INVESTIGATION OF TOXICITY

IN

PALOS VERDES SEDIMENTS

Final Report

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Prepared for Santa Monica Bay Restoration Project

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I. EXECUTIVE SUMMARY

This research was conducted to accomplish two objectives. The first objective was to document the magnitude of Palos Verdes (PV) shelf sediment toxicity and bioaccumulation to infaunal and epibenthic organisms (amphipods and sea urchins, respectively). The second objective was to determine the dose-response relationship for two selected contaminants (sediment-sorbed DDE and dissolved sulfide) thought to play important roles in PV sediment toxicity.

Sediment and interstitial water samples were collected in the summer of 1992 from 12 locations off PV in depths ranging from 30 to 300 meters. Sediment was also collected from a relatively uncontaminated site near Dana Pt. Toxicity was measured using four methods. Interstitial water toxicity was measured using a sea urchin fertilization test. The toxicity of bulk sediment was measured using a 10 day amphipod survival test, a 28 day amphipod growth test, and a 35 day sea urchin growth test. Gonad tissues from laboratory exposed and resident sea urchins were also analyzed to determine contaminant exposure levels.

Reductions in sea urchin growth and fertilization were produced by sediment and interstitial water from some PV stations. The general spatial pattern of toxicity appeared to be influenced by two factors, distance from the outfall and depth. Greater toxic effects were usually associated with sediments located near the outfall and in depths greater than 30 m.

Amphipod tests conducted at a limited number of stations did not detect toxicity. Data from the 10 d survival test were compared to previous results and indicated that a reduction in toxicity measured in 1983 had persisted. The data were unable to determine whether toxicity has remained constant or continued to decline since 1983.

Statistical analysis and dose-response test results showed that among the interstitial water parameters measured, hydrogen sulfide (H_2S) was an important cause of interstitial water toxicity to sea urchin sperm. Ammonia, though elevated in some interstitial water samples, was not present at toxic concentrations. A significant correlation between sediment organic contaminants and interstitial water toxicity was also present, but additional research is needed to verify potential contaminant-toxicity relationships.

Tissue contaminant data were helpful in validating the sediment exposure system used for the sea urchin growth test and in identifying potential contaminant-toxicity relationships. A close correspondence between DDT, PCB, and PAH concentrations in gonads of laboratory and field exposed sea urchins was present, indicating that the laboratory test provided a realistic contaminant exposure. Trace metal accumulation by gonads was not increased by

exposure to contaminated sediments, indicating metals were not likely to be significant causes of sediment toxicity.

Most organic contaminants were accumulated by sea urchins and showed significant correlations with growth variations. Specific contaminants most likely to cause toxicity could not be identified by statistical procedures because of a high degree of covariance between chemicals.

The approach used in this project has been successful in improving our understanding of the causes of PV sediment toxicity. The results suggest that the combined effects of H_2S and multiple organics are important factors. The spiked sediment test demonstrated that growth effects were not caused by exposure to *p,p'*-DDE, the most prevalent contaminant measured in PV sediments.

Deficiencies in our understanding of PV sediment toxicity still exist due to the difficulties inherent in this area of study and technical limitations in this specific project. Results from the amphipod growth test were not acceptable, so we can not evaluate the potential for sublethal PV sediment effects on crustaceans, an important group of benthic animals. Chemical analysis of interstitial water samples was limited in scope and of questionable accuracy for dissolved sulfide. Two of the toxicity tests used in this project (sea urchin growth on sediment and sea urchin fertilization in interstitial water) have not been widely used so their reproducibility is not known.

This project was not of sufficient scope to make a conclusive identification of the cause of altered PV sediment quality. Additional studies are needed to examine the effects of specific contaminants on sea urchin growth, characterize the chemical composition of interstitial water, and confirm the relationship between sulfide and interstitial water toxicity.

The amount of additional information needed depends upon the specific objectives of SMBRP. Replication of the sea urchin toxicity studies is highly recommended so that their reproducibility can be determined. Once this is accomplished, the toxicity data are sufficient to describe the spatial extent of altered sediment quality and provide a reference for future studies intended to document temporal changes or the effectiveness of remediation efforts.

Additional dose-response research is essential if the objective is to identify specific contaminants responsible for altered PV sediment quality. The results of this study indicate that a complex chemistry-toxicity relationship exists that will require many additional laboratory tests to understand. Our limited knowledge of toxic mechanisms and variations in sensitivity between species precludes reliance solely on the work of others (e.g., fish or mammalian toxicologists) to resolve this question for PV.

There are two approaches that hold the greatest promise for useful results. First, additional dose-response studies using mixtures of contaminants similar to those present at PV

can be conducted. The results of these experiments, combined with tissue chemistry measurements, have the potential allow rapid confirmation of the presumed link between organic contaminants and biological effects at PV. A second recommended approach is to conduct a Toxicity Identification Evaluation (TIE) of PV interstitial water. A successful TIE would be able to identify those contaminants or contaminant groups most likely to be causing interstitial water toxicity in the laboratory.

I. INTRODUCTION

Background. The presence of sediment contamination and biological impacts on the Palos Verdes (PV) coastal shelf is well documented (Smith and Greene 1976; Word *et al.* 1979; Stull *et al.* 1986; Swartz *et al.* 1986). The most obvious biological impacts are the changes in the composition of benthic invertebrate populations living in or on the sediments. Alterations in PV sediment quality are probably responsible for these effects, but it is not known which characteristic(s) of the sediments are responsible.

Prior studies (LACSD 1992) have documented the presence of many different types of potentially toxic chemicals in PV sediments (e.g. hydrogen sulfide, chlorinated hydrocarbons, trace metals, polynuclear aromatic hydrocarbons). Toxicity resulting from some or all of these materials may be responsible for the observed biological effects. This assumption is supported by previous studies showing some PV sediments to be toxic to crustaceans and echinoderms (Swartz *et al.* 1986 and Anderson *et al.* 1988). Marine animals living at PV also contain elevated concentrations of some contaminants (e.g. chlorinated hydrocarbons, mercury) in their tissues (Brown *et al.* 1986; Eganhouse and Young 1978; MBC 1993), demonstrating that at least some of the sediment-sorbed chemicals in the area are biologically available and have the potential to cause toxicity.

Other sediment constituents (e.g. grain size, organic matter) can also affect benthic composition. Changes in these constituents are often correlated with contamination increases and may cause benthic population changes that can be confused with chemical contamination effects.

The documentation of PV sediment toxicity is deficient in several respects, making it difficult to determine the most appropriate remediation alternatives for the area. Information on the magnitude and spatial extent of sediment toxicity in the area is very limited. Studies by Swartz *et al.* (1986) provide data describing toxicity for multiple locations (eight stations) at PV in 1980. However, this study was restricted to a single water depth (60 m) and used a test method (amphipod survival) that is not sensitive to the sublethal nature of the sediment toxicity currently found in the area. Additional studies using this test conducted in 1983 and 1986 generally failed to detect toxicity at the same stations (Ferraro *et al.* 1991).

More recent experiments have shown that exposure of marine amphipods and sea urchins to PV sediment (LACSD station 7C) impairs growth (Nipper *et al.* 1989 and Thompson *et al.* 1989). These studies did not examine multiple locations, however.

The identity of the specific sediment constituent(s) responsible for PV sediment toxicity is another critical piece of information that is not known. Previous studies have attempted to

address this issue by correlating sediment contaminant concentrations with toxicity data (Anderson *et al.* 1988 and Swartz *et al.* 1986). These investigations identified relationships between measures of sediment contamination and biological effects, but were unable to associate toxicity with specific contaminants. This is because numerous contaminants are present in PV sediments and their concentrations are intercorrelated. Moreover, it is not known what portion of these contaminants are biologically available. These uncertainties limit the usefulness of the correlation approach.

Project description. The research described in this report was designed to address two objectives. The first objective was to document the magnitude of Palos Verdes shelf sediment toxicity to infaunal and epibenthic organisms (amphipods and sea urchins, respectively). Data on sediment contamination, tissue concentration, and sediment toxicity to multiple species were collected for a variety of stations near the White Pt. outfall on PV.

Results from the first phase of the study improves our knowledge in several ways. We have compiled the most comprehensive chemical description of the study area using recently developed analytical approaches (e.g., congener-specific PCB analysis). Information on the acute and chronic toxicity of PV sediments has been greatly augmented by obtaining results for stations that represent gradients in depth, sediment type, and distance from the outfall. Inclusion of toxicity tests used previously at PV has provided data useful to document temporal patterns in toxicity. Lastly, bioaccumulation data produced in the first phase provides valuable information on contaminant bioavailability and the relevance of laboratory exposures to the field.

The second objective of this study was to determine the dose-response relationship for two contaminants (DDE and hydrogen sulfide) thought to play important roles in PV sediment toxicity. Such information is generally not available, either because the experiments have not been conducted, or because the data cannot be applied to the exposure environment and species of concern at PV. Laboratory experiments were conducted to determine if the PV concentrations of these contaminants cause toxicity.

Data from the second phase improve our ability to predict biological effects from various chemical dose estimates (e.g., water concentration or tissue concentration). These data can be used to evaluate hypotheses regarding the role played by DDE and sulfide in PV sediment toxicity.

III. METHODS

A. Field Sampling

1. Sampling Design

Twelve stations located off the Palos Verdes Peninsula were selected for study (Figure 3.1). Station depths ranged from 30 to 300 meters (Table 3.1). An additional station near Dana Point in Orange County (SCCWRP station R52-60) was sampled for use as a reference to indicate test performance in relatively uncontaminated sediment. This station was located about 12 km south of the Dana Pt. Harbor at a depth of 60 meters. This site was selected because prior studies indicated it was representative of reference conditions and low contaminant concentrations, it had also been used in previous toxicity tests at SCCWRP (Thompson *et al.* 1987 & 1989).

Station locations off Palos Verdes were selected from the monitoring grid currently used by the County Sanitation Districts of Los Angeles. Previous monitoring data were used to select nine stations that were relatively similar in grain size characteristics and exhibited a wide range of contamination. One of these sites, station 0A, served as a local reference. This site, located in deeper water (300 m), had relatively low contaminant concentrations and similar in grain size and organic carbon characteristics to many of the sites closer to the outfall. Station 0A was included to provide a reference site more representative of PV sediment characteristics (other than contaminants) that may affect toxicity test results (e.g., grain size).

Two additional stations (6D and 9D) were selected to represent sites used for collection of resident sea urchins for bioaccumulation analysis. These stations were located in shallow water (30 m) and were markedly different in grain size and organic carbon from the other sites.

Replicate sediment samples were collected from each station by box core. An otter trawl was used to collect sea urchins from four stations for analysis of contaminant levels in gonad tissue.

The box cores were subsampled and used to provide material for chemical and toxicity analyses. The number of cores and the types of subsamples taken at each station varied depending on the types of toxicity tests conducted. Four different toxicity tests were conducted on sediment from five of the stations (R52, 1C, 5C, 6C, and 8C). Interstitial water toxicity was measured using a sea urchin fertilization test and sediment toxicity was measured using sea urchin growth, amphipod survival, and amphipod growth tests. Six box cores were taken to provide material for these tests. Toxicity at the remaining stations was measured

using only the sea urchin fertilization and sea urchin growth tests. Four cores were needed to provide test material from these stations.

Two replicate cores from each station were used for the sea urchin growth test. The additional four cores taken at stations R52, 1C, 5C, 6C, and 8C were subsampled as shown in Figure 3.2. Two subsamples were collected from each core and used for amphipod toxicity testing. A subsample for chemical analysis was also taken from each of the four cores. An additional sediment subsample was taken from two of the four cores for extraction and testing of interstitial water in the laboratory. A sample of interstitial water was also collected on board ship for dissolved sulfide measurement.

The subsampling protocol used for the remaining stations (no amphipod toxicity testing) differed in that only two replicate cores were taken in addition to those used for the sea urchin growth test. Subsamples for interstitial water extraction, chemical analysis, and sulfide analysis were taken as described previously.

2. Sampling Methods

a) Sediment

Sediment samples were collected between June 24 and July 6, 1992 using a GOMEX box core (Boland and Rowe 1991) obtained from the U.S. Army Corps of Engineers (Vicksburg, Mississippi). The box core sampled a surface area of 0.05 m^2 and was fitted with an acrylic core liner to facilitate removal of the sediment. Only cores having at least 10 cm of penetration and minimal evidence of sediment disturbance were used for testing.

Special precautions were taken to minimize sediment disturbance in samples used for the sea urchin growth, sea urchin fertilization, and amphipod growth tests. A two-piece core liner was developed that enabled the surface layer of the entire core to be removed with minimal disturbance for sea urchin growth testing. The position of the sediment within the liner was adjusted so that the top 4 cm was in the upper portion of the liner. The upper portion (and its sediment) was then separated from the rest of the liner and fitted with an acrylic base to form the test chamber for the sea urchin toxicity test. The chambers were stored at 15^{o}C.

Cylindrical polycarbonate subcores having a 3 inch diameter were used to collect undisturbed samples for interstitial water extraction and the amphipod growth test. A 10 cm column of sediment was removed and stored in the subcore until used for testing. These subcores were submerged in a seawater bath and held at 5^{o}C until used. The upper 2 cm of each subcore was used for testing.

Subsamples for chemical analysis, sulfide analysis, and amphipod survival tests were removed from an undisturbed area of the box core with a plastic scoop. The chemistry sample was placed in a clean glass beaker and combined with samples from the other replicates and thoroughly mixed to form a composite. Portions of the composite sample were placed in separate containers for trace organics, trace metals, organic carbon, and grain size analyses. The amphipod toxicity test sample was placed in a plastic jar and stored at 5°C. The sediment sample for sulfide analysis was immediately placed in a hydraulic press for extraction of interstitial water.

b) Sea urchins

Sea urchins for chemical analysis and toxicity testing were collected using an otter trawl (7.6 meter headrope). A summer collection of individuals from four stations was made between June 24 and July 1, 1992. Approximately 100 live individuals from each station were placed in buckets containing cooled seawater and returned to SCCWRP. Specimens for chemical analysis were held in aerated seawater and dissected the next day.

An additional 400 sea urchins were collected from Dana Pt. for use in toxicity tests. These individuals were placed in a large aquarium containing sediment from station R52 and acclimated to laboratory conditions for approximately two weeks.

Sea urchins were obtained from Dana Pt. because previous studies measured low contaminant concentrations and acceptable growth in test animals from this site. Acclimation of the sea urchins was intended to allow sufficient time to identify animals of poor health (i.e., injured during collection) and enable the sea urchins to adjust to the feeding regime used during the test.

Additional collections were made in November 1992 and March 1993 to provide sea urchins for chemical analysis and spiked sediment toxicity tests, respectively.

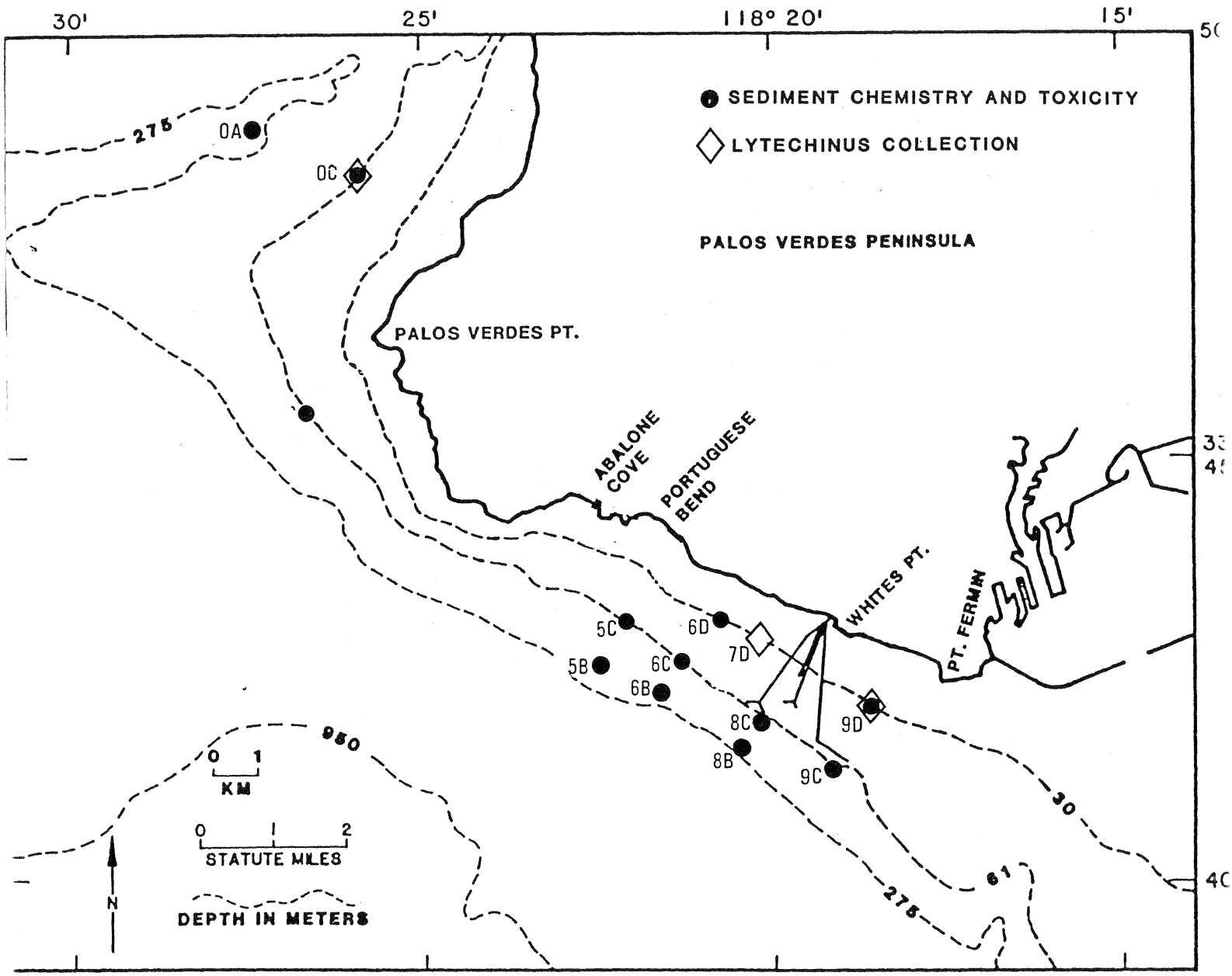
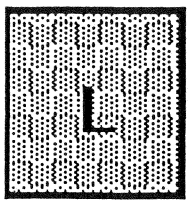


Figure 3.1 Location of Palos Verdes sediment and sea urchin collection stations. Station numbers are those used by the Los Angeles County Sanitation Districts.

Table 3.1. Station locations and depths.

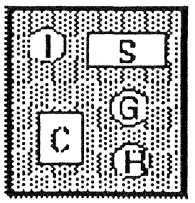
Station	Location[a]	Depth (meters)	Latitude	Longitude	Date sampled
Sediment Sampling					
OA	PV	300	33°49.15	118°27.31	07/06/92
OC	PV	60	33°48.44	118°25.90	07/06/92
1C	PV	60	33°45.51	118°26.36	07/06/92
5B	PV	150	33°42.65	118°22.03	07/02/92
5C	PV	59	33°42.91	118°21.89	07/02/92
6B	PV	150	33°42.65	118°22.03	06/30/92
6C	PV	60	33°42.51	118°21.20	06/30/92
6D	PV	30	33°43.03	118°20.82	07/02/92
8B	PV	150	33°41.65	118°20.11	07/01/92
8C	PV	60	33°42.00	118°20.05	07/02/92
9C	PV	60	33°41.38	118°19.00	06/30/92
9D	PV	30	33°42.05	118°18.70	07/02/92
R52-60	OC	60	33°23.82	117°40.00	06/24/92
Trawling					
OC-200	OC	60	30°48.45	118°25.91	07/06/92
DPT1	OC	45	33°20.58	117°36.65	06/24/92
DPT2	OC	28	33°21.80	117°37.00	11/30/92
T4-90	PV	27	33°42.70	118°20.31	07/01/92
T5-100	PV	30	33°42.19	118°18.79	07/01/92
T5-75	PV	29	33°42.25	118°18.95	11/10/92

[a] PV, Palos Verdes; OC, Orange County (stations located approximately 12 km south of Dana Pt. Harbor).



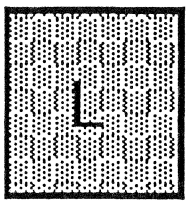
Grab #1

Sea urchin growth test (entire core)



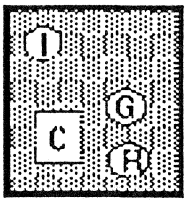
Grab #2

I: Subcore for interstitial water toxicity
C: Subsample for chemistry composite
S: Subsample for dissolved sulfides
G: Subcore for amphipod growth test (selected stations)
R: Subsample for amphipod survival test (selected stations)



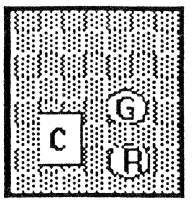
Grab #3

Sea urchin growth test (entire core)



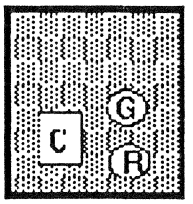
Grab #4

I: Subcore for interstitial water toxicity
C: Subsample for chemistry composite
G: Subcore for amphipod growth test (selected stations)
R: Subsample for amphipod survival test (selected stations)



Grab #5 (selected stations)

C: Subsample for chemistry composite
G: Subcore for amphipod growth test
R: Subsample for amphipod survival test



Grab #6 (selected stations)

C: Subsample for chemistry composite
G: Subcore for amphipod growth test
R: Subsample for amphipod survival test

Figure 3.2. Box core subsampling strategy used for sediment toxicity testing and chemical analysis. At least four box cores were taken at all stations. Six box cores were taken at selected stations to provide additional material for amphipod toxicity tests.

B. Chemical Analysis

1. Interstitial water

Interstitial water for chemical analysis and toxicity testing was extracted from the sediment by centrifugation. The upper 2 cm of sediment was removed from two subcores and placed in a polyethylene centrifuge tube. The tube was flushed with nitrogen gas and sealed to minimize oxidation of the sample. The sample was then centrifuged at 3,000 x g for 15 minutes. At least 30 ml of interstitial water was obtained from most of the samples. The dissolved oxygen content of the interstitial water was measured with an electrode and then the water was transferred to nitrogen-flushed glass vials and stored for 1-4 hours until analyzed.

A sample of interstitial water for sulfide analysis was taken immediately after opening the storage vial and preserved with zinc acetate. Sulfide concentration was analyzed at a later date using a colorimetric procedure (APHA 1989). Portions of interstitial water were diluted with seawater to produce test concentrations of 50% and 10%.

The dissolved oxygen content of excess interstitial water in the storage vial was measured while the toxicity test was in progress. Measurements of interstitial water salinity and pH were also made the day of the toxicity test. Subsamples of water were stored under refrigeration and measured for ammonia concentration the next day. Ammonia concentration was measured using a specific ion electrode.

2. Sediment

Grain size. The percentages of sand, silt, and clay in each sample were determined by the wet sieving and pipette analysis method of Plumb (1981).

Organic carbon and nitrogen. A modification of the procedure of Hedges and Stern (1984) was used for the determination of total organic carbon and total nitrogen in sediment. A dried sediment sample was exposed to concentrated HCl vapor to remove inorganic carbon. The acidified sample was then combusted at high temperature in a Carlo Erba CHN analyzer for analysis of evolved carbon and nitrogen. Quantification was based on the analysis of acetanilide standards.

Trace organics Sediment and tissue samples were analyzed for chlorinated hydrocarbons (DDTs and PCBs) and polynuclear aromatic hydrocarbons (PAH) using methods employed by NOAA's National Status and Trends Program (MacLeod *et al.* 1985 and Sericano *et al.* 1990). Samples were analyzed by the Geochemical and Environmental Group (GERG) at Texas A&M University.

Approximately 50 g of sediment or 1 g of tissue was extracted with methanol/methylene chloride, concentrated, and fractionated by alumina/silica gel chromatography. Tissue extract fractions for PAH analysis were passed through a Sephadex column to remove lipids.

Internal standards and recovery surrogates were added to each sample for quality assurance purposes. Additional quality assurance samples were included with each batch of samples; these included blanks, standard reference materials, duplicates of actual samples, and spiked duplicate samples.

Chlorinated hydrocarbons were quantified using capillary column gas chromatography and electron capture detection (GC/ECD). DDT (and metabolites) and 20 PCB congeners were quantified against authentic standards. Additional groups of PCB congeners were quantified based on the ECD response of a single reference congener having the same chlorination level as the group. Concentrations of all detected congeners were summed to calculate the total PCB concentration.

