Toxicity of Sediments on the Palos Verdes Shelf

The Palos Verdes Shelf is the site of one of the largest municipal wastewater outfall systems in Southern California. An average of 330 million gallons of treated effluent was discharged each day in 1992 through two outfalls at a depth of 60 m (SCCWRP 1993a). Historically, the discharged effluent contained high levels of contaminants and settling particles created a deposit of contaminated sediments in depths greater than 30 m (CSDLAC 1991).

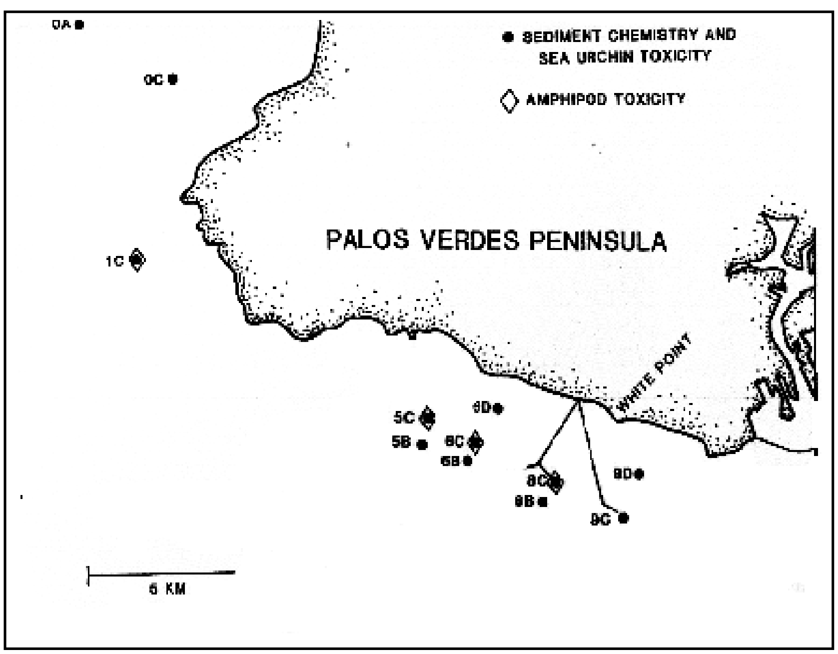
Sediment contamination and biological impacts on the Palos Verdes (PV) Shelf are well documented (Stull *et al*. 1986, Swartz *et al*. 1986, Ferraro *et al*. 1991, CSDLAC 1991). The most obvious biological impacts are changes in the composition and abundance of benthic invertebrate populations living in or on the sediments. Over the past two decades, biological and chemical conditions have improved in response to changes in wastewater treatment; however, benthic communities near the outfalls continue to show effects. Alterations in sediment quality as a result of wastewater discharge are probably responsible for these changes, but the cause is unknown.

Many potentially toxic chemicals are present in sediments on the Palos Verdes Shelf (e.g., hydrogen sulfide, chlorinated hydrocarbons, trace metals, polynuclear aromatic hydrocarbons). The tissues of some animals living on the sediments have elevated concentrations of chlorinated hydrocarbons and mercury (Eganhouse and Young 1978, Brown *et al*. 1986, SCCWRP 1993b), and sediments from the shelf are toxic to crustaceans and echinoderms (Swartz *et al*. 1986, Anderson *et al*. 1988). Changes in the benthic community may be caused by toxic responses to chemicals in the sediments, or it may be caused by responses to other sediment constituents (e.g., grain size, organic matter, Thompson *et al*. 1993). Sediment organic content, which is elevated along with contamination on the PV Shelf, may affect the composition of the benthic community (Swartz *et al*. 1985).

Information on the magnitude and spatial extent of sediment toxicity on the Palos Verdes Shelf is limited. Swartz *et al*. (1986) measured toxicity at eight stations along the 60 m depth contour. However, their results are based on short-term amphipod survival, a test that is no longer sensitive to the level of toxicity in the sediments (Swartz *et al*. 1986, Anderson *et al*. 1988). More recent experiments demonstrate that exposure to PV sediments causes sublethal effects on the growth of amphipods and sea urchins (Nipper *et al*. 1989, Thompson *et al*. 1989); however, these studies did not test multiple locations.

The objective of this study was to measure the toxicity of sediments from the Palos Verdes Shelf to infaunal (amphipods) and epibenthic (sea urchins) organisms. Data on sediment and tissue contamination, and sediment toxicity were collected at 12 stations on the PV Shelf. The study described herein was part of a larger study funded by the Santa Monica Bay Restoration Project (Bay *et al*. 1994).

FIGURE 1. Location of Palos Verdes sediment collection stations. Station numbers were established by County Sanitation Districts of Los Angeles County.



MATERIALS AND METHODS

Sediment and interstitial water samples were collected in June and July 1992 from 12 stations on the Palos Verdes Shelf in depths from 30 to 300 m (Figure 1). Sediment was also collected from an uncontaminated site near Dana Point (station R52). Sediments were collected with a 0.05 m^2 GOMEX box core (Boland and Rowe

1991) fitted with a two-piece, acrylic core liner that minimized sediment disturbance during sample handling and storage. The upper portion of the liner contained the top 4 cm of sediment. It was removed, fitted with a base, and used as the container for the sea urchin growth test. Undisturbed sediment for interstitial water samples was removed from replicate box cores with polycarbonate cores. Surface sediment (top 2 cm) was removed from an undisturbed area of the box core with a plastic scoop for chemical analysis, sulfide analysis, and amphipod survival tests. Subsamples from replicate cores were combined to create a composite for chemical analysis.

Analyses of sediment and tissue samples for trace metals and organics were conducted by the Geochemical and Environmental Research Group (GERG) of Texas A&M University and are described in detail in Bay *et al.* (1994). Silver (Ag), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) were measured by flame or graphite furnace atomic absorption spectrometer. The average recovery of metals from spiked duplicates was 100% and the average percent difference between laboratory duplicates was 10%.

Sediment and tissue samples were analyzed for chlorinated hydrocarbons [DDT compounds and 20 polychlorinated biphenyl (PCB) congeners] and polynuclear aromatic hydrocarbons (PAH) using the methods of NOAA's National Status and Trends Program (MacLeod *et al.* 1985, Sericano *et al*. 1990). Chlorinated hydrocarbons were quantified by capillary column gas chromatography and electron capture detection. Total PCB concentration (ΣPCB) concentration was the sum of the detected congeners; total DDT concentration (ΣDDT) was the sum of DDT+DDE+DDD. Typical detection limits were 0.25 ng/g for sediments and 15 ng/g for tissues. The average recovery of chlorinated hydrocarbons from spiked sediments was 87% and laboratory duplicates differed by an average of 14%. The average recovery for tissues was 82% and the average percent difference between laboratory duplicates was 54%. Tissue lipid content was determined gravimetrically from a portion of the solvent extract.

Sediment and tissue samples were analyzed for 27 parent and alkylated PAH compounds by GC-mass spectrometer. The total PAH (ΣPAH) concentration was the sum of all compounds plus alkylated homologue groups (e.g., C1-fluorenes). Typical detection limits were 2 ng/g for sediments and 100 ng/g for tissues. The average recovery for sediment was 102% and the average percent difference between laboratory duplicates was 10%. Average recovery and duplicate differences for tissue PAH were both 82%.

