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ORGANIC CONTAMINANTS IN PENINSULA BERMS AND AGRICULTURAL SOILS AT THE SONOMA BAYLANDS WETLAND DEMONSTRATION PROJECT SITE AND ADJACENT SEASONAL WETLANDS, SONOMA COUNTY, CALIFORNIA

by
Wilfred E. Pereira, Frances D. Hostettler, Keith A. Kvenvolden,
Robert J. Rosenbauer and Fred Murphy

U. S. GEOLOGICAL SURVEY

Open-File Report 97-831

Menlo Park, California
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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	*By*	*To obtain*
feet	3.048 X 10^{-4}	kilometers
centimeter (cm)	3.94 X 10^{-1}	inch
gram (gm)	3.53 X 10^{-2}	ounce, avoirdupois
microgram (µg)	3.53 X 10^{-8}	ounce, avoirdupois
micrometer (µm)	3.94 X 10^{-5}	inch
milligram (mg)	3.53 X 10^{-5}	ounce, avoirdupois
millimeter (mm)	3.94 X 10^{-2}	inch
nanogram (ng)	3.53 X 10^{-11}	ounce, avoirdupois
nanometer	3.94 X $^{10\text{-}8}$	inch
acre	4,047	meter^2
yard^3 (yd^3)	0.7646	meter^3 (m^3)

Degree Celsius (^{0}C) may be converted to degree Farenheit (^{0}F) by using the following equation:

$$^0\mathrm{F} = [9 \text{ X } {}^0\mathrm{C} / 5] + 32$$

Abbreviated water-quality units used in this report:

ng/g	nanogram per gram

Other units used in this report:

^{0}C/min	degrees Celsius per minute

Other abbreviations and symbols used in this report:

PAHs	polycyclic aromatic hydrocarbons
DDT	4,4'-dichlorodiphenyltrichloroethane
DDD	4,4'-dichlorodiphenyldichloroethane
DDE	4,4'-dichlorodiphenyldichloroethene

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ABSTRACT

A geochemical study was conducted to establish baseline data of organic contaminants in soils of artificial peninsulas developed as barriers, at the Sonoma Baylands Wetland Demonstration site. This study also included soils of the adjacent hayfields, Leonard Ranch, and North Point Properties, which are seasonal wetlands. This information is helpful as reference data for monitoring the progress of wetland development and restoration. Compounds were identified by gas chromatography/mass spectrometry, and included aliphatic hydrocarbons, biomarker hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides DDT and its degradates DDD and DDE, chlordanes, and dieldrin. Aliphatic and biomarker hydrocarbons are mainly biogenic, whereas the PAHs and chlorinated pesticides are mainly anthropogenic. Ratios of DDE/DDT were less than 1.0, indicating that the DDT in these soils has not been subjected to significant long term weathering. Concentrations of total DDTs were the greatest in soils from the North Point Properties (9.7 ng/g, or ppb). Concentrations of total PAHs were the greatest in soils from Leonard Ranch (680 ng/g) and peninsula 15 at the Main site (600 ng/g). Concentrations of total PAHs and DDTs in soils were generally below the Effects Range-Low values. Therefore, the potential for toxic effects to biota that may be exposed to these soils is low, making these soils suitable for wetland construction and restoration.

INTRODUCTION

The Sonoma Baylands Wetland Demonstration Project (SBWDP) was authorized by Congress under the Water Resources Development Act of 1992. The U. S. Army Corps of Engineers is currently investigating the feasibility of using dredged sediment from the Petaluma River across-the-flats navigation channel and the Oakland Harbor Deepening Project to raise the elevation of this former diked tideland to historic tidal marsh elevation and thus reestablish lost wetland habitat in San Francisco Bay. If this project is successful, it will provide a beneficial use of dredged sediments from other parts of the bay, expand the feeding and nesting areas for waterfowl along the Pacific flyway, and provide habitat for several endangered species such as the salt marsh harvest mouse and the California clapper rail.

To assist in this important project, the U. S. Geological Survey has begun an investigation on the occurrence and fate of organic contaminants in sediments at the Sonoma site and the adjacent marshlands. This geochemical study will provide base-line contaminant concentrations of fill material at the site and on soils from the adjacent farms and marshlands. This study enables a geochemical comparison of these sediments. A limited contaminant data base exists for the fill material prior to emplacement at the site (U. S. Army Corps of Engineers, 1994), but no contaminant data exist for these sediments after the fill was in place and the site was raised to historic tidal marsh elevation and opened to tidal action in 1996. A report in progress, will provide these data.

During site excavation, and prior to emplacement of fill material, these agricultural soils, formerly used for oat hay farming, were bulldozed and numerous peninsulas were constructed from soils at the site. This report provides organic geochemical data for soils from these peninsulas. In addition, this report also provides comparative data on agricultural soils from two adjacent hayfield properties, the Leonard Ranch and North Point properties.

Purpose and Scope

The purpose of this study is to report base-line organic contaminant data on peninsula soils of the Sonoma Baylands Wetland Demonstration Project site and two adjacent pieces of agricultural land, the North Point Properties and the Leonard Ranch, both of which were used in the past for oat hay farming and which are now classified as seasonal wetlands.

Study Area

The Sonoma Baylands Wetland Demonstration Project site is a 348 acre parcel of diked former tidelands located on the northwestern shoreline of San Pablo Bay near the mouth of the Petaluma River. The site is 11 miles south of the city of Petaluma and 4 miles east of the city of Novato (fig. 1). The site was used in the past for oat hay farming. This tideland restoration project consists of a 39 acre western Pilot unit and a 309 acre eastern Main unit; these units are divided by an interior levee (fig. 2). Within each unit a series of low interior berms or peninsulas was constructed with former farmland soils. The function of these peninsulas is to provide tidal deflection and facilitate sediment deposition by breaking up long lengths of wave-fetches once the site is opened to tidal action. The site is bounded on the north by the Northwestern Pacific Railroad and the Leonard Ranch, on the west by a diked wetland parcel, on the east by North Point Property hayfields, and on the south by a tidal marsh that is mostly within the San Pablo Bay Wildlife Refuge. In 1994, the Pilot unit was filled with about 264,000 cubic yards of maintenance-dredged material from the Petaluma River across-the-flats navigation channel. After a period of settling and compaction of sediments, the Pilot unit was exposed to tidal action in January 1995 by breaching an existing bay-front levee. The eastern Main unit was similarly filled with about 2.5 million cubic yards of dredged sediment from the Oakland Harbor Deepening Project. After a period of settling and compaction of sediment, this unit was exposed to tidal action in October 1996. The purpose of the fill material is to partially restore the ground elevation to historic tidal marsh elevation. It is anticipated that the use of dredged material would accelerate the