The PAH fractions were analyzed by GC-mass spectrometer (GC/MS). Identification of the target compounds was based on relative retention time. PAH concentrations were quantified using standards for the compounds and corrected for surrogate recoveries.

Method detection limits for individual pesticides and congeners in sediment were 0.25 ng/g (assuming typical sample weight of 10 g). Detection limits for individual PAH in sediments were 2 ng/g. Method detection limits were higher for sea urchin tissues because only about 0.4 g of gonad was available for analysis. The method detection limits for tissue chlorinated hydrocarbons and PAH were 15 and 100 ng/g, respectively. All data reported by the analytical laboratory were included in the results (i.e., the data were not censored on the basis of detection limits).

Trace metals. All trace metal analyses were carried out by GERG. Sediment and tissue samples were homogenized and dried prior to analysis. A 200 mg aliquot of sample was digested at 130^{o}C in a closed Teflon vessel using a mixture of nitric and perchloric acids. The resulting digest was brought to a known volume and stored in a polyethylene bottle.

Digests were analyzed using either a flame or graphite furnace atomic absorption spectrometer (AAS). Quantification was based on standards analyzed with each batch of samples. Blanks, standard reference materials, duplicate samples, and spiked duplicates were analyzed with every set of 10 samples for quality assurance purposes.

Acid volatile sulfides. The draft EPA procedure of Allen *et al.* (1991) was followed for the digestion and analysis of sediment acid volatile sulfides. Sulfide concentrations were quantified using the calorimetric method specified in the procedure.

C. Toxicity Testing

1. Interstitial Water Toxicity

A sea urchin fertilization test was used to measure the toxicity of interstitial water samples. Gametes from purple sea urchins (*Strongylocentrotus purpuratus*) were exposed to the test samples according to the methods of Dinnel *et al.* (1987).

Concentrations of 100, 50, and 10% interstitial water were tested at all stations except one. An insufficient volume of water was available from station 9D, preventing testing of 100% sample. All dilutions were prepared using filtered seawater. The test was conducted in glass culture tubes at a temperature of 15°C. Duplicates of each interstitial water concentration were tested. Sperm were exposed to the samples for 60 min and then unfertilized eggs were added. The percentage of eggs fertilized after 20 minutes was determined by microscopic examination of formalin-preserved samples.

Similar test procedures were used in the spiked seawater experiment to determine the toxicity of hydrogen sulfide (H_2S). Five replicates of each test concentration were tested in the sulfide experiment.

The sample concentration producing a 50% reduction in fertilization relative to the control (EC50) was calculated using probit analysis. Interstitial water toxicity was also expressed as toxicity units (TU), calculated as 100/EC50.

2. Sediment Toxicity

Three different methods were used to measure sediment toxicity. Long-term exposures (28-35 days) were used to measure effects on amphipod and sea urchin growth. A 10 day exposure test was also conducted to measure sediment effects on amphipod survival.

Sea urchin growth. The white sea urchin, *Lytechinus pictus*, was used for this test. Sea urchins were collected from Dana Point at the same time that individuals were collected for contaminant analysis and acclimated to laboratory conditions for two weeks. The exposure chamber was the upper portion of the acrylic core liner used to remove the surface sediment layer. Duplicate samples from each station were tested.

The diameter and wet weight of each test animal was measured at the start of the test. The initial wet weight of gonad tissue was measured for a representative subsample of the test organisms. This test was conducted for 35 days at 15°C under flow through conditions according to procedures used previously at SCCWRP (Thompson *et al.* 1989).

Each exposure chamber was checked daily to record any mortalities and determine the proportion of sea urchins on the sediment surface. The diameter and total weight of each sea

urchin was measured at the end of the experiment. Sea urchins were then dissected for measurement of gonad weight and to provide tissue for contaminant analysis. Growth (change in diameter or total weight) and gonad production (change in tissue weight) rates for each individual were calculated from the initial and final measurements.

Amphipod survival. The amphipod, *Rhepoxynius abronius*, was exposed to sediment from selected stations for 10 days according to standard guidelines (ASTM 1991). Test organisms were collected from Yaquina Bay in Oregon and shipped to SCCWRP. Amphipods were acclimated to laboratory conditions for four days. Sediment from the amphipod collection site was included in the test as a control. Four replicates of each sample were tested.

The static exposure system consisted of 2 cm of sediment in one liter glass beakers maintained at a temperature of 15°C. The number of surviving amphipods were counted at the end of the exposure and used to calculate percent survival in each sediment type.

Amphipod growth. Sediment effects on amphipod growth were measured using a different species, *Grandidierella japonica*. Juvenile amphipods were obtained from ovigerous females collected from Newport Bay and exposed to duplicate sediment samples according to the methods of Nipper *et al.* (1989).

The test was conducted at 20°C under flow through conditions. Sediment samples were tested while still inside the polycarbonate subcores used to sample the box core. A divider consisting of a 3 inch diameter polycarbonate ring containing a plastic mesh center was inserted into each core to isolate the surface 2 cm of the sediment for testing. The purpose of this step was to preserve chemical gradients in the 10 cm sediment column while facilitating recovery of the amphipods at the end of the experiment.

The length of animals surviving the 28-day exposure was determined. Growth (mm/28 days) was determined by comparison of the length data to the average size of juveniles at the start of the experiment.

3. Water Spiking

The toxicity of sulfide in water was measured using the sea urchin fertilization test. Various concentrations of dissolved sulfide were prepared by adding a stock solution of sodium sulfide ($Na_2S \cdot 9H_2O$) to dilution water. The stock solution was prepared by adding reagent grade sodium sulfide to seawater that had been deaereated by bubbling with nitrogen. A small amount of 1N HCl was added to the stock solution to compensate for pH changes.

Ten treatments containing nominal concentrations of total sulfide ranging from 0.06 to 10 mg/L in seawater were prepared. A preliminary analysis of the test was conducted in order

to select a subset of five concentrations (0.06-0.56 mg/L) for complete analysis. Interstitial water was also spiked at two sulfide concentrations (0.56 and 5.6 mg/L) to check for interferences due to the type of dilution water used.

Interstitial water was obtained from a sample of station 0C sediment that had been stored in the laboratory for approximately one month. Station 0C was selected because it was relatively far from the outfall and had nontoxic interstitial water.

Water quality measurements (DO and pH) were made of each dilution at the time they were apportioned to the test chambers. Samples for sulfide analysis were taken at the beginning and end of the sperm exposure period.

4. Sediment Spiking

A sea urchin growth test was conducted to measure the toxic effects of sediment spiked with DDE. A preliminary experiment was conducted in order to determine the rate of DDE bioaccumulation by the test organisms (*L. pictus*). This experiment consisted of a 28 day exposure to sediments containing nominal DDE concentrations of 2,000, 9,000, and 34,000 ng/g.

Samples of gonad tissue were taken at various times during the exposure period. Total and gonad weight measurements were also made at each time interval. The results were used to select DDE concentrations of 360, 2,700, and 8,700 ng/g for use in the final experiment.

The procedure used to spike sediment for the preliminary and final experiments was similar to that developed by the U.S. Environmental Protection Agency (Lee et al. 1989). A stock solution containing reagent grade *p,p'*-DDE and a trace amount of ^{14}C-DDE was prepared in methylene chloride. A volume of stock solution containing the desired mass of DDE was added to a 3.9 L glass jar. Separate jars were used for each test concentration. The solvent was allowed to evaporate while gently rolling the jars in a fume hood. Sediment from station R52 was then added to each jar, which was then sealed and placed on a roller table for mixing.

Jars were mixed at a temperature of 5^{o}C for four days. Jars were rolled for approximately six hours each day. An overhead stirrer was used to thoroughly mix the sediment at the beginning and end of each day's mixing period. The jars were stored upright at 5^{o}C until the start of mixing on the next day. A two day equilibration period was used between mixing and addition of the spiked sediment to test chambers. The jars were stored at 5^{o}C without mixing during equilibration. Overlying water was mixed back into the sediment, which was then added to polyethylene exposure chambers to produce a sediment layer of about 1.5 cm. Sea urchins were added to the chambers the next day to start the experiment.

IV. TOXICITY AND EXPOSURE PATTERNS

A. Sediment Characteristics

1. General Characteristics

Measurements of sediment grain size and organic carbon varied with depth and proximity to the outfall. Most PV stations located in depths greater than 30 m were relatively similar in grain size, containing 43-69% silt, 10-23% clay, and 10-47% sand (Table 4.1). Sediment from the shallow PV stations (6D and 9D) contained a higher percentage of sand, as expected. Sediment from the Dana Point reference site was almost exclusively composed of silt.

Total organic carbon (TOC) concentration was generally highest at stations nearest the outfall; a maximum value of 4.3% was measured at station 8B (Table 4.1). Both carbon and nitrogen values tended to increase with greater depth. Measurements of acid volatile sulfide concentration (AVS) in PV sediments varied by nearly two orders of magnitude, from 0.1 to 9.3 μMole/g. The highest AVS concentrations were generally found in the sediments containing elevated TOC levels.

2. Trace Metals

All seven trace metals measured had elevated concentrations at the silty stations near the outfall (Table 4.2). The two shallow water PV stations (30 m depth) had relatively low metal concentrations.

The reference station, R52, had the lowest concentration of each of the metals measured. Among the silty PV stations (all stations greater than 30 m in depth), 0C was always lowest in metal concentration. There was less than a factor of 2 difference in the concentrations of chromium, copper, nickel, lead, and zinc between R52 and 0C. The relative concentrations of silver and cadmium were very different between these two stations, with 5-7 times higher concentrations at 0C.

The magnitude of metal enrichment between the silty PV stations varied with different metals. Nickel concentrations varied by only a factor of 2 between stations. The greatest degree of enrichment was found for copper and cadmium, with concentrations varying by factors of 8 and 15, respectively.

The sediment extracts produced during the AVS analysis procedure were analyzed for trace metal content (Table 4.3). The proportion of the total sediment metals present in the extract varied widely, with 30-70% of the total metals usually found in the extracts. There

were few trends among the extract data. A relatively low proportion of the total metals was usually found in extracts from station R52. The proportion of total metals extracted by the AVS procedure was usually lowest for nickel. The concentration of extracted metal exceeded the total concentration in two cases, a theoretically impossible situation. It was assumed that heterogeneity between subsamples accounted for the discrepancy.

The mass of each metal extracted from each AVS sediment sample was calculated and expressed as μMoles of simultaneously extracted metal (SEM). SEM concentrations of Ag, Cd, Cu, Ni, Pb, and Zn were summed to indicate the total amount of divalent cations available for binding to sulfide (Table 4.3). Silver SEM concentrations were multiplied by 0.5 to correct for differences in sulfide binding.

Ratios of total SEM to AVS were calculated and ranged from 0.2 to 55 (Table 4.3). The highest ratios (>10) were obtained for stations having very low AVS concentrations (Table 4.1). Stations with the highest sediment metal concentrations had ratios of 0.8-1.8.

3. Trace Organics

Chlorinated hydrocarbon pesticides. The pesticide DDT and its principal metabolites (DDE, DDD) were by far the most abundant organic contaminants found. Even the least contaminated PV site (9D) had a total DDT concentration (454 ng/g dry wt) 30 times greater than that present at R52, the Dana Pt. reference (Table 4.4). Total DDT concentrations varied greatly between PV stations, following the same general trends observed for the trace metals (e.g., highest near outfalls, lowest at remote or shallow stations). The highest concentration measured was at station 8C (16,900 ng/g). The most abundant metabolite present was *p,p'*-DDE, which accounted for about 70-80% of the total DDT concentration at each station.

Additional chlorinated pesticides were present in low concentrations. Chlordanes (oxy, gamma, alpha forms) were the most abundant member of this group, with concentrations up to 75 ng/g at the most contaminated site (Table 4.4). Hexachlorobenzene (HCB), Dieldrin, and Mirex were present at lower concentrations in some sites. Lindane (and related forms), Heptachlor, Nonachlor, Aldrin, and Endrin were not usually present at concentrations above 1 ng/g (data not shown).

Polychlorinated biphenyls. Polychlorinated biphenyl (PCB) compounds were also present in high concentrations in PV sediment samples (Table 4.4). Total PCB concentrations were approximately one fifth of total DDT levels for the same site. The total PCB values listed in Table 4.4 represent the summed concentrations of up to 88 individual congeners resolved into 77 distinct chromatograph peaks (some peaks may contain 2 or 3 congeners).

Individual congener data listed in Table 4.4 are limited to 20 congeners representing the range of chlorination levels (2-10) present. This subset is the same as that used in the NOAA National Status and Trends program and is the most reliable since standards for each congener were present in the calibration mixture. Concentrations of the remaining congeners were calculated using the average response factor for each chlorination level and are not as accurate. Concentrations for some of the congeners not listed were greater than the values shown in Table 4.4 for compounds with the same chlorination level.

Stations with the highest DDT concentrations also tended to have the most PCBs. The highest total PCB concentration was measured at station 8C (3,420 ng/g). Individual congeners with 3-6 chlorines generally had the greatest sediment concentrations (50-100 ng/g) at the most contaminated sites.

Polynuclear aromatic hydrocarbons. The PV sediment samples contained detectable levels of all polynuclear aromatic hydrocarbon (PAH) compounds on the analytical list (Table 4.5). The list included 27 parent compounds (e.g., naphthalene, benzo[a]pyrene) as well as 19 groups of alkylated compounds (e.g., 1-methylnaphthalene, C1-naphthalenes). Alkylated PAH are parent compounds containing one or more alkyl groups (e.g., methyl, ethyl). Multiple alkylated forms are often present for some PAH and they are not always quantified separately. Groups of related alkylated PAH are designated by a prefix (C1, C2, etc.) indicating the number of carbon atoms present in the alkyl group(s). Accuracy of concentration values for groups of alkylated PAHs may be variable, since these data were calculated using the instrument response factor for the parent compound instead of authentic standards.

Total PAH concentration (sum of parent and alkylated forms) varied between stations in a pattern similar to that described for the chlorinated hydrocarbons. The highest concentration (10,600 ng/g) was found in sediment from station 8C (Table 4.5). PAH concentrations between PV stations varied by a factor of 15. The Dana Pt. reference station (R52) contained 756 ng/g PAH, a relatively high value similar to that of the lowest PV stations.

PAH of relatively high molecular weight (e.g., pyrene, fluoranthene, benzo[a]pyrene, perylene) were usually present in the highest concentrations at PV. The Dana Pt. reference station (R52) was dominated by some of the same compounds and also contained relatively high concentrations of two smaller PAH, phenanthrene and naphthalene. Alkylated PAH were much more abundant than the parent compounds. About 70-80% of the total PAH concentration at most stations was composed of alkylated forms.

Table 4.1. General sediment characteristics of stations.

Station	Sand (%)	Silt (%)	Clay (%)	TOC (%)	TN (%)	C:N	AVS (μMole/g)
OA	26	53	21	2.4	0.22	11	4.1
OC	21	69	11	1.1	0.07	15	0.1
1C	40	49	11	1.2	0.10	13	0.1
5B	11	68	21	3.8	0.25	15	6.7
5C	19	67	14	2.4	0.16	16	7.6
6B	10	68	23	4.5	0.30	15	7.4
6C	21	65	15	2.8	0.22	13	9.3
6D	78	16	6	0.8	0.07	11	1.7
8B	11	66	23	4.3	0.35	12	3.7
8C	42	47	11	3.1	0.21	14	9.3
9C	47	43	10	1.4	0.11	12	5.6
9D	85	11	4	0.6	0.11	5	1.0
R52	4	88	9	1.0	0.08	13	0.0

Table 4.2 Trace metal concentrations in sediment samples. Abbreviations: Ag, silver; Cd, cadmium; Cr, chromium; Cu, copper; Ni, nickel; Pb, lead; Zn, zinc.

	Concentration (mg/dry kg)						
Station	Ag	Cd	Cr	Cu	Ni	Pb	Zn
OA	2.94	1.35	151	50.7	34.8	42.0	119
OC	1.35	0.80	108	25.9	23.5	28.1	86.3
1C	1.68	1.99	143	52.3	32.2	37.9	126
5B	5.29	11.7	337	187	45.7	108	409
5C	3.72	7.72	213	108	31.5	66.8	129
6B	5.79	11.7	353	189	46.3	114	425
6C	5.16	11.4	296	154	39.4	100	470
6D	0.76	2.31	77.7	19.0	19.8	15.5	88.3
8B	3.49	12.1	373	208	42.2	113	438
8C	6.19	9.81	272	206	37.6	189	477
9C	1.85	2.98	402	59.6	25.3	46.6	160
9D	0.41	1.52	69.3	12.1	16.3	12.3	78.0
R52	0.19	0.17	57.2	14.4	21.7	15.7	85.9
% Recovery[a]	90	98	99	94	129	91	101
% Difference[b]	12	5	6	4	7	4	3

[a] Results from a single sediment sample spiked with metal.

[b] Average percent difference between laboratory duplicates ((sample/duplicate) X 100; N=2).

Table 4.3. Concentrations of metals extracted by AVS procedure. Values are expressed relative to the dry weight of the extracted sediment.

Station	Concentration (mg/kg)							ΣSEM[a] μMole/g	Ratio[b]
	Ag	Cd	Cr	Cu	Ni	Pb	Zn		
0A	1.50	0.71	42.3	13.4	5.44	23.4	40.2	1.0	0.2
0C	1.29	0.64	39.1	7.7	5.86	23.4	81.7	1.6	16.0
1C	0.81	0.71	29.6	13.1	2.49	22.4	50.5	1.1	11.0
5B	1.02	8.72	94.9	88.7	7.65	71.4	225.0	5.4	0.8
5C	0.71	3.17	55.0	52.4	2.96	43.5	146[c]	3.3	0.4
6B	1.57	9.35	132	101	10.5	95.6	289	6.7	0.9
6C	0.41	6.45	88.3	12.4	2.58	59.4	225	4.0	0.4
6D	0.25	2.93	26.2	5.1	1.64	12.8	42.4	0.8	0.5
8B	0.97	9.28	131	95.9	7.94	95.2	280	6.5	1.8
8C	0.38	8.74	90.7	35.9	5.53	103	375	7.0	0.8
9C	0.67	1.24	50.6	18.4	3.54	32.9	111	2.2	0.4
9D	0.26	0.57	19.6	95.9	2.09	9.9	42.4	2.2	2.2
R52	0.07	0.00	3.8	55.8[c]	1.39	5.9	10.1	1.1	55.0

[a] Summed concentration of Ag, Cd, Cu, Ni, Pb and Zn extracted during AVS analysis (μMole/g).

[b] ΣSEM/AVS

[c] Concentration greater than total sediment value.

Table 4.4. Chlorinated hydrocarbon concentrations in sediment samples. Values are expressed on a dry weight basis.

Compound	Concentration (ng/g)														
	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R[a]	%D[b]
Total Chlordane	4	3	7	58	40	75	40	2	68	21	8	2	1	nc[c]	12
Total DDT	629	773	2380	10240	6530	8480	8530	609	13600	18000	2600	454	15	nc	25
Total PCB	162	136	409	1740	993	1790	1740	111	2480	3420	462	128	8	110	10
HCB	0	0	0	0	0	0	0	0	0	1	0	0	0	45	nc
Dieldrin	0	1	0	0	0	0	0	0	0	25	1	0	0	85	nc
Mirex	0	0	0	1	0	0	0	0	1	0	0	0	0	101	nc
o,p'-DDE	62	74	265	1000	713	832	882	57	1470	2070	282	42	1	84	22
p,p'-DDE	533	665	1970	8550	5240	6830	6600	490	11200	9900	1970	351	11	nc	28
o,p'-DDD	4	6	17	57	38	52	84	7	133	316	37	6	0	111	15
p,p'-DDD	21	25	99	488	388	482	520	40	658	3000	208	36	2	nc	12
o,p'-DDT	3	2	3	6	0	0	2	1	5	142	9	0	0	75	26
p,p'-DDT	6	1	23	132	149	284	450	13	170	2590	93	17	1	nc	49
PCB8(2)	1	0	1	4	1	5	4	0	5	11	1	0	0	nc	9
PCB18(3)	1	0	1	5	3	6	6	0	6	17	1	0	0	nc	6
PCB28(3)	2	2	6	35	18	42	48	2	44	102	8	2	0	nc	11
PCB52(4)	3	2	10	63	32	77	54	3	76	119	13	3	0	nc	8
PCB44(4)	2	2	9	59	30	77	52	2	73	111	12	2	0	nc	10
PCB66(4)	4	6	24	166	83	55	151	6	232	172	27	5	0	nc	8

Table 4.4. Continued.

Compound	Concentration (ng/g)													%R[a]	%D[b]
	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52		
PCB101(5)	7	6	19	0	40	77	58	5	91	114	19	4	0	nc	15
PCB77/110(4/5)	10	9	26	97	58	83	92	6	138	149	26	4	0	nc	8
PCB118/108/149(5/5/6)	10	8	22	54	46	45	68	6	105	121	23	4	0	nc	11
PCB153(6)	14	10	21	78	46	65	64	6	103	110	21	4	1	nc	8
PCB105(5)	6	5	15	13	30	74	45	3	71	70	14	2	0	nc	11
PCB138(6)	15	11	25	83	41	42	73	6	116	133	24	4	0	nc	9
PCB126(5)	0	0	0	0	0	0	0	0	0	0	0	0	0	nc	nc
PCB187/182/159(7/7/6)	4	3	5	17	10	17	13	1	19	25	5	2	0	nc	10
PCB128(6)	3	2	5	19	10	20	14	1	23	26	4	1	0	nc	14
PCB180(7)	7	5	10	40	22	42	35	3	46	51	14	3	0	nc	8
PCB170(7)	0	3	9	15	6	17	0	1	21	0	5	1	0	nc	10
PCB195(8)	1	1	1	5	2	5	16	0	4	4	1	8	0	nc	14
PCB206(9)	2	1	2	6	3	6	6	0	7	7	2	19	0	nc	12
PCB209(10)	2	0	2	7	4	9	6	1	6	5	2	4	0	nc	15

[a] Average percent recovery from analyses of 4 spiked sediment samples.
[b] Average percent difference from duplicate analyses of 2 sediment samples.
[c] Not calculated because of matrix interference, nondetectable concentrations, or no spike added.

Table 4.5. Polynuclear aromatic hydrocarbon concentrations in sediment samples. Values are expressed on a dry weight basis.

	Concentration (ng/g)														
	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R	%D
Total PAH	2440	1480	1500	4500	3000	6560	3690	760	4210	10600	2590	685	756	nc[c]	nc
Naphthalene	33	15	14	46	33	37	29	7	50	199	21	5	12	103	6
C1-Naphthalenes	33	15	17	84	53	76	60	8	96	609	50	5	8	nc	8
C2-Naphthalenes	33	16	18	85	55	85	60	9	99	429	56	6	9	nc	8
C3-Naphthalenes	42	24	26	91	64	75	59	11	86	468	56	9	16	nc	9
C4-Naphthalenes	57	34	29	123	88	122	27	9	63	99	36	8	21	nc	15
Biphenyl	10	3	4	25	13	23	19	2	28	195	10	1	1	108	0
Acenaphthylene	14	7	17	82	46	66	56	5	95	55	35	2	0	105	14
Acenaphthene	2	0	1	5	3	4	3	0	5	21	3	0	0	90	0
Fluorene	5	3	4	17	10	13	12	2	19	49	11	1	1	96	0
C1-Fluorenes	20	12	11	49	34	45	36	6	45	72	25	5	7	nc	7
C2-Fluorenes	69	33	34	118	76	97	62	15	101	110	51	18	27	nc	18
C3-Fluorenes	95	97	79	243	183	276	111	30	131	252	75	32	59	nc	30
Phenanthrene	41	24	19	61	39	59	44	12	65	181	63	8	12	89	0
Anthracene	12	6	11	39	22	36	29	4	39	69	26	2	1	78	21
C1-Phenanthrenes/ anthracenes	92	58	46	122	82	146	107	25	126	239	108	23	38	nc	14
C2-Phen/anthr	136	103	79	184	122	255	166	41	195	293	129	44	60	nc	14
C3-Phen/anthr	148	98	72	224	159	387	180	42	177	393	118	49	57	nc	11
C4-Phen/anthr	121	82	55	190	165	466	144	32	126	421	91	38	36	nc	24
Dibenzothiophene	10	6	4	15	8	13	10	2	15	30	10	2	4	77	17
C1-Dibenzothiophenes	42	27	21	61	37	64	40	10	58	84	33	12	21	nc	23
C2-Dibenzothiophenes	98	74	49	112	97	215	139	32	109	180	84	32	47	nc	14
C3-Dibenzothiophenes	177	80	58	129	87	219	112	29	125	304	88	35	48	nc	20

Table 4.5. Continued.

