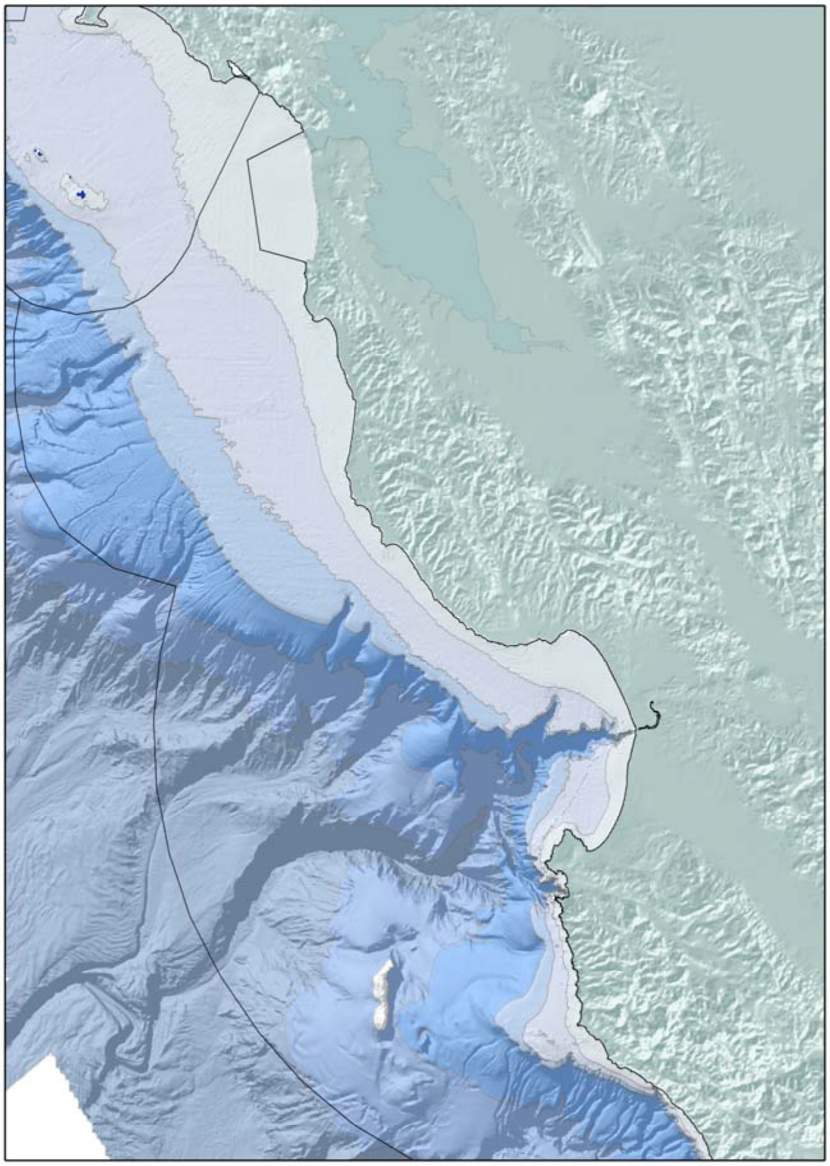
Distribution of Persistent Organic Contaminants in Canyons and on the Continental Shelf off Central California



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Distribution of Persistent Organic Contaminants in Canyons and on the Continental Shelf off Central California

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EXECUTIVE SUMMARY

The National Status and Trends (NS&T) Program has conducted studies to determine the spatial extent and severity of chemical contamination and associated adverse biological effects in coastal bays and estuaries of the United States since 1991. Sediment contamination in U.S. coastal areas is a major environmental issue because of its potential toxic effects on biological resources and often, indirectly, on human health. Thus, characterizing and delineating areas of sediment contamination and toxicity and demonstrating their effect(s) on benthic living resources are therefore important goals of coastal resource management at NOAA.

The National Centers for Coastal Ocean Science, and the Office of National Marine Sanctuaries, in cooperation with the U.S. Geological Survey (USGS), University of California Moss Landing Marine Lab (MLML), and the Monterey Bay Aquarium Research Institute (MBARI), conducted ecosystem monitoring and characterization studies within and between marine sanctuaries along the California coast in 2002 and 2004 on the NOAA RV McArthur. One of the objectives was to perform a systematic assessment of the chemical and physical habitats and associated biological communities in soft bottom habitats on the continental shelf and slope in the central California region. This report addresses the magnitude and extent of chemical contamination, and contaminant transport patterns in the region. Ongoing studies of the benthic community are in progress and will be reported in an integrated assessment of habitat quality and the parameters that govern natural resource distributions on the continental margin and in canyons in the region.

In 2002, site selection targeted potential depositional areas, locations of major outfalls and terrestrial river discharges, and areas lacking data, to specifically address the potential transport routes and sinks of contaminants. Stations were initially laid out in a grid pattern on the continental shelf. Stations were then added based on known contaminant release areas, sediment depositional zones, the heads of canyons, and in the canyon leads beyond the shelf break from San Francisco to Monterey Bay. In 2004, sample sites were selected based upon results from 2002. Sampling was prioritized to include a variety of canyons and shelf/slope areas to allow evaluation of contaminant transport patterns along the continental shelf and potential delivery to canyons, based on bathymetry from detailed side scan sonar maps. Preliminary grid lines were laid out to sample eight locations from the mid shelf, to the shelf break, and down the canyons to a depth of 1,200m in Pioneer, Ascension, Año Nuevo, Soquel, Monterey and Carmel Canyons. Samples were taken along five transects from mid-shelf to the shelf break and down the continental slope in 5 transects between Pioneer Canyon and approximately 20 km southeast of Pt. Sur. In addition to water quality measurements and physical characteristics of the sediment, chemical analyses following the NOAA NS&T program and USGS methods, analyzed a broad suite of chemicals, including PAHs, PCBs, chlorinated pesticides, and trace elements. Contaminant concentrations and concentrations normalized for sediment characteristics were calculated and plotted by

location to assess distribution patterns. Analysis of Variance and Duncan's Multiple Range Test were calculated to subset location groups.
Most of the sediments in the Gulf of the Farallones, Pioneer Canyon, the southern transects, and around the margins of Monterey Bay are sandy. Sediments at sampling stations south of Half Moon Bay, the mid-shelf sediments, in Ascension, Soquel, and Monterey Canyons were finer in texture. In contrast, Año Nuevo Canyon does not exhibit accumulation of fine grained sediments at depths shallower than 800m. Total organic carbon (TOC) content of sediments generally increased with depth at all locations. Dissolved oxygen at the bottom of the water column exhibited the expected decline with depth to an oxygen minimum zone below 700m. Total metals analyzed in the 2002 samples revealed few notable trends. Organic contaminant concentrations were relatively low throughout the sampling area, compared to typical estuarine concentrations found in nearby San Francisco Bay. Concentrations of organic contaminants indicate a very inhomogeneous distribution however. Accumulation of contaminants was evident in finer grained sediments in Monterey Bay, Ascension Canyon, on the continental shelf between those features, and in the immediate vicinity of the Golden Gate and the San Francisco POTW outfall. Contaminant concentrations in Carmel Canyon and on the shelf south of Monterey Bay did not appear to be elevated above background levels. Organic carbon normalization of the data show that for PAHs and PCBs, the sediments in the Gulf of the Farallones appear to receive organic contaminants from San Francisco Bay through tidal exchange at the Golden Gate to a greater extent than from longshore drift up the coast. In contrast, DDT concentrations are highest in Monterey Bay, Ascension Canyon, and the continental shelf between them (but not the slope) with or without TOC normalization. Concentrations of DDT are elevated above sediment quality guidelines in several locations. Low level accumulation in other areas only occurs at depth. Other persistent pesticides were also detected throughout the region, but at very low concentrations.

Compared to other continental shelf locations sampled by NS&T, sediments on the continental shelf off California have generally higher concentrations of DDT than elsewhere, including areas in and around Massachusetts and Cape Cod Bays, off the mouths of Delaware and Chesapeake Bays, and outside the mouth of Galveston Bay, TX. In contrast, PAH and PCB concentrations are higher in Massachusetts and Cape Cod Bays than off central California, or even Galveston. Other persistent pesticides were somewhat higher in the California canyons than elsewhere, but were more uniform across the areas where they were found.

DDT enters Monterey Bay in stormwater runoff from agricultural land. Although DDT is no longer used on crops, there is a large residual volume stored in sediments within the watersheds. Ocean sediment concentrations similar to those seen in the early '70s indicates a continuous input 30 years after it was banned.

Contaminants accumulate in fine grained sediments which do not necessarily correspond to source locations. The continental shelf north of Monterey Bay contains the so-called mid-shelf mud belt, where fine grained sediments accumulate. Organic contaminants are concentrated in this region. Canyons that accumulate fine grained sediments (Ascension, Soquel, and Monterey) accumulate higher concentrations than canyons with coarser sediments. The continental slope only accumulates higher concentrations of organic contaminants at depth, where fine grained material is deposited in relatively static habitats.

The presence of DDT at equal concentrations in Monterey Bay and at the head of Ascension Canyon indicates transport of fine-grained materials out of the Monterey Bay system to the shelf. The fate of fined grained sediment derived from the watersheds within Monterey Bay is not accurately known. Water currents are complex and seasonably variable. Net flow in the Bay delivers water and sediments to the northern rim of the Bay most of the time, which may then be transported north or south on the continental shelf, depending on the prevailing coastal current direction and depth. Within the Bay, sediments may also be lost down Monterey Canyon in large sediment sloughing events.

In the mid-shelf mud belt, fine grained sediments move from south to north. Estimated sediment flux values from Monterey Bay do not account for the observed mass of material being transported on the continental shelf. Either the source estimates need revision, there are other sources, or sediments are by-passing the canyon from the southern portion of Monterey Bay. Data is needed to determine what suspended sediment dynamics are present in the shallower portions of Monterey Canyon. Satellite imagery indicates that large volumes of sediment may move across Monterey Canyon from south to north during the wet season. Data from joint NOAA/USGS instrument moorings retrieved in 2006 are currently being analyzed to help address this question. The transport and fate of sediment-borne contaminants in Monterey Bay and it’s canyon system are of central importance to assessing the fate and effects of anthropogenic contaminants in the Monterey Bay National Marine Sanctuary. A major question is what impact does low level, but continuous, input of DDT have on the biological community. Tissue concentrations in mussels exceed local screening values and guidelines indicating that contamination of nearshore shellfish in the Monterey Bay area may be of concern for both human and wildlife health.

Submarine canyons are prominent conduits of sediment/contaminant transport to deeper waters. DDT body burdens observed in fish is a reflection of local sediment concentrations and food chain transfer from the benthic community. DDT concentrations in Monterey Bay biota indicate bioaccumulation is occurring at depth. Bottom feeding fish in Monterey Bay have higher body burdens of DDT than pelagic fish. Also, deep dwelling species have higher body burdens than shallow species. Body burdens in fish from the Monterey Bay area are higher than comparable deep and surface water species from the Atlantic Ocean. Benthic invertebrate species have higher body burdens than fish. Benthic community assessment studies are currently under way.

INTRODUCTION

The National Status and Trends (NS&T) Program conducts studies to determine the spatial extent and severity of chemical contamination and associated adverse biological effects along the coast and in estuaries of the United States. Sediment contamination in U.S. coastal areas is a major environmental issue because of its potential toxic effects on biological resources and often, indirectly, on human health. A large variety of contaminants from industrial, agricultural, urban, and maritime activities are associated with bottom sediments, including persistent organic chemicals, polycyclic aromatic hydrocarbons (PAHs), and trace metals.

Critical habitats and food chains supporting many fish and wildlife species involve the benthic environment both inshore and offshore. Contaminants in the sediments may pose ecological risks through degraded habitats, loss of fauna, and biomagnification of contaminants in the ecosystem. Thus, characterizing and delineating areas of sediment contamination are viewed as important goals of coastal resource management. This report addresses the physical and chemical contaminant characteristics of the soft bottom benthic habitat on the continental shelf and upper continental slope of the central California region. This information will be integrated with biological data on benthic infaunal communities, and additional chemical and biological sample collections taken during subsequent years, which are still being analyzed. The intent is to contrast the benthic communities between canyons, between canyon flanks and central axis habitats, and between canyons and adjacent slope habitats. The broader objective is to assess the potential impact(s) of physical stressors and contaminants on the benthic community in differing habitats found in this region. Macrobenthic organisms play an important role in the marine environment. As secondary consumers in the offshore ecosystem, they represent an important link between detritus-based food webs and higher trophic levels. They are also an important food source for juvenile fish and crustaceans.

2002 Sampling

The National Centers for Coastal Ocean Science, and the Office of National Marine Sanctuaries, in cooperation with the U.S. Geological Survey and the Monterey

Bay Aquarium Research Institute (MBARI), conducted ecosystem monitoring and characterization studies within and between marine sanctuaries along the California coast in 2002 and 2004 on the NOAA RV McArthur. The primary objectives of the 2002 cruise included:

- Evaluate historical and recent contaminants in depositional sediments and at other priority target sites in the Gulf of Farallones (GFNMS), Monterey Bay (MBNMS), and Channel Islands (CINMS) National Marine Sanctuaries
- Evaluate sediment characteristics in the Gulf of Farallones and Monterey Bay National Marine Sanctuaries
- Examine mesoscale physical and biological characteristics of the water column in the region during the spring seasonal transition period and use these measurements to calibrate interpretations of satellite ocean color images
- Teach sanctuary staff methods that may be used for Sanctuary monitoring programs
- Strengthen partnerships among organizations involved in monitoring in the sanctuaries on the West Coast
- Support MBARI data collection efforts along the California Cooperative Oceanic Fisheries Investigations (CalCOFI) Line 67
- Identify protocols that can be continued during expeditions planned for later in the year and those that might be implemented in a system-wide monitoring program being planned for the National Marine Sanctuaries

The expedition included collection of physical and biological oceanographic data via Conductivity/Temperature/Depth (CTD) meters, fluorometry, Acoustic Doppler Current Profiler (ADCP), sediments samples, net tows, and seabird and marine mammal observations. Midday, on-board chamber incubations were conducted to evaluate water column productivity, as well as bongo net tows at stations along a permanent transect extending from Monterey Bay 400 km to the west.

2004 Sampling

Based upon the 2002 results, a follow-up sampling cruise was conducted in 2004 to further explore the distribution of contaminants and benthic community composition on the continental shelf off central California. The primary objectives of the 2004 cruise included:

- Baseline characterization of sediment contaminant distribution in depositional habitats of canyons and the continental shelf/slope in Monterey Bay National Marine Sanctuary
- Baseline characterization of the biodiversity and distribution of benthic communities in depositional habitats in canyons and the continental shelf/slope in Monterey Bay National Marine Sanctuary
- Identify habitat factors that govern species and community distributions
- Identify natural and anthropogenic stressors that influence habitat quality and living resources.

Little published information is available on the living resources of soft bottom benthic habitats off central California except for selected areas in Monterey Canyon. Outside of the canyon, little detailed specific knowledge about the benthic community on the outer continental shelf or continental slope is known beyond broad generalizations of the boundaries of biogeographical zones (Lissner, 1989). Obtaining the biological and physical data in this region was intended to expand our knowledge of the ocean's characteristics, document poorly known areas, and aid in developing an understanding of the ecology of the continental shelf region and the general health of the system. The research was designed to investigate and document the soft bottom benthic infaunal community in a systematic approach in the central California region, and to delineate habitats as defined by the resident biological communities. These habitats will then be characterized to determine how bathymetry, disturbance, and sediment characteristics influence the distribution of the communities. These are currently unknowns. The central California shelf break and slope contain one of the more diverse benthic communities in the ocean. The diversity and spatial heterogeneity of this area have not been systematically explored. The research project was also designed to assess what the physical and ecological processes are that enable these highly diverse communities to exist in a seemingly simple habitat that is stable over long periods of time.

In contrast, canyons experience periodic sediment sloughing that opens up new habitat space by removing the existing benthic community. The frequency of these natural disturbances are partially dependent on sedimentation rate, storm activity, and earthquakes, and resident communities are expected to be evolutionarily adapted for periodic disturbance. The similarity or dissimilarity of the faunal assemblages present in different canyon habitats in this region have not been explored. Submarine canyons are also the conduits to the deep ocean for material accumulated on the shelf. It is unknown to what extent sediment contaminant loads moving down the canyons may be impacting benthic communities.

Data from the NS&T sediment chemical contaminant profile from the 2002 cruise indicated a very inhomogeneous distribution of organic tracer chemicals in the canyon heads between San Francisco and Monterey Bay. Relative to the continental shelf and Pioneer Canyon stations, dichloro diphenyl trichloroethane (DDT) and other contaminants were found at higher concentrations at the heads of Ascension and Monterey Canyons. Monterey Bay still receives DDT input from terrestrial runoff and may be the source of DDT found in Ascension Canyon. The presence of DDT at equal concentrations at the head of Ascension Canyon and Monterey Bay indicates transport of fine-grained materials out of the Monterey Bay system to the shelf. Monterey Canyon sediments also contain DDT at depths of over 3,200 m (Paull et al., 2002). DDT concentrations in Monterey Bay biota indicate bioaccumulation is also occurring at depth (Looser at al., 2000). It is unknown to what extent sediment loads moving down the canyons may be impacting the deep communities. Contrasting the benthic communities on the slope and within these canyon systems will also allow an assessment of the impact, if any, of anthropogenic inputs into these important systems which are also the routes of continental runoff to abyssal ecosystems.

Deep benthic regions are difficult to observe and thus are not well understood. The lack of documentation and inventory of sediment contamination and of the benthic biota of oceans and coastal areas are a widespread deficiency in the technical knowledge base. Another utility of the assessment is to provide information to regulatory agencies and local stakeholders on how to prioritize and monitor areas, and as a predictive tool to guide regulation of commercial and recreational activities in the ocean, or watershed land use activities, that can lead to degraded coastal habitats. This report is intended to address sediment chemistry data obtained from the 2002 and 2004 sampling cruises. Biological data will be addressed in subsequent reports following further data analysis.

NOAA RV McArthur I

METHODS

In 2002, sediment samples were taken for chemical analysis with a Kynar-coated $0.1m^2$ Young-modified Van Veen grab sampler. In 2004, sediment samples were taken to assess the chemical and biological content of the sediment with a dual Young-modified stainless steel Van Veen grab. This allowed simultaneous sampling for biota and contaminant assessment at the exact same location. Sampling gear was initially washed and rinsed, followed by an acid wash with 10% HCl and rinsed with deionized water, rinsed with acetone and again with deionized water. At each site, the sampler was rinsed with acetone and deionized water immediately prior to sampling. Subsamples were collected for chemical analyses and grain size characterization with a Teflon coated titanium scoop. Only the upper 2-3 cm of the sediment was used in order to assure collection of recently deposited materials. Samples for chemical analyses were stored in pre-cleaned glass jars with teflon liners. All subsamples were either stored on ice or frozen (-23^oC), as appropriate, prior to shipment to analytical laboratories. The entire second sample from the dual grab was sieved onboard through a 0.5 mm screen to retain the dominant proportion of the benthos. All retained organisms were preserved in

Deploying a dual Van Veen grab sampler from the RV McArthur II.

buffered formalin with Rose Bengal and stored for shipment to the laboratory. These data will be reported at a later date when they become available.

The 2002 site selection was based upon existing data. Sites were selected to target potential depositional areas, locations of major outfalls and terrestrial river discharge, and in areas lacking data. Fifty six locations were sampled (Fig. 1). Stations were selected in advance to specifically address the potential transport routes and sinks of contaminants emanating from San Francisco Bay via the Golden Gate and from the municipal Publicly Owned Treatment Works (POTW) discharge site (Southwest Ocean Outfall - SWOO) approximately 6 km offshore. Stations were initially laid out in a grid pattern on the continental shelf. Stations were then added based on release point locations, the presence of fine-grained depositional zones north and south of the release areas, the approaches to the heads of Pioneer Canyon, and in the canyon leads beyond the shelf break. Additional stations were included at a fine-grained site south-west of Half Moon Bay, at the head of Ascension Canyon, and six locations in Monterey Bay. Sampling at deeper stations in Ascension Canyon was precluded due to severe weather. The Monterey Bay stations were located near the mouths of the three major freshwater tributaries to Monterey Bay, and in depositional zones around the canyon rim, offshore from the tributaries.