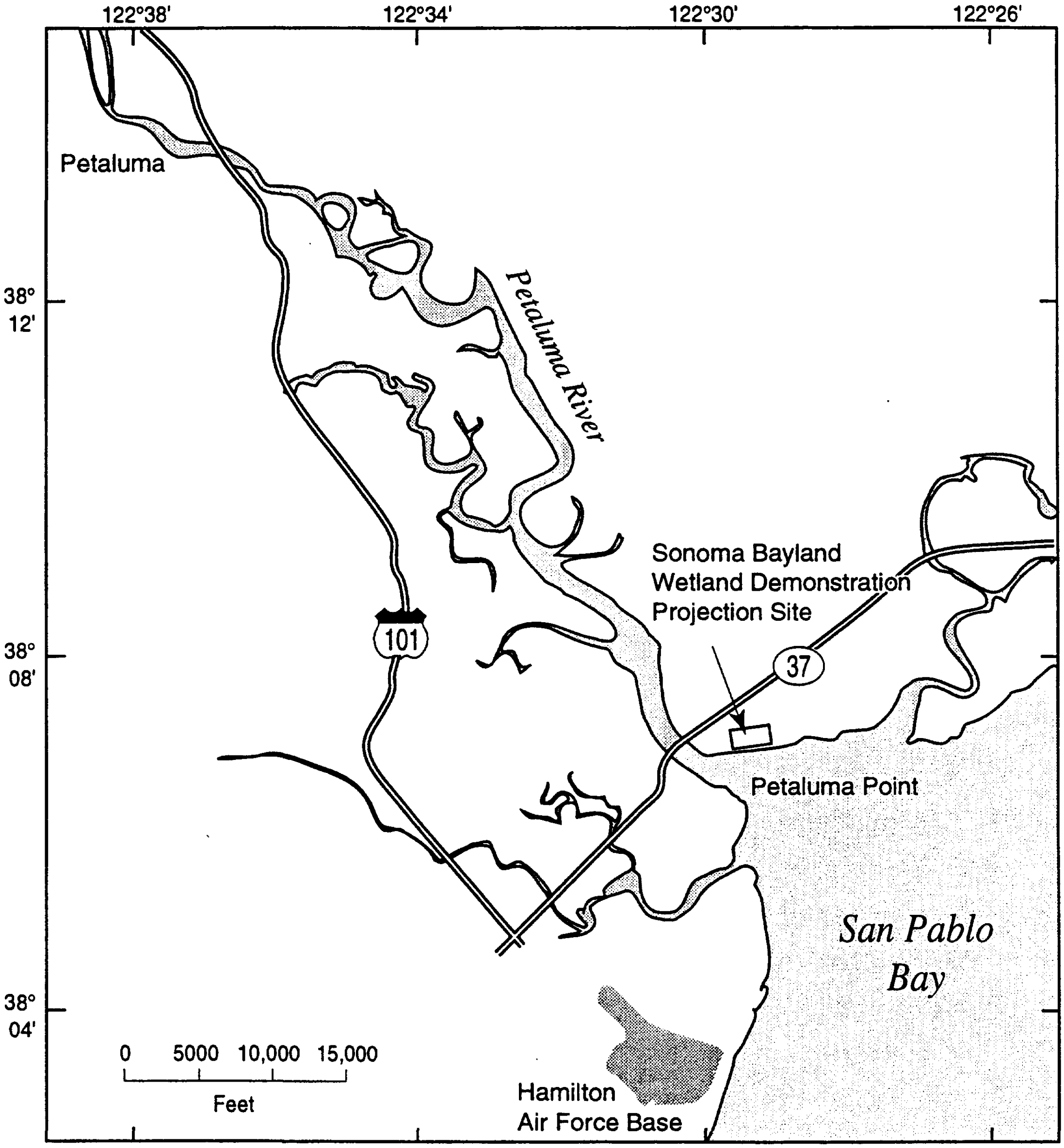


Figure 1. **Map showing location of the Sonoma Baylands Wetland Demonstration Project site.**

