

Literature Review To Characterize Environmental Contaminants That May Affect The Southern Sea Otter

FINAL REPORT



Prepared for:

MONTEREY BAY NATIONAL MARINE SANCTUARY



Prepared by:

Dane Hardin
Bryan Bemis
Katharine Starzel
Clare Dominik

APPLIED *marine* SCIENCES

With assistance from
Dave Paradies

**Literature Review To Characterize Environmental Contaminants
That May Affect The Southern Sea Otter**

A report submitted to the Monterey Bay National Marine Sanctuary
Sanctuary Integrated Monitoring Network (SIMoN)
and
Monterey Bay Sanctuary Foundation

May 1, 2007

Dane Hardin
Bryan Bemis
Clare Dominik
Applied Marine Sciences, Inc.
2125 Delaware Avenue, Suite D, Santa Cruz, CA 95060

Katharine Starzel
California Department of Fish and Game

Dave Paradies
Morro Bay Foundation

Project Summary

Applied Marine Sciences, Inc. (AMS) submits this report to the Monterey Bay National Marine Sanctuary (MBNMS), with investigators from the Central Coast Long-term Environmental Assessment Network (CCLEAN), and the Central Coast Regional Water Quality Control Board (Regional Board). The objectives of this study were to

- characterize environmental contaminants present in sea otter habitats that may affect population recovery,
- synthesize existing data on contaminant concentrations and
- map their distribution.

The literature search was focused on sources of anthropogenic contaminants. Several classes of chemical contaminants may affect otters. These include trace metals and organic compounds, such as polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides (e.g., chlordane and DDT), butyl tins (BTs), and organophosphorous pesticides (e.g., diazinon). The search was concentrated on organic compounds and those metals with the greatest potential for toxicity (e.g., lead and mercury).

Numerous sources of relevant data were searched, as follows:

- Data from peer-reviewed publications
- Bay Protection and Toxic Cleanup Program of the California State Water Resources Control Board sediment chemistry data for 1992–1997
- Central Coast Long-term Environmental Assessment Network sediment and bivalve chemistry data from 2002–2004
- Coastal Fish Contamination Program of the California State Water Resources Control Board bivalve and fish tissue chemistry data for 1999–2000
- Moss Landing Harbor District sediment chemistry data related to dredging activities from 1993–2002
- National Status and Trends Mussel Watch Program (NS&T) of the National Oceanic and Atmospheric Administration sediment chemistry data from 1986–1997 and bivalve chemistry data from 1986–2003
- Santa Cruz Harbor District sediment chemistry data related to dredging activities from 1995–2003
- State Mussel Watch Program of the California State Water Resources Control Board bivalve tissue chemistry data for 1977–2000
- Toxic Substances Monitoring Program of the California State Water Resources Control Board sediment and fish tissue chemistry data for 1978–2000

Several other state, municipal, or industrial sources of data were identified as follows:

- California Coastal Commission 1997 compilation of monitoring data for the Elkhorn Slough Watershed and the lower Salinas River drainage area
- California Department of Fish and Game sea otter prey contamination chemistry data for bivalves and other invertebrates from 1999 in Elkhorn Slough
- Central Coast Regional Water Quality Control Board special investigative report on the lead slagpile near Monterey from 2003

- City and County of San Francisco Southwest Ocean Outfall monitoring program sediment and fish chemistry data from 1997–2002
- City of Santa Cruz sediment and fish chemistry data from 1988–1997
- City of Watsonville sediment, fish and shrimp chemistry data from 1988–1996
- Monterey Regional Water Pollution Control Agency sediment chemistry data from 1977–1994, and fish and shrimp chemistry data from 1982–1991
- Union Pacific report on the historic lead slagpile near Monterey from 2003

Data were screened for geographic relevance (i.e., between San Francisco and Point Conception) and entered into an Excel workbook. The large number of parameters entered into separate columns in the workbook required that the data span multiple worksheets. The database includes 3,432 rows (one row per sample) and over 900 columns (one column per analyte per measurement basis; e.g., dry weight, lipid weight, or wet weight).

Inconsistencies among datasets in the analytes measured, matrices analyzed and measurement bases complicated comparisons across programs to determine areas with high contaminant concentrations. Visual determination of areas with higher contaminant concentrations was made possible by converting contaminant concentrations into percentiles and graphing the most common matrices for a single group of contaminants on one figure. Using this method, the Elkhorn Slough and Salinas River areas, as well as more urbanized areas, contained samples that often had higher percentile concentrations of contaminants. Most of the organic contaminants evaluated in this study have been banned from use since the 1970s or 1980s. Nevertheless, analysis of mussel data from NS&T indicated no significant ($p < 0.05$) downward trends in contaminant concentrations and some marginally significant ($p < 0.10$) increases in PAHs and PCBs and concentrations of DDT in sea otter livers have not declined significantly since 1970, which was three years before agricultural use of this pesticide was banned. Sediment data collected by CCLEAN also indicate that concentrations of DDT from several locations in Monterey Bay have not significantly declined since 1970. The concentrations of dieldrin, DDT and PCBs in mussels at some locations varied according to rainfall, suggesting storm runoff as a pathway from the land into nearshore waters. Moreover, only for dieldrin at Lovers Point and DDT at Point Santa Cruz have there been significant or marginally significant declines in the amount of contaminant relative to rainfall, suggesting no discernable decline in contaminant concentrations from most legacy terrestrial sources.

TABLE OF CONTENTS

1.0	INTRODUCTION	1
2.0	APPROACH AND METHODS	1
2.1	LITERATURE SEARCH	2
2.2	DATA SCREENING AND FORMATTING	3
3.0	RESULTS	4
3.1	CONSTRUCTING THE DATABASE	4
3.2	CONTAMINANT RESULTS	6
3.2.1	<i>Butyltins</i>	7
3.2.1.1	Background	7
3.2.1.2	Spatial Patterns	7
3.2.1.3	Temporal Trends	7
3.2.2	<i>Chlordanes</i>	10
3.2.2.1	Background	10
3.2.2.2	Spatial Patterns	11
3.2.2.3	Temporal Trends	13
3.2.3	<i>Dichlorodiphenyltrichloroethane</i>	14
3.2.3.1	Background	14
3.2.3.2	Spatial Patterns	16
3.2.3.3	Temporal Trends	16
3.2.4	<i>Dieldrin</i>	16
3.2.4.1	Background	16
3.2.4.2	Spatial Patterns	19
3.2.4.3	Temporal Trends	19
3.2.5	<i>Polynuclear Aromatic Hydrocarbons</i>	23
3.2.5.1	Background	23
3.2.5.2	Spatial Patterns	23
3.2.5.3	Temporal Trends	23
3.2.6	<i>Polychlorinated Biphenyls</i>	26
3.2.6.1	Background	26
3.2.6.2	Spatial Patterns	27
3.2.6.3	Temporal Trends	29
4.0	DISCUSSION	30
5.0	ACKNOWLEDGEMENTS	37
6.0	LITERATURE CITED	37
7.0	APPENDIX 1: RELEVANT CITATIONS	41

LIST OF TABLES

Table 1. Concentrations of chlorinated organic contaminants in sea otter liver tissues reported by Bacon <i>et al</i> (1999).....	1
Table 2. Databases and search words used to find published literature related to chemical contaminants that could affect sea otters.....	5
Table 3. Results of linear regressions of lipid-normalized butyltin concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program..	10
Table 4. Results of linear regressions of lipid-normalized chlordane concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch Program.	13
Table 5. Results of linear regressions of lipid-normalized DDT concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.	18
Table 6. Results of linear regressions of lipid-normalized dieldrin concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program..	22
Table 7. Results of linear regressions of lipid-normalized PAH concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.	25
Table 8. Uses of various Aroclors.	27
Table 9. Results of linear regressions of lipid-normalized PCB concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.	29

LIST OF FIGURES

Figure 1. Spatial distribution and percentile of concentrations for samples in which MBTs were analyzed.....	8
Figure 2. Spatial distribution and percentile of concentrations for samples in which DBTs were analyzed.....	9
Figure 3. Concentrations of butyltins in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1989 and 2004.	10
Figure 4. Relationship between lipid-normalized butyltin concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites.....	11
Figure 5. Spatial distribution and percentile of concentrations for samples in which chlordanes were analyzed.	12
Figure 6. Concentrations of chlordanes in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1986 and 2004.	13
Figure 7. Relationships between lipid-normalized chlordane concentrations in mussels and rainfall at six NS&T sites.	14
Figure 8. Temporal variation in DDT concentrations near four CCLEAN sites.....	15
Figure 9. Spatial distribution and percentile of concentrations for samples in which DDT was analyzed.....	17
Figure 10. Concentrations of DDTs in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1986 and 2004.	18
Figure 11. Relationships between lipid-normalized DDT concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites.....	19
Figure 12. Spatial distribution and percentile of concentrations for samples in which dieldrin was analyzed.....	20

Figure 13. Comparison of dieldrin concentrations in mussels at Scott Creek, Laguna Creek, Point Santa Cruz, The Hook, Moss Landing Beach, Lovers Point, Pacific Grove, Fanshell Overlook and Carmel River Beach with the OEHHA human health screening value.....	21
Figure 14. Concentrations of dieldrin in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1986 and 2004.	21
Figure 15. Relationship between lipid-normalized dieldrin concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites.....	22
Figure 16. Spatial distribution and percentile of concentrations for samples in which PAHs were analyzed.....	24
Figure 17. Concentrations of PAHs in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1989 and 2004.	25
Figure 18. Relationship between lipid-normalized PAH concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites.....	26
Figure 19. Spatial distribution and percentile of concentrations for samples in which PCBs were analyzed.....	28
Figure 20. Concentrations of PCBs in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1988 and 2004.	29
Figure 21. Relationships between lipid-normalized PCB concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites.....	30
Figure 22. Temporal trends in concentrations of DDTs in sea otter livers in central California. .	33
Figure 23. Comparison of replicate values for two studies of DDTs in the livers of sea otters from central California.	33
Figure 24. Concentrations of the DDD, DDE and DDT isomers in water samples analyzed by CCLEAN from the Pajaro and Salinas rivers.	35
Figure 25. Concentrations of DDTs in sediments at eight CCLEAN sites measured over a five-year period.	36
Figure 26. Concentrations of DDTs measured in mussels at five CCLEAN sites over a four-year period compared to a coastal background site and a contaminated estuarine site.....	36

1.0 INTRODUCTION

The southern sea otter, *Enhydra lutris nereis*, was thought to be extinct after it was heavily hunted for its pelts in the 18th and 19th centuries. A small remnant population was rediscovered near Big Sur in the 1930s, and the species was designated as threatened by the United States Fish and Wildlife Service in 1977. Recovery of the southern sea otter has been slow, with the California population growing at a rate that is only 25–30% of the growth rate for populations in Alaska (Estes, 1990). Moreover, in the late 1990s, counts of southern sea otters indicated that the population was either stable or declining. The population currently is approximately 2,200 animals. Causes of this lack of population growth are uncertain, but concerns exist for fishery operations, malnutrition, disease, and chemical contaminants.

Concerns for the effects of chemical contaminants on the southern sea otter are based on the results of several articles in the scientific literature. High concentrations of chlorinated organic contaminants have been reported in sea otters from the Monterey Bay area, relative to otters from Alaska (Bacon *et al.*, 1999) (Table 1). It also has been reported that sea otters in the Central California area that die from disease have higher concentrations of some organic contaminants than sea otters that die from other causes (Kannan *et al.*, 1998; Nakata *et al.*, 1998).

Table 1. Concentrations of chlorinated organic contaminants in sea otter liver tissues reported by Bacon *et al* (1999).

Location	Pollutant Concentration
Aleutian Islands	Total PCB 310 $\mu\text{g/kg}$ Total DDT 40 $\mu\text{g/kg}^b$
Southeast Alaska	Total PCB 8 $\mu\text{g/kg}$ Total DDT 1 $\mu\text{g/kg}^b$
Monterey Bay	Total PCB 190 $\mu\text{g/kg}$ Total DDT 850 $\mu\text{g/kg}^b$

^b = Concentrations given for wet weight.

This project provides valuable information to help determine the effects of chemical contaminants on sea otters and will contribute to the fulfillment of several research and monitoring efforts in the Monterey Bay National Marine Sanctuary (MBNMS).

2.0 APPROACH AND METHODS

The objectives of this study are to characterize environmental contaminants present in sea otter habitats that may affect population recovery, synthesize existing data on contaminant concentrations, and map their distributions. To achieve these objectives, the literature search was

focused on sources of anthropogenic contaminants. Several classes of anthropogenic chemical contaminants could affect otters. These include trace metals and organic compounds, such as polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides (e.g., chlordane and DDT), tributyl tins (TBTs), and organophosphorous pesticides (e.g., diazinon). The search was concentrated on organic compounds and those metals with the greatest potential for toxicity (e.g., lead and mercury).

2.1 Literature Search

Two methods of literature search were used to obtain both published and unpublished (“grey literature”) data. First, the project team compiled a list of sampling programs and principal investigators in the region. Internet searches were performed for data available from major monitoring programs in the region and personal contacts were made with principal investigators to obtain data that were not available *via* the internet. When investigators were contacted and the literature search was described, they often provided information regarding other monitoring programs or sources of data. The second method of searching for literature and data involved general and specific electronic searches for pertinent published literature. In many cases, references taken from initial literature findings suggested other sources of material, which were then pursued.

Through the first method of searching for literature and data, several institutional monitoring programs were identified and the data were obtained, as follows:

- Bay Protection and Toxic Cleanup Program of the California State Water Resources Control Board sediment chemistry data for 1992–1997
- Central Coast Long-term Environmental Assessment Network (CCLEAN) sediment and bivalve chemistry data from 2002–2004
- Coastal Fish Contamination Program of the California State Water Resources Control Board bivalve and fish tissue chemistry data for 1999–2000
- Moss Landing Harbor District sediment chemistry data related to dredging activities from 1993–2002
- National Status and Trends Mussel Watch Program (NS&T) of the National Oceanic and Atmospheric Administration sediment chemistry data from 1986–1997 and bivalve chemistry data from 1986–2003
- Santa Cruz Harbor District sediment chemistry data related to dredging activities from 1995–2003
- State Mussel Watch Program of the California State Water Resources Control Board bivalve tissue chemistry data for 1977–2000
- Toxic Substances Monitoring Program of the California State Water Resources Control Board sediment and fish tissue chemistry data for 1978–2000

Several other state, municipal, or industrial sources of data were identified as follows:

- California Coastal Commission 1997 compilation of monitoring data for the Elkhorn Slough Watershed and the lower Salinas River drainage area

- California Department of Fish and Game sea otter prey contamination chemistry data for bivalves and other invertebrates from 1999 in Elkhorn Slough
- Central Coast Regional Water Quality Control Board special investigative report on the lead slagpile near Monterey from 2003
- City and County of San Francisco Southwest Ocean Outfall monitoring program sediment and fish chemistry data from 1997–2002
- City of Santa Cruz sediment and fish chemistry data from 1988–1997
- City of Watsonville sediment, fish and shrimp chemistry data from 1988–1996
- Monterey Regional Water Pollution Control Agency sediment chemistry data from 1977–1994, and fish and shrimp chemistry data from 1982–1991
- Union Pacific report on the historic lead slagpile near Monterey from 2003

The second method of searching for literature and data used broad search strategies to explore Cambridge Scientific Abstracts for pertinent literature. The Aquatic Science and Fisheries Abstracts database was searched from 1977 to 2004 and Environmental Sciences and Pollution Management database was searched from 1968 to 2004 with 20 combinations of words that were allowed to appear anywhere in the citation records (Table 2). These searches resulted in 2,217 records, which were all imported into an EndNote (version 6.0.2, ISI ResearchSoft) bibliography. Duplicates were eliminated and the resulting bibliography of 1,039 citations was visually searched for citations that are specifically relevant to chemical contaminants in water, sediment or animal tissues in the Monterey Bay National Marine Sanctuary. The Sanctuary-specific bibliography includes 71 citations (Appendix 1). Every effort was made to obtain all of these relevant citations and any data they contained were entered into the database. The GIS coordinates for these data are imprecise because latitudes and longitudes were not included in most of the published manuscripts. Both the entire bibliography, minus the duplicate citations, and the Sanctuary-specific bibliography are included as appendices to this report and the original EndNote files have been provided.

