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Marine Chemistry 64 (1999) 115–127

MARINE CHEMISTRY

A record of hydrocarbon input to San Francisco Bay as traced by biomarker profiles in surface sediment and sediment cores

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Received 31 July 1997; revised 6 July 1998; accepted 28 July 1998

Abstract

San Francisco Bay is one of the world's largest urbanized estuarine systems. Its water and sediment receive organic input from a wide variety of sources; much of this organic material is anthropogenically derived. To document the spatial and historical record of the organic contaminant input, surficial sediment from 17 sites throughout San Francisco Bay and sediment cores from two locations—Richardson Bay and San Pablo Bay—were analyzed for biomarker constituents. Biomarkers, that is, 'molecular fossils', primarily hopanes, steranes, and *n*-alkanes, provide information on anthropogenic contamination, especially that related to petrogenic sources, as well as on recent input of biogenic material. The biomarker parameters from the surficial sediment and the upper horizons of the cores show a dominance of anthropogenic input, whereas the biomarker profiles at the lower horizons of the cores indicate primarily biogenic input. In the Richardson Bay core the gradual upcore transition from lower maturity background organics to a dominance of anthropogenic contamination occurred about 70–100 years ago and corresponds to the industrial development of the San Francisco Bay area. In San Pablo Bay, the transition was very abrupt, reflecting the complex depositional history of the area. This sharp transition, perhaps indicating a depositional hiatus or erosional period, dated at pre-1952, is clearly visible. Below, the hiatus the biomarker parameters are immature; above, they are mature and show an anthropogenic overlay. Higher concentrations of terrigenous *n*-alkanes in the upper horizons in this core are indicative of an increase in terrigenous organic matter input in San Pablo Bay, possibly a result of water diversion projects and changes in the fresh water flow into the Bay from the Delta. Alternatively, it could reflect a dilution of organic material in the lower core sections with hydraulic mining debris. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: sediment; hydrocarbons; San Francisco Bay; biomarkers

1. Introduction

Hydrocarbons are ubiquitous constituents of estuarine sediments. They originate from a wide variety of autochthonous and allochthonous sources and exhibit broad differences in structure, reactivity, and refractivity. The more refractive of these compounds are deposited into the sediment and are preserved over time. Because estuarine sediments thus serve as sinks and integrators of these hydrocarbons, sediment cores have been used in widely differing loca-

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PII: S0304-4203(98)00088-7

tions to reconstruct the geochemical history of estuarine or deltaic environments. These studies include work in Narragansett Bay, RI (Wade and Quinn, 1979), Puget Sound, WA (Barrick et al., 1980; Barrick and Hedges, 1981), and the Black Sea near the mouth of the Danube River (Wakeham, 1996).

The sediments of San Francisco Bay (SFB) receive inputs of organic material from a wide variety of sources. These sources include terrigenous, urban, and riverine inputs, industrial, agricultural, and sewage discharges, atmospheric deposition, shipping traffic, and other anthropogenic inputs (Nichols et al., 1986), as well as autochthonous marine material such as algae, phytoplankton, and zooplankton (Jassby et al., 1993). Due to these variations in sources, there is high spatial and temporal variability of organic constituents in surface sediment throughout SFB (Canuel et al., 1995; Canuel and Cloern, 1996). There is also significant variation in the reactivity of this organic matter, and therefore in its susceptibility for remineralization or preservation. In addition, SFB has seen a significant growth in urbanization, industrialization, and population since 1900. Increased agricultural activity and water management throughout the area drained by the Bay has resulted in changes in water flow regimes, both of which have, in turn, impacted the influx of hydrocarbons to SFB. All of these factors contribute to the complexity of

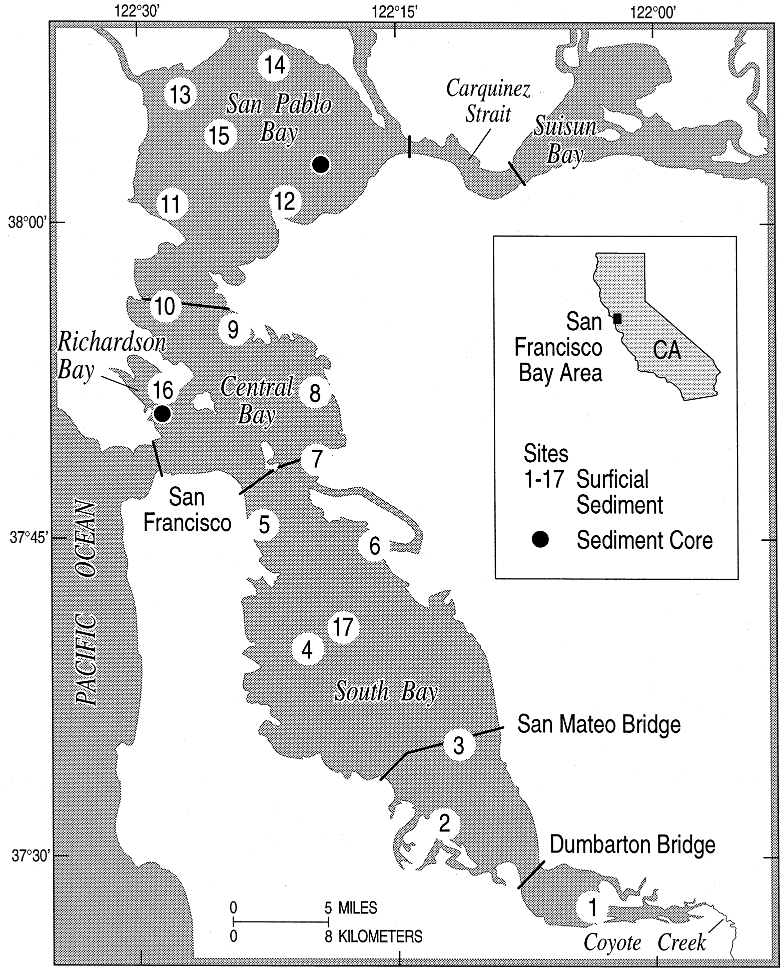

Fig. 1. Map of the study area, San Francisco Bay, CA. Specific locations are given in Table 1.

the hydrocarbon record in the sediments of the Bay. Furthermore, because SFB sediments are typically highly mixed or bioturbated (Nichols and Thompson, 1985; Fuller et al., 1999), there is little information in the literature regarding the history of organic inputs. As part of an ongoing investigation into sources of organic input to San Francisco Bay, we have examined a suite of surficial sediment samples from 17 sites throughout the Bay, as well as sediment from two cores collected from two embayments within SFB, Richardson and San Pablo Bays (Fig. 1). The purpose of this work was to evaluate how selected organic inputs have varied, both spatially and historically. The core study was part of a larger, multi-investigator project looking at the historical record of several types and sources of contaminant input to San Francisco Bay (see van Geen and Luoma, 1999).