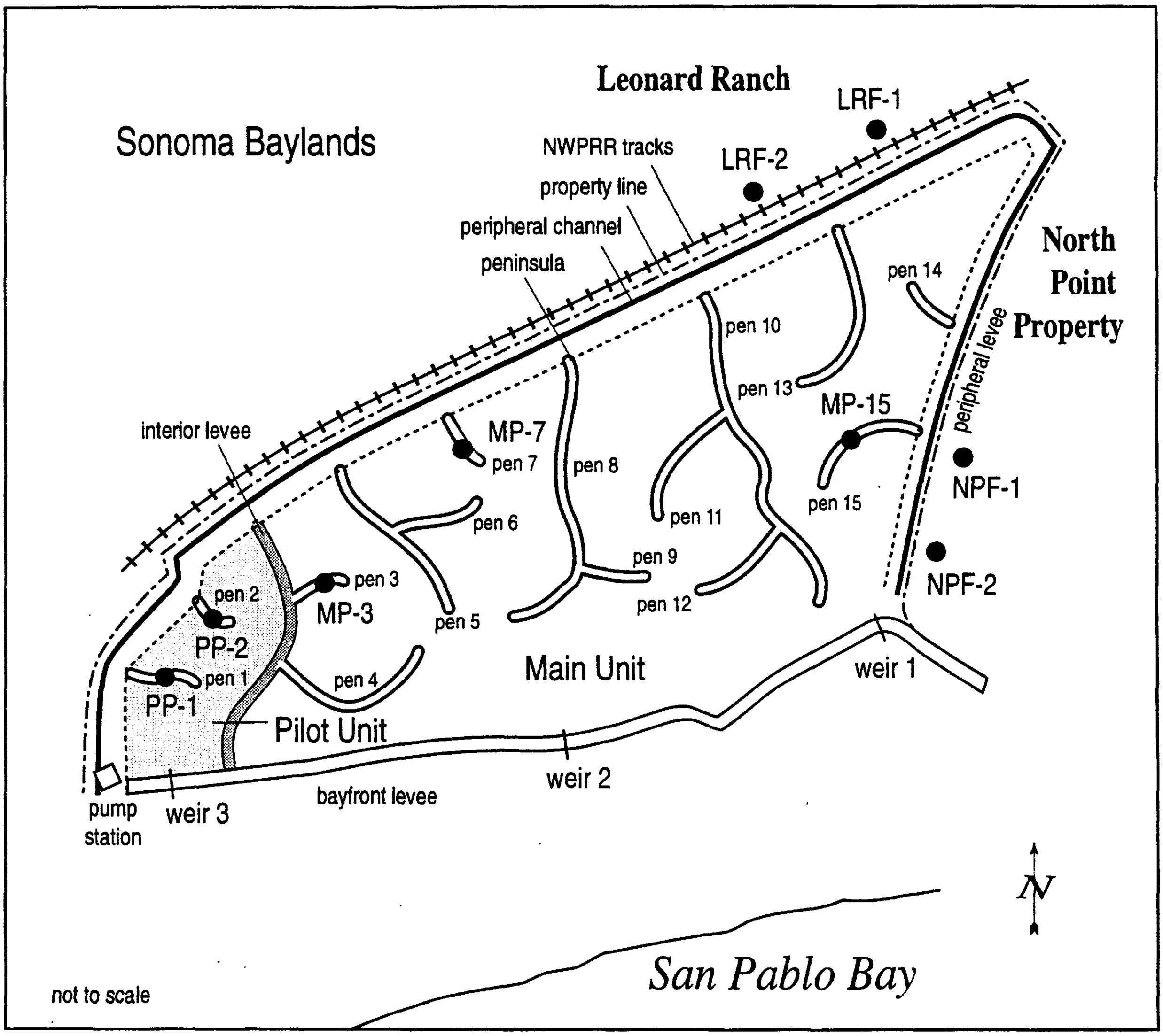


Figure 2. Map showing sampling locations at the Sonoma Baylands Wetland Demonstration Project site and the adjacent Leonard Ranch and North Point Properties.

restoration of vegetated tidal wetlands by an estimated 15-45 years. A detailed description of the SBWDP site has been reported (U. S. Army Corps of Engineers, 1994).

The North Point Properties, located east of the site, and the Leonard Ranch, located to the Northwest, are farmed for oat hay. They are seasonal wetlands.

ACKNOWLEDGMENT

This project was funded by the U. S. Geological Survey's San Francisco Bay Ecosystem Program. The cooperation of Scott Miner, U. S. Army Corps of Engineers, the Coastal Conservancy, and the Sonoma Land Trust, is greatly appreciated. The financial and administrative support of Sarah Gerould, Ecosystem Program Coordinator, U. S. Geological Survey, is gratefully acknowledged.

METHODS

Sample Collection

Sampling sites were located using a Global Positioning Satellite receiver with positions good to within ± 100 meters (table 1). Sampling locations of the soil cores are shown in fig. 2. Two soil cores were collected from peninsulas in the Pilot site (PP-1, PP-2), and three soil cores were collected from peninsulas in the Main site (MP-3, MP-7, and MP-15). In addition, two soil cores were collected from the North Point Property hay field (NPF-1, NPF-2), and two soil cores were collected from the Leonard Ranch hay field (LRF-1, LRF-2). Soil cores were collected with a slide-hammer coring device equipped with a pre-cleaned cellulose acetate butyrate liner. The upper ~ 25-35 cm section of each core was used for analysis. The soils were air-dried in pre-cleaned and baked (450 ^{0}C) aluminum pans. Samples were ground in a pre-cleaned mortar with a pestle until they passed a #32 stainless steel mesh screen, mixed thoroughly, and stored in a freezer in pre-cleaned and baked glass jars provided with Teflon™ lined screw caps. All sampling equipment was washed with soap and water, distilled water, and rinsed with acetone or methanol prior to sampling.

Table 1. Sampling sites at the Sonoma Baylands

(Peninsulas and adjacent Hay Fields, January 1997)

Site	Description	Latitude	Longitude
Pilot Site			
1. PP-1	Mid-peninsula 1	38° 07.049′ N	122° 29.413′ W
2. PP-2	Mid-peninsula 2	38° 07.127′ N	122° 29.438′ W
Main Site			
MP-3	Mid-peninsula 3	38° 07.166′ N	122° 29.274′ W
MP-7	Mid-peninsula 7	38° 07.353′ N	122° 29.049′ W
MP-15	Peninsula 15	38° 07.353′ N	122° 28.374′ W
North Point Properties			
NPF-1	Hay Field	38° 07.286′ N	122° 28.350′ W
NPF-2	Hay Field	38° 07.291′ N	122° 28.350′ W
Leonard Ranch			
LRF-1	Hay Field	38° 07.682′ N	122° 28.341′ W
LRF-2	Hay Field	38° 07.664′ N	122° 28.432′ W

Sample Preparation and Analysis

About 10g of dry soil was weighed into the Teflon vessel of a MES-1000 microwave extraction system (CEM Corporation, North Carolina). The sample was spiked with deuterium labeled standards (d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, d12-perylene, d8-4,4′-DDT, d8-4,4′-DDD, and d8-4,4′-DDE. After a 15 minute equilibration period with occasional mixing, 30ml of hexane:acetone (1:1) was added. The labeled internal standards were used to correct for analyte losses that may occur during sample extraction and analysis. The sample was extracted by microwave assisted extraction (Temp., 115^0 C; Pressure, 80 psi; Time, 20 min.). The sample was cooled and centrifuged. The supernatant was decanted and filtered through a bed of anhydrous Na_2SO_4 placed over a plug of glass wool into the concentrator vessel of a Zymark Turbovap II concentrator. The sample in the extraction vessel was treated with two successive 10 ml portions of hexane:acetone (1:1), mixed, centrifuged, and the rinses were transferred to the concentrator vessel. The solution was concentrated to a volume of 1 ml. The solvent was exchanged with 3 successive portions of 3 ml of hexane, and once with 3 ml of cyclohexane, each time evaporating the sample down to a volume of 1 ml. The cyclohexane extract was passed through a Bakerbond 3 ml solid phase extraction cartridge containing sulphonic acid (SO_3H) resin, that was topped with a small amount of HCl-activated copper powder to remove sulfur. The eluate and 3 hexane washings were collected in a graduated vessel, and the volume made up to 5 ml. This extract was chromatographed on a column of 5g and 2.5g activated silica gel (Davison, Nos. 923 and 62, respectively) and deactivated (5 percent water) alumina. The column was eluted with hexane (alkane fraction), followed by 30 percent dichloromethane in hexane (aromatic and pesticide fraction). The hexane fraction was analyzed for alkanes using external standards by GC-MS. A further analysis of the alkane fraction for biomarkers was done by GC-MS using the single ion monitoring (SIM) mode for hopanes (m/z 191) and steranes (m/z 217). The aromatic fraction was spiked with 4,4′-dibromooctafluorobiphenyl as the injection standard and analyzed for polycyclic aromatic hydrocarbons (PAHs) and chlorinated pesticides by GC-Ion Trap mass spectrometry. The alkanes and biomarkers were analyzed on a Hewlett Packard 5973 Mass Selective Detector GC-MS system. For the alkane analysis, the gas chromatograph was maintained at 90^0 C for 2 minutes and programmed at 5^0 C/min to 315^0 C. For the biomarker analysis, the gas chromatograph was maintained at 150^0 C for 0.5 minutes and programmed at 30^0 C/minute to 200^0 C, followed by a program rate of 1^0 C/minute to 300^0C. The aromatic fraction was analyzed on a Finnigan Mat GCQ ion trap mass spectrometer in the SIM mode. The gas chromatograph was maintained at 60^0 C for 5 minutes and programmed at 6^0 C/min. to 300^0 C. The capillary column (30m X 0.25 mm internal diameter, containing 0.25 µm bonded phase of DB-5MS) was interfaced directly to the ion source of the mass spectrometer. Quantitation of the PAHs and DDTs was based on the deuterium labeled surrogate standards and 5 point calibration curves which were linear over the concentration range investigated. Laboratory and glassware blanks were processed with the samples. A Standard Reference Marine Sediment (HS-4, National Research Council, Canada) was analyzed in triplicate for PAHs. Results of analyses of marine sediment (NRC, HS-4) are shown in table 2. Duplicate soil samples from one of the peninsulas also were analyzed.