In 2004, sample sites were selected based upon results from 2002. Sampling was prioritized to include a variety of canyons and shelf/slope areas to allow evaluation of contaminant transport patterns along the continental shelf and potential delivery to canyons. Stations were initially stratified on the basis of depth, and were situated in specific locations that were believed to be depositional environments (as opposed to the canyon axis), based on bathymetry from detailed side scan sonar maps and inferred sediment texture (NMFS, 2004). In addition, sites were selected to provide the widest possible range of habitat types to contrast benthic communities in different canyons and between canyons and stable slope areas. Preliminary grid lines were laid out to sample sediment at up to eight depths from the mid-shelf (80, 110m), the shelf break (150, 250m), and down the canyons/slope through the oxygen minimum zone (475, 700, 950m), and below to 1200m. Initial target areas included Pioneer, Ascension, Año Nuevo, Soquel, Monterey and Carmel Canyons (Fig. 1). Two sampling lines on the continental shelf and slope were placed between Pioneer and Ascension Canyons (S1 and

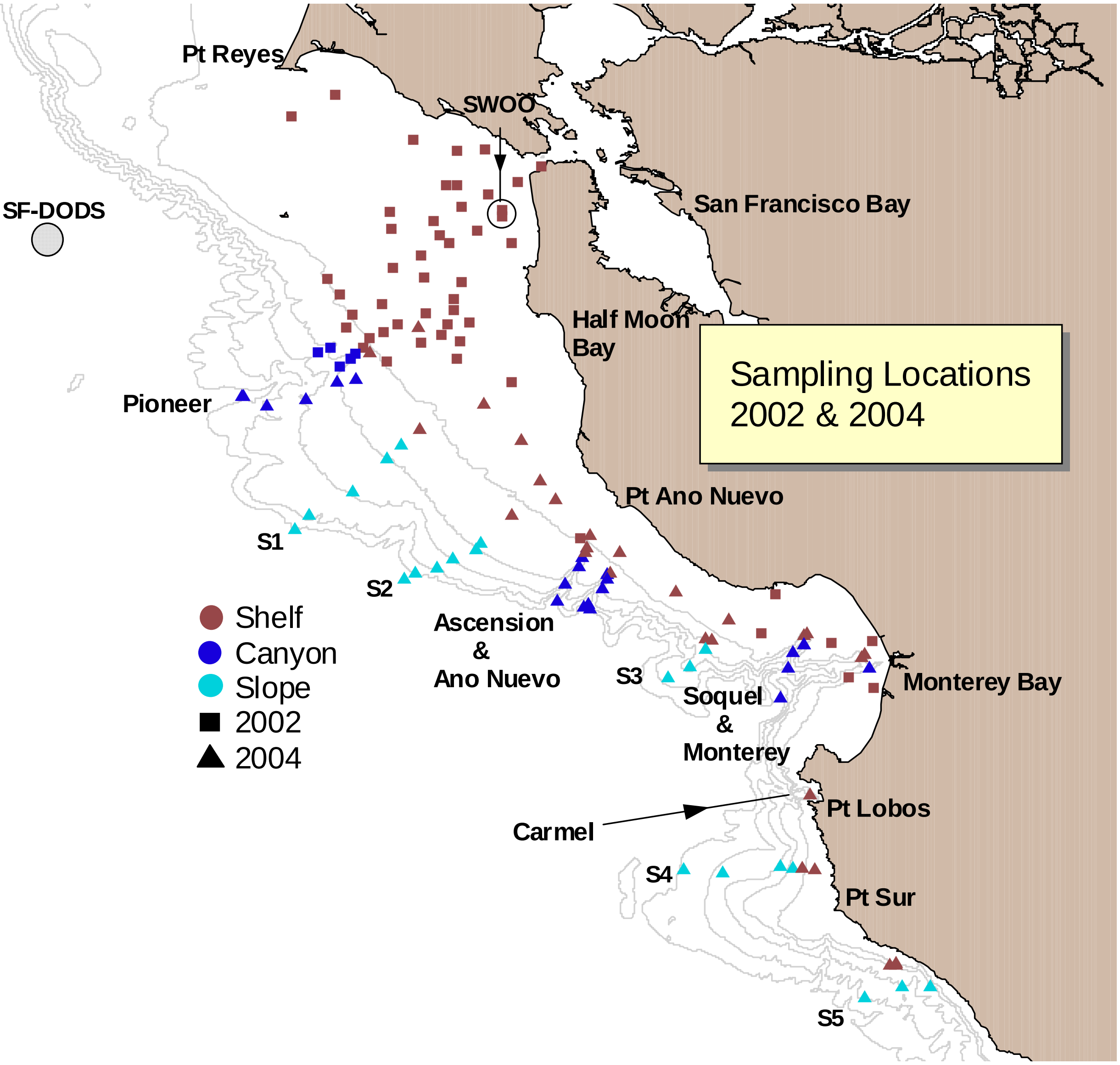


Figure 1 Sampling locations. See text for site selection description.

S2 in Figure 1), a line between Año Nuevo and Soquel Canyons to the so-called Smooth Ridge area (S3), and a line between Pt. Lobos and Pt. Sur (S4). A fifth series of sites approximately 20 km southeast of Pt. Sur were samples to provide a contrast between the slope1-4 transects and an area where the continental shelf is typically narrow (S5). This was not so much a transect as a sequence of presumptively depositional locations at the target depths. A true transect was not possible as the bathymetry in this area is irregular and cut by many small gulleys.

A water quality profile (salinity, temperature, etc.) was measured with a CTD at selected stations. Dissolved oxygen was measured at the deep stations in 2004 by retrieving water samples from the bottom in replicate Nisken bottles and measuring oxygen immediately with a hand-held Yellow Springs Instruments (YSI) meter. Sediments were analyzed for moisture content, grain size, and organic contaminants including polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides (Tables 1 & 2). Sediments were analyzed for trace metals (Table 3) and selected pharmaceuticals in 2002 only. Results of the pharmaceutical analyses are reported in Pait et al. (2006). All sampling methods and analytical techniques followed routine NOAA, NS&T methods (Hartwell et al., 2001; Lauenstein and Cantillo, 1998). Organic compounds were extracted using a Soxhlet apparatus. Quantitation of PAHs and their alkylated homologues was performed

Sampling sediment for chemical analysis

Table 1. Polynuclear aromatic hydrocarbons analyzed in sediment samples, and minimum detection limits (MDL, ppb).

Analyte	**MDL**	**Analyte**	**MDL**
Naphthalene	0.17	C2-Fluoranthenes/Pyrenes	0.39
C1-Naphthalenes	0.33	C3-Fluoranthenes/Pyrenes	0.39
C2-Naphthalenes	0.35	Benz(a)anthracene	0.13
C3-Naphthalenes	0.35	Chrysene	0.17
C4-Naphthalenes	0.35	C1-Chrysenes	0.35
Biphenyl	0.14	C2-Chrysenes	0.35
Acenaphthylene	0.19	C3-Chrysenes	0.35
Acenaphthene	0.13	C4-Chrysenes	0.35
Fluorene	0.19	Benzo(b)fluoranthene	0.29
C1-Fluorenes	0.39	Benzo(k)fluoranthene	0.23
C2-Fluorenes	0.39	Benzo(e)pyrene	0.31
C3-Fluorenes	0.39	Benzo(a)pyrene	0.22
Anthracene	0.19	Perylene	1.38
Phenanthrene	0.14	Indeno(1,2,3-c,d)pyrene	0.28
C1-Phenanthrenes/Anthracenes	0.29	Dibenzo(a,h)anthracene	0.15
C2-Phenanthrenes/Anthracenes	0.29	Benzo(g,h,i)perylene	0.14
C3-Phenanthrenes/Anthracenes	0.29	18a-Oleanane	1.11
C4-Phenanthrenes/Anthracenes	0.29	Naphthobenzothiophene	0.20
Dibenzothiophene	0.15	C1-Naphthobenzothiophenes	0.41
C1-Dibenzothiophenes	0.31	C2-Naphthobenzothiophenes	0.41
C2-Dibenzothiophenes	0.31	C3-Naphthobenzothiophenes	0.41
C3-Dibenzothiophenes	0.31	C29-Hopane	1.11
Benzothiophene	0.17	C30-Hopane	1.11
C1-Benzothiophenes	0.35		
C2-Benzothiophenes	0.35		
C3-Benzothiophenes	0.35	**Additional PAHs**	
Carbazole	0.33	2-Methylnaphthalene	0.20
Dibenzofuran	0.20	1-Methylnaphthalene	0.13
Fluoranthene	0.21	2,6-Dimethylnaphthalene	0.20
Pyrene	0.19	1,6,7-Trimethylnaphthalene	0.10
C1-Fluoranthenes/Pyrenes	0.39	1-Methylphenanthrene	0.20

Table 2. Chlorinated pesticides and PCBs analyzed in sediment samples, and minimum detection limits (MDL, ppb).

Pesticides	**MDL**	**PCBs**	**MDL**
Aldrin	0.10	PCB8/5	0.10
Dieldrin	0.07	PCB18	0.06
Endrin	0.12	PCB28	0.05
Heptachlor	0.09	PCB44	0.10
Heptachlor-Epoxide	0.18	PCB52	0.05
Oxychlordane	0.05	PCB66	0.04
Alpha-Chlordane	0.04	PCB101/90	0.04
Gamma-Chlordane	0.05	PCB 103	0.19
Trans-Nonachlor	0.04	PCB105	0.10
Cis-Nonachlor	0.07	PCB118	0.06
		PCB128	0.11
Alpha-HCH	0.09	PCB138	0.06
Beta-HCH	0.07	PCB153/132/168	0.06
Delta-HCH	0.08	PCB170/190	0.06
Gamma-HCH	0.05	PCB180	0.06
		PCB187	0.04
2,4'-DDD	0.07	PCB195/208	0.04
4,4'-DDD	0.11	PCB 198	0.19
2,4'-DDE	0.05	PCB206	0.04
4,4'-DDE	0.04	PCB209	0.07
2,4'-DDT	0.10		
4,4'-DDT	0.08		
Endosulfan II	0.10		
Endosulfan I	0.10		
Endosulfan Sulfate	0.11		
Mirex	0.04		
Chlorpyrifos	0.10		

Table 3. Trace elements analyzed in sediment samples by the USGS, and minimum detection limits (MDL, ppm).

Element	**Symbol**	**MDL**	**Element**	**Symbol**	**MDL**
Silver	Ag	1.0	Manganese	Mn	0.02
Aluminum	Al	1.0	Nickel	Ni	0.2
Arsenic	As	0.2	Lead	Pb	0.1
Cadmium	Cd	0.004	Antimony	Sb	0.04
Chromium	Cr	0.9	Selenium	Se	0.1
Copper	Cu	0.1	Tin	Sn	0.12
Iron	Fe	1.0	Thallium	Tl	0.05
Mercury	Hg	0.004	Zinc	Zn	0.2

by gas chromatography/mass spectrometry (GC/MS). Chlorinated hydrocarbons were quantitatively determined by capillary gas chromatography with an electron capture detector (ECD). Metals were analyzed using USGS analytical methods (USGS, 2002) by inductively coupled plasma mass spectroscopy (ICP/MS) or atomic emission spectroscopy (AES), with the exception of cold vapor atomic absorption spectroscopy (CV AAS) for As, Se, and Hg. Quality control samples were processed in a manner identical to actual samples and included method blanks, duplicates, and matrix spike/matrix spike duplicate (MS/MSD) samples. Certified reference materials were extracted with each batch of samples (NIST SRM 2260). Method detection limits were determined following the procedures outlined in CFR 40, part 136 (1999). Surrogate and internal standards were spiked into every sample and quality control sample.

Special samples were collected at six locations for analysis of polybrominated diphenyl ethers (PBDE) and polybrominated biphenyls (PBB). These compounds are emerging contaminants of concern and little data is available on environmental concentrations. PBDEs are flame retardants that are used in a large variety of products including consumer goods (e.g. fabrics, carpets, plastic containers, foam, electrical circuitry) and industrial products (ATSDR, 2004). Deca-brominated diphenyl ethers are still produced but penta- and octa- brominated diphenyl ethers were phased out of U.S. production in 2004. More stringent restrictions are in place in Europe. PBBs were also used as flame retardants in plastic products but have not been manufactured in the U.S.

since 1976 due to environmental and human health concerns (ATSDR, 2004). Like. PCBs, these are highly recalcitrant compounds with bioaccumulative potential. The selected stations were all located behind the ebb tidal shoal south of the Golden Gate. Two sites were adjacent to the SWOO (Fig. 1) and four other sites where fine-grained sediments were believed to exist. The intent was not to comprehensively assess PBDE and PBB distributions on the shelf, but to determine whether they are present in sufficient quantities, in presumptively depositional habitats near likely sources, to warrant expenditure of resources to pursue a more thorough assessment.

Grain size sorting was calculated using an inclusive graphical method based on equations from Folk (1974). Chemical data were plotted geographically to assess spatial distributions. Sediments with higher concentrations of TOC will tend to accumulate higher concentrations of non-polar organic contaminants than sediments with low TOC that receive similar loadings of contaminants. Comparison of sediment chemical concentration data from different locations was made following organic carbon normalization, specifically by dividing the contaminant concentrations by organic carbon content. Normalizing concentration data for the relative bulk of organic matter in a given sediment sample allows an examination of the relative input pattern (as opposed to accumulation potential) of sediments in differing locations. Normalized contaminant concentrations were plotted to assess relative distributions. Sediments with less than 0.1% TOC were eliminated (6 stations) because very small values will lead to spurious calculations. Stations were divided into five groups based on depth and latitude : 1) continental shelf sites north of Half Moon Bay, 2) shelf sites south of Half Moon Bay, 3) continental slope sites [all were south of Half Moon Bay], 4) canyon sites north of Half Moon Bay [Pioneer], and 5) canyon sites south of Half Moon Bay. Shelf sites were arbitrarily defined as being in water depths of 150 m or less. Slope and canyon sites were designated as being at depths greater than 150 m. Regressions and Duncan's Least Significant Difference (LSD) groupings were calculated using concentration data and organic carbon normalized data to examine potential source and sink areas for the various organic contaminants. Throughout this report "DDT" is defined as the sum of concentrations of DDT and the degradation products DDD and DDE.

Sandy sediment vs fine-grained sediment

RESULTS

Most of the sediments in the Gulf of the Farallones are sandy at all depths on the shelf and slope (Fig. 2), as are the slope deposits on the southern transects, and around the margins of Monterey Bay. Sediments in Pioneer Canyon are coarser than material in the canyons to the south. South of Half Moon Bay shelf sediment deposits are finer in the so-called mid-shelf mud belt (Eittriem et al., 2002). Sample locations were deliberately targeted at this depth to assess contaminant concentrations where they were likely to accumulate. Closer to shore, sediments are typically coarser. Ascension, Soquel, and Monterey Canyons exhibit finer grained sediments than elsewhere. Soquel Canyon has particularly fine-grained sediments (Fig. 3) relative to the other canyon locations. In contrast, Año Nuevo Canyon does not exhibit accumulation of fine-grained sediments at depths shallower than 800 m. Sediments were poorly or very poorly sorted throughout most of the sampling area, except in areas where tidal currents and/or riverine input were prominent (Fig. 4). Total organic carbon content of the sediments followed the grain size distribution. Percent TOC ranged from less than 0.1 % to 2.3% and averaged 0.7%. Total organic carbon content of sediments generally increased with depth at all locations. Ascension, Año Nuevo, Soquel and Monterey Canyons all exhibited higher TOC concentrations than elsewhere (Fig. 5).

Dissolved oxygen at the bottom of the water column exhibited the expected decline with depth to an oxygen minimum zone below 700 m. An unequivocal oxygen rise was not evident at deeper stations but the maximum depth was only 1,200 m. There was no apparent difference in bottom oxygen concentrations between the slope and canyon stations, indicating that tidal currents were not moving the oxygen minimum up and down the canyons within this depth range (Fig. 6). The water column was thermally stratified between 20 and 50 m. The thermocline was typically located at shallower depths on the shelf than offshore. Figure 7 shows data from Slope 1 stations, which was typical of all sampling transects. The local thermal reversal below 100 m was also seen in the nearby Pioneer Canyon transect, but faded away closer to shore, probably indicating a local transient internal current or wave disturbance. It was not present in the Ascension Canyon transect further south (and a day later).

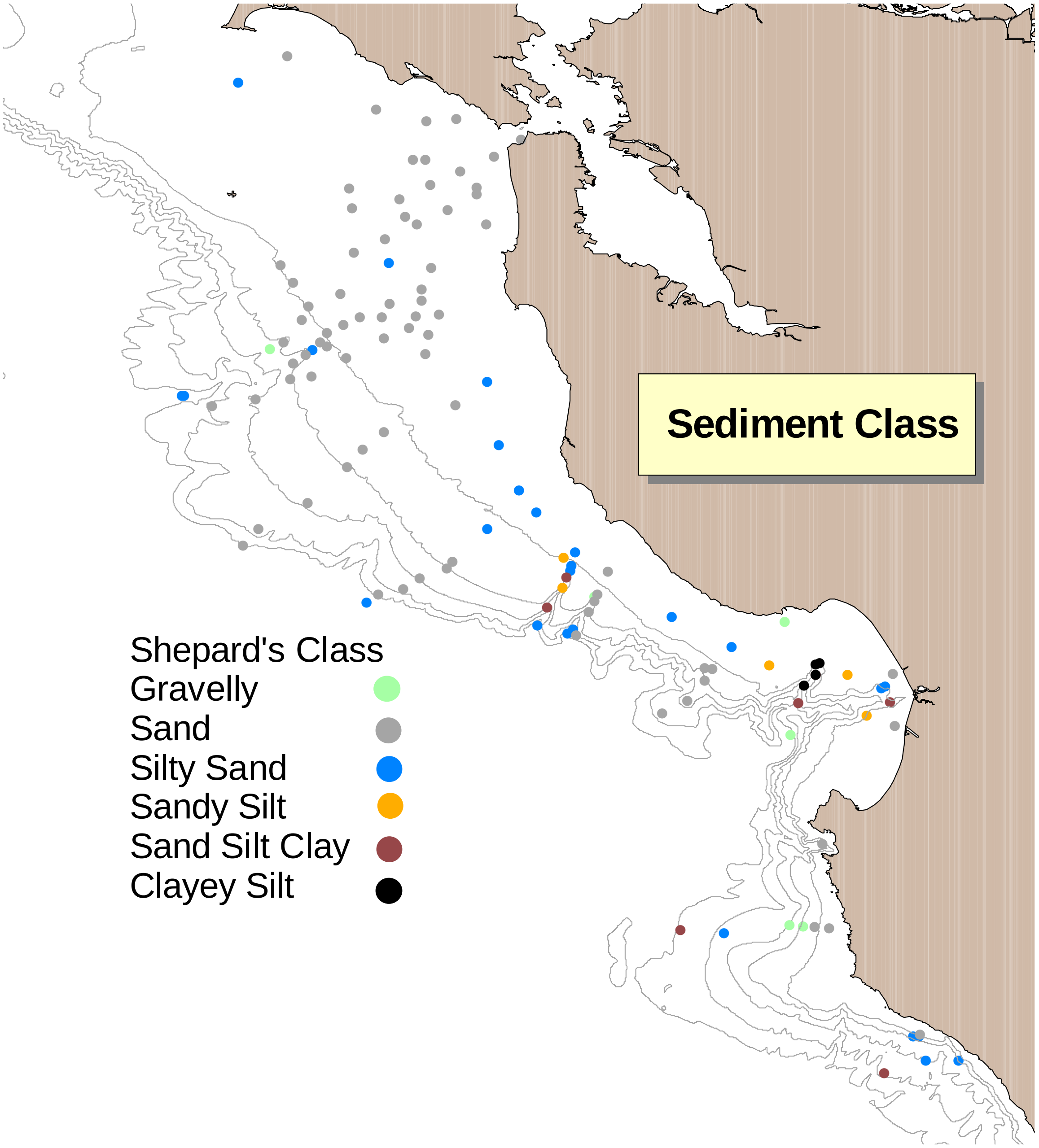


Figure 2. Shepards classification of sediment types.

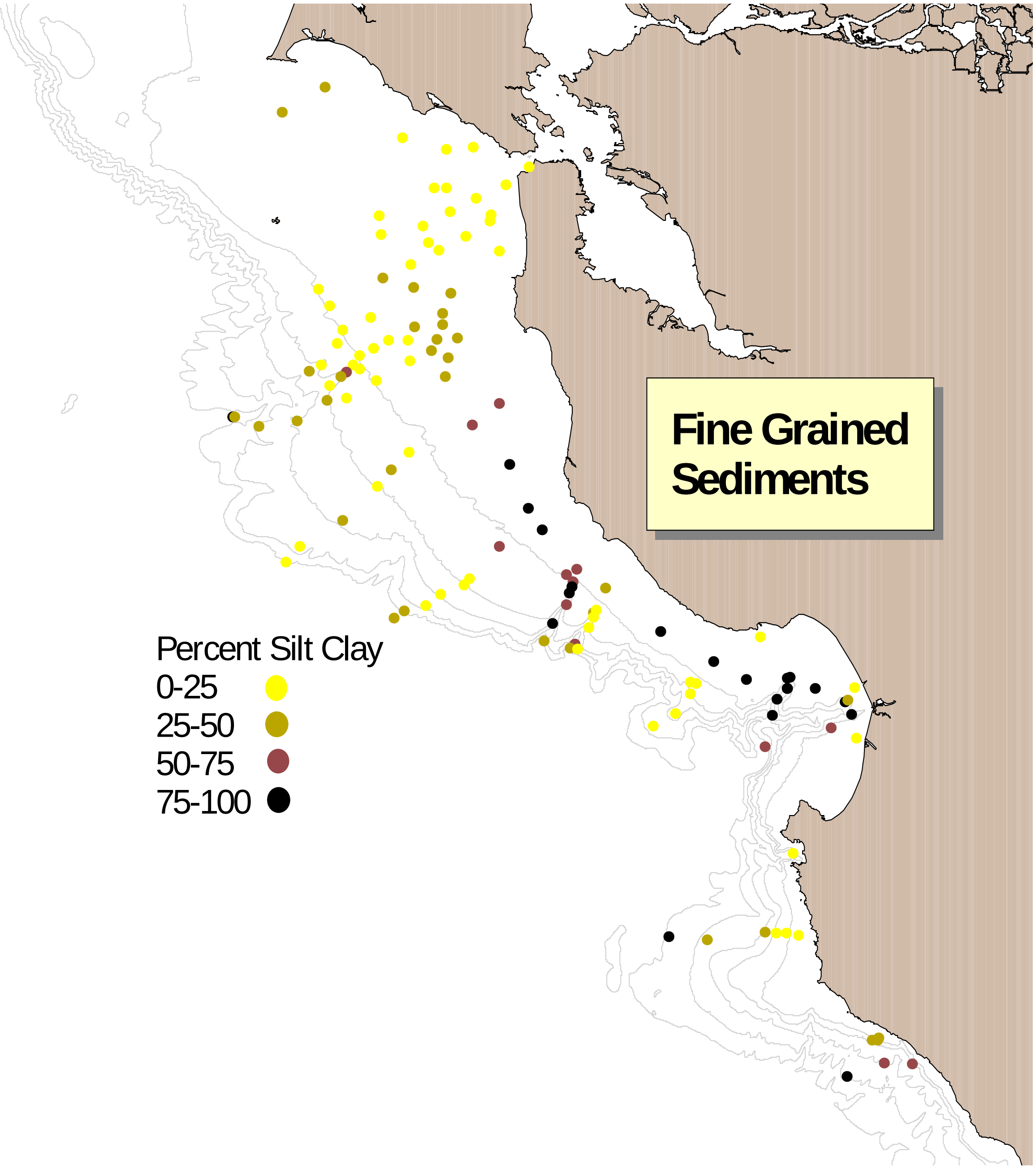


Figure 3. Distribution of fine grained sediments.