Sediment grain size, organic carbon, nitrogen, and acid volatile sulfides were measured at SCCWRP. Percent sand, silt, and clay was measured by sieving and pipette analysis (Plumb 1981). Organic carbon was measured by high temperature combustion (Hedges and Stern 1984). Acid volatile sulfides (AVS) was measured by weak acid digestion and a colorimetric quantitation procedure according to EPA draft method 376.3 (Allen *et al.* 1993). Interstitial water sulfide was measured by the methylene blue colorimetric method (APHA 1989). Electrodes were used to measure interstitial water ammonia, pH, and dissolved oxygen.

Interstitial water was obtained by centrifugation and tested for toxicity with a sea urchin fertilization test (Dinnel *et al.* 1987). Sperm were collected from the purple sea urchin, *Strongylocentrotus purpuratus*, and exposed to solutions of 100, 50, and 10% interstitial water for one hour. Seawater carried through the interstitial water collection process was used as the control. The percentage of eggs fertilized by the sperm was measured with a microscope.

Whole sediments were tested for toxicity with amphipod (*Rhepoxynius abronius*) and white sea urchin (*Lytechinus pictus*) tests at 15°C. A 10-day test was used to measure the effects on amphipod survival (ASTM 1991). Amphipods were collected from Yaquina Bay; sediment from the collection site was used as a control. A 35-day test was used to measure the effects on sea urchin growth (Thompson *et al.* 1989). White sea urchins were collected at Dana Point (R52); sediment from the collection site was used as a control. Growth was measured by change in wet weight, body diameter, and gonad weight. Gonad tissues from all individuals in a replicate were composited and analyzed for contaminants.

Differences in sea urchin fertilization and growth among stations were tested by Kruskal-Wallis analysis of variance by ranks. Differences in amphipod survival among stations were tested by analysis of variance (Jandel Scientific 1994). The relations among chemical measurements, sediment characteristics, and toxicity test responses were examined with Spearman rank correlation coefficients (SYSTAT 1992).

Sediment organic contaminant concentrations were normalized to TOC prior to analysis by:

TOC normalized concentration (µ/g OC) = C_s/TOC

where:

C_s = sediment concentration in µg/kg dry weight, and

TOC = organic carbon content in g/kg dry weight.

Tissue organic contaminant concentrations were normalized to lipid prior to analysis by:

lipid normalized concentration (µg/g lipid) = C_t/lipid where:

C_t = tissue concentration in µg/kg wet weight, and
lipid = lipid concentration in g/kg wet weight.

Tissue accumulation factors (AF) were calculated by:

AF = lipid normalized tissue concentration/TOC normalized sediment concentration.

RESULTS

Sediment and Interstitial Water Characteristics

The physical and chemical characteristics of the sediment on the Palos Verdes Shelf varied with depth and proximity to the outfall (Tables 1 and 2). Most stations in depths ≥60 m were sandy-silts; the two shallow stations (6D and 9D) had a higher sand content (silty-sands). Organic carbon content increased with depth and proximity to the outfalls (for stations located northwest of the outfall system). Sediment trace metals and trace organics had similar patterns; the highest concentrations occurred at stations nearest and northwest of the "Y" outfall and lowest levels usually at the 30 m stations.

Concentrations of sediment acid volatile sulfides (AVS) ranged from undetectable to >9 µMole/g near the outfall (Table 1). The average percent (relative to sediment concentration) of total metal extracted during AVS digestion (simultaneously extracted metal or SEM) was highest for Cd, Pb, and Zn (59-68%). Significantly lower percentages of Ni (14%), Cr (27%), Ag (36%), and Cu (43%) were removed by the extraction (Kruskal-Wallis test, H=46.3, $p<0.0001$). There were no significant differences in SEM percentages among stations, although R52 had the lowest values for Cd, Cr, Ni, Pb, and Zn. The summed concentration of divalent SEM percentages(Ag, Cd, Cu, Ni, Pb, and Zn) exceeded AVS concentration (SEM/AVS>1) at stations 0C, 1C, 8B, 9D, and R52 (Table 1). Ratios >1 for R52, 0C, and 1C were due to levels of AVS ≤0.1 µMole/g.

Total ammonia and sulfide concentrations were elevated in some interstitial water samples (Table 3); the sulfide data were determined on separate samples collected in November 1992. Sulfide was not detected in interstitial water samples in July, apparently because of problems with sample filtration or storage. Interstitial water pH was similar among the stations and about 0.5 units below seawater values. Dissolved oxygen (Table 3) was measured during the toxicity tests and reflects oxygenation during sample handling and storage. Dissolved oxygen was usually <2 mg/L in interstitial water samples when they were extracted.

TABLE 1. General characteristics of sediments on the Palos Verdes Shelf in June–July 1992. One composite sample was analyzed from each station. All values are dry weight.

Station	Depth (m)	Sand (%)	TOC (%)	AVS[a] (µMole/g)	ΣSEM[b] (µMole/g)
0A	300	26	2.4	4.1	1.0
0C	60	21	1.1	0.1	1.6
1C	60	40	1.2	0.1	1.1
5B	150	11	3.8	6.7	5.4
5C	59	19	2.4	7.6	3.3
6B	150	10	4.5	7.4	6.7
6C	60	21	2.8	9.3	4.0
6D	30	78	0.8	1.7	0.8
8B	150	11	4.3	3.7	6.5
8C	60	42	3.1	9.3	7.0
9C	60	47	1.4	5.6	2.2
9D	30	85	0.6	1.0	2.2
R52	60	4	1.0	<0.1	1.1

[a]Acid volatile sulfides.
[b]Summed concentration of Ag, Cd, Cu, Ni, Pb, and Zn extracted during AVS analysis.

TABLE 2. Chemical characteristics of sediments on the Palos Verdes Shelf in June–July 1992. One composite sample was analyzed from each station.

	Metals (mg/kg)							Organics (ng/g)		
Station	Ag	Cd	Cr	Cu	Ni	Pb	Zn	ΣDDT	ΣPCB	ΣPAH
0A	2.94	1.35	151	50.7	34.8	42.0	119	629	162	2,440
0C	1.35	0.80	108	25.9	23.5	28.1	86.3	773	136	1,480
1C	1.68	1.99	143	52.3	32.2	37.9	126	2,380	409	1,500
5B	5.29	11.7	337	187	45.7	108	409	10,240	1,740	4,500
5C	3.72	7.72	213	108	31.5	66.8	129	6,530	993	3,000
6B	5.79	11.7	353	189	46.3	114	425	8,480	1,790	6,560
6C	5.16	11.4	296	154	39.4	100	470	8,530	1,740	3,690
6D	0.76	2.31	77.7	19.0	19.8	15.5	88.3	609	111	760
8B	3.49	12.1	373	208	42.2	113	438	13,600	2,480	4,210
8C	6.19	9.81	272	206	37.6	189	477	18,000	3,420	10,600
9C	1.85	2.98	402	59.6	25.3	46.6	160	2,600	462	2,590
9D	0.41	1.52	69.3	12.1	16.3	12.3	78.0	454	128	685
R52	0.19	0.17	57.2	14.4	21.7	15.7	85.9	15	8	756

There was a high degree of covariance among most of the sediment constituent measurements, except for total PAH (Table 4). Percent sand and percent silt were not significantly correlated with any contaminant. There were no significant correlations between interstitial water ammonia or sulfide concentration and any sediment constituent except AVS (Table 4). Ammonia and sulfide were highly correlated with each other despite the fact that different batches of interstitial water collected were analyzed about four months apart.

