

Organic markers as source discriminants and sediment transport indicators in south San Francisco Bay, California

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Abstract—Sediment samples from nearshore sites in south San Francisco Bay and from streams flowing into that section of the Bay have been characterized in terms of their content of biogenic and anthropogenic molecular marker compounds. The distributions, input sources, and applicability of these compounds in determining sediment movement are discussed. By means of inspection and multivariate analysis, the compounds were grouped according to probable input sources and the sampling stations according to the relative importance of source contributions. A suite of polycyclic aromatic hydrocarbons (PAHs) dominated by pyrene, fluoranthene and phenanthrene, typical of estuarine environments worldwide, and suites of mature sterane and hopane biomarkers were found to be most suitable as background markers for the Bay. A homologous series of long-chain *n*-aldehydes (C_{12} – C_{32}) with a strong even-over-odd carbon number dominance in the higher molecular weight range and the ubiquitous *n*-alkanes (n - C_{24} – C_{34}) with a strong odd-over-even carbon number dominance were utilized as terrigenous markers. Several ratios of these terrigenous and Bay markers were calculated for each station. These ratios and the statistical indicators from the multivariate analysis point toward a strong terrigenous signal in the terminus of South Bay and indicate net directional movement of recently introduced sediment where nontidal currents had been considered to be minimal or nonexistent and tidal currents had been assumed to be dominant.

INTRODUCTION

SAN FRANCISCO BAY, which receives drainage from 40% of the land area of California, is subjected to vast inputs of organic chemicals in largely unknown amounts from land, street and river runoff, industrial, agricultural and sewage discharges, atmospheric fallout, shipping traffic, and other anthropogenic sources (NICHOLS *et al.*, 1986). The Bay has not been as thoroughly investigated in terms of organic components as many other estuaries in the United States (PHILLIPS, 1987). Local stream inputs of chlorinated hydrocarbons (LAW and GOERLITZ, 1974), the distribution of "total hydrocarbons" (GUARD *et al.*, 1983), and the occurrence of *n*-alkanes in Bay sediments (KVENVOLDEN, 1962) have been considered. SPIES *et al.* (1987) and CHAPMAN *et al.* (1987) demonstrated that sediments in several localities in the Bay reflect anthropogenic introduction of organic contaminants, specifically polycyclic aromatic hydrocarbons (PAHs), chlorinated hydrocarbons, and polychlorinated biphenyls (PCBs). These contaminants appear to adversely affect at least one species of fish in the Bay (SPIES *et al.*, 1985). The sources of organic components are largely unknown, and rigorous separation of natural from anthropogenic components have not been undertaken.

It has long been recognized that one way to investigate the geochemical setting and/or history of an estuarine environment is through its sedimentary record (WADE and QUINN, 1979; PRAHL, 1985; READMAN *et al.*, 1986). For example, understanding the origin of recent sediments and their movement within an estuary may improve understanding of the fate and distributions of many important anthropogenic contaminants. However, processes determining the disposition of sediments in an estuary may be complex. Sediments at any specific locality can originate from a variety of sources,

and net directional movement of sediments may be influenced by complex tidal and nontidal hydrodynamic processes.

The origin and movement of sediments in San Francisco Bay are poorly known (NICHOLS *et al.*, 1986). Homogenous minerology precludes the use of inorganic markers in studying the disposition of sediments in South Bay (SERNE and MERCER, 1975; LUOMA *et al.*, unpubl. data). Hydrodynamic influences on sediment movement at specific localities are poorly understood in general, and understanding is especially deficient in the semi-enclosed reach near the South Bay terminus where large inputs of anthropogenic contaminants occur.

This present study was undertaken primarily as a preliminary investigation of selected categories of organic constituents, mainly hydrocarbons, including biomarkers and other biogenic lipids, in surficial sediments from south San Francisco Bay. The sampling was concentrated around a small perennial stream that discharges into the reach at the south terminus of the Bay, adjacent to an intertidal sewage outfall. Our objectives included characterization of sediment constituents from estuarine, terrigenous (plant), and anthropogenic sources and assessment of the use of hydrocarbon markers for such sources in this area. The suitability of these markers for determining the origin and net movement of sediment in this South Bay locality was then investigated. Results were compared to an earlier study in the same locality where the distribution of trace metals originating from the sewage treatment plant (THOMSON *et al.*, 1984) showed a southerly bias despite the fact that nontidal currents in this area have been considered to be weak or nonexistent (CONOMOS, 1981).

Figure 1 shows the primary study area. Seven intertidal sites were sampled in South Bay, six (#2–7) in the terminus reach and one in central South Bay, away from local stream

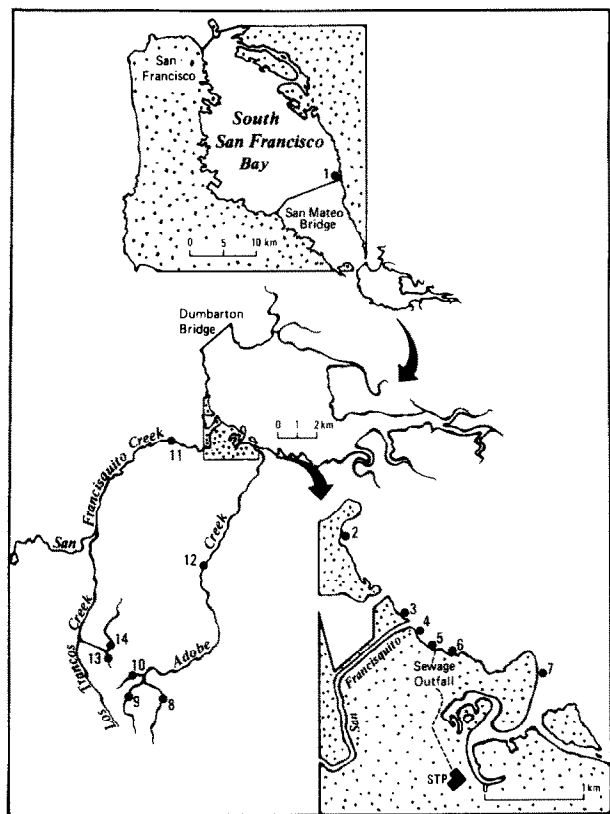


FIG. 1. Location of sampling stations in south part of San Francisco Bay and streams flowing into it.

inputs (#1). Table 1 lists their specific locations. Of particular interest were trends in the distributions of hydrocarbons to the north and south of San Francisquito Creek where substantial terrigenous (plant) input from the creek flow was expected, and to the north and south of the sewage outfall from the sewage treatment plant (STP) where we wanted to identify any organic input that might correlate with the high input of the trace metals Cu and Ag found by THOMSON *et al.* (1984). In order to identify terrigenous plant input more clearly, a second set of samples (#8–14) was taken from beds of streams flowing into this area.

EXPERIMENTAL METHODS

Methods used in this study focused on the unbound organic constituents that are extractable with dichloromethane. The extracts of the Bay sediments were separated into three fractions and the extracts of the upstream sediments into six fractions in order of increasing polarity using liquid chromatography (see below). The larger number of fractions in the upstream samples resulted from a sub-fractionation to obtain a cleaner class separation of constituents. The hexane fraction contains aliphatic hydrocarbons, including several suites of biomarkers, which are "molecular fossils" of natural products present in the sediments. The benzene fraction(s) contains aromatic hydrocarbons, PAHs, and possible S- or O-containing molecules, including molecules with a carbonyl functional group (aldehydes and possible

ketones). The methanol fraction contains the most polar constituents, that is, the more polar N-, S-, O-containing compounds. The hexane and benzene eluates were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) to identify constituents; the methanol eluates were only weighed. The chromatograms of the fractions were analyzed by visual inspection and by multivariate analysis in order to determine how individual and groups of compounds varied with respect to each other. Wherever possible, the input source of the constituents was identified, and then ratios of representative compounds from terrigenous and Bay input were used to indicate sediment transport.

Sample collection

Surficial sediment samples from 14 sites were collected by spooning the wet sediment into clean aluminum cans. Seven samples (#1–7) from along the South Bay intertidal perimeter were taken in April 1986, just after the end of the rainy season, and seven samples (#8–14) were obtained from beds of streams flowing into this area of the Bay (see Fig. 1 and Table 1) during the dry summer season of the following year. Because of seasonal lack of water flow some of the upstream samples were only moist. The Bay samples were mainly fine silt and sand, and the upstream samples fine sand and gravel. Five of the seven upstream samples (#8, 9, 10, 13 and 14) were collected in the hills above any urban influence; two samples (#11 and 12) were collected from near-urban areas where local urban runoff would be expected. The samples were frozen as soon as possible after collection and then freeze-dried to remove water.