COMPOUND	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R	%D
Fluoranthene	43	23	19	46	32	69	45	14	49	213	64	9	11	89	6
Pyrene	116	75	60	131	91	207	124	38	152	394	124	35	48	97	13
C1-Fluoranthenes/ pyrenes	157	91	82	241	144	373	174	45	221	459	166	48	70	nc	5
Benzo[a]anthracene	27	14	15	48	34	69	64	9	56	196	44	5	4	114	3
Chrysene	32	18	22	58	40	86	51	11	67	212	52	8	7	118	2
C1-Chrysenes	76	42	57	180	117	263	174	35	146	418	112	26	10	nc	6
C2-Chrysenes	129	76	127	387	276	638	454	52	424	833	168	42	12	nc	11
C3-Chrysenes	106	61	117	320	223	683	249	35	248	440	99	23	4	nc	14
C4-Chrysenes	25	12	25	48	34	104	47	8	43	73	22	5	2	nc	41
Benzo[b]fluoranthene	27	15	21	51	35	98	60	12	62	182	39	7	3	100	9
Benzo[k]fluoranthene	27	15	21	51	36	98	60	12	63	183	39	7	3	101	9
Benzo[e]pyrene	29	16	26	61	48	122	83	14	83	218	45	8	3	86	2
Benzo[a]pyrene	38	21	34	79	62	165	96	19	108	283	62	11	4	112	4
Perylene	62	29	44	208	1	267	105	38	137	287	80	33	8	115	12
Indeno[1,2,3-cd]pyrene	29	16	21	36	29	82	48	10	49	139	34	5	3	105	3
Dibenz[ah]anthracene	10	7	11	19	17	47	28	5	25	62	14	2	1	119	0
Benzo[ghi]perylene	36	20	28	43	36	118	64	14	60	179	42	8	4	110	2
2-Methylnaphthalene	22	10	11	58	37	52	41	6	66	417	34	3	5	118	0
1-Methylnaphthalene	10	5	6	25	16	23	18	3	30	191	16	1	3	116	0
2,6-Dimethylnaphthalene	13	7	8	37	25	31	27	4	40	215	24	2	3	95	6
2,3,5-Trimethylnaphth.	11	7	6	25	17	20	19	3	25	68	16	2	4	118	0
1-Methylphenanthrene	28	17	11	35	19	41	27	8	32	59	25	7	12	85	4
2,3-Benzofluorene	71	47	37	171	130	92	99	19	145	113	66	28	34	nc	17
Diphenylanthracene	3	2	2	12	9	7	5	1	7	4	2	0	0	nc	17

[a] Average % recovery from analyses of 2 spiked samples.
[b] Average % difference between duplicate analyses of 2 samples.
[c] Not calculated due to nondetectable concentrations or no spike added.

B. Interstitial Water Characteristics

Water quality measurements were made on samples of interstitial water extracted for toxicity testing in the laboratory. An insufficient volume of water was obtained from station 9D to allow water quality measurements.

Total ammonia concentrations were 0.8 to 4.7 mg/L, substantially higher than typical seawater values of less than 0.1 mg/L (Table 4.6). Ammonia concentration tended to be highest at stations located nearest the sewage outfall. Interstitial water pH was similar at each station and about 0.5 units below typical seawater values.

No dissolved sulfide was detected in samples of interstitial water samples extracted in the laboratory and on board ship (data not shown). These results were unexpected since previous measurements and the odor of some samples indicated the presence of sulfide. Loss of sulfide due to the type of filters used or storage conditions was suspected. An additional set of interstitial water samples was collected in November 1992 and analyzed for sulfide. These results indicated detectable levels of sulfide at five stations located near the outfall (Table 4.6). Sulfide concentrations were relatively low, except for a value of 5.2 mg/L at station 6C. The proportion total sulfide present as the toxic species, hydrogen sulfide (H_2S), varies as a function of pH, temperature, and salinity. H_2S concentrations reported in Table 4.6 were calculated for the interstitial water conditions present at the time of toxicity testing.

Interstitial water dissolved oxygen was measured both at the time of extraction and during the toxicity test. The initial values were low (0.5-2.6), indicating that the low oxygen conditions characteristic of the sediment environment had been maintained during storage and extraction of the sediment samples. The higher values reported at the final sampling indicate that the samples were rapidly oxidized on contact with air.

Table 4.6. Interstitial water characteristics.

Station	Ammonia mg/l	pH	Sulfide[a] mg/L	H_2S[b] μM	Dissolved oxygen(mg/L) Initial	Final
OA	0.78	7.5	0.0	0	1.0	4.0
OC	0.33	7.5	0.0	0	1.4	4.6
1C	0.71	7.6	0.0	0	1.4	5.2
5B	1.13	7.7	0.0	0	0.8	5.2
5C	3.70	7.4	0.3	2	1.0	4.6
6B	1.29	7.7	0.0	0	1.0	5.1
6C	4.72	7.5	5.2	32	1.2	4.8
6D	1.35	7.9	0.0	0	1.5	5.2
8B	1.49	7.7	0.1	1	0.7	5.5
8C	3.36	7.7	0.3	2	0.5	5.6
9C	3.63	7.8	0.3	2	1.6	5.1
R52	1.07	7.8	0.0	0	2.6	5.6

[a] Samples collected in November 1992.

[b] Value estimated from pH of interstitial water extracted in the laboratory.

C. Sediment Contamination Patterns

Principal components analysis (PCA) was the method selected to identify distinctive patterns among the many sediment characteristics measured in the study. Two approaches were used to eliminate irrelevant or redundant variables prior to PCA in order to improve the chances of identifying useful patterns.

Sediment concentrations were first compared to verify that each parameter showed substantial differences between PV stations. The concentration of each parameter at station 0A was compared to that of all other stations located at a depth of 60 m or greater. Chemicals that did not have at least a factor of three enrichment relative to 0A were eliminated from further analysis. For example, station 0A sediment contained 34.8 mg/kg of nickel and the highest concentration at any of the other stations was 46.3 mg/kg (station 6B). Nickel was dropped from the list of parameters because there was not a factor of three enrichment (46.3/34.8 = 1.3). Data for the shallow stations (6D and 9D) were not subject to this criterion because of interferences caused by large differences in grain size and organic carbon content.

Three trace metals (Ag, Cr, and Ni) did not meet this criterion and were dropped from the data set. One chlorinated hydrocarbon (PCB126) and several PAH compounds (C2-C3 fluorenes, C1-C3 phenanthrenes/anthracenes, and C1-C3 dibenziothiophenes) were also dropped due to lack of enrichment.

Station 0A was used as a reference for comparisons between PV stations because this station was more representative of sediment grain size and TOC characteristics at PV while containing lower contaminant concentrations compared to sites closer to the PV outfall. Contaminant concentrations were elevated in station 0A sediment compared to other stations in southern California (e.g., R52) but the effect of these chemicals was assumed to be minor for the purposes of this project.

Correlation analysis was used to identify and eliminate variables that were highly redundant (provided the same information about contamination pattern). The data were standardized (zero mean and unit variance) and then Pearson correlations were calculated for pairs of contaminants within groups of similar type (e.g., metals, chlorinated hydrocarbons, PAH). Correlations of ≥ 0.9 between pairs was judged to indicate high redundancy. Variables with high correlations were usually dropped from further analysis or combined to create a single summary variable.

Sediment carbon and nitrogen were highly correlated with each other (0.96, Table 4.7). Total nitrogen was therefore eliminated from the data set. Copper concentration was highly

correlated with the other metals in the data set (Table 4.7). The standardized concentrations for the metals were summed to create a new variable (METSUM).

Similar correlations were calculated for chlorinated hydrocarbons and PAH. Correlations for only selected compounds are presented in this report due to the large amount of data generated. High correlations were present between DDT metabolites and many PCB congeners (Table 4.8). Of the various forms of DDT and metabolites, only *p,p'*-DDE (the most abundant compound) was retained in the final data set. The standardized concentrations of 13 PCB congeners that were highly correlated with each other (Nos. 8, 18, 28, 52, 44, 77, 118, 153, 105, 138, 187, 128, and 180) were combined to create a summary variable called PCBSUM1. The remaining congeners were retained as individual variables for PCA.

High correlations were also present between many PAH compounds (Table 4.9). Two summary variables (PAHSUM4 and PAHSUM5) composed of the combined concentrations of highly redundant compounds were created to simplify the data set. PAHSUM4 was composed of data for perylene and the C1-C4 chrysenes. The components of PAHSUM5 were: naphthalene, C1-C3 naphthalenes, biphenyl, acenaphthene, fluorene, C1-fluorenes, phenanthrene, dibenzothiophene, fluoranthene, pyrene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene. Six PAH variables (acenaphthylene, anthracene, C4-phenanthrenes/anthracenes, C1-fluoranthenes/pyrenes, benzo[a]anthracene, and diphenylanthracene) were retained in the final data set.

The remaining sediment chemistry variables were factored using PCA to identify patterns in contaminant distribution. Concentrations of organic contaminants were normalized to TOC content prior to analysis. A VARIMAX rotation was used.

The first four PCA factors obtained accounted for 77% of the variance in the input data (Table 4.10). Two general patterns in the data were indicated by this analysis. The first pattern was represented by PCA factor 1 which was strongly correlated with PAH and PCB. The PCB summary variable, most PAH variables, Dieldrin, and HCB had strong correlations ($r \geq 0.75$) with this factor.

The second major contamination pattern was represented by factor 2. This factor had strong correlations with TOC, grain size, metals, Mirex, and BHC. Data for three PCB congeners (170, 206, 209) were strongly correlated with factor 3 which represented a minor pattern accounting for about 12% of the variance (Table 4.10).

There was not a strong correlation between DDE and any one PCA factor. Variations in DDE concentration were moderately correlated ($0.75 > r \geq 0.5$) with factors 1, 2 and 4.

Plots of the factor scores shown in Figure 4.1 illustrate relationships between stations and the characteristics of the patterns identified by PCA. The factor 1 scores were dominated

by a large value for station 8C, a reflection of the fact that this station usually had much higher contaminant concentrations that the other stations. Surprisingly, factor 2 scores for 8C were similar to other stations with lower contaminant levels.

The plot of factors 1 and 2 also showed a cluster of four stations (0C, 9D, 1C, and 6D). This group represented stations having relatively coarse grain size and low contaminant levels.

Scores for factor 3 were dominated by a large absolute value for station 9D. These scores were probably influenced by relatively high concentrations at station 9D for the three PCB congeners that were strongly correlated with factor 3.

Table 4.7. Pearson correlations (r) of sediment grain size, organic matter, and trace metals.

	Sand	Clay	TOC	TN	AVS	Cd	Cu	Pb	Zn
Sand	1.00								
Clay	-0.72	1.00							
TOC	-0.60	0.89	1.00						
TN	-0.50	0.88	0.96	1.00					
AVS	-0.27	0.45	0.69	0.61	1.00				
Cd	-0.43	0.66	0.90	0.85	0.79	1.00			
Cu	-0.48	0.70	0.94	0.88	0.77	0.96	1.00		
Pb	-0.36	0.52	0.81	0.73	0.80	0.85	0.94	1.00	
Zn	-0.40	0.61	0.86	0.82	0.75	0.93	0.95	0.91	1.00

Table 4.8. Pearson correlations (r) of sediment concentrations of selected chlorinated hydrocarbons.

	TOC	CHLD	DIEL	Mirex	DDE	P28	P52	P101	P138	P180	P195	P206
TOC	1.00											
Chlordane	0.92	1.00										
Dieldrin	0.16	-0.07	1.00									
Mirex	0.83	0.88	-0.21	1.00								
p,p'-DDE	0.89	0.83	0.41	0.64	1.00							
PCB28	0.68	0.53	0.77	0.32	0.85	1.00						
PCB52	0.82	0.72	0.64	0.54	0.94	0.96	1.00					
PCB101	0.68	0.58	0.61	0.29	0.80	0.88	0.88	1.00				
PCB138	0.76	0.64	0.59	0.46	0.96	0.91	0.92	0.81	1.00			
PCB180	0.90	0.83	0.46	0.66	0.98	0.90	0.97	0.83	0.93	1.00		
PCB195	0.32	0.37	0.03	0.22	0.40	0.44	0.38	0.35	0.39	0.44	1.00	
PCB206	0.11	0.18	0.12	0.16	0.22	0.23	0.24	0.18	0.21	0.22	0.51	1.00

Table 4.9. Pearson correlations (r) of sediment concentrations of selected PAH compounds.

	NAPH	Biphenyl	ACENPL	ACENPH	FLUOR	PHEN	ANTHR	FLUR	Pyrene	CHRYS	BaPY	PERYL
Naphthalene	1.00											
Biphenyl	0.99	1.00										
Acenaphthylene	0.43	0.35	1.00									
Acenaphthene	0.99	0.99	0.46	1.00								
Fluorene	0.97	0.95	0.61	0.98	1.00							
Phenanthrene	0.96	0.95	0.55	0.98	0.98	1.00						
Anthracene	0.86	0.82	0.80	0.88	0.95	0.93	1.00					
Fluoranthene	0.97	0.97	0.42	0.98	0.96	0.98	0.88	1.00				
Pyrene	0.94	0.92	0.56	0.95	0.96	0.98	0.92	0.98	1.00			
Chrysene	0.96	0.95	0.55	0.98	0.98	0.98	0.93	0.98	0.99	1.00		
Benzo[a]pyrene	0.90	0.89	0.63	0.92	0.94	0.94	0.94	0.94	0.98	0.98	1.00	
Perylene	0.72	0.69	0.70	0.74	0.79	0.79	0.88	0.76	0.86	0.83	0.88	1.00

Table 4.10. Summary of principal components analysis of sediment characteristics.

	ROTATED LOADINGS			
	Factor 1	Factor 2	Factor 3	Factor 4
Benzo[a]anthracene	0.989	-0.026	0.078	0.031
PAHSUM5	0.980	-0.050	0.067	0.072
Dieldrin	0.946	-0.094	0.053	0.145
HCB	0.944	0.144	0.006	0.080
PAHSUM4N	0.910	0.254	0.001	0.000
Anthracene	0.887	0.073	0.153	-0.269
C1-Flur/pyrenes	0.855	-0.232	-0.000	0.185
PCBSUM1	0.847	0.406	0.010	-0.279
PCB101	0.825	0.179	0.015	-0.215
C4-Phen/anthr	0.764	0.089	-0.027	0.406
DDE	0.623	0.544	0.014	-0.532
AVS	0.563	0.693	-0.005	0.022
PCB66	0.521	0.546	-0.067	-0.526
TOC	0.170	0.934	0.163	-0.001
Chlordane	-0.001	0.873	-0.045	-0.387
CLAY	-0.188	0.855	0.361	0.091
METSUM	0.497	0.819	0.024	-0.144
Mirex	-0.276	0.787	0.095	-0.126
SAND	0.074	-0.781	-0.469	0.084
BHC	-0.472	-0.760	0.057	0.095
Acenaphthylene	0.365	0.526	0.172	-0.645
PCB209	-0.064	-0.046	-0.972	0.071
PCB195	-0.062	-0.125	-0.967	0.071
PCB206	-0.114	-0.267	-0.922	0.117
PCB170	-0.348	0.003	0.234	-0.633
Diphenylanthracene	-0.283	0.393	0.077	-0.379
	PERCENT OF TOTAL VARIANCE EXPLAINED			
	38	26	12	8

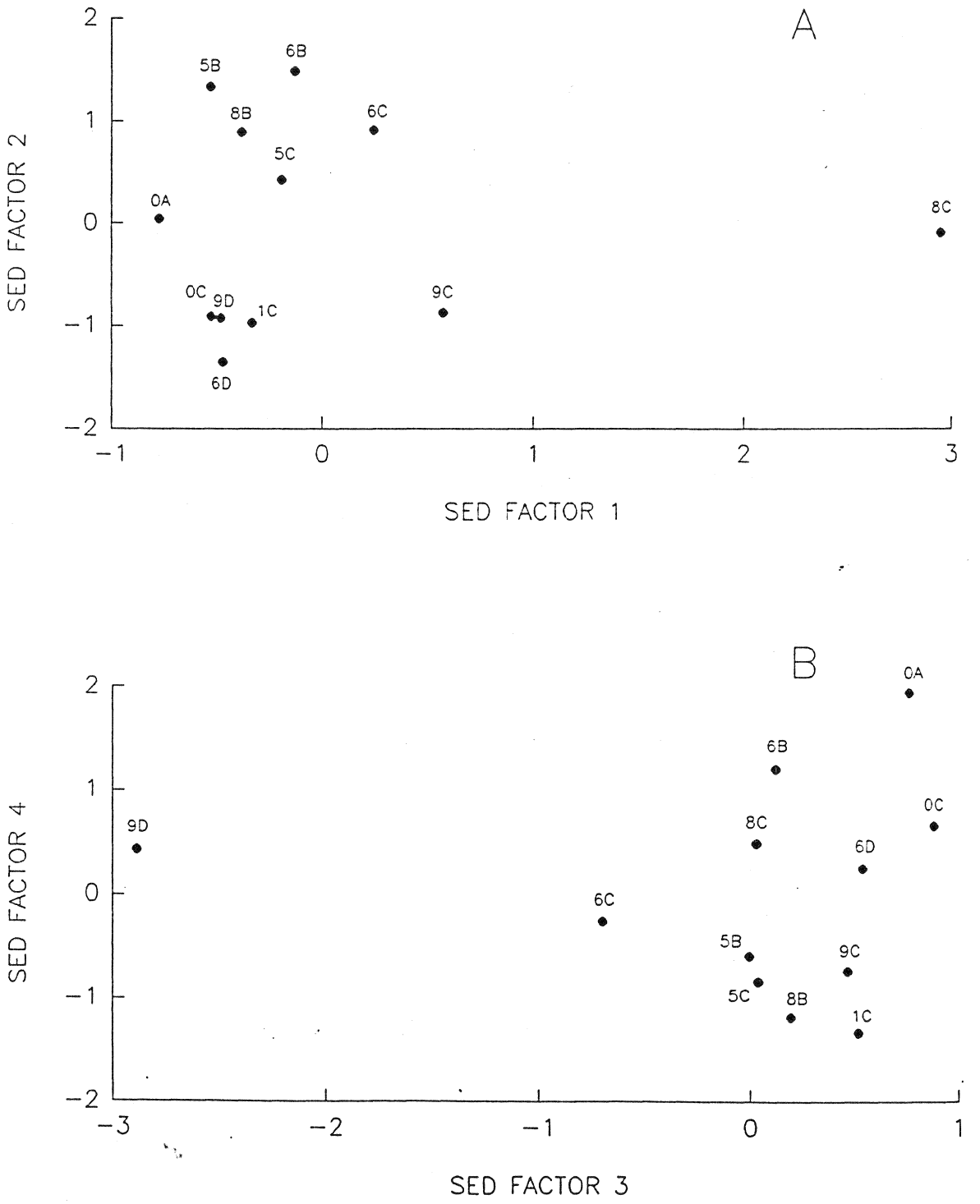


Figure 4.1. Scatter plots of factor scores obtained from PCA.

D. Toxicity

1. Interstitial Water

The sea urchin fertilization test identified toxicity in interstitial water samples from 6 stations (Table 4.11). Dilution of the samples with seawater to produce interstitial water concentrations of 50 and 10% usually produced a dose response, allowing an EC50 to be calculated for some samples.

Control fertilization was 81%, well within the range considered acceptable. Interstitial water from the two reference stations (R52 and 0A) was somewhat lower, possibly a response to differences in general composition between seawater and interstitial water.

A spatial pattern in toxicity related to the outfall is evident when data for the 50% concentration are plotted according to location (Figure 4.2). The greatest toxicity occurred in samples from locations near the outfall and at depths of 60 meters or greater. Samples from some of these stations were still highly toxic after dilution with seawater to a concentration of 10%. Much less toxicity was found at the shallow stations near the outfall.

2. Sediment

Amphipod survival. A 10 day survival test with *Rhepoxynius abronius* was conducted with sediment from 5 stations. Amphipods exposed to sediment from station 8C had the lowest survival (81%), but this result was not significantly different from the survival at the other stations (Table 4.12). There was no clear trend in the data related to the outfalls.

Amphipod growth. Juvenile *Grandidierella japonica* were exposed to sediment samples from 5 stations for 28 days. Poor survival was observed in all treatments, ranging from 0% at station 1C to 52% in control sediment from the collection site (Table 4.13). The variation in survival did not appear to correspond to the outfall locations or changes in sediment type.

Amphipod growth rates in the two treatments having the best survival were similar and within the range found for controls in other experiments. These data suggest that the surviving amphipods were in good health. Comparisons of growth rates between stations is not appropriate because of the poor survival results.

Sea urchin growth. White sea urchins (*Lytechinus pictus*) were exposed for 35 days to sediments from all 13 stations. This experiment generated data for a variety of endpoints, ranging from survival to behavior.

Daily observations of the position of sea urchins in the exposure chambers were made for the purpose of documenting sediment avoidance behavior. Few trends in behavior were

observed. An average of 69-86% of the urchins were observed to be on the sediment each day (Table 4.14). Individuals not on the sediment were attached to the side walls of the exposure chamber and restricted to a space a few millimeters above the sediment surface by the height of the overlying water's surface.

The highest percentage of sea urchins on the bottom was observed for stations 6D and 9D (Table 4.14), suggesting that they tended to favor sandy sediments. Sediment contact percentage was usually similar throughout the experiment, as shown in Figure 4.3. A noticeable change with time is evident only for station 6D, where the percentage of sea urchins on the sediment increased somewhat after the first week.

Measurements of sea urchin survival, body weight, diameter, and gonad weight were taken following 35 days of exposure. These data were used in conjunction with measurements taken at the start of the exposure to determine the net change in diameter or weight during the experiment. Survival was high in all treatments, the lowest value measured was 96% (Table 4.15).

Increases in body weight and diameter were recorded for animals in all treatment groups. The response of sea urchins exposed to Dana Pt. reference sediment (R52) was similar to that measured in previous experiments. A larger increase in body weight and diameter occurred in animals exposed to the PV reference sediment (0A). Change in body weight varied from a high of 0.25 g/35 days at station 6D to a low of 0.06 g/35 days at station 0C.

A plot of the body weight data by location indicates an overall pattern similar to that found for interstitial water toxicity (Figure 4.4). The data shown in Figure 4.4 have been normalized to the value for station 0A to facilitate comparisons between different test endpoints. Among the PV stations, low body growth was found for stations located nearest the outfalls and high growth resulted during exposure to the shallow stations. Body growth for the Dana Pt. reference was less than that recorded for many of the PV stations. An anomalous result was obtained for station 0C, which produced the lowest body growth even though the station was located relatively far from the outfall.

Sea urchin diameter change did not vary much between stations (Table 4.15). Exposure to station 9D sediment produced the greatest change (1.14 mm/35 days) while the lowest growth was again measured in animals from station 0C (0.67 mm/35 days). There did not appear to be any relationship between diameter change and location of the stations relative to the outfall.

Sea urchin gonad weight change was the test parameter that showed the greatest relative response between stations (Table 4.15). Station 0A sediment prompted the greatest gonad change (0.068 g/35 days) while no gonad growth was observed in animals exposed to station

R52 sediment. A plot of the normalized data indicates a pattern among the PV stations similar to that shown for body weight (Figure 4.5). Sediment from shallow stations near the outfall stimulated relatively high gonad growth, while low values were recorded for the deeper stations near the outfall. An unusually low value was again recorded for animals exposed to station 0C sediment.

Table 4.11. Sea urchin fertilization test results for interstitial water concentrations of 100, 50, and 10%.

Station	% Fertilized 100%	50%	10%	EC50[a]	Toxicity units[b]
Control	81				
0A	66	75	92	>100	<1
0C	90	92	94	>100	<1
1C	89	93	91	>100	<1
5B	72	82	90	>100	<1
5C	75	90	92	>100	<1
6B	7	44	80	53	1.9
6C	0	0	8	<10	>10
6D	92	97	95	>100	<1
8B	1	11	60	18	5.6
8C	1	0	1	<10	>10
9C	38	64	85	91	1.1
9D	[c]	66	75	>50	<2
R52	76	92	92	>100	<1

[a] Calculated by probit analysis.

[b] Toxicity units = 100/EC50.

[c] Insufficient sample to test at 100%. Data are for single replicate due to removal of outliers.