TABLE 3. Characteristics of sediment interstitial water (n=1) from the Palos Verdes Shelf in June–July 1992. Sulfide was measured on samples collected in November 1992. Dissolved oxygen was measured after storing and preparing the samples for testing; it was higher than in situ measurements.

Station	Ammonia (mg/L)	pH	Total sulfide (mg/L)	H_2S[a] (µM)	Dissolved oxygen (mg/L)
0A	0.78	7.5	<0.1	<1	4.0
0C	0.33	7.5	<0.1	<1	4.6
1C	0.71	7.6	<0.1	<1	5.2
5B	1.13	7.7	<0.1	<1	5.2
5C	3.70	7.4	0.3	2	4.6
6B	1.29	7.7	<0.1	<1	5.1
6C	4.72	7.5	5.2	32	4.8
6D	1.35	7.9	<0.1	<1	5.2
8B	1.49	7.7	0.1	1	5.5
8C	3.36	7.7	0.3	2	5.6
9C	3.63	7.8	0.3	2	5.1
9D[b]			0.1	1	6.4
R52	1.07	7.8	<0.1	<1	5.6

[a]Hydrogen sulfide calculated using pH of interstitial water extracted from June–July samples.
[b]Insufficient sample for ammonia and pH analyses.

Toxicity

Interstitial water

Interstitial water concentrations as low as 10% caused reductions in sea urchin fertilization (Table 5). Dose response relations were used to estimate EC50s, which is the interstitial water concentration causing 50% reduction in fertilization.

Statistical analyses were conducted on the 50% interstitial water treatment instead of the 100% because data were available for all stations and diluted samples were less likely to produce artifacts due to differences unrelated to contaminants (e.g., differences in major ion composition). Exposure to 50% interstitial water from stations 6B, 6C, 8B, 8C, 9C, and 9D caused significant reductions in fertilization (Kruskal-Wallis test, H=22.6, p=0.047), but Dunn's multiple comparison test could not identify which stations were different from the control (p>0.05). The use of only two replicates per station probably reduced the power of the test. Recent fertilization tests with 3–5 replicates had an average minimum significant difference of 11% (SCCWRP, unpublished data).

Fertilization was normalized to the response at station 0A, which had grain size and TOC characteristics similar to the stations at 60-150 m near the outfalls. The spatial pattern of toxicity was influenced by distance from the outfalls and depth (Figure 2). Greater toxic effects were observed near the "Y" outfall (e.g., 8B and 8C) and in depths greater than 30 m.

TABLE 4. Spearman rank correlations (r_s) between sediment and interstitial water measurements. Trace organics were normalized to organic carbon content (µg/g organic carbon). Coefficients in bold type are significantly different from zero ($p \leq 0.05$). For n=13 (sediment constituents), $r_{s\ 0.05(2)11}=0.618$; $r_{s\ 0.01(2)11}=0.755$. For n=12 (interstitial water), $r_{s0.05(2)10}=0.648$; $r_{s\ 0.01(2)10}=0.794$.

	Sand	Silt	TOC	AVS	Ag	Cd	Cr	Cu	Ni	Pb	Zn	DDT_{oc}	PCB_{oc}	PAH_{oc}	Ammonia
Sand															
Silt	**-0.920**														
TOC	-0.538	0.339													
AVS	-0.041	-0.097	**0.684**												
Ag	-0.278	0.140	**0.902**	**0.882**											
Cd	-0.272	0.019	**0.835**	**0.698**	**0.790**										
Cr	-0.218	0.036	**0.817**	**0.645**	**0.731**	**0.812**									
Cu	-0.375	0.179	**0.944**	**0.708**	**0.896**	**0.889**	**0.841**								
Ni	-0.537	0.349	**0.968**	**0.612**	**0.868**	**0.790**	**0.753**	**0.885**							
Pb	-0.413	0.237	**0.957**	**0.769**	**0.945**	**0.820**	**0.808**	**0.973**	**0.896**						
Zn	-0.218	0.025	**0.864**	**0.810**	**0.896**	**0.850**	**0.813**	**0.945**	**0.824**	**0.934**					
DDT_{oc}	-0.063	-0.116	**0.666**	**0.702**	**0.753**	**0.831**	**0.621**	**0.846**	0.615	**0.769**	**0.868**				
PCB_{oc}	-0.088	-0.088	**0.707**	**0.763**	**0.808**	**0.858**	**0.648**	**0.852**	**0.670**	**0.802**	**0.890**	**0.978**			
PAH_{oc}	0.160	-0.069	0.368	0.559	0.583	0.281	0.506	0.451	0.327	0.525	0.525	0.407	0.468		
Ammonia	0.140	-0.354	0.329	**0.744**	0.462	0.557	0.524	0.483	0.182	0.462	0.643	0.622	0.636	0.277	
Sulfide	0.252	-0.347	0.187	0.634	0.349	0.371	0.403	0.361	0.066	0.349	0.512	0.608	0.620	0.431	**0.889**

TABLE 5. Results of sea urchin (*Strongylocentrotus purpuratus*) fertilization test. Sperm were exposed to interstitial water from sediments collected off Palos Verdes and Dana Point (R52). Interstitial water was diluted with lab seawater for 50% and 10% treatments; lab seawater was the control. Values are the mean of two replicates (n=5 for control); standard deviation in parentheses. The EC50 was calculated by probit analysis; values preceded by ">" or "<" did not have sufficient data to calculate an EC50.

	Fertilization						
Station	100%		50%		10%		EC50
Control	81	(6)					
0A	66	(8)	75	(4)	92	(1)	>100
0C	90	(3)	92	(5)	94	(5)	>100
1C[a]	89		93		91		>100
5B	72	(12)	82	(1)	90	(0)	>100
5C	75	(8)	90	(2)	92	(3)	>100
6B	7	(5)	44	(12)	80	(1)	53
6C	0	(0)	0	(0)	8	(12)	<10
6D	92	(2)	97	(2)	95	(2)	>100
8B	1	(2)	11	(15)	60	(13)	18
8C	1	(0)	0	(0)	1	(0)	<10
9C	38	(5)	64	(17)	85	(6)	91
9D[ab]			66		75		>50
R52	76	(7)	92	(1)	92	(4)	>100

[a]Data for single replicate.
[b]Insufficient sample to test at 100%.

Sediment

Sediments from station 8C had the lowest amphipod survival (Table 6), but none of the stations was significantly different from the control (ANOVA, F=1.874, $0.10<p<0.25$). Sea urchin survival was also unaffected by sediment exposure; the lowest survival obtained was 96% (data not shown).

A wider range of responses was obtained with sea urchin growth (Table 6). Change in body weight varied by up to a factor of four among treatments. Change in gonad weight varied by more than a factor of 20. Change in test diameter was similar among all treatments. However, the growth responses were not significantly different among stations (for gonad growth: H=19.5, p=0.077). In fact, growth on most PV sediments was similar to, or greater than, growth on sediment from the control (R52).