Sample fractionation

One hundred grams (from Bay sites) or 200 to 300 g (from upstream sites) were broken up to approximately 30 mesh, then placed in a bottle and extracted serially with dichloromethane (DCM) on a wrist-action shaker: 200 ml for 2 h, 100 ml for 2 h, then washed with 100 ml for 15 min. Each time, the bottles were centrifuged for 5 min at 1500 rpm and the supernatant decanted and filtered through glass wool. Each total extract was evaporated to 5 to 10 ml on a rotary evaporator. Elemental sulfur was removed by filtering the extract through HCl-activated copper powder. Moderate amounts of sulfur were observed in the Bay samples, and almost none in the upstream samples. The solvent of the sulfur-free eluate (SFE) was exchanged for 5 ml hexane, and the SFE was then applied to a column layered with 5 g and 2.5 g activated silica gel (Davidson Nos. 923 and 62, respectively) and 2.5 g deactivated (5% water) alumina, all in hexane. The SFE flask was further rinsed by the sequential elution solvents. Two fractionation procedures were used: for the Bay sediments (#1–7), three solvents, hexane, benzene and methanol, were used serially to elute the constituents, and three corresponding fractions (H, B and M) were collected; for the upstream samples (#8–14), the solvents used were hexane, then 20, 40 and 60% benzene in hexane, then benzene and methanol, and six corresponding fractions were collected. Aliquots (50 μ l from the 5–10 ml volume) of the SFE and of the three or six fractions were removed for weight percentage calculations. Weights are given in Table 1 (weights for the upstream 20, 40, 60 and 100% benzene fractions are combined). A method blank was carried through each extraction procedure. The hexane and the benzene fractions, particularly the 20% and 60% benzene for the upstream samples, were examined by GC and GC/MS.

Gas chromatography and mass spectrometry

Gas chromatography of the fractions was done on a Varian Model 3700 Gas Chromatograph¹ using a 30 m $\times$ 0.3 mm DB-1 bonded phase, fused silica capillary column with flame ionization detection (FID). Conditions were: column temperatures, 90°C for 3 min followed by 4°C/min temperature increase to 310°C and held for 20 min; injection port and detector temperatures, 300°C; column pressure, 10 psi helium; splitless injection. Quantitation of *n*-alkanes, isoprenoid hydrocarbons, and PAHs was carried out by GC using external standards. GC/MS was done on a Hewlett-Packard Model 5995A GC/MS using a 30 m $\times$ 0.3 mm DB-5 bonded phase, fused silica capillary column, also by splitless injection. Identification of

¹ The use of trade names here and elsewhere in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 1. Geochemical Analyses

Station	Location	EOM ^a		Fractions, % EOM		[ΣPAH] ^b (ppb)	ΣC ₂₅₋₃₁ ^h	CPI ^c		ald-C ₃₀ Fluoranthene	Cmax ^d		Σ n-Alk ^e Σ n-Ald
		(μg/g)	H(%)	B(%) ^f	M(%)			TOC ^g	n-Alk		n-Ald	n-Alk	
South Bay Samples:													
1	San Mateo Bridge	160	19	30	48	0.80	46	4.8	-	0.25	29	30	8.4
2	University Ave. site	405	20	15	48	1.17	152	6.2	-	0.55	29	30	4.7
3	100 m. N. of San Francisco Cr.	222	32	27	36	1.13	181	5.6	4.1	0.88	29	30	2.9
4	100 m. S. of San Francisco Cr.	212	25	25	43	0.80	441	9.8	6.8	1.79	29	30	3.9
5	100 m. N. of sewage outfall	456	29	19	39	1.04	314	7.2	-	0.41	29	30	7.9
6	200 m. S. of sewage outfall	262	37	25	33	1.18	217	5.2	-	0.81	29	30	5.6
7	1 km. S. of sewage outfall	197	34	25	35	0.83	204	7.4	-	0.73	29	30	4.0
Upstream Samples:													
8	Adobe Cr., East fork	26	8	11	78	0.29	267	11.7	4.7	34	29	30(28)	4.7
9	Adobe Cr., middle fork	28	24	25	46	0.23	245	8.4	4.4	40	29	30(28)	7.4
10	Adobe Cr., Bunny Cr. fork	59	27	31	29	0.31	718	10.6	5.7	72	29	30	6.1
11	San Francisco Cr., URBAN	76	28	25	33	-	-	3.1	6.3	1.4	29	28	7.8
12	Adobe Creek, URBAN	358	35	29	20	0.36	1440	5.8	9.9	1.5	29	30	2.9
13	Los Trancos Cr., Foothill Pk	82	10	23	48	-	50	11.8	6.6	22	29	28	3.8
14	Los Trancos Cr., Foothill Pk	47	22	38	34	-	-	12.5	7.3	34	29	28(26)	3.3

^a EOM = Extractable Organic Material; μg/g = μg of fraction/g of dry sediment^e Sum of n-alkanes C_{28,29,30,31,32}; sum of n-aldehydes C_{22,24,26,28,30,32}; ratio of peak areas^b Sum of "combustion" PAHs^f Benzene: South Bay samples = fraction B; Upstream samples = Σ20,40,60,80,100% benzene eluates

$$CPI = \frac{1}{2} \left[\frac{\sum_{n=24}^{32} \text{evens} + \sum_{n=26}^{34} \text{odds}}{\sum_{n=25}^{33} \text{odds}} \right]^{-1/n}, \text{ where } n = 2 \text{ for aldehydes and } 1 \text{ for alkanes}$$

^d Carbon number of most abundant member of series; () refers to second most abundant if very close^g TOC = Total Organic Carbon^h Sum of n-alkanes C_{25,27,29,31} normalized to TOC, μg/g OC

compounds was accomplished by comparison of obtained spectra with archived and literature spectra, and, in most cases, was verified by comparison with known compounds. In the case of the *n*-aldehydes, only the lower molecular weight homologs were available as standards; therefore, for the higher *n*-aldehyde homologs, literature spectra were used (HELLER and MILNE, 1978), as well as retention time extrapolation and molecular ions. Calculations of the Carbon Preference Index (CPI, defined below and in Table 1) for *n*-alkanes were carried out using concentrations. However, when the calculations were repeated using peak areas only, the two values were almost identical, differing by less than one percent. CPIs for the *n*-aldehyde suite, where no standards were available, were calculated using peak areas and an inverted form of the formula for *n*-alkanes (Table 1). The aldehyde CPIs were calculated for all upstream samples, but only for two Bay samples because of interfering peaks in the latter case. The two Bay values are considered the best estimate. Biomarker identifications were made as in previous studies (KVENVOLDEN *et al.*, 1987). Selected-Ion-Monitoring (SIM) was done on the hexane fractions, monitoring *m/z* 191 for terpanes and triterpanes, 217 for steranes, and 57 for alkanes, with dwell times of 600, 600 and 10 msec, respectively. Two temperature programs were used: 1) injection at 60°C, fast ramp to 90°C, then 6°/min to 300°C, holding for 10 min; and 2) injection at 150°C, fast ramp to 200°C, then 1°/min to 300°C.

Multivariate analysis

After the chromatography, the GC areas of the major peaks of each of the Bay (#1–7) and the upstream (#8–14) hexane fractions and the Bay benzene fractions were placed into three respective data matrices for statistical analysis (for relevant discussions on the use of multivariate analysis in geochemical studies, see ØYGARD *et al.*, 1984; DAVIS, 1986; SHAW and JOHNS, 1986; ZUMBERGE, 1987). The data matrix for the benzene fraction of the Bay samples consisted of 32 compounds (known PAHs and unknowns that appear most frequently in the samples). Initially, Q mode factor analysis was used with cosine theta as the similarity index. The objective of Q mode analysis is to determine the relationships between sample sites. Then R mode factor analysis was done with correlation coefficients used as the similarity index. The objective of R mode analysis is to determine the relationships between variables (here, compounds). In both types of analysis, Varimax Rotation was used to optimize the results. The "composition" of a factor is obtained from the factor loadings in R mode and from the factor scores in Q mode. A high factor loading at a site means that a large amount of the total information for that site is explained by that factor. In quantitative terms, the square of the factor loading times 100 gives the percentage of the total information at that site explained by that factor.