Table 2. Results of analyses of NRC, HS-4 Standard Reference Marine Sediment (μg/g).

Compound	HS-4A	HS-4B	HS-4C	Mean (μg/g)	Relative standard deviation, percent	NRC (μg/g)
naphthalene	0.08	0.09	0.06	0.08	15.6	0.15*
acenaphthylene	0.04	0.03	0.04	0.04	11.8	0.15*
acenaphthene	0.02	0.03	0.02	0.02	23.6	0.15*
9[H]fluorene	0.03	0.04	0.04	0.04	10.4	0.15*
phenanthrene	0.51	0.52	0.52	0.52	0.9	0.68
anthracene	0.09	0.09	0.09	0.09	0.0	0.14
fluoranthene	1.01	1.16	1.07	1.08	5.7	1.25
pyrene	0.94	1.05	1.0	1.0	4.5	0.94
benz[a]anthracene	0.40	0.43	0.42	0.42	3.0	0.53
chrysene	0.62	0.63	0.62	0.62	0.8	0.65
benzo[b]fluoranthene	1.01	0.88	1.03	0.97	6.8	0.70
benzo[k]fluoranthene	0.48	0.38	0.47	0.44	10.2	0.36
benz[a]pyrene	0.48	0.42	0.46	0.45	5.5	0.65
indeno[1,2,3-cd]pyrene	0.59	0.53	0.75	0.62	15.0	0.51
dibenz[a.h]anthracene	0.19	0.12	0.18	0.16	19.3	0.12
benzo[g.h.i]perylene	0.73	0.47	0.63	0.61	17.5	0.58

Upper limit-* Amount present is not greater than 0.15μg/g.

RESULTS AND DISCUSSION

The target contaminants for this investigation included alkanes (aliphatic hydrocarbons), hydrocarbon biomarkers (tri-and pentacyclic terpanes and steranes), polycyclic aromatic hydrocarbons (PAHs), and chlorinated pesticides (DDT and it's degradates DDD and DDE), cis and trans chlordane, trans nonachlor, and dieldrin.

Alkanes (aliphatic hydrocarbons)

Distributions of alkanes in soil cores from peninsulas in the Pilot and Main sites, and agricultural soils from the Leonard Ranch and the North Point Properties are shown in fig. 3. Concentrations of alkanes at these sites are shown in tables 3-6. Apart from differences in concentrations, the chromatograms of alkanes in figure 3 from the peninsulas and adjacent agricultural fields are all similar, showing bimodal distributions. The first mode is dominated by n-C_{16} and n-C_{17} , indicative of recent algal (Gelpi and others, 1970) or biogenic inputs. The second mode is dominated by n-C_{29} and n-C_{31} with a strong odd carbon number predominance. This pattern of compound distribution is indicative of inputs of higher plant waxes from terrigenous vascular plants (Eglinton and Hamilton, 1967). These chromatograms are different from those of the fill material at the Sonoma Baylands site (Pereira and others, unpublished data). The peninsula and agricultural field soil chromatograms from this study are unique in that they contain the first alkane mode, whereas the alkane distributions in chromatograms of fill-material