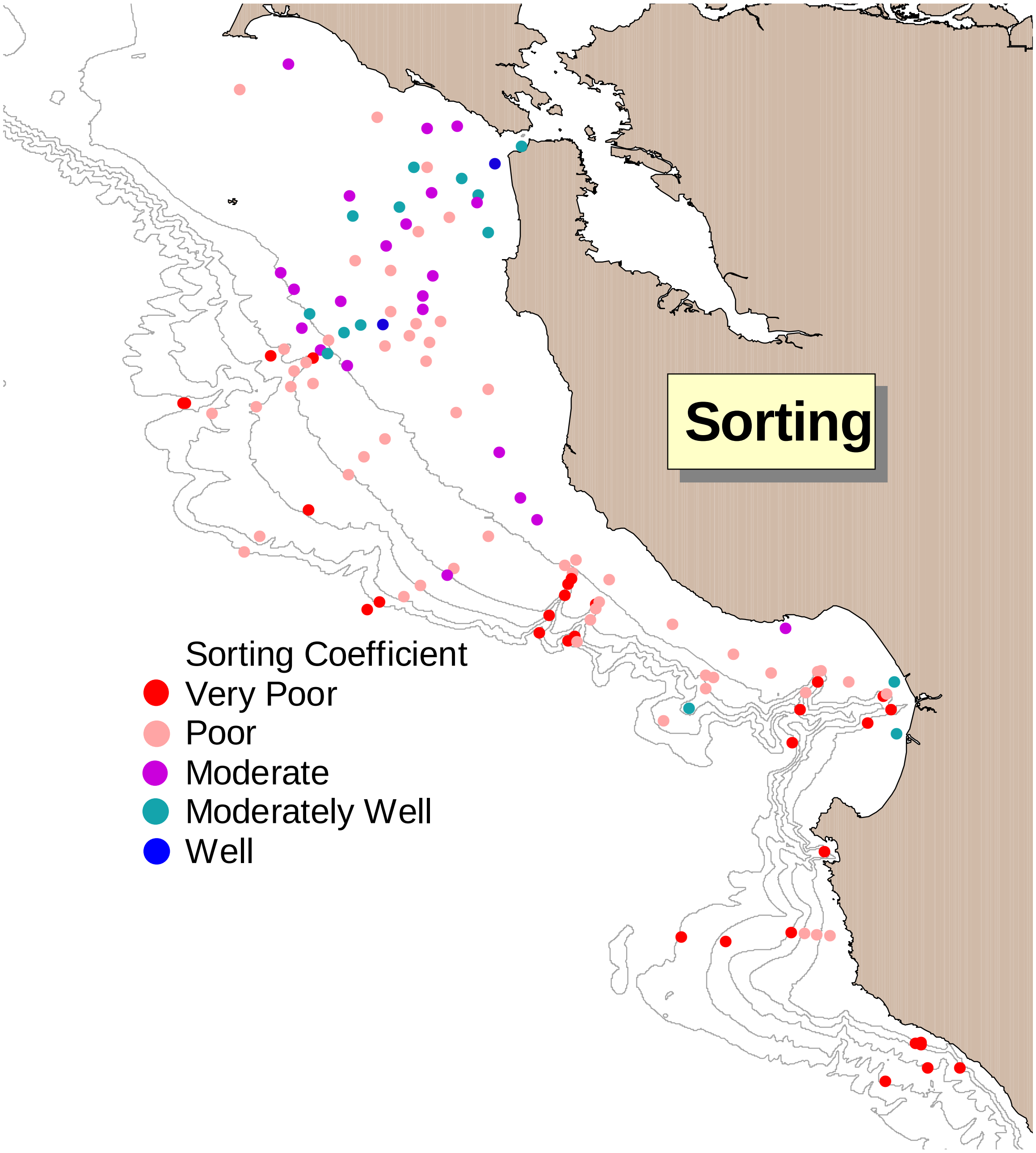


Figure 4. Calculated sorting coefficient for sediments.

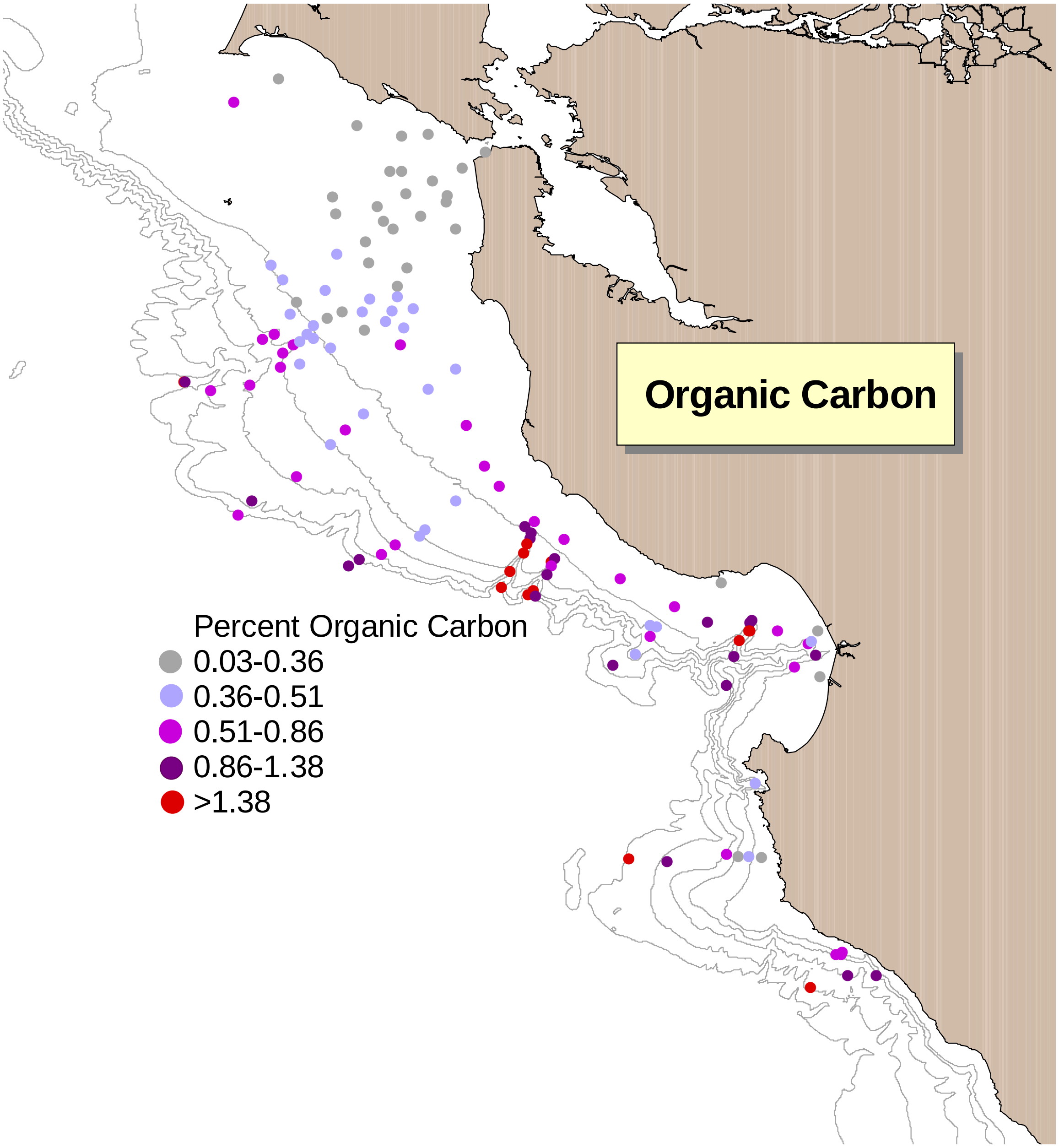


Figure 5. Percent organic carbon content of sediments.

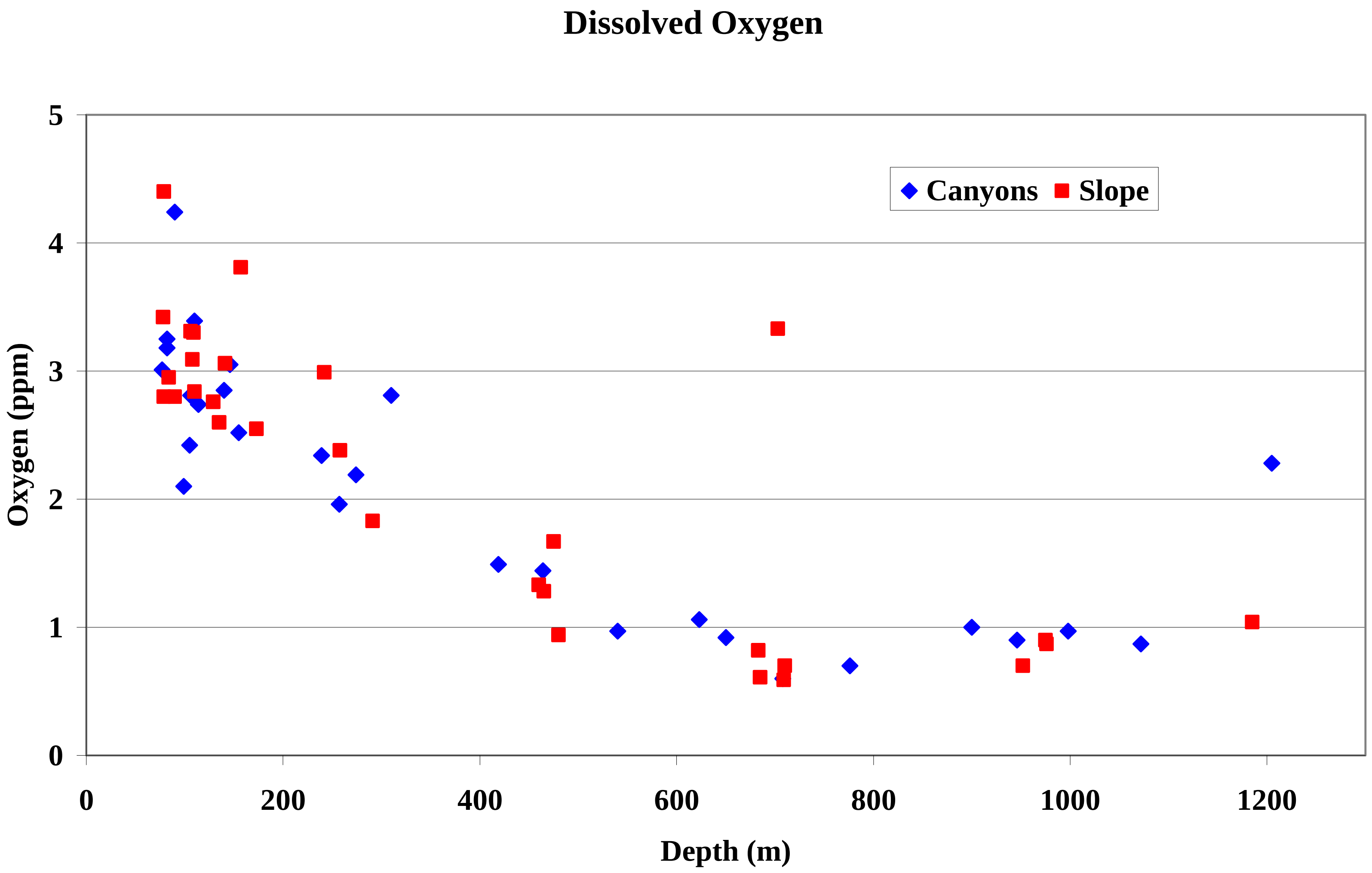
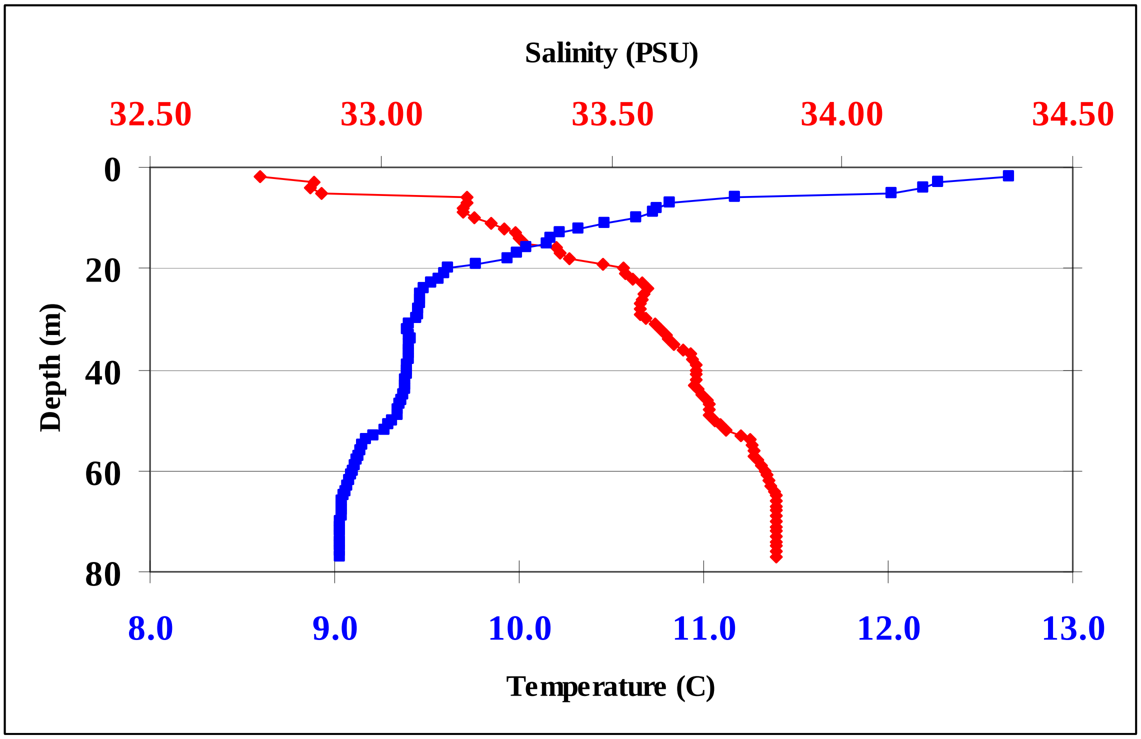


Figure 6. Bottom water dissolved oxygen concentrations in canyons and on the continental shelf/slope off central California in 2004.



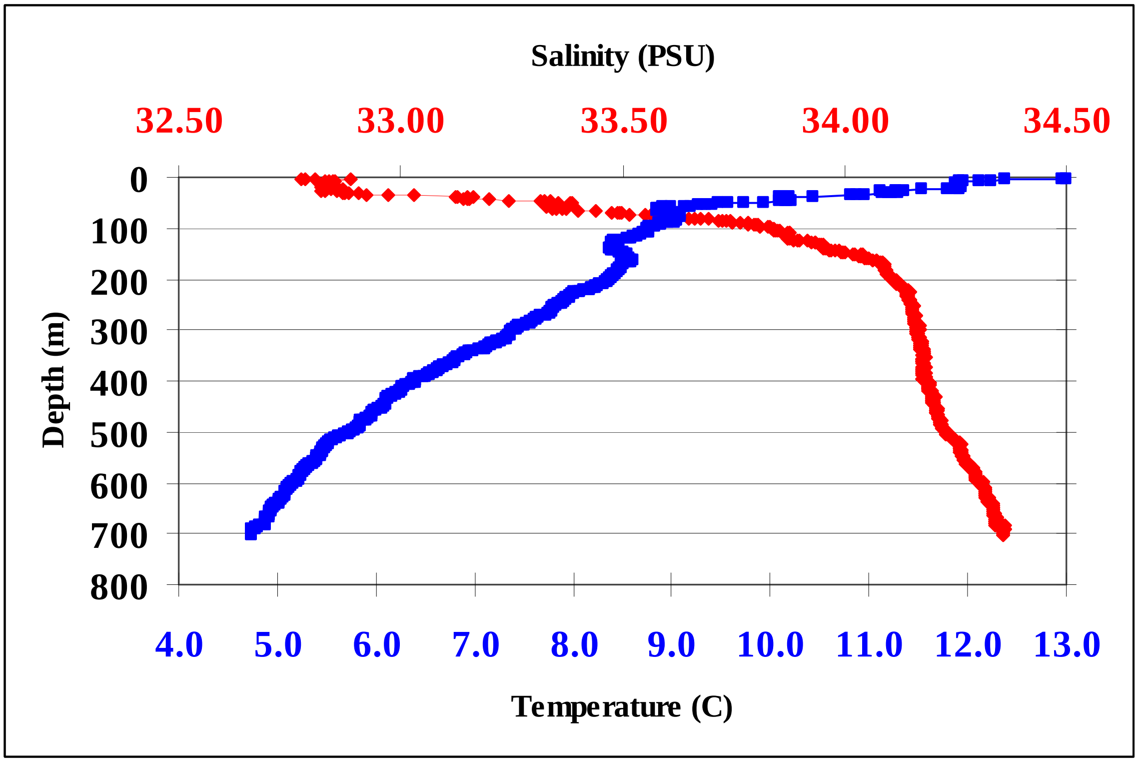


Figure 7. Salinity-temperature depth profiles for Slope 1 stations #1 (above) and #6 (below).

Total metals analyzed in the 2002 samples revealed few notable trends. Selenium concentrations increased with depth, and were higher in Monterey Bay than in the Gulf of Farallones (Fig. 8). However, Se was rarely above detection limits in sediments with low TOC levels, including those in Monterey Bay. Mean concentration throughout the sampling area was 0.14 mg/kg, whereas mean Se concentration in nearby San Francisco Bay was 0.3 mg/kg (SD = 0.197) (NOAA, unpublished data). Mean Se concentrations in other recent NS&T assessments of coastal sediments include 0.19 mg/kg (Massachusetts Bay), 1.0 mg/kg (Chesapeake Bay mouth), 0.03 mg/kg (Delaware/New Jersey coast) and 0.13 (off Galveston Bay) (Harmon et al., 2003; Hartwell et al., 2001, 2007; Hartwell and Hameedi, 2007). Numerical sediment quality guidelines (Table 4) developed by Long and Morgan (1990) and Long et al. (1995) known as ERM and ERL (effects range-median, effects range-low) express statistically derived levels of contamination, above which toxic effects would be expected to be observed with at least a 50% level of frequency (ERM), and below which effects were rarely (at most 10%) expected (ERL). It should be noted that these guidelines were developed to assess estuarine habitats, not offshore deposits. There were no exceedances of ERL concentrations for Ag, Cu, Pb, or Zn. Cadmium slightly exceeded ERL levels in some locations, primarily in the deeper shelf stations (Fig. 9) with lower concentrations away from this zone. Arsenic and Hg concentrations were elevated at one station each. Concentrations of Cr exceeded ERL levels at virtually every site, and the ERM at select stations. However, the concentration of Cr is higher in West Coast sediments than in the Gulf of Mexico and Atlantic coasts in general. There was a gradient from high to low concentrations leading from the Golden Gate area to the outlying shelf stations (Fig. 10). Away from the Golden Gate, Cr concentrations observed in this study are comparable with other data sets in this region from shallower waters (EMAP, 1999).

PAH concentrations ranged from 13 to 614 ug/kg (Table 5). These concentrations were relatively low, compared to typical estuarine concentrations found in nearby San Francisco Bay, for example. Accumulation of PAHs was evident in finer grained sediments (Fig. 11). Concentrations of PAHs were also elevated in the vicinity of the San Francisco POTW outfall (SWOO), relative to other locations on the shelf. PCB

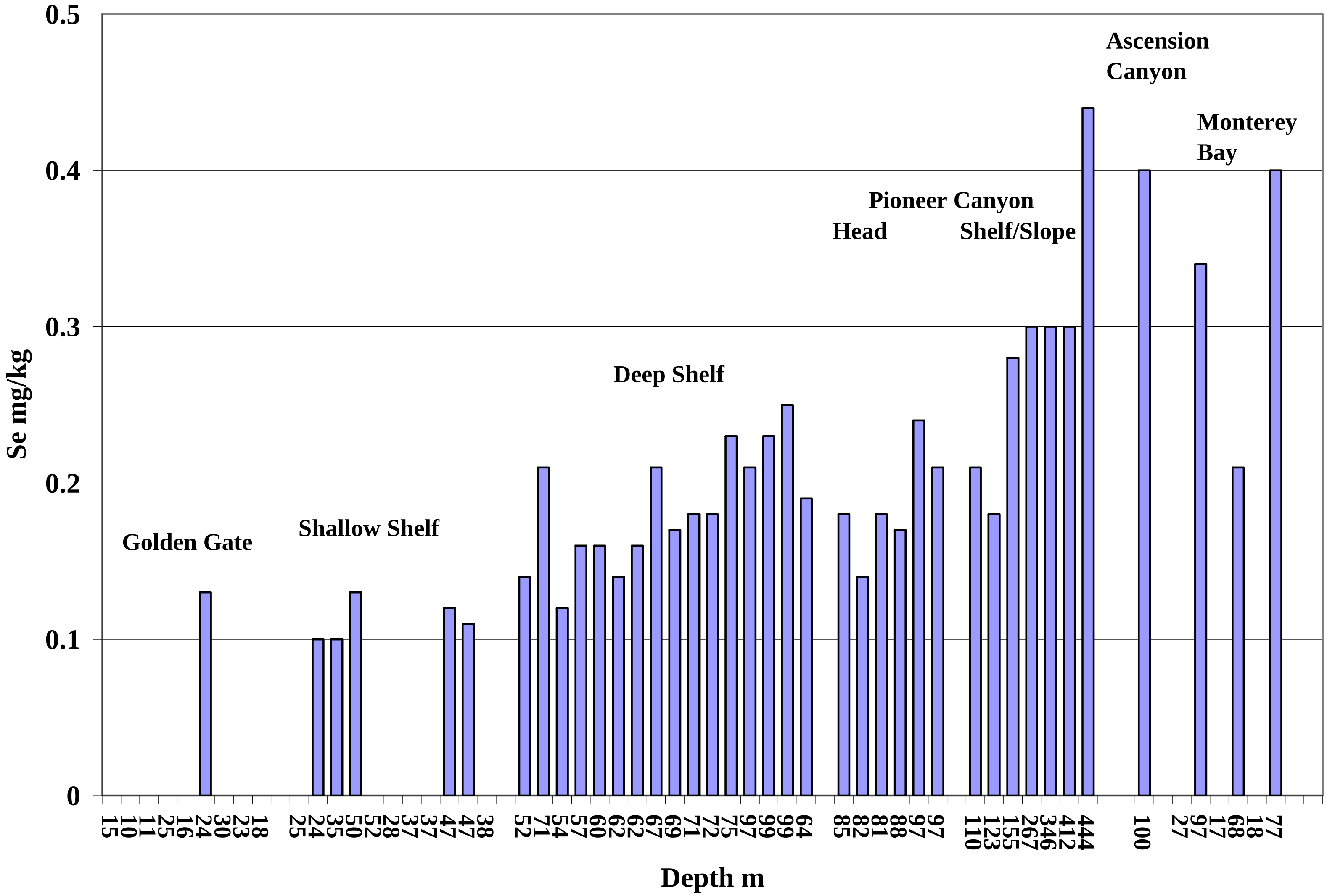


Figure 8. Selenium concentrations in sediments on the continental shelf and the heads of selected canyons off central California in 2002.