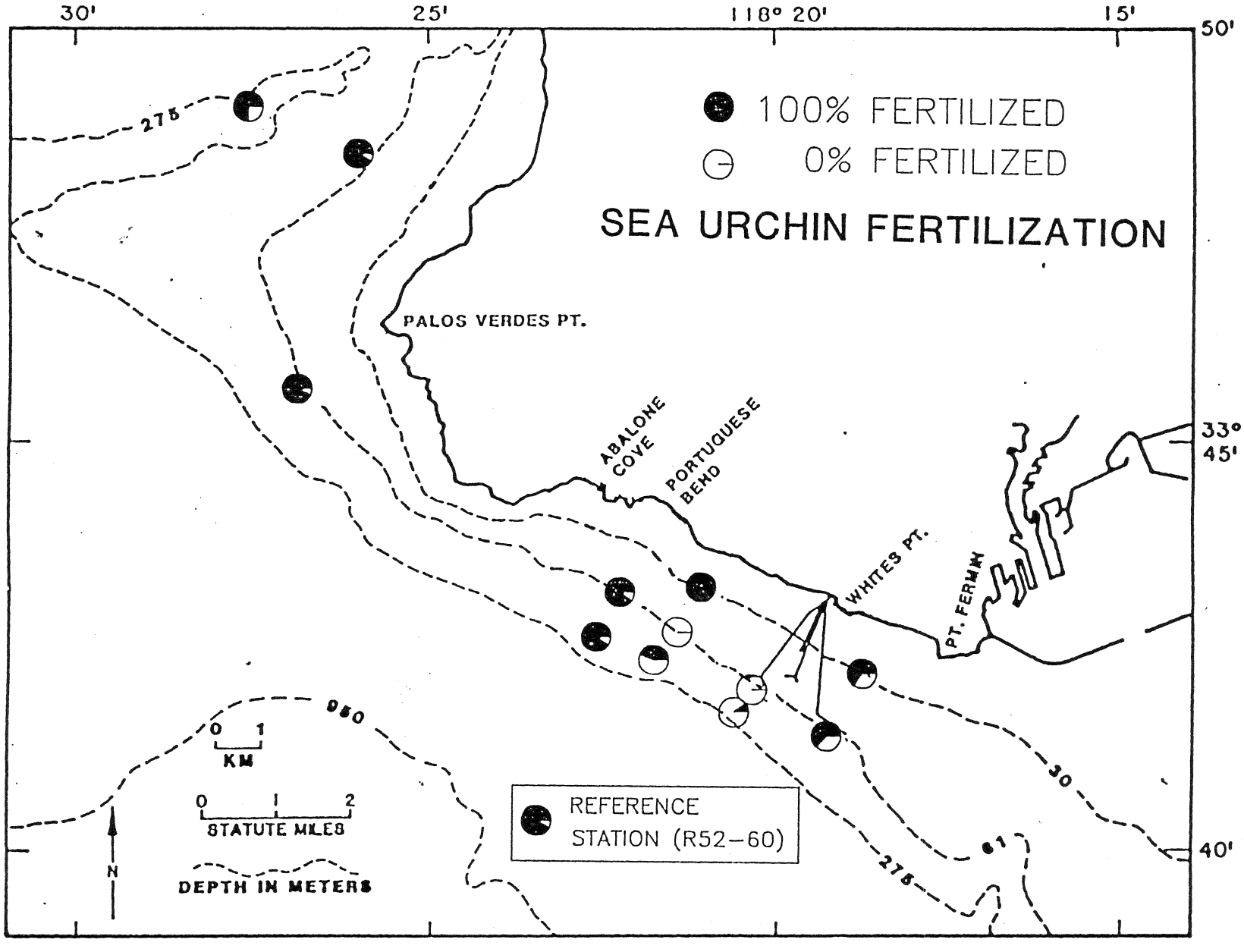


Figure 4.2. Sea urchin fertilization test results for samples of 50% interstitial water.

Table 4.12 Amphipod *(Rhepoxynius abronius)* survival following 10 day sediment exposure.

	Percent Survival	
Station	Mean	SD
Control	95	6
1C	86	15
5C	91	8
6C	95	6
8C	81	11
R52	95	4

Table 4.13 Mean amphipod (*Grandidierella japonica*) survival and growth following 28 day sediment exposure. Standard deviations are shown in parentheses.

Station	Survival %		Growth (mm/28 days) Non-males		Males	
Control	52	(22)	3.7	(0.9)	4.6	(0.01)
1C	0	(0)				
5C	8	(4)	2.7	(0.7)		
6C	32	(32)	3.8	(0.4)	4.4	
8C	18	(25)	2.0			
R52	12	(18)	1.6		3.8	

Table 4.14 Percentage of sea urchins on sediment during 35 day sediment exposure.

Station	Percent on bottom	
	Mean	SD
OA	72.3	1.5
OC	70.7	2.7
1C	79.5	4.0
5B	73.8	0.6
5C	75.5	11.4
6B	72.6	3.4
6C	69.2	2.9
6D	86.5	12.3
8B	78.1	4.7
8C	72.9	0.1
9C	79.8	3.7
9D	81.4	8.1
R52	78.2	6.6

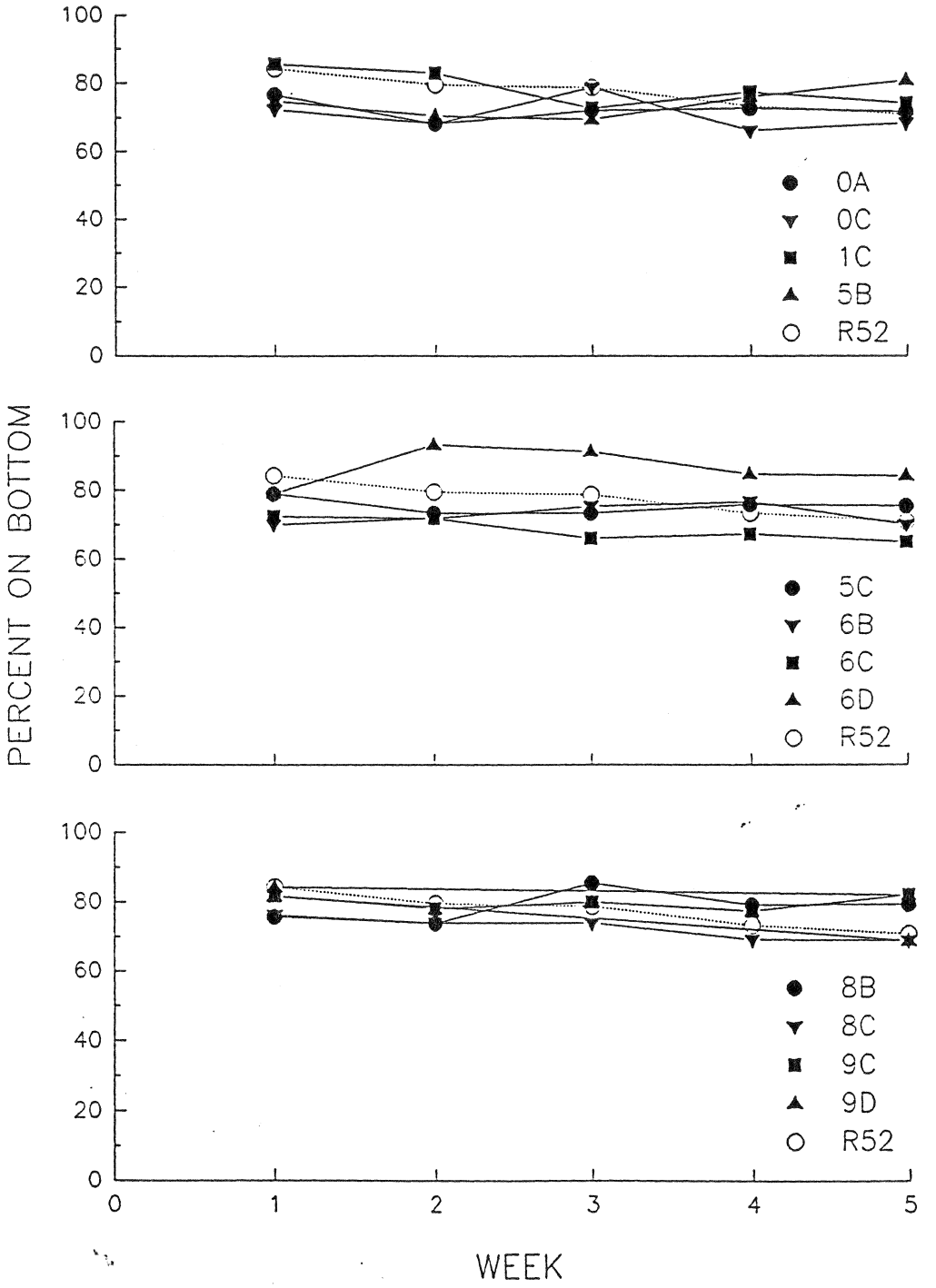


Figure 4.3. Mean percent of sea urchins on sediment surface during each week of the exposure. Data for the Dana Pt. reference has been included on each graph for comparison.

Table 4.15 Sea urchin survival and growth following 35 day sediment exposure.

Station	Survival %	Wet weight change (g)		Diameter change (mm)		Gonad weight change (g)	
OA	100	0.21	(0.10)	1.01	(0.43)	0.068	(0.021)
OC	100	0.06	(0.04)	0.67	(0.09)	0.007	(0.001)
1C	100	0.15	(0.03)	0.93	(0.08)	0.036	(0.034)
5B	100	0.08	(0.07)	0.88	(0.21)	0.013	(0.013)
5C	96	0.16	(0.07)	0.79	(0.01)	0.044	(0.020)
6B	100	0.16	(0.03)	0.97	(0.06)	0.017	(0.001)
6C	100	0.14	(0.08)	0.76	(0.08)	0.022	(0.015)
6D	100	0.25	(0.08)	0.95	(0.07)	0.061	(0.008)
8B	96	0.07	(0.09)	0.93	(0.15)	0.024	(0.010)
8C	96	0.07	(0.09)	0.80	(0.05)	0.012	(0.003)
9C	96	0.12	(0.04)	0.82	(0.12)	0.033	(0.005)
9D	100	0.23	(0.00)	1.14	(0.17)	0.046	(0.020)
R52	100	0.13	(0.08)	0.82	(0.06)	-0.003	(0.006)

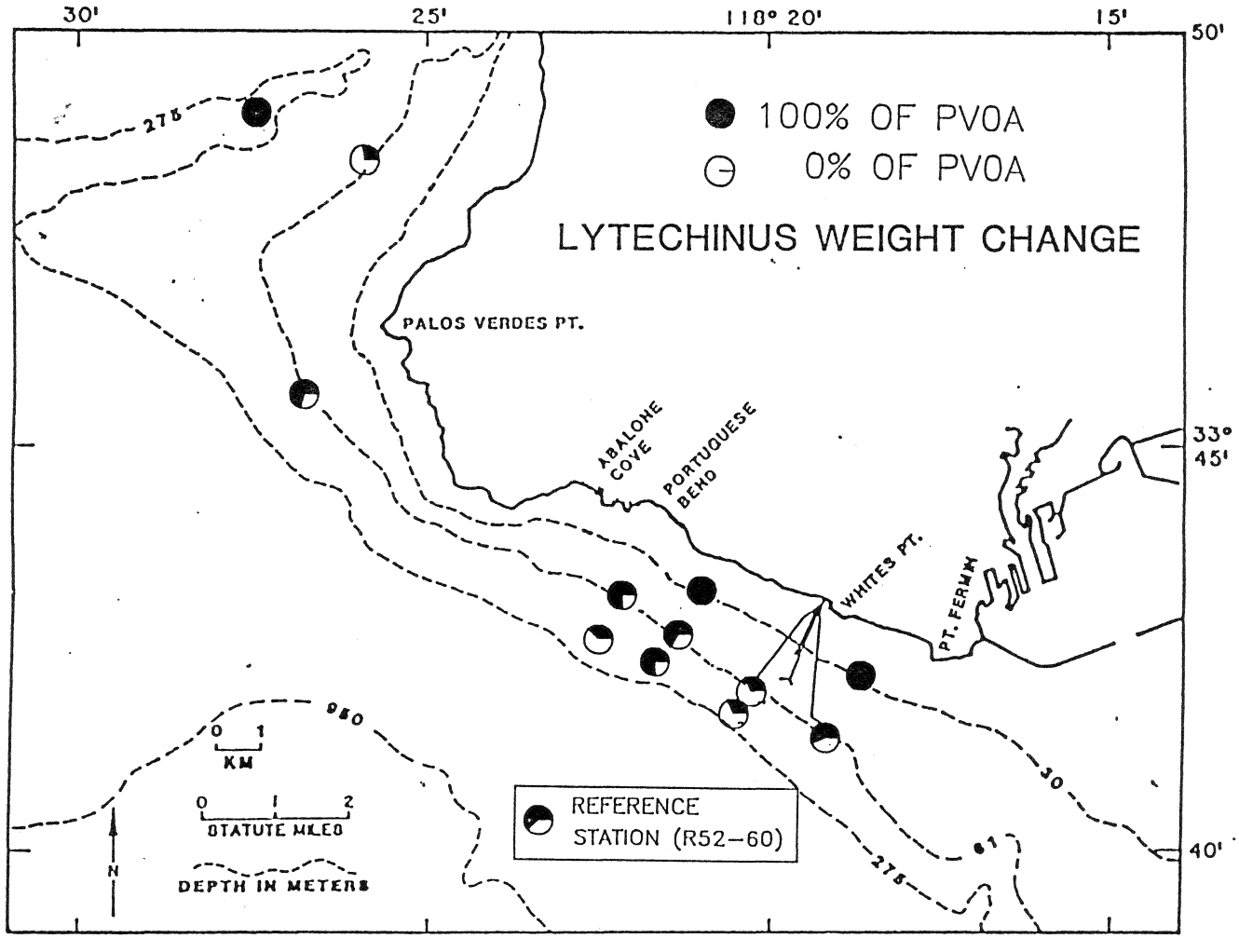


Figure 4.4. Relative change in sea urchin body weight following 35 day sediment exposure. Data are expressed as a percentage of the value for station 0A.

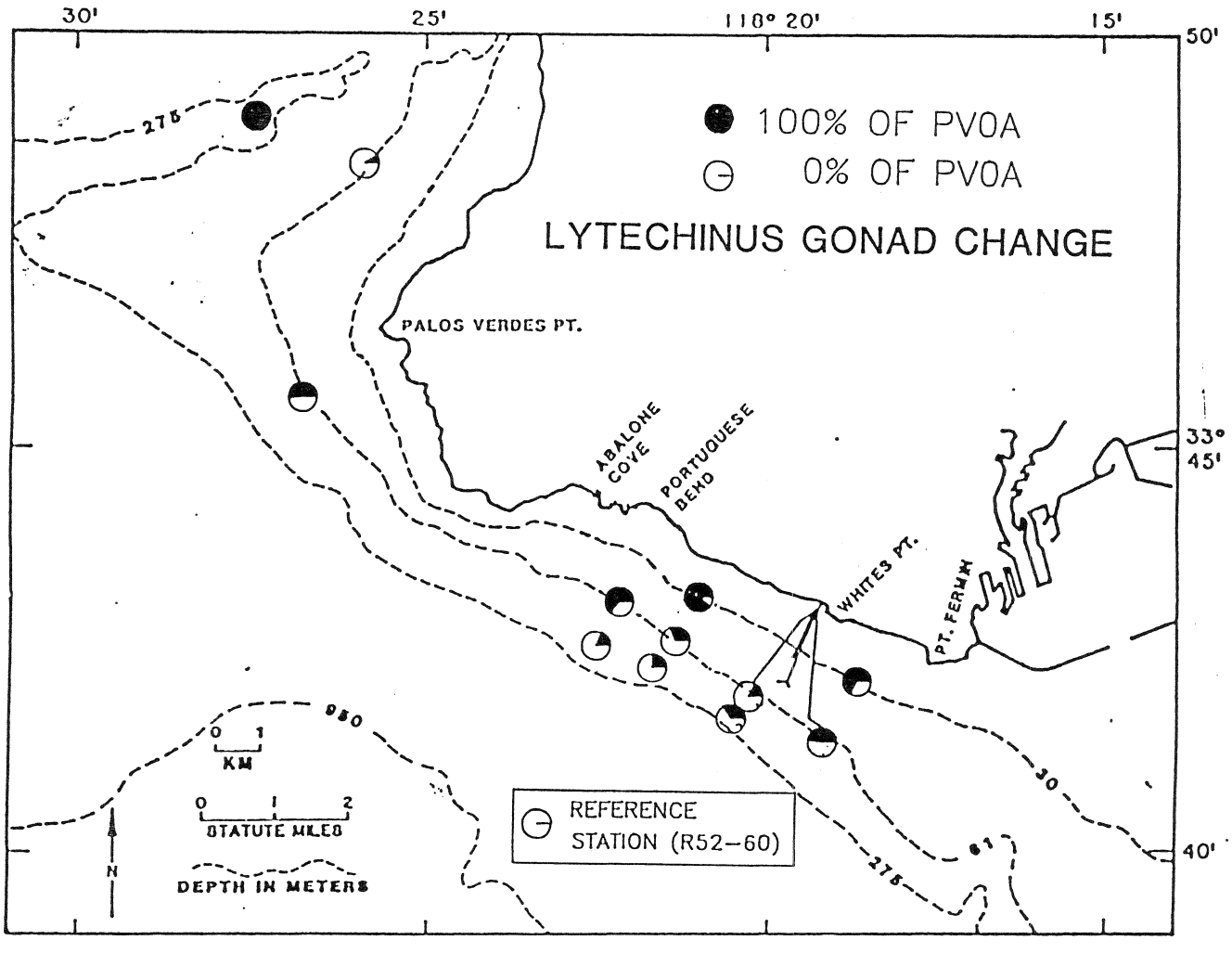


Figure 4.5. Relative change in sea urchin gonad weight following 35 day sediment exposure. Data are expressed as a percentage of the value for station 0A.

E. Bioaccumulation

1. Laboratory Exposure

All sea urchins surviving the 35 day exposure to the test sediments were dissected to provide gonad tissue for chemical analysis. Both male and female gonads were combined to produce a single composite sample from each duplicate exposure chamber. Two samples of sea urchins were also dissected at the start of the exposure to provide data on initial gonad contaminant concentrations.

Trace metals. There was no evidence of trace metal bioaccumulation in any of the samples of gonad tissue (Table 4.16). Comparisons with initial concentration data indicated that the concentrations of silver, cadmium, chromium, copper, and nickel declined in most treatment groups. Gonad concentrations of lead and zinc were generally similar between sample times.

There was no obvious trend in the data that suggested an influence of the outfall. Trace metal concentrations in animals exposed to sediments with the greatest levels of metal contamination were often similar to those of animals exposed to sediments from the reference stations (0A and R52). The shallow stations (6D and 9D) usually had relatively low trace metal concentrations, suggesting influences related to low sediment metal concentrations or growth dilution (the stations had the greatest gonad growth).

Growth dilution (reduction in tissue concentration caused by increased tissue mass without corresponding change in contaminant mass) did not appear to be the principal cause of the overall pattern of trace metal reductions for two reasons. First, reductions were noted for animals exposed to station R52 sediment, even though no net increase in gonad weight was detected in this group. Second, consistent reductions were not observed for all metals (e.g., lead and zinc).

Chlorinated hydrocarbons. Sediment exposure in the laboratory resulted in the accumulation of chlorinated hydrocarbons in all treatments (Table 4.17). Virtually every pesticide or PCB congener detected in the sediments (Table 4.4) was bioaccumulated by the gonad. Only some of the most highly chlorinated PCB congeners (170, 195, 206, and 209) did not show evidence of accumulation. The greatest amount of bioaccumulation occurred in animals exposed to station 8C sediment. Sea urchins from this treatment accumulated approximately 22,300 ng/g of total DDTs and approximately 6,900 ng/g of total PCBs during the 35 day exposure.

The general pattern of relative tissue concentration between compounds and stations was similar to that observed in the sediment samples. The highest absolute tissue

concentrations for any compound were usually found in samples from PV stations 8B or 8C, sites which had the highest sediment contaminant concentrations. DDT compounds were present at higher concentrations than PCBs, with *p,p'-D*DE the most abundant metabolite measured. Among the PCBs, congeners having 4-6 chlorines were present at the highest concentrations.

An unexpectedly high degree of bioaccumulation was measured in sea urchins exposed to the least contaminated sediment (station R52). Sea urchins collected from the general area of this station had gonad concentrations of total DDT or PCB of 27 ng/g at the start of the experiment. By the end of the sediment exposure, gonad DDT and PCB concentrations had increased to 327 and 181 ng/g, respectively (Table 4.17). This increase represented approximately a 20 fold increase relative to the sediment concentration. Tissue increases relative to sediment were much less for samples from the other stations, rarely exceeding a 7 fold increase.

Polynuclear aromatic hydrocarbons. Total tissue PAH concentrations were higher (relative to an initial sample) following exposure to sediments from each station (Table 4.18). These data provide evidence that sediment PAHs were bioavailable during the laboratory experiment.

Exposure to station 8C sediment produced the greatest amount of total PAH accumulation (approximately 3,600 ng/g). Accumulation relative to sediment concentration was much less than that calculated for chlorinated hydrocarbons. Total tissue PAH concentration was only 13-82% of the sediment concentration, compared to values as high as 700% for total PCB.

The pattern of accumulation of individual PAH was not consistent. Some compounds (e.g., biphenyl and dibenzothiophene) did not show a strong accumulation trend; tissue concentrations were less than double those measured in the initial sample. Tissue concentrations for some compounds (e.g., naphthalene and dibenz[a,h]anthracene) did not correspond to the pattern of sediment concentrations, having relatively high values for the least contaminated station (R52).

Table 4.16. Trace metal concentrations in sea urchin gonads following 35-day laboratory exposure to sediments. Values are the mean of two composites and are expressed on a wet weight basis.

	Concentration (mg/kg)															
	Initial[a]	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R[b]	%D[c]
Silver	0.16	0.06	0.09	0.08	0.05	0.05	0.04	0.07	0.05	0.05	0.05	0.05	0.04	0.06	nc[d]	0
Cadmium	0.75	0.14	0.23	0.16	0.21	0.15	0.17	0.23	0.11	0.18	0.18	0.15	0.16	0.28	86	4
Chromium	0.40	0.16	0.34	0.19	0.31	0.17	0.20	0.36	0.19	0.46	0.22	0.21	0.12	0.26	110	9
Copper	0.72	0.42	0.60	0.35	0.52	0.42	0.49	0.54	0.44	0.56	0.48	0.38	0.36	0.56	91	1
Nickel	0.73	0.24	0.62	0.30	0.57	0.26	0.26	0.34	0.10	0.38	0.38	0.26	0.12	0.60	82	9
Lead	0.09	0.08	0.13	0.09	0.18	0.09	0.10	0.10	0.08	0.18	0.11	0.10	0.07	0.08	145	57
Zinc	66.8	43.2	86.6	27.8	37.1	26.4	66.7	88.0	28.9	67.8	63.3	58.2	25.5	63.4	84	9

[a] Concentration in sample of sea urchins prior to exposure.

[b] Percent recovery from analysis of standard reference material (dogfish muscle).

[c] Percent difference of duplicate analysis of standard reference material

[d] Not calculated because certified value not available.

Table 4.17. Chlorinated hydrocarbon concentrations in sea urchin gonads following 35-day laboratory exposure to sediments. Values are the mean of two composites and are expressed on a wet weight basis. Chlorination level of PCB congeners is shown in parentheses.

	Concentration (ng/g)															
	INITIAL[a]	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R[b]	%D[c]
Total Chlordane	1	7	9	36	69	36	72	57	8	70	132	42	6	2	nc[d]	34
Total DDT	27	1400	3760	14000	15200	8890	14450	10700	2320	14900	22400	8170	1970	327	nc	32
Total PCB	27	449	647	2980	4780	3060	5290	3950	779	6360	6940	2420	548	181	90	47
HCB	0	0	0	0	0	0	0	0	0	0	0	0	0	0	49	nc
Dieldrin	0	0	0	0	1	2	1	2	1	4	15	1	1	1	87	0
Mirex	0	1	0	1	1	0	4	0	0	0	3	1	0	0	94	0
o,p'-DDE	1	154	334	1580	1960	958	2060	1370	417	1770	4600	1020	233	16	80	36
p,p'-DDE	26	1180	3340	11900	11700	6890	10800	8150	1730	11800	12000	6070	1630	303	nc	31
o,p'-DDD	0	10	18	109	234	124	263	161	18	313	739	136	14	1	91	36
p,p'-DDD	0	48	70	316	1260	821	1250	944	130	920	3520	726	71	6	71	52
o,p'-DDT	0	0	0	4	8	7	16	11	1	11	87	17	1	0	90	75
p,p'-DDT	0	6	3	30	55	92	68	97	25	70	1440	209	16	1	86	44
PCB8(2)	0	0	0	0	0	1	0	0	0	3	0	0	0	0	nc	nc
PCB18(3)	0	0	0	0	1	2	3	4	0	5	18	1	0	0	nc	nc
PCB28(3)	1	6	7	35	63	37	75	62	8	89	111	29	11	4	nc	42
PCB52(4)	1	9	10	90	197	112	210	167	21	269	329	88	15	3	nc	52

Table 4.17. Continued.