The data matrix for the hexane fractions of the seven Bay samples consisted of 42 compounds, and that of the seven upstream samples, 26 compounds (*n*-alkanes, isoprenoids and unknowns which appear most frequently in these fractions). As above, Q mode analysis was used with cosine theta as the similarity index. Because >95% of the total information in both sets of hexane fractions was explained by one factor using unrotated principal components, Varimax Rotation was not applied.

Geochemical ratios

The following calculations were made to show relationships among recent terrigenous (plant) input and background Bay constituents of the sediments:

1. Carbon Preference Index, a measure of the ratio of odd- to even-carbon number *n*-alkanes, calculated according to the method of COOPER and BRAY (1963), using concentrations:

$$\text{CPI} = \frac{1}{2} \left(\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right)$$

2. From the benzene fraction, using GC total areas:

$$\frac{[\text{Major terrestrial aldehyde}]}{[\text{Major background PAH}]} = \frac{[n\text{-}C_{30} \text{ aldehyde}]}{[\text{Fluoranthene}]}$$

3. From the hexane fraction, using GC/MS SIM areas:

$$\frac{[\text{Major terrestrial } n\text{-alkane, } m/z \text{ 57}]}{[\text{Major background biomarker, } m/z \text{ 191}]} = \frac{[n\text{-}C_{29}]}{[\alpha, \beta\text{-Hopane, } C_{30}]}$$

RESULTS AND DISCUSSION

Chromatography

The hexane and benzene fractions were examined in detail by GC and GC/MS. The following sections outline the types of compounds found in the two fractions and the geochemical information that was obtained from them.

Hexane fraction. Figure 2 shows chromatograms of a typical Bay and a pristine upstream hexane extract, and Table 2 lists the identifications of constituents of this and later fractions. All of the hexane fractions are dominated by the C_{24} – C_{34} *n*-alkanes with a strong odd-over-even carbon number predominance, giving high CPI values (see Table 1). Values for CPI can theoretically range from about 20 down to 1 and even lower, with the high values representing distributions of original unaltered plant waxes, and 1 (no odd or even preference) representing a mixture that has been substantially modified, especially by time and temperature as, for example, in oils and other petroleum products (HUNT, 1979). Intermediate values represent intermediate modifications or, in the case of recent sediments, where catagenesis cannot have occurred, possible dilution with anthropogenic (petroleum)

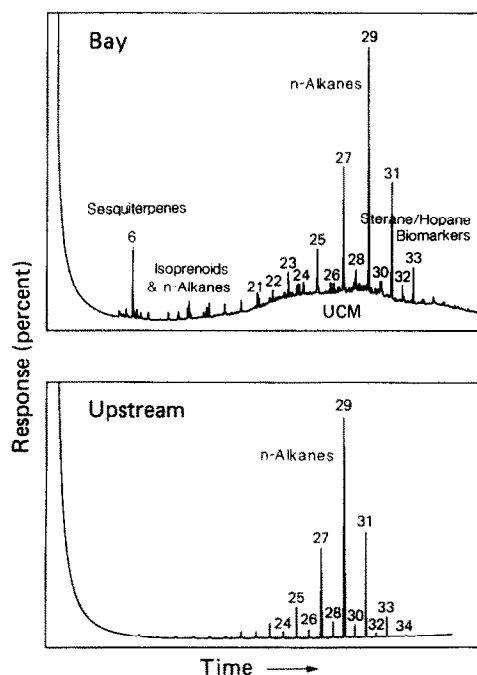


FIG. 2. Gas chromatograms of hexane fractions of typical Bay and Upstream (pristine) samples. Numbers 21–34 are *n*-alkanes; 6 is a sesquiterpene as shown in Table 2, Aliphatic hydrocarbons.

Table 2. Identification of fraction constituents (see figs. 2,3,5, and 6)

Peak	Compound
Polycyclic aromatic hydrocarbons (PAH's)	
a	Biphenyl
b	C ₂ -naphthalene
c	3-Methylbiphenyl
d	2-Methylbiphenyl
e	Cadalene
f	Phenanthrene
g	Fluoranthene
h	Pyrene
i	Benanthracene
j	Chrysene
k	Benzo(b) and (k) fluoranthenes
l	Benzo(e)pyrene
m	Benzo(a)pyrene
n	Perylene
o	Indeno(1,2,3-cd)pyrene
p	Benzo(ghi)perylene
q	Coronene
Aliphatic and partially aromatized hydrocarbons	
n#	n-alkane of # carbon chain length
i#	isoprenoid of # carbon atoms
Pr	Pristane (i19)
Ph	Phytane (i20)
1-8	Major sesquiterpenoid hydrocarbon isomers, MW 204
A-D	Major sesquiterpenoid hydrocarbon isomers, MW 202
	A. Cuparene
	B. Calamanene
	C. Unknown
	D. 5,6,7,8-Tetrahydrocadalene
Aldehydes	
a#	n-aldehyde of # carbon chain length
Unknowns	
x#	Unknown, # = base peak on MS
u	Unknown, not relevant

contaminants (WADE and QUINN, 1979). The CPI for the *n*-alkanes can therefore be viewed in our limited system as an approximate measure of the balance between recent terrigenous and contaminant contributions to the sediment.

Although the lower molecular weight *n*-alkanes and isoprenoids are present in Bay sediment fractions, they are present in significantly lower concentrations than are the higher molecular weight *n*-alkanes. These low molecular weight hydrocarbons could have a biogenic or anthropogenic (fossil fuel) source. The minor amount of the isoprenoid pristane that is present suggests little or no zooplankton contribution (BOEHM, 1984). Low *n*-C₁₅ and *n*-C₁₇ abundances also indicate little marine phytoplankton or freshwater algal input (WADE and QUINN, 1979). These small amounts of lower molecular weight hydrocarbons seem much more likely to be artifacts of petroleum contamination, especially in view of the other petroleum markers discussed below. There is, however, a possibility that some preferential degradation of the lower molecular weight *n*-alkanes is occurring and thus contributing to an apparent enhancement of the amount of

the higher molecular weight terrigenous contribution (PRAHL *et al.*, 1980; BRASSELL *et al.*, 1983).

A series of several sesquiterpenes (C₁₅) is present in the Bay samples and, in lower concentrations, in the upstream samples. Because many sesquiterpenes occur in the essential oils of higher plants, and therefore are of terrigenous origin (SIMONEIT and MAZUREK, 1982), it was of interest to further identify the compounds. The C₁₅ compounds are found in both the hexane and benzene fractions, distributed according to their degree of aromaticity; they are all discussed in this section for continuity. Figure 3 shows these early-eluting compounds on chromatograms from the GC/MS of typical hexane and benzene fractions. Three groups of sesquiterpenes, categorized by molecular weight, are seen: eight cycloalkene isomers, nos. 1-8 in Fig. 3, molecular weight 204; four partially aromatized isomers, A-D, molecular weight 202; and one fully aromatic compound, cadalene (e) (structure I in Appendix 1), molecular weight 198. The mass spectra of all the sesquiterpenes are given in Appendix 2. Only cadalene and cuparene (A) (II in Appendix 1), a constituent of a higher plant resin (GRANTHAM and DOUGLAS, 1980), could be positively identified by comparison with authentic standards. Two of the remaining molecular weight 202 isomers, discussed below, are tentatively identified by comparison with literature spectra, and the remaining sesquiterpenes could not be unambiguously identified without authentic standards.