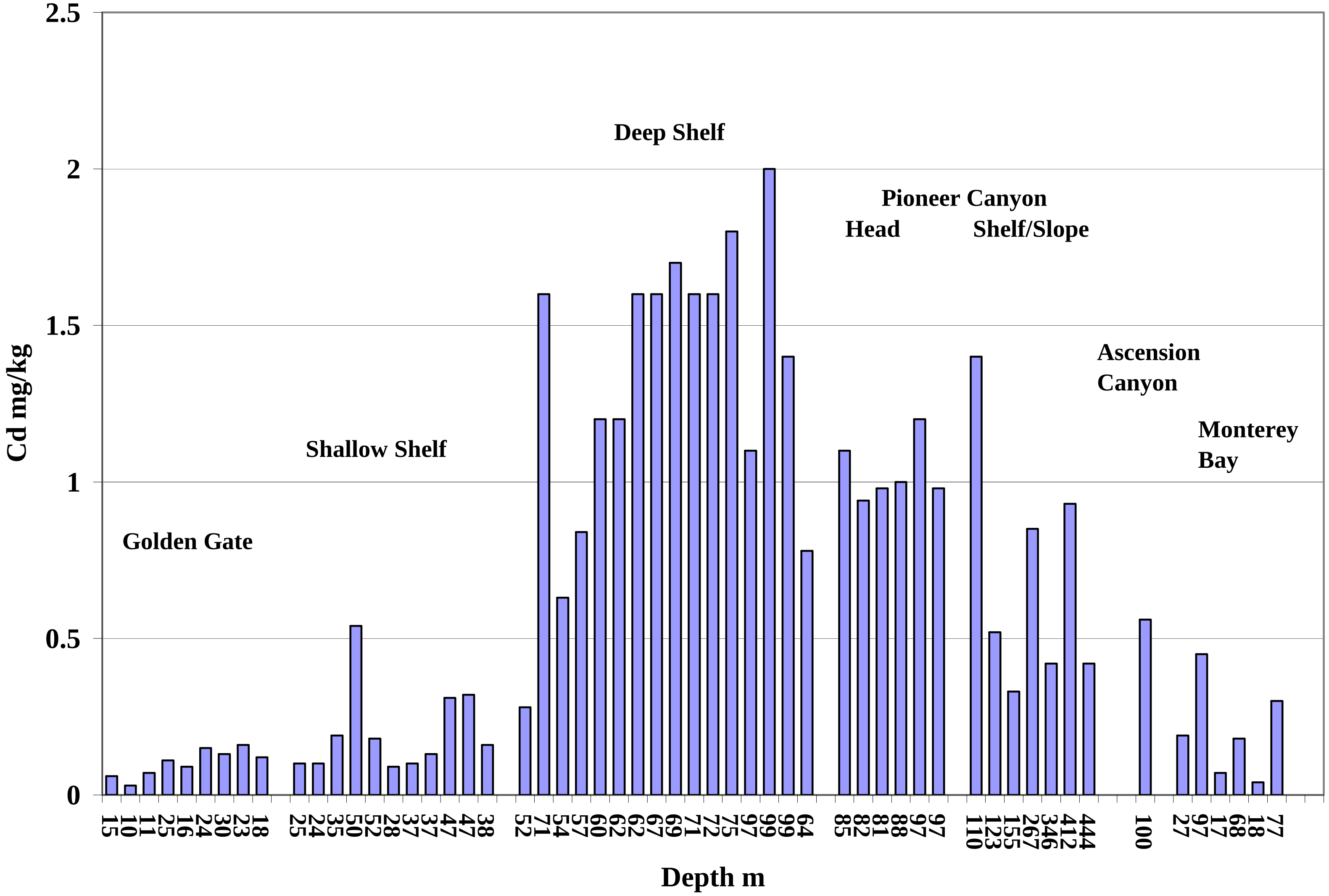


Figure 9. Cadmium concentrations in sediments on the continental shelf and the heads of selected canyons off central California in 2002.

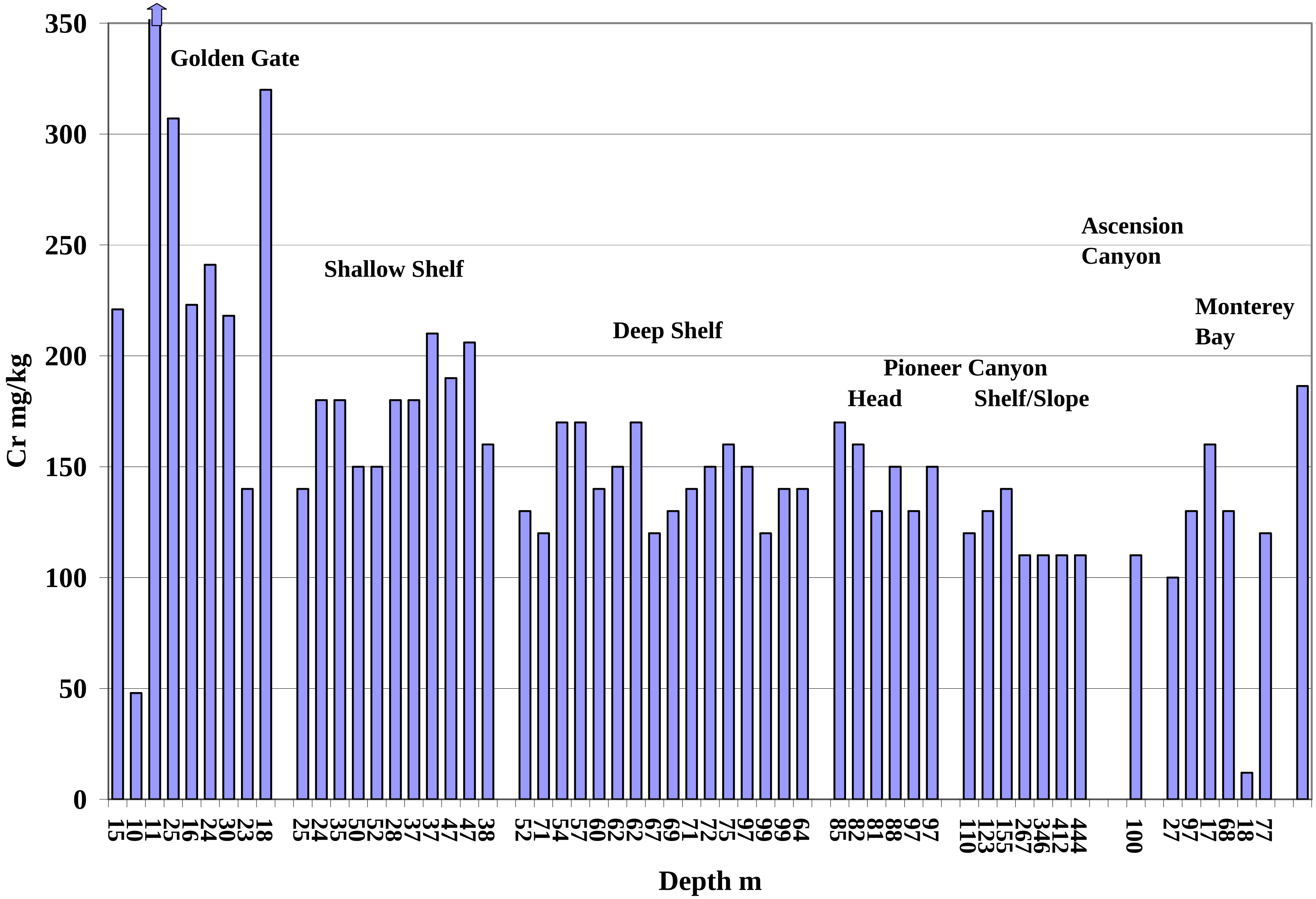


Figure 10. Chromium concentrations in sediments on the continental shelf and the heads of selected canyons off central California in 2002.

Table 4. Chemicals and chemical groups for which ERLs and ERMs have been derived (organics ppb, metals ppm, dry weight).

	ERL	ERM
Total DDT	1.58	46.1
pp'-DDE	2.2	27
Total PCBs	22.7	180
Total PAHs	4022	44792
High weight PAHs (≥ 4 rings)	1700	9600
Low weight PAHs (≤ 3 rings)	552	3160
Acenaphthene	16	500
Acenaphthylene	44	640
Anthracene	85.3	1100
Flourene	19	540
2-Methyl Naphthalene	70	670
Naphthalene	160	2100
Phenanthrene	240	1500
Benzo-a-anthracene	261	1600
Benzo-a-pyrene	430	1600
Chrysene	384	2800
Dibenzo(a,h)anthracene	63.4	260
Fluoranthene	600	5100
Pyrene	665	2600
As	8.2	70
Cd	1.2	9.6
Cr	81	370
Cu	34	270
Pb	46.7	218
Hg	0.15	0.71
Ni	20.9	51.6
Ag	1.0	3.7
Zn	150	410

Table 5. Descriptive statistics of organic contaminant concentrations found in sediments off the central California coast from depths between 80 and 1200 m.

	Low Molecular Weight PAHs	High Molecular Weight PAHs	Total PAHs	Total PCBs	Total DDTs	Chlorpyrifos	Cyclodienes	Total HCHs	Total Chlorinated Benzenes	Total Endosulfan	Mirex
Min	8.1	4.4	13.2	0.13	0.15	0.00	0.00	0.00	0.01	0.00	0.00
Max	198.6	448.6	614.3	2.60	16.72	0.34	1.61	0.80	1.18	1.86	0.12
Ave	67.8	121.9	189.7	1.01	3.83	0.03	0.27	0.08	0.12	0.09	0.02
Med	51.2	91.2	144.4	0.81	2.20	0.02	0.20	0.06	0.05	0.04	0.00
Std Dev	46.2	86.4	129.5	0.56	3.99	0.05	0.23	0.10	0.19	0.19	0.03

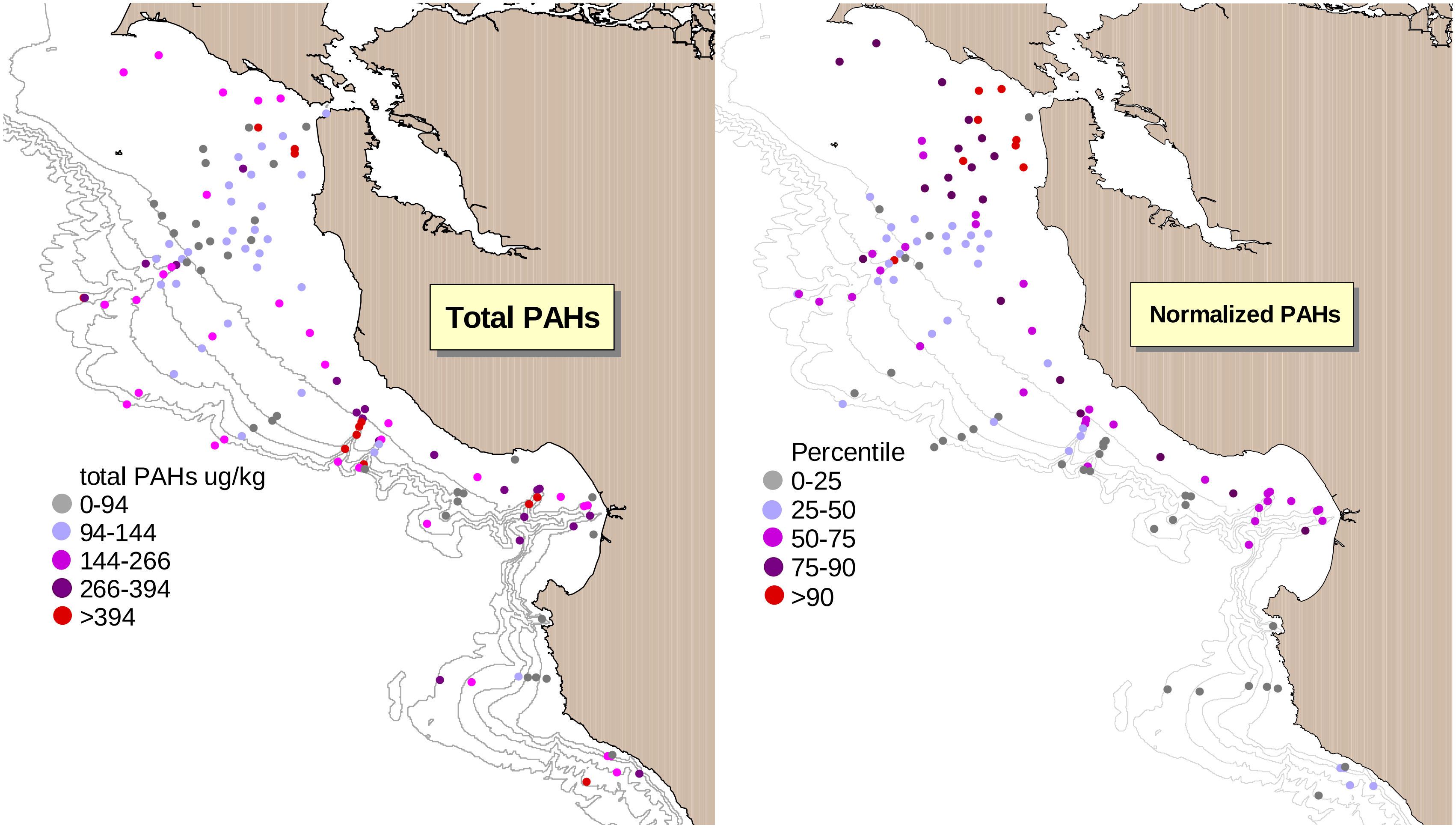


Figure 11. Total measured PAH concentrations and concentration normalized for %TOC in sediments off central California. Color scale represents concentration range (left) and percentile rank (right).

concentrations were relatively low throughout the study area (Fig. 12, Table 5). The spatial distribution of PCBs was very similar to the PAHs. Concentrations of both groups of compounds were well below their respective ERLs. The Duncan LSD groupings demonstrate that the canyons south of Half Moon Bay have significantly higher concentrations of PAHs and PCBs than all other locations (Table 6). The shelf stations north of Half Moon Bay have the lowest concentrations. The concentrations of DDTs (DDT and metabolites DDE and DDD) are elevated above the ERL in several locations (Fig. 13). The highest concentrations of DDT are concentrated in Monterey Bay, Ascension Canyon, and the continental shelf (but not the slope) in between them. Low level accumulation in other areas only occurs at depth.

Other persistent pesticides were also detected throughout the region. However, all the concentrations of these pesticides were very low in the sediments (Table 5). Cyclodienes (e.g. chlordanes, dieldrin, heptachlor, nonachlors, etc.) accumulated to the highest concentrations in the canyons and the shelf in the southern half of the study area (Fig. 14), but were also widely distributed in the Gulf of the Farallones. These are highly toxic compounds to most animal groups and are banned or severely restricted in most countries. Chlorinated benzenes were used as pesticides and in the manufacture of a variety of other pesticides and industrial compounds. The distribution of these compounds is similar to that of the cyclodienes (Fig. 15). Chlorpyrifos is a highly toxic insecticide which is now severely restricted, but was widely used as a termiticide on building foundations and an insecticide on a variety of food and fiber crops. Chlorpyrifos is widely distributed along the entire study area (Fig. 16). Hexa-chloro-hexane (HCH, sometimes wrongly called hexa-chloro benzene) is also widely distributed throughout the study area (Fig. 17). The gamma isomer of HCH is more commonly known as Lindane, which is highly toxic to insects, but less so to crustaceans. Lindane is no longer used on crops, but is still used in restricted products such as shampoos used to eradicate head lice. Endosulfans were above detection limits in only roughly half the stations and were never above 1 ppb.

Lethal concentrations of these compounds to marine organisms range from less than 1 to several hundred ppb, depending on test species and exposure conditions.

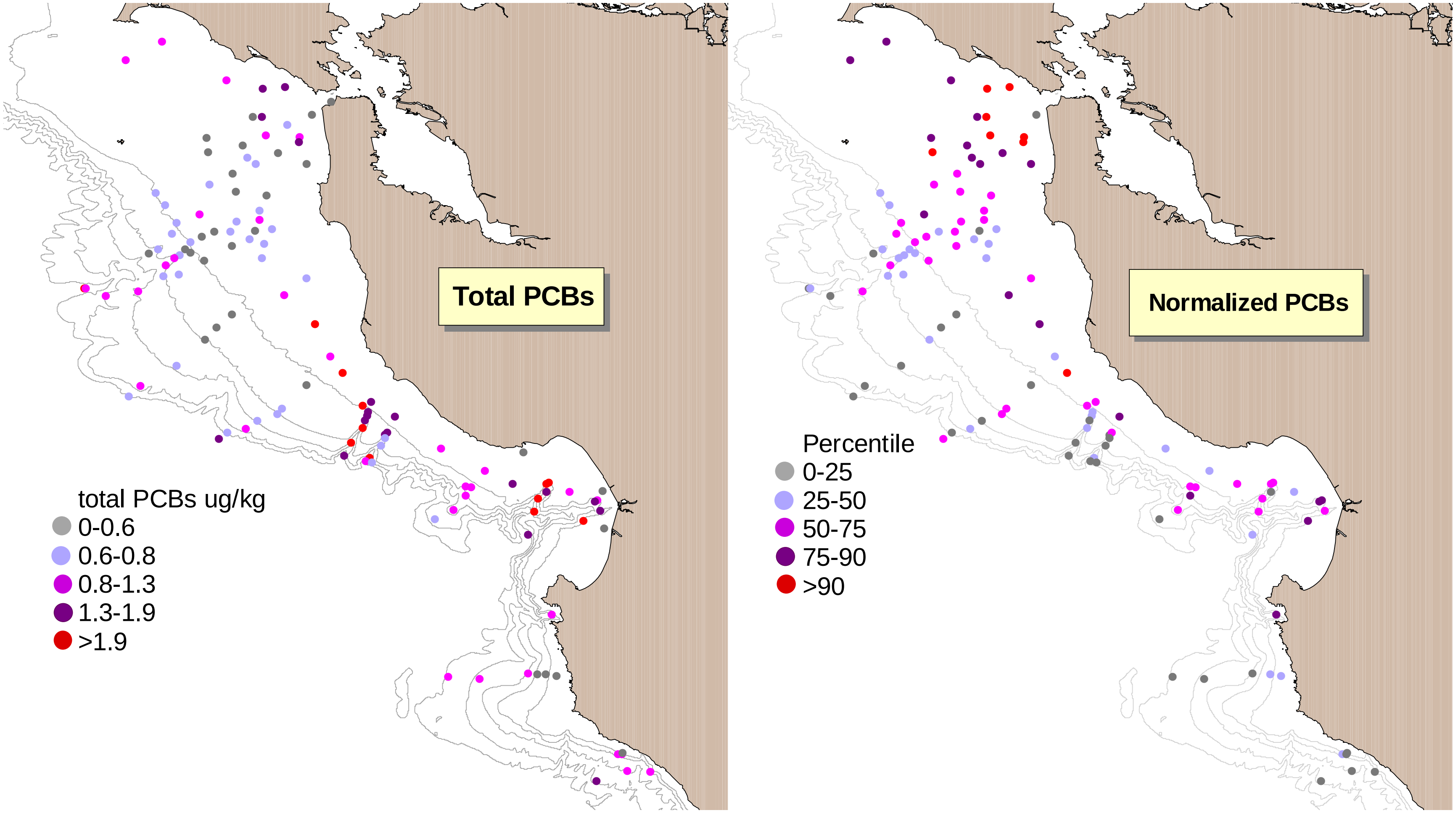


Figure 12. Total measured PCB concentrations and concentration normalized for % TOC in sediments off central California. Color scale represents concentration range (left) and percentile rank (right).

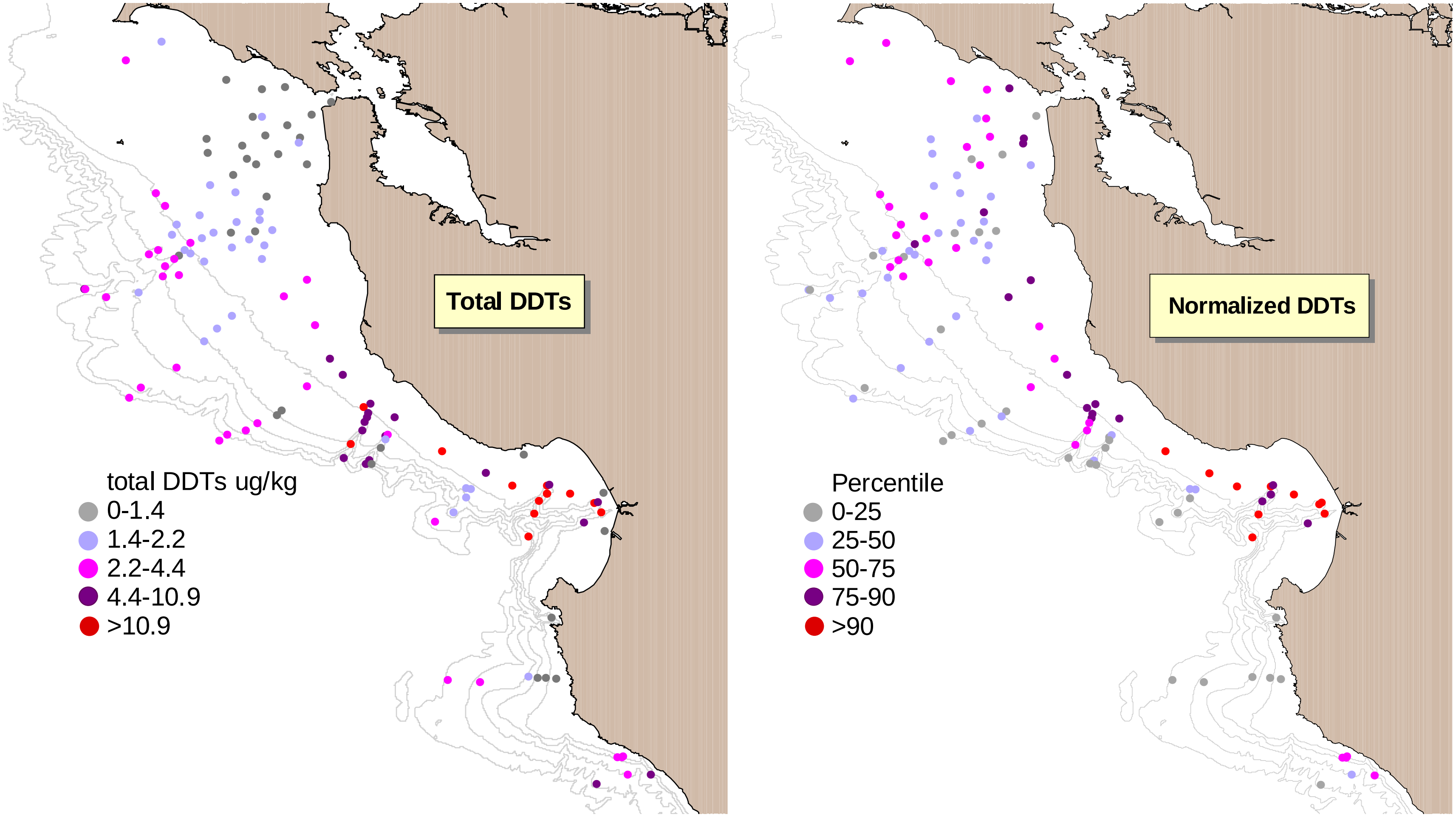


Figure 13. Total DDTs (DDT, and metabolites DDD and DDE) concentrations, and concentrations normalized for % TOC in sediments off central California. Color scale represents concentration range (left) and percentile rank (right).