	Concentration (ng/g)															
	INITIAL[a]	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R[b]	%D[c]
PCB44(4)	1	6	13	68	158	92	175	137	15	226	300	66	10	3	nc	45
PCB66(4)	1	21	24	168	316	217	372	273	64	488	399	146	36	6	nc	37
PCB101(5)	2	25	45	198	291	173	320	243	43	346	474	160	28	5	nc	59
PCB77/110(4/5)	1	48	102	440	630	291	709	503	75	649	958	362	59	9	nc	31
PCB118/108/149 (5/5/6)	1	39	60	218	310	222	343	255	73	403	393	168	48	10	nc	56
PCB153(6)	2	33	36	145	181	114	180	140	31	209	216	97	24	12	nc	69
PCB105(5)	1	22	28	122	196	143	233	149	45	285	224	89	27	8	nc	55
PCB138(6)	2	44	60	204	232	187	257	193	60	329	321	141	36	13	nc	60
PCB126(5)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	nc	nc
PCB187/182/159 (7/7/6)	1	13	14	45	48	33	50	37	11	50	58	31	8	2	nc	52
PCB128(6)	1	9	10	32	49	36	48	32	11	63	50	24	6	3	nc	33
PCB180(7)	2	6	6	15	34	26	35	29	15	24	61	38	17	6	nc	60
PCB170(7)	2	2	2	3	1	0	2	0	2	0	1	0	2	4	nc	62
PCB195(8)	1	1	0	0	0	0	0	0	1	0	0	0	0	0	nc	100
PCB206(9)	0	1	0	0	0	0	0	0	1	0	0	0	0	2	nc	100
PCB209(10)	0	1	0	0	0	0	0	0	1	1	0	0	0	0	nc	200
% Lipids	1.2	2.6	2.8	3.1	2.4	2.6	2.9	2.2	2.4	3.0	2.6	2.2	2.4	1.5	nc	15

[a] Concentration in sample of sea urchins prior to exposure.

[b] Average percent recovery of 3 spiked tissue samples.

[c] Average percent difference between duplicate analyses of 2 tissue samples.

[d] Not calculated because of matrix interference, nondetectable concentrations or no spike added.

Table 4.18. Polynuclear aromatic hydrocarbon concentrations in sea urchin gonads following laboratory exposure to sediments. Values are the mean of two composites and are expressed on a wet weight basis.

	Concentration (ng/g)															
	Initial[a]	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R[b]	%D[c]
Total PAH	138	324	355	823	2260	1670	1570	2140	440	1820	3670	2140	324	477	nc[d]	nc
Naphthalene	22	26	36	70	55	25	34	36	36	62	51	31	21	70	80	47
C1-Naphthalenes	20	36	37	65	67	36	53	40	43	81	52	52	19	95	nc	60
C2-Naphthalenes	0	0	0	0	0	0	0	0	0	0	0	0	0	0	nc	nc
C3-Naphthalenes	0	0	0	0	0	0	0	0	0	0	177	0	0	0	nc	nc
C4-Naphthalenes	0	0	0	0	0	0	0	0	0	0	235	0	0	0	nc	nc
Biphenyl	10	15	9	17	17	8	13	8	14	12	15	14	16	14	90	64
Acenaphthylene	2	10	6	9	14	9	14	12	9	18	7	10	8	7	77	48
Acenaphthene	8	5	15	18	12	5	5	9	8	13	14	7	5	15	82	19
Fluorene	3	10	3	25	9	5	21	8	7	6	4	3	2	4	89	50
C1-Fluorenes	0	0	0	0	0	0	0	0	0	0	49	0	0	0	nc	nc
C2-Fluorenes	0	0	0	0	0	0	0	0	0	0	67	0	0	0	nc	nc
C3-Fluorenes	0	0	0	0	0	0	0	0	0	0	0	0	0	0	nc	nc
Phenanthrene	9	13	14	18	18	7	11	10	9	9	18	12	9	5	77	57
Anthracene	1	5	6	5	7	4	6	6	7	3	12	3	3	8	73	14
C1-Phenanthrenes/anthracenes	0	0	0	0	0	12	0	35	0	0	86	52	0	0	nc	nc
C2-Phenanthrenes/anthracenes	0	0	0	0	56	22	0	72	0	0	172	97	0	0	nc	nc
C3-Phenanthrenes/anthracenes	0	0	0	0	106	93	0	242	0	0	400	227	0	0	nc	nc
C4-Phenanthrenes/anthracenes	0	0	0	0	146	85	0	240	0	0	322	111	0	0	nc	nc
Dibenzothiophene	3	6	6	5	6	3	5	2	3	2	5	4	2	4	72	151
C1-Dibenzothiophenes	0	0	0	0	0	0	0	0	0	0	15	0	0	0	nc	nc
C2-Dibenzothiophenes	0	0	0	0	62	121	0	87	0	0	183	90	0	0	nc	nc
C3-Dibenzothiophenes	0	0	0	0	64	103	0	116	0	0	172	115	0	0	nc	nc

Table 4.18 (Continued).

	Concentration (ng/g)															
	Initial[a]	0A	0C	1C	5B	5C	6B	6C	6D	8B	8C	9C	9D	R52	%R	%D
Fluoranthene	2	11	7	25	15	11	16	14	11	11	33	19	11	8	81	306
Pyrene	3	22	15	44	77	48	79	63	22	80	146	54	17	16	87	89
C1-Fluoranthenes/pyrenes	0	0	42	123	289	198	263	238	23	263	355	263	40	0	nc	nc
Benz[a]anthracene	2	4	10	9	14	10	11	8	8	11	16	12	3	9	96	43
Chrysene	3	10	6	23	39	26	38	36	16	38	50	37	13	5	91	84
C1-Chrysenes	0	0	0	40	258	172	211	168	14	243	229	210	0	0	nc	nc
C2-Chrysenes	0	0	0	50	422	270	339	285	29	431	286	298	0	0	nc	nc
C3-Chrysenes	0	0	0	0	17	13	0	13	0	0	19	19	0	0	nc	nc
C4-Chrysenes	0	0	0	0	0	8	0	16	0	0	15	17	0	0	nc	nc
Benzo[b]fluoranthene	1	4	3	15	29	23	26	22	8	33	29	23	5	6	82	67
Benzo[k]fluoranthene	1	4	2	16	31	24	27	24	8	35	31	24	7	6	84	73
Benzo[e]pyrene	1	21	23	70	111	85	100	75	37	118	94	79	26	10	74	72
Benzo[a]pyrene	1	8	5	13	34	29	28	21	6	41	20	24	4	6	80	68
Perylene	2	11	7	26	44	29	34	35	19	39	56	48	19	5	78	40
Indeno[1,2,3-cd]pyrene	2	6	4	11	16	16	12	10	6	20	11	11	3	13	74	172
Dibenz[ah]anthracene	2	3	3	4	5	5	5	5	4	8	4	6	2	10	73	117
Benzo[ghi]perylene	2	12	8	30	37	30	30	23	12	42	28	26	9	11	76	93
2-Methylnaphthalene	12	17	15	42	35	21	13	19	17	42	30	33	10	56	112	80
1-Methylnaphthalene	8	19	22	23	32	15	41	21	25	38	22	19	8	38	84	35
2,6-Dimethylnaphthalene	5	6	17	50	18	15	36	15	9	10	13	11	8	10	83	177
2,3,5-Trimethylnaphthalene	7	19	9	30	16	11	26	23	7	16	14	14	9	21	86	31
1-Methylphenanthrene	2	8	10	15	5	7	10	12	4	6	9	5	11	9	73	55
2,3-Benzofluorene	2	9	12	27	72	59	60	64	11	85	104	55	14	12	nc	86
Diphenylanthracene	2	4	3	5	4	5	6	2	3	5	2	1	2	4	nc	96

[a] Concentration in sample of sea urchins prior to exposure.

[b] Average percent recovery from analyses of 3 spiked samples.

[c] Average percent difference between duplicate analyses of 3 samples.

[d] Not calculated due to nondetectable concentrations or no spike added.

2. Field Exposure

Resident *L. pictus* were collected from four field sites in summer and two sites in fall for tissue analysis. The summer collection included one site near the Dana Pt. reference station and three locations off PV, including sites near the outfall (7D and 9D) and one distant site (0C). Fall sampling was restricted to Dana Pt. and station 9D.

Gonad condition. Marked differences were noted in the relative gonad size of animals from some stations, even though sampling was conducted at the same time. The gonad index (gonad weight/total weight) was lowest in sea urchins collected from Dana Pt. in summer. Gonad tissue from these individuals accounted for about 2% of the total body weight (Figure 4.6). Sea urchins from the summer Dana Pt. collection were also used in the laboratory exposure experiment and therefore had a similar initial gonad index.

Relative gonad size increased in samples of Palos Verdes sea urchins. The highest gonad index values (6%) were measured in individuals collected nearest the outfall.

A seasonal trend in gonad size was also present (Figure 4.6). A larger gonad index was calculated for sea urchins sampled in the fall, possibly reflecting gonad maturation in preparation for spawning. Relative gonad size was similar for males and females during both seasons sampled.

Trace metals. Trace metal concentrations in gonad samples from the two stations nearest the outfall were usually lowest (Table 4.19). Summer gonad concentrations of five of seven metals were highest in individuals from the PV station (0C) farthest from the outfall. Copper and nickel concentrations were highest in Dana Pt. sea urchins. Except for lead, gonad metal concentrations in sea urchins from stations 7D and 9D were usually less than half of those measured for the other stations.

Trace metal measurements made in the fall confirmed the pattern observed in summer. Concentrations of all metals measured in station 9D individuals were one half or less of the concentration in Dana Pt. sea urchins (Table 4.19). Summer and fall concentrations within a station were similar for most metals.

Chlorinated hydrocarbons. Elevated levels of chlorinated hydrocarbons were found in all gonad samples from Palos Verdes sea urchins. Compared to the Dana Pt. reference station, total DDT and PCB concentrations were elevated approximately 100 and 20 fold, respectively (Table 4.20). Detectable levels of most DDT metabolites and PCB congeners were present in the tissue samples. Compounds not detected (e.g., PCB congeners 8 and 126) were generally those present at low concentrations in the sediment.

There were no consistent trends between the PV stations. Sea urchins from stations 7D and 9D (near the outfall) contained chlorinated hydrocarbon concentrations similar to those

from station 0C. Sediment concentrations were also similar between the three stations (Table 4.4). There was also no pronounced difference in gonad concentration between the summer and fall collections.

Polynuclear aromatic hydrocarbons. Measurements of gonad total PAH indicated a pattern of increased concentration near the PV outfall. Total gonad PAH concentrations at stations 7D and 9D were approximately six times higher than the value for Dana Pt. in the summer collection (Table 4.21).

Station 0C gonads contained an intermediate PAH concentration compared to the other sites. This trend corresponded to the relative distance from the outfall, but did not match the sediment concentrations. Sediment PAH concentrations were similar for sea urchins from the Dana Pt., 7D, and 9D stations, while station 0C concentrations were about twice as high (Table 4.5). Tissue concentrations were similar between the summer and fall collections (Table 4.21).

The relative concentration of individual PAH compounds between samples was variable. Some compounds (e.g., naphthalene and phenanthrene) had similar concentrations between stations, while others (e.g., fluoranthene and benzo[e]pyrene) displayed a pattern typical of the total PAH data (Table 4.21).

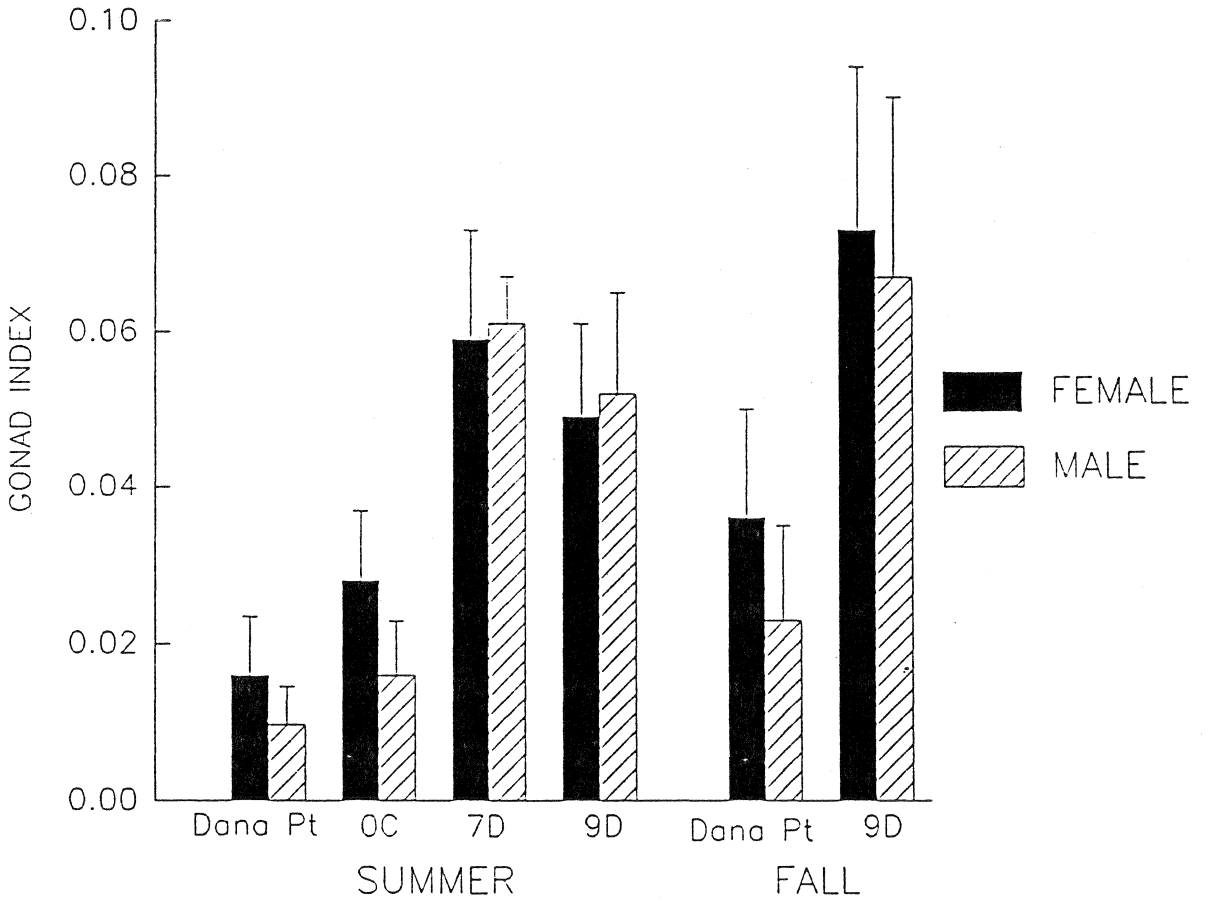


Figure 4.6. Relative gonad size of sea urchins collected from the field during summer and fall. Gonad index was calculated as: gonad wt./body wt.

Table 4.19. Trace metal concentrations in gonads of sea urchins collected from the field. Values are the mean of two composites and are expressed on a wet weight basis.

	Concentration (mg/kg)					
	Summer				Fall	
	0C	7D	9D	Dana Pt.	9D	Dana Pt.
Silver	1.60	0.02	0.02	0.16	0.03	0.07
Cadmium	0.95	0.09	0.06	0.75	0.06	0.22
Chromium	0.69	0.16	0.16	0.40	0.12	0.35
Copper	0.48	0.42	0.38	0.72	0.46	0.90
Nickel	0.52	0.12	0.18	0.73	0.17	0.48
Lead	0.15	0.12	0.10	0.09	0.03	0.06
Zinc	123	42.6	45.8	66.8	40.5	150

Table 4.20. Chlorinated hydrocarbon concentrations in gonads of sea urchins collected from the field. Values are the mean of two composites and are expressed on a wet weight basis.

	Concentration (ng/g)							
	Summer				Fall			
	0C	7D	9D	Dana Pt.	9D	Dana Pt.	%R[a]	%D[b]
Total Chlordane	7	12	8	1	21	3	nc[c]	8
Total DDT	3040	3820	2870	27	3650	62	nc	24
Total PCB	570	706	508	27	701	27	89	7
HCB	0	0	0	0	0	0	26	nc
Dieldrin	0	1	0	0	0	0	95	8
Mirex	1	1	0	0	0	0	115	25
o,p' DDE	262	407	298	1	429	3	125	14
p,p'-DDE	2700	3210	2420	26	3080	58	nc	29
o,p' DDD	14	25	17	0	14	0	112	16
p,p'-DDD	54	157	112	0	103	1	nc	10
o,p' DDT	1	1	1	0	5	0	107	75
p,p'-DDT	3	20	15	0	16	0	125	6
PCB8(2)	0	0	0	0	0	0	nc	nc
PCB18(3)	0	0	0	0	1	0	nc	nc
PCB28(3)	2	3	2	1	10	0	nc	14
PCB52(4)	6	15	10	1	24	1	nc	2
PCB44(4)	4	9	6	1	12	0	nc	17
PCB66(4)	17	27	21	1	41	1	nc	1
PCB101(5)	36	48	36	2	46	1	nc	13
PCB77/110(4/5)	82	106	75	1	46	1	nc	11
PCB118/108/149(5/5/6)	62	60	44	1	58	3	nc	11
PCB153(6)	41	38	26	2	36	1	nc	4
PCB105(5)	35	43	30	1	24	1	nc	13
PCB138(6)	71	63	45	2	59	5	nc	1
PCB126(5)	0	0	0	0	0	0	nc	nc
PCB187/182/159(7/7/6)	13	9	7	1	18	2	nc	10
PCB128(6)	12	10	8	1	10	1	nc	13
PCB180(7)	8	35	27	2	28	3	nc	10
PCB170(7)	1	1	1	2	0	0	nc	nc
PCB195(8)	0	2	0	1	0	0	nc	50
PCB206(9)	0	2	0	0	0	0	nc	100
PCB209(10)	0	2	0	0	0	0	nc	200
%Lipid	2.9	1.4	1.8	1.2	3.6	2.8	nc	15

[a] Percent recovery of single spiked sample.

[b] Average percent difference between duplicate analyses of 2 samples.

[c] Not calculated due to matrix interference, nondetectable concentrations or no spike added.

Table 4.21. Polynuclear aromatic hydrocarbon concentrations in gonads of sea urchins collected from the field. Values are the mean of two composites and are expressed on a wet weight basis.

	Concentration (ng/g)							
	Summer				Fall			
	0C	7D	9D	Dana Pt.	9D	Dana Pt.	%R	%D
Total PAH	242	752	1100	138	709	275	nc[c]	nc
Naphthalene	26	29	23	22	28	18	90	42
C1-Naphthalenes	33	32	23	20	55	61	nc	39
C2-Naphthalenes	0	0	0	0	0	0	nc	nc
C3-Naphthalenes	0	0	107	0	0	0	nc	nc
C4-Naphthalenes	0	0	85	0	0	0	nc	nc
Biphenyl	9	9	7	10	18	15	83	24
Acenaphthylene	5	10	6	2	11	6	78	26
Acenaphthene	4	7	4	8	14	18	81	15
Fluorene	6	4	3	3	12	7	77	19
C1-Fluorenes	0	0	0	0	0	0	nc	nc
C2-Fluorenes	0	0	25	0	0	0	nc	nc
C3-Fluorenes	0	0	41	0	0	0	nc	nc
Phenanthrene	7	10	10	9	17	7	90	40
Anthracene	3	5	6	1	5	6	76	75
C1-Phenanthrenes/anthracenes	0	0	31	0	0	0	nc	nc
C2-Phenanthrenes/anthracenes	0	56	52	0	0	0	nc	100
C3-Phenanthrenes/anthracenes	0	104	107	0	0	0	nc	100
C4-Phenanthrenes/anthracenes	0	26	45	0	0	0	nc	100
Dibenzothiophene	2	2	4	3	4	4	75	41
C1-Dibenzothiophenes	0	0	0	0	0	0	nc	nc
C2-Dibenzothiophenes	0	22	69	0	0	0	nc	15
C3-Dibenzothiophenes	0	38	69	0	0	0	nc	16
Fluoranthene	3	9	11	2	26	12	84	26
Pyrene	8	16	18	3	29	9	91	34
C1-Fluoranthenes/pyrenes	29	76	97	0	95	0	nc	17
Benz[a]anthracene	2	8	3	2	5	2	86	12
Chrysene	7	12	16	3	19	3	85	6
C1-Chrysenes	0	45	38	0	53	0	nc	17
C2-Chrysenes	0	81	64	0	81	0	nc	12
C3-Chrysenes	0	0	0	0	0	0	nc	nc
C4-Chrysenes	0	0	0	0	0	0	nc	nc
Benzo[b]fluoranthene	2	6	5	1	8	2	89	27
Benzo[k]fluoranthene	2	6	5	1	8	2	89	27
Benzo[e]pyrene	15	32	29	1	42	3	89	26
Benzo[a]pyrene	1	3	3	1	6	2	89	37

Table 4.21 (Continued).

	Concentration (ng/g)							
	Summer				Fall			
	0C	7D	9D	Dana Pt.	9D	Dana Pt.	%R	%D
Perylene	5	9	14	2	22	2	88	14
Indeno[1,2,3-cd]pyrene	2	6	4	2	7	2	90	30
Dibenz[ah]anthracene	3	4	3	2	2	2	92	50
Benzo[ghi]perylene	8	9	10	2	12	2	93	13
2-Methylnaphthalene	19	19	13	12	35	31	117	41
1-Methylnaphthalene	14	13	11	8	20	30	96	43
2,6-Dimethylnaphthalene	6	10	11	5	16	12	86	36
2,3,5-Trimethlynaphthalene	8	17	11	7	25	7	84	60
1-Methylphenanthrene	7	3	8	2	6	5	72	45
2,3-Benzofluorene	4	12	9	2	22	0	nc	27
Diphenylanthracene	2	2	2	2	6	5	nc	50

[a] Average percent recovery from analyses of 2 spiked samples.
[b] Average percent difference between duplicates of 2 samples.
[c] Not calculated due to nondetectable concentrations or no spike added.

F. Tissue Contamination Patterns

1. Laboratory vs. Field

Sea urchin gonad contaminant data obtained from laboratory and field exposed individuals were compared within stations. Comparisons were made for four sets of stations, each representing similar sediment types: R52 (lab exposure)/Dana Pt. (field exposure), 0C/0C, 6D/7D, and 9D/9D.

Trace metals. Gonad metals showed varying levels of agreement within each station group (Figure 4.7). The best agreement was obtained for stations 6D and 9D, where concentrations were usually similar between the summer and laboratory data sets.

A similar pattern of concentration changes between metals was also present in the comparison for station R52 (i.e., lowest values for silver and lead). Greater differences were noted for silver, cadmium, and chromium, where laboratory sample concentrations were only about half that of field individuals.

Substantial differences were also observed for the station 0C metals data (Figure 4.7). Large differences were again noted for silver, cadmium, and chromium concentrations. The pattern of relative magnitude between metals also varied. For example, silver and cadmium concentrations were much higher than copper in the field samples, while the opposite trend was present in the laboratory data.

Hydrocarbons. Gonad concentrations of selected chlorinated and polynuclear aromatic hydrocarbons, representing a range of sediment concentrations and characteristics were compared for the four pairs of laboratory/field data (Figure 4.8). These data indicate that organic contaminant concentrations were in good agreement for three of four lab/field exposure groups (0C/0C, 6D/7D, and 9D/9D). Laboratory and field concentrations of the same compound were generally within a factor of two, which is remarkable considering that tissue concentrations of some compounds increased by more than an order of magnitude during the laboratory exposure.

There was a poor correspondence between the lab and field data for the Dana Pt. stations (Figure 4.8). Higher concentrations of virtually all organic contaminants were measured in laboratory exposed sea urchins. These results indicated bioaccumulation of chlorinated hydrocarbons to a greater degree than would be expected from the relatively low sediment concentrations.