The Bay samples (#1-7) contained more of the cycloalkene isomers (MW 204) than the aromatic (MW 202 and 198) sesquiterpenes, and the upstream samples (#8-14) contained more of the aromatic sesquiterpenes, especially cadalene. Among all the samples there is one dominant cycloalkene (6), seven minor isomers (1-5, 7, 8), and traces of other isomers not shown. The mass spectra of the cycloalkene isomers all show molecular ions of *m/z* 204, several (1, 3, 5, 6 and 7) with major ions at 161 and 189. The spectra of these are similar, but not clearly identical, to literature spectra of sesquiterpenoid cycloalkenes like longifolene (III in Appendix 1; PHILP, 1985) or members of the cadinene family (IV in Appendix 1; ALBAIGES *et al.*, 1984a). The cadinene family of compounds, with two double bonds endo- or exo- to the bicyclic system, has many naturally occurring isomers. The presence of cadinene-type sesquiterpenoids in our sediments is further indicated by the presence of their partially and fully aromatized counterparts, B, D and e, for which they are the reported precursors (SIMONEIT and MAZUREK, 1982). Cadinenes are easily degraded, and a suggested degradation pathway leads first to the partially aromatized isomers, calamanene (B) (V in Appendix 1), and 5,6,7,8-tetrahydrocadalene (D) (VI in Appendix 1), and then to the fully aromatized cadalene (e) (I in Appendix 1), all of which are seen in the benzene fraction of some of the upstream samples.

Interpretation of the distributions of these compounds is not clear-cut. For example, the dominant cycloalkene member (6) shows a maximum concentration in the Bay at site #4, south of San Francisco Creek (Fig. 3), but it is not highly concentrated upstream. The observation that the more reduced members of the cadinene family dominate in Bay sediments, whereas the partially and fully aromatized members are seen upstream, is contrary to the simple precursor-product relation described above. Differing sedimentary en-

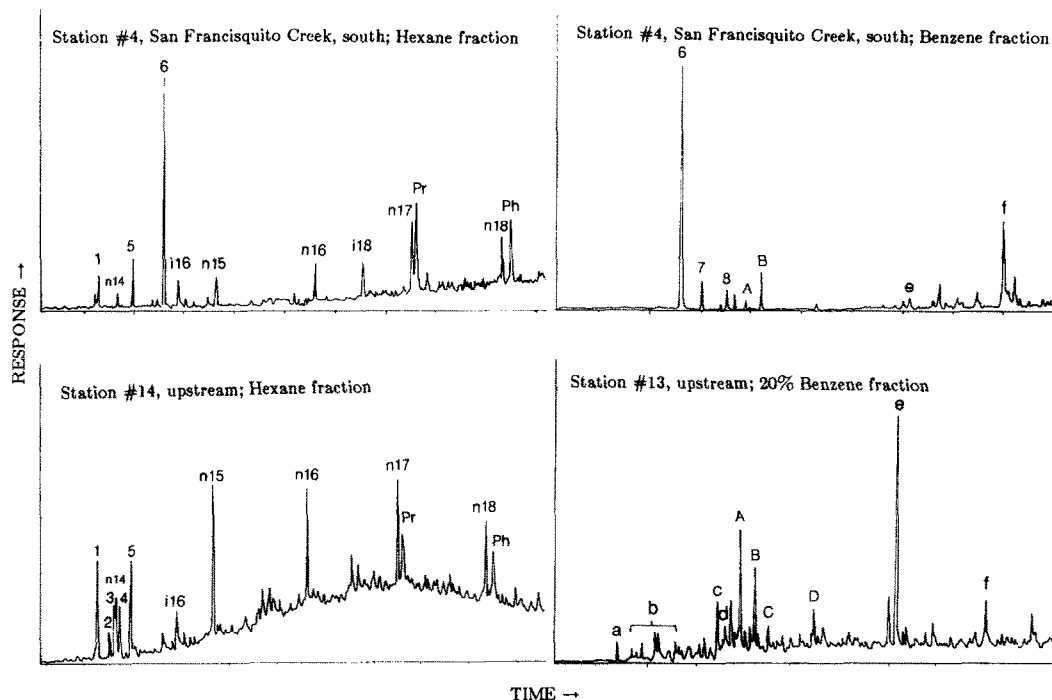


FIG. 3. Sesquiterpenes from mass chromatograms of representative hexane and benzene fractions. See Table 2 for identifications.

vironments (*i.e.*, reducing or oxidizing) or the seasonality of the sediment collection could explain these results. SIMONEIT (1986), in studying analogous diterpenoid systems, has noted that more reducing environmental conditions, such as we have in the Bay, favor preservation of the more saturated members; and more oxidizing conditions, as in our upstream samples, favor the more aromatized analogs; and notes that seasonality affects concentrations (SIMONEIT and MAZUREK, 1982).

Although these compounds are most likely derived from resinous higher plants and therefore are terrigenous markers, their relative lability limits their usefulness for this study. Further work is necessary to determine the exact plant origin of these sesquiterpenes and, if standards are available, their structures and their interactions.

A significant Unresolved Complex Mixture (UCM) is also present in the hexane fractions of the Bay samples, but is absent in the upstream samples collected away from urban input. The UCM is a mixture of chromatographically unresolvable components seen as a "hump" in the chromatogram (Fig. 2). It is usually considered indicative of petroleum contamination or biodegradation (BRASSELL and EGLINTON, 1980).

The chromatograms of the most pristine upstream sediment hexane fractions are considerably simpler than those of the Bay samples, showing only the *n*-alkanes with a high CPI, no UCM, and only minimal sterane and hopane biomarkers (see below). This observation is not surprising, but because one of the purposes of this work is to differentiate different types of input to the Bay sediments, it is important in distinguishing terrigenous input.

Biomarkers. The hexane extracts were also examined for sterane and hopane biomarkers. Figure 4 gives the biomarker

mass chromatograms of a representative Bay sample; all the Bay samples and the two urban stream samples are similar. The five non-urban upstream samples show the same distributions but with much lower amounts. In contrast to the *n*-alkanes (m/z 57), which clearly indicate very recent terrigenous sources because of their strong odd-even predominance, the steranes (m/z 217) and hopanes (m/z 191) show the complex signature of mature or highly reworked constituents. The 17 α (H),21 β (H)-hopane (C_{30}), especially, is the mature end-member of the naturally occurring 17 β (H),21 β (H)-ho-

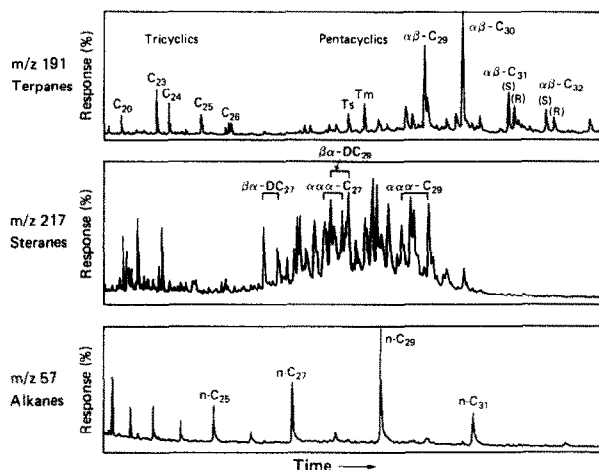


FIG. 4. Chromatograms, GC/MS SIM, of biomarkers. For Terpanes, $\alpha\beta$ refers to compounds in the 17 α (H),21 β (H)-hopane series; for Steranes, $\alpha\alpha\alpha$ and $\beta\alpha\alpha$ refer to compounds in the 5 α (H),14 α (H),17 α (H)-cholestane and 13 β (H),17 α (H)-diacholestane series, respectively.

pane, as are the $17\alpha(H),21\beta(H)$ -30-homohopanes with their C22-S/R-isomer ratio of 1.6 (ENSMINGER *et al.*, 1974). The steranes have a high diasterane content and the complex equilibrium mixture of mature isomers (BRASSELL and EGLINTON, 1980). Because of the maturity of these two latter signatures and their consistency in the Bay samples, and because the pristine upstream samples show minimal amounts of these biomarkers, we consider the terpanes and steranes to be background for the Bay, most likely from anthropogenic petroleum contamination. An anthropogenic petroliferous origin is supported by work in other systems (BRASSELL and EGLINTON, 1980; FARRAN *et al.*, 1987; VENKATESAN *et al.*, 1980). Contrasting the SIM response of the dominant *n*-alkane, as a terrigenous marker, to that of the dominant hopane, as Bay background, enables us to compare terrigenous input to background Bay input (Table 1).

Benzene fraction. Gas chromatograms of all of the Bay benzene fractions are shown in Fig. 5, and identifications are given in Table 2. The sesquiterpenes found here have been discussed with their counterparts in the section on the hexane fraction. In the Bay samples, two major suites of components are observed. The first is a suite of PAHs indicated by lowercase letters, and the second is a suite of straight-chain aldehydes, indicated by the prefix "a" followed by numerals which give their chain length (only the even-carbon-numbered constituents are labeled; the odd-carbon-numbered homologs are present, but in much lower concentrations).