Changes in body weight and gonad weight were highly correlated (r_s=0.758, $p<0.01$), but there were no significant correlations with change in diameter. The spatial pattern of sea urchin weight change was similar to the interstitial water toxicity — high at the 30 m stations and low close to the "Y" outfall (Figure 2). Sea urchin fertilization in the interstitial water test was not correlated with growth in the sediment test (Table 7). The lowest sea urchin growth occurred on 0C sediment, but 0C interstitial water had high fertilization. Low growth also occurred on 5B sediment, but 5B interstitial water had high fertilization.

Toxicity-sediment chemistry relations

Fertilization was inversely correlated with dissolved hydrogen sulfide (r_s=-0.663, $p<0.05$), but not with ammonia. Fertilization was also correlated with sediment concentrations of Ag, Cr, Cu, Pb, Zn, PCB, TOC, and AVS (Table 7). Silt was the only sediment parameter that had a significant correlation with sea urchin gonad growth.

Bioaccumulation

Trace metals were not accumulated by sea urchins during the 35-day exposure (Table 8). Gonad concentrations of Ag, Cd, Cr, Cu, and Ni declined during the experiment. Concentrations of Pb and Zn were similar to pre-exposure levels. Trace metal concentrations in sea urchins exposed to sediments with the highest metal levels (e.g., 8B and 6B) were similar to concentrations in urchins exposed to sediments from less contaminated stations (e.g., 0A and R52). Gonad concentrations were correlated with sediment concentrations only for Pb (r_s=0.735, $p<0.05$).

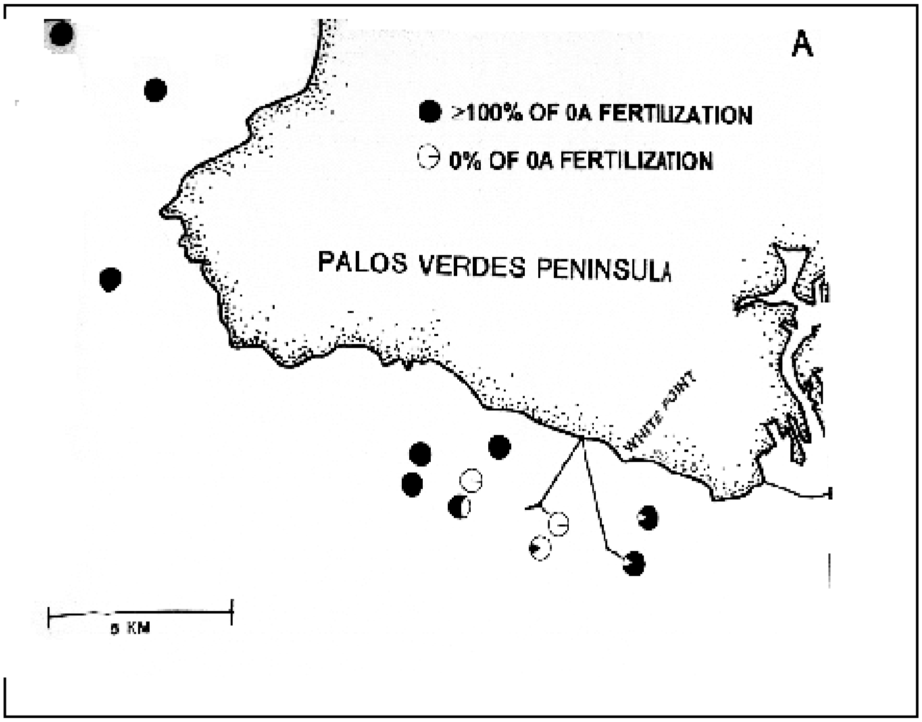
Trace organics were accumulated by sea urchins during the 35-day exposure (Table 8). Gonad concentrations of DDT, PCB, and PAH among sea urchins exposed to the more contaminated sediments were higher than the initial values, and higher than urchins exposed to less contaminated sediments. Lipid normalized gonad concentrations of total DDT (r_s=0.874, $p<0.001$) and total PCB (0.945, $p<0.001$) were correlated with TOC normalized sediment concentrations. Tissue PAH was not correlated with sediment PAH (r_s=0.377, $p>0.05$).

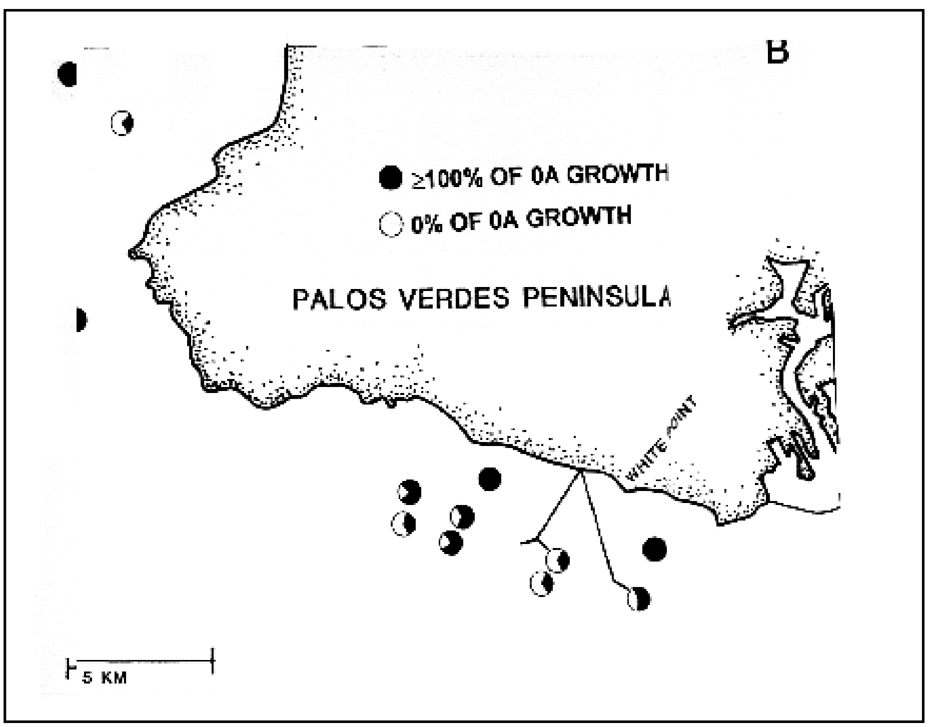
Of all the trace organics, DDT compounds were present in the highest concentrations in the tissues, and *p,p'*-DDE was the most abundant metabolite. Among PCBs, congeners with 4-6 chlorines were present the highest concentrations. Sea urchins exposed to sediment from station 8C contained in the highest concentrations of DDT, PCB, and PAH.

Chlorinated hydrocarbons were accumulated to a greater extent than PAHs (AF_{PCB}=2.9; AF_{DDT}=1.8; AF_{PAH} = 0.4). The mean AFs for PCB congeners ranged from 1.1–6.8; from 0.67–3.0 for DDT and metabolites; and from 0.26–2.2 for PAH compounds. Data from station R52 were excluded from the chlorinated hydrocarbon AF calculations because many congeners were not detected in the sediment.

At least one of the urchin growth parameters was inversely correlated with the gonad concentration of every contaminant (Table 9). Change in total weight was inversely correlated with all contaminants.