In all cases, priority was placed on populating the database with data that came from within the Sanctuary, that came from within the known range of the southern sea otter, or that could inform assessments about sources of contaminants coming into the Sanctuary.

2.2 Data Screening and Formatting

Data were initially screened for geographic relevance (i.e., between San Francisco and Santa Barbara) and entered into a single database. The database fields (columns) included:

- data source (i.e., monitoring program or publication author)
- site name
- site code
- latitude
- longitude
- matrix (e.g., sediment, prey species)
- date
- one column for the concentration of each chemical contaminant
- data qualifiers (i.e., identification of concentrations that are below detection limits)

The data were then screened for discrepancies in nomenclature so that all the data for one chemical appear in a single column. According to discussions with MBNMS, the data were put into an Excel spreadsheet for importing into the MBNMS' GIS system to facilitate detailed mapping. Due to the large number of fields entered in the database and Excel's limitation of 256 columns per worksheet, the data spanned several worksheets. The sheets included one that lists all sites (Sites), one with general information (General), one for metals and related data (Metals), two for organic compound data (Org1, Org2), and two for PCB data (PCB1, PCB2). Data on the General sheet were repeated on all other data sheets to allow cross-referencing. In addition, there were duplicate data sheets ("BDL" suffix, e.g., Metals_BDL) with concentration values replaced by a coding variable that corresponds to data that were below detection limits.

The necessary ancillary data (i.e., percent fines, percent total organic carbon, percent lipids) were included to allow normalization for each type of data (e.g., sediment and tissue) to adjust for temporal trends in these parameters. Because many organic contaminants are associated with the surfaces of sediment particles or organic material, trends could be obscured if there is high annual variation, or high spatial variation that appears as temporal variation, in percent fines or total organic carbon. Moreover, since many organic contaminants are lipophilic, trends in tissue contaminants are often best detected by normalizing to percent lipid content. This normalization effectively reduces variation in the data due to interannual variation in lipid content.

Initial database development was based upon templates used for the Central Coast Regional Water Quality Control Board's Central Coast Ambient Monitoring Program (CCAMP) and the State of California Surface Water Ambient Monitoring Program (SWAMP). Both of these databases have been configured to easily export data to the EPA STORET system. Discussions were held with Dave Paradies (CCAMP) and Chad King (MBNMS) to ensure that the project database would be compatible with the Sanctuary's GIS requirements.

3.0 RESULTS

3.1 Constructing the Database

Synthesizing contaminant data from a variety of literature sources and entering them into the database in a consistent and efficient manner proved to be more difficult than expected. Because data were obtained from many sources, including different authors and funding agencies, the data varied greatly in format. For example, inconsistencies in analyte name, concentration units, matrix description (e.g., wet weight or dry weight for sediment, mussels, fish muscle, sea otter liver), latitude and longitude notation, identification of values below detection limits, and physical arrangement of data fields and records were common. These differences required careful renaming, conversion, and rearrangement of data from each source before values could be manually entered into the database. Because the number of data values entered was large, a series of computer macros was developed to reformat the data for each source more rapidly and accurately than could be done otherwise. Despite the speed improvements provided by these efforts to automate data preparation, the additional formatting and calculations necessary at each step of data entry added a significant amount of time to the original estimates for constructing the database.

Table 2. Databases and search words used to find published literature related to chemical contaminants that could affect sea otters.

Database	Search Words	Citations Found
Aquatic Science and Fisheries Abstracts	California Contaminant Coast	12
	California Contaminant Marine	110
	California Hydrocarbon Coast	25
	California Hydrocarbon Marine	202
	California Pesticide Coast	10
	California Pesticide Marine	39
	California Pollutant Coast	31
	California Pollutant Marine	237
	California Polychlorinated Coast	32
	California Polychlorinated Marine	125
	Monterey Contaminant	3
	Monterey Hydrocarbon	16
	Monterey Pesticide	4
	Monterey Pollutant	8
	Monterey Polychlorinated	9
	Sea Otter Contaminant	3
	Sea Otter Hydrocarbon	4
	Sea Otter Pesticide	4
	Sea Otter Pollutant	4
	Sea Otter Polychlorinated	4
Environmental Sciences and Pollution Management	California Contaminant Coast	24
	California Contaminant Marine	125
	California Hydrocarbon Coast	56
	California Hydrocarbon Marine	219
	California Pesticide Coast	20
	California Pesticide Marine	80
	California Pollutant Coast	123
	California Pollutant Marine	388
	California Polychlorinated Coast	27
	California Polychlorinated Marine	143
	Monterey Contaminant	9
	Monterey Hydrocarbon	23
	Monterey Pesticide	14
	Monterey Pollutant	28
	Monterey Polychlorinated	33
	Sea Otter Contaminant	3
	Sea Otter Hydrocarbon	6
	Sea Otter Pesticide	1
	Sea Otter Pollutant	5
	Sea Otter Polychlorinated	8
Total		2,217

3.2 Contaminant Results

The inconsistencies in analytes reported and matrices analyzed for the various datasets obtained in this literature search made analysis of spatial and temporal patterns difficult. Consequently, for purposes of this report, emphasis was placed upon showing spatial patterns for a select set of persistent organic pollutants (POPs) that had been measured in numerous investigations within the range of the southern sea otter. Although trace metal data are included in the database, they are not considered in this report, as published articles have suggested that the greatest contaminant risk to sea otters in the central California region is from POPs (Kannan *et al.*, 1998; Nakata *et al.*, 1998). In an attempt to show spatial patterns across several different matrices, data within each of several common matrices (i.e., sea otter liver, sea otter kidney, mussels, sediments, and fish fillets/muscle/tissue) were converted to percentiles and displayed together for each analyte group (i.e., dibutyl tins, monobutyl tins, sum of chlordanes, dieldrin, sum of DDTs, sum of PAHs, and sum of PCBs). In this way, spatial patterns across numerous matrices could be observed, regardless of differences in the original concentrations or data reporting conventions for each matrix. Because many of the datasets included in this analysis are based upon repeated sampling at fixed locations, there are many sampling points that have numerous samples. These sampling points are displayed in the following figures as the mean percentile for all samples in a given matrix from that location. This has had the tendency to reduce the percentiles displayed for locations with periodic high concentrations.

Analysis of temporal trends must be based upon consistent long-term, site-specific monitoring and account for environmental and biological variation that could affect contaminant concentrations. Mussel data from some NS&T central California sites go back to 1986 and the analysis of temporal trends was based on these data. Because many of the organic contaminants in the database are lipophilic, their concentrations in samples can vary according to the lipid content (Hebert & Keenleyside, 1995). Not all programs analyze lipid content, but fortunately NS&T does. Consequently, variation due to lipid content of the mussels was corrected by examining lipid-normalized data (dry-weight concentrations \div percent lipid). Because an initial screening of the mussel data suggested some interannual variation might be related to differences among years in rainfall, the significance of this relationship was examined by performing linear regressions of mussel pollutant concentrations against the cumulative rainfall in the three months prior to each mussel sampling date. It has previously been shown that mussels require 90–100 days to come to equilibrium for most contaminants (Stephenson, 1992). For Monterey Bay sites, rainfall at Salinas was used for this analysis, and for San Simeon and Point San Luis, rainfall at San Luis Obispo was used. For sites where significant relationships were observed between rainfall and contaminant concentrations, a linear regression was performed between contaminant/rainfall and time to see whether there have been trends in this relationship (i.e., increase or attenuation in contaminant concentration relative to rainfall). Results of statistical tests with probabilities <0.05 are termed significant and those with probabilities from 0.05–0.10 have been termed marginally significant. Sediment data from several investigations that sampled similar locations also were analyzed for temporal variation in DDT.

3.2.1 Butyltins

3.2.1.1 Background

Butyltins are used in antifouling bottom paints on boat hulls, as well as stabilizers in PVC pipe and catalysts in the production of electrodeposited coatings. The primary compound in antifouling paints is tributyltin oxide, whereas mono- and dibutyltins are used in PVC pipe and electrodeposited coatings (World Health Organization, 2006). Tributyltin degrades in the environment and can be metabolized to dibutyltin and monobutyltin by mammals. Regulation of butyltins began after the collapse of oyster growing in Arcachon Bay, France in the late 1970s and early 1980s (Bray & Langston, 2006). This collapse was traced to high concentrations of butyltins from antifouling paints. Subsequently, the use of butyltin paints on boat hulls became regulated in most industrial countries. In the United States, several states enacted laws limiting the use and allowable concentrations of butyltins in water. As a result of inconsistent regulations among states, the federal government enacted the Organotin Antifouling Paint Control Act of 1988. This act prohibited the use of butyltin paints on boats shorter than 25 feet long, except for aluminum boats. In 1990, regulations were enacted that limited the leaching of butyltins from bottom paint on larger vessels to no more than 4 mg/cm²/day for boats longer than 25 feet and required that butyltin paints be applied only by certified applicators.

Butyltins are fairly persistent in the environment. They exhibit low solubility in water and readily adhere to sediment particles (Extension Toxicology Network Pesticide Information Profiles, 1996). In sediments, butyltins have a half-life of 122 days (World Health Organization, 2006) and breakdown takes longer in anaerobic conditions (Extension Toxicology Network Pesticide Information Profiles, 1996).

Butyltins have exhibited low acute toxicities to laboratory animals. Laboratory toxicity tests have reported LD₅₀ concentrations from oral exposure in rats ranging from 58 mg/kg body weight for dibutyltin to 2,300 mg/kg body weight for monobutyltin. The lowest observable adverse effect level (LOAEL) reported for immunological effects in rats was 2.5 mg/kg body weight (World Health Organization, 2006).

3.2.1.2 Spatial Patterns

Butyltins were analyzed in relatively fewer samples than many of the other contaminants discussed in this report and were generally reported separately for monobutyltin (MBT) and dibutyltin (DBT). Figures showing the spatial patterns of butyltin percentiles are presented here separately for these two compounds (Figure 1 and Figure 2). In both cases, the highest percentiles occurred in Elkhorn Slough and at the mouth of the Salinas River (sediments) and in Monterey Harbor (sea otters).

3.2.1.3 Temporal Trends

Concentrations of monobutyltin and dibutyltin were added together to show temporal trends in the NS&T mussel data (Figure 3). There was substantial variation among years, with generally lower concentrations since 2000. Trends in lipid-normalized concentrations were downward at all sites except Lovers Point and San Simeon, although none was significant (Table3). Temporal variation in butyltins was not related to rainfall (Figure 4).

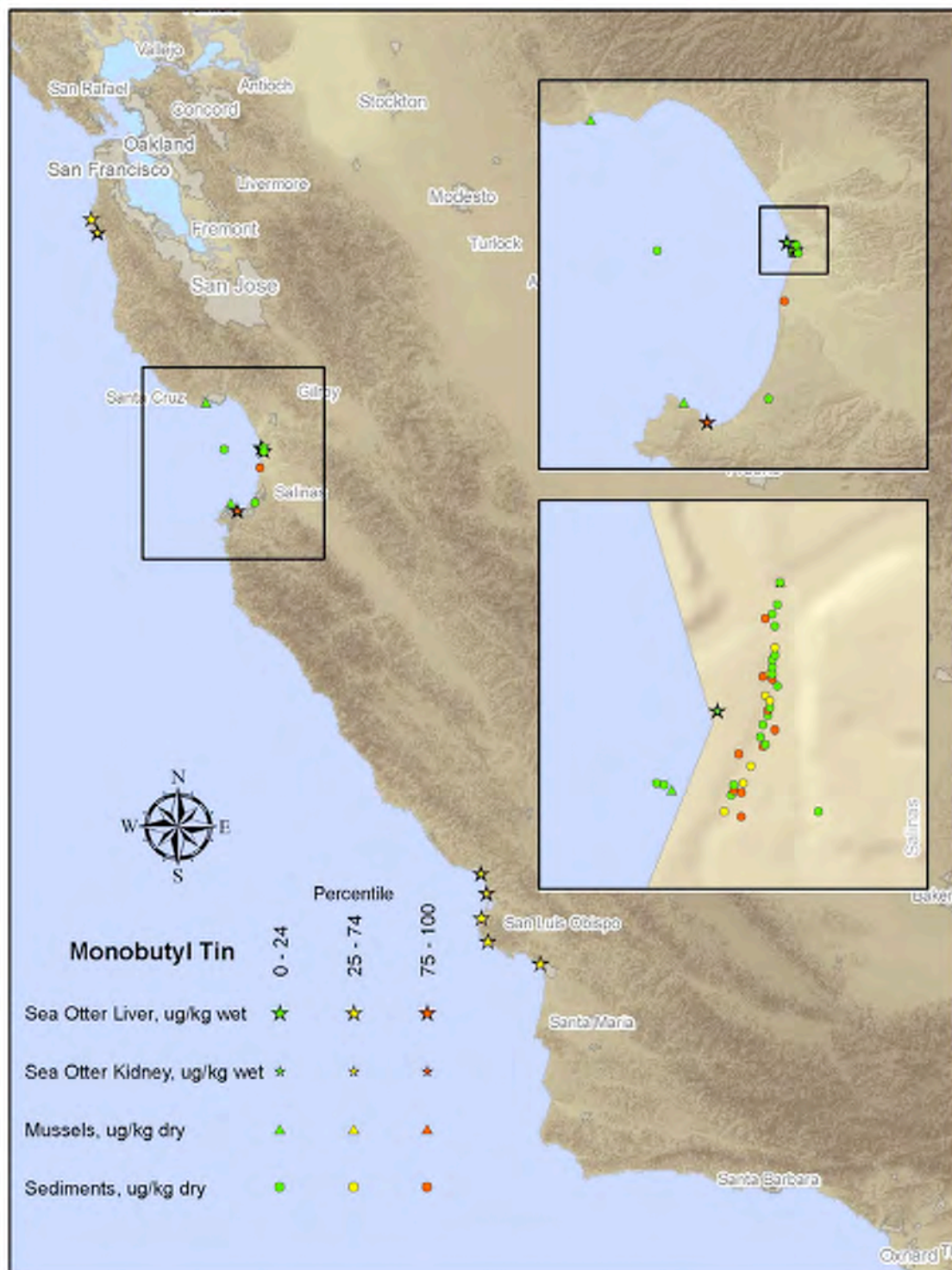


Figure 1. Spatial distribution and percentile of concentrations for samples in which MBTs were analyzed.