The PAHs throughout this area of the Bay are dominated by pyrene, fluoranthene and phenanthrene. In all probability at least two sources are responsible for the observed distributions of Bay PAHs. The first and probably major contributor includes a group whose distribution is typical of that

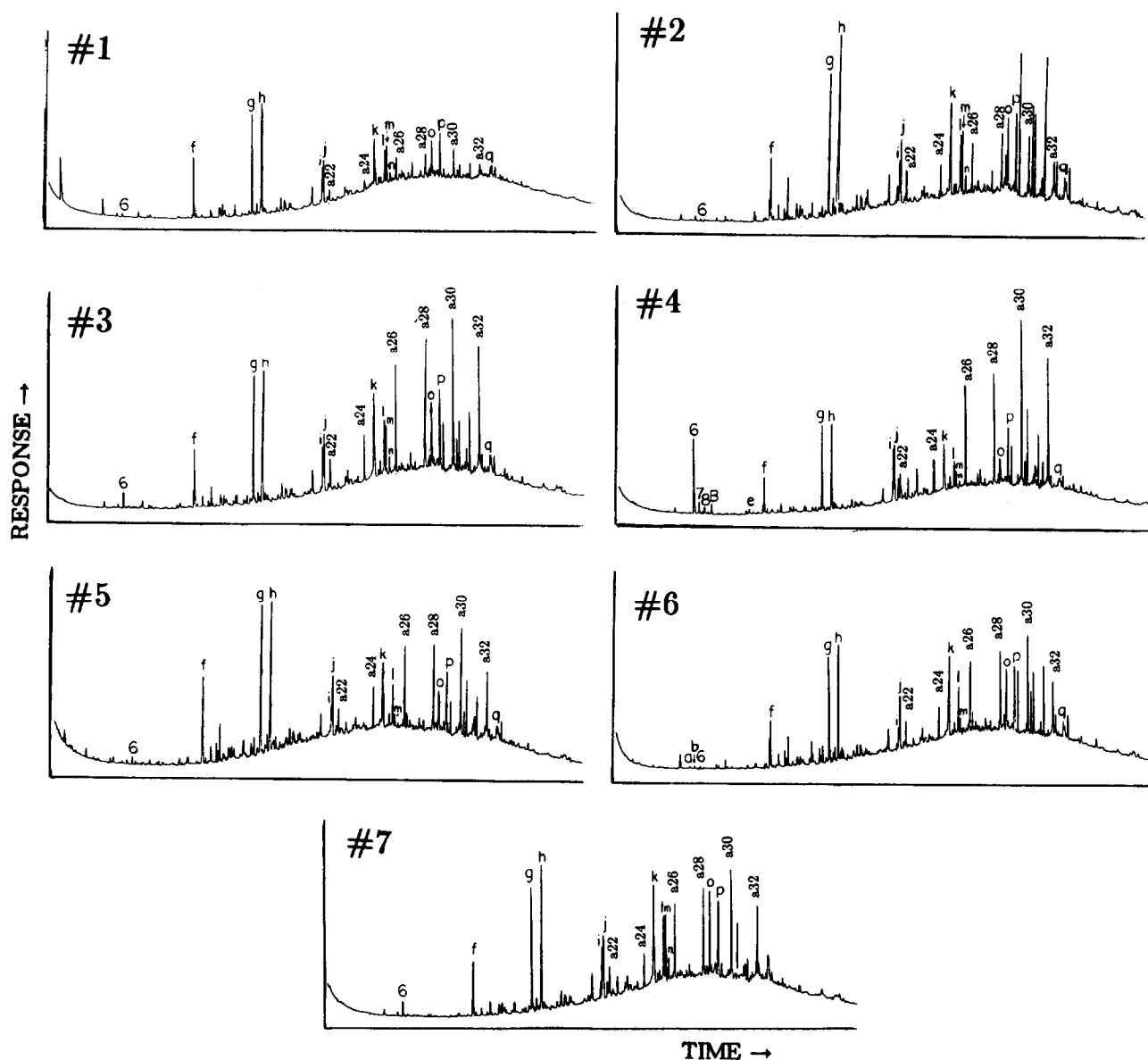


FIG. 5. Gas chromatograms of benzene fractions of Bay sediments. Identifications given in Table 2.

found all over the world in this type of an estuarine environment, both in highly populated areas like the Charles River in Boston and in remote areas (*e.g.*, LAFLAMME and HITES, 1978; PRAHL and CARPENTER, 1983; JOHNSON *et al.*, 1985; PRUELL and QUINN, 1985). These compounds are considered to be derived from pyrolytic sources like forest fires and anthropogenic combustion, spread primarily by aeolian transport (LAFLAMME and HITES, 1978), and from urban runoff, especially asphaltic street dust (WAKEHAM *et al.*, 1980). Because their distribution in estuarine environments is ubiquitous, for the purposes of this paper they also are considered background Bay constituents. Although pyrene is the dominant PAH in the entire assemblage, fluoranthene is present in only slightly lower amounts, and is shown by multivariate analysis to be the most representative in this first PAH suite. Thus, fluoranthene is used in source ratio calculations.

That there is at least one more group of PAHs contributing to the combustion suite is most obvious in the relative proportions of benz(e)pyrene and benz(a)pyrene. At most sites, the chromatograms (Fig. 5) show the concentrations to be approximately the same. However, north and south of the sewage outfall (sites #5 and #6) benz(e)pyrene is significantly dominant over benz(a)pyrene. In the multivariate analysis (Appendix 3) the benzpyrene isomers fall into different factors with benz(a)pyrene in the pyrene/fluoranthene group and benz(e)pyrene in a group of higher molecular weight PAHs. This latter group maximizes around the sewage outfall with multivariate analysis showing a weak bias to the south, indicating probable southward sediment transport.

Other studies (LAFLAMME and HITES, 1978; KILLOPS and HOWELL, 1988) have also shown that different combustion sources can contribute to similar PAH distributions. Further differentiation of sources of combustion PAHs in the Bay was not attempted.

The PAHs from the pristine upstream sites have only minimal representation from the above groups; rather, the upstream sites are dominated by PAHs like cadalene which, as discussed above, is considered to be a product of natural diagenesis of plant constituents. In the fractionation of the upstream samples, all the PAHs eluted in the 20% benzene fraction; Fig. 6a presents a typical upstream PAH distribution. The two urban upstream samples have distributions closer to the Bay samples, reinforcing the concept of a strong anthropogenic contribution to the Bay PAHs.

The aldehyde suite consists of normal-aldehydes from C_{12} to C_{32} . The entire range is not obvious in the Bay samples because of the low concentration of the early homologs, but when the upstream samples were subfractionated, the entire suite of aldehydes was separated in the 60% benzene fraction, and the lower molecular weight homologs were observed (Fig. 6b). In the higher molecular weight range, the aldehydes have a strong even-over-odd carbon number dominance. These compounds have been reported elsewhere (PRAHL and PINTO, 1987, and references therein) to be primary material from terrigenous plants, which our analyses of upstream samples substantiate. These aldehydes have not been previously reported in San Francisco Bay. ALBAIGES *et al.* (1984b) identified aldehydes in lagoon sediments, but they were found in considerably lower concentrations than are present in our study, and as bound rather than unbound constituents. The

aldehyde concentrations were low enough in the lagoon sediments that they were considered to be secondary diagenetic material, in contrast to the conclusions of PRAHL and PINTO (1987). The high concentrations seen in our samples corroborate the conclusions of PRAHL and PINTO (1987) that these aldehyde suites are more widespread than previously recognized.