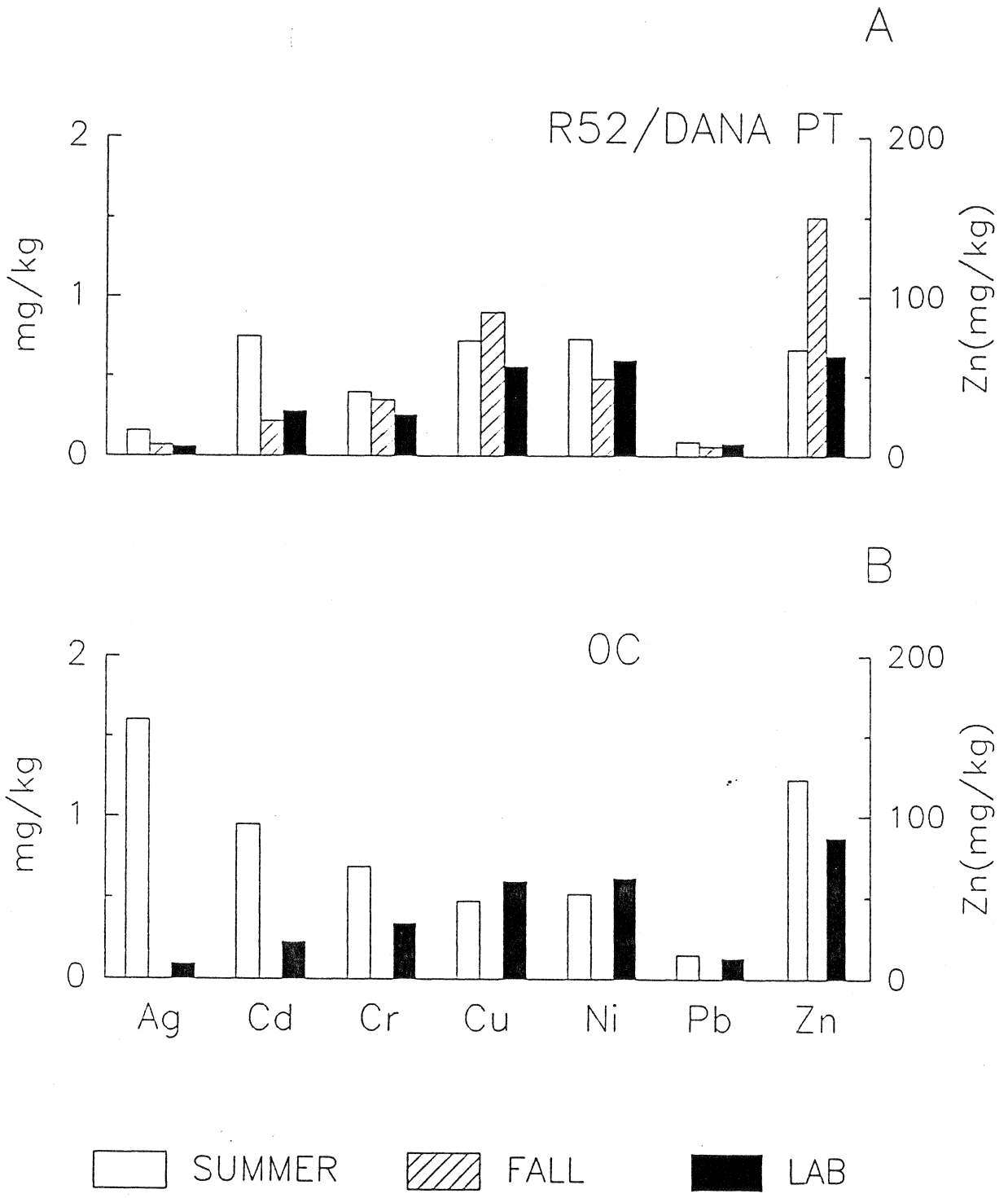


Figure 4.7. Comparison of sea urchin gonad metals concentrations between laboratory and field exposed individuals. Data for Ag, Cd, Cr, Cu, Ni, and Pb are plotted using the vertical axis on the left. (A) Lab samples from R52 and field samples from Dana Pt. (B) Field and lab samples from 0C.

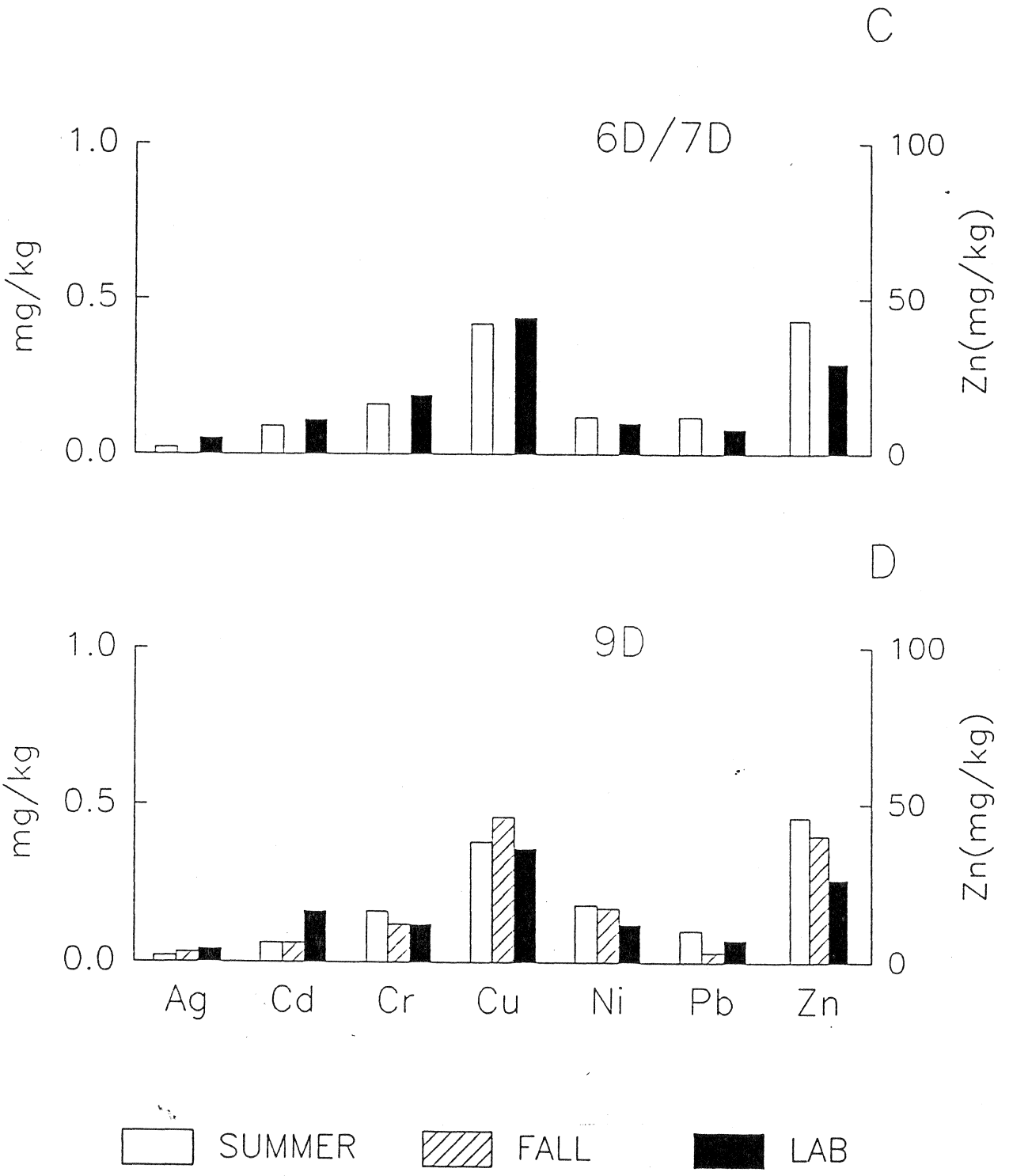


Figure 4.7 (continued). (C) Lab samples from 6D and field samples from 7D. (D) Field and lab samples from 9D.

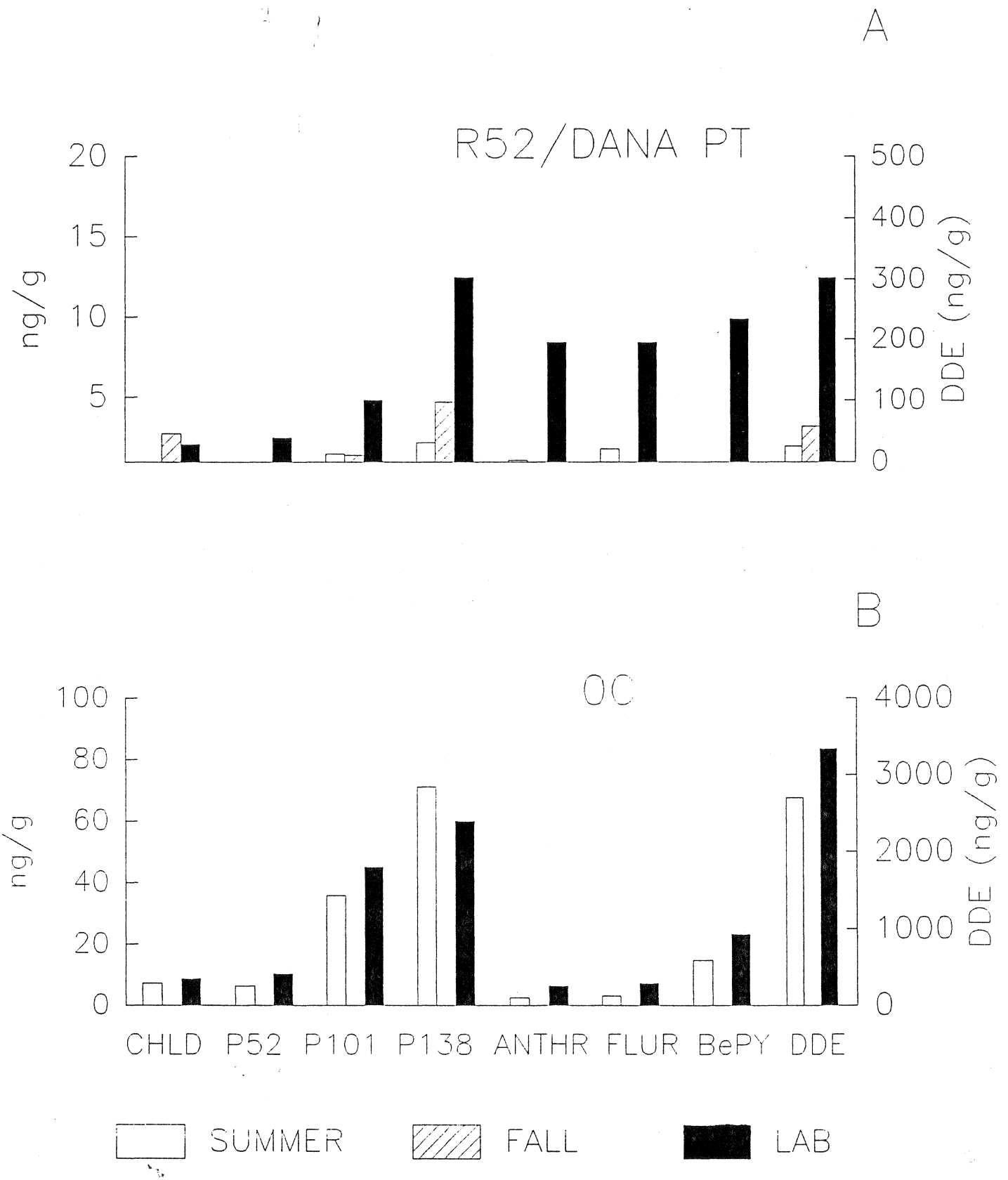


Figure 4.8. Comparison of gonad concentrations of selected organic hydrocarbons in field and laboratory exposed sea urchins. Abbreviations: CHLD, Chlordane; DDE, *p,p'*-DDE; P52, PCB congener 52; P101, PCB congener 101; P138, PCB congener 138; ANTHR, anthracene; FLUR, fluoranthene; BePY, benzo[e]pyrene. All compounds except DDE are plotted using the left vertical axis. (A) Lab samples from R52 and field samples from Dana Pt. (B) Field and lab samples from 0C.

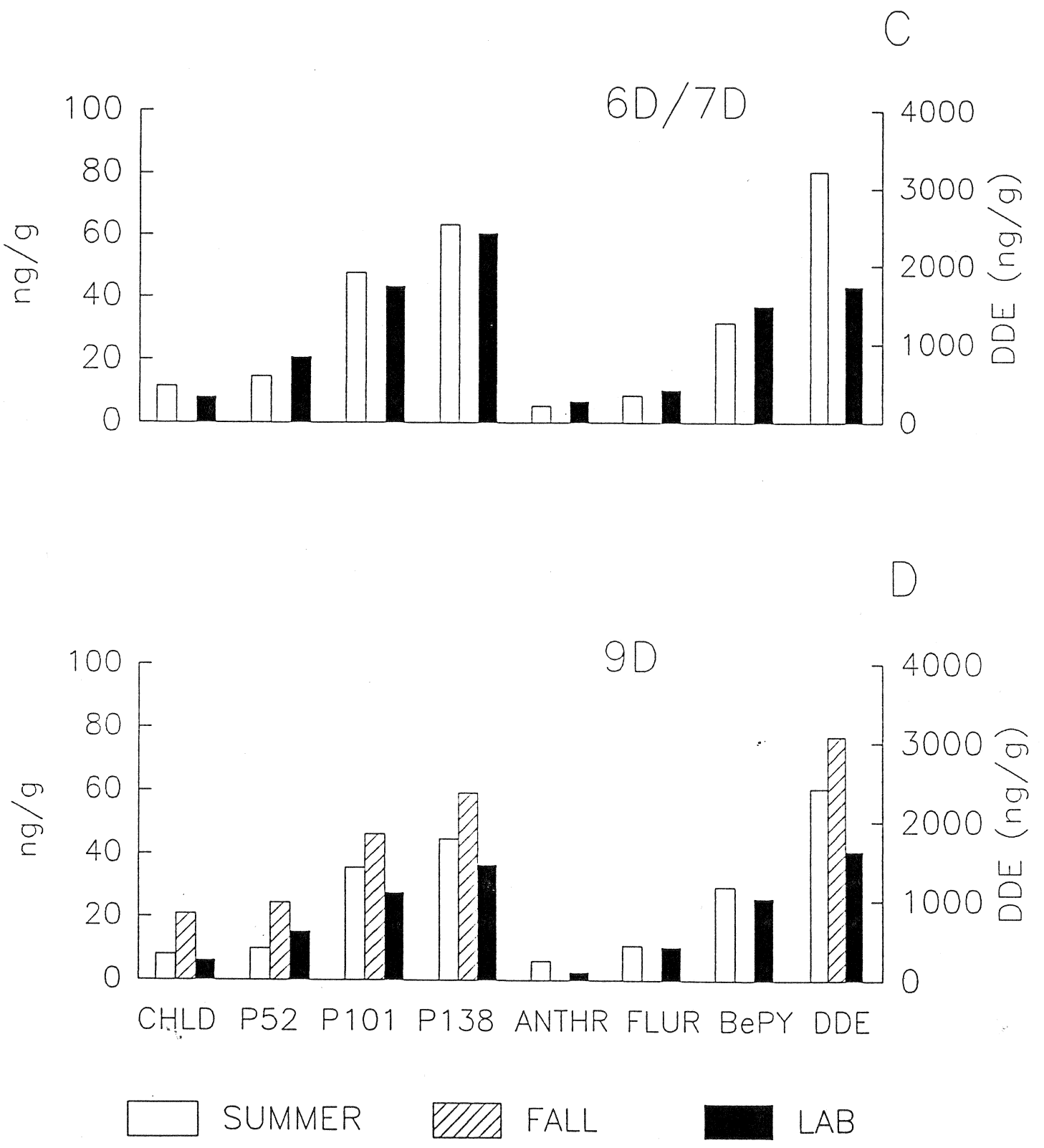


Figure 4.8 (continued). (C) Lab samples from 6D and field samples from 7D. (D) Field and lab samples from 9D.

2. Between stations

Principal components analysis (PCA) was used to identify patterns in tissue contamination (from laboratory exposure) between stations. The screening procedure used to eliminate irrelevant or redundant tissue chemistry variables prior to PCA was the same as that used for the sediment data. None of the tissue trace metal data were included in the analysis because there was no evidence of substantial bioaccumulation relative to sea urchins exposed to sediment from the PV reference station (Table 4.16).

Several chlorinated hydrocarbons (BHC, HCB, PCB8, PCB126, PCB195, PCB206, and PCB209) were also removed from the data set for lack of bioaccumulation. About one half of the tissue PAH compounds were dropped from further analysis because of failure to meet the bioaccumulation criterion. The PAH variables retained for analysis were: C4-phenanthrenes/anthracenes, fluoranthene, pyrene, C1-fluoranthenes/pyrenes, benz[a]anthracene, chrysene, C1, C2, C3, and C4-chrysenes, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene.

Correlation analyses were performed on the reduced set of data to identify redundant pesticide, PCB, and PAH variables. Pearson correlations of standardized chlorinated hydrocarbon concentrations identified high correlations (>0.90) among most PCB congeners and total PCB (selected results shown in Table 4.22). Total DDT and *p,p'*-DDE were also strongly correlated with each other and many of the PCB congeners. Data for *p,p'*-DDE and all individual PCB congeners except P180 were deleted from the data set to reduce the number of redundant variables.

Pearson correlations on standardized data indicated that high correlations were present between 8 tissue PAH (selected results shown in Table 4.23). The standardized concentrations of these compounds (chrysene, C1 and C2-chrysenes, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, and perylene) were summed to create a single variable (PAHSUM1) that was used to replace the redundant data. All other PAH data were retained in the final data set used for PCA.

Analysis of the remaining tissue chemistry data using PCA resulted in four factors that accounted for a total of 86% of the total variance (Table 4.24). Two general patterns reflecting variations in tissue chlorinated hydrocarbon and PAH concentrations were obtained. PCA factor 3 accounted for the greatest proportion of the variance (36.8%). This factor was most strongly correlated with total DDT, PCBs, and other pesticides. Two PAH groups, pyrene and C1-fluoranthenes/pyrenes also had relatively high correlations with this factor.

PCA factor 1 appeared to represent a pattern characteristic of most tissue PAH. This factor had strong correlations with PAHSUM1 (8 PAH groups) and two individual PAH (Table 4.24). PCA factors 2 and 4 were most strongly correlated with additional PAH

compounds. C3 and C4 alkylated chrysenes were strongly correlated with factor 2, while factor 4 was most strongly correlated with fluoranthene and benzo[a]anthracene.

Table 4.22. Pearson correlations (r) of selected tissue chlorinated hydrocarbons.

	CHLD	DIEL	Mirex	DDT	DDE	PCB	PCB28	PCB52	PCB101	PCB138
Chlordane	1.00									
Dieldrin	0.72	1.00								
Mirex	0.57	0.38	1.00							
Total DDT	0.90	0.62	0.64	1.00						
*p,p'-D*DE	0.77	0.41	0.55	0.95	1.00					
Total PCB	0.93	0.61	0.53	0.93	0.89	1.00				
PCB28	0.94	0.67	0.49	0.89	0.82	0.98	1.00			
PCB52	0.95	0.66	0.46	0.88	0.80	0.98	0.98	1.00		
PCB101	0.97	0.64	0.53	0.93	0.86	0.98	0.97	0.98	1.00	
PCB138	0.85	0.58	0.53	0.94	0.93	0.97	0.91	0.91	0.93	1.00
PCB180	0.81	0.70	0.61	0.80	0.67	0.74	0.75	0.72	0.75	0.71

Table 4.23. Pearson correlations (r) of selected tissue polynuclear aromatic hydrocarbons.

DahAN	FLUR	Pyrene	CHRYS	BbFL	BaPY	PERYL
Fluoranthene	1.00					
Pyrene	0.68	1.00				
Chrysene	0.56	0.84	1.00			
Benzo[b]fluoranthene	0.40	0.81	0.90	1.00		
Benzo[a]pyrene	0.09	0.59	0.76	0.89	1.00	
Perylene	0.59	0.84	0.85	0.84	0.61	1.00
Dibenz[a,h]anthracene	0.03	0.36	0.56	0.70	0.81	0.43

Table 4.24. Summary of principal components analysis of tissue contaminants.

	ROTATED LOADINGS			
	Factor 1	Factor 2	Factor 3	Factor 4
Indeno[1,2,3-cd]pyrene	0.93	-0.02	0.11	0.14
Dibenz[a,h]anthracene	0.92	-0.07	0.12	-0.05
PAHSUM1	0.76	0.18	0.58	0.11
Total PCB	0.56	0.03	0.76	0.21
C1-Fluoranthenes/pyrenes	0.55	0.32	0.70	0.13
Benzo[a]anthracene	0.54	0.12	0.32	0.62
C4-Chrysenes	-0.02	0.92	0.06	0.10
C3-Chrysenes	0.04	0.89	0.19	0.09
C4-Phenanthrenes/anthracenes	-0.01	0.52	0.73	-0.15
PCB180	0.19	0.07	0.89	0.14
Chlordane	0.33	0.17	0.84	0.30
Total DDT	0.40	-0.04	0.81	0.32
Pyrene	0.38	0.32	0.75	0.32
Dieldrin	0.02	0.19	0.74	0.28
Mirex	-0.08	-0.35	0.61	0.54
Fluoranthene	0.06	0.42	0.37	0.66
	PERCENT OF TOTAL VARIANCE EXPLAINED			
	23	16	37	10

G. Chemistry-Toxicity Relationships

1. Sediments

Correlation analysis was used to examine the relationship between toxicity and sediment contamination level. Coefficients for each of the four factors developed by PCA were used to calculate scores for the 12 PV stations. The correlation of these scores with the results of the sea urchin growth and fertilization tests was calculated.

None of the three growth endpoints had statistically significant correlations ($p > 0.05$) with the sediment chemistry factor scores (Table 4.25). The highest correlation coefficient was obtained for diameter change and factor 3. PCB congeners having 8-10 chlorines had the strongest loadings on this factor (Table 4.10). This correlation did not indicate a potential toxic relationship since greater growth appeared to be associated with higher congener concentrations.

Gonad growth was most highly correlated with scores for factors 1 and 2. These two factors were strongly correlated with most of the contaminant data (Table 4.10). The size of the correlation coefficient between weight change and each of the four factors was similar.

Interstitial water toxicity (fertilization test) was significantly ($p < 0.05$) correlated with PCA factor 1 scores (Table 4.25). Factor 1 represented a large number of contaminants, including most PAH and PCB compounds. DDE was also partly correlated with this factor.

Correlations between interstitial water toxicity and contaminant chemistry have a relatively high degree of uncertainty since the analyses were not made on the exposure solutions. Additional correlations were conducted on four parameters measured directly in interstitial water: ammonia, pH, dissolved oxygen, and dissolved sulfide. The highest correlations were obtained between fertilization and ammonia or sulfide (Table 4.26). Both correlations were slightly less than 0.58, the value denoting significance at the 0.05 level.

2. Tissues

Correlations were also calculated between the sea urchin growth test endpoints and scores for the four tissue chemistry PCA factors. Results from these correlations may be a superior indicator of biologically significant relationships because the tissue chemistry data reflect contaminant concentrations within affected individuals.

Gonad and body weight change were significantly correlated ($p \leq 0.05$) with scores for different tissue PCA factors (Table 4.27). Gonad growth impacts were correlated with factor 3, which represented the principal bioaccumulation pattern of chlorinated hydrocarbons,

pyrene, and C1-fluoranthenes/pyrenes. Change in body weight was significantly correlated with a different suite of contaminants, those represented by factor 1. Tissue PCA factor 1 represented the principal bioaccumulation pattern of polynuclear aromatic hydrocarbons.

3. Response thresholds

Multivariate and correlation analyses were not able to identify specific contaminants responsible for sediment toxicity. Instead, these procedures indicated the presence of statistical associations between most bioaccumulated trace organic compounds and sea urchin growth. The gonad concentration of three summary groups of contaminants (total DDT, total PCB, and total PAH) were plotted against gonad growth in order to illustrate relationships with the raw data.

A pattern suggesting the presence of a threshold body burden was seen for each of the three contaminant groups (Figure 4.9). Gonad growth was highly variable at relatively low gonad concentrations, reflecting in part the unexpectedly low growth for station 0C. Consistently low growth (less than 50% of station 0A) was present in samples having the highest tissue contaminant concentrations.