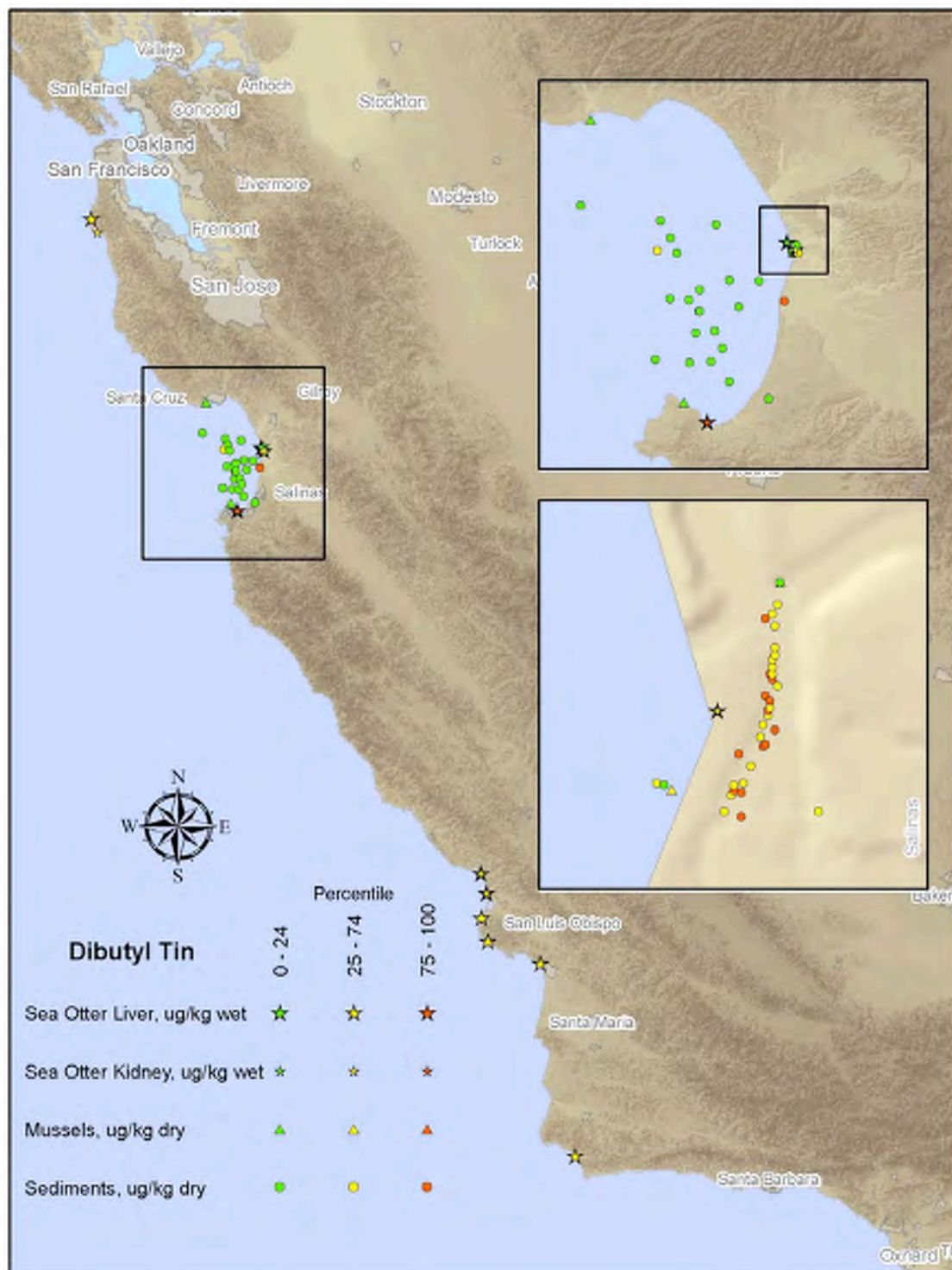


Figure 2. Spatial distribution and percentile of concentrations for samples in which DBTs were analyzed.

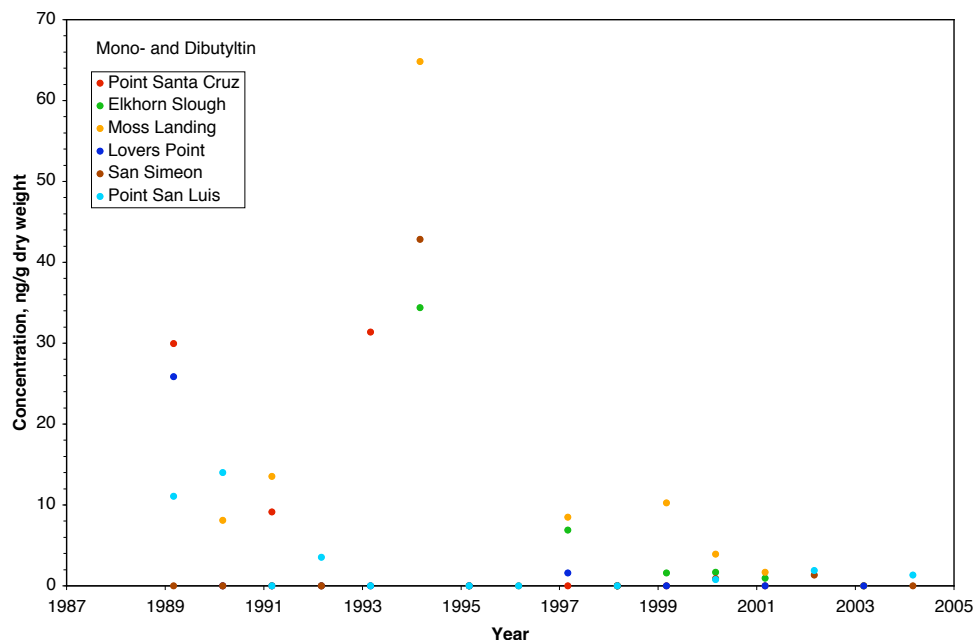


Figure 3. Concentrations of butyltins in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1989 and 2004.

Table 3. Results of linear regressions of lipid-normalized butyltin concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.

Site	R ²	Regression Results	
		Slope	p
Point Santa Cruz	0.0925	down	0.3928
Elkhorn Slough	0.3756	down	0.1062
Moss Landing	0.0312	down	0.5829
Lovers Point	0.0077	up	0.8097
San Simeon	0.0001	up	0.9820
Point San Luis	0.0870	down	0.4410

3.2.2 Chlordanes

3.2.2.1 Background

Chlordane was an insecticide first registered in the U.S. in 1948. Before 1978, chlordane was applied to a wide variety of uses, including agricultural crops, lawns and gardens. It was regularly used to control turf insects on golf courses (Baskin C.G., 1975; Miami-Dade County Department of Environmental Resource Management, 2002). From 1983 to 1988, chlordane's only approved use was for controlling termites in homes and the registration of chlordane for

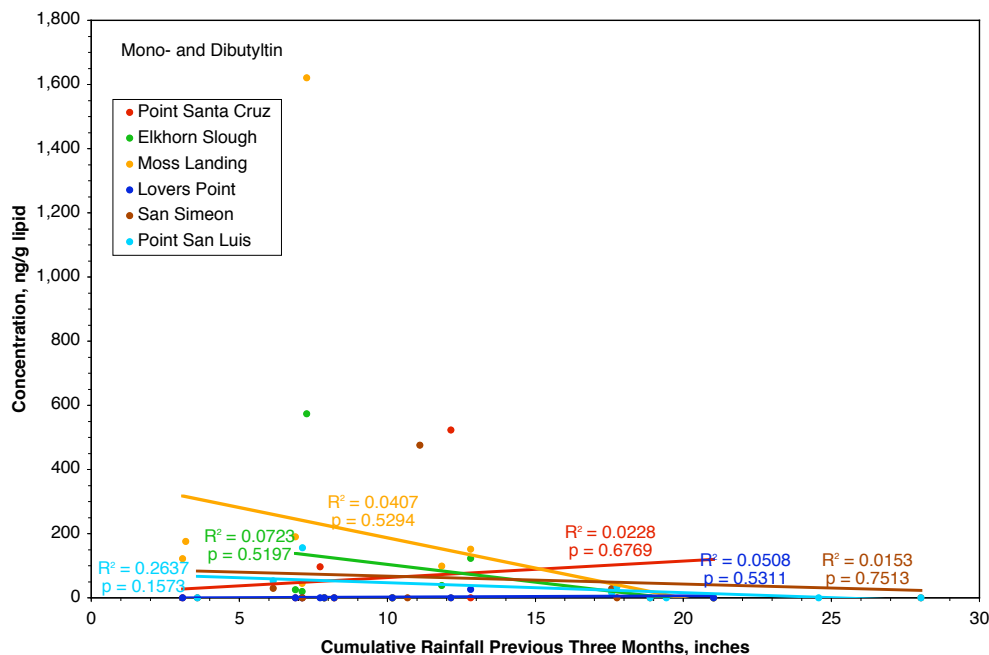


Figure 4. Relationship between lipid-normalized butyltin concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites. Rainfall data from Salinas were used for Point Santa Cruz, Elkhorn Slough, Moss Landing and Lovers Point. Rainfall data from San Luis Obispo were used for Point San Luis and San Simeon.

commercial production, delivery, sale and use in the United States was canceled in April 1988 (Agency for Toxic Substances and Disease Registry, 1994).

Chlordane is a mixture of compounds, primarily including *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, oxychlordane, heptachlor and heptachlor epoxide. It is relatively insoluble in water and required mixing with a wetting agent or emulsifier in order to be sprayed. The half-life of chlordane in cropped and fallow sandy loam has been measured at 93.2 and 154 days, respectively (Agency for Toxic Substances and Disease Registry, 1994). LOAEL doses in rats have ranged from 40 mg/kg/day to 590 mg/kg/day. The oral dose below which there was no observed adverse effect (NOAEL) for immunosuppression in mice was 8 mg/kg/day (Agency for Toxic Substances and Disease Registry, 1994). The LD₅₀ for acute toxicity in mink was observed at an oral dose of 63.84 mg/kg/day (Parametrix, 2001). In humans, chlordane exposure has been linked to breast tumors, liver damage and increased incidence of leukemia in agricultural workers. Chlordane has been found in human fat samples at concentrations of 0.03-0.4 mg/kg (Oregon State University, 1996a) and is also transmissible through lactation to nursing offspring.

3.2.2.2 Spatial Patterns

Most of the samples with high percentile concentrations of chlordanes came from the Elkhorn Slough and Salinas Valley areas, although high percentile sediment and fish samples were found in the Santa Cruz and Point San Luis areas and high percentile otter samples occurred at Half Moon Bay (Figure 5).

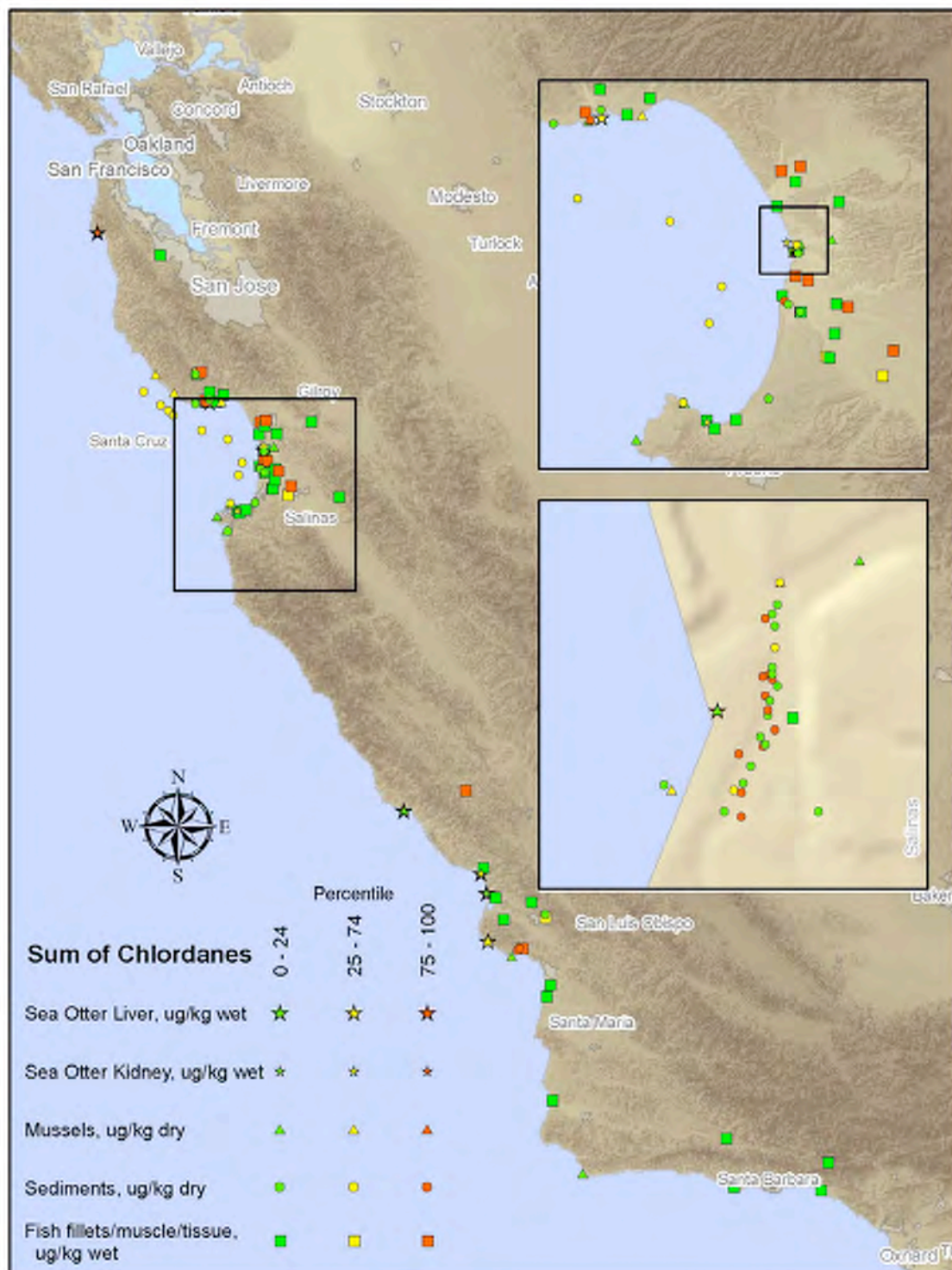


Figure 5. Spatial distribution and percentile of concentrations for samples in which chlordanes were analyzed.