Table 6. Duncan groupings for contaminant concentrations (left) and TOC normalized concentrations (right) in five habitat settings on the central California coast.

	Mean	Zone	Group			Mean	Zone	Group	
PAHs	ug/kg					ug/gm OC			
	329.41	South Canyons	A			600.10	North Shelf	A	
	230.12	Pioneer Canyon		B		346.60	Pioneer Canyon	A	B
	191.29	South Shelf		B	C	289.70	South Shelf	A	B
	162.50	South Slopes		B	C	218.40	South Slopes		B
	143.07	North Shelf			C	215.80	South Canyons		B
PCBs									
	1.57	South Canyons	A			2.84	North Shelf	A	
	1.19	South Shelf		B		2.08	South Shelf	A	B
	0.95	Pioneer Canyon		B	C	1.53	South Slopes		B
	0.91	South Slopes		B	C	1.36	Pioneer Canyon		B
	0.73	North Shelf			C	1.06	South Canyons		B
DDTs									
	7.44	South Canyons	A			8.52	South Shelf	A	
	5.86	South Shelf	A			4.81	South Canyons		B
	2.88	Pioneer Canyon		B		4.72	North Shelf		B
	2.82	South Slopes		B		4.01	South Slopes		B
	1.45	North Shelf		B		3.98	Pioneer Canyon		B
Cyclodienes									
	0.58	South Canyons	A			0.13	South Shelf	A	
	0.31	South Shelf		B		0.09	North Shelf	A	B
	0.21	South Slopes		B	C	0.04	South Canyons	A	B
	0.20	North Shelf		B	C	0.03	Pioneer Canyon		B
	0.16	Pioneer Canyon			C	0.00	South Slopes		B
Chlorinated Benzenes									
	0.25	South Canyons	A			0.27	South Shelf	A	
	0.17	South Shelf	A	B		0.20	South Slopes	A	
	0.11	South Slopes		B	C	0.17	North Shelf	A	
	0.07	Pioneer Canyon		B	C	0.16	South Canyons	A	
	0.05	North Shelf			C	0.11	Pioneer Canyon	A	
Chlorpyrifos									
	0.06	South Canyons	A			0.72	North Shelf	A	
	0.05	South Shelf	A	B		0.60	South Shelf	A	B
	0.03	North Shelf		B	C	0.39	South Canyons	A	B
	0.02	Pioneer Canyon			C	0.26	South Slopes		B
	0.00	South Slopes			C	0.24	Pioneer Canyon		B
HCHs									
	0.15	South Canyons	A			0.25	North Shelf	A	
	0.09	South Shelf		B		0.14	South Shelf	A	B
	0.07	North Shelf		B		0.10	South Canyons	A	B
	0.04	Pioneer Canyon		B		0.07	Pioneer Canyon	A	B
	0.04	South Slopes		B		0.04	South Slopes		B

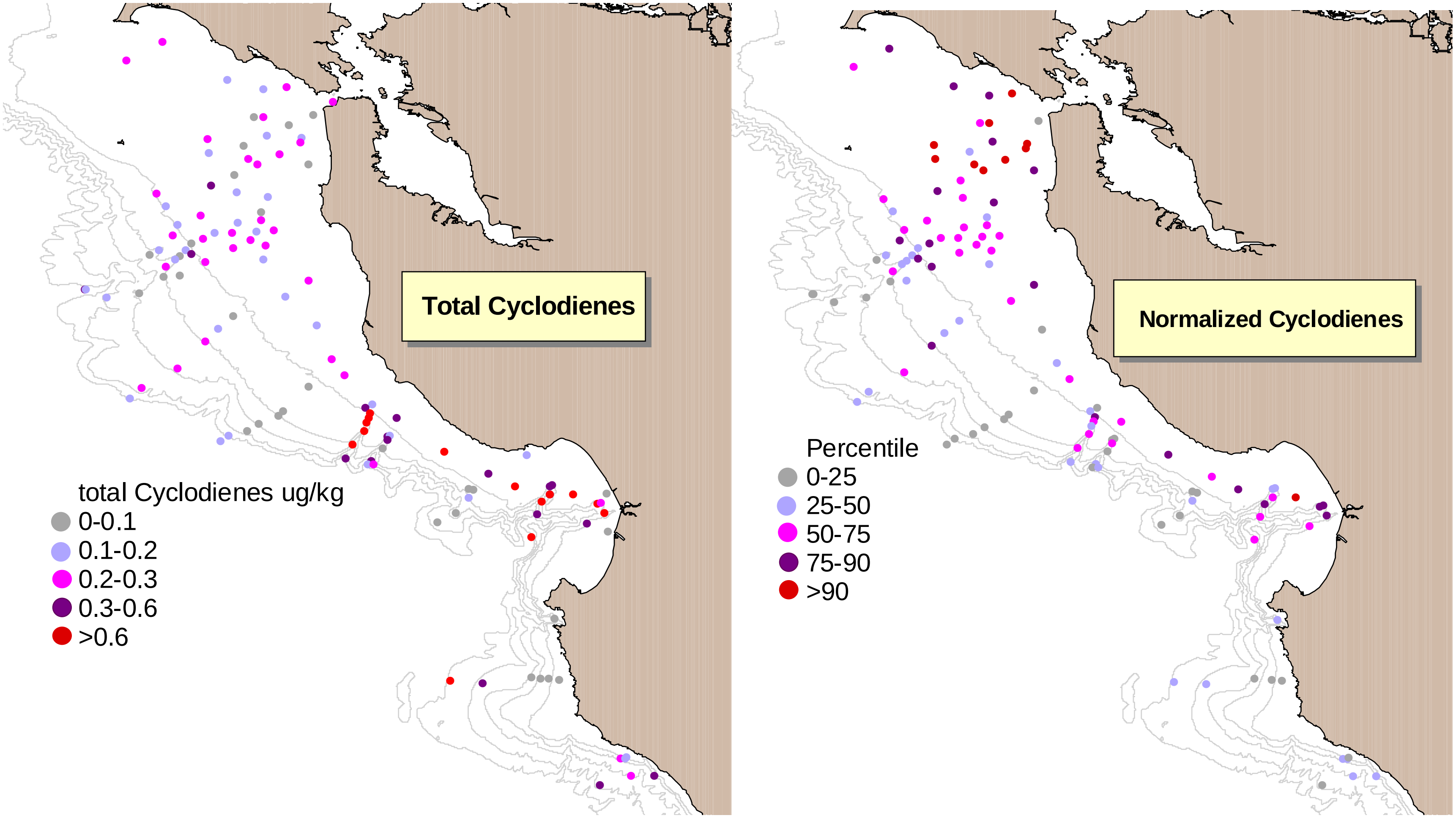


Figure 14. Total cyclodiene concentrations (chlordanes, dieldrins, nonachlors, heptachlors) and concentrations normalized for % TOC in sediments off central California. Color scale represents concentration range (left) and percentile rank (right).

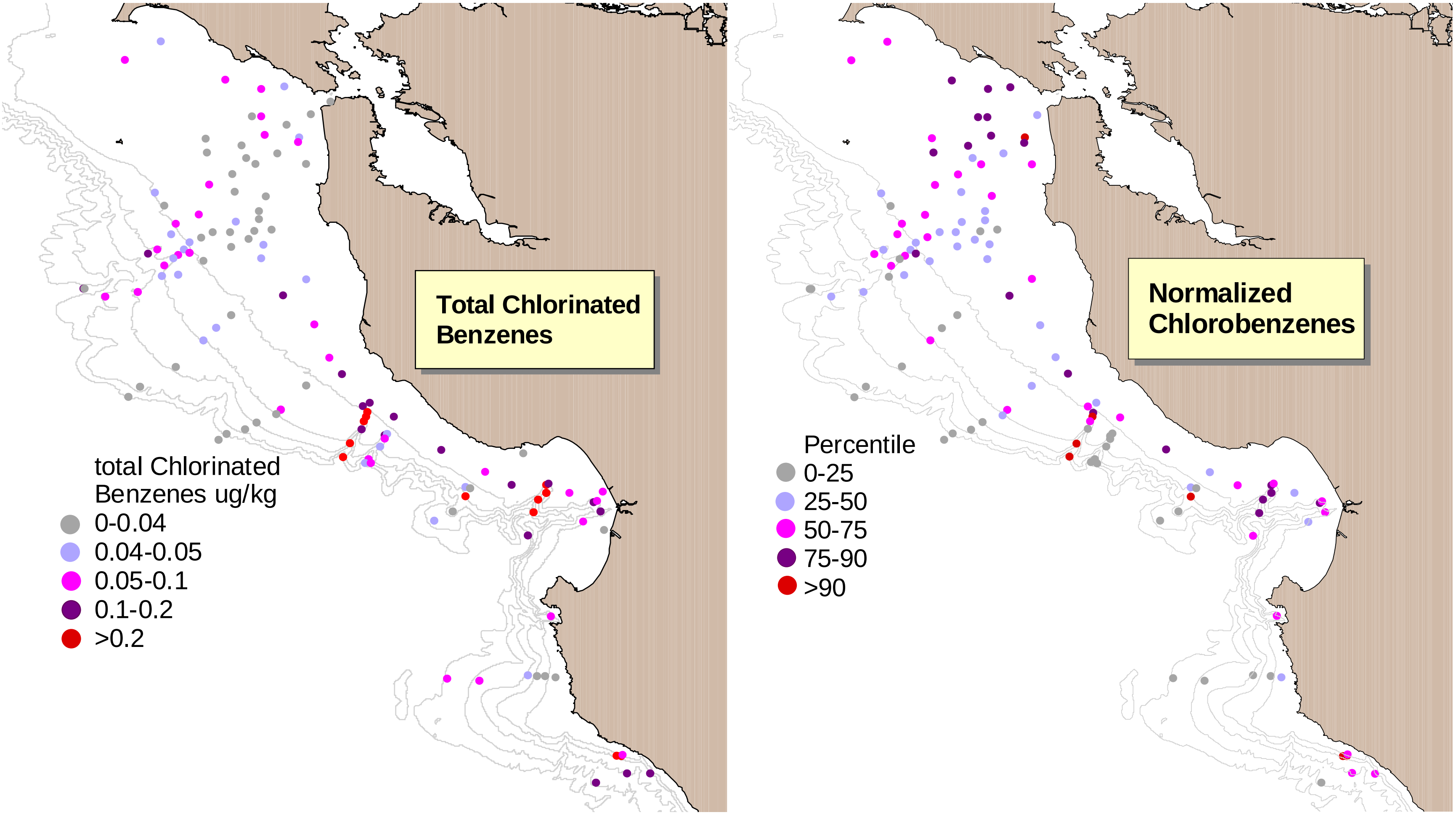


Figure 15. Total chlorinated benzene concentrations and concentrations normalized for % TOC in sediments off central California. Color scale represents concentration range (left) and percentile rank (right).

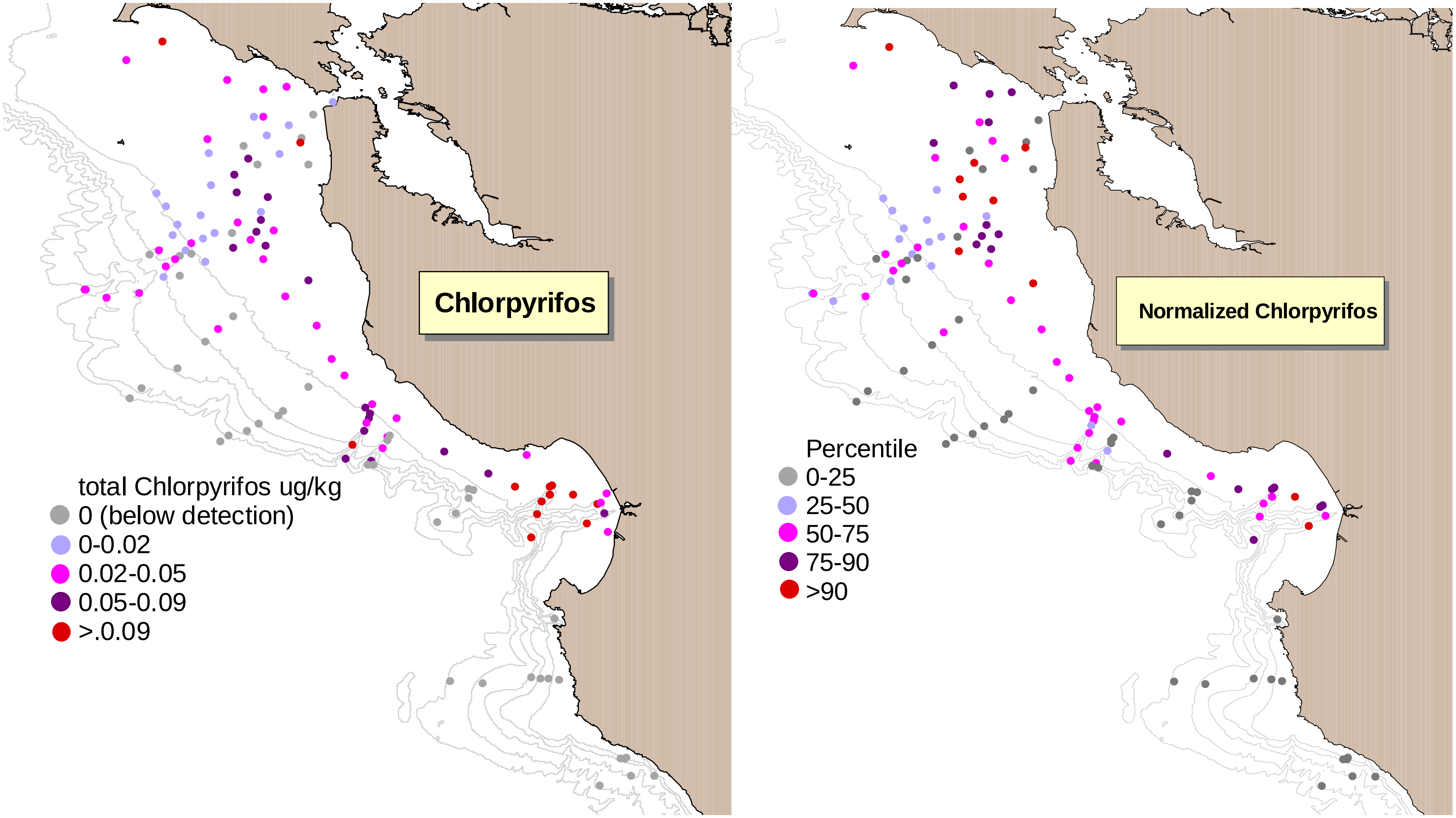


Figure 16. Total chlorpyrifos concentrations and concentrations normalized for % TOC in sediments off central California. Color scale represents concentration range (left) and percentile rank (right).

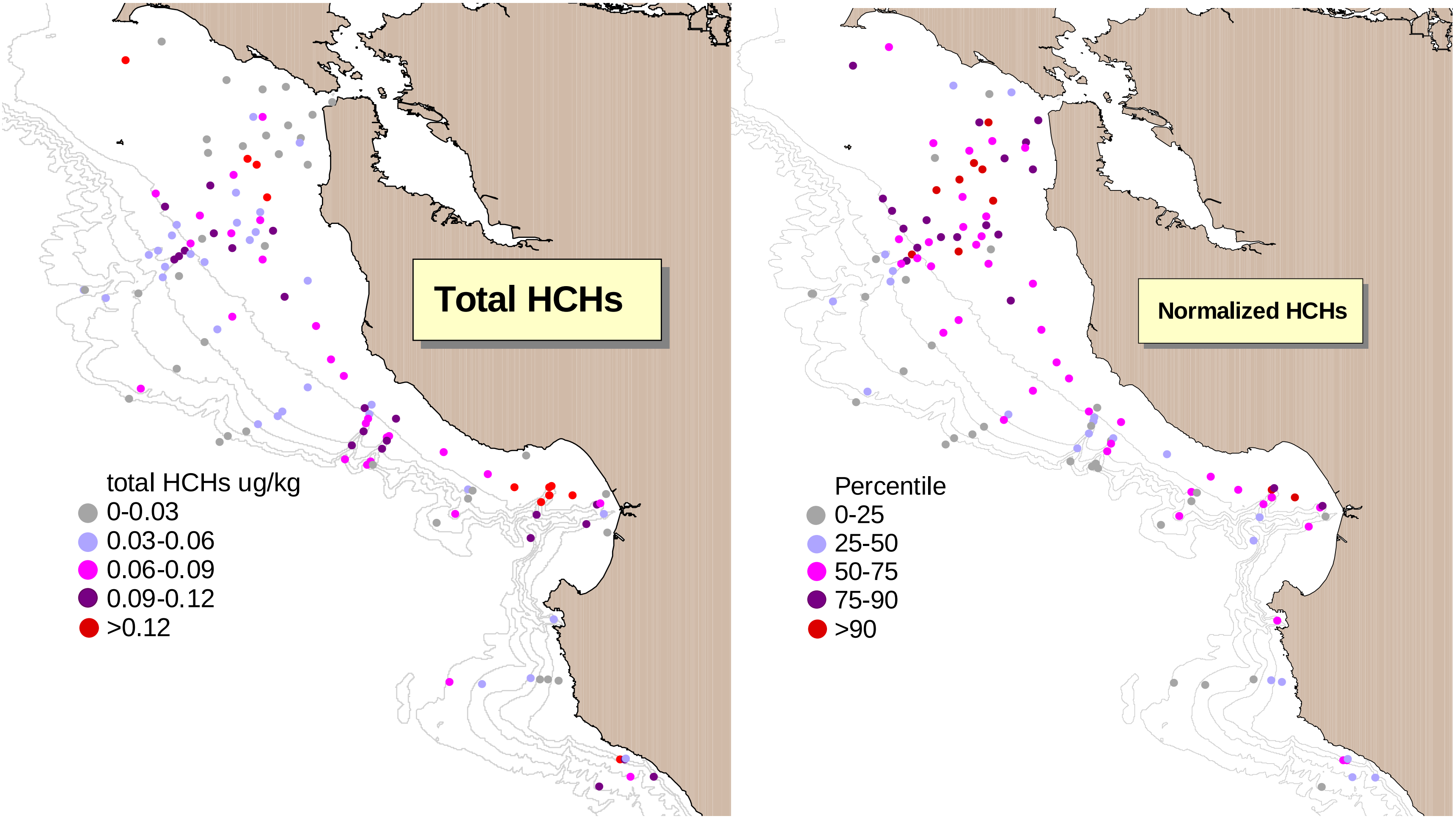


Figure 17. Total HCHs (Hexachloro-cyclo-hexane) concentrations and concentrations normalized for % TOC in sediments off central California. Color scale represents concentration range (left) and percentile rank (right).

However, these bioassay data are typically from tests conducted in aquatic solutions. Toxicity data from sediment tests for these compounds are virtually non-existent in the published literature. Toxicity in sediment is presumed to occur at much higher concentrations than in water-only test systems due to equilibrium partitioning in complex substrates (Landrum et al., 1987; DeToro and DeRosa, 1996).

Relative concentrations of the organic contaminants following organic carbon normalization are illustrated on the right panel in Figures 11-17. (Stations with less than 0.1 % TOC were excluded to eliminate artificially extreme values.) Normalized data show where concentrations are elevated after adjusting for the affinity of the sediment for organic compounds. For the PAH and PCB data, this procedure illustrates that the sediments in the Gulf of the Farallones appear to receive organic contaminants from San Francisco Bay through tidal exchange through the Golden Gate to a greater extent than from longshore drift up the coast. The other pesticides tend to exhibit a pattern similar to PAHs and PCBs. Normalized concentrations in Monterey Canyon sites and the intervening slope and canyons are lower than in the vicinity of San Francisco. The shelf sites north and south of Half Moon Bay are in the same Duncan grouping for both PAHs and PCBs (Table 6). In contrast, DDT concentrations are still highest in the Monterey Bay region after TOC normalization.

The three shallow stations in Monterey Bay were sandy sites with TOC less than 0.1%. The deeper sites were muddier with higher TOC levels. The Ascension Canyon sites also had fine-grained sediment with higher TOC. Concentrations of DDT were elevated at all these stations when normalized for TOC (Fig. 13). Stephenson et al. (1997) found a similar relationship in sediments from Monterey Bay. DDT concentrations demonstrate a nonlinear relationship with TOC, indicating that areas in the vicinity of Monterey Bay and down current from there are receiving higher inputs of DDT than other areas (Figure 18), independent of sediment affinity for organic compounds.