An effects threshold concentration was determined for the three contaminant groups. This value was defined as the lowest tissue concentration producing a consistent reduction in gonad growth of at least 50%. A threshold concentration of 13,500 ng/g was calculated for total DDT. Gonad growth reductions of at least 50% were always measured at tissue concentrations $\geq$13,500 ng/g (Figure 4.9). Similar analyses produced threshold concentrations of 3,360 ng/g for total PCB and 1,500 ng/g for total PAH.

Patterns similar to those shown in Figure 4.9 exist for most organic contaminants present in PV sediments since most compounds are highly correlated with each other. As with correlation coefficients, the patterns shown in Figure 4.9 may be the result of other sediment characteristics besides contaminant concentrations and thus do not demonstrate cause and effect.

Table 4.25. Correlation of sediment and interstitial water toxicity with sediment chemistry PCA factors for Palos Verdes stations. Asterisks indicate statistically significant correlation coefficients ($r_{0.05(2)10}$=0.58).

	Sediment[a]			Interstitial water[b]
	Weight	Diameter	Gonad	Fertilization
Weight	1.00			
Diameter	0.67*	1.00		
Gonad	0.86*	0.57	1.00	
Fertilization	0.38	0.12	0.43	1.00
Factor 1	-0.39	-0.34	-0.39	-0.60*
Factor 2	-0.35	-0.07	-0.42	-0.48
Factor 3	-0.33	-0.50	-0.06	0.22
Factor 4	0.34	0.24	0.21	0.00

[a] Change in sea urchin weight, diameter, or gonad weight following 35 day sediment exposure.
[b] Fertilization of sea urchin eggs following 60 minute exposure to 50% interstitial water.

Table 4.26. Pearson correlations (r) between interstitial water characteristics and toxicity. Toxicity was expressed as the percentage of unfertilized eggs in samples exposed to 50% interstitial water. Asterisks indicate statistically significant correlation coefficients ($r_{0.05(2)10}=0.58$)

	Toxicity	Ammonia
Ammonia	0.55	
pH	-0.14	-0.33
Dissolved oxygen	0.27	0.03
Dissolved sulfide	0.54	0.66*

Table 4.27. Correlation of sediment toxicity (change in sea urchin weight, diameter, or gonad weight) with tissue chemistry PCA factors for Palos Verdes stations. Asterisks indicate statistically significant correlation coefficients ($r_{0.05(2)22}=0.40$)

	Weight	Diameter	Gonad
Weight	1.00		
Diameter	0.48*	1.00	
Gonad	0.70*	0.53*	1.0
Factor 1	-0.51*	-0.15	-0.29
Factor 2	-0.11	-0.34	0.02
Factor 3	-0.26	-0.09	-0.51*
Factor 4	-0.04	-0.19	-0.14

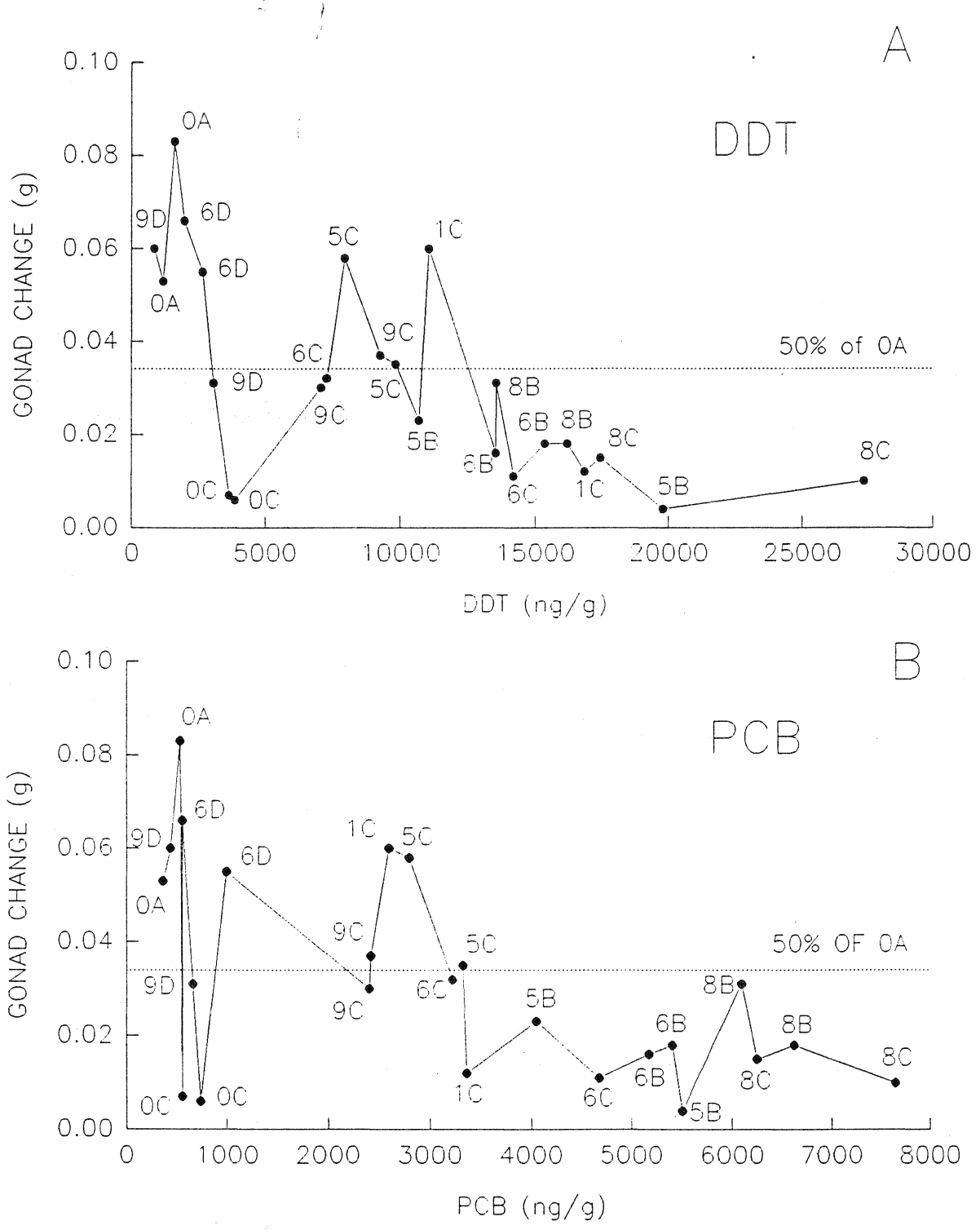


Figure 4.9. Sea urchin gonad growth and concentration of selected contaminant groups. The dotted line indicates a gonad growth rate corresponding to 50% of the average value for animals exposed to the PV reference sediment (0A). Data for duplicate groups of sea urchins exposed to each sediment type are shown. (A) Total DDT. (B) Total PCB.

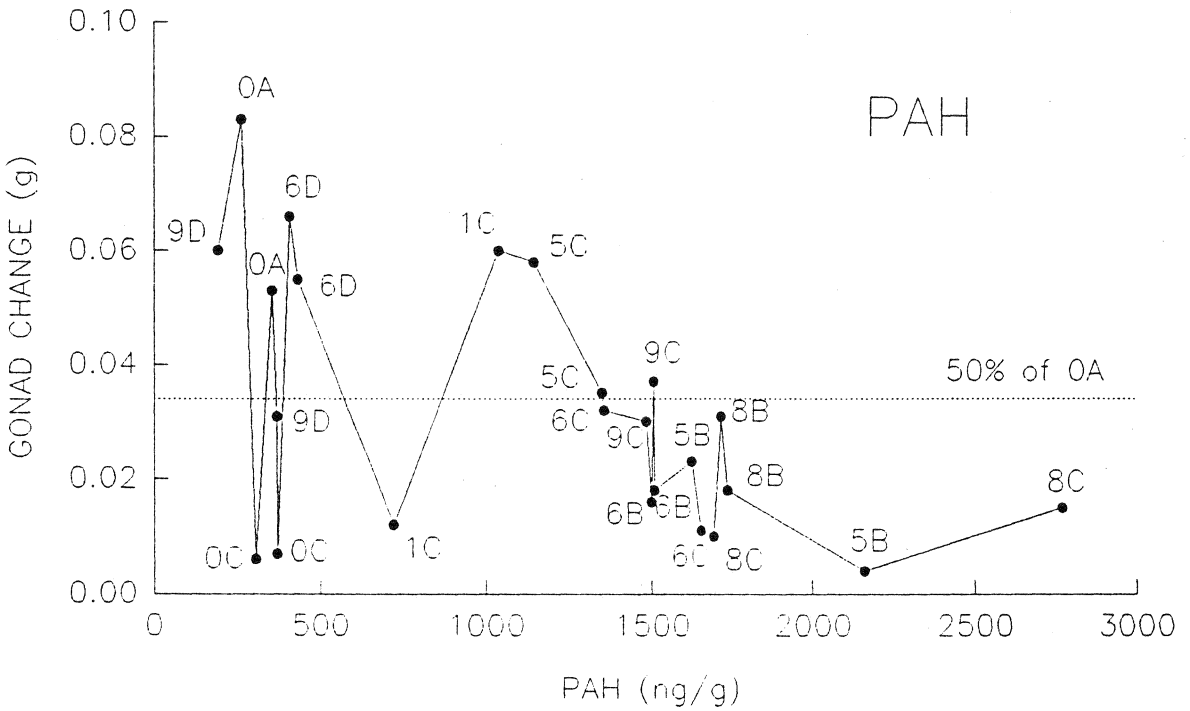


Figure 4.9 (continued). (C) Total PAH.

V. Dose-Response Relationships

A. Sulfide in Seawater

Filtered seawater and interstitial water from station 0C were spiked with sodium sulfide to measure the effect on sea urchin sperm. Nominal seawater concentrations ranging from 0.06 to 0.56 mg/L of dissolved sulfide were tested. Measured sulfide concentrations were very similar to nominal levels (Table 5.1), indicating that sulfide concentrations were stable during the experiment. Salinity, pH, and temperature measurements during the test were used to calculate the concentration of unionized hydrogen sulfide (H_2S), regarded as the most toxic chemical form. Hydrogen sulfide concentrations ranged from 0.1 to 0.9 μM (Table 5.1).

Control fertilization was low (49%) but adequate to permit the detection of toxic effects. Fertilization was significantly reduced by sulfide at a concentration of 0.29 mg/L in seawater (Table 5.1). Expressed as H_2S, a NOEC (no observed effect concentration) of 0.4 μM and an EC50 (median effect concentration) of 0.5 μM were calculated.

Sulfide concentrations were less stable in the two interstitial water treatments. Nominal total sulfide concentrations of 0.56 and 5.6 mg/L rapidly declined to much lower levels during the experiment (Table 5.1). Concentrations of H_2S were high (0.9 and 1.8 μM), however, because of the effects of low interstitial water pH on sulfide speciation. No fertilization occurred in either sample of spiked interstitial water. These results were consistent with the data for spiked filtered seawater, where very low fertilization was present at 0.9 μM H_2S.

The relationship between the spiked seawater and field sediment interstitial water test results is shown in Figure 5.1. These data indicate that all of the detectable sulfide concentrations measured in interstitial water from field samples were potentially toxic. Considerable variation in fertilization was present at H_2S concentrations of 0 and 2 μM. This pattern indicates that either fertilization was influenced by factors in addition to sulfide or that the field sulfide measurements were inaccurate.

Table 5.1. Summary of sea urchin fertilization test of hydrogen sulfide toxicity. Samples of laboratory seawater or interstitial water were spiked with sodium sulfide. The EC50 calculated for these data was 0.24 mg/l total sulfide (0.5 μM H_2S).

Total sulfide (mg/L)				Percent fertilized		
Nominal	Measured	H2S μM	pH	Mean	SD	Significance[a]
Seawater						
0 (control)			8.15	49	6	
0.06	0.07	0.1	8.10	69	9	NS
0.10	0.11	0.2	8.10	64	5	NS
0.18	0.18	0.4	8.12	45	4	NS
0.32	0.29	0.6	8.12	19	3	S
0.56	0.45	0.9	8.13	6	2	S
Interstitial water						
0 (control)			7.50	44	6	
0.56	0.14	0.9	7.52	0	0	
5.60	0.43	1.8	7.79	0	[b]	

[a] S indicates fertilization is significantly less than control (Dunnetts test, $p<0.05$).

[b] Only one replicate counted for this treatment.

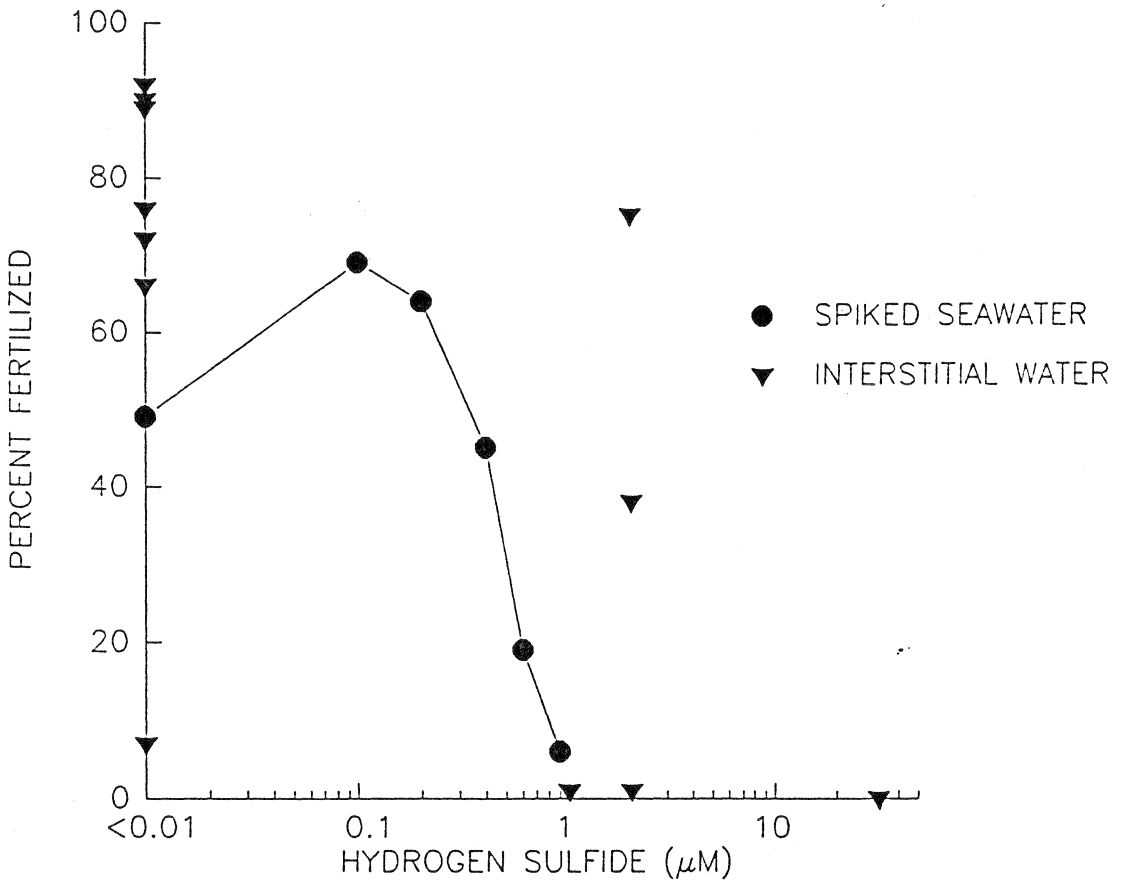


Figure 5.1. Effect of hydrogen sulfide on sea urchin fertilization. Toxicity data for PV interstitial water samples are also shown.

B. DDE in Sediment

A 35 day exposure of sea urchins to sediments spiked with *p,p'-D*DE was conducted during March-April 1993. Reagent grade DDE containing ^{14}C-DDE as a radiolabel was added to sediment from station R52 to produce three treatment levels (270, 1400, and 8,700 ng/g). A fourth treatment containing unspiked sediment was included as a control. The DDE concentrations used were selected on the basis of a preliminary test and were intended to produce gonad DDE concentrations spanning the range measured in tissue samples from the laboratory exposure to field sediments.

The sea urchins used in the experiment had substantially larger gonads than individuals used in the previous toxicity test (Figure 5.2). Gonad size was similar to that measured in resident sea urchins collected from Palos Verdes in summer and fall (Figure 4.6). Large gonad size was an indication of increased reproductive activity in the Dana Pt. individuals, as would be expected in a winter spawning animal such as *L. pictus*.

The experiment produced the desired level of DDE bioaccumulation in the sea urchins. The spiked sediment exposure produced average gonad DDE concentrations ranging from 1,300-38,000 ng/g, while PV sediment exposure produced tissue concentrations of 1,400-22,400 ng/g.

Sea urchins exposed to spiked sediment accumulated similar amounts of DDE as animals exposed to field sediment of similar TOC normalized concentration (Figure 5.3). These data suggest that the spiked sediment adequately represented the bioavailability of DDE in PV sediments.

No relationship between DDE exposure level or gonad concentration and sea urchin growth was present. Change in body weight, diameter, and gonad weight during exposure to DDE was similar to or greater than control values (Table 5.2).

Gonad DDE concentration was measured on individual sea urchins in the experiment. Tissue concentrations were found to vary greatly within exposure levels, possibly obscuring toxic responses in some individuals. Sea urchins were grouped on the basis of gonad DDE concentration instead of exposure level in an effort to reduce variability in the data. Growth data for individuals having gonad concentrations falling within intervals of 10,000 ng/g (e.g., 40,000-49,999 ng DDE/g) were averaged and plotted against the average tissue concentration for the group.

No correspondence between DDE concentration and reduced gonad growth was found using this method of analysis (Figure 5.4). Variable gonad growth rates were calculated for some groups, but there was no pattern suggesting an effect of DDE even though tissue concentrations were more than four times greater than those associated with growth inhibition

in the field sediment exposure. A similar plot of change in wet weight also failed to indicate an effect of DDE (data not shown).

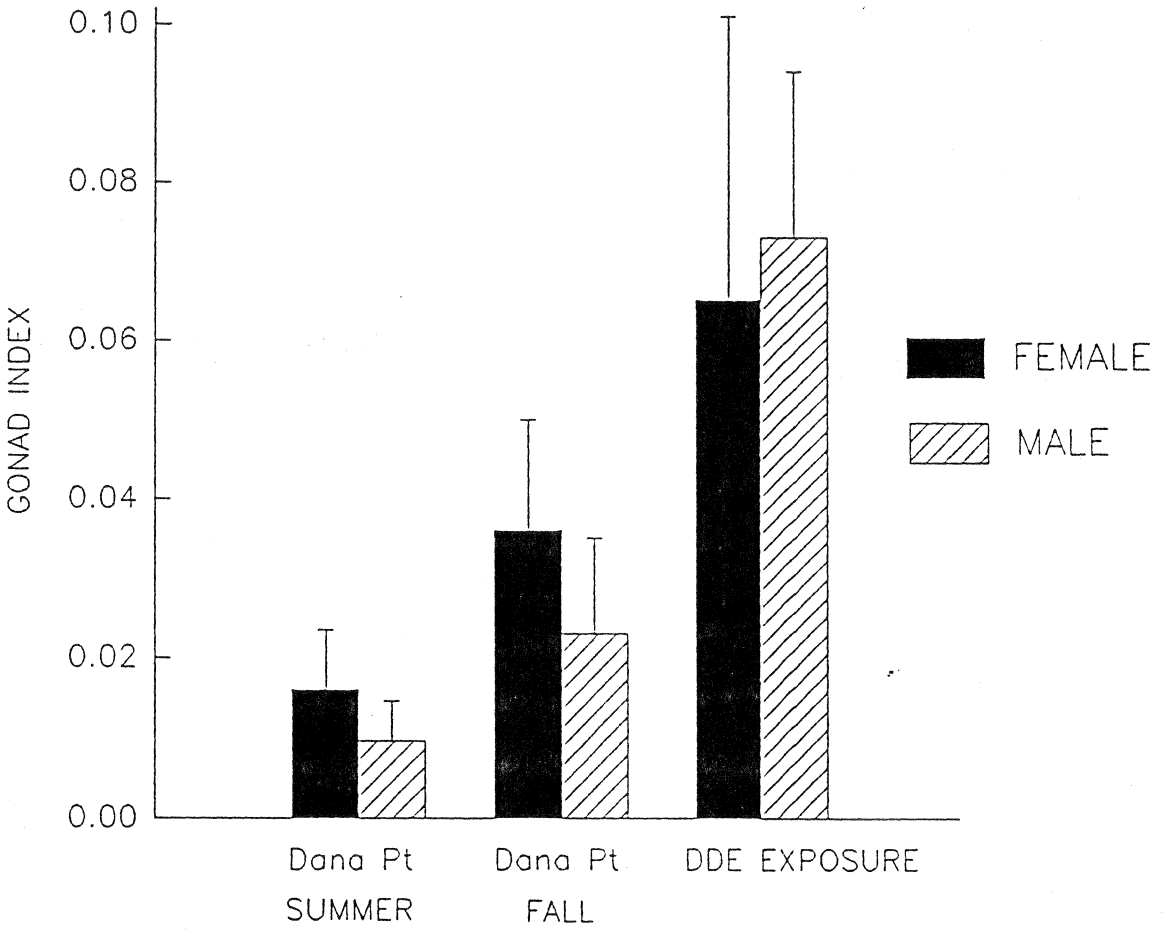


Figure 5.2. Initial gonad index of sea urchins used in spiked DDE experiment. Data for summer and fall field collections are included for reference.

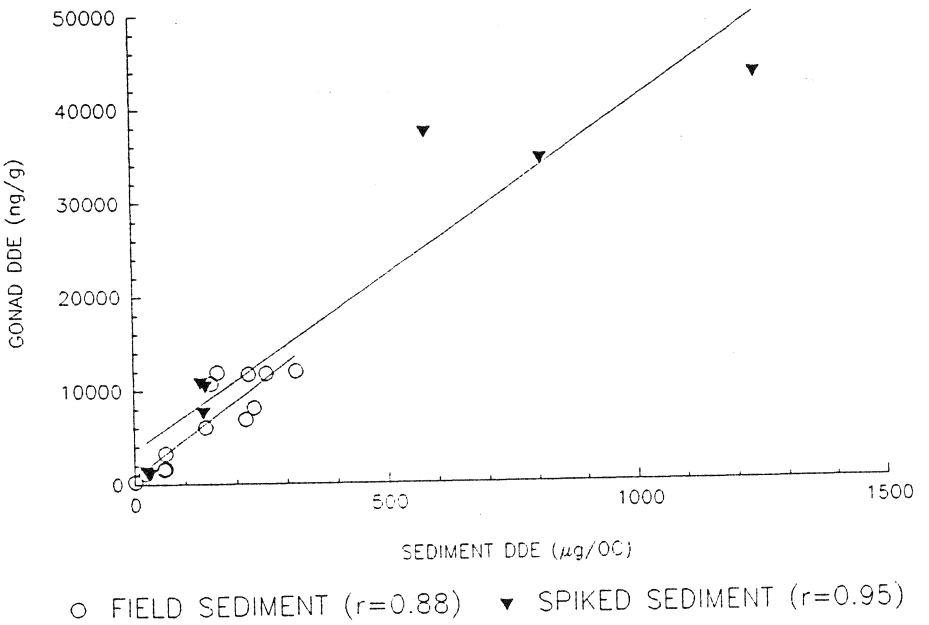


Figure 5.3. Relationship between sediment and gonad *p,p'*-DDE concentration for sea urchin toxicity tests. Lines and regression coefficients (r) were produced by linear regressions between sediment and gonad concentrations.

Table 5.2. Summary of sea urchin growth and bioaccumulation results for the 35 day spiked DDE experiment. Values are the mean of three replicate exposure chambers (standard deviation in parentheses).

DDE Concentration (ng/g)		35 day growth		
Sediment	Gonad	Wet Weight g	Diameter mm	Gonad Weight g
Control	na[a]	0.06(0.09)	0.28(0.16)	0.024(0.007)
270	1,300	0.13(0.06)	0.22(0.20)	0.019(0.014)
1,400	9,800	0.17(0.10)	0.50(0.40)	0.020(0.057)
8,700	38,000	0.09(0.04)	0.46(0.26)	0.051(0.041)

[a] Not analyzed because no DDE added. Sediment and gonad concentrations should be similar to those measured for station R52 in field sediment toxicity test (approximately 300 ng/g).