3.2.2.3 Temporal Trends

Concentrations of chlordanes in mussels from most of the central California NS&T sites varied little among years, except for a very high concentration at Elkhorn Slough in 2000 (Figure 6). The direction of temporal trends in lipid-normalized concentrations was inconsistent among sites and none were significant (Table 4). Variation in chlordanes also was not related to rainfall at any of the sites (Figure 7).

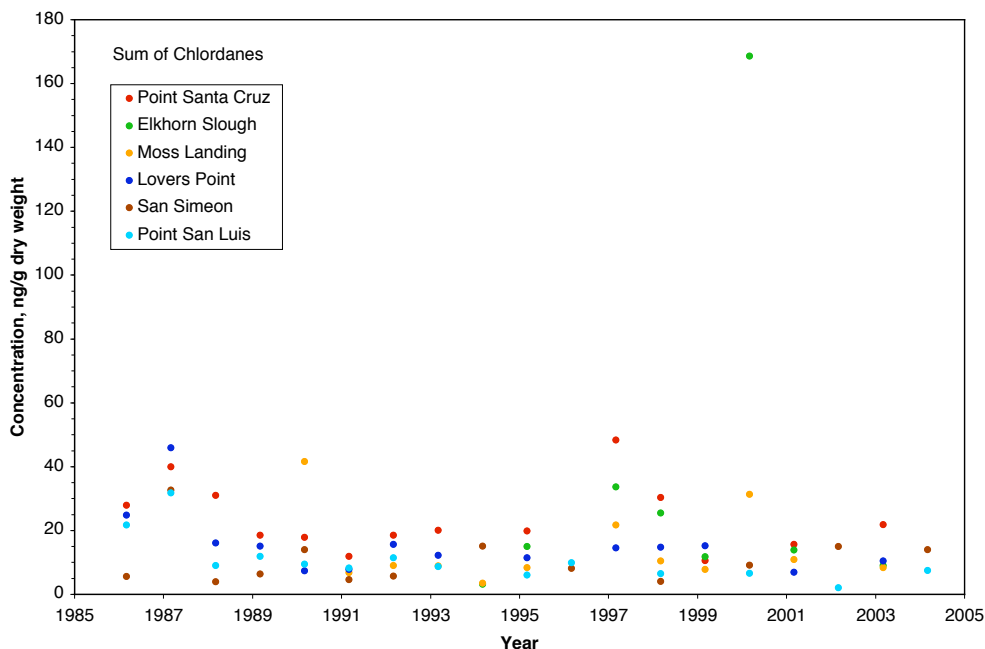


Figure 6. Concentrations of chlordanes in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1986 and 2004.

Table 4. Results of linear regressions of lipid-normalized chlordane concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch Program.

Site	R ²	Regression Results	
		Slope	p
Point Santa Cruz	0.0014	up	0.9032
Elkhorn Slough	0.0471	up	0.6057
Moss Landing	0.0142	up	0.7125
Lovers Point	0.0266	down	0.5944
San Simeon	0.0024	up	0.8786
Point San Luis	0.1546	down	0.2060

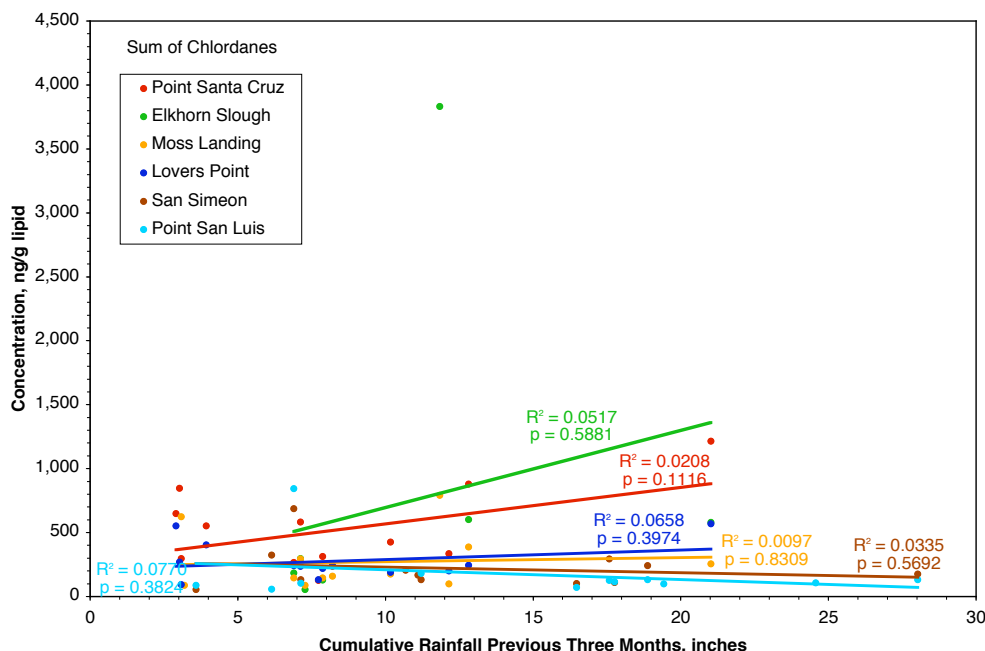


Figure 7. Relationships between lipid-normalized chlordane concentrations in mussels and rainfall at six NS&T sites. Rainfall data from Salinas were used for Point Santa Cruz, Elkhorn Slough, Moss Landing and Lovers Point. Rainfall data from San Luis Obispo were used for Point San Luis and San Simeon.

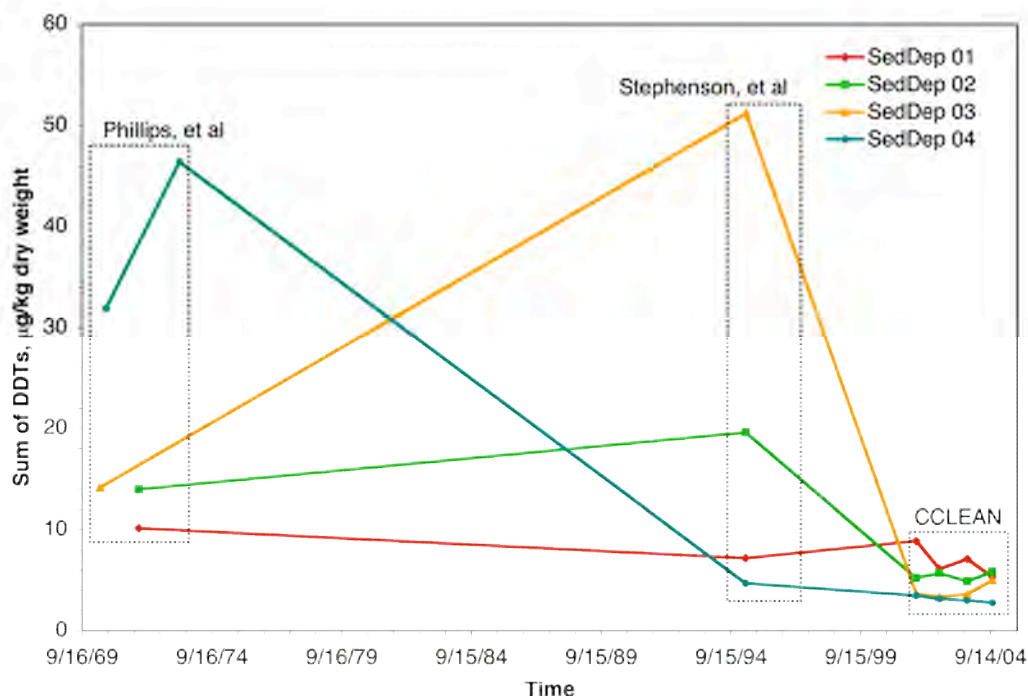
3.2.3 Dichlorodiphenyltrichloroethane

3.2.3.1 Background

Dichlorodiphenyltrichloroethane (DDT) was one of the most widely used pesticide chemicals used in the United States. It was first synthesized in 1874, but its effectiveness as an insecticide was only discovered in 1939 (U.S. Environmental Protection Agency, 1975). During World War II it was most widely used in combating the vector-borne diseases spread by mosquitoes such as typhus and malaria. Agricultural and commercial uses of DDT increased after 1945 with a total of approximately 1,350,000,000 pounds applied domestically during the next 30 years (U.S. Environmental Protection Agency, 1975). On December 2, 1970 all major responsibility of Federal regulation of pesticides went to the EPA and on December 31, 1973 the EPA cancelled all remaining crop uses of DDT (U.S. Environmental Protection Agency, 1975).

DDT is extremely persistent in the environment with a half-life ranging from 2-15 years and is immobile in most soils (Oregon State University, 1996b). The DDT breakdown products in soil are dichlorodiphenylethane (DDE) and dichlorodiphenyldichloroethane (DDD), which also are highly persistent in the environment and have similar chemical and physical properties. Because DDT is highly insoluble in water it is more likely to be retained to a greater degree in soils with higher proportions of organic matter. DDT has been widely detected in ambient surface water sampling in the United States at a mean level of 1 ng/L (Oregon State University, 1996b) probably associated with soil erosion. Despite the length of time since the use of DDT was

banned for crops in the U.S., CCLEAN has consistently reported discharges of all DDT isomers from area wastewater treatment plants and rivers, with river discharges, especially from the Pajaro and Salinas rivers, contributing 394 times the loads coming from wastewater during the period 2002-2006 (i.e., 24 kg versus 62 g) (CCLEAN, 2007). Moreover, sediment data for Monterey Bay spanning the period from 1970 to 2004 indicated only one out of four sites that were sampled over that time span exhibited a significant decline in DDT concentrations (Figure



8) (CCLEAN, 2006).

Figure 8. Temporal variation in DDT concentrations near four CCLEAN sites. Non-CCLEAN data are from (Phillips *et al.*, 1975) and (Stephenson *et al.*, 1997). Only SedDep 04 exhibited a significant decline in DDT concentrations since 1970.

Effects of DDT in the environment have historically been widespread, but have declined in the United States since its use was banned. Some bird species were exposed to DDT by preying on contaminated prey with body burdens of DDT. In some bird species chronic exposure caused detrimental effects on reproduction, such as eggshell thinning and embryo deaths (Oregon State University, 1996b). The LD₅₀ of orally administered DDT has been reported from 113-800 mg/kg in rats, to 300 mg/kg in guinea pigs, 400 mg/kg in rabbits and 500-750 mg/kg in dogs (Oregon State University, 1996b). Tests with minks, which provide a mustelid surrogate for sea otters, have indicated LD₅₀s for food-administered p,p-DDD, p,p-DDE and p,p-DDT of 94.39, 676.86, and 576.87 mg/kg body weight/day, respectively (Parametrix, 2001). Chronic exposure in animals has caused effects on the nervous system, liver, kidneys, and immune systems (Oregon State University, 1996b). DDT is equivocally a carcinogen in humans causing increased production of tumors mainly in the liver and lungs (Agency for Toxic Substances and Disease

Registry, 2002b). DDT is still used in some developing countries to combat mosquito-borne malaria. It has been detected in children from these areas and has been implicated in the early onset of puberty in young girls (Parent *et al.*, 2005).

3.2.3.2 Spatial Patterns

With the exception of two sea otter liver samples from near Half Moon Bay and Morro Bay, all samples with high percentiles of DDT concentrations came from Monterey Bay near or within Elkhorn Slough or the Salinas Valley (Figure 9). This pattern is consistent with sources of DDT that are associated with previous agricultural applications.

3.2.3.3 Temporal Trends

Concentrations of DDT in mussels collected in Elkhorn Slough and other nearby sites have shown substantial variation through time (Figure 10), but there have been no significant trends at any site (Table 4). Rainfall accounted for most of the temporal variation in lipid-normalized DDT concentrations at Elkhorn Slough and Point Santa Cruz (Figure 11), with significant positive relationships between DDT concentrations and rainfall at Elkhorn Slough, Moss Landing and Point Santa Cruz. Nevertheless, regressions of DDT/rainfall against time indicated that only at Point Santa Cruz has there been a decrease in the amount of DDT relative to rainfall ($R^2 = 0.3476$, $p = 0.0340$), suggesting that concentrations of DDT in the legacy agricultural sources nears Elkhorn Slough have not appreciably decreased with time.

3.2.4 Dieldrin

3.2.4.1 Background

Dieldrin is a chlorinated hydrocarbon, with a ring structure based on naphthalene. It was originally produced as an alternative to DDT. Dieldrin was first synthesized in the United States in 1948 by the epoxidation of aldrin. Sunlight and bacteria can degrade aldrin into dieldrin. Dieldrin was used as an insecticide and in mothproofing and is active through contact or ingestion. Both dieldrin and aldrin were used as insecticides on crops such as corn, cotton and citrus (Agency for Toxic Substances and Disease Registry, 2002a). The USDA cancelled all food-crop uses of aldrin and dieldrin in 1970. In 1972, EPA approved their below-ground insertion for killing termites, which continued until 1987 when the main manufacturer voluntarily cancelled the chemicals' registrations. EPA halted the remaining uses of aldrin and dieldrin in 1989.

Dieldrin is persistent in the environment and readily adheres to soil. Its half-life in temperate soils is approximately 5 years (Agency for Toxic Substances and Disease Registry, 2002a). LOAEL for oral doses in rats have ranged from 6 mg/kg/day to 168 mg/kg/day, depending on the selected toxicity endpoint. It has been found that dieldrin can act as a mutagen and has an LD₅₀ for oral ingestion by rats of 38 mg/kg (National Toxicology Program, 2000). The immunosuppressive effects of dieldrin in mice were documented by impaired antigen processing by macrophages that was observed at a food-borne dose of 0.065 mg/kg/day (Agency for Toxic Substances and Disease Registry, 2002a). The LD₅₀ for acute toxicity in mink was observed at an oral dose of 4.08 mg/kg/day (Parametrix, 2001).

