reported to be the dominant PAH in peat samples (Venkatesan, 1988). Because the Sacramento–San Joaquin Delta contains large peat deposits, the perylene precursor could possibly be derived from peat soils in the delta. Thus, the upcore decrease in the concentration profile of perylene in San Pablo Bay may represent loss of marsh inputs of natural organics with development of the watershed or diking that sealed peat areas from erosion. Diking of marshlands around San Francisco Bay created land for farming, for salt evaporation ponds, and for residential and industrial uses. Of the original 2200 km^2 of tidal marsh around the bay, only about 125 km^2 of undiked marsh remains today (Conomos, 1979).

An unknown compound (Compound X) was tentatively identified by mass spectrometry (m/z 258) in the San Pablo Bay core. A mass spectral library search tentatively identified this compound as hexahydroperylene. Compound X was not detected in the Richardson Bay sediment core. Lack of a commercially available standard of this compound precludes definite confirmation at this time. The ratio of Compound X to the internal standard, plotted as a function of depth in the sediment core is shown in Fig. 3f. The profile of Compound X indicates that this compound appears at a depth of about 60 cm and gradually increases with increasing depth in the core. Similarities in the depth profiles of perylene and

Compound X suggest that Compound X may be a partially aromatized diagenetic precursor of perylene. The precursor of Compound X is not known at this time.

3.5. Triaromatic steroid hydrocarbons

A series of triaromatic steroid hydrocarbons (m/z 231), were present in sediment cores from Richardson and San Pablo Bays. These compounds are biomarkers and are components of fossil-fuels. Triaromatic steroid hydrocarbons have been found in estuarine sediments (Killops and Howell, 1988), and in natural bitumens and pyrolysates of humic coals (Lu and Kaplan, 1992).

The concentration of the C_{21} triaromatic steroid hydrocarbon was observed to increase with increasing depth in the sediment column relative to the other members (C_{26}–C_{28}). Depth profiles of the ratio of $C_{21}/(C_{26}R + C_{27}S)$ triaromatic steroids in Richardson and San Pablo Bays are shown in Fig. 4. This ratio is relatively consistent down to a depth of about 80–90 cm in Richardson Bay, then it increases significantly below a depth of 90 cm. The dominant source of the C_{21} triaromatic steroid hydrocarbons in the upper horizons of the Richardson Bay core is probably from fossil-fuels containing these biomarkers. The increase in the ratio below a depth of 90 cm suggests in situ formation from biogenic precursors during early diagenesis in the older sediments. Because these aromatic hydrocarbons have retained the steroid skeleton, they are probably derived from sterols that have undergone successive dehydrogenation, progressive aromatization, and side chain scission.

A similar trend in the ratio of these compounds also is seen in San Pablo Bay. Again, the ratio is greater in San Pablo Bay than Richardson Bay, presumably because of closer proximity of San Pablo Bay to riverine inputs of biogenic precursors. The anomalously high ratio in the surficial horizon is still unclear. However, in general, there is a sharp upcore decrease in the ratio in sediment deposited since 1950. This transition from diagenetic to pyrogenetically derived C_{21} triaromatic steroid hydrocarbons presumably results, as with the other PAHs, from a combination of increased urbanization, and increased municipal and industrial inputs to San Pablo Bay after World War II.

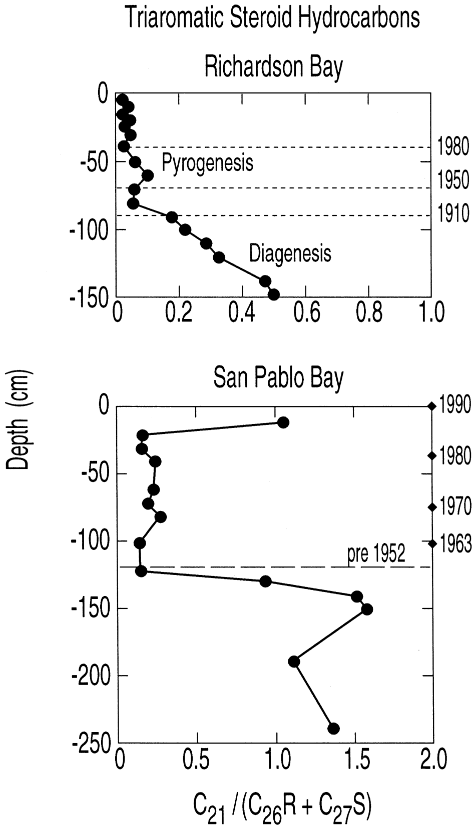

Fig. 4. Ratios of $C_{21}/(C_{26}R+C_{27}S)$ triaromatic steroid hydrocarbons in sediment cores from Richardson and San Pablo Bays.

4. Conclusions

This report demonstrates that PAHs are indicators of anthropogenic activities, and can be used to track the history of PAH contamination from the past to the present in sediments of San Francisco Bay. The dominant sources of PAHs in San Francisco Bay appear to be from combustion processes (atmospheric, urban runoff, industrial discharges etc.) rather than from direct petroleum input. These sources of recalcitrant PAHs appear to be more important on a regional scale, than PAH discharges from refineries or frequent small oil spills (Luoma and Cloern, 1982). In contrast to many estuaries, sediments from the more seaward Richardson Bay are substantially more contaminated with PAHs than sediments from the landward site, nearer oil refineries. The profile of perylene in San Pablo Bay suggests that eroding peat from the Delta may be a major source of this compound in pre-industrial times. This input has declined in recent times probably reflecting land reclamation by diking of marshlands. Sediment chronologies of PAHs suggest that San Francisco Bay Estuary has been significantly modified by urbanization, industrialization, and possibly by water management during the past century. This information may be useful in designing future strategies for protection and management of the estuary.

Acknowledgements

This study was partly funded through a cooperative agreement between USGS and National Oceanic and Atmospheric Administration under Grant #1434-93-A-1016. The core from 1991 was collected by Roberto Anima and Ed Clifton of the USGS. The 1992 core collection was led by Roberto Anima and Lex van Geen. The authors gratefully acknowledge the assistance of Keith Kvenvolden, Michelle Hornberger and Liz Canuel, for their assistance in collection of the sediment cores. The assistance of Byron Richards and Francis Parchaso in the collection of surficial sediment samples is appreciated.

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