Biomarker profiles of the surficial and core sediments are used in this report to track specific types of organic input. Biomarkers are ‘molecular fossils’. They are organic molecules that have originated in a biologic system, were preserved in the geologic record, and have been ‘geologically matured’ while retaining enough of their original biologic configuration (or molecular skeleton) so that information about their source and maturity can be obtained. In sediments, biomarker compounds can vary from immature, that is, very recently deposited with configurations or distributions close to that of the biogenic precursor(s), to mature, with configurations, or ‘equilibrium’ distributions of configurations, of high thermodynamic stability, such as those commonly found in petroleum. For example, certain *n*-alkanes, specifically the odd-carbon numbered *n*-alkanes from C_{25} to C_{31}, are known to originate from the epicuticular waxes of higher (vascular) land plants (Eglinton and Hamilton, 1967). A distribution of *n*-alkanes with a pronounced dominance of these odd numbered alkanes is, therefore, a marker for terrigenous input. Conversely, ratios calculated from the relative proportions of specific hopane and sterane isomers and their progressive diagenetic and catagenic counterparts are widely used as maturity and source indicators (Peters and Moldowan, 1993); as such, they are particularly useful as indicators of petrogenic (petroleum) contamination. Biomarkers, therefore, can give a perspective on sources of organic input, including anthropogenic contamination sourced from petroleum (Dastillung and Albrecht, 1976; Lichtfouse et al., 1997). Thus, they are complementary to other molecular tracers of contaminant and other inputs to San Francisco Bay sediments discussed elsewhere in this volume.

2. Experimental methods

2.1. Sample collection

The surficial sediment samples were collected in January, 1992 with a Van Veen grab sampler from 17 sites throughout SFB (Fig. 1, Table 1). Water depths varied from 2 to 13 m, and the top 7 cm of sediment were used for analysis. A gravity core, 240 cm in length, was collected from San Pablo Bay in 1991 (SFB020790-8 in Fuller et al., 1999; hereafter referred to as SP90-8), and a gravity and box core, 150 cm and 40 cm in length, respectively, were collected from Richardson Bay specifically for organic analysis in August, 1992 [SFB082092-3 in Fuller et al., 1999; hereafter referred to as RB92-3(org)]. Other cores were collected at the Richardson Bay site and the cores investigated in parallel; the age model for RB92-3(org) established from a correlation of physical properties with the well-dated adjacent core RB92-3 (Fuller et al., 1999) is described in Pereira et al. (1999). All samples were refrigerated immediately after collection, then transported to the laboratory. The surficial sediment samples and the Richardson Bay cores were frozen until the time of analysis; the San Pablo Bay core was kept refrigerated at 2–5°C. The gravity cores were divided into 10-cm subsections for analysis, and the box core divided into 5-cm subsections. The same San Pablo Bay core was used by all investigators participating in this study.

2.2. Extraction and fractionation

Analysis focused on the unbound lipid or solvent-extractable constituents of the sediment. This analysis has been described previously (Hostettler et al., 1989) and is summarized here. Sediment sub-

Table 1
Site information and hydrocarbon parameters for surficial samples, San Francisco Bay

Site	Location	Water depth [m]	EOM[a] [μg/g]	ΣC^{b}_{25-31}	CPI[c]	m/z 191[d]		m/z 217[d]	PAH: ΣCOMB[e]
						T_m/T_s	$\alpha\beta C_{31}$ $(S/(S+R))$	$\alpha\alpha\alpha C_{29}$ $(S/(S+R))$	
Surface sediment									
1	Coyote Creek mouth	3	391	2.72	4.7	1.1	0.56	0.51	1.37
2	Redwood Creek mouth	3	255	1.70	5.1	1.3	0.56	0.51	2.15
3	San Mateo Bridge, SE	2	132	0.91	5.3	1.2	0.55	0.49	0.92
4	Oyster Point Entrance	3	292	1.20	4.8	1.2	0.57	0.45	3.05
5	Army Street pier	13	261	1.11	3.9	1.3	0.57	0.44	5.34
6	Alameda shoreline	3	179	0.58	4.2	1.2	0.57	0.49	0.87
7	Oakland Outer Harbor	4	232	1.02	4.5	1.2	0.57	0.42	2.52
8	Berkeley Marina	3	183	0.89	5.0	1.2	0.57	0.43	1.74
9	Richmond Longwharf	4	332	1.34	4.5	1.3	0.55	0.43	1.75
10	Larspur Channel	6	232	1.52	5.4	1.3	0.54	0.43	2.01
11	Rat Rock, China Camp	2	297	1.81	5.4	1.3	0.57	0.45	1.22
12	Pinole Point, East	4	30	0.87	7.2	0.3	0.48	0.19	0.23
13	Petaluma	2	233	1.77	5.3	1.2	0.55	0.48	0.88
14	Sonoma Creek mouth	2	209	1.84	5.1	1.3	0.56	0.47	1.02
15	Petaluma, East	4	224	1.53	5.2	1.3	0.56	0.44	1.48
16	Richardson Bay, Shallow	4	202	1.10	5.1	1.5	0.54	0.42	2.10
17	San Bruno shoal, mid-channel	10	247	1.54	4.9	1.3	0.52	0.41	2.50
Cores									
Richardson Bay, 0–148 cm		6	(TOC)[a]	Fig. 3	Fig. 3	Fig. 5a	Fig. 5c	Fig. 5d	Fig. 7c
San Pablo Bay, 0–239 cm		5	(TOC)[a]	Fig. 3	Fig. 3	Fig. 5e	Fig. 5g	Fig. 5h	Fig. 7d

[a] EOM = Extractable organic matter [μg/g dry weight]. For cores, TOC values were calculated. See Pereira et al. (1999).