Away from Monterey Bay, the relative concentrations of DDT are more pronounced on the shelf in the immediate area around the Golden Gate than in the slope transects. The north and south shelf stations are always in the same Duncan grouping. Sites in Pioneer Canyon and the slope sites are always separated into the lower group. Normalized trends indicate source input from both San Francisco Bay and the

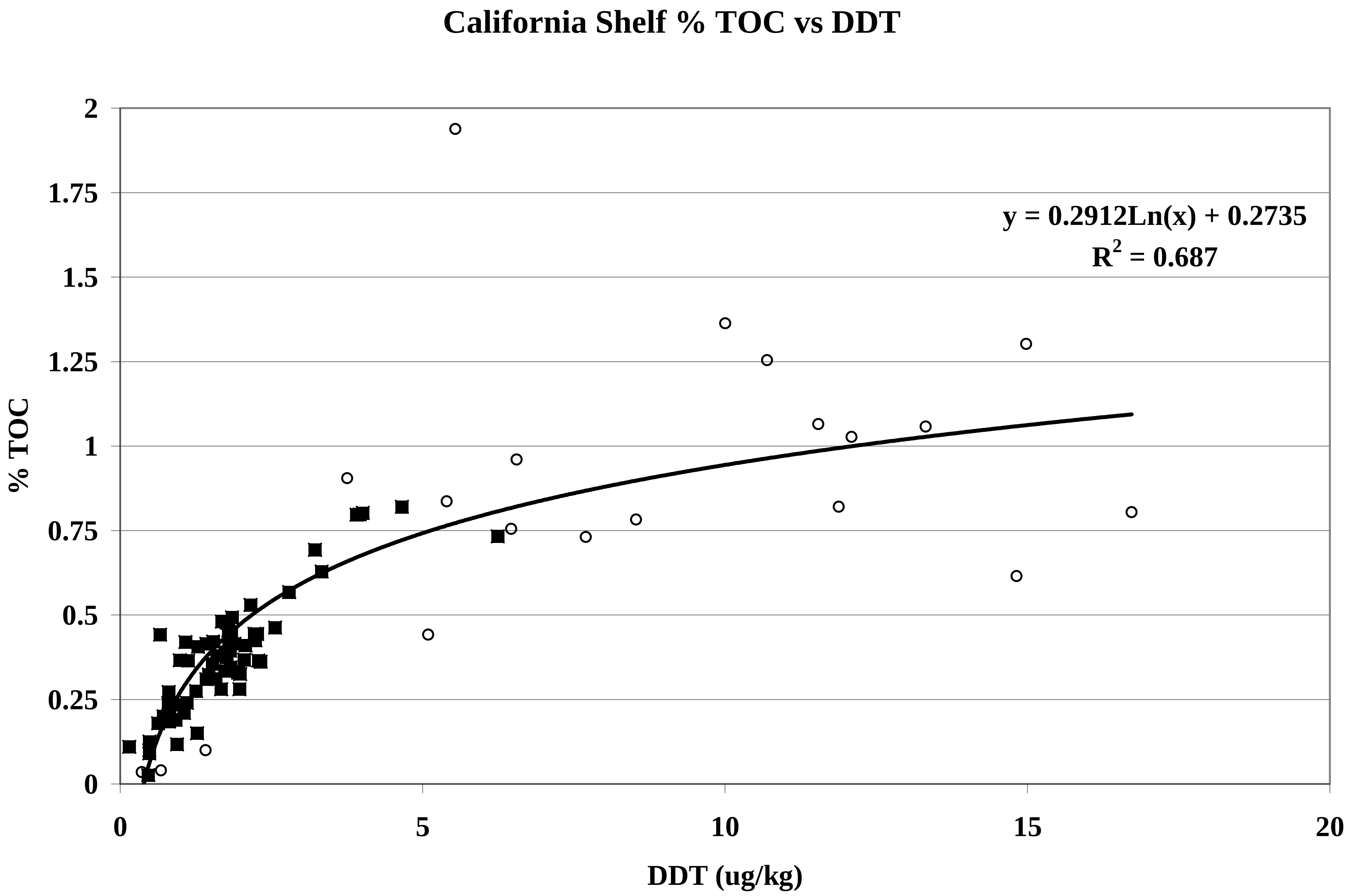


Figure 18. Regression of DDT and sediment % TOC showing Ascension, Ano Nuevo, and Monterey Canyon sites (O) and all other sites in Pioneer and Carmel Canyons and the shelf and slope transects (■).

Monterey Bay watershed for all constituents except DDT.

Concentrations of PBDE and PBB congeners were below detection limits at most stations, and at relatively low concentrations where they were found. PBDE 47 and 99 were found at all stations. Trace levels of PBDE 100 was found at 5 out of 6 stations (Table 7). Stations 115 and 114 close to the SWOO were only slightly higher than those further away.

Pacific white sided dolphins are constant companions.

Table 7. Measured concentrations of PBDEs and PBBs in sediment at selected stations in the Gulf of the Farallones. Inset shows sample site locations.

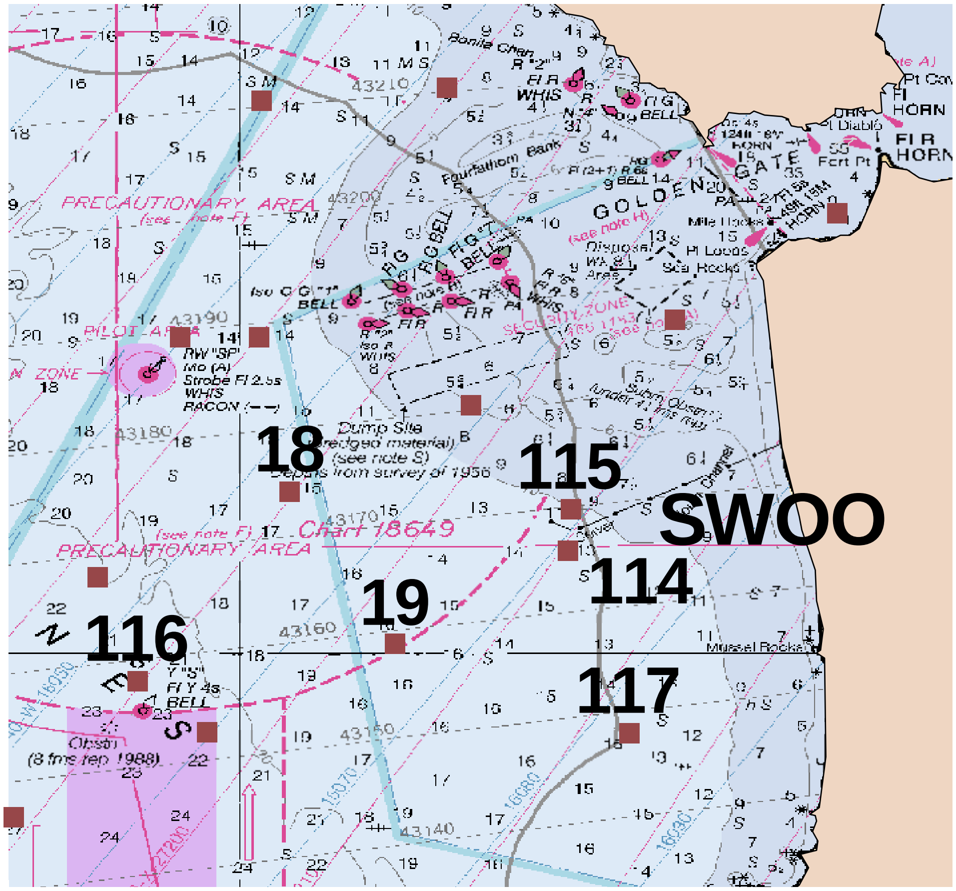
Station	SF114	SF115	MB18	SF19	SF117	MB116
Polybrominated Diphenyl Ethers	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
BDE 1 (2-MonoBDE)	ND	ND	ND	ND	ND	ND
BDE 2 (3-MonoBDE)	ND	ND	ND	ND	ND	ND
BDE 3 (4-MonoBDE)	ND	ND	ND	ND	ND	ND
BDE 7 (2,4-DiBDE)	ND	ND	ND	ND	ND	ND
BDE 8/11 (2,4'-DiBDE/3,3'-DiBDE)	ND	ND	ND	ND	ND	ND
BDE 10 (2,6-DiBDE)	ND	ND	ND	ND	ND	ND
BDE 12 (3,4-DiBDE)	ND	ND	ND	ND	ND	ND
BDE 13 (3,4'-DiBDE)	ND	ND	ND	ND	ND	ND
BDE 15 (4,4'-DiBDE)	ND	ND	ND	ND	ND	ND
BDE 17 (2,2',4-TriBDE)	ND	ND	ND	ND	ND	ND
BDE 25 (2,3',4-TriBDE)	ND	ND	ND	ND	ND	ND
BDE 28 (2,4,4'-TriBDE)	ND	ND	ND	ND	ND	ND
BDE 30 (2,4,6-TriBDE)	ND	ND	ND	ND	ND	ND
BDE 32 (2,4',6-TriBDE)	ND	ND	ND	ND	ND	ND
BDE 33 (2',3,4-TriBDE)	ND	ND	ND	ND	ND	ND
BDE 35 (3,3',4-TriBDE)	ND	ND	ND	0.011*	ND	ND
BDE 37 (3,4,4'-TriBDE)	ND	ND	ND	ND	ND	ND
BDE 47 (2,2',4,4'-TetraBDE)	0.20	0.19	0.12	0.11	0.13	0.14
BDE 49 (2,2',4,5'-TetraBDE)	ND	ND	ND	ND	ND	ND
BDE 66 (2,3',4,4'-TetraBDE)	ND	ND	ND	ND	ND	ND
BDE 71 (2,3',4',6-TetraBDE)	ND	ND	ND	ND	ND	ND
BDE 75 (2,4,4',6-TetraBDE)	ND	ND	ND	ND	ND	ND
BDE 77 (3,3',4,4'-TetraBDE)	ND	ND	ND	ND	ND	ND
BDE 85 (2,2',3,4,4'-PentaBDE)	ND	ND	ND	ND	ND	ND
BDE 99 (2,2',4,4',5-PentaBDE)	0.17	0.18	0.14	0.13	0.13	0.14
BDE 100 (2,2',4,4',6-PentaBDE)	0.064*	ND	0.03*	0.031*	0.039*	0.03*
BDE 116 (2,3,4,5,6-PentaBDE)	0.023*	ND	ND	ND	ND	ND
BDE 118 (2,3',4,4',5-PentaBDE)	ND	ND	ND	0.042*	0.01*	ND
BDE 119 (2,3',4,4',6-PentaBDE)	0.013*	ND	ND	ND	0.011*	ND
BDE 126 (3,3',4,4',5-PentaBDE)	ND	ND	ND	ND	ND	ND
BDE 138 (2,2',3,4,4',5'-HexaBDE)	ND	ND	ND	ND	ND	ND
BDE 153 (2,2',4,4',5,5'-HexaBDE)	ND	ND	0.04*	ND	ND	ND
BDE 154 (2,2',4,4',5,6'-HexaBDE)	ND	ND	ND	ND	ND	ND
BDE 155 (2,2',4,4',6,6'-HexaBDE)	ND	ND	ND	ND	ND	ND
BDE 166 (2,3,4,4',5,6-HexaBDE)	ND	ND	ND	ND	ND	ND
BDE 181 (2,2',3,4,4',5,6-HeptaBDE)	ND	ND	ND	ND	ND	ND
BDE 183 (2,2',3,4,4',5',6-HeptaBDE)	ND	ND	ND	ND	ND	ND
BDE 190 (2,3,3',4,4',5,6-HeptaBDE)	ND	ND	ND	ND	ND	ND

* below method detection limit

Table 7 (cont.). Measured concentrations of PBDEs and PBBs in sediment at selected stations in the Gulf of the Farallones. Inset shows sample site locations.

Station	SF114	SF115	MB18	SF19	SF117	MB116
Polybrominated Biphenyls	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
PBB 1 (2-MonoBB)	ND	ND	ND	ND	ND	ND
PBB 2 (3-MonoBB)	ND	ND	ND	0.04*	0.03*	ND
PBB 3 (4-MonoBB)	ND	ND	ND	0.07	0.08	0.09
PBB 4 (2,2'-DiBB)	ND	ND	ND	ND	ND	ND
PBB 10 (2,6-DiBB)	ND	ND	ND	ND	ND	ND
PBB 7 (2,4-DiBB)	ND	ND	ND	ND	ND	ND
PBB 9 (2,5-DiBB)	ND	ND	ND	ND	ND	ND
PBB 15 (4,4'-DiBB)	ND	ND	ND	ND	ND	ND
PBB 30 (2,4,6-TriBB)	ND	ND	ND	ND	ND	ND
PBB 18 (2,2',5-TriBB)	ND	ND	ND	ND	ND	ND
PBB 26 (2,3,',5-TriBB)	ND	ND	ND	ND	ND	ND
PBB 31 (2,4',5-TriBB)	ND	ND	ND	ND	ND	ND
PBB 53 (2,2',5,6'-TetraBB)	ND	ND	ND	ND	0.03*	ND
PBB 52 (2,2',5,5'-TetraBB)	ND	ND	ND	ND	ND	ND
PBB 49 (2,2',4,5'-TetraBB)	ND	ND	ND	ND	ND	ND
PBB 103 (2,2',4,5',6-PentaBB)	ND	ND	ND	ND	ND	ND
PBB 80 (3,3',5,5'-TetraBB)	ND	ND	ND	ND	ND	0.04*
PBB 77 (3,3',4,4'-TetraBB)	ND	ND	ND	ND	ND	ND
PBB 155 (2,2',4,4',6,6'-HexaBB)	ND	ND	ND	ND	ND	ND

* below method detection limit



DISCUSSION

Data for the NS&T sediment chemical contaminant profile and physical analyses indicate a very inhomogeneous distribution of trace chemicals on the continental shelf, the slope, and in the canyons between San Francisco and Pt Sur. Contaminant concentrations in Carmel Canyon and on the shelf south of Monterey Bay did not appear to be elevated above background levels. North of Carmel, concentrations of organic contaminants on the shelf appear to be derived from the San Francisco Bay and Monterey Bay watersheds. Contaminants accumulate in fine-grained sediments which do not necessarily correspond to source locations. The continental shelf north of Monterey Bay contains the so-called mid-shelf mud belt, where fine-grained sediments accumulate. Organic contaminants are concentrated in this region. Canyons that accumulate fine-grained sediments (Ascension, Soquel, and Monterey) accumulate higher concentrations than canyons with coarser sediments. The continental slope accumulates higher concentrations of organic contaminants at depth, where fine-grained material is deposited in relatively static habitats. While a variety of organic contaminants and pesticides are delivered to the shelf in the Gulf of the Farallones and Monterey Bay, most of the DDT appears to be derived from the Monterey Bay watershed (Fig. 13).

Pioneer Canyon and the depositional zones of the shelf in the vicinity of San Francisco do not appear to accumulate DDT. The station off Half Moon Bay was included as a depositional site (based on known grain size distributions) but away from the immediate influence of releases from the Golden Gate area. San Francisco Bay contains sediments that have a large reservoir of contaminants, including DDT (Figure 19 - note Y axis log scale) and other pesticides, PCBs, PAHs, and a suite of trace elements (Marine Chemistry, 1999). Many locations in San Francisco Bay, especially in some of the smaller tributaries and harbors, have concentrations far greater than those seen in Monterey Bay (Perkowski and Beckvar, 1997; Davis, 2004; NOAA, unpub.). San Francisco Bay exports contaminants to the continental shelf via tidal exchange through the Golden Gate. Export rates are not well studied and estimates of the releases are highly variable, even for those few that are the focus of current concern (Davis, 2004). Municipal and industrial releases of pollutants also contribute to the contaminant load on

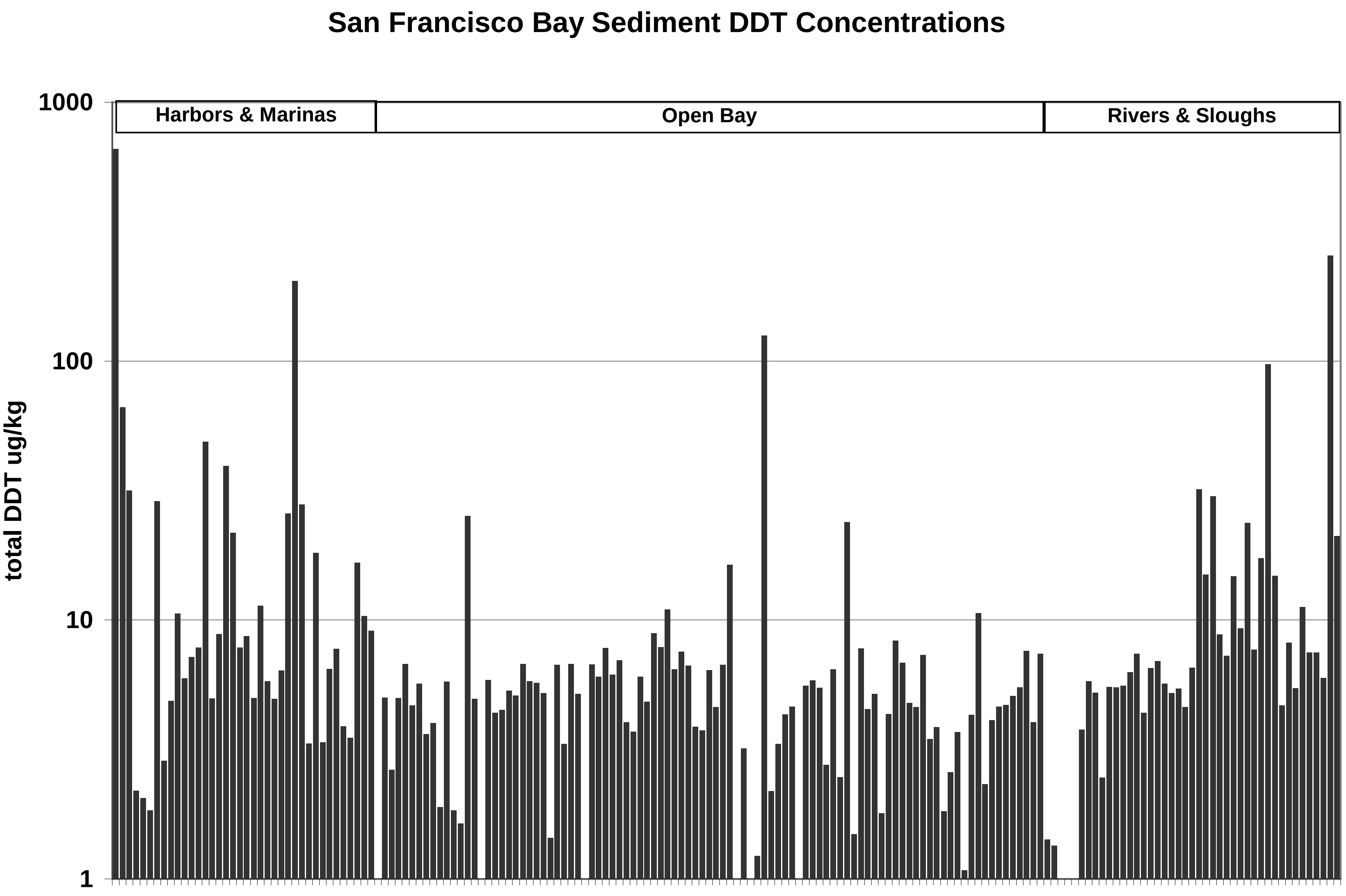


Figure 19. Concentration of total DDT in sediments in San Francisco Bay (unpublished NS&T data).

the continental shelf in the Gulf of Farallones region. The question arises as to whether contaminants exiting the Bay become advected off the shelf by tidal and other currents, and/or are sediments in the Gulf of the Farallones an unsuitable collection area for persistent organic contaminants?

Forecasting persistent contaminant concentrations within the estuary and contaminant export to the coastal ocean is a major issue within the San Francisco Bay research community (Phillips, 1987; Risebrough, 1997; Davis et al., 2000; Davis, 2004; Leatherbarrow et al., 2005; Daviset al., in press) and has serious ramifications with respect to existing and proposed dredging operations within the system. Sediment budgets within the Bay suggest that it is becoming a net sediment exporting system due to anthropogenic changes in sediment delivery processes within the watershed (Geen and Luoma, 1999; Jafee et al., 1998; McKee et al., 2006). Data from Bodega Canyon samples collected in 2005 may shed light on the fate of contaminants emanating from San Francisco Bay.

There are other factors that may impact contaminant delivery to the continental shelf in this vicinity. There are three smaller POTW sewage outfalls off San Francisco and Half Moon Bay. Two are located in relatively shallow water (~10 m) and one currently discharges into an artificial wetland on shore. However, these are relatively small (2.3, 3.7 , and 7.5 million gallons per day [mgd], 2006 data) releases of secondary and tertiary treated domestic sewage without industrial input (RWQCB, 2007). In contrast, the SWOO discharge varies between 18-175mgd (depending on season) containing treated domestic sewage, industrial effluents and stormwater runoff (SFPUC, 2003).

There are two active dredge spoil disposal sites in the region. One is used for sidecasting of sand from the main ship channel leading into San Francisco Bay onto the ebb tidal shoal adjacent to it. This is reportedly clean sand that shoals in the channel, and is placed immediately to the south of the channel so as to keep it in the same overall littoral transport system. Fairly large volumes are moved in this way each year (500,000-750,000 cy) (EPA, 2007). Since it is moved from one place on the shelf to an adjacent place, there is no net transfer of contaminants to the system. The second site (San Francisco Deep Ocean Disposal Site, SF-DODS) is approximately 92 km offshore at a depth of 3,000 m, in a trough at the base of the continental slope (Fig. 1). Several million cubic yards of material from harbor areas in San Francisco Bay have been disposed of there. Dredge spoil from US Navy facilities and military munitions have also been dumped in the vicinity of this site. While it is much deeper and further offshore than the current study area, upwelling currents and lateral transport of fine-grained material is possible during disposal. However, material that is currently dumped there must pass screening toxicity and chemical analysis testing.

Although sampling intensity is lower in other areas, compared to continental shelf locations sampled by NS&T using the same field methods and analytical lab procedures, sediments on the continental shelf off California have generally higher concentrations of DDT than elsewhere (Fig. 20). Figures 20-23 compare contaminant concentrations in Massachusetts Bay, Stellwagen Bank (east of Massachusetts Bay), Cape Cod Bay, off the mouth of Delaware Bay, off the Virginia Capes (immediately south of Chesapeake Bay), and outside the mouth of Galveston Bay, Texas (Harmon et al., 2003; Hartwell et al., 2001, 2007; NOAA unpublished data). In California, elevated levels of DDT are obvious in Ascension, Año Nuevo, Soquel, and Monterey Canyons, and shelf sites in the mid-shelf mud belt south of Pioneer Canyon. In contrast, PAH concentrations are much higher in Massachusetts and Cape Cod Bays than off central California, or even Galveston (Fig 21). The central region of Massachusetts Bay features a depression where fine-grained sediments accumulate. These sediments retain contaminants from disposal operations and effluents from Boston into Massachusetts Bay. Stellwagen Bank is a remnant glacial moraine. It is shallow, sandy and exposed to North Atlantic winter storms. Sampling sites off Delaware Bay were located north and south of the mouth of the Bay. While large industrial and commercial port facilities are present in Delaware Bay, they are far from the mouth of the Bay, which has a wide unrestricted opening to the Atlantic. Sampling sites off the Virginia Capes and Galveston do have large industrial and port facilities in the vicinity of the shoreline. Concentrations of PCBs were also higher in the Massachusetts/Cape Cod Bays and off Galveston than off California (Fig 22). Cyclodiene pesticide concentrations (chlordanes, aldrin, etc.) were somewhat higher in the California canyons than elsewhere, but were more uniform across the areas where they were found (Fig. 23). They were noticeably absent in the mid-Atlantic and Gulf of Mexico stations.