PRAHL and PINTO (1987) note that in Washington state coastal sediments the plantwax *n*-alkane series is present at about twice to equal the amount of *n*-aldehydes (as opposed to widely varying proportions, from eight times to less than one, in actual locally occurring plant and pollen samples). In our Bay sediments the *n*-alkane concentrations dominate the *n*-aldehyde concentrations by a larger margin with a wider range (see Table 1) than in the Washington coastal sediments, but the aldehydes are still prominent constituents. At least one biosynthetic pathway has been shown to occur (CHEESBROUGH and KOLATTUKUDY, 1984) whereby *n*-aldehydes are directly decarbonylated to *n*-alkanes. Our sample set provides some evidence that this could be occurring here, in that all of the Bay samples have as their dominant member (Cmax, Table 1) C_{30} in the aldehyde series and C_{29} in the alkane

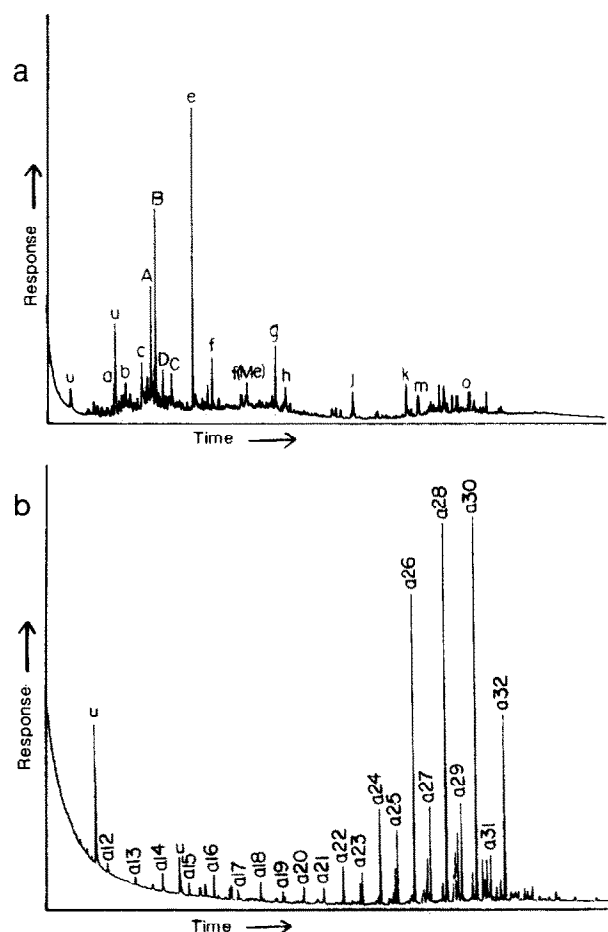


FIG. 6. Gas chromatograms of typical benzene fractions of upstream sediment. (a) 20% benzene fraction (PAHs and aromatic sesquiterpenes); (b) 60% benzene fraction (*n*-aldehydes). Identifications given in Table 2.

series, which implies a possible precursor-product relation. However, upstream samples do not allow quite such a simplistic interpretation, because the dominant aldehyde members are both C_{28} and C_{30} . Also, the even-odd dominance of the aldehyde series, measured by CPI, is lower than the odd-even dominance of the n -alkanes, except for the two Urban upstream samples where the n -alkane CPI is lower, probably due to dilution with petrogenic n -alkanes. In addition, the spatial distribution of the aldehyde series is not nearly as sharply defined as that of the n -alkane series. Clearly, other factors contribute to their geochemical relationship, and these are beyond the scope of this paper.

Of major importance in this study is the respective variation of these two suites of compounds, the background PAHs and the terrigenous aldehydes, at each of the different sampling sites. Figure 5 shows that two extremes exist in the Bay sample set, sites #1 and #4. At #1, San Mateo Bridge in Central South Bay, the background PAHs dominate, whereas at #4, south of San Francisco Creek, the aldehydes dominate, as a result of local terrigenous input. The other Bay sites have intermediate balances between these two suites of compounds. A ratio of the GC response of the most representative member of each suite, that is, the C_{30} -aldehyde to fluoranthene, gives us another comparison of terrigenous input to background Bay input (see Table 1 and Fig. 7).

Parameter comparisons

The three independent ratios of organic parameters discussed above were used to compare terrigenous input to background constituents of the Bay sediments. Trends developed from absolute concentrations were not useful; absolute concentrations are known to be highly variable with fluctuations of two to three orders of magnitude (FARRAN *et al.*, 1987). Comparative data are considered to be more reliable (BRASSELL and EGLINTON, 1986). The first parameter is the n -alkane Carbon Preference Index (CPI), that is, the quantitation of the magnitude of the odd-over-even dominance of the C_{24} to C_{34} n -alkanes. The second parameter is a ratio from the benzene fractions of the most prominent terrestrial aldehyde to fluoranthene, the most representative background PAH. The third parameter is a ratio from the SIM biomarker mass chromatography of the major terrestrial

n -alkane n - C_{29} to the major Bay background biomarker, $17\alpha(H),21\beta(H)$ -hopane.

The highest values in this sample set for the three ratios come from the five most pristine upstream samples (Table 1). This result is expected, especially for CPI, because the n -alkanes in this range are known to originate from the leaf waxes of vascular land plants (EGLINTON and HAMILTON, 1967). The two urban upstream samples (#11 and #12) have lower values comparable to values observed in the Bay; these samples were collected where anthropogenic contamination inputs, that is, petroleum product contamination from urban run-off, were expected. The lowest value for CPI in our Bay samples occurs at station #1, the station furthest from direct terrigenous inputs.

The results of the parameter comparisons for the South Bay sites alone (#1–7) are listed in Table 1 and graphed in Fig. 7. All three ratios have a fairly broad but distinct range among most sites. At site #4, the site just south of San Francisco Creek, all three ratios show a clear maximum, indicative of input of terrigenous components from San Francisco Creek. The occurrence of the maxima at the site south of the creek and not at the site equidistant north of the creek is evidence that more terrigenous sediment accumulates in the southward direction. Another parameter which further substantiates the dominance of terrigenous input at site #4 is ΣC_{25-31} , the sum of the concentrations of the four major terrigenous alkanes (n - C_{25} , n - C_{27} , n - C_{29} and n - C_{31}) normalized to total organic carbon (PRAHL and CARPENTER, 1984). This ratio is not included in Fig. 7, but values from Table 1 indicate that it also maximizes south of the Creek, indicating southward sediment transport. The values of the first three parameters calculated for stations #11 and #12, the urban upstream sites, are within the ranges of stations #1 through #7, the Bay sites, indicating a strong influence throughout this area from the mix of urban (anthropogenic) and terrestrial hydrocarbons characteristic of the lower Bay watershed. The above conclusions are supported and expanded by the statistical analysis of the chromatography of the hexane and benzene fractions. The results of the multivariate analysis are described in Appendix 3.

CONCLUSIONS

This preliminary survey of the hydrocarbon constituents of the sediments from an area of south San Francisco Bay has established the presence of several organic markers or suites of markers that can be used as terrigenous and Bay source indicators. One of these suites of markers is a homologous series of n -aldehydes with a strong even-over-odd carbon number dominance, reported here for the first time in San Francisco Bay. Others include n -alkanes, mature steranes and hopanes, combustion-derived PAH, and a suite of sesquiterpenes. The sesquiterpenes appear too labile for use other than as terrigenous indicators. Specific signatures differentiated the two stations furthest from the discharge of a small creek (predominant PAH estuarine signal) from the two stations closest to the discharge (predominant terrigenous aldehyde signal). Sediments of all stations near the discharge of the creek showed a detectable influence from the mix of terrestrial material and anthropogenic contaminants typical

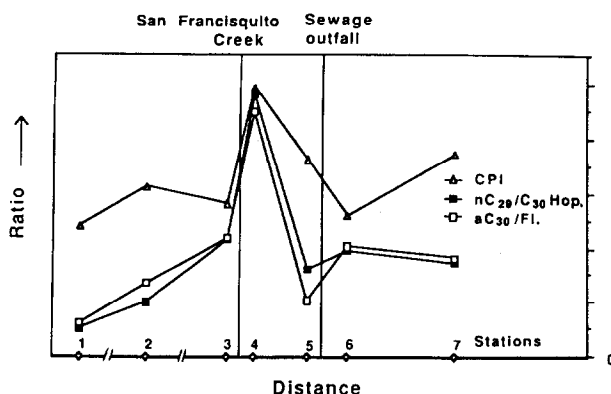


FIG. 7. Results of parameter comparisons of Bay samples.

of the watershed. Sediments closest to sewage outfall adjacent to the creek had a weak but unique signature, despite the strong influence of the creek.