[b] Sum of concentrations of terrigenous *n*-alkanes C_{25}, C_{27}, C_{29}, C_{31} [μg/g dry weight].

[c] CPI_{24-34}. Calculated according to the method of Cooper and Bray (1963): $1/2([(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})]+[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})])$.

[d] Biomarker ratios are defined in Table 2.

[e] Sum of 'combustion' PAH [μg/g dry weight] (see Prahl and Carpenter, 1983). Total is the same except this summation omits benz[e] pyrene (see also Hostettler et al., 1994).

samples (100 g for the surficial samples, 10–14 g for the core samples, air-dried and ground to pass a 32-mesh sieve) were extracted with dichloromethane on a wrist-action shaker. Sulfur was removed with HCl-activated copper. The extracts were then fractionated chromatographically on a silica gel and alumina column. Two fractions were collected: a hexane fraction containing aliphatic hydrocarbons, including *n*-alkanes, isoprenoids, and cyclic biomarkers; and, a 20 or 30% benzene in hexane fraction containing mainly polycyclic aromatic hydrocarbons (PAH). This paper is concerned primarily with the hexane fraction; analysis of the latter fraction is described in Pereira et al. (1999).

2.3. Gas chromatography and mass spectrometry

The extracts were analyzed by gas chromatography and gas chromatography/mass spectrometry (GCMS) as described elsewhere (Hostettler et al., 1989). The biomarkers were analysed by monitoring m/z 191 (hopanes) and 217 (steranes) using GC/MS Selected Ion Monitoring (SIM). Ratios of various compounds for the biomarker parameters (see Table 2 for definitions) were calculated using peak heights.

2.4. Age dating of cores

Depositional chronologies of the two cores are discussed in detail in Fuller et al. (1999), van Geen

Table 2
Biomarker ratios

Ratios	Parameter	Immature → mature
C_{27}: T_m/T_s[a]	Maturity indicator	Higher → lower[a]
C_{27}: $T_e/(T_s+T_m)$[b]	Indicates relative biogenic character	Higher → lower[b]
$\alpha\beta C_{31}$-hopane $S/(S+R)$[c]	Maturity indicator	0 → 0.6
$\alpha\alpha\alpha C_{29}$-sterane $S/(S+R)$[d]	Maturity indicator	0 → 0.5

[a] Seifert and Moldowan, 1978. See Fig. 5a and e, and Table 1. Range in this system: 4.8–0.30.
[b] See Fig. 5b and f. Range in this system: 2.4–0.12.
[c] Mackenzie (1984). See Fig. 5c and g, Table 1.
[d] Mackenzie et al., 1980. See Fig. 5a and h, and Table 1.

et al. (1999), and Pereira et al. (1999): calculations of sedimentation rate utilized radioisotope profiles of fallout nuclides (^{137}Cs, ^{239,240}Pu) as well as ^{210}Pb and ^{234}Th and a finite rate mixing model; the oldest sediments in the core were identified with ^{14}C AMS dates; ^{10}Be data were used as indicators of changes in erosion patterns from the watershed that preceded occurrence of detectable ^{210}Pb.

3. Results

3.1. Gas chromatography—hexane fraction (surface and cores)

Gas chromatograms of the hexane fraction of the surficial sediment samples and the upper horizons of the cores showed fairly uniform patterns of aliphatic hydrocarbons throughout the Bay. Fig. 2a is a chromatogram from the surficial horizon of the Richardson Bay core, and is typical of all but one (Pinole Point, #12) of the surficial sediments sampled in the study area. Two dominant features of the chromatogram are obvious: an *n*-alkane distribution containing an homologous series maximizing at *n*-C_{29} with $CPI_{24\text{-}34}$ values >4, indicative of terrigenous plant input, superimposed on a broad Unresolved Complex Mix (UCM). This pattern is very similar to the compound distributions reported by Wakeham (1996) in sediments near the mouth of the Danube River and other studies where input from industrialized urban areas is significant (Wade and Quinn, 1979; Barrick et al., 1980).

The *n*-alkanes in SFB sediments range from C_{13} to C_{38} or higher. However, C_{25} to C_{31} *n*-alkanes with a strong odd-over-even carbon number predominance (OEP) are by far the most prominent. Both total concentrations of terrigenous alkanes (C_{25}, C_{27}, C_{29}, and C_{31}, ΣC_{25-31}; Prahl and Carpenter, 1984) and Carbon Preference Indices, CPI_{24-34}, for all the sediment samples were calculated and are given in Table 1 (surficial) and Fig. 3 (cores). These *n*-alkanes, as noted above, are from vascular plants and so constitute a signature for terrigenous input. The Richardson Bay core has a fairly narrow range (0.90–1.6 μg/g dry weight) of ΣC_{25-31} concentrations throughout the entire length of the core, indicating a consistent rate of terrigenous input over time. The San Pablo Bay core, however, shows levels of terrigenous alkanes comparable to those in the Richardson Bay core only in the lower, older horizons of the core (0.72–1.6 μg/g) up to a depth of approximately 120 cm, and then a two- to three-fold increase in concentrations (2.2–3.2 μg/g) at around 1950, the depth of penetration of ^{137}Cs; these higher concentrations continue to the top of the core.