FIGURE 2. Results of the sea urchin toxicity test plotted according to station location. The area shaded in each circle corresponds to the percent response relative to station 0A. A) *Strongylocentrotus purpuratus* fertilization test with 50% interstitial water. Percent fertilization was greater at stations 0C, 1C, 5B, 5C, and 6D than at OA. B) *Lytechinus pictus* growth (change in body weight) on sediment. Growth was greater at stations 6D and 9D than at 0A.





DISCUSSION

Sediment Chemistry

Sediment concentrations of trace metals and PCB generally agreed with those reported by the County Sanitation Districts of Los Angeles County (CSDLAC) for the same stations. However, CSDLAC measurements of DDT were 116–204% higher than the values obtained in this study for 10 of 11 stations (CSDLAC 1992). This may have been due to different analytical methods, sampling techniques, or sediment heterogeneity. The apparent bias between DDT measurements made by CSDLAC and GERG should be investigated so data from these sources can be combined to examine spatial and temporal trends.

The bioavailability and toxicity of divalent trace metals can be predicted from sediment acid volatile sulfides (AVS) and the concentration of simultaneously extracted metals (SEM) (Di Toro *et al*. 1992). Sediments with SEM/AVS ratios <1 probably have sufficient metal binding capacity to maintain dissolved concentrations below acutely toxic levels. In sediments with ratios >1, the binding capacity of the sediment is probably exceeded and toxicity may result. Sediment SEM/AVS ratios were >1 for some PV stations (Table 1), but metal concentrations were not elevated in sea urchin tissues (Table 8). These results suggest that Ag, Cd, Cr, Cu, Ni, Pb, and Zn in PV sediments were not bioavailable during the toxicity tests. Resident marine life on the Palos Verdes Shelf do not accumulate trace metals (Brown *et al*. 1986, Bay *et al*. 1994).

TABLE 6. **Results of 10-day amphipod (*Rhepoxynius abronius*) survival tests and 35-day sea urchin (*Lytechinus pictus*) growth tests with sediment collected off Palos Verdes and Dana Point (R52). Control sediments were from Yaquina Bay, Oregon (*R. abronius*) and station R52 (*L. pictus*). Values are means and standard deviation in parentheses; n=2 except for amphipod data (n=4).**

	R. abronius		*L. pictus*					
Station	Survival (%)		Body diameter change (mm)		Body weight change (g)		Gonad weight change (g)	
Control	95	(6)						
0A	NT[a]		1.01	(0.43)	0.21	(0.10)	0.068	(0.021)
0C	NT		0.67	(0.09)	0.06	(0.04)	0.007	(0.001)
1C	86	(15)	0.93	(0.08)	0.15	(0.03)	0.036	(0.034)
5B	NT		0.88	(0.21)	0.08	(0.07)	0.013	(0.013)
5C	91	(8)	0.79	(0.01)	0.16	(0.07)	0.044	(0.020)
6B	NT		0.97	(0.06)	0.16	(0.03)	0.017	(0.001)
6C	95	(6)	0.76	(0.08)	0.14	(0.08)	0.022	(0.015)
6D	NT		0.95	(0.07)	0.25	(0.08)	0.061	(0.008)
8B	NT		0.93	(0.15)	0.07	(0.09)	0.024	(0.010)
8C	81	(11)	0.80	(0.05)	0.07	(0.09)	0.012	(0.003)
9C	NT		0.82	(0.12)	0.12	(0.04)	0.033	(0.005)
9D	NT		1.14	(0.17)	0.23	(0.00)	0.046	(0.020)
R52	95	(4)	0.82	(0.06)	0.13	(0.08)	-0.003	(0.006)

[a]Not tested.

TABLE 7. **Spearman rank correlations (r_s) between sea urchin (*Lytechinus pictus*) growth parameters, 50% interstitial water sea urchin (*Strongylocentrotus purpuratus*) fertilization test, and sediment contaminants and characteristics. Trace organics were normalized to organic carbon content (µg/g organic carbon). Coefficients in bold type are significantly different from zero (n=13; $r_{s\ 0.05(2)11}$=0.618; $r_{s\ 0.01(2)11}$=0.755).**

	Sediment (growth test)			Interstitial water (fertilization test)
	Body diameter	Body weight	Gonad weight	Fertilization
Body diameter	1.000			0.039
Body weight	0.588	1.000		0.300
Gonad weight	0.544	**0.758**	1.000	0.193
Ag	-0.176	-0.275	-0.165	**-0.656**
Cd	0.022	-0.234	-0.058	-0.607
Cr	-0.066	-0.401	-0.060	**-0.650**
Cu	-0.176	-0.484	-0.231	**-0.664**
Ni	-0.016	-0.352	-0.231	-0.567
Pb	-0.198	-0.462	-0.302	**-0.708**
Zn	-0.253	-0.407	-0.203	**-0.738**
DDT_{oc}	-0.280	-0.330	-0.077	-0.573
PCB_{oc}	-0.264	-0.335	-0.154	**-0.669**
PAH_{oc}	-0.410	-0.358	-0.281	-0.474
Sand	0.240	0.369	0.532	0.061
Silt	-0.435	-0.465	**-0.635**	0.121
TOC	-0.058	-0.393	-0.231	**-0.646**
AVS	-0.223	-0.030	-0.044	**-0.695**

Interstitial Water Toxicity

The spatial pattern of interstitial water toxicity was consistent with the spatial pattern of sediment contamination (Figure 2). Ammonia concentrations were not high enough to affect sea urchin fertilization (Bay *et al*. 1993), although ammonia was elevated in some interstitial water samples. Interstitial water toxicity was correlated with the dissolved sulfide concentration, but this relation was suspect because the sulfide data were obtained from different samples. Some toxic PV interstitial water samples contained 1–32 µM H_2S. Reductions in sea urchin fertilization occurred in seawater spiked with H_2S at concentrations ≥0.6 µM (Bay *et al*. 1994). The significant correlations between fertilization and the sediment concentration of PCB and several trace metals suggested that other contaminants contributed to interstitial water toxicity. Extensive covariation among sediment contaminants (Table 4) precluded identifying the responsible contaminants.

Sediment Toxicity

Amphipod survival

Sediments from the Palos Verdes Shelf were not acutely toxic to *R. abronius* (Table 6). In 1986, survival of *R. abronius* was 83-91% in sediments collected near the outfall (Ferraro *et al*. 1991), which is similar to the results in this study. Toxicity declined during 1980-83 and generally has not been detectable since then. However, resident macrofauna on the PV Shelf are impacted by wastewater discharges (CSDLAC 1991) indicating that the

Station	Metals (mg/kg) Ag	Cd	Cr	Cu	Ni	Pb	Zn	Organics (ng/g) ΣDDT	ΣPCB	ΣPAH
Initial[a]	0.16	0.75	0.40	0.72	0.73	0.09	66.8	27	27	138
0A	0.06	0.14	0.16	0.42	0.24	0.08	43.2	1,400	449	324
0C	0.09	0.23	0.34	0.60	0.62	0.13	86.6	3,760	647	355
1C	0.08	0.16	0.19	0.35	0.30	0.09	27.8	14,000	2,980	823
5B	0.05	0.21	0.31	0.52	0.57	0.18	37.1	15,200	4,780	2,260
5C	0.05	0.15	0.17	0.42	0.26	0.09	26.4	8,890	3,060	1,670
6B	0.04	0.17	0.20	0.49	0.26	0.10	66.7	14,450	5,290	1,570
6C	0.07	0.23	0.36	0.54	0.34	0.10	88.0	10,700	3,950	2,140
6D	0.05	0.11	0.19	0.44	0.10	0.08	28.9	2,320	779	440
8B	0.05	0.18	0.46	0.56	0.38	0.18	67.8	14,900	6,360	1,820
8C	0.05	0.18	0.22	0.48	0.38	0.11	63.3	22,400	6,940	3,670
9C	0.05	0.15	0.21	0.38	0.26	0.10	58.2	8,170	2,420	2,140
9D	0.04	0.16	0.12	0.36	0.12	0.07	25.5	1,970	548	324
R52	0.06	0.28	0.26	0.56	0.60	0.08	63.4	327	181	477

[a]Concentration in Dana Pt. sea urchins prior to exposure; two composites of 48 and 63 individuals.