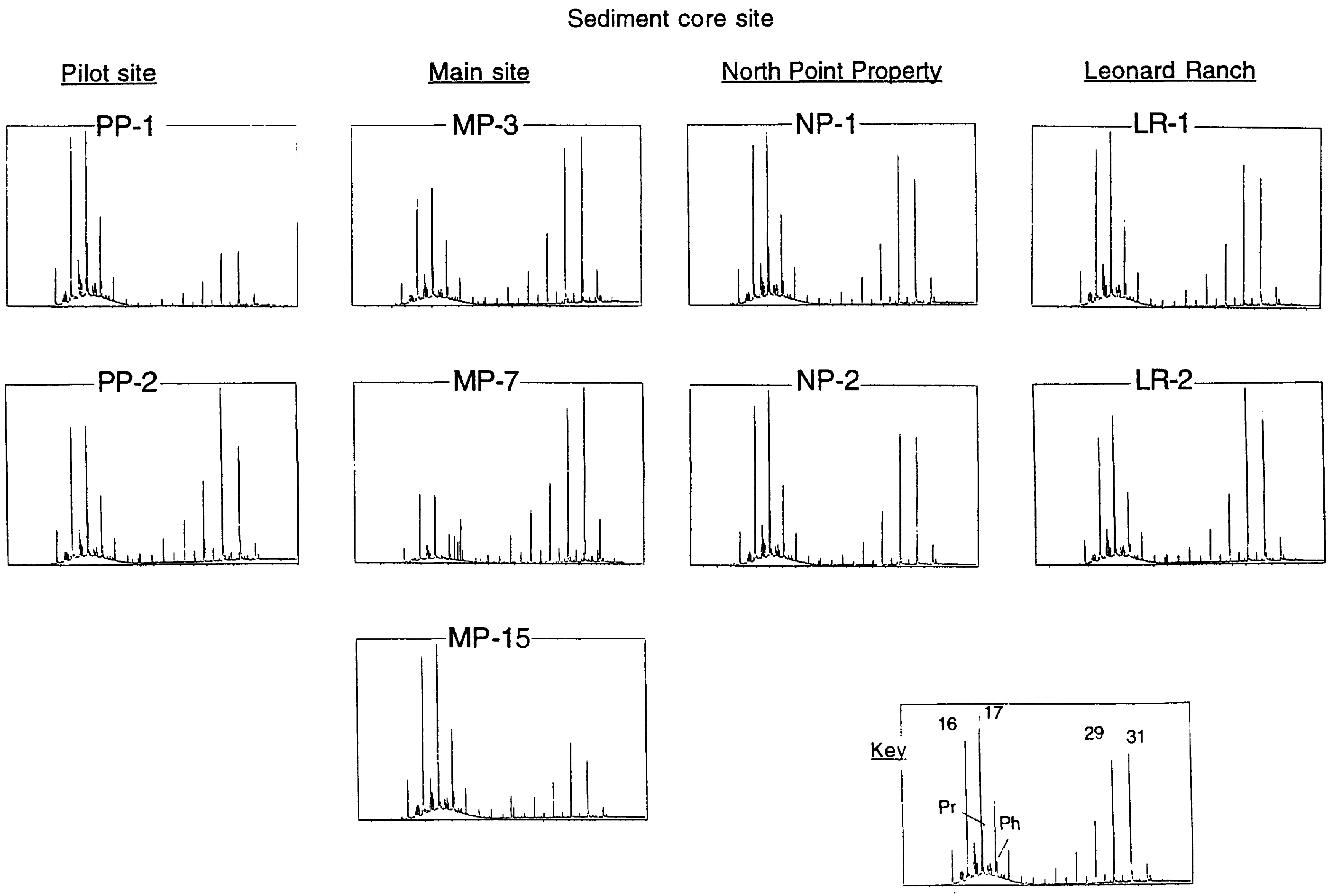


Figure 3. Total ion chromatograms of alkanes in peninsula soils from the Sonoma Baylands and soils from adjacent agricultural lands.

Table 3. Concentrations of aliphatic hydrocarbons in peninsula soils from the Pilot site (ng/g).

Compound	Peninsula-1	Peninsula-2
n-C_{13}	<1.0	<1.0
n-C_{14}	70	30
n-C_{15}	1480	270
n-C_{16}	5500	770
n-C_{17}	4960	640
Pristane	1700	240
n-C_{18}	2090	270
Phytane	580	110
n-C_{19}	700	110
n-C_{20}	150	30
n-C_{21}	70	40
n-C_{22}	50	30
n-C_{23}	240	210
n-C_{24}	140	130
n-C_{25}	420	330
n-C_{26}	200	170
n-C_{27}	1040	670
n-C_{28}	190	140
n-C_{29}	1750	1180
n-C_{30}	180	140
n-C_{31}	3520	1570
n-C_{32}	180	150
n-C_{33}	520	290
n-C_{34}	150	<1.0
n-C_{35}	220	170
n-C_{36}	<1.0	4.0
Total Alkanes	**26100**	**7700**

Table 4. Concentrations of aliphatic hydrocarbons in peninsula soils from the Main site (ng/g).

Compound	Peninsula-3	Peninsula-7	Peninsula-15	Peninsual-15*
n-C_{13}	<1.0	<1.0	<1.0	<1.0
n-C_{14}	<1	60	60	50
n-C_{15}	190	870	750	740
n-C_{16}	680	2800	2320	2380
n-C_{17}	660	2400	2060	2100
Pristane	270	790	760	800
n-C_{18}	300	960	910	980
Phytane	120	320	290	320
n-C_{19}	120	380	340	340
n-C_{20}	20	130	80	80
n-C_{21}	30	260	100	90
n-C_{22}	20	180	40	30
n-C_{23}	190	980	230	220
n-C_{24}	120	380	130	120
n-C_{25}	310	1950	360	350
n-C_{26}	170	510	180	160
n-C_{27}	680	4540	780	750
n-C_{28}	150	660	150	150
n-C_{29}	1300	6990	1420	1400
n-C_{30}	160	570	160	150
n-C_{31}	2770	16700	1950	1910
n-C_{32}	170	460	160	150
n-C_{33}	440	1830	340	330
n-C_{34}	<1	150	<1	<1
n-C_{35}	200	410	170	170
n-C_{36}	10	180	<1	<1
Total Alkanes	**9100**	**45500**	**13700**	**13800**

*Duplicate sample

Table 5. Concentations of aliphatic hydrocarbons in agricultural soils from the Leonard Ranch (ng/g).

Compound	Site 1	Site 2
n-C_{13}	<1.0	<1.0
n-C_{14}	40	30
n-C_{15}	520	340
n-C_{16}	1950	1390
n-C_{17}	1780	1360
Pristane	570	530
n-C_{18}	770	620
Phytane	270	200
n-C_{19}	280	240
n-C_{20}	60	70
n-C_{21}	60	70
n-C_{22}	40	60
n-C_{23}	250	240
n-C_{24}	140	140
n-C_{25}	450	460
n-C_{26}	190	180
n-C_{27}	1100	1100
n-C_{28}	170	170
n-C_{29}	2020	2120
n-C_{30}	180	190
n-C_{31}	3840	4300
n-C_{32}	170	160
n-C_{33}	470	470
n-C_{34}	<1.0	150
n-C_{35}	180	170
n-C_{36}	<1.0	<1.0
Total Alkanes	**15500**	**14800**

Table 6. Concentations of aliphatic hydrocarbons in agricultural soils from the North Point Properties (ng/g).

Compound	Site 1	Site 2
n-C_{13}	<1.0	<1.0
n-C_{14}	40	50
n-C_{15}	690	670
n-C_{16}	2360	2320
n-C_{17}	2200	2140
Pristane	800	760
n-C_{18}	1000	1060
Phytane	330	320
n-C_{19}	370	390
n-C_{20}	80	150
n-C_{21}	70	130
n-C_{22}	50	120
n-C_{23}	250	210
n-C_{24}	140	130
n-C_{25}	490	410
n-C_{26}	180	160
n-C_{27}	1320	1120
n-C_{28}	190	160
n-C_{29}	2400	2090
n-C_{30}	200	180
n-C_{31}	4970	4400
n-C_{32}	180	160
n-C_{33}	580	520
n-C_{34}	<1.0	<1.0
n-C_{35}	200	190
n-C_{36}	<1.0	<1.0
Total Alkanes	**19100**	**17800**

from the site (Pereira and others,unpublished data) contained only the second mode with n-alkanes characteristic of terrigenous plant inputs. Moreover, this second mode from fill material has generally been underlain by a substantial Unresolved Complex Mix (UCM), indicative of degraded petrogenic contamination. The chromatograms from the peninsula and field soils have no high range UCM. Thus, the chromatograms show the peninsulas and adjacent agricultural fields to contain primarily recently deposited natural biogenic material, with essentially no indication of anthropogenic petrogenic contamination. They also have low levels of biomarker constituents as monitored by m/z 191 and 217 amu ion profiles; this result also indicates a lack of any substantial anthropogenic input.