Convergent results from ratios of critical marker compounds and multivariate analyses proved useful in determining sediment transport direction within the area of study. These results suggest that sediment-associated contaminants input from point sources in the terminus reach of South Bay will be more concentrated south of the input than north. The hydrodynamics of south San Francisco Bay are not well established, but it has been generally accepted that nontidal, residual currents are very weak in this part of the Bay (CONOMOS, 1981). Nevertheless, the several lines of evidence in this study clearly show southward sediment transport from the major input source of its sedimentary components, San Francisquito Creek, and imply southward sediment transport from the sewage outfall. This conclusion is consistent with earlier observations of trace metal distributions in this area (THOMSON *et al.*, 1984). The sediment input distribution and transport patterns help unravel the hydrodynamic complexities of this area of the Bay. This study demonstrates the general utility of hydrocarbon characterization, ratios from inputs, and multivariate analysis in defining sources of sedimentary input and sediment transport in a complex estuarine environment.

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APPENDIX 1

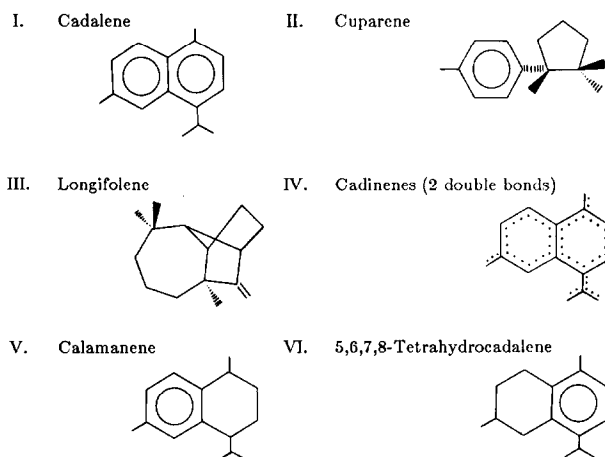
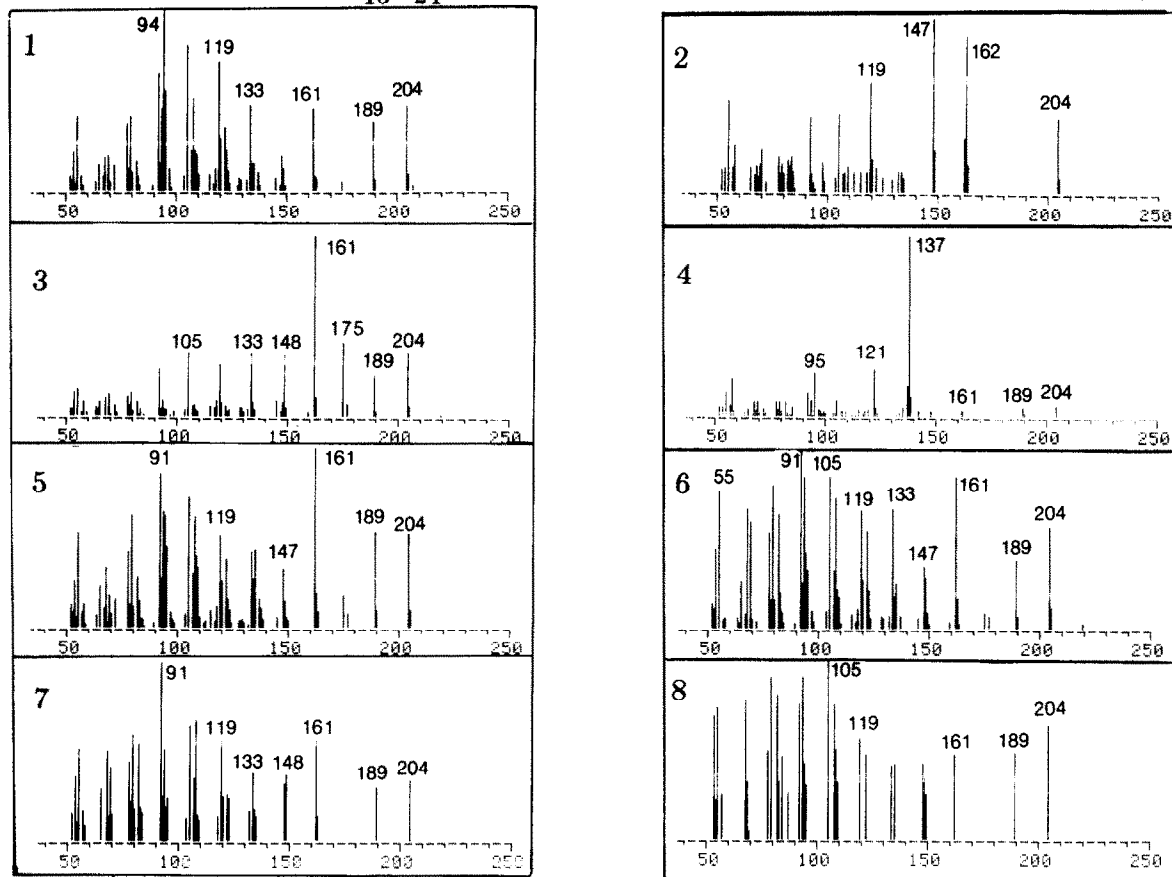
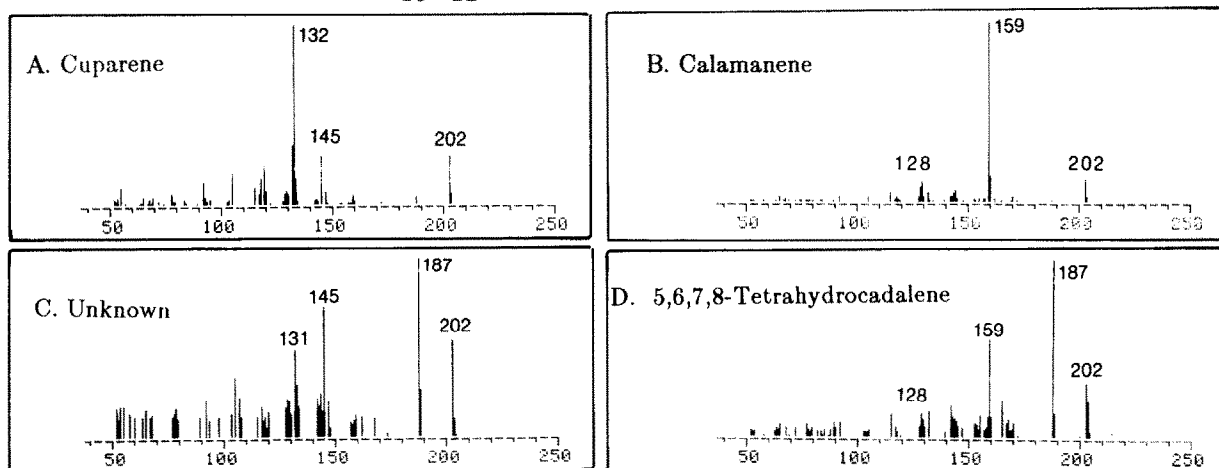
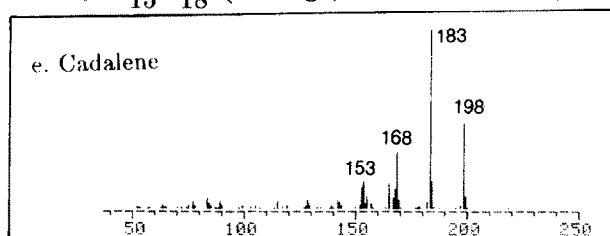


FIG. A-1. Structures of organic compounds cited in the text.

(Appendix 2 follows on next page)

APPENDIX 2

1. Molecular weight 204, $C_{15}H_{24}$ (2 rings, 2 double bonds or 3 rings, 1 double bond)2. Molecular weight 202, $C_{15}H_{22}$ (2 rings, 1 fully aromatized)3. Molecular weight 198, $C_{15}H_{18}$ (2 rings, both aromatic)

APPENDIX 3

MULTIVARIATE ANALYSIS

The data from the factor analysis were used in R mode to group the various compounds in the fractions according to source, and in Q mode to compare sample sites with respect to input sources. In the case of the hexane fractions, one factor each (unrotated) explained >95% of the total information in both the Bay sample set and the upstream sample set. Within these factors, 88% (Bay) and 94% (upstream) of the information was contained in only three compounds (the major plant wax alkanes, n -C₂₇, n -C₂₉ and n -C₃₁), supporting the contention that the great majority of the material in the hexane fraction of the Bay sediments has a terrigenous origin.