These ΣC_{25-31} profiles from the cores are similar in appearance to the Total Organic Carbon (TOC) profiles (TOC figure shown in Pereira et al., this volume). This similarity is particularly evident in the San Pablo Bay core, where a very high correlation ($R=0.97$) exists between $\Sigma C_{25\text{-}31}$ and TOC, indicating that terrigenous input is especially significant in San Pablo Bay. Similar results are reported in other river-fed estuarine systems like the Rhone Delta (Bouloubassi and Saliot, 1993) and the Columbia River drainage basin (Hedges and Prahl, 1993). This observation of correlation is also in agreement with

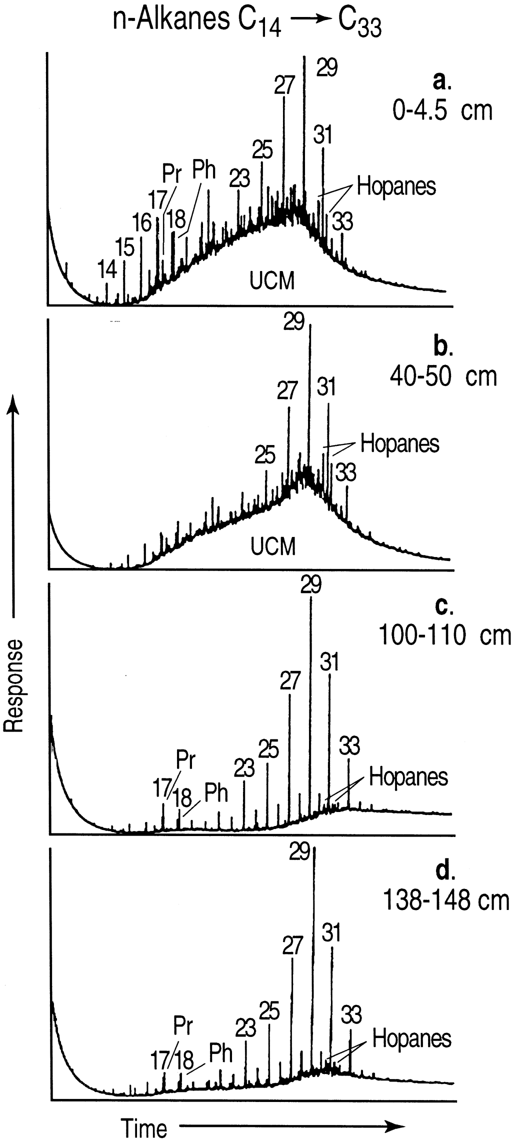

Fig. 2. Gas chromatograms of aliphatic hydrocarbons at four depths, Richardson Bay core. *n*-Alkanes are numbered 14–33, Pr = pristane; Ph = phytane; Hopanes = 17α(*H*),21β(*H*)-30-norhopane (αβ C_{29}) and 17α(*H*)21β(*H*)-hopane (αβ C_{30}); UCM = Unresolved Complex Mix.

Jassby et al. (1993) who demonstrated that the most important source of organic carbon to the northern reaches of SFB is riverine input. However, the two parameters do not show a correlation in San Pablo Bay ($R = 0.07$). This lack of correlation may be indicative of a greater mix of input sources, including anthropogenic contamination (Bouloubassi and Saliot, 1994) and marine input (Pereira et al., 1999).

The CPI_{24-34} values also show interesting trends. The surficial sediments have a range of 3.9–7.2 (Table 1), with nearly identical levels in South Bay (4.7–5.3) and San Pablo Bay (4.7–5.4, except for Pinole Point, 7.2), but somewhat lower levels in the more industrialized Central Bay (3.9–5.1). CPI values in the top horizons of the two cores (Fig. 3) are similar to the other surficial sediments. These values persist downcore to about 80 cm (RB92-3org) and 120 cm (SP90-8) but then increase to 6.6 and 7.9, respectively. There is one exception, the 50–60 cm horizon in RB92-3org where the value exhibits a sudden episodic increase. The higher values of CPI at depth in the cores, at 50–60 cm in RB92-3org, and at Pinole Point most likely represent more pristine terrigenous input. The sudden increase in the 50–60 cm horizon of RB92-3org may be indicative of high terrigenous input from flooding, possibly

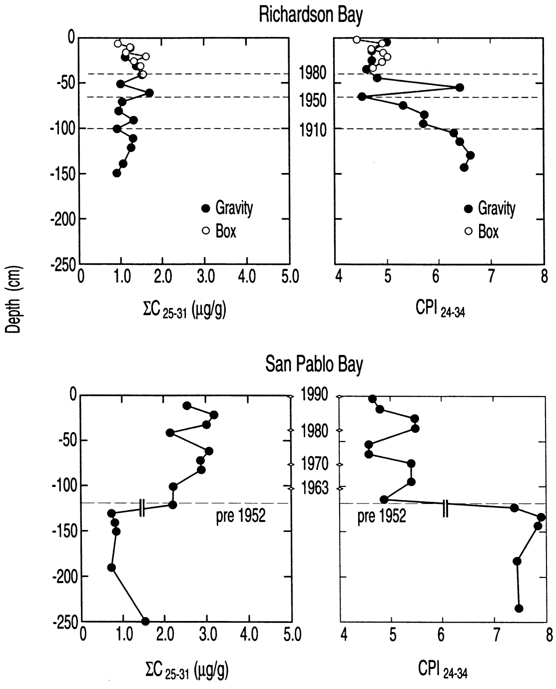

Fig. 3. Depth profiles of the (1) total concentration of the terrigenous alkanes, ΣC_{25-31}, *n*-C_{25}, C_{27}, C_{29}, and C_{31}; and (2) CPI_{24-34} from the Richardson Bay and San Pablo Bay cores. ‖ lines indicate depositional hiatus in SPB. Dates shown are the most recent date of deposition.

from the 1950s—the 1957–1958 winter season was one of the highest rainfall years in SF history and 1951–1952 and 1955–1956 also had winter months with very high rainfall (unpublished data, http://ggweather.com/sf/monthly.html). By contrast, the lower CPI values upcore may indicate an increasing input of anthropogenic hydrocarbons, possibly an admixture with fossil fuel *n*-alkanes which are characterized by no OEP (Wade and Quinn, 1979). Bacterial reworking of the complex anthropogenically-impacted sediments may also have an influence (Bouloubassi and Saliot, 1994).

Chromatograms in Fig. 2 also include low levels of a short-chain (C_{15}–C_{19}) suite of *n*-alkanes, indicative of autochthonous algal input (Peters and Moldowan, 1993). This feature diminishes downcore in the horizons shown in Fig. 2 compared to the C_{25-31} *n*-alkanes. The San Pablo Bay core and the surficial sediments also include an algal input (data not shown), although in varying amounts with no clearly discernible downcore or spatial patterns. The decreased short-chain alkanes below the surface in RB92-3org may reflect higher productivity in recent times in this area of the bay. However, high spatial and temporal variability in organic input throughout the Bay has already been noted (Canuel et al., 1995). It is also known that algal- or phytoplankton-derived *n*-alkanes are more subject to degradation in the water column and in the aerobic upper layer of the sediment than are the more refractory plantwax *n*-alkanes (Prahl and Carpenter, 1984). Jassby et al., 1993 have demonstrated that autochthonous primary production (mostly phytoplankton) is the main source of organic carbon in South SFB, but this conclusion is not reflected in the sediment record of this study. Therefore, the presence of this input source can be noted, but no conclusions can be drawn here as to its relative importance.