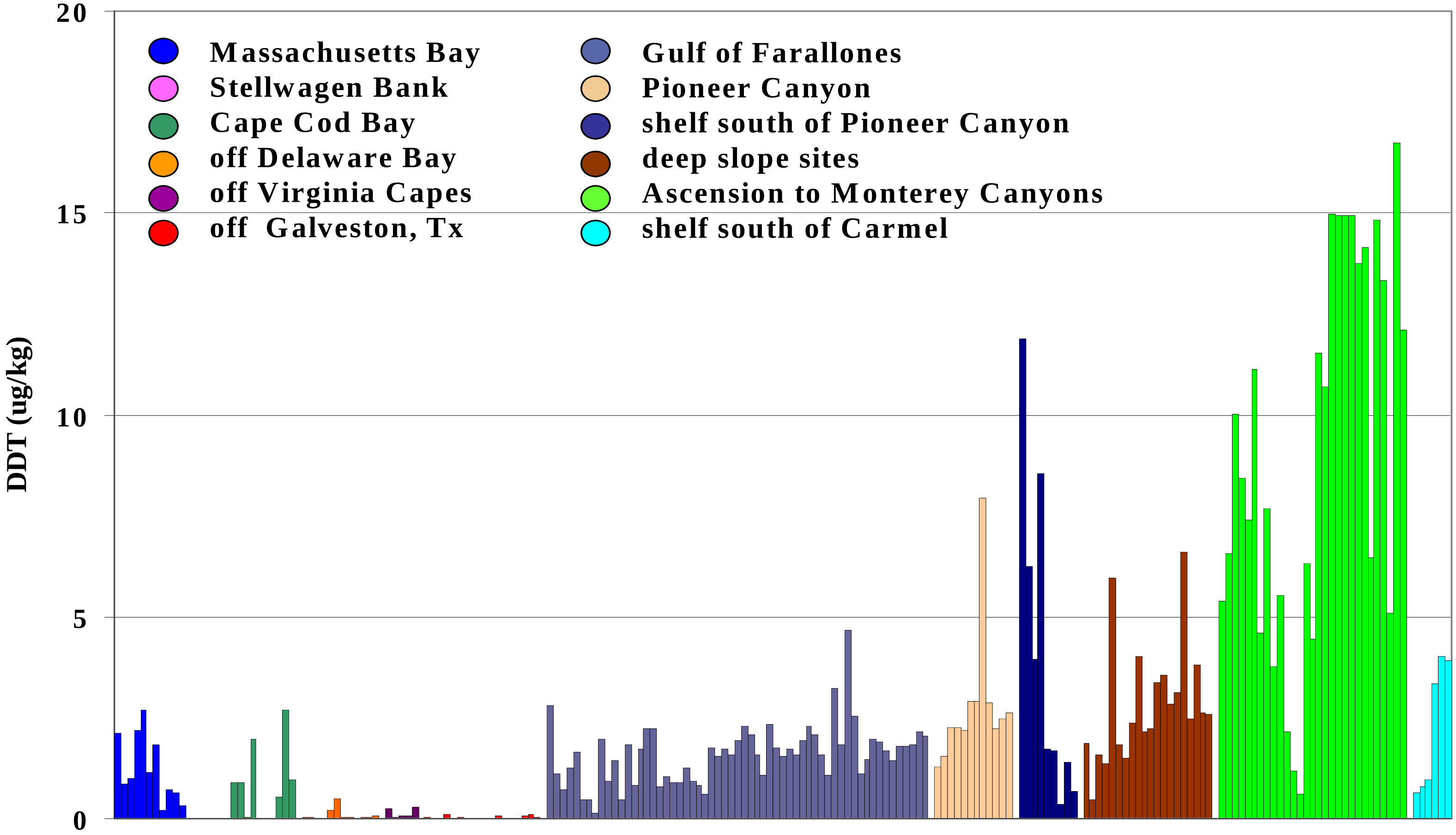


Figure 20. Concentration of total DDT in continental shelf and canyon sediments from various locations in the USA.

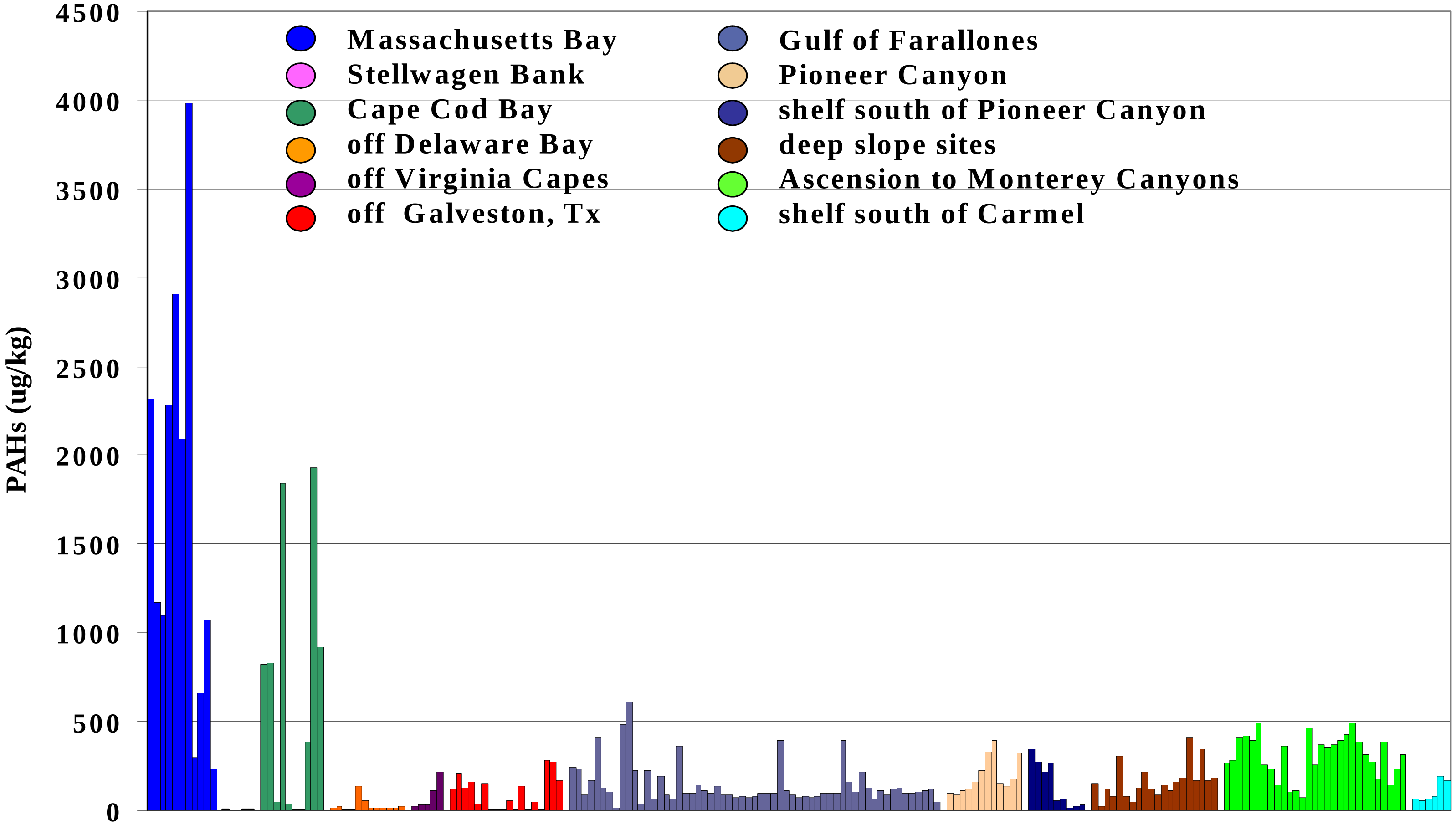


Figure 21. Concentration of PAHs in continental shelf sediments from various locations in the USA.

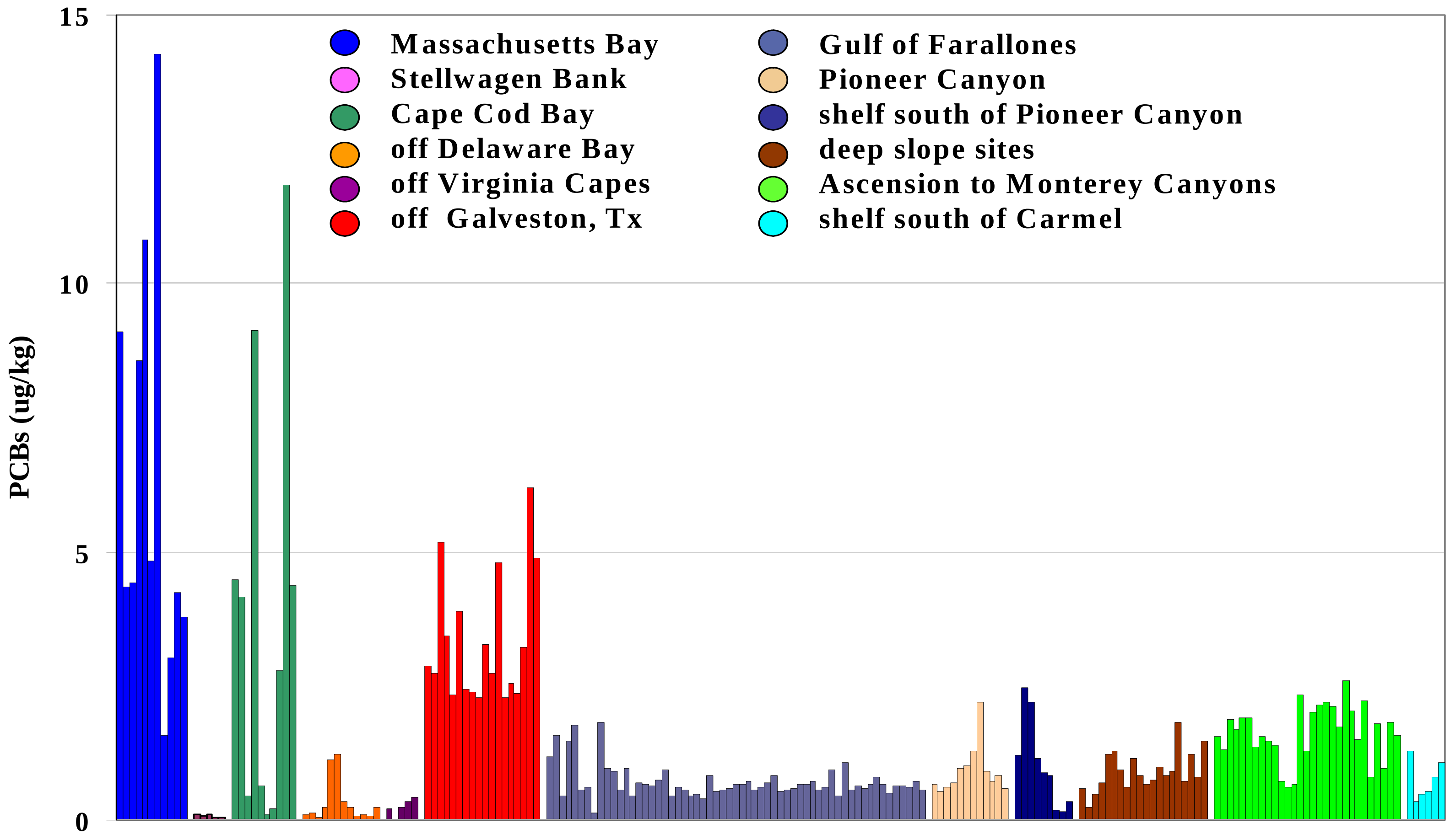


Figure 22. Concentration of PCBs in continental shelf sediments from various locations in the USA.

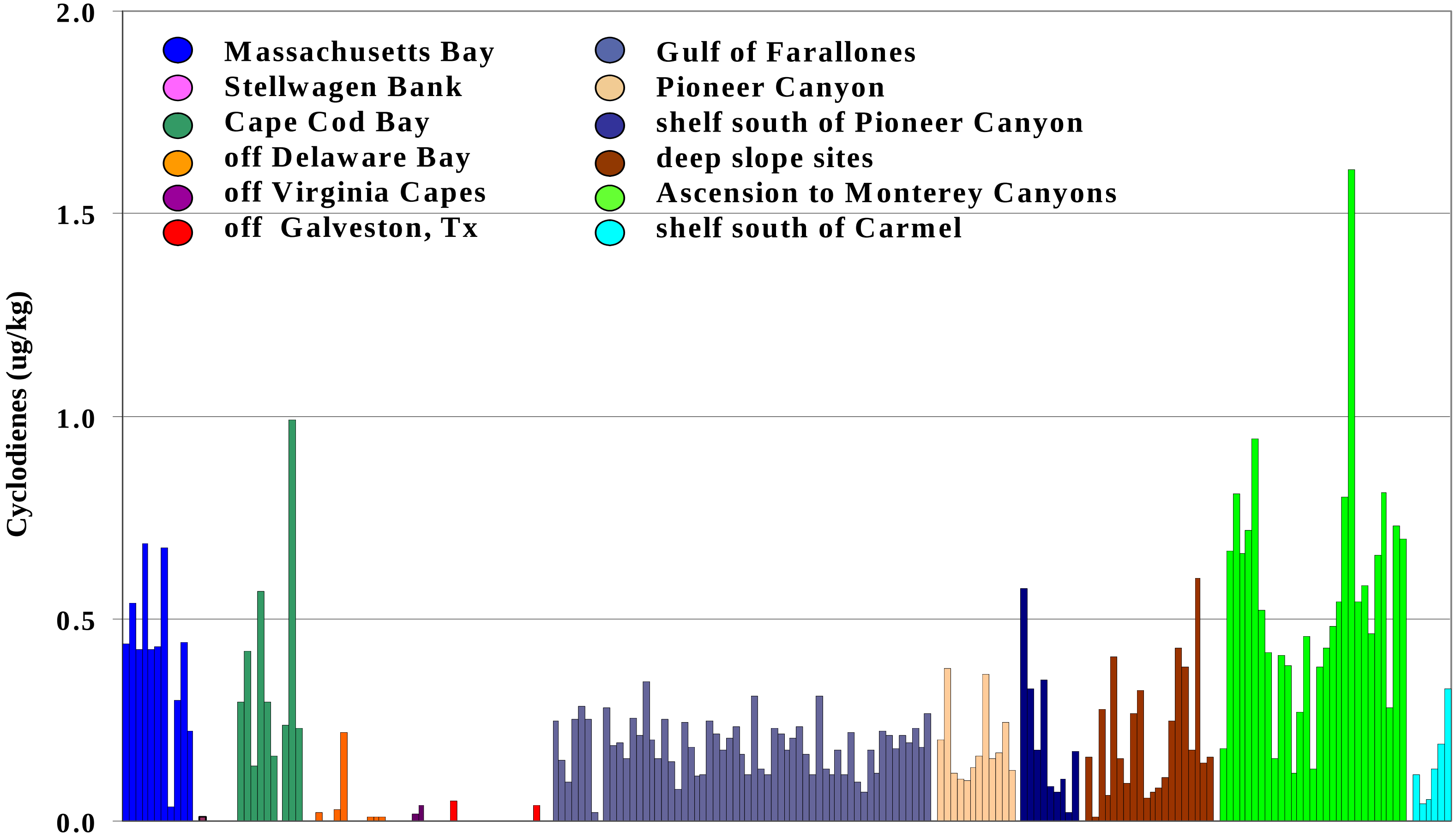


Figure 23. Concentration of cyclodiene pesticides in continental shelf sediments from various locations in the USA.

In contrast to San Francisco Bay, the Monterey Bay watershed does not have large urban areas and the open nature of the Bay is not conducive to large port facilities or marine industrial complexes that require sheltered harbor areas. The watershed is mostly forested or agricultural. Monterey Bay still receives DDT input from terrestrial runoff and is the likely source of DDT found in Ascension and AnoNuevo Canyons. MBARI sampled Monterey Canyon sediments to a depth of over 3,200 m (Paull et al., 2002). They found surface sediment concentrations similar to the shelf concentrations as seen in this data set and others dating back to the early '70s. The presence of DDT at equal concentrations at the head of Ascension Canyon indicates transport of fine-grained materials out of the Monterey Bay system to the shelf.

DDT and it's metabolites enter Monterey Bay in stormwater runoff from agricultural land (Routh, 1972; Mischke et al., 1985; Rice, Seltenrich et al., 1993, CCLEAN, 2005). Although DDT is no longer used on crops, there is a large residual mass stored in sediments within the watersheds. Measured loads of DDT and other persistent organic contaminants from the rivers in the wet season are an order of magnitude greater than during the dry season. There are three shallow offshore POTW discharges into Monterey Bay and one in Carmel Bay. As with the smaller POTWs in the Gulf of the Farallones, these receive input primarily from domestic sanitary input. Flow from the Monterey Regional plant varies between 3-15mgd depending on season. The Santa Cruz and Watsonville Regional plants discharge approximately 10mgd or less, regardless of season. The discharge from the Carmel Bay plant discharge is generally below 1mgd. Annual loadings from the watersheds are several times greater than the loadings seen from sewer discharges (CCLEAN, 2005) for all organic constituents. Moss Landing Harbor sediment contains elevated levels of DDT derived from the watershed. That harbor is dredged periodically, and some of the spoil is dumped at the head (~150 m) of Monterey Canyon as a slurry. Clean, sandy dredge spoil is used for beach renourishment. The volume of permitted spoil material may be as much as 76,000m^3, but this is an upper permit limit. Estimates of sediment input to Monterey Bay from the Salinas River alone are nearly 2,000,000m^3 (Eittreim et al., 2002).

DDT has a low water solubility and transport is primarily associated with fine-grained sediment. The Salinas River is estimated to contribute more fine-grained sediment material to Monterey Bay than the Pajaro and San Lorenzo Rivers, although the bulk of DDTs appears to come from both the Pajaro and Salinas Rivers (CCLEAN, 2005). DDT was used heavily in agricultural areas in coastal California from the late 1940s through the early 1970s, when it was phased out and ultimately banned. Reliable use statistics are not available prior to 1970. In that year, 33,931 pounds of DDT were applied to 19,387 acres in Monterey County (Phillips et al., 1975), which includes the Salinas River watershed. DDT was also applied in the watershed of the Pajaro River which empties into Monterey Bay north of the Salinas River. Airborne sources to Monterey Bay were also a likely factor. In the watersheds, sediment concentration values as high as 170,000 ppb were reported in some canals and sloughs (Phillips et al., 1975). Sediment transport during periods of high flow in the Salinas River above Moss Landing were estimated at 1,207 kg/day (Routh, 1972). In that same study, the concentration of DDT in sediments in depositional areas near Moss Landing were observed to be as high as 190 ppb. Sampling in the 1980s (Rice et al., 1993) showed average total DDT concentrations in Monterey Bay, Elkhorn Slough, and Moss Landing Harbor to be 8.4, 23.6 and 559.8 pbb, respectively. They found no significant differences in annual concentrations indicating a relatively constant supply from runoff. In the same time frame, the California Dept. of Food and Agriculture took soil samples from agricultural fields across the state (Mischke et al., 1985). Concentrations in the Salinas River valley ranged from 2,099 to 3,217 ppb. Recent sampling (MEC 2002) in Moss Landing Harbor showed concentrations ranging from 11.7 up to 122 ppb depending on specific location within the harbor area. Most of these samples were composites of cores from areas which had been dredged in previous years and had accumulated new sediment. Monterey Bay was extensively sampled for DDT at depths above 200 fathoms (~364 m) in the early 1970s by Phillips et al. (1975). They found a wide range of concentrations from 0.5 to 87.9 ppb (mean= 14.1, SD=17.8). The higher concentrations were located around the rim of the canyon, particularly on the south side, where the sampling grid was denser. The areas that they determined contained elevated concentrations of DDT correspond to areas of fine-grained, high TOC sediments. Stephenson et al. (1997) found a similar pattern and also concluded DDT was being transported in a generally net south to north direction within the Bay.

The fate of fine-grained sediment in Monterey Bay is not accurately known. Water currents in this area are complex, and are influenced by the geology of the region. Upwelling is common during the spring/summer months, bringing deep ocean water onto the shelf. Upwelling currents are most prominent near Pt. Reyes, Pt. Año Nuevo, and Pt. Sur. While upwelling up the Monterey Canyon axis to the surface has not been documented (Rosenfeld et al., 1994), strong tidal currents oscillate in the canyon with a net up-canyon transport of deep water (Broenkow and Smethie, 1978). Offshore, the surface flow is dominated by the southward flowing California current. The California undercurrent flows north beneath the surface current. During the winter months the surface flow reverses to the north in a phase referred to as the Davidson Current.

Within Monterey Bay, circulation is cyclonic 2/3 of the year with periodic reversals in early spring and fall (Breaker and Broenkow, 1994). The net flow delivers water and sediments to the northern rim of the Bay which may be transported north or south on the continental shelf, depending on the prevailing coastal current direction and depth. During calm summer months, fine-grained sediments derived from the previous winter's watershed and shoreline erosion deposit on the shelf north and south of the canyon along with settling plant material, resulting in highly organically enriched conditions. DDT accumulates in these deposits. These sediments are transported by bottom currents to either Monterey Canyon or out of Monterey Bay onto the mid-shelf mud belt north of Monterey Bay. The rim of the canyon accumulates large volumes of fine-grained sediment. With the onset of winter season storm-driven wave action, these materials may be disrupted and move down the canyon. The frequency of these events is unknown. Large sediment turbidity flow events have been observed at all depths in the canyon, and may last for a week or more, resulting in large suspended sediment volumes moving down the canyon (Martini, 2004; Xu et al., 2002a). Paull et al. (2002) concluded that DDT laden sediment delivered to Monterey Canyon was diluted with clean sediment from other sources and transported down the canyon during the winter storm season. Their estimates do not take bioturbation into consideration and the terrestrial source term may be underestimated. They also concluded that little DDT is deposited on the flanks of the canyon, and virtually none is deposited in the inter-canyon areas on the continental shelf south of Monterey Bay.

NOAA maintains three Mussel Watch sites in Monterey Bay (http://NSandT.noaa.gov). Over time, the pattern of body burdens in mussels near Santa Cruz, on the north side of the Bay, follows the pattern from Moss Landing samples, in contrast to samples from Pacific Grove on the south side of the Bay (Figure 24). This is also consistent with a net transport from south to north within the Bay.

A preliminary sediment budget for Monterey Bay and the adjacent Santa Cruz shelf was generated by Eittreim et al. (2002).Their calculations indicate a fine-grain sediment deficit on the mid-shelf mud belt north of Monterey Bay, unless a significant portion of the material from the Salinas River watershed is transported across Monterey Canyon to the northern bay for export to the continental shelf. Eittreim et al. (2002) concluded that shelf by-passing to the slope is the dominant sink of fine-grained sediment from the shelf south of Monterey Canyon based on ^{210}Pb accumulation rates. They further conclude that significant sediment by-passing from south to north is not a major transport pathway over the canyon because it is too wide for sediment plumes to cross.