Biomarker Hydrocarbons (tri- and pentacyclic triterpanes and steranes)

Tri- and pentacyclic triterpanes or hopanes (m/z 191) and steranes (m/z 217) were examined in soil cores from the Peninsula and Main sites, the Leonard Ranch, and North Point Properties. Hopanes and steranes evolve from biogenic molecules whose carbon skeletons remain intact through processes of diagenesis and thermal maturation. Thus, they serve as molecular tracers that are useful for correlation of oils with each other and with their proposed source rocks, and for the assessment of thermal maturity (Mackenzie, 1984). The biomarker ratios may indicate petrogenic contamination at this study site. Ratios of these geochemical parameters are shown in table 7. Typical mass chromatograms of hopane (m/z 191) and sterane (m/z 217) distributions in soil from Main peninsula 15 is shown in Figure 4. The biomarker ratios shown are standard source parameters (Tm/Ts and C_{30}/C_{29}) and maturity parameters [hopane S/(S+R) and sterane S/(S+R)], and a diploptene index. The hopane and sterane maturity parameters have

Table 7. Biomarker parameters of soils from peninsulas from the Pilot and Main sites and adjacent agricultural fields from the Sonoma Baylands.

	Hopanes (m/z 191)				Steranes (m/z 217)
Site	Tm/Ts	C_{30}/C_{29}	$\alpha\beta C_{31}$-S/(S+R)	Dipl./$\alpha\beta C_{30}$	$\alpha\alpha\alpha C_{29}$-S/(S+R)
Pilot site					
PP-1	1.7	1.4	0.57*	2.3	0.24
PP-2	2.3	1.3	0.49	1.0	0.20
Main site					
MP-3	1.9	1.3	0.58*	2.1	0.25
MP-7	1.4	1.3	0.48	2.1	0.20
MP-15	1.6	1.3	0.50	1.4	0.24
Leonard Ranch					
LR-1	1.8	1.5	0.52	1.9	0.26
LR-2	1.5	1.5	0.55	2.0	0.24
North Point Property					
NP-1	1.9	1.4	0.55	6.2	0.20
NP-2	1.2	1.2	0.53	4.5	0.20

*--Value anomalously high due to interfering peak

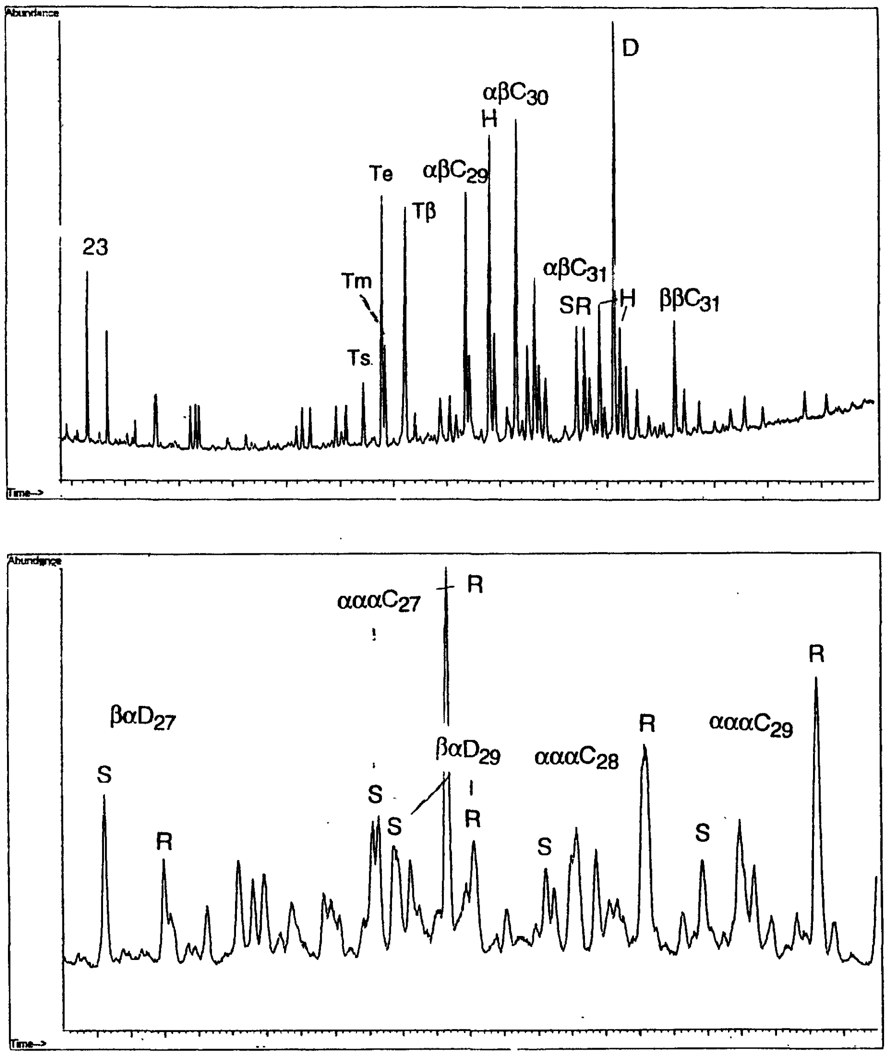
Tm/Ts, 17α(H)-22,29,30-trisnorhopane/18α(H)-22,29,30-trisnorneohopane.

C_{30}/C_{29}, 17α(H),21β(H)-hopane/17α(H),21β(H)-30-norhopane.

$\alpha\beta C_{31}$ S/(S+R), 17α(H),21β(H)-homohopane(22S)/17α(H),21β(H)-homohopane (22S)+(22R).

Dipl./$\alpha\beta C_{30}$, 17β(H),21β(H)-hop-22(29)-ene/17α(H),21β(H)-hopane

C_{29} S/(S+R), 24-ethyl-5α(H),14α(H),17α(H)-cholestane (20S)/24-ethyl-5α(H),14α(H),17α(H)-cholestane (20S)+(20R).