The analysis of the data from the Bay benzene fractions was more complex. Factor loadings for R mode are shown in Fig. A-3 (a and c); factor loadings for Q mode are shown in Fig. A-3 (b and d). Because the order of the factors is the same in both modes, Q mode and R mode will be discussed together for each factor. In the Q mode, four factors account for 99% of the total variance of the data:

Factor 1. This factor explains 34% of the total information in the Q mode. Figure A-3a shows the R mode factor loadings of the constituents of factors 1 and 2, and Table A-1 gives identifications of the dominant compounds. Factor 1 is composed mainly of the low to medium molecular weight PAHs, phenanthrene, fluoranthene, pyrene, benzo(a)pyrene, and perylene, given in their GC elution order. As discussed above, this is the suite of compounds found in many diverse parts of the world in estuarine environments, that we are considering to be background in the Bay. Figure A-3b shows that the sample with the highest loading in this factor (−0.83) is site #1, the

northernmost site. The sample with the second highest loading (−0.67) is #7, the southernmost site.

Factor 2. This factor explains 35% of the total information in the Q mode. Figure A-3a shows that factor 2 consists of a homologous series of n -aldehydes, with the C₂₆, C₂₈, C₃₀ and C₃₂ homologs being present in the highest concentrations. As discussed earlier, these aldehydes come from terrigenous sources. Figure A-3b shows that the sample with the highest loading (−0.89) is site #4 (south of San Francisco Creek), and #3 (north of San Francisco Creek) has the second highest loading (−0.70). This result implies that: 1) the creek is the local source of the aldehydes (which we confirmed with the upstream sediment samples), and 2) more terrigenous sediment is transported southward from the mouth of the creek than northward. Quantitatively, factor 2 explains $(-0.89)^2 \cdot 100 = 79\%$ of the information in #4 and only $(-0.70)^2 \cdot 100 = 49\%$ of the information in #3; if there were uniform mixing at the mouth, the values would be similar.

In Fig. A-3b, 69% [34% (factor 1) plus 35% (factor 2)] of the total variation in the 224 data points (7 samples, 32 compounds) is represented in two dimensions. Stations #1, 7, 3 and 4 all have >75% of their information explained by adding variable amounts of two end-members (stations #1 and #7 are predominantly estuarine, dominated by background PAHs, factor 1; stations #3 and #4 are predominantly terrigenous, dominated by the terrestrial aldehydes, factor 2). Stations #5, 6 and 2 have 59 to 44% of their information explained by factors 1 and 2 and thus need other factors to explain fully their total variance.

Factor 3. This factor explains 24% of the total information in the Q mode analysis. Figure A-3c is a graph of the factor loadings of the

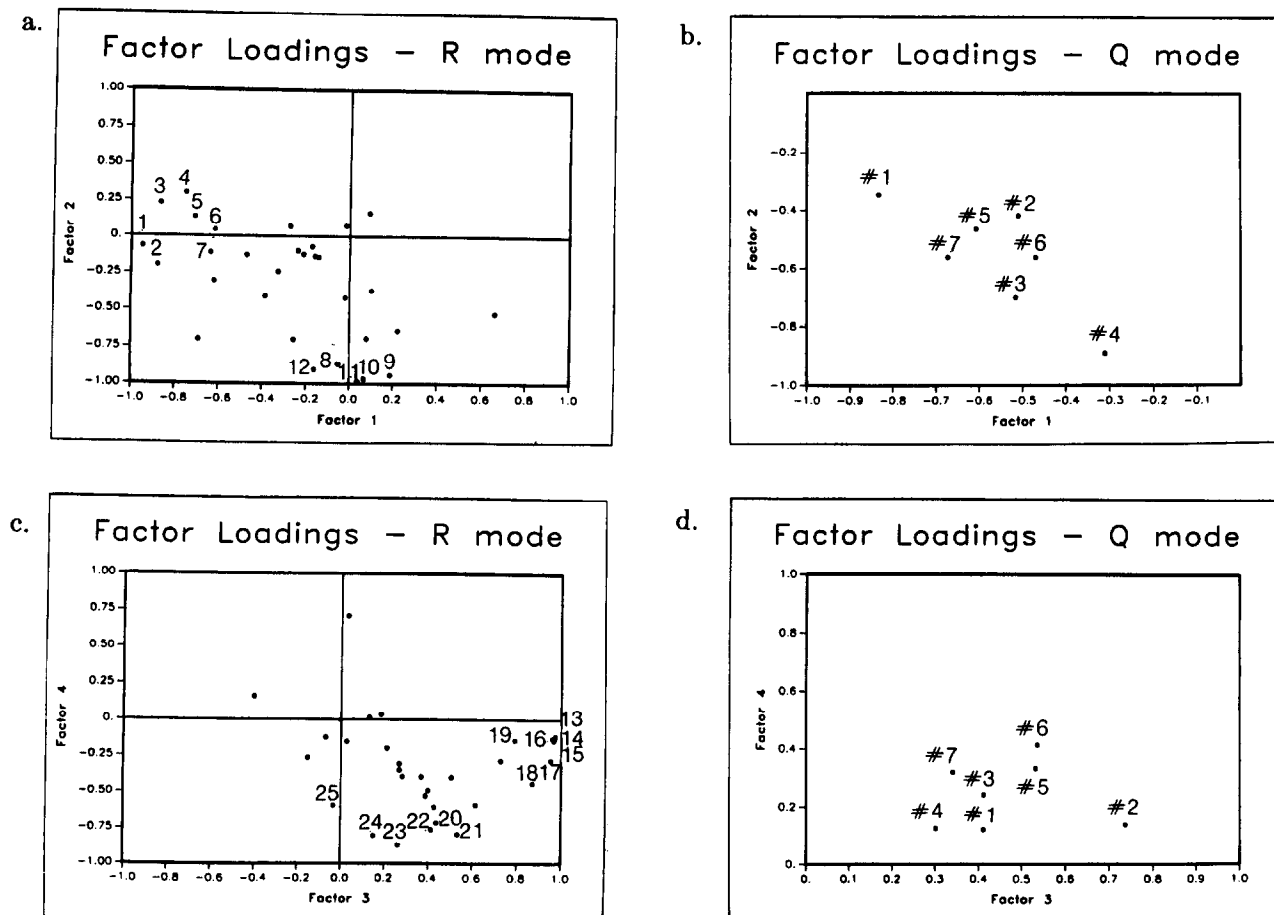


FIG. A-3. Multivariate analysis factor loadings. Compounds in R mode are given in Table A-1; #'s in Q mode refer to sampling sites.

Table A-1. Compound identifications for factor analysis of Bay benzene fractions (Fig. A-3)

1. Benzo(a)pyrene	10. n-C ₂₈ aldehyde
2. Perylene	11. n-C ₃₀ aldehyde
3. 2-Me phenanthrene	12. n-C ₃₂ aldehyde
4. Unknown	13-20. Unknowns
5. Phenanthrene	21. Benzo(b)fluoranthene
6. Pyrene	22. Benzo(e)pyrene
7. Fluoranthene	23. Indeno(1,2,3-cd)pyrene
8. n-C ₂₄ aldehyde	24. Benzo(ghi)perylene
9. n-C ₂₆ aldehyde	25. Coronene

compounds (R mode) for factor 3 vs. factor 4. Compounds with the highest loading in factor 3 are a highly correlated group of high molecular weight unknown compounds. These unknown compounds

elute from a DB-1 capillary column between 288 and 310°C, and their retention times indicate that they may be a homologous series. The compounds are most predominant at station #2 (loading = 0.74) where they are second only to the PAH suite in concentration. The stations near the sewage outfall, #5 and #6, are intermediate between #2 and a group with low loadings (1, 3, 4 and 7). Presently we have no interpretation of this factor, but we are working on the identification of the unknowns.

Factor 4. This factor explains 7% of the information in the Q mode. This factor consists of a group of co-occurring high molecular weight PAHs (benzo(b)fluoranthene, benzo(e)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene and coronene). This group of compounds is most prominent (*i.e.*, has the highest loading, 0.41) at station #6 (south of the sewage outfall) followed by #5 (0.33; north of the sewage outfall) and #7 (0.32). This distribution of #6 > #5 implies that 1) either the sewage outfall is a source of these compounds, or components of the sewage discharge facilitate higher inclusions of these high molecular weight PAHs in the sediments; and 2) there is a net southward movement of material from the sewage outfall.