The second dominant feature of the gas chromatogram in Fig. 2 is the UCM—the chromatographically undifferented 'hump' that underlies most of the chromatogram. A UCM indicates petrogenic input and (or) biodegradation (Brassell and Eglinton, 1980). Its magnitude in this setting gives a qualitative indication of anthropogenic contamination. All the surficial sites but one (Pinole Point, #12), have chromatograms which contain a significant UCM. In contrast, RB92-3org contains the UCM down to about the 40–50 cm horizon, below which the hump diminishes sharply and disappears (Fig. 2). The San Pablo Bay core (not shown) shows a similar trend, although the transition point is deeper in the core, corresponding to a higher sedimentation rate in recent times.

The chromatograms in Fig. 2 also show two peaks on either side of *n*-C_{31} which are the two most abundant hopanes, $17\alpha(H),21\beta(H)$-30-norhopane (C_{29} hopane) and $17\alpha(H),21\beta(H)$-hopane (C_{30} hopane). These hopanes are two of the most recalcitrant organic compounds from petrogenic sources found in the environment; they predominate in the m/z 191 SIM profiles, Fig. 4, as discussed below. These hopanes are relatively prominent with respect to the terrigenous alkanes in all the surficial sediment samples (again, with the exception of site #12), and in the upper part of the core (Fig. 2a,b). However, they diminish significantly in the lower part of the core (Fig. 2c,d).

3.2. GC/MS of biomarkers (hopanes and steranes)

GC/MS SIM analysis of the hopanes and steranes provides more information on spatial and historical patterns. Fig. 4 shows SIM-based biomarker chromatograms of a typical surficial sediment (Fig. 4a, hopanes, and Fig. 4c, steranes) and a downcore horizon (Fig. 4b, hopanes, and Fig. 4d, steranes) from the Richardson Bay core. Chromatograms from the San Pablo Bay core are similar. The definitions of ratios of various constituents in the SIM profiles used for biomarker parameters are listed in Table 2; the values of these ratios are found in Table 1 (surficial sediments) or shown graphically in Fig. 5 (cores). The ratios T_m/T_s, $\alpha\beta$ C_{31}-hopane $S/(S+R)$, and $\alpha\alpha\alpha$ C_{29} sterane $S/(S+R)$ are standard geochemical maturity parameters; $T_e/(T_s+T_m)$ is more source-related and measures relative biogenic character. Other studies have used a different compound, the C_{30} hopene diploptene, to indicate biogenic character (e.g., Wakeham, 1996).

Throughout the Bay the biomarker chromatograms of the surficial sediments (again, with the exception of site #12) and those of the upper sections of the cores are quite uniform and similar to Fig. 4a and c; they include biomarkers that indicate

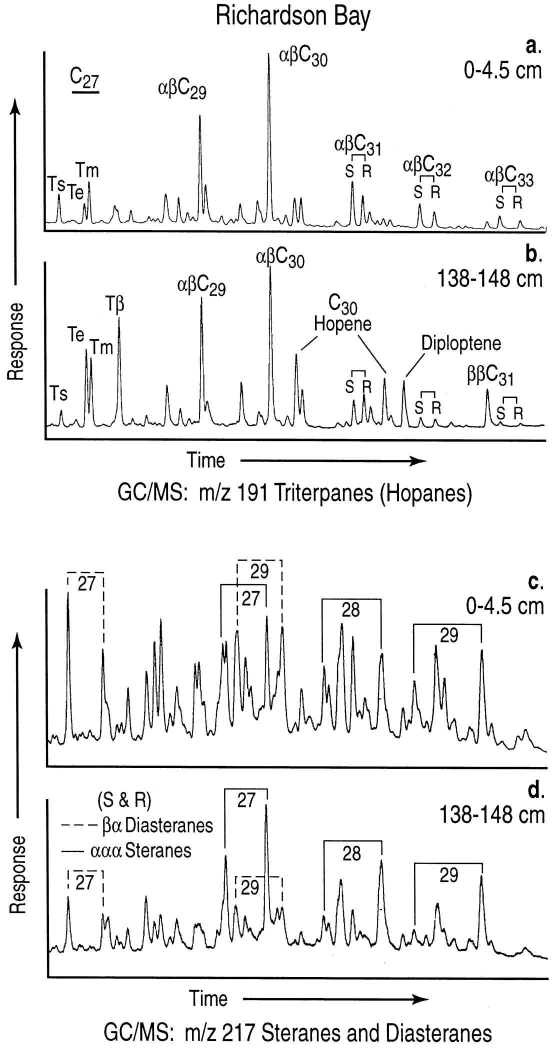

Fig. 4. Mass chromatograms of m/z 191 (hopanes) and 217 (steranes) from top and bottom horizons of Richardson Bay core. Peaks identified are—Hopanes: C_{27}: $T_s = 18\alpha(H)$-22,29,30-trisnorneohopane; $T_m = 17\alpha(H)$-22,29,30-trisnorhopane; $T_e =$ 22,29,30-trisnorhop-17(21)-ene; $T\beta = 17\beta(H)$-22,29,30-trisnorhopane; $\alpha\beta = 17\alpha(H),21\beta(H)$-hopane series; Diploptene $= 17\beta(H),21\beta(H)$-hop-22(29)-ene; $\beta\beta$ $C_{31} = 17\beta(H),21\beta(H)$-homohopane. Steranes: $\beta\alpha = 13\beta(H),17\alpha(H)$ diasterane series (20R and 20S epimers); $\alpha\alpha\alpha = 5\alpha(H),14\alpha(H),17\alpha(H)$ sterane series (20R and 20S epimers).