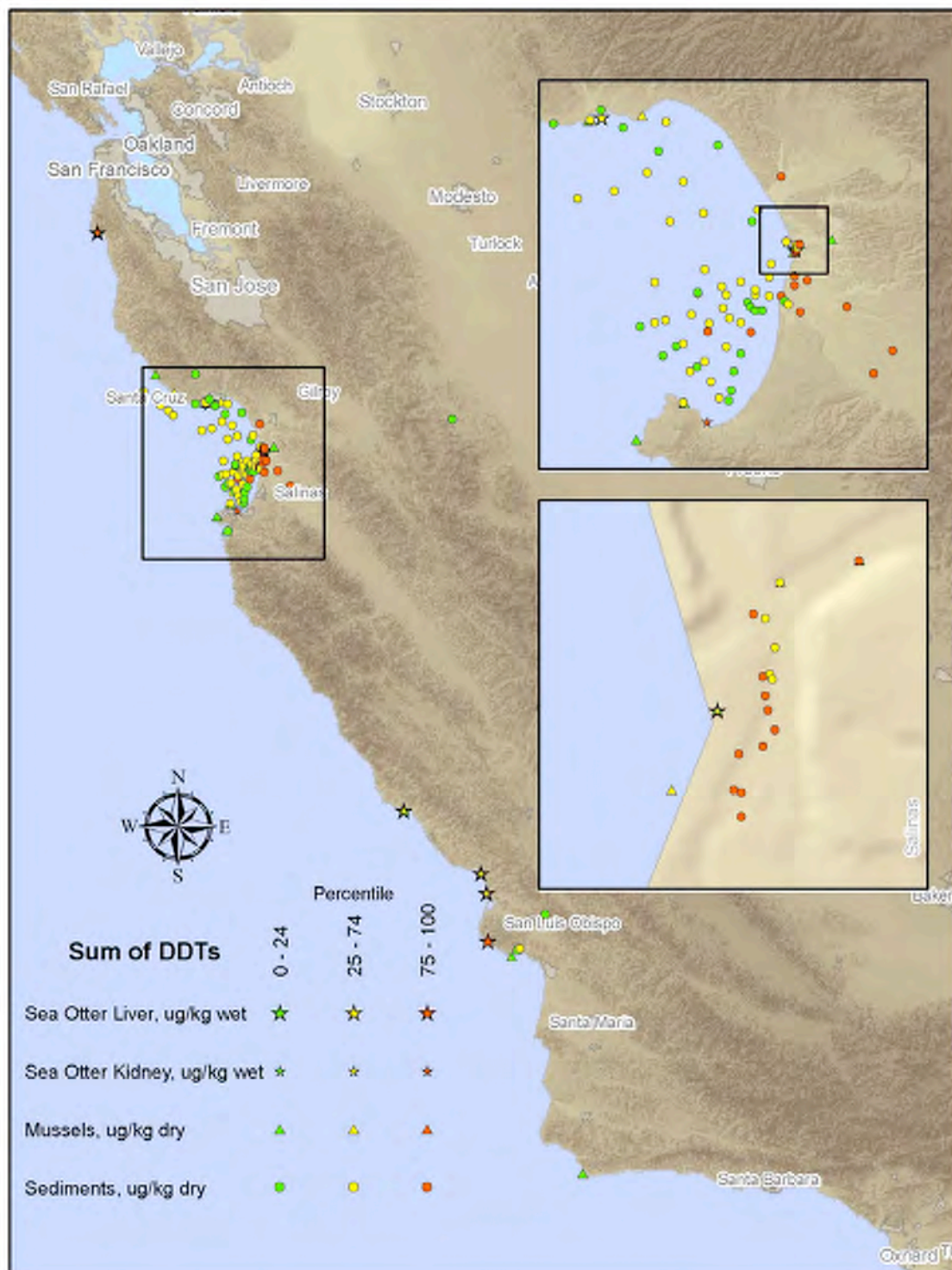


Figure 9. Spatial distribution and percentile of concentrations for samples in which DDT was analyzed.

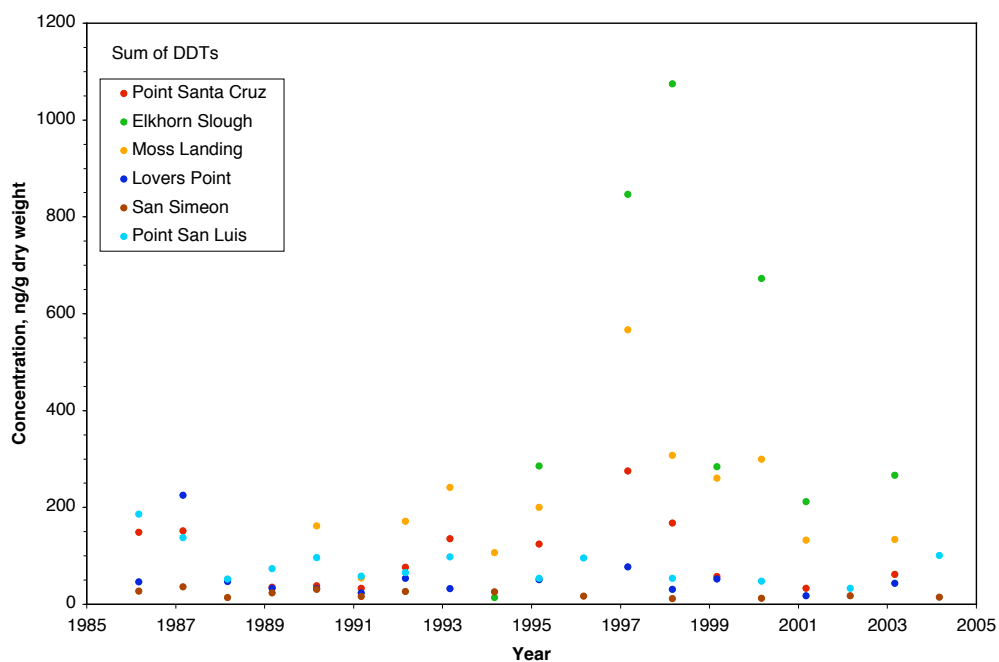


Figure 10. Concentrations of DDTs in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1986 and 2004.

Table 5. Results of linear regressions of lipid-normalized DDT concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.

Site	R ²	Regression Results	
		Slope	p
Point Santa Cruz	0.0176	up	0.6655
Elkhorn Slough	0.0066	up	0.8484
Moss Landing	0.1675	up	0.1864
Lovers Point	0.0304	down	0.5686
San Simeon	0.0891	down	0.3640
Point San Luis	0.0831	down	0.3636

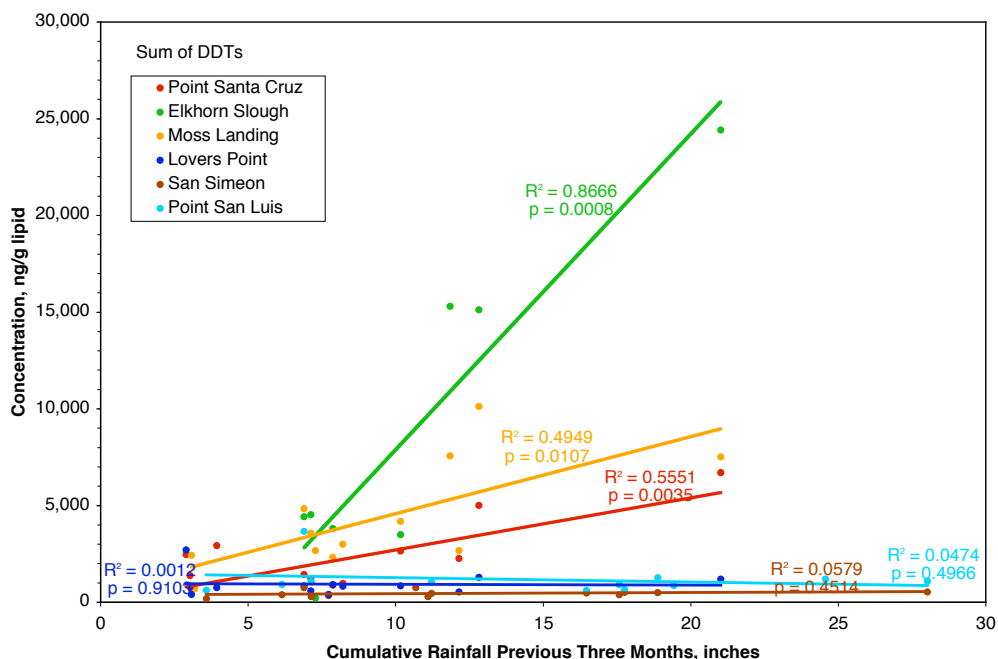


Figure 11. Relationships between lipid-normalized DDT concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites. Rainfall data from Salinas were used for Point Santa Cruz, Elkhorn Slough, Moss Landing and Lovers Point. Rainfall data from San Luis Obispo were used for Point San Luis and San Simeon.

3.2.4.2 Spatial Patterns

The samples with the highest percentile concentrations of dieldrin came from the Elkhorn Slough and Salinas Valley areas, except for high-percentile sediment samples from the mouth of the Carmel River and Point San Luis and a high-percentile fish sample in the drainage from Oso Flaco Lake (Figure 12). Recent analyses by the CCLEAN program have shown that mussels from numerous sites in Monterey Bay exceed the human health alert level for dieldrin established by the California Office of Environmental Health Hazard (Brodberg & Pollock, 1999) (Figure 13).

3.2.4.3 Temporal Trends

There was high interannual variability in concentrations of dieldrin in mussels sampled by NS&T in central California (Figure 14), but no long-term trends in lipid-normalized data (Table 6). Similar to the findings for DDT, much of the temporal variation in lipid-normalized dieldrin concentrations at Elkhorn Slough, Moss Landing and Point Santa Cruz was due to rainfall, with significant positive relationships between rainfall and dieldrin at all three sites (Figure 15). Regressions of lipid-normalized dieldrin/rainfall against time indicated that there has been no significant change in the relationship between rainfall and dieldrin concentrations (e.g., Elkhorn Slough $R^2 = 0.0246$, $p = 0.7108$). As was the case for DDT, this indicates there has been no change in the amount of dieldrin relative to rainfall, suggesting that concentrations of dieldrin in the legacy sources have not changed.

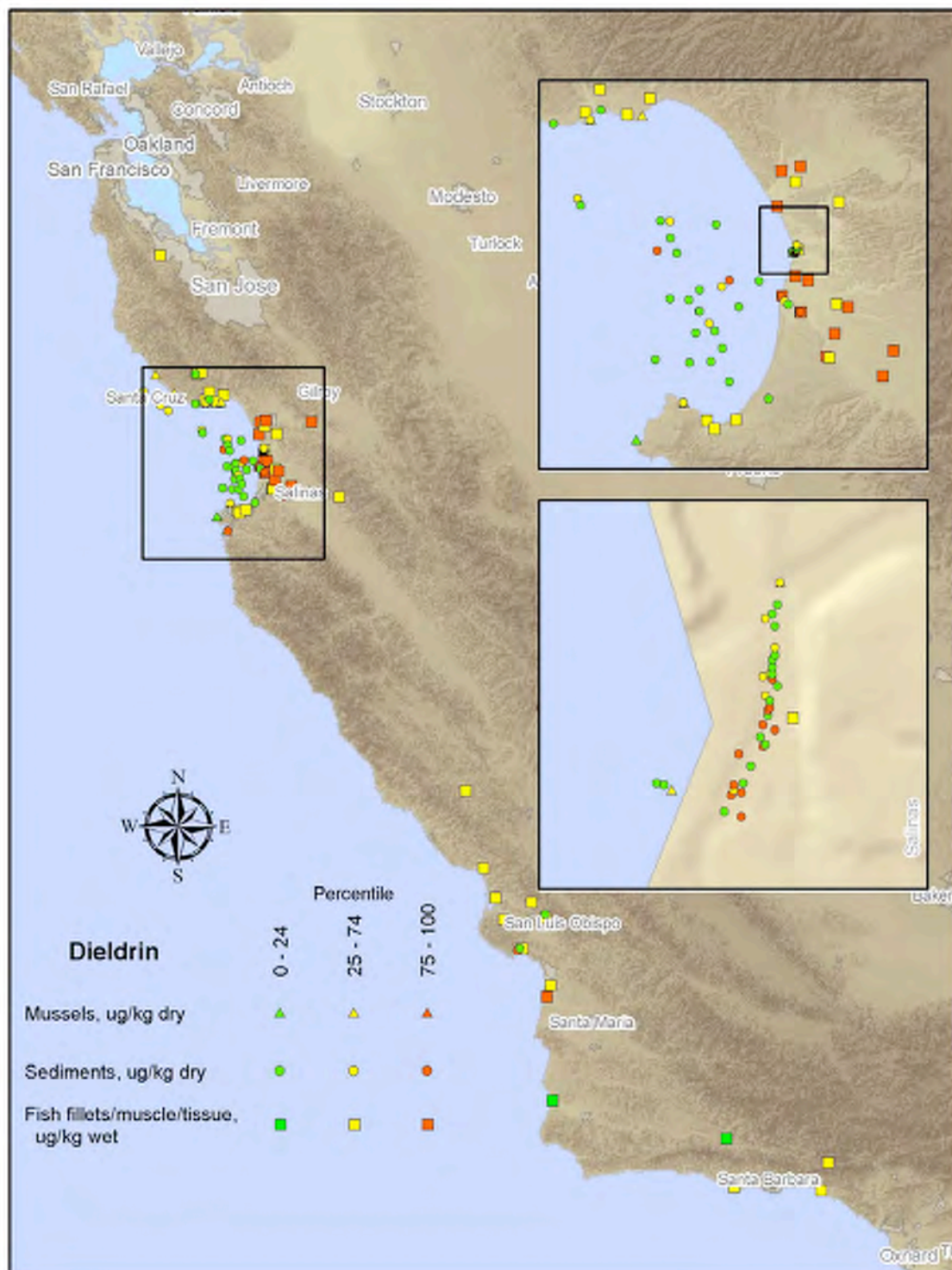


Figure 12. Spatial distribution and percentile of concentrations for samples in which dieldrin was analyzed.

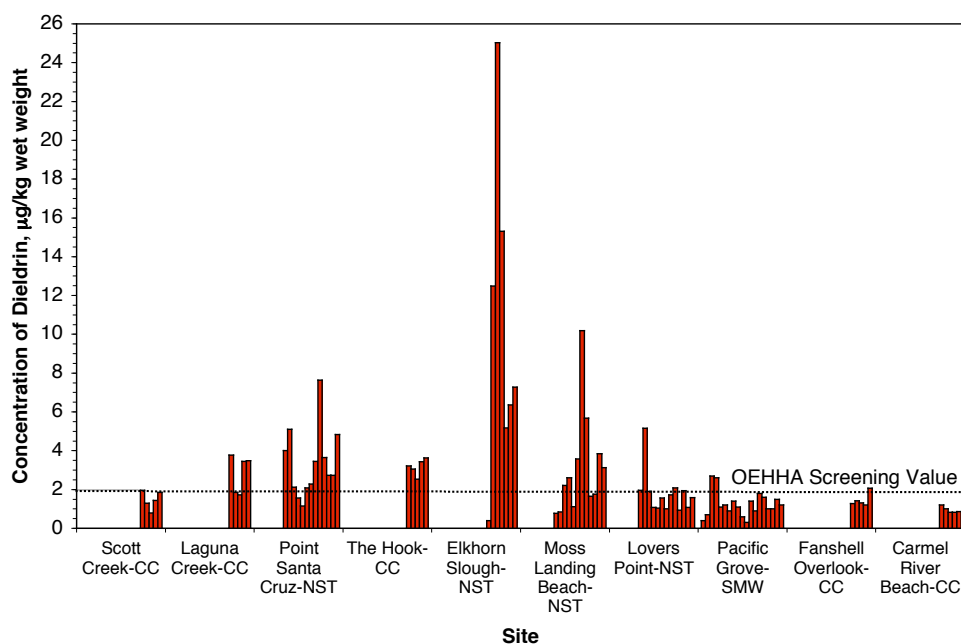


Figure 13. Comparison of dieldrin concentrations in mussels at Scott Creek, Laguna Creek, Point Santa Cruz, The Hook, Moss Landing Beach, Lovers Point, Pacific Grove, Fanshell Overlook and Carmel River Beach with the OEHHA human health screening value. Oldest samples are toward the left side of each site category and most recent samples are toward the right. CC = CCLEAN; NST = National Status and Trends Mussel Watch program; SMW = State Mussel Watch program (CCLEAN, 2007).