TABLE 8. Contaminant concentrations in sea urchin (*Lytechinus pictus*) gonad collected off Dana Pt. after 35-day laboratory exposure to sediments. All values are wet weight. Data are mean of two composites of 15 individuals each.

R. abronius test is not sensitive to ambient factors that affect sediment quality.

<u>Sea Urchin Growth</u>

The failure to detect statistically significant differences in sea urchin growth among treatments was not unexpected. The growth experiment was not designed to differentiate among sites, but rather to describe the pattern of response. Exposure to sediments from 0C, 5B, 8B, and 8C resulted in growth (body weight) reductions relative to the control (R52) (Table 6). None of the PV stations resulted in substantial reductions in test diameter or gonad weight relative to R52. However, more replicates probably would have improved the power of the test to detect significant differences (Thompson *et al*. 1991).

The growth reductions on sediments collected at the "Y" outfall were consistent with previous sea urchin tests on sediments from a nearby station (7C). Thompson *et al*. (1989) observed reductions in test diameter and gonad weight (body weight change was not measured). Anderson *et al*. (1988) observed reductions in test diameter and body weight, but not gonad weight. Differences in the pattern of response may reflect variations in the magnitude or mechanism of toxicity among experiments, or perhaps seasonal differences in sea urchin physiology (e.g., reproductive cycle).

Surprisingly, the lowest sea urchin growth occured in sediments from 0C (Table 6), which was relatively low in contaminants (Table 2), located far from the outfalls, and inhabited by *L. pictus*. Sediment characteristics unrelated to contamination may have affected the results. Station 0C had relatively little TOC and AVS for a silty sediment (Table 1). The influence of grain size and TOC on the *L. pictus* growth test is unknown, but these factors influence the results of sediment tests with other species (Widerholm *et al*. 1987, DeWitt *et al*. 1988, Ankley *et al*. 1994). Sea urchins exposed to sediments from stations 0A and 6D had relatively high growth over a wide range of grain size, TOC, and AVS.

Different spatial patterns were obtained for the interstitial water and sediment growth test responses (Figure 2), which was not surprising considering that the tests differed in duration, lifestage tested, and potential route of exposure. Both methods are appropriate for assessing sediment quality because they account for the diversity of lifestyles among benthic macrofauna.

TABLE 9. Spearman rank correlations (r_s) between sea urchin (*Lytechinus pictus*) growth parameters and tissue contaminant concentrations after 35-day sediment exposure. Data for replicates from each station were used in calculations (n=26). Coefficients in bold type are significantly different from zero ($r_{s\ 0.05(2)24}$=0.406; $r_{s\ 0.01(2)24}$ =0.521).

	Body diameter	Body weight	Gonad weight
Body weight	0.312	1.000	
Gonad weight	**0.414**	**0.610**	1.000
Ag	**-0.447**	**-0.425**	-0.297
Cd	-0.323	**-0.713**	**-0.728**
Cr	-0.302	**-0.671**	**-0.483**
Cu	-0.131	**-0.583**	-0.371
Ni	**-0.473**	**-0.828**	**-0.600**
Pb	-0.066	**-0.687**	-0.262
Zn	-0.151	**-0.541**	-0.383
DDT	-0.022	**-0.458**	-0.279
PCB	0.033	**-0.406**	-0.205
PAH	-0.057	**-0.537**	-0.317

Bioaccumulation

The decline in the concentrations of trace metals in sea urchin tissue may have been due to increases in gonad mass (growth dilution) during the experiment. The average gonad weight of individuals exposed to sediment from 0A, 5C, 6D, and 9D more than doubled from the estimated initial weight; gonads in other treatments grew less than 50%. Gonad concentrations were corrected for growth by dividing the mass of contaminant measured after 35 days by the initial gonad weight (0.04 g) (Figure 3). The inverse correlations between tissue metals and growth (Table 9) were an artifact of gonad growth. The maximum change in Cd concentration produced by growth correction (0.23 mg/kg) was greater than the range in measured values among sea urchins exposed to PV sediments (0.12 mg/kg).

The correction for gonad growth did not affect the tissue concentrations of organics to the same extent as the tissue concentration of metals (Figure 3). The maximum change in DDT concentration produced by growth correction (11,000 ng/g) was about half the range in measured values among the Palos Verdes treatment groups (21,000 ng/g). Growth dilution effects were less for organics because accumulation was greater than growth.

Change in sea urchin body weight was weakly correlated with tissue concentrations of DDT and PAH (Figure 4). The range of growth in treatment groups with the lowest concentrations of organics was nearly as large as the range for all stations combined. There was also substantial variation in growth between replicates that was unrelated to tissue concentration (e.g., 0A).

Chronic toxicity-chemistry relations

The DDTs, PCBs, and PAHs in PV sediments were more likely than metals to affect sea urchin growth (Tables 7 and 9). Metals in the sediments were not bioavailable in the laboratory exposure. The statistically significant correlations between growth and tissue metal concentrations (Table 9) are probably an artifact of gonad growth. Tissue concentration is a better measure of effective dose for predicting toxic effects of some contaminants than sediment concentration (McCarty and Mackay 1993).

The effects range approach of Long *et al*. (1995) was of limited use for determining the cause of sea urchin growth reductions in this study. Sediments that caused growth reductions (8B and 8C) had concentrations of DDT (1.58–46.1 ng/g dry weight), PCB (22.7–180 ng/g dry weight), and PAH (4,022–44,792 ng/g dry weight) that were within the “possible-effects” ranges (concentrations between the Effects Range-Low and Effects Range-Median). Long *et al*. (1995) caution that their concentration-effects relations for PCB and DDT are relatively weak.

Swartz *et al*. (1994) examined the relation between sediment toxicity and amphipod abundance in PV sediments and at two other sites contaminated predominantly by DDTs. They concluded that chronic effects on amphipod populations occurred at DDT concentrations >100µg/g OC (organic carbon normalized concentration). Total DDT concentrations at 8B, 8C, and 5B, which caused reduced sea urchin growth, were 269–580µg/g OC. However, sea urchin growth (body weight change) was not affected at 1C, 5C, 6B, 6C, and 9C, which had total DDT concentrations >100µg/g OC.