high maturity (Table 1, Fig. 5). The dominant hopanes all have the $17\alpha(H),21\beta(H)$ (that is, $\alpha\beta$) configuration, as opposed to the less stable natural $\beta\beta$ stereochemistry or the mono-unsaturated configuration present in immature biological precursors. At all the surficial sites (except #12) and the upper horizons of the cores, the C22 $S/(S+R)$ epimer ratios of $\alpha\beta$ C_{31} hopane have a narrow range, from 0.52–0.57, close to the value of 0.60 for full maturity. T_m/T_s values are closely clustered, from 1.1 to 1.6. T_s and T_m are strongly dominant over any other C_{27} trisnorhopanoids, which is reflected in the low

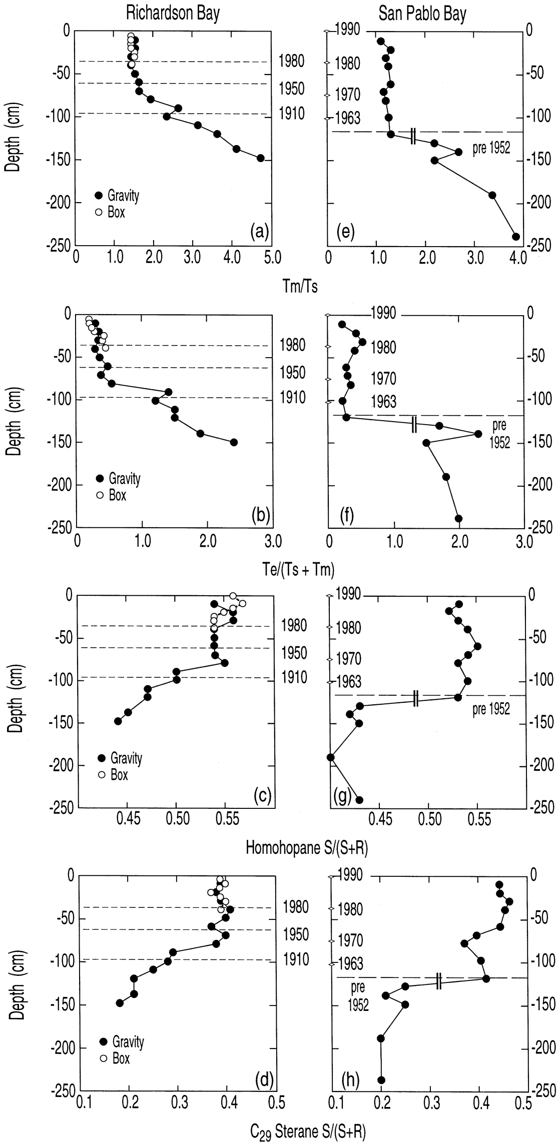

Fig. 5. Biomarker parameter profiles in the cores from Richardson Bay and San Pablo Bay. Ratios defined in text and Table 2. || lines indicate depositional hiatus in SPB. Dates shown are the most recent date of deposition.

values (0.20–0.53) of the biogenic trisnorhopene ratio $T_e/(T_s + T_m)$.

These characteristics are contrasted with those of the downcore horizons (e.g., Fig. 4b). These deeper deposits show a mixture of mature and immature constituents. The mature constituents gradually decrease, leaving more prominent the immature constituents, notably the C_{27} 17β(*H*)-trisnorhopane (T_β) and the C_{31} ββ-hopane, along with the mono-unsaturated hopenes—17β(*H*)-trisnorhopene (C_{27}, T_e) and several C_{30} hopenes including diploptene. Diploptene is a biogenic hopane, widely reported in marine environments like the Columbia River basin (Prahl and Carpenter, 1984), as well as in terrigenous soils that were former SFB wetlands (Pereira et al., 1997). The mass chromatogram in Fig. 4b shows the αβ C_{31} epimers and the trisnorhopanes, T_s and T_m, in distributions indicating lower maturity. The lower horizons from core RB92-3org have T_m/T_s values steadily increasing downcore, from 1.9 to 4.7, the C_{31} epimer ratio decreasing from 0.50 to 0.44, and the biogenic factor (T_e) ratio increasing from 0.54 to 2.4. The San Pablo Bay core exhibits similar trends. The anomalous sediment from surface site #12 (Table 1) contains hydrocarbons exhibiting low maturity similar to the downcore horizons, rather than the higher maturity parameters of the surface sediment samples.

The sterane chromatograms from the surficial sediment samples and upper levels of the cores (e.g., Fig. 4c) also indicate fairly mature constituents. The 5α(*H*),14α(*H*),17α(*H*) (that is, ααα) C_{29} $S/(S+R)$ epimer ratios range from 0.37 to 0.51 (near the equilibrium distribution of 0.50) and high levels of the mature βα-diasteranes are observed relative to ααα-steranes. The downcore horizons (e.g., Fig. 4d) are quite different. As with the hopanes, the steranes exhibit a greater prominence of the immature constituents. The 20*R* (biogenic configuration) epimers of the ααα-C_{27}, -C_{28}, and -C_{29} steranes strongly dominate over the 20*S* epimers (giving C_{29} $S/(S+R)$ ratios from 0.29 to 0.18, Fig. 5), and the mature βα-diasteranes are much less prominent than the ααα-steranes.

The downcore profiles of biomarker parameters differ between RB92-3org and SP90-8 (Fig. 5). For Richardson Bay sediment, all biomarker graphs (Fig. 5a–d) show a progressive change from bottom to top. In sediments deposited before about 1900 the immature biogenic background dominates. From the early 1900s to about the 1930s a transition occurs where the more mature components become prominent. After that time (at approximately 80 cm) to the present time, the pattern of mature constituents remains strongly dominant. In San Pablo Bay, in the lower part of the core the immature, biogenic hydrocarbons also give way upwards to the mature, anthropogenic biomarkers. However, this transition is very sharp at about 120 cm. Fuller et al. (1999) attribute the sharp transition of these and other properties at this horizon to an extended period of erosion. This conclusion is consistent with bathymetric data of Jaffe et al., 1998.