Hopanes

23: C_{23} tricyclic terpane
Ts: C_{27},18α(H)-22,29,30-trisnorneohopane
Te: C_{27}, 22,29,30-trisnorhop-17(21)-ene
Tm: C_{27}, 17α(H)-22,29,30-trisnorhopane
Tβ: C_{27}, 17β(H)-22,29,30-trisnorhopane
αβC_n: 17α(H),21β(H)-hopane series,
if applicable, C22 S and R epimers
D: diploptene, 17β(H),21β(H)-hop-22(29)-ene
H: other C_{30} hopenes
ββC_{31}: C_{31}, 17β(H),21β(H)-homohopane

Steranes

βαD_n: 13β(H),17α(H)-diasterane series,
(C20 S and R epimers)
αααC_n: 5α(H),14α(H),17α(H)-sterane series,
(C20 S and R epimers)

Figure 4. **Mass chromatograms of hopane (m/z 191) and sterane (m/z 217) distributions in soils from Main peninsula MP-15.**

equilibrium values (that is, values indicating high maturity) of approximately 0.60 and 0.50 respectively. When these values are lower, it indicates input or a mixing with input from less mature sources; that is, more recently deposited biogenic material. Diploptene is a hopene that is a marker for very immature natural biogenic input in the sediments. It is present as a constituent of the bottom sediment from below any fill material in the Pilot and Main sites (Pereira and others, unpublished data), but it is not in the fill material. The ratio of diploptene to the $\alpha\beta C_{30}$-hopane, a marker of mature input, frequently of petrogenic origin, gives an indication of whether the sediment is dominated by anthropogenically contaminated material (ratio $\cong 0$) or the agricultural soil (ratio > 0).

In these agricultural soils, both from peninsulas within the Sonoma Baylands site (which were constructed out of the old hay-field soils), and from the adjacent hayfields (Leonard Ranch and North Point Properties), the parameters all indicate a dominance of immature natural biogenic material. The hopane and sterane S/(S+R) ratios are well below maturity, particularly the sterane ratios, and the diploptene ratios are very high. In fact, the biomarker chromatograms (fig. 4) are dominated by diploptene and other hopenes indicative of recent biogenic inputs. There is no indication of significant petrogenic contamination in any of these soils.

Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are higher cyclic homologs of benzene with the aromatic rings arranged in different configurations. PAHs are derived from anthropogenic or natural sources. By far, the largest source of PAHs in the environment is anthropogenic. Pyrolysis of organic materials produce PAHs by a step-wise free radical mechanism. Anthropogenic sources include a) combustion of fossil fuels (Hites and others, 1977); b) long range atmospheric transport of PAHs adsorbed onto soot or airborne particulate matter (Lunde and Bjorseth, 1977; LaFlamme and others, 1978); c) urban runoff containing PAHs derived from abrasion of street asphalt and automobile tires and vehicular emissions (Wakeham and others, 1980); and d) spillage of petroleum and its refined products containing complex assemblages of PAHs (Boehm and others, 1991). Natural sources include a) forest or prairie fires (Blumer and Youngblood, 1975); b) natural petroleum seeps; and c) post-depositional transformations of biogenic precursors over relatively short time frames (Wakeham and others, 1980).

Concentrations of PAHs in the peninsula soils from the Pilot and Main sites are shown in tables 8-9, and in the agricultural soils from the adjacent hayfields Leonard Ranch and the North Point properties in Tables 10-11. PAHs ranged in ring size from 2-ring naphthalene to six ring benzo[g.h.i]perylene. In general, PAH concentrations at all these sites were low, except for soil from peninsula 15 and Leonard Ranch site 2, where the levels of indeno[1,2,3-cd]pyrene, dibenz[a.h]anthracene, and benzo[g.h.i]perylene were elevated. The reason for the elevated concentrations of these three PAHs is not known at this time. However, concentrations of total PAHs at all the study sites are within the range of concentrations of total PAHs that have been reported previously by the National Status and Trends Program for San Francisco Bay (Long and others, 1988).

The potential for toxic effects of PAHs in these soils were evaluated using the criteria of Long and Morgan (1990), and Long and Markel, (1992). The Effects Range-Low (ER-L) value is the concentration above which adverse biological effects may be expected 10 percent of the time. The Effects Range Median (ER-M) value is the

Table 8. Concentrations of polycyclic aromatic hydrocarbons and chlorinated pesticides in peninsula soils from the Pilot site (ng/g).

compound	peninsula 1 (PP-1)	peninsula 2 (PP-2)
naphthalene	37.0	32.0
2-methylnaphthalene	17.0	24.0
1-methylnaphthalene	12.0	17.0
acenaphthylene	0.9	0.9
acenaphthene	4.1	1.9
fluorene	12.0	6.4
phenanthrene	30.0	22.0
anthracene	1.1	1.0
2-methylphenanthrene	7.0	7.3
1-methylphenanthrene	4.2	4.8
fluoranthene	7.0	12.0
pyrene	2.2	3.9
benz[a]anthracene	2.2	3.3
chrysene	9.1	9.6
benzo[b]fluoranthene	6.8	7.5
benzo[k]fluoranthene	1.1	6.7
benz[a]pyrene	1.5	7.4
perylene	4.0	10.0
indeno[1,2,3-cd]pyrene	1.5	2.8
dibenz[a.h]anthracene	1.5	1.3
benzo[g.h.i]perylene	4.6	5.0
Total PAHs	**170**	**190**
gamma chlordane	0.06	0.02
alpha chlordane	0.06	-
trans nonachlor	0.04	0.02
dieldrin	-	-
p,p'- DDE	0.5	0.3
p,p'-DDD	0.1	0.4
p,p'-DDT	1.5	0.9
Total DDT	**2.1**	**1.6**

Table 9. Concentrations of polycyclic aromatic hydrocarbons and chlorinated pesticides in peninsula soils from the Main site (ng/g).