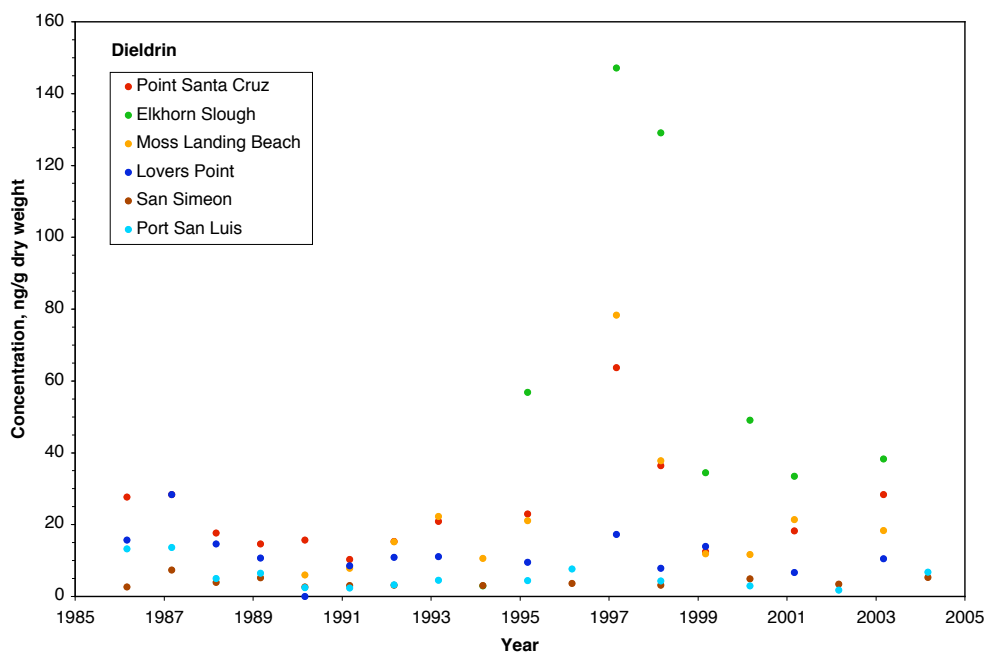


Figure 14. Concentrations of dieldrin in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1986 and 2004.

Table 6. Results of linear regressions of lipid-normalized dieldrin concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.

Site	R^2	Regression Results	
		Slope	p
Point Santa Cruz	0.1078	up	0.2733
Elkhorn Slough	0.0011	down	0.9391
Moss Landing	0.1137	up	0.2838
Lovers Point	0.0083	up	0.7669
San Simeon	0.0097	up	0.7604
Point San Luis	0.0943	down	0.3316

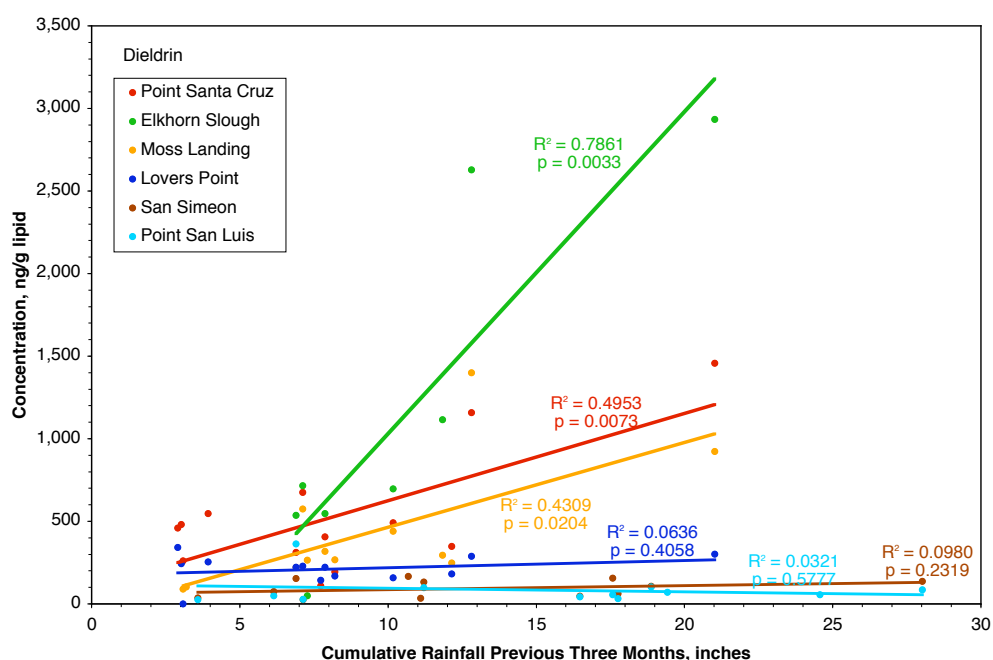


Figure 15. Relationship between lipid-normalized dieldrin concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites. Rainfall data from Salinas were used for Point Santa Cruz, Elkhorn Slough, Moss Landing and Lovers Point. Rainfall data from San Luis Obispo were used for Point San Luis and San Simeon.

3.2.5 Polynuclear Aromatic Hydrocarbons

3.2.5.1 Background

PAHs consist of a group of over 100 compounds that are present in crude oil, coal and other petroleum products. They also are formed during the incomplete oxidation of garbage, or other organic substances, such as wood, tobacco or charbroiled meat (Agency for Toxic Substances and Disease Registry, 1995). Chemically, PAHs are composed of five- or six-sided fused carbon rings, with hydrogen atoms attached to available bonds on the carbon atoms. They range in complexity from biphenyl, with two rings, to indeno[1,2,3-cd]pyrene, with six rings. In addition, methyl groups can be attached to the carbon atoms of some PAHs, instead of hydrogen atoms, providing dozens of alkylated compounds. PAHs are released to the environment primarily from volcanoes, forest fires, burning coal, motor vehicle exhaust and oil spills. There also are numerous natural oil seeps in central California (United States Geological Survey, 2001).

PAHs tend to not be as persistent in the environment as chlorinated hydrocarbons. Most PAHs can be broken down by microorganisms in soil or water after a period of time. Laboratory studies have shown that the rate of degradation of PAHs depends on the number of rings. Two-ring PAHs in sandy soils have half-lives of approximately 2 days. Three-ring PAHs in sandy soil have half-lives of 16–134 days, whereas four- to six-ring PAHs generally have half-lives >200 days (Agency for Toxic Substances and Disease Registry, 1995).

PAHs induce the P450-1A enzyme system in vertebrates and are relatively easily metabolized. Consequently, high body burdens of PAHs normally are found only in acute situations, such as oil spills. The toxic effects of PAHs differ among the individual compounds, with NOAEL for oral doses in mice ranging from 10 mg/kg/day to 1000mg/kg/day. PAHs have been shown to be related to increased cancer risks in humans and the NOAEL oral dose related to gastric tumors in mice is 1.3 mg/kg/day (Agency for Toxic Substances and Disease Registry, 1995).

Investigations related to the *Exxon Valdez* oil spill found significantly higher mortality rates, compared to controls, for salmon embryos exposed to a PAH concentration 1.0 µg/L derived from very weathered oil (Heintz *et al.*, 1999). Moreover, salmon exposed to a PAH concentration of 5.4 µg/L experienced a 15% decrease in marine survival compared to unexposed salmon (Heintz *et al.*, 2000).

3.2.5.2 Spatial Patterns

The samples with the highest percentile concentrations of PAHs came from Elkhorn Slough and the Monterey Peninsula, although a relatively small number of programs report total PAHs, which provided a correspondingly smaller number of sample points (Figure 16).

3.2.5.3 Temporal Trends

Most sites displayed little variation through time, although high PAH concentrations were periodically measured at Elkhorn Slough, Moss Landing and Point San Luis (Figure 17). Marginally significant increases in lipid-normalized PAHs have occurred over time at Point Santa Cruz, Moss Landing and Lovers Point (Table 7). The very high concentration at Point San Luis in 1991 predates the oil spill from the Unocal pipeline, which occurred in August 1992. None of the sites exhibited a significant relationship between PAHs and rainfall (Figure 18).

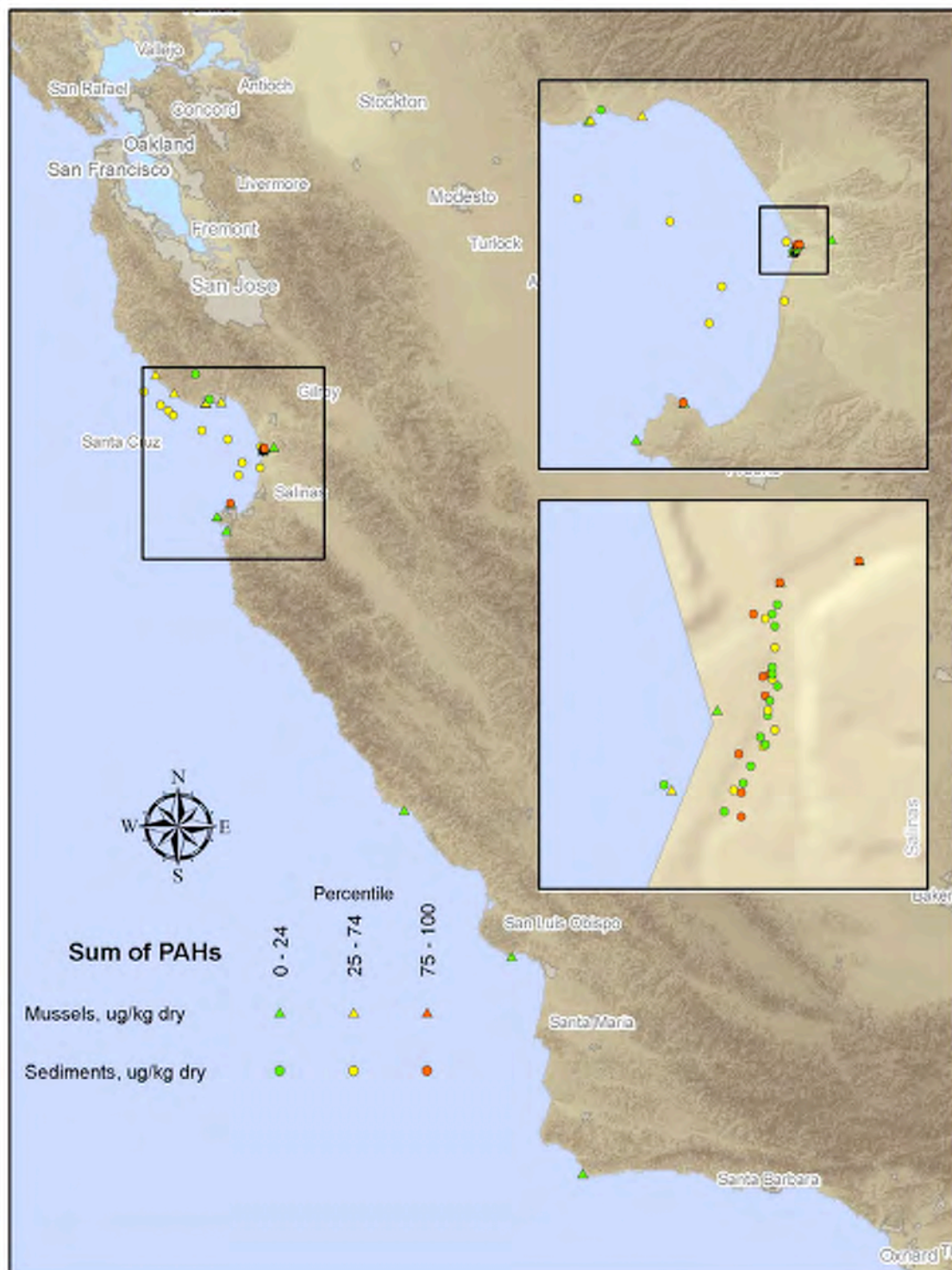


Figure 16. Spatial distribution and percentile of concentrations for samples in which PAHs were analyzed.

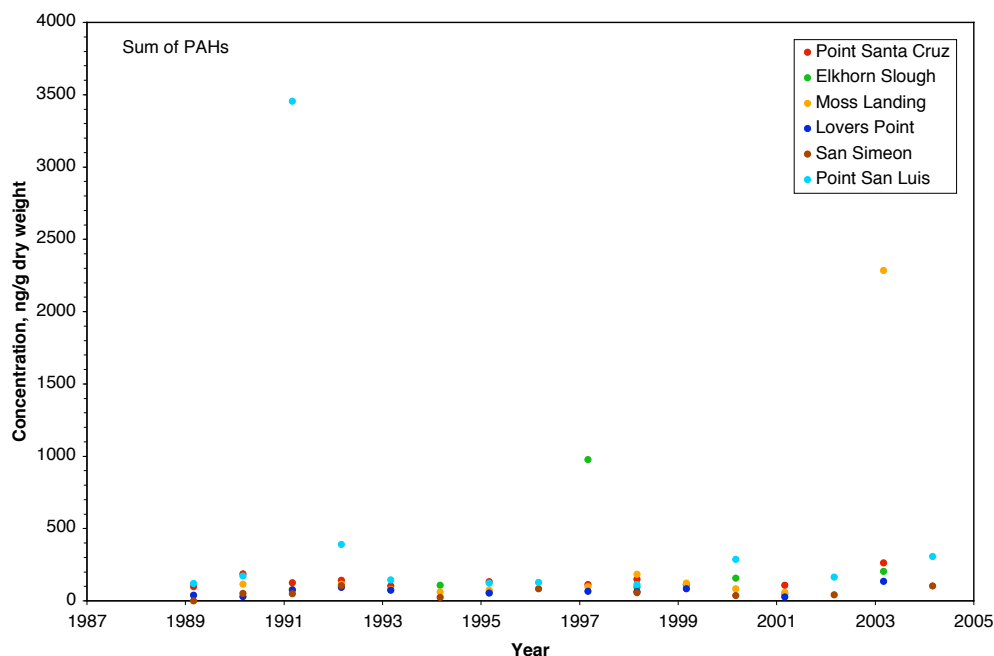


Figure 17. Concentrations of PAHs in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1989 and 2004.

Table 7. Results of linear regressions of lipid-normalized PAH concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.