Imagery from Sea-viewing Wide Field-of-View Sensor (SeaWiFS) satellite ocean color data can be used to track sediment plumes. Turbidity can be inferred from sea surface reflectance at a wavelength of 670nm, which indicates red light reflected from the water. At 670nm, chlorophyll pigment absorption is weak, and reflectance indicates scattering due to sediments (Stumpf et al., 2005). Figure 25 shows the median reflectance at that wavelength for the peak rainfall months during the wet season from late 2001to early 2004. The pattern varies from year to year, but sediment plumes appear to be moving around the perimeter of Monterey Bay from south to north during the wet season, when DDT laden sediment is being flushed from the watersheds. Figure 26 shows the SeaWiFS image from Feb. 9, 1998, two days after a particularly large rain storm. The movement of sediment across the canyon head is clear. Large rain events are particularly important in sediment mass movement contributing to overall sediment budgets. Mertes and Warrick (2001) estimated the sediment load in the plume from the Salinas River alone to be 83,030 tons during this single event. What proportion of the sediment load is settling out before crossing the canyon is not known, nor is the distribution of coarse and fine grained particles. Presumably, DDT would be primarily associated with fine grained materials that will tend to stay in suspension longer than coarse grained material.

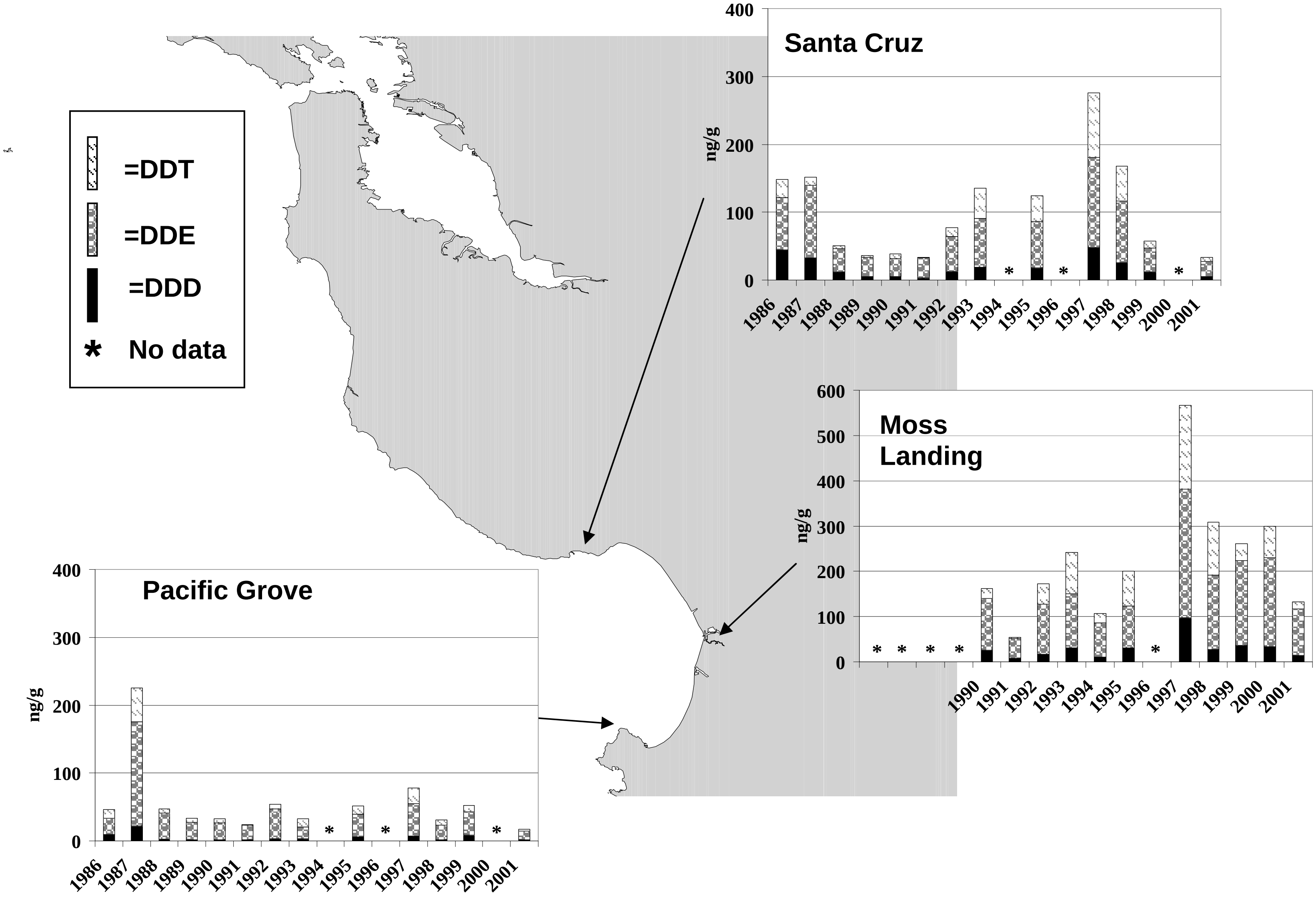


Figure 24. Concentrations of DDT and metabolites in NOAA Mussel Watch tissue samples over time in Monterey Bay.

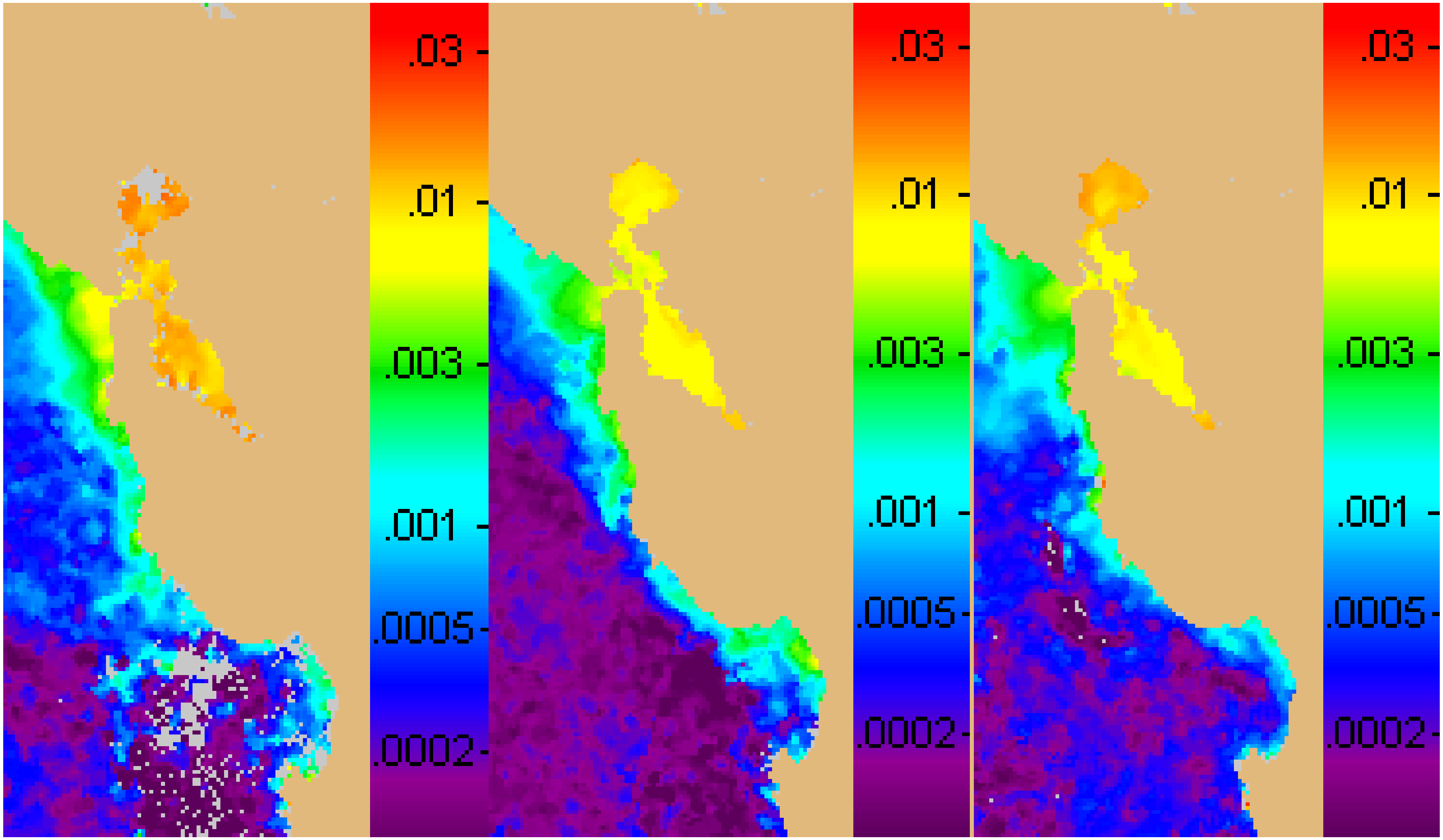


Figure 25. Median SeaWiFS turbidity spectral analysis image for the months of Dec. 2001, Dec. 2002, and Jan. 2004 (left to right). Color scale is in units of Steradian^{-1} at 670nm. Higher values represent higher sea surface reflectance (=higher turbidity).

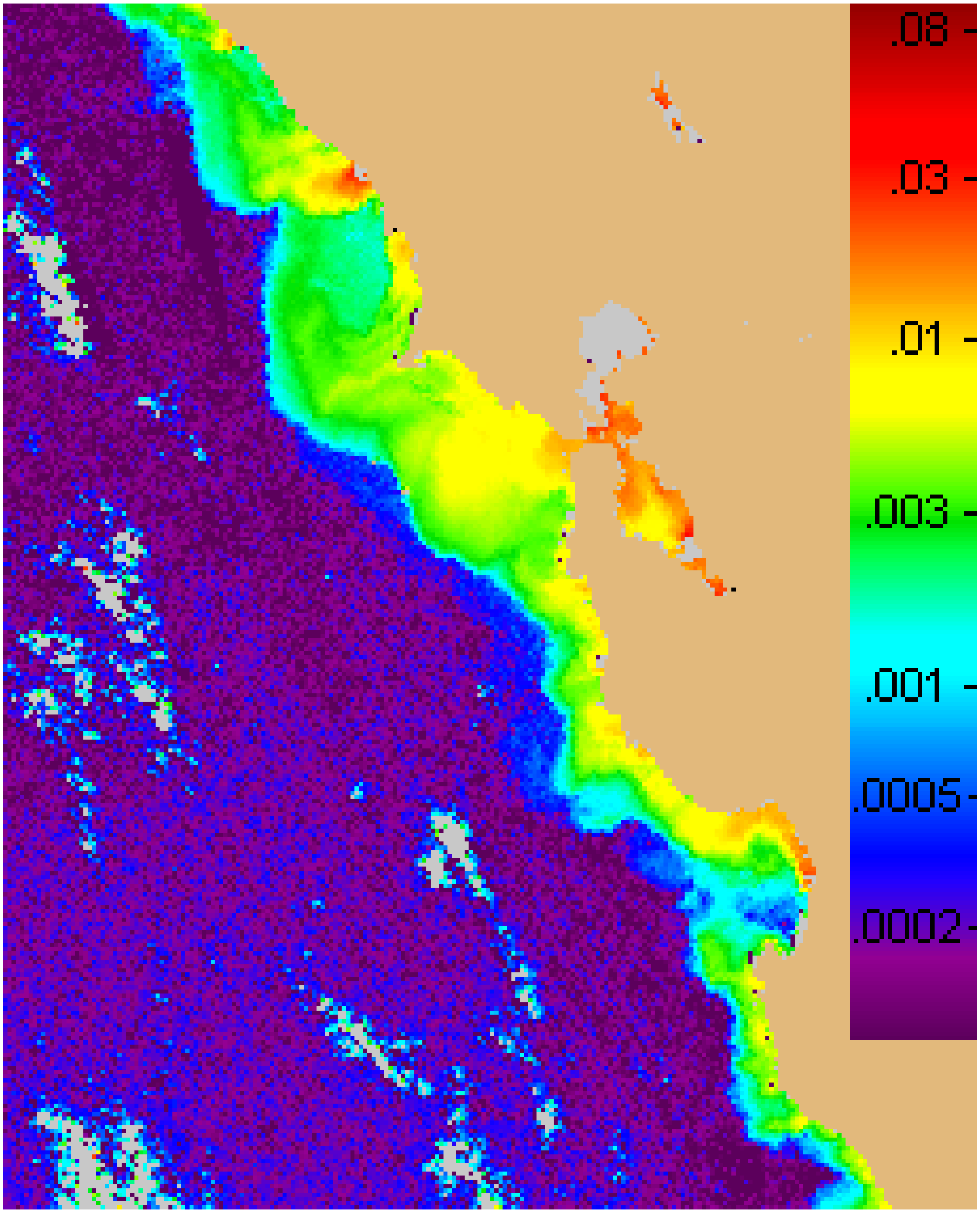


Figure 26. SeaWiFS turbidity spectral analysis image for February 9, 1998. Color scale is in units of Steradian^{-1} at 670nm. Higher values represent higher sea surface reflectance (=higher turbidity).

Another technique being investigated to track plumes, known as Synthetic Aperture Radar (SAR), utilizes satellite radar signals to generate images of ocean surface features based on phase and Doppler shift measurements. This technique can distinguish surface roughness patterns, which in turn can be resolved into surface current boundaries and wave fronts. An advantage of SAR is that the process does not require light, and is generally unaffected by cloud cover (Jackson and Apel, 2004). The latter is a particularly important aspect compared to optical systems when trying to assess plumes during the rainy season, as is the case with Monterey Bay. An example SAR image of the Salinas River plume is shown in Figure 27 (Canadian Space Agency, 2004, image processed by the Alaska Satellite Facility, University of Alaska, Fairbanks). The image clearly shows the outflow plume from the Salinas River crossing Monterey Canyon and impacting the north shore of Monterey Bay on November 2, 2004, following several inches of rain in the region in late October. What is unknown from either SeaWiFS or SAR images, is

Figure 27. Synthetic Aperture Radar (SAR) image of a plume from the Salinas River into Monterey Bay, CA, on Nov. 2, 2004. Color is an artifact of radar image processing.

how much sediment is transported by the plumes. Quantitation of sediment transport will require field measurements.

So, where does the sediment accumulating on the mid-shelf mud belt primarily come from? In the mid-shelf mud belt, fine-grained sediments move from south to north and the source of material is from Monterey Bay (Eittreim et al., 2002; Xu et al., 2002b). As noted above, existing data indicate there is an inadequate volume of fine-grained material emanating from northern Monterey Bay to account for the mass of material observed to be moving over the mid-shelf mud belt. The source estimates probably need revision, as sediments appear to be by-passing the canyon from the southern portion of Monterey Bay based on satellite imagery. Based on measured sediment loads from Mertes and Warrick (2001), SeaWiFS data largely underestimates sediment loads and cannot be used to estimate sediment transport without real-time field measurements. Eittreim et al. (2002) and Xu et al. (2002b) have demonstrated that unlike the offshore movement of fine-grained material, coarse grained sediment moves south in the near shore zone between Half Moon Bay and Monterey Bay, and that source material is shoreline erosion, riverine input and possibly ebb tidal shoals off the Golden Gate. This material does not appear to be a significant source of material for the middle shelf however. Eittrem et al. (2002) also note that if sediment loss down canyons is significant (as Paull et al. contend), the deficits would be even greater than calculated. The 2004 NS&T data clearly show that sediment transport down both canyons in Monterey Bay and in Ascension and AnoNeuvo canyons is a significant sink based upon the DDT concentrations. Xu et al. (2002a) demonstrated that oscillating tidal currents within Monterey Canyon are sufficient to resuspend fine-grained bottom sediments on a regular basis, if not continuously at depths below 1000 m. They reported that a nephaloid layer was persistent at the bottom. The water currents at the rim of the canyon showed a distinct disconnect between the surface water and water in the canyon. Eittreim et al. (2002) also noted a “pervasive” bottom nephaloid layer up on the shelf.

Data is needed to determine what suspended sediment dynamics are present in the shallower portions of Monterey Canyon, where the width of the canyon may not preclude transport of large volumes of suspended sediments from the southern to northern shelf, and where sediments may be entrained from up-canyon tidal currents into surface layer currents to be carried away to the north. Submarine canyons are prominent conduits of sediment/contaminant transport to deeper waters. It needs to be determined if all the DDT goes down to the depths from the submarine canyons first and then redistributes to the deep slopes, or if there is another down-slope transport mechanism. Does this down-canyon transport account for most of the DDT found both in the canyons and on the slope? No data currently exists on current regimes or sediment dynamics within Soquel Canyon. Turbidity, water current, and deposition data will be obtained from moorings placed in Monterey and Soquel Canyons in 2005 by NOAA and USGS. If sediment source terms in the sediment budgets for the Santa Cruz shelf area are correct, alternative sources of contaminants will need to be investigated. Conversely, if the sediment source terms are not correct, the relative magnitude of contaminant inputs to MBNMS from differing watersheds must be addressed. The transport and fate of sediment-borne contaminants in Monterey Bay and it's canyon system are of central importance to assessing the fate and effects of anthropogenic contaminants in the MBNMS.

The larger question is what impact does low level, but continuous, input of DDT have on the biological community. Tissue concentrations in mussels sampled by both the NS&T Mussel Watch and the CCLEAN Programs (http://NSandT.noaa.gov; CCLEAN, 2005) exceed local screening values and guidelines indicating that contamination of nearshore shellfish in the Monterey Bay area may be of concern for both human and wildlife health, such as sea otters, that consume mussels and other bivalves. All data indicate a continuous input at depth 30 years after DDT was banned. DDT concentrations in Monterey Bay biota indicate bioaccumulation is occurring at depth. It is unknown to what extent contaminant loads moving down the canyons may be impacting the deep communities. Contrasting the benthic communities on the slope and within these canyon systems will also allow an assessment of the impact, if any, of anthropogenic inputs into these important systems which are also the routes of continental runoff to abyssal ecosystems. Benthic community assessment examinations are currently under way.

Relatively little is known about the biota of deep water, soft bottom benthic habitats on the shelf or slope in this region (MBNMS, 1996), and few systematic benthic community data sets exist. The USGS collected sediment samples in the Monterey Bay National Marine Sanctuary in 1995 and '97 for sediment texture analysis but with limited concurrent sampling of the benthos. Samples from transects along potential fiber optic cable routes exist, but analyses have not been published. MBARI has samples from a limited set of locations within the canyon, but not on the flanks or the shelf and slope.

It is well established that patterns of DDT body burdens observed in fish is a reflection of local sediment concentrations (Beyer et al., 1994; McCain et al., 1996; Pereira et al., 1994; Spies et al., 1985; Stehr et al., 1997) and food chain transfer from the benthic community (Brown et al., 1986; Foster et al., 1987; Gaston et al., 1998; McLeese et al., 1980). Shaw (1972) found that benthic feeding flatfishes in Monterey Bay and deep epibenthic feeders (sablefish and roughscale rattail) had higher body burdens of DDT and metabolites than did pelagic fish. More recent surveys (Looser et al., 2000) observed the same pattern of deep water, benthic species having higher body burdens than pelagic species. Looser et al. (2000) further observed that deep dwelling species had higher body burdens than shallow species. This was not true for cyclodiene pesticides, indicating DDT has been building up in the deep habitats for a much longer period of time and continues to do so. Body burdens in fish from the Monterey Bay area were higher than comparable deep and surface water species from the Atlantic Ocean. The benthic brittle star *Amphiura archystata* had higher body burdens than any of the fish species (3,340 ug/kg lipid). Eganhouse et al. (2000), and Zeng and Tran (2002) concluded that DDT is constantly being remobilized from sediments to the water column and the benthic food chain at Palos Verdes, California. Smokler et al. (1979), and Young and McDermott-Ehrlich (1977) demonstrated that DDT body burdens in bottom feeding fish in the Palos Verdes area did not reflect reductions in DDT input to the region whereas pelagic feeders did. It is reasonable to assume the same processes are operating in the central California shelf and slope environments.

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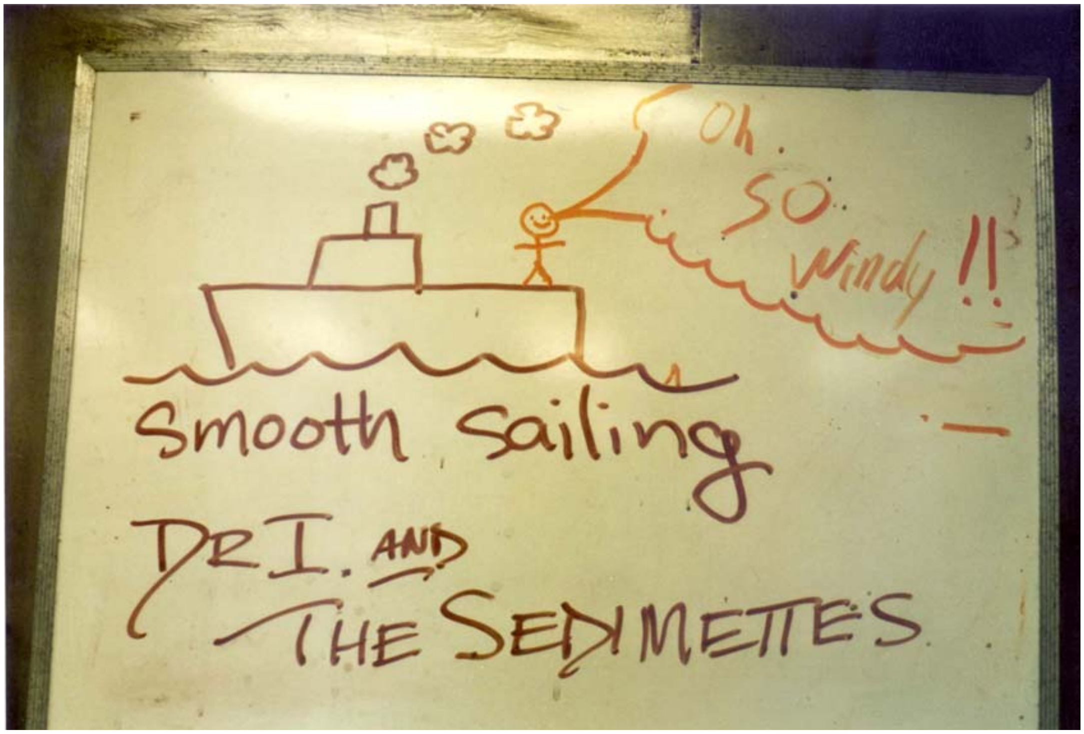

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