4. Discussion

The high degree of maturity of the biomarkers in the surficial sediment and the top levels of the SFB cores is uncharacteristic of pristine surficial estuarine sediment (Hostettler et al., 1989). Therefore, we consider these mature biomarkers to be derived from petroliferous sources. There are no reports of natural petroleum seeps in the SFB area, and no parameters in this report such as UCM or high maturity biomarkers at depth, which could indicate natural seeps. The parameters show no significant increase near the oil refineries around Richmond. The predominance of mature hydrocarbons is widespread throughout the Bay, so a single petroleum point source is unlikely. Therefore, it appears that this constituent maturity reflects an anthropogenic overprint on naturally occurring lower levels of immature background biogenic markers. The UCM observed in the gas chromatograms of the sediment extracts from these sites is also characteristic of weathered petrogenic input. CPI data also reflects an anthropogenic impact. An anthropogenic petroliferous origin is supported by work in sediments from similar systems, that is, highly urbanized estuarine or deltaic locations (Dastillung and Albrecht, 1976; Wade and Quinn, 1979; Barrick and Hedges, 1981; Hostettler et al., 1989; Lichtfouse et al., 1997). All the surficial sediment samples from SFB, with the exception of site #12 from Pinole Point, contained this high level of anthropogenic contamination. Site #12, where all the parameters indicate low maturity and low concentrations of organic constituents in general, has apparently not been subjected to the accumulation of anthropogenically modified sediments common to our other sites in the Bay. Comparative bathymetry studies in SFB (Jaffe et al., 1998) show that this site, unlike all the other surficial sites in our study area, is currently undergoing sedimentary erosion rather than deposition.

The timing of the gradual upcore transition in RB92-3org from primarily background biogenic constituents to a dominance of anthropogenic constituents corresponds to a change from the pre-industrial to the industrial age in the Bay area, from about 1900 to the 1930s. In San Pablo Bay the abrupt change in the biomarker constituents occurs only after the depositional hiatus documented in the dating study (Fuller et al., 1999), in the 1950s. The pattern of terrigenous input seen in the *n*-alkane profiles (Fig. 3) also indicates that the rate of deposition of terrigenous hydrocarbons in San Pablo Bay is two to three times greater after the hiatus than before, in contrast to Richardson Bay. TOC data (Pereira et al., 1999) show similar trends. RB92-3org shows a fairly constant rate of deposition throughout the core, with levels of input at the same concentra-

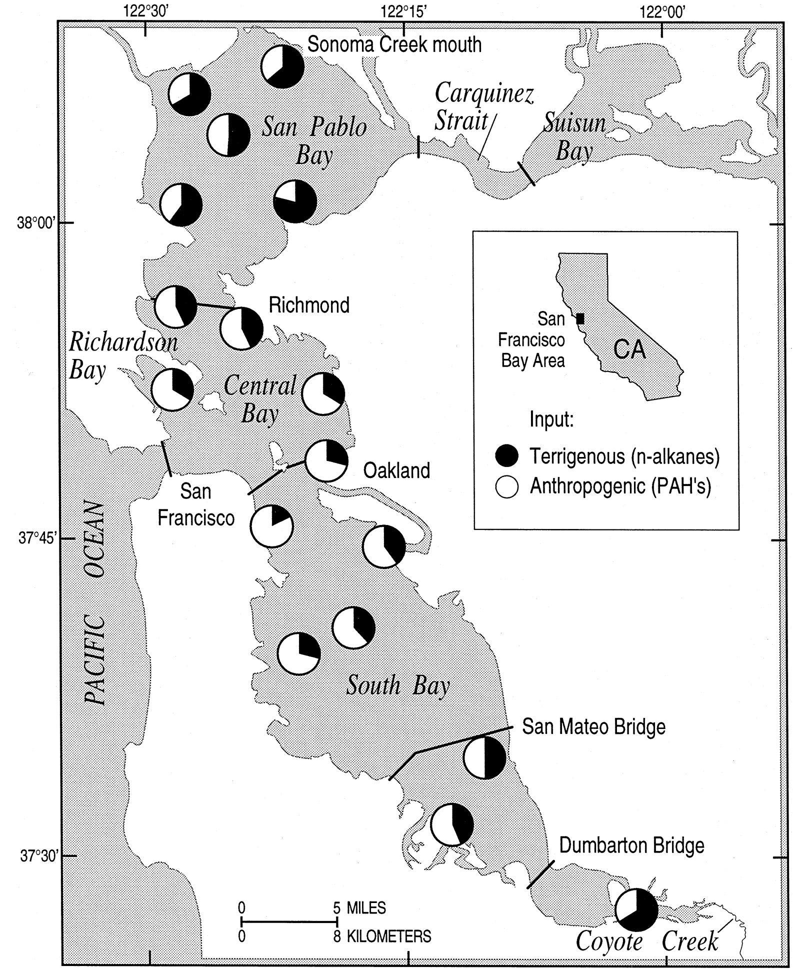

Fig. 6. Comparison of selected terrigenous and anthropogenic input signals in surficial sediments, San Francisco Bay.

tions as the lower section of the San Pablo Bay core. Modern sedimentation rates have been greater in San Pablo Bay after about 1950 (~ 4 cm/year) than in Richardson Bay (~ 0.9 cm/year). Between 1930 and 1950, the large water-diversion projects in the San Francisco Bay Delta significantly changed the fresh-water flow regimes into the Bay. Lower fresh water inflow from the Delta may have reduced the flushing of Bay sediments, and lengthened residence time for organic input in areas of net sediment deposition. One outcome could have been an increase in terrigenous organic matter inputs at sites of deposition in San Pablo Bay. The 1950s were also a time when agricultural activity around the Bay increased rapidly, which also could have increased the terrigenous organic input to San Pablo Bay. An alternative possibility is that debris from early hydraulic mining in the Sierra Nevada could have diluted the organic content in the lower core horizons, below the hiatus point. The difference in the trends in *n*-alkanes and TOC between the two bays may be due in part to the fact that Richardson Bay is near the Golden Gate, closer to the ocean, protected, and, therefore, not as affected by the changes in the Delta watershed as is San Pablo Bay. Overall, however, cores from both Bays record a transition from biogenic constituents in the pre-industrial period to anthropogenically contaminated sediments from the 1930s (Richardson Bay) or 1950s (San Pablo Bay) to the present time.