Site	R ²	Slope	Regression Results
			p
Point Santa Cruz	0.3150	up	0.0914*
Elkhorn Slough	0.0107	down	0.8077
Moss Landing	0.2965	up	0.0672*
Lovers Point	0.3522	up	0.0705*
San Simeon	0.1711	up	0.2684
Point San Luis	0.0970	down	0.4147

* = Result is marginally significant (p = 0.10–0.05)

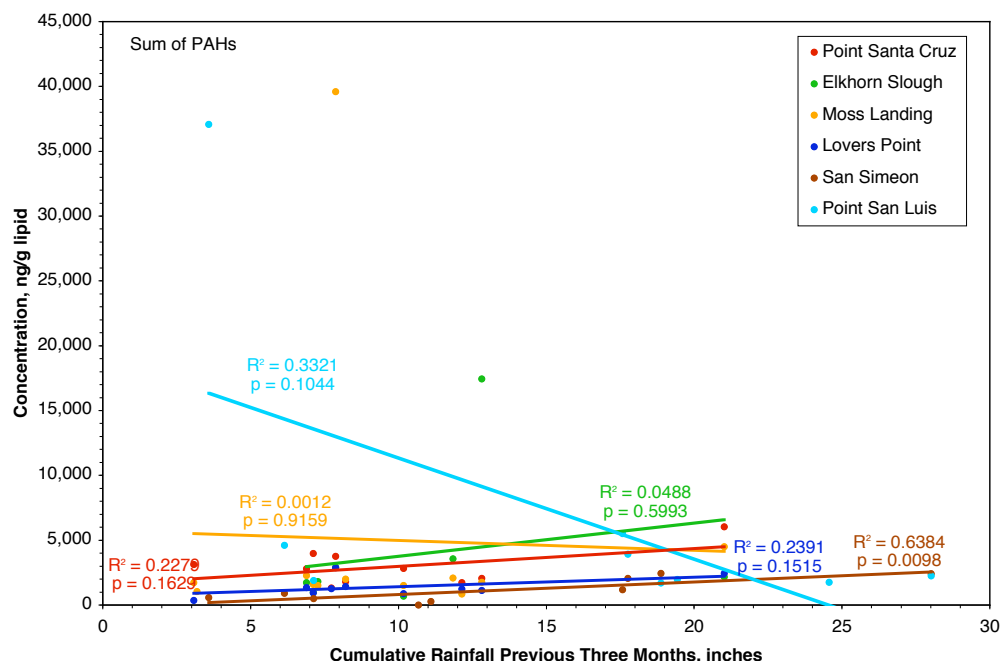


Figure 18. Relationship between lipid-normalized PAH concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites. Rainfall data from Salinas were used for Point Santa Cruz, Elkhorn Slough, Moss Landing and Lovers Point. Rainfall data from San Luis Obispo were used for Point San Luis and San Simeon.

3.2.6 Polychlorinated Biphenyls

3.2.6.1 Background

PCB's are oily or waxy substances that are relatively non-flammable, environmentally stable, have a high boiling point and are good electrical insulators. For these reasons, they were used in numerous industrial and commercial applications. The first PCB-like chemical was discovered in 1865 as a by-product of coal tar but it was not until 1881 that the first PCB was synthesized (Katers, 2004). By 1914 enough PCB's had already been released into the environment to leave measurable amounts in the feathers of birds in museums today (Katers, 2004). PCBs were manufactured in the U.S. between 1929 and 1977. Annual U.S. production peaked in 1970 at 39,000,000 kg (Agency for Toxic Substances and Disease Registry, 2000).

There are 209 PCB congeners that differ according to the number and position of chlorine atoms attached to a biphenyl base. PCBs often were sold as products called Aroclors, which differed in the proportions of individual congeners they contained. The last two digits of each Aroclor name indicates the approximate percent weight of chlorine it contained. Each Aroclor had slightly different physical properties and certain Aroclors predominated in different types of uses (Table 8). More than 1.5 billion pounds of PCB's were manufactured in the U.S. prior to the halt in production in 1977 (U.S. Environmental Protection Agency, 2006). Widespread concern over the toxicity and persistence of PCB's in the environment led the Congress in 1976

to enact Section 6(e) of the Toxic Substances Control Act (TSCA) that outlined prohibitions of the manufacture, processing and distribution in commerce of PCB's (U.S. Environmental Protection Agency, 2006).

Table 8. Uses of various Aroclors (Agency for Toxic Substances and Disease Registry, 2000).

End use	Aroclor							
	1016	1221	1232	1242	1248	1254	1260	1268
Capacitors	*	*				*		
Transformers				*		*	*	
Heat transfer				*				
Hydraulics/lubricants								
Hydraulic fluids			*	*	*	*	*	
Vacuum pumps					*	*		
Gas transmission turbines		*		*				
Plasticizers								
Rubbers		*	*	*	*	*		*
Synthetic resins					*	*	*	*
Carbonless paper				*				
Miscellaneous:								
Adhesives		*	*	*	*	*		
Wax extenders				*		*		*
Dedusting agents						*	*	
Inks						*		
Cutting oils						*		
Pesticide extenders						*		
Sealants and caulking compounds						*		

The environmental persistence of PCB congeners differs according to the number of chlorine atoms. The reported half-life of PCB18 (three chlorines) ranges from 0.02–0.03 years, while the half-life of PCB170 (seven chlorines) ranges from 3.9–71 years (Agency for Toxic Substances and Disease Registry, 2000).

Determining the toxicity of PCBs is problematic because they are complex mixtures of different compounds. In general, the most toxic congeners are those that have no or one chlorine atom in the *ortho* position on the biphenyl rings, some of which approach dioxins in toxicity. The LOAEL in rats exposed through PCB-laced food ranged from 0.74 µg/kg/day to 425 µg/kg/day for hepatic effects (Agency for Toxic Substances and Disease Registry, 2000). Moreover, immunosuppression caused by PCB mixtures in experiments on monkeys has been observed at doses ranging from 5 µg/kg/day to 7.5 µg/kg/day (Agency for Toxic Substances and Disease Registry, 2000). PCBs are endocrine disruptors, with reported effects on the thyroid and both agonistic and antagonistic effects of estrogen production.

3.2.6.2 Spatial Patterns

As with DDT, most of the samples with high percentile concentrations of PCBs came from the Elkhorn Slough and Salinas Valley area (Figure 19). Nevertheless, there were relatively high sediment concentrations of PCBs indicated for Santa Cruz and Point San Luis and high sea otter liver concentrations indicated for the Half Moon Bay area.

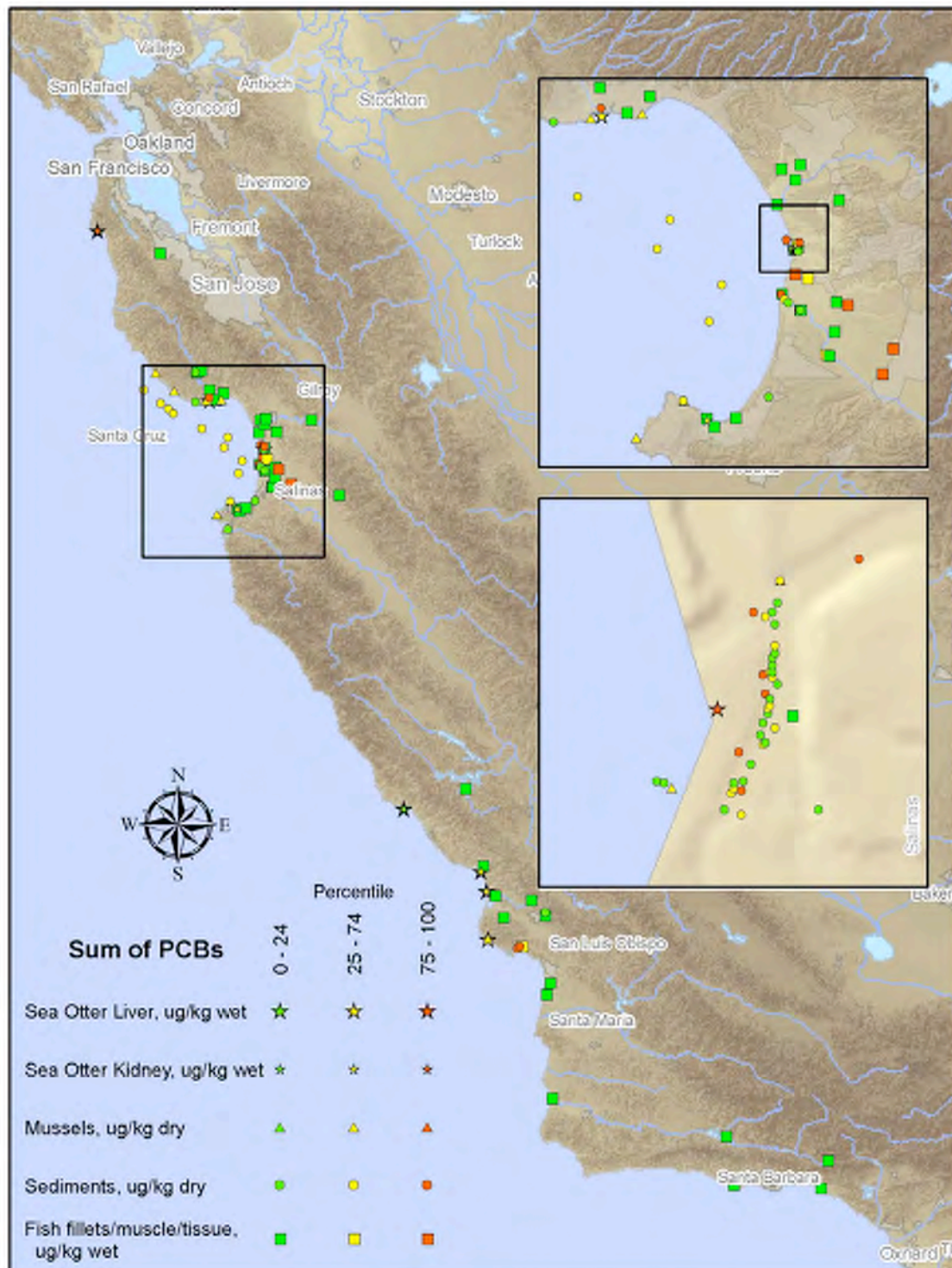


Figure 19. Spatial distribution and percentile of concentrations for samples in which PCBs were analyzed.

3.2.6.3 Temporal Trends

Concentrations of PCBs in mussels from all the central California NS&T sites have exhibited high interannual variability, with Elkhorn Slough and Point San Luis being the most variable (Figure 20). There has been a marginally significant increase in lipid-normalized PCBs at Moss Landing (Table 9). There were significant relationships between rainfall and lipid-normalized PCB concentrations in mussels at Point Santa Cruz and Lovers Point and marginally significant relationships between rainfall and PCBs at Elkhorn Slough and Moss Landing (Figure 21). Nevertheless, regressions of lipid-normalized PCB/rainfall against time revealed no significant changes in the relationship between rainfall and PCB concentrations at any site (e.g., Lovers Point $R^2 = 0.0725$, $p = 0.4233$), which suggests no attenuation in the terrestrial background of PCBs at these sites.

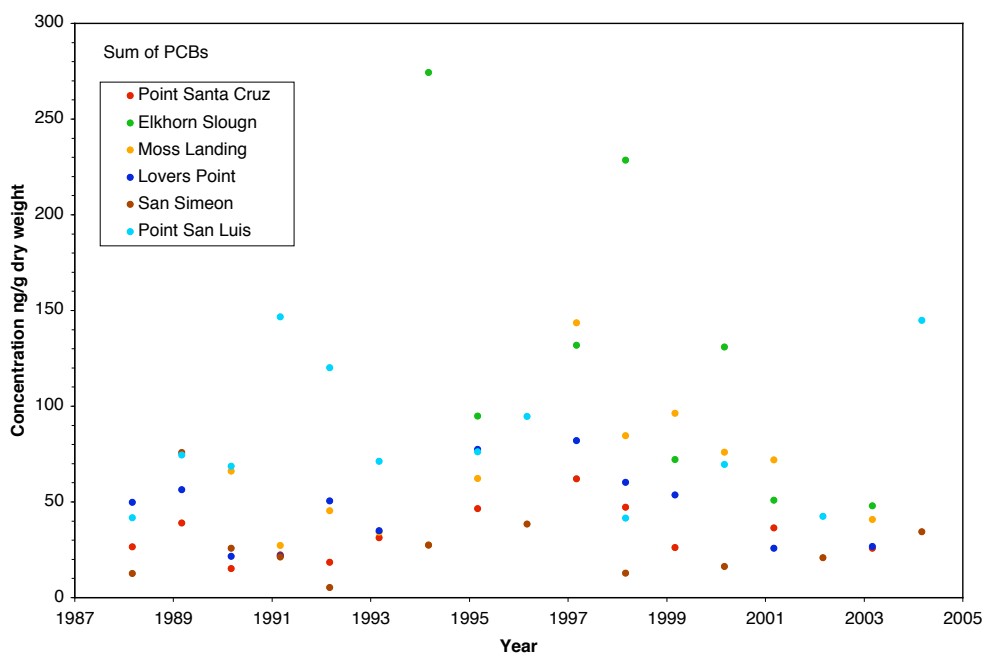


Figure 20. Concentrations of PCBs in mussels analyzed by the National Status and Trends Mussel Watch program from six sites between 1988 and 2004.

Table 9. Results of linear regressions of lipid-normalized PCB concentration in mussels versus time at six sites monitored by National Status and Trends Mussel Watch program.

Site	R^2	Regression Results	
		Slope	p
Point Santa Cruz	0.1503	up	0.2387
Elkhorn Slough	0.2329	down	0.2258
Moss Landing	0.2874	up	0.0724*
Lovers Point	0.1043	up	0.3326
San Simeon	0.0322	down	0.6200
Point San Luis	0.0714	up	0.4555

* = Result is marginally significant ($p = 0.10-0.05$)

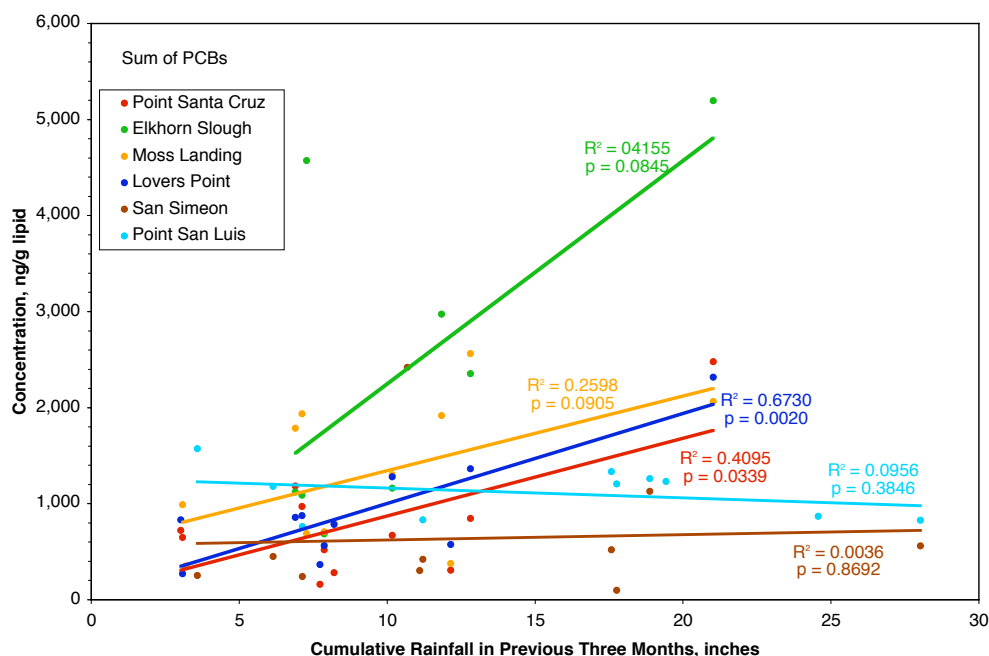


Figure 21. Relationships between lipid-normalized PCB concentrations in mussels and rainfall at six National Status and Trends Mussel Watch program sites. Rainfall data from Salinas were used for Point Santa Cruz, Elkhorn Slough, Moss Landing and Lovers Point. Rainfall data from San Luis Obispo were used for Point San Luis and San Simeon.