In a separate experiment, *L. pictus* was exposed to sediments spiked with *p,p'*-DDE (Bay *et al*. 1994), the dominant contaminant in sea urchins exposed to PV sediments. Their growth was unaffected by tissue DDE concentrations that were four times higher than the concentrations in the PV sediment exposure. The *p,p'*-DDE is probably not the cause of growth effects in *L. pictus* exposed to PV sediments. The relations between chronic toxicity and tissue residues of *p,p'*-DDD and *o,p'*-DDE, as well as PCBs and PAHs, need to be examined to determine if the correlations identified in this study represent meaningful causal relations. Laboratory tests with spiked sediments may lead to a better understanding of the cause of toxicity in sediments from the Palos Verdes Shelf.

CONCLUSIONS

Acute toxicity (amphipod survival) was not observed at the four PV sites investigated. Chronic toxicity (sea urchin fertilization and sea urchin growth) was detected at stations nearest the “Y” outfall. Sea urchin growth was also affected by exposure to sediments with low contaminant levels, demonstrating the need for more information on the influence of non-contaminant factors on chronic toxicity tests. Further studies are also needed before the factors influencing interstitial water toxicity can be resolved. Statistical analyses identified significant correlations between biological effects and most of the contaminants measured, including hydrogen sulfide, chlorinated hydrocarbons, polynuclear aromatic hydrocarbons, and metals. Laboratory dose-response tests could determine the biological significance of these correlations. Limited results confirmed the important role of hydrogen sulfide in invertebrate toxicity and discounted the importance of *p,p'*-DDE.

Measurement of contaminant concentrations in sea urchin gonads provided useful information about contaminant bioavailability and dose during the laboratory exposures. Tissue concentration data were useful for evaluating

FIGURE 3. Dilution effects of growth on *Lytechinus pictus* gonad concentrations of Cd and ΣDDT after 35-day sediment exposure. The corrected data are predicted concentrations assuming no change in tissue mass during the experiment (initial gonad weight of 0.04 g used in calculations).

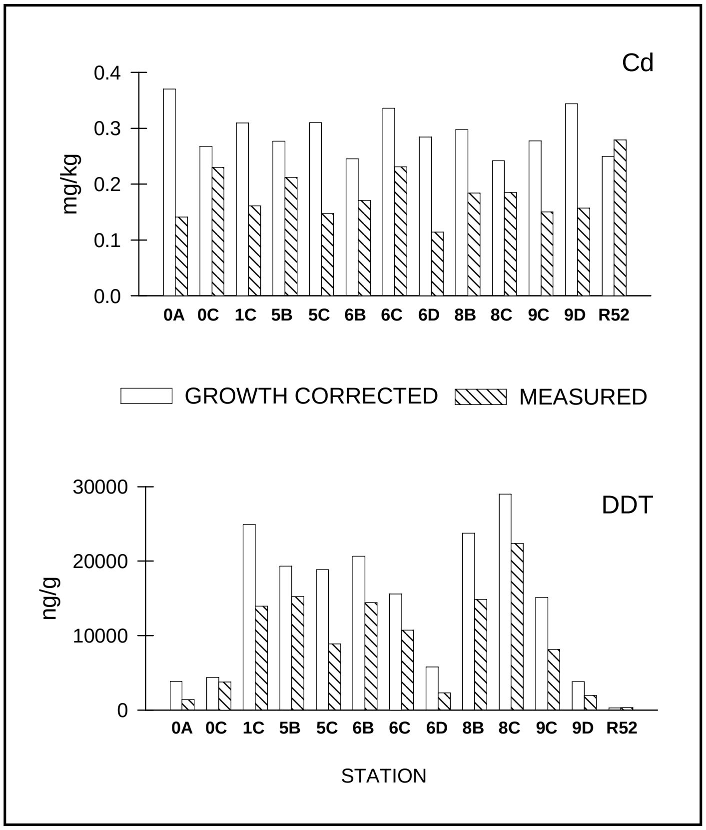
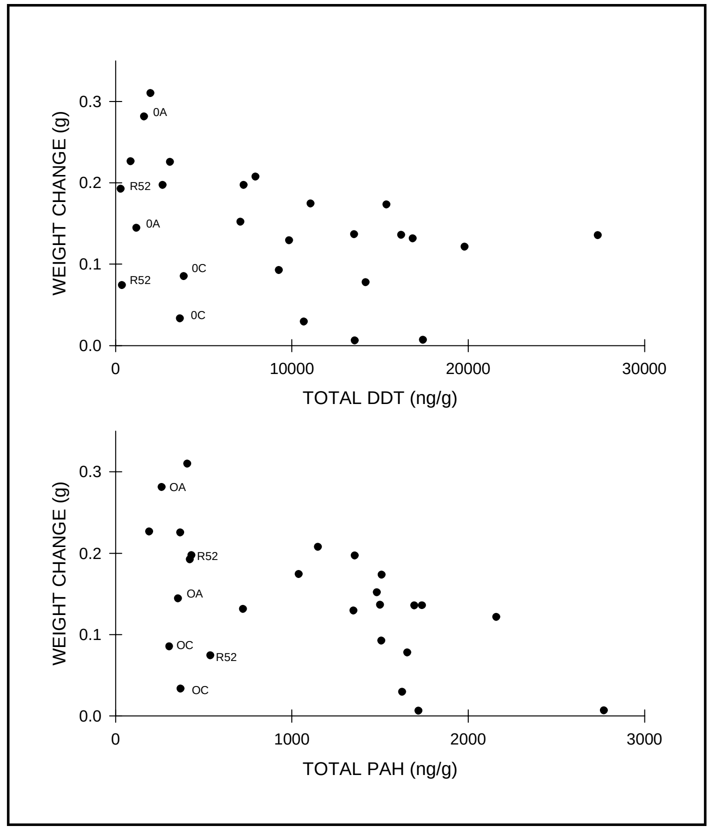


FIGURE 4. Relation between *Lytechinus pictus* growth (weight change) and gonad concentratiuons of ΣDDT and ΣPAH. Values for each replicate are plotted. Data for the three silty stations (>30 m depth) with the lowest sediment contaminant concentrations are labeled.



the significance of correlations with trace metals, and for linking the results of experiments with field data and spiked sediment studies. Further spiked sediment tests are needed to evaluate the biological significance of the contaminant correlations. The tissue contaminant data from this study provide a basis for future dose-response experiments.

REFERENCES

Allen, H.E., G. Fu, and B. Deng. 1993. Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem*. 12:1441-1453.

APHA. see *American Public Health Association*.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. 1989. Method 4500-S^{2-} Sulfide, *In:* Standard Methods for the Examination of Water and Wastewater, 17th ed. L.S. Clesceri, A.E. Greenberg, and R.R. Trussell (eds.), American Public Health Association, Wash. DC.

American Society for Testing and Materials. 1991. Guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. E 1367-90, *In:* Annual Book of ASTM Standards, vol. 11.04. ASTM, Philadelphia, PA.

Anderson J.W., S.M. Bay, and B.E. Thompson. 1988. Characteristics and effects of contaminated sediments from Southern California. Final Report to California State Water Resources Control Board, June 1988. Southern California Coastal Water Research Project, Long Beach. 120 pp.