compound	peninsula 3	peninsula 7	peninsula 15	peninsula 15*
naphthalene	28.0	39.0	19.0	25.0
2-methylnaphthalene	13.0	13.0	31.0	25.0
1-methylnaphthalene	12.0	12.0	16.0	17.0
acenaphthylene	0.3	0.7	1.3	1.4
acenaphthene	3.4	3.8	3.9	3.0
fluorene	7.2	6.3	8.7	7.4
phenanthrene	22.0	27.0	23.0	24.0
anthracene	0.6	0.9	1.9	2.2
2-methylphenanthrene	7.6	7.9	8.2	7.9
1-methylphenanthrene	3.6	4.6	5.4	6.7
fluoranthene	8.1	8.5	27.0	29.0
pyrene	3.1	2.6	17.0	17.0
benz[a]anthracene	2.5	2.5	13.0	11.0
chrysene	8.8	12.0	20.0	18.0
benzo[b]fluoranthene	7.1	8.5	27.0	24.0
benzo[k]fluoranthene	2.0	3.3	11.0	7.9
benz[a]pyrene	4.7	7.4	9.6	6.7
perylene	12.0	11.0	23.0	19.0
indeno[1,2,3-cd]pyrene	7.6	7.8	123.0	132.0
dibenz[a.h]anthracene	7.1	5.4	68.0	82.0
benzo[g.h.i]perylene	14.0	18.0	129.0	139.0
Total PAHs	**180**	**200**	**590**	**600**
gamma chlordane	-	0.02	0.06	0.02
alpha chlordane	0.02	0.02	0.04	0.02
trans nonachlor	0.02	0.02	0.08	0.02
dieldrin	-	-	-	-
p,p'- DDE	0.3	0.6	0.8	0.4
p,p'-DDD	-	-	0.6	0.3
p,p'-DDT	-	2.4	1.6	1.1
Total DDT	**0.3**	**3.0**	**3.0**	**1.8**

* duplicate analysis

Table 10. Concentrations of polycyclic aromatic hydrocarbons and chlorinated pesticides in agricultural soils from the North Point Properties (ng/g).

compound	site 1	site 2
naphthalene	42.0	47.0
2-methylnaphthalene	35.0	31.0
1-methylnaphthalene	18.0	18.0
acenaphthylene	2.0	1.1
acenaphthene	2.7	3.6
fluorene	5.3	4.8
phenanthrene	35.0	33.0
anthracene	1.7	1.3
2-methylphenanthrene	9.0	9.9
1-methylphenanthrene	6.2	5.2
fluoranthene	19.0	16.0
pyrene	4.7	4.5
benz[a]anthracene	3.1	3.6
chrysene	16.0	15.0
benzo[b]fluoranthene	12.0	11.0
benzo[k]fluoranthene	2.7	2.4
benz[a]pyrene	8.0	7.5
perylene	0.8	3.6
indeno[1,2,3-cd]pyrene	3.7	4.0
dibenz[a.h]anthracene	1.0	1.5
benzo[g.h.i]perylene	5.0	5.3
Total PAHs	**230**	**230**
gamma chlordane	0.06	0.06
alpha chlordane	0.10	0.06
trans nonachlor	0.08	0.08
dieldrin	-	-
p,p'- DDE	1.7	2.3
p,p'-DDD	0.8	0.8
p,p'-DDT	7.2	6.4
Total DDT	**9.7**	**9.5**

Table 11. Concentrations of polycyclic aromatic hydrocarbons and chlorinated pesticides in agricultural soils from the Leonard Ranch (ng/g).

compound	site 1	site 2
naphthalene	22.0	33.0
2-methylnaphthalene	34.0	22.0
1-methylnaphthalene	46.0	14.0
acenaphthylene	0.6	0.6
acenaphthene	2.6	5.5
fluorene	5.7	6.3
phenanthrene	24.0	28.0
anthracene	0.8	1.5
2-methylphenanthrene	7.2	6.8
1-methylphenanthrene	4.5	4.4
fluoranthene	8.4	25.0
pyrene	2.7	19.0
benz[a]anthracene	2.5	16.0
chrysene	9.7	31.0
benzo[b]fluoranthene	8.8	41.0
benzo[k]fluoranthene	1.4	18.0
benz[a]pyrene	0.6	24.0
perylene	9.7	14.0
indeno[1,2,3-cd]pyrene	21.0	151.0
dibenz[a.h]anthracene	14.0	76.0
benzo[g.h.i]perylene	31.0	145.0
Total PAHs	**260**	**680**
gamma chlordane	0.06	0.06
alpha chlordane	0.10	0.06
trans nonachlor	0.08	0.08
dieldrin	-	-
p,p'- DDE	0.7	1.0
p,p'-DDD	0.3	0.2
p,p'-DDT	1.7	2.2
Total DDT	**2.7**	**3.4**

concentration above which adverse effects may be expected 50 percent of the time. The ER-L values of PAHs at all the sites investigated are well below the established ER-L limit of 4,022 ppb (ng/g) for total PAHs in sediments. Therefore, the potential for toxic effects from PAHs adsorbed to soils at all these study sites is relatively low.

Chlorinated pesticides

Low concentrations of first generation chlorinated pesticides were found in soil from the peninsulas of the Main and Pilot sites, the Leonard Ranch, and North Point Properties. Concentrations of the chlorinated pesticides are shown in tables 8-11. These concentrations are within the range of concentrations of total DDT in sediments of San Francisco Bay (Long and others, 1988). Chlorinated pesticides probably were applied on these agricultural lands as insecticides prior to the banning of DDT in 1972. Surprisingly, ratios of DDE/DDT were less than 1.0, indicating that DDT in these soils has not undegone extensive aerobic degradation to DDE, as is common with DDT treated western agricultural soils that have been subjected to long-term weathering, resulting in ratios of DDE/DDT greater than 1.0 (Hitch and Day, 1992). Concentrations of total DDT in soils from the North Point Properties were greater relative to all other sites in this study. Dieldrin was not detected in any of these soils, and concentrations of total chlordane were 0.2 ppb (ng/g) or lower.

The potential for toxic effects of these DDT contaminated soils were examined using the criteria of Long and Morgan (1990), and Long and Markel (1992). The Effects Range-Low (ER-L) value for total DDT is 3.0 ppb (ng/g), and the Effects Range-Median (ER-M) value is 350 ppb (ng/g). Except for the North Point Properties soil, the potential for toxic effects of DDT to biota exposed to these soils, would be low. Dilution with existing fill material at the site would lower even further any potential for toxicity. Even though the total DDT concentration of 9.7 and 9.5 ng/g at the North Point Properties site is greater than the ER-L value for DDT, the value is still closer to the ER-L value than the ER-M value. Determination of the bioavailability and toxicity of sediment associated contaminants to biota requires that other factors be considered such as grain size, porosity, and organic carbon.

CONCLUSIONS

The results of this geochemical study of soils from the peninsulas in the Sonoma Baylands Wetland Demonstration Project site and from the adjacent hayfields at Leonard Ranch and North Point Properties, which are seasonal wetlands, clearly show that these soils are contaminated with low levels of PAHs and chlorinated pesticides. However, the potential for toxic effects from these soils, should they ever contaminate the site, would be very low. It is important to understand the baseline contaminant concentration of the underlying soil and neighboring land parcels with like characteristics, and of the dredged fill material, in evaluating the feasibility of using dredge spoils to restore historic tidelands in San Francisco Bay.

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