Finally, we examined the relative levels of anthropogenic vs. terrigenous input in the surficial sediments and in the two cores to determine where input sources were most prominent. Although the presence of specific marker compounds does not allow for a quantitative extrapolation to the amount of organic matter from that source, molecular tracers can provide a good qualitative measure for the input of organic matter from the biomarkers' established source (Brassell and Eglinton, 1986; Hedges and Prahl, 1993). In the surface sediments a comparison was made between two major source signals, namely the concentrations of the terrigenous *n*-alkanes (ΣC_{25-31}) and, from a parallel study (Hostettler et al., 1994), the anthropogenically-derived combustion PAHs (ΣCOMB; Table 1). This relative distribution is shown in Fig. 6. The anthropogenic influence is highest in the urbanized Central and South SFB and along the mid-bay channel. The terrigenous influence is higher in the less urbanized San Pablo Bay and the southernmost site in South Bay.

In the cores, similar trends come from (a) comparing the two major hopane biomarkers ($\alpha\beta$ C_{29} and $\alpha\beta$ C_{30}, representing anthropogenic input) with the C_{31} *n*-alkane (representing terrigenous input) from the gas chromatograms as discussed above with Fig. 2, and (b) comparing the sum of the concentrations of the combustion PAH (anthropogenic; data given in Pereira et al., 1999) with the sum of the concentrations of the terrigenous *n*-alkanes. In Richardson Bay (Fig. 7a,c) the upcore transition from background to anthropogenic prominence is seen up to the 1930s; however, after that there are significant variations. Although these variations may correspond to specific events, such as the changeover from coal to oil, the Great Depression, major flood events, or changing industrial patterns having to do with wars (Pereira et al., 1999), uncertainty in the dating in these substantially mixed sediments does not allow definitive conclusions. In San Pablo Bay (Fig. 7b,d),

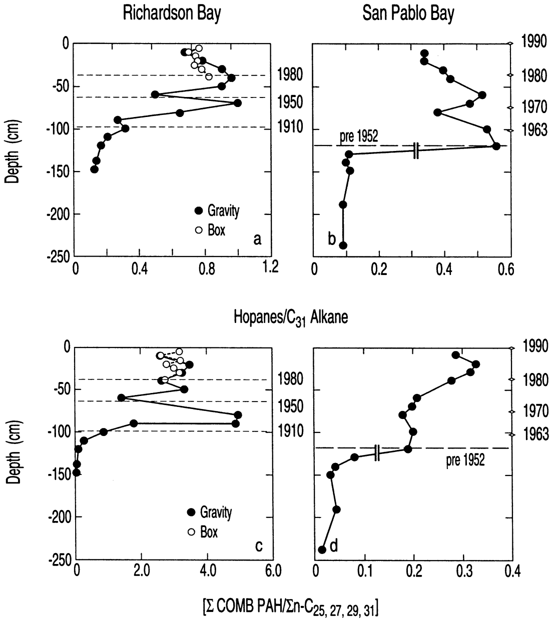

Fig. 7. Profiles of selected anthropogenic vs. terrigenous input signals in cores from Richardson Bay and San Pablo Bay. See Pereira et al. (this volume) for PAH data. || lines indicate depositional hiatus in SPB. Dates shown are the most recent date of deposition.

the lower horizons of the core show no anthropogenic (i.e., petrogenic) impact before about 1880, where the record moving upcore is interrupted by the hiatus. From the 1950s on, a similar though somewhat less pronounced pattern to that in Richardson Bay implies a similar impact of specific events. The generally higher levels of anthropogenic relative to terrigenous input in the Richardson Bay core vis-a-vis the San Pablo Bay core are in agreement with the trends seen in the surficial study, Fig. 6, and probably reflects the greater proximity of Richardson Bay to the urban center.

5. Conclusions

The dominant organic source signals in the surficial sediments of San Francisco Bay are: (1) the OEP *n*-alkanes, from vascular land plants and, therefore, a marker for terrigenous input; (2) mature hopane and sterane biomarkers, in this setting markers for anthropogenic petroliferous contaminant input; and (3) PAHs, primarily of a combustion origin and a marker of anthropogenic input. A comparison of representative members of these input signals (Fig. 6) shows that the anthropogenic signal dominates in the urbanized Central San Francisco Bay and the mid-Bay channel, and the terrigenous signal dominates in San Pablo Bay and the southernmost site in South Bay. In the historical record from two cores, one from Richardson Bay and one from San Pablo Bay, the main feature in the profiles of the biomarkers (Fig. 5) is the transition from the dominance of biogenic constituents in the lower sections of the cores to the dominance of anthropogenic hydrocarbons in the upper sections of the cores. This record indicates an anthropogenic overprint of contaminant input on naturally occurring lower levels of immature biogenic input, and corresponds to a transition from the pre-industrial to the industrial era in the San Francisco Bay area. The transition in Richardson Bay appears gradual, and input from the two sources reaches a relatively steady state by about the 1930s. The transition in San Pablo Bay is much more abrupt. The sedimentary record of this transition has a major disruption due to a change in sedimentation patterns in San Pablo Bay, where a prolonged period of erosion interrupts the sedimentary record. Dating of the core shows that sedimentary deposition resumed around the early 1950s. After the resumption of sedimentary deposition, concurrent with water diversion projects and more intense agricultural activity in the riverine/delta area impacting the northern reaches of SFB, inputs of terrigenous organic matter increased in San Pablo Bay. The levels of these hydrocarbons were greater than those observed in the ~1850–1880 period in San Pablo Bay, and also greater than those observed overall in Richardson Bay. All of these results show that the biomarker and aliphatic hydrocarbon profiles work well to track the historical record of natural and anthropogenically derived hydrocarbon inputs to sediments of San Francisco Bay.

Acknowledgements

The coring work presented in this paper is part of a multi-investigator project partially funded through a cooperative agreement between USGS and NOAA under Grant #1434-93-A-1016. The core from 1991 was collected by Roberto Anima and Ed Clifton of USGS. The 1992 core collection was led by R. Anima and A. van Geen. The authors gratefully acknowledge the assistance of Michelle Hornberger and Elizabeth Canuel in the collecting of sediment cores, Byron Richards and Francis Parcheso in the collection of surficial sediment samples, and Robert Rosenbauer and Jeanne Dileo for help with the graphics. This paper profited greatly from reviews by M. Moldowan, J. Hedges, P. Meyers, and an anonymous reviewer.

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