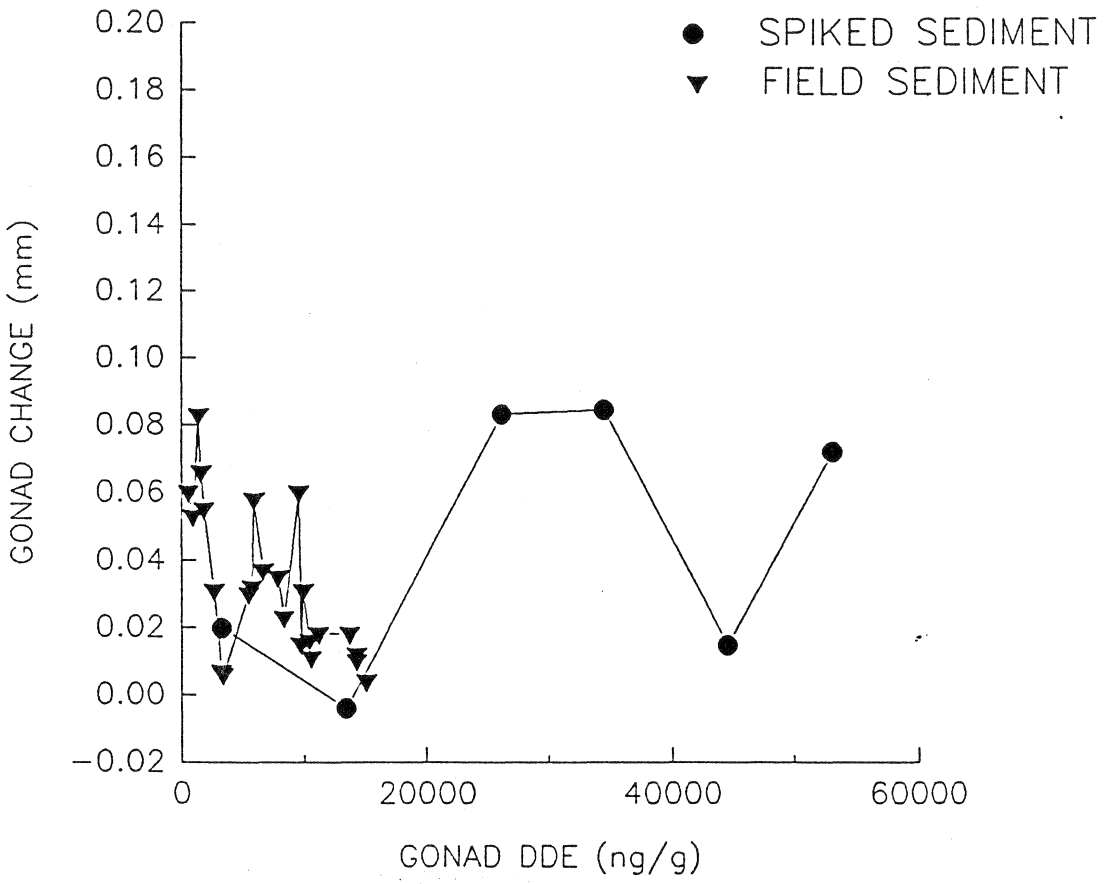


Figure 5.4. Relationship between sea urchin gonad growth and DDE concentration. Spiked sediment data are means of individuals grouped on the basis of tissue concentration. Data from the field exposure are included for comparison.

VI. DISCUSSION

Sediment Chemistry

The sediment chemistry analyses conducted for this project represent one of the most extensive sets of data for the stations sampled. This is the first time that information on AVS, PCB congeners, and PAH has been reported for most of these stations.

The Los Angeles County Sanitation Districts (LACSD) measures sediment chemistry at these same sites every year, providing excellent data for comparison. Sediment concentrations of trace metals and total PCBs reported here generally agree well with LACSD measurements of samples collected in July 1992 (LACSD 1992). PCB concentrations differed sharply for three stations 0C, 6D, and 9C. Nondetectable PCB concentrations (<50 ng/g dry wt) were reported by LACSD while measurements conducted during this study found concentrations of 111-462 ng/g (Table 4.4). Such discrepancies may have been caused by the use of different analytical methods by each agency. An analysis of PCB quantitation methods by SCCWRP (1990) demonstrated that errors of over 100% could result from laboratories analyzing the same sample with different techniques.

Comparison of total DDT measurements with LACSD results indicates a consistent bias in the data. Concentrations of total DDT reported by LACSD were always higher than those reported here. For example, a July 1992 sample from station 8B was reported by LACSD to contain 27,700 ng/g compared to 13,600 ng/g for a July 1992 sample analyzed for this study by Texas A&M University (Table 4.4). A similar pattern was evident in analyses of split sediment samples by SCCWRP and LACSD during a laboratory intercalibration study (unpublished data). This apparent bias should be investigated further so that data from diverse sources can be combined for examining spatial and temporal trends off PV.

Limited data on PV sediment PAH is available for comparison. Published PAH measurements by LACSD (1992) using the NPDES required methodologies have a detection limit (2 mg/kg), too high to be useful off PV. Total PAH concentrations reported for the PV shelf area by others range from 660 to 3,200 ng/g (Nipper *et al.* 1988, NOAA 1991) which is within the range reported here.

Sediment acid volatile sulfides (AVS) and the concentration of simultaneously extracted metals (SEM) were measured because recent studies indicate this parameter may be useful for predicting the toxicity of divalent trace metals (Di Toro *et al.* 1992). Sediments having SEM/AVS ratios <1 are likely to have sufficient metal binding capacity to maintain concentrations below acutely toxic levels. Ratios >1 indicate the potential for metals to exceed the binding capacity of the sediment and produce toxicity.

Sediment SEM/AVS ratios were >1 for some PV stations and highest (55) for the least contaminated station, R52 (Table 4.3). Tissue concentrations of trace metals were not elevated in sea urchins exposed to PV sediments exposed to sediments with high SEM/AVS ratios (Table 4.16), suggesting that bioavailable trace metal concentrations were not present in excessive concentrations during the toxicity tests.

Interstitial Water Chemistry

Measurements of interstitial water pH and hydrogen sulfide (H_2S) conducted by LACSD (1992) provide a basis for comparison with the data from this study. Measurements of pH were similar between studies, and indicated that interstitial water pH was usually lower than that of the overlying seawater.

Measurements of H_2S (Table 4.6) were in partial agreement with LACSD measurements. Similar values were obtained for most stations. A high concentration (263 μM) was reported by LACSD for 8C, while only 2 μM was measured during this study. Accurate sulfide measurements are difficult to obtain because this compound is distributed unevenly in the sediments and very sensitive to loss during sample collection.

The sulfide measurements reported in this study were obtained from a repeat sampling conducted in November to replace unsuccessful analyses of the July samples. The data have been used in this report because of the high toxicity of this compound, but it should be noted that the concentrations used in statistical analysis of the interstitial water toxicity experiment (Table 4.4) are probably inaccurate.

Interstitial Water Toxicity

This study marks the first reported use of interstitial water toxicity testing for multiple sites off PV. Consequently, no comparisons can be made to indicate the consistency of the results. Interstitial water toxicity was greatest for silty sediments collected nearest the outfall (Figure 4.2), a pattern consistent with that expected based on sediment contamination levels in the area, however.

The sea urchin fertilization test used to measure interstitial water toxicity is well-suited to the task because of its small sample and short time requirements. The test uses the response of highly specialized cells (sperm and eggs) to detect toxicity, which leads to concerns that the results may not be applicable to more traditional measures of toxicity (e.g. reduced survival or growth). This possibility was investigated by conducting a concurrent sea urchin embryo development test on some interstitial water samples. Reductions in normal embryo

development were measured in samples causing reduced fertilization (data not shown), indicating that the fertilization test results were a reliable measure of toxicity.

Sediment Toxicity

Amphipod survival. The amphipod survival test with *R. abronius* was not sensitive to PV sediment toxicity (Table 4.12). This test has been used previously by the EPA to measure sediment toxicity at the the same stations (Ferraro *et al.* 1991). In 1986 *R. abronius* survival in PV sediments near the outfall was 83-91%, very similar to the results obtained in this study. PV sediment toxicity data using *R. abronius* now span a 12 year period and indicate a temporal pattern of declining toxicity during 1980-83 (Swartz *et al.* 1986) followed by a generally consistent period of no toxicity between 1983 and the present.

Resident macrofauna along the PV outfall gradient still appear to be impacted, indicating that the *R. abronius* test is not sensitive to the current level of PV sediment toxicity. Because of this low sensitivity, the test results since 1983 demonstrate that toxicity has not increased, but cannot determine whether sediment toxicity has stabilized or continued to decline.

Amphipod growth. The 28 day growth test using *G. japonica* did not indicate survival impacts related to the outfall (Table 4.13). The lowest survival (0%) was measured for the PV station (1C) located the furthest from the outfall. Survival in sediment from stations nearest the outfall (35-61% of the control) was higher than a previous measurement at a similar station (29% of control; Nipper *et al.* 1988).

Survival in all field sediment samples (including the least contaminated sites) was lower than the collection site control (screened Newport Bay sediment), which suggests the presence of a systematic problem in the test. Two factors, poor animal condition and predation, may have interacted to produce the relatively low and variable survival in the test.

Poor animal health was indicated by the results of a concurrent reference toxicant test (96 hour exposure to dissolved cadmium). All juvenile amphipods in the reference test (including those exposed to control seawater) died. Previous reference toxicant tests have been conducted with older animals and usually result in 60-80% survival in the control.

Predation effects may have been inadvertently enhanced in the sediment exposure by sample handling procedures used to minimize sample disturbance. Subcores collected for field sediment testing were not mixed prior to use. This precaution, intended to preserve chemical gradients in the sediment sample, may have enabled some resident predators to survive and eat the juvenile *G. japonica* during the test. Cursory examination of the sediment samples at the

end of the test did not detect obvious predators, however. Control sediment from Newport Bay did not contain predators, as it was screened prior to use.

Sea Urchin Growth. Two measures of sea urchin growth (gonad production and change in body weight) had a pattern of response to the PV stations that was similar to the interstitial water toxicity results. Relatively low growth resulted from exposure to silty sediments located near the outfall, while relatively high growth resulted from exposure to PV sediment from reference (0A) and shallow stations (Figures 4.4 & 4.5). Similar depressions in growth have been found in previous studies at a single station near the PV outfall (Anderson *et al.* 1988, Thompson *et al.* 1989).

Anomalous growth results were obtained for two of the least contaminated stations, 0C and R52. Growth measures for station 0C were among the lowest reported for each endpoint (Table 4.15). No obvious explanation for these data is evident. There is no prior sea urchin toxicity data for 0C for comparison. *Lytechinus pictus* is abundant at 0C, so it is unlikely that sediment from this station is of poor quality. Accidental contamination of the samples during collection is suspected but cannot be documented.

The lowest gonad production was measured in animals exposed to the Dana Pt. reference sediment. This sediment has been used as a reference in previous sea urchin toxicity tests and usually produces a gonad production of about 0.12 g during a 35 day exposure (Anderson *et al.* 1988, Thompson *et al.* 1989). Change in test diameter and wet weight were similar to values obtained in previous tests of R52 sediment, suggesting that the poor gonad production was caused by a mechanism different from that producing the effects reported for station 0C.

The sea urchin growth data were used to describe patterns in response that could be compared to chemical characteristics, not to determine which stations were significantly toxic. Data for station R52 was excluded from additional statistical analyses because the sediment was from a different region and was dissimilar in grain size and TOC compared to the PV stations showing outfall-related responses. It was felt that the test results for this station may reflect regional differences in sediment characteristics not related to contamination level. Inclusion of such data was likely to interfere with identifying relationships between PV contamination and biological responses.

Station 0A was a more appropriate reference station because this site was relatively low in contaminants and had grain size and TOC characteristics similar to most of the other silty PV stations. OA was used as a reference for data comparisons (e.g., Figure 4.4) in an attempt to limit variability produced by noncontaminant sediment characteristics.

Gonad growth was selected as the endpoint for examining contaminant relationships for two reasons. First, this endpoint had the greatest relative response between stations, which

would increase the chance of detecting relationships with chemical concentrations. Second, it was felt that relationships between tissue chemistry and biological responses would be strongest for the gonad, since this was the tissue analyzed for contaminant concentrations.

Bioaccumulation

Data from the chemical analysis of gonads from laboratory and field exposed sea urchins was used several ways. First, bioaccumulation was used as a filter to identify some of the contaminants that were bioavailable and thus had the potential to cause toxicity. Some of the contaminants excluded by this filter may have been bioavailable, but did not accumulate due to metabolism by the sea urchins. Second, tissue concentrations from field exposed sea urchins were compared to laboratory data in order to determine if bioavailability was similar between exposure types. Finally, the data were compared with the toxicity test results (gonad production) to identify relationships that might indicate which chemicals were causing toxic effects.

There was no evidence that PV sediment exposure in the laboratory caused metal bioaccumulation (Table 4.16). In addition, metal concentrations in resident sea urchins from locations nearest the outfall tended to show reductions in some metals. A similar pattern has been observed previously for fish and invertebrates collected from PV (Brown *et al.* 1986). These results suggest that the increased concentrations of sediment metals near PV are not bioavailable or that contaminant effects may be interfering with normal processes of metal regulation in these animals.

Most organic compounds were accumulated by *L. pictus* following laboratory or field exposure, indicating that sediment chlorinated hydrocarbons and polynuclear aromatic hydrocarbons were bioavailable to the test organisms.

There was relatively good agreement between the tissue concentrations of organic contaminants in laboratory and field samples (Figure 4.8). These results are important in that they demonstrate that the laboratory test provided a contaminant exposure similar to that occurring at PV. It is therefore valid to use tissue contaminant data from the laboratory test to estimate the dose received by individuals exposed to the different sediments in the field.

Poor agreement was obtained between lab and field tissue contaminant levels for the Dana Pt. reference station (R52). Tissue concentrations from the laboratory exposure were higher even though sediment concentrations were similar between lab and field. Contamination from the laboratory exposure system is suspected, possibly from the food

provided during the test. Accumulation from this contamination is minor compared to the effects of PV sediment exposure and should not have influenced the test results.

Previous measurements of trace organics in other invertebrate species collected from PV are available for comparison with this study. Gonads from red sea urchins (*Strongylocentrotus franciscanus*) collected near the outfall contained about one third the concentration of DDTs and PCBs measured in *L. pictus* from stations 7D and 9D (LACSD 1992). Red sea urchins from the PV reference area contained even lower levels of contaminants, a pattern not seen in *L. pictus*.

The differences in tissue contaminants between sea urchin species may be related to variations in trophic level and habitat. Red sea urchins analyzed by LACSD were collected from shallower locations that probably had lower sediment contaminant concentrations. *L. pictus* ingests a variety of food sources, such as drift algae, sediments, and animal carcasses. Red sea urchins are primarily herbivores and thus probably receive a lower exposure to organic contaminants from their diet of algae.

Other data on contaminant concentrations in invertebrates collected from PV differ greatly from concentrations measured in *L. pictus* (MBC 1993). Muscle tissue from yellow rock crabs living near the outfall contained low concentrations of DDT (31 ng/g; SCCWRP 1992) while PV shrimp hepatopancreas contained very high DDT levels (49,000 ng/g; Brown *et al.* 1986). PCB concentrations in these organisms show a similar trend. The wide range of tissue concentrations probably reflect the influence of tissue lipid content (highest in hepatopancreas) and species specific differences in contaminant uptake processes.

Resident *L. pictus* collected from PV stations nearest the outfall had increased total PAH concentrations (Table 4.21). This pattern does not correspond with sediment PAH concentrations (Table 4.5) or tissue DDT and PCB concentrations (Table 4.20). It is possible that the unexpected pattern for PAH is an artifact of unreliable data caused by small sample sizes. Tissue concentrations of individual PAH compounds were often below the method detection limit (approximately 100 ng/g) and were variable between duplicate composites and laboratory duplicates. The data have been included in this report because they are the best data available for this important group of toxic contaminants. Comparable tissue PAH data from other PV invertebrates are not available for comparison.

Chemistry-Toxicity Relationships

Interstitial water toxicity. The identification of statistical relationships between contaminants and interstitial water toxicity was constrained by limited chemical data. Only a few interstitial water parameters (pH, ammonia, and sulfide) were measured due to funding

limitations. Results from sediment contaminant analyses were also compared to interstitial water toxicity but the relationships must be cautiously interpreted since an assumption has been made that interstitial water concentrations were proportional to TOC normalized sediment levels.

Sulfide was identified as a likely toxic constituent in interstitial water on the basis of correlation tests (Table 4.26) and prior toxicity data (Thompson *et al.* 1991). Dissolved ammonia concentration, although significantly correlated with toxicity, was not present at high enough concentrations to impact sea urchin fertilization (Bay *et al.* 1993).

Results from the sulfide exposure experiment (Table 5.1) demonstrated that sulfide at the concentrations measured in PV interstitial water is toxic to sea urchin sperm. The relationship between toxicity and sulfide concentration in interstitial water was not as consistent as the relationship found in the dose-response experiment (Figure 5.1). Variations in sulfide concentration accounted for only about 30% of the variability in interstitial water toxicity. This remaining (unaccounted) toxicity is probably related to analytical problems in the sulfide measurements and the presence of other toxic constituents in interstitial water. Since sulfide data from a separate set of samples were used for statistical comparisons, they may not have provided an accurate measure of sulfide levels in the July samples tested for toxicity.

Two aspects of the results suggest that other chemical contaminants also contributed to the toxicity found in PV sediment. First, interstitial water toxicity was measured at some stations (6B and 9D) where no sulfide was detected. In addition, a significant correlation between toxicity and a principal components analysis (PCA) factor was present (Table 4.25). This factor was strongly correlated with the sediment concentrations of many PAH and PCB compounds but not strongly correlated with sediment TOC (Table 4.10). Changes in TOC are often correlated with sulfide concentration. Additional toxicity studies that include more extensive chemical analysis are needed to before additional contaminants causing interstitial water toxicity can be identified.

Sediment Toxicity. Multivariate analysis (PCA) had only limited success in identifying distinctive patterns of sediment or tissue contamination because the distributions of most contaminants were highly correlated with one another. This result was anticipated since most of the contaminants originated from a single source (LACSD outfall) and had chemical similarities (i.e., nonionic organics). Similar difficulties were encountered in previous studies of PV sediments (Anderson *et al.* 1988, Swartz *et al.* 1986). PCA was tried again in this study to determine if methodological differences (e.g., PCB congener analysis, TOC normalization of data) would aid in the identification of patterns.

PCA was useful in reducing the influence of variations in sediment grain size and organic content on chemistry-toxicity correlations. Toxicity tests attempting to associate effects with chemical contaminants in field sediments are often confounded by changes in grain size or TOC, which may influence the test results. Sediment PCA factor 1, which was correlated with most of the organic contaminants, was not correlated with TOC or grain size (Table 4.10).

DDE, a prime suspect in causing biological effects at PV, was not strongly correlated with any one sediment PCA factor. Consequently, this analysis was not useful for assessing the potential influence of DDT compounds on sediment toxicity.

Sea urchin growth was not significantly correlated with any sediment chemistry PCA factor (Table 4.25). The lack of significant correlations do not necessarily mean that sediment contamination had no impact on sea urchin growth. Approximately 37-50% of the variation in sea urchin growth was accounted for by variation in sediment characteristics represented by these four PCA factors.

The low correlations obtained for this phase of the data analysis may have been partially related to a small sample size (N=12), poor precision in the data (only two replicates used in the sea urchin test), and error resulting from the use of sediment concentrations to represent the chemical dose. The above limitations were partially remedied by using tissue concentration data in subsequent correlation analyses. Tissue data were available for twice as many samples (each toxicity test replicate) and provide a better measure of the dose received for slowly metabolized chemicals such as DDT. Tissue concentration may not be a superior indicator of dose for contaminants that are readily metabolized such as some PAH.

The tissue chemistry data provide strong evidence that the high concentrations of trace metals in PV sediments were not bioavailable and therefore unlikely to be the principal cause of sediment toxicity. This conclusion is supported by tissue analyses of laboratory and field exposed sea urchins that show no evidence of bioaccumulation following exposure to metal contaminated sediments (Tables 4.16 & 4.19).

Significant correlations between sea urchin growth and PCA factors representing tissue concentrations of organic contaminants were obtained (Table 4.27). Specific contaminants producing the effects cannot be identified from this analysis because the PCA factors were composites strongly correlated with many compounds (Table 4.24). Two growth endpoints, body weight and gonad weight, were correlated with different suites of contaminants (PCA factors 1 and 3, respectively), which suggest that growth impacts may be related to the combined effects of multiple contaminants. DDTs were included in the group of contaminants most strongly correlated with changes in gonad weight. Correlations cannot prove cause-effect

relationships, however. The biological effects measured in this study may not have been caused by the contaminants measured.

Experiments with specific organic contaminants are required to verify and improve contaminant relationships indicated by the correlation tests. The objective of the spiked sediment experiment was to determine if *p,p'-D*DE (a DDT metabolite and the most concentrated organic contaminant off PV) was responsible for the sea urchin growth responses measured in the laboratory.

The spiked sediment exposure failed to demonstrate a dose-response relationship between DDE and reduced sea urchin growth. Gonad production was unaffected by tissue DDE concentrations that were up to four times greater than those produced by PV sediment exposure (Figure 5.4).

Sea urchins used in the DDE exposure appeared to be in a different physiological state compared to animals used in the PV sediment toxicity test. Control animals had reduced rates of change in diameter and body weight compared to sea urchins exposed to the same sediment type (R52) in the previous experiment (Table 4.15). The sea urchins exposed to DDE were probably in a more active portion of their reproductive cycle, as indicated by their larger relative gonad size (Figure 5.2).

It is not known if these physiological differences had a significant influence on the sensitivity of *L. pictus* to DDE. Physiological changes can alter the effects of contaminants through differences in contaminant metabolism, distribution, and sites of toxic action. Additional experiments to confirm the results presented here are needed to resolve this issue. Until such experiments are conducted, the appropriate conclusion is that *p,p'-D*DE is not responsible for the sea urchin growth effects produced by exposure to PV sediments.

The influence of DDTs in PV sediment on resident macrofauna or laboratory test animals should not be dismissed on the basis of this study. The spiked sediment experiment studied only the most abundant metabolite, *p,p'-D*DE. Other forms of DDT (i.e., *p,p'-D*DT, *o,p'-D*DT, *p,p'-D*DD, *o,p'-D*DD, and *o,p'-D*DE) are present in PV sediments at concentrations exceeding those of most other organic contaminants (Table 4.4). Toxicity can vary greatly among closely related chemicals, so the results for *p,p'-D*DE cannot be extrapolated to related forms without additional information.

A recent synthesis of sediment toxicity and ecological information concludes that DDTs are important factors in PV sediment toxicity. Swartz *et al.* (in press) estimates that a total sediment DDT concentration of about 100 μg/g organic carbon represents a minimum threshold above which effects on resident biota occur. This estimate is consistent with the sea urchin growth data, which found strong growth responses at sediment DDT concentrations $\geq$189 μg/g oc (concentration at station 6B). Swartz *et al.* also calculated a DDT threshold of

300 ug/g oc for mortality effects in 10 day sediment toxicity tests using amphipods. No significant mortality was seen in the 10 day amphipod test conducted in this study (Table 4.12), even though total DDT concentrations were as high as 545 ug/g oc (station 8C).

This project has made progress in refining our hypotheses regarding the causes of PV sediment toxicity, yet more research is needed. An important aspect of the approach used here for investigating chemistry toxicity relationships was the use of tissue contaminant concentrations to indicate bioavailability and exposure dose. This approach has been advocated by others as essential for assessing the environmental risk of contaminants (McCarty and Mackay 1993). Additional factors such as metabolism and subcellular distribution are also important for predicting the risk of contaminants.

Additional dose-response experiments that determine the critical body residues associated with contaminant effects should be conducted with *L. pictus*. These studies are needed to verify that sediment contaminants are causing toxic effects in the macrofauna and to determine which contaminants are most important.

It is recommended that future spiked sediment tests use mixtures of several contaminants (e.g., DDTs or PCB congeners) present in PV sediments. The bioaccumulation data show that sea urchins were exposed to many toxic organic contaminants. As mixtures of contaminants are thought to contribute to chronic toxicity in an additive manner (Swartz *et al.* 1988, McCarty and Mackay 1993), it is unlikely that only one or two compounds will be responsible for PV sediment toxicity. Conducting tests on contaminant mixtures is the most cost-effective method to demonstrate chemistry-toxicity relationships and also provides an exposure that is more representative of PV sediments.

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