Ankley, G.T., D.A. Benoit, J.C. Balogh, T.B. Reynoldson, K.E. Day, and R.A. Hoke. 1994. Evaluation of potential confounding factors in sediment toxicity tests with three freshwater benthic invertebrates. *Environ. Toxicol. Chem*. 13:627-635.

ASTM. see *American Society for Testing and Materials*.

Bay, S., R. Burgess, and D. Nacci. 1993. Status and applications of echinoid (phylum Echinodermata) toxicity test methods. Pp. 281-302, *In:* Environmental Toxicology and Risk Assessment, ASTM STP 1179. W. G. Landis, J. S. Hughes, and M. A. Lewis (eds.). ASTM Philadelphia, PA.

Bay, S., D. Greenstein, J. Brown, and A. Jirik. 1994. Investigation of Toxicity in Palos Verdes Sediments. Final report to Santa Monica Bay Restoration Project. Southern California Coastal Water Research Project, Westminster. 103 pp.

Boland, G.S. and G.T. Rowe. 1991. Deep-sea benthic sampling with the GOMEX box corer. *Limnol. Oceanogr*. 36:1015-1020.

Brown, D.A., R.W. Gossett, G.P. Hershelman, C.G. Word, A.M. Westcott, and J.N. Cross. 1986. Municipal wastewater contamination in the Southern California Bight: Part I-Metal and organic contaminants in sediments and organisms. *Mar. Environ. Res*. 18:291-310.

CSDLAC. see *County Sanitation Districts of Los Angeles County*.

County Sanitation Districts of Los Angeles County. 1991. Palos Verdes Ocean Monitoring. 1991 Annual Report. Los Angeles County Sanitation Districts, Whittier, CA.

County Sanitation Districts of Los Angeles County. 1992. Palos Verdes Ocean Monitoring. 1992 Annual Report: Appendices. Los Angeles County Sanitation Districts, Whittier, CA.

DeWitt, T.H., G.R. Ditsworth, and R.C. Swartz. 1988. Effects of natural sediment features on survival of the phoxocephalid amphipod, *Rhepoxynius abronius. Mar. Environ. Res*. 25:99-124.

Dinnel, P.J., J. Link, and Q. Stober. 1987. Improved methodology for sea urchin sperm cell bioassay for marine waters. *Arch. Environ. Contam. Toxicol*. 16:23-32.

Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, A.R. Carlson, and G.T. Ankley. 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environ. Sci. Technol*. 26:96-101.

Eganhouse, R.P. and D.R. Young. 1978. Total and organic mercury in benthic organisms near a major submarine wastewater outfall system. *Bull. Environ. Contam. Toxicol*. 19:758-766.

Ferraro, S.P., R.C. Swartz, F.A. Cole, and D.W. Schults. 1991. Temporal changes in the benthos along a pollution gradient: discriminating the effects of natural phenomena from sewage-industrial wastewater effects. *Estuar. Coast. Shelf Sci*. 33:383-407.

Hedges, J.I. and J.H. Stern. 1984. Carbon and nitrogen determinations of carbonate-containing solids. *Limnol. Oceanogr*. 29:657-663.

Jandel Scientific. 1994. SigmaStat Statistical Software: User's Manual. Jandel Scientific, San Rafael, CA.

Long, E.R., D.D. MacDonald, S.L. Smith, and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ. Mngt*.19:81-97.

MacLeod, W.D., Jr., D.W. Brown, A.S. Friedman, D.G. Burrows, O, Maynes, R. Pearce, C.A. Wigren, and R.G. Bogar. 1985. Standard analytical procedures of the NOAA National Analytical Facility, 1985-1986: Extractable toxic organic compounds, 2nd edition. NOAA Tech. Mem. MFS F/NWC-92. 121pp.

McCarty, L.S. and D. Mackay. 1993. Enhancing Ecotoxicological Modeling and Assessment. *Environ. Sci. Technol*. 27:1719-1728.

Nipper, M.G., D. J. Greenstein, and S.M. Bay. 1989. Short- and long-term sediment toxicity test methods with the amphipod *Grandidierella japonica*. *Environ. Toxicol. Chem*. 8:1191-1200.

Plumb, R. 1981. Procedures for handling and chemical analysis of sediment and water samples. Tech. Rep. EPA/CE-81-1, US Army Corps of Engrs., Vicksburg, MS.

SCCWRP. see *Southern California Coastal Water Research Project.*

Sericano, J.L., E.L. Atlas, T.L. Wade, and J.M. Brooks. 1990. OAA's Status and Trends mussel watch program: chlorinated pesticides and PCBs in oysters (*Crassostrea virginica*) and sediments from the Gulf of Mexico, 1986-1987. *Mar. Environ. Res*. 29:161-203.

Southern California Coastal Water Research Project. 1993a. Characteristics of effluents from large municipal wastewater treatment facilities in 1992. Pp.10-19, *In:* Annual Report 1992-93. Southern California Coastal Water Research Project, Westminster.

Southern California Coastal Water Research Project. 1993b. Contamination of recreational seafood organisms off southern California. Pp.100-110, *In:* Annual Report 1992-93. Southern California Coastal Water Research Project, Westminster.

Stull, J.K., C.I. Haydock, R.W. Smith, and D.E. Montagne. 1986. Long-term changes in the benthic community on the coastal shelf of Palos Verdes, southern California. *Mar. Biol*. 91:539-551.

Swartz, R.C., D.W. Schults, G.R. Ditsworth, W.A. DeBen, and F.A. Cole. 1985. Sediment toxicity, contamination, and macrobenthic communities near a large sewage outfall. Pp. 152-175, *In:* Validation and Predictability of Laboratory Methods for Assessing the Fate and Effects of Contaminants in Aquatic Ecosystems, ASTM STP 685. T.P. Boyle (ed.), ASTM, Philadelphia, PA.

Swartz R.C., F.A. Cole, D.W. Schults, and W.A. DeBen. 1986. Ecological changes in the Southern California Bight near a large sewage outfall: benthic conditions in 1980 and 1983. *Mar. Ecol. Prog. Ser*. 31:1-13.

Swartz R.C., F.A. Cole, J.O. Lamberson, S.P. Ferraro, D.W. Schults, W.A. DeBen, H. Lee II, and R.J. Ozretich. 1994. Sediment toxicity, contamination, and amphipod abundance at a DDT- and Dieldrin-contaminated site in San Francisco Bay. *Environ. Toxicol. Chem*. 13:949-962.

SYSTAT. 1992. SYSTAT for Windows: Statistics, Version 5 Edition. SYSTAT, Inc., Evanston, IL. 750 pp.

Thompson, B.E., S.M. Bay, J.W. Anderson, J. Laughlin, D. Greenstein, and D. Tsukada. 1989. Chronic effects of contaminated sediments on the urchin *Lytechinus pictus*. *Environ. Toxicol. Chem*. 8:629-637.

Thompson, B., S. Bay, D. Greenstein, and J. Laughlin. 1991. Sublethal effects of hydrogen sulfide in sediments on the urchin *Lytechinus pictus*. *Mar. Environ. Res*. 31:309-321.

Thompson, B., J. Dixon, S. Schroeter, and D.J. Reish. 1993. Benthic Invertebrates. Pp. 369-458, *In:* Ecology of the Southern California Bight. M.D. Dailey, D.J. Reish, and J.W. Anderson (eds.), University of California Press, Berkeley.

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Preparing for sediment toxicity tests.