4.0 DISCUSSION

The analysis of spatial and temporal patterns in contaminants that could affect sea otters has been hampered by a general lack of consistent long-term data and differing analytical and reporting conventions among programs. Nevertheless, analysis of the available data has shown the highest concentrations of many of the contaminants in the database have occurred in the Elkhorn Slough and Salinas Valley areas and are probably associated with legacy agricultural applications. High percentile samples also were noted in populated and industrial areas, such as Santa Cruz, Monterey and Point San Luis. No statistically significant declines have been observed in lipid-normalized mussel data from NS&T over the last 15–20 years and marginally significant increases have been noted for PAHs and PCBs at some sites. Moreover, significant relationships between rainfall and lipid-normalized concentrations of dieldrin, DDT and PCB in mussels from Elkhorn Slough, Moss Landing and Point Santa Cruz suggest storm runoff as the pathway into the marine environment for some contaminants. Steeper slopes of regressions of lipid-normalized contaminant concentrations against rainfall in Elkhorn Slough are consistent with erodible legacy sources in surrounding watersheds. Only for DDT at Point Santa Cruz has there been a significant decrease through time in the amount of contaminant relative to rainfall. For other contaminants and other locations, there has been no measurable attenuation in the legacy

contaminants. This is surprising, given that most of the organic contaminants considered in this study have been banned from use for 20–30 years.

There are numerous processes and human activities that could account for high contaminant concentrations in the Monterey Bay National Marine Sanctuary. These processes include agricultural practices, urbanization with increasing areas of impervious surfaces, and recreational activities. Agricultural and rural lands have different hydrological processes from urbanized areas, since most of the land is not developed into impervious surfaces. The CCLEAN program has demonstrated that discharges from the Pajaro and Salinas rivers contribute large loads of legacy agricultural and other POPs to Monterey Bay. For example, an average of nearly 50 kg per year of PAHs and 5 kg per year of DDTs are discharged from the rivers around Monterey Bay.

Urban runoff also is widely acknowledged as a source of contaminants to aquatic systems (U.S. Environmental Protection Agency, 2000). Petroleum hydrocarbons from motor vehicles, current and historic residential and municipal pesticide use, degraded electrical equipment and accidental spills all contribute to POPs in urban runoff. Construction and installation of impervious surfaces like streets and parking lots increases the chances of contaminants reaching the ocean, rather than being kept on land, by increasing runoff rates and attendant resuspension of sediment particles. Permitting practices that allow inappropriate or conflicting land uses adjacent to waterways also are problematic. There currently are no monitoring programs measuring a wide range of POPs in urban watersheds that discharge directly into the ocean around Monterey Bay.

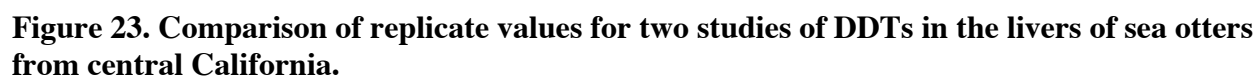
Many POPs, especially chlorinated pesticides, are found predominantly in the particulate phase, rather than in the dissolved phase, from both riverine and urban runoff sources (Leatherbarrow *et al.*, 2005; McKee *et al.*, 2006). Leatherbarrow *et al.* (2005) found significant positive correlations in the lower Sacramento-San Joaquin Delta between concentrations of suspended sediments and chlorinated pesticides, but not for PCBs, whereas McKee *et al.* (2006) found significant positive correlations between suspended sediment concentrations and PCBs and polybrominated diphenylethers (PBDEs) in the Guadalupe River in San Jose, CA. Dr. Donald Weston of University of California, Berkeley, has found that cultivated soils of the Salinas Valley are especially erodible, when compared to those in the Central Valley of California (personal communication). Consequently, sedimentation from flooding and erosion of agricultural and urban lands is probably a major pathway for contaminants entering aquatic ecosystems. These findings suggest that actions taken to reduce concentrations of suspended sediments in runoff from all sources could reduce loads of organic contaminants into the Sanctuary.

Marinas and boating recreation also can contribute to the loads of contaminants in the Bay through maintenance and construction of boats and boating facilities, as well as incidental spills directly into the water. Boatyard and underwater hull cleaning including pressure washing to remove marine growth on the hulls of ships done in boatyards or physical removal by divers underwater removes heavy metals and other toxics to the adjacent environment. Petroleum products are common toxics in harbors due to accidental or illegal discharge or improper disposal of fuel and oil, bilge water, sewage discharge, vessel flooding, and parking lot or boatyard runoff.

Permitted discharges of wastewater also contribute to contaminants. Permitted discharges receive considerable regulatory scrutiny and are a much smaller source of POPs than are the rivers. For example, CCLEAN has reported that rivers discharge many times more DDTs and other POPs to Monterey Bay than do permitted wastewater discharges. Nevertheless, there are other emerging contaminants of concern, such as PBDEs and endocrine disrupting compounds, that are not widely measured, and which have been measured in high concentrations in wastewater (North, 2004).

The general absence of declines in POPs reported in this project conflicts with some other studies. Many investigators have reported declines in DDTs in wildlife over the last 30 years, whereas PCBs, depending on the mixture of congeners, have not consistently shown similar declines. PCB degradation is complex due to the existence of different congeners and the different chemical properties and interactions with the environment of each congener or mix of congeners. The global inventory of PCB's in soils is greater than in surface waters for all congeners, with larger differences for highly chlorinated PCB's (Jurado *et al.*, 2004) but the ocean is enriched in lower chlorinated PCBs, probably because they are more soluble in water and, therefore, not as effectively removed by the settling of particulate matter as are those congeners with more chlorine atoms. Estimated global half lives of PCB congeners in water and sediment have ranged from 20 years for PCB 101 to 170 years for PCB 194 (Wania & Daly, 2002). Nevertheless, a recent study of PCBs and DDTs in sea lions off the coast of California reported mean PCB concentrations in California sea lions collected during 1991-1997 were 5 times higher than those measured in 2000 (Kannan *et al.*, 2004) and there were significantly higher concentrations of PCBs in central California sea lions than in those from the north or the south.

Historic declines in DDTs have been reported in some marine mammals. Kannan *et al* (2004) reported 10-fold declines in DDT concentrations in California sea lions between 1970 and 2000. Moreover, comparisons of historic DDT concentrations in sea otters from California also suggest substantial declines. A publication that was not found in time to include in this database reported DDT concentrations in 10 sea otters that stranded in central California in 1969 and 1970 (Shaw, 1971). Shaw (1971) reported total DDT residues in livers ranging from 0.032 ppm wet weight to 15 ppm wet weight. Shaw's mean value was 1.6–3.4 times higher than those from two more recent studies (Figure 22), which analyzed otters that died between 1988 and 1996 (Bacon *et al.*, 1999; Nakata *et al.*, 1998), with an R^2 of 0.6477 in the downward trend. Nevertheless, when replicate values in Shaw (1971) and Nakata *et al* (1998) are considered, it is apparent that the difference between the mean concentrations for these two studies was due to two 1970 otters with extremely high concentrations (Figure 23) and the differences between 1970 and 1994 are, in fact, not statistically significant ($p = 0.3427$). This suggests that maximum values in sea otters might be declining, but exposure of the overall population has not changed since before the agricultural application of DDT in the United States was halted in 1973.



On a regional scale, POPs may not show declines because of inputs from nearby sources or because of transport from distant locations. One such transportation pathway that is not normally considered is *via* migrating wildlife. For example, high concentrations of PCBs in wildlife from the Aleutian Archipelago appear to be due to local contamination from old military bases (Arctic Monitoring and Assessment Programme, 2004). Many wildlife species migrate from higher latitudes in the winter to lower latitudes in the summer and the Arctic Monitoring and Assessment Programme (2004) estimated that the total load of PCB's and DDT's contained in the Eastern Pacific stock of grey whales was 20-150 kg and 1-40 kg respectively. This estimate suggests that loads of POPs deposited in the Sanctuary in dead whale carcasses may not be trivial.

The general lack of declines in POPs observed in mussels in this study also is an indication of nearby, continuing discharges from large "reservoirs" of contaminated sediments. For example, CCLEAN data have shown high concentrations of the DDT isomer of DDTs in samples from the Salinas and Pajaro rivers (Figure 24), especially in wet-season samples (CCLEAN, 2006). In the environment, DDT degrades into DDE in aerobic conditions and into DDD in anaerobic conditions (Aislabie *et al.*, 1997). Leatherbarrow *et al* (2005) suggest that greater than 10% DDT isomers in total DDTs indicates recent inputs of undegraded DDT. Consequently, consistently high proportions of the DDT isomer in wet-season samples from the Salinas and Pajaro rivers indicate fresh DDT is being transported into the Sanctuary and the high proportions of DDE indicate that whatever degradation is taking place is occurring in aerobic conditions, probably in surficial sediments or the water.

Concentrations of some POPs in mussels and sediments in Monterey Bay are comparable to, or exceed, those found in San Francisco Bay. San Francisco Bay has been listed on the State of California 303(d) list as impaired due to concentrations of legacy pesticides, including DDTs, chlordanes and dieldrin. Using dry-weight concentrations of DDTs as an example, concentrations in Monterey Bay sediments along the 80-meter contour are roughly twice the average concentration in San Francisco (Figure 25). DDT concentrations in mussels in the Monterey Bay area are comparable to those measured in transplanted mussels studies in San Francisco Bay (Figure 26).

Sea otters are exposed to POPs through their prey. Suspension-feeding prey organisms, primarily bivalve mollusks, concentrate POPs in their tissues because they do not have efficient metabolic mechanisms for breaking down or depurating these compounds. Consequently, they have much higher concentrations of contaminants than are found in either the water or sediments. For example, CCLEAN typically reports DDT concentrations in rivers from <5 parts per trillion to 55 parts per trillion. In sediments, the concentration of DDTs ranges from 3 parts per billion to 9 parts per billion and in wet-season mussel samples it ranges from 16 parts per billion to over 110 part per billion. While we are not aware of published estimates of the primary route of contaminant accumulation in California mussels, *Mytilus californianus*, the primary dietary uptake of contaminants by zebra mussels, *Dreissena polymorpha*, is through ingestion of suspended sediment particles, although at very high water concentrations, direct uptake from the water is greater than from food (Bruner *et al.*, 1994). Consequently, it is suggested that ingestion by mussels and other bivalves of contaminated suspended sediments is an important pathway of contaminants to sea otters that prey on suspension feeders.

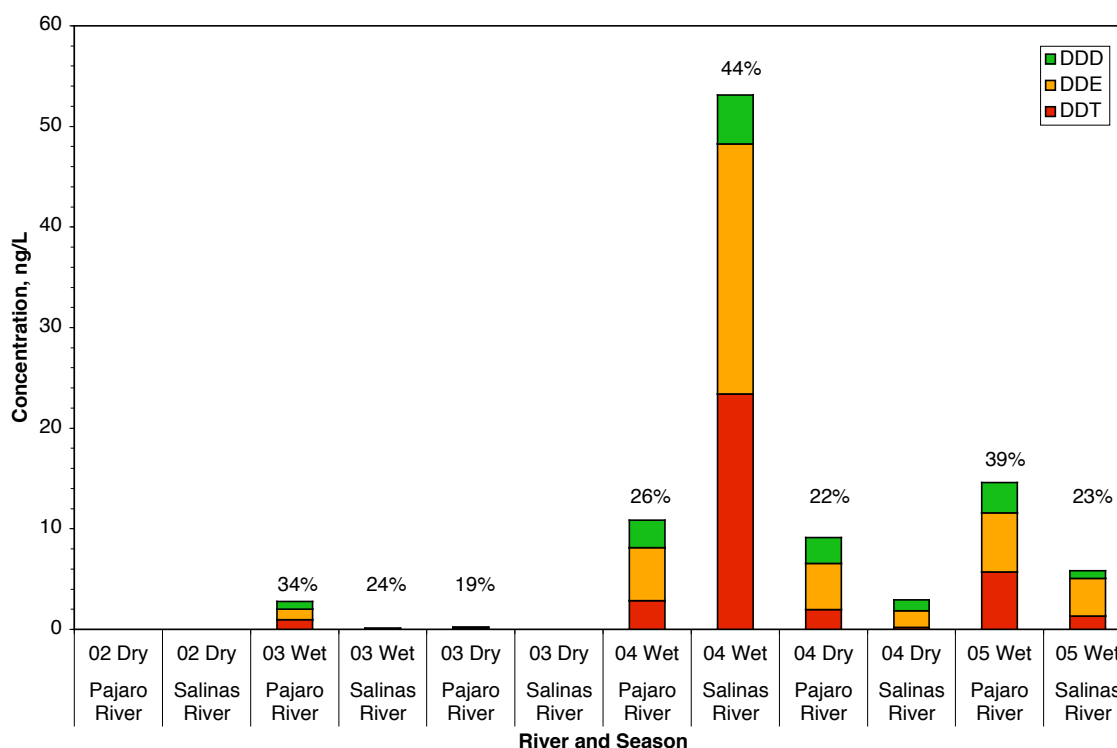


Figure 24. Concentrations of the DDD, DDE and DDT isomers in water samples analyzed by CCLEAN from the Pajaro and Salinas rivers. Percent of total DDTs contributed by DDT isomers are indicated above the bars.

The continuing discharges of POPs from rivers is a concern, especially as they are likely a major source of contaminants accumulated by suspension feeders and transferred to sea otters. Management practices are being implemented on irrigated agricultural lands that should reduce the runoff of contaminated sediments into rivers, streams and the ocean, although improvements in water quality from such practices are not yet apparent. Moreover, the potential negative effects of these POPs on sea otters is still being investigated in a large-scale study by CCLEAN, California Department of Fish and Game and University of California, Davis funded by Proposition 13 funds. Consequently, it is important to continue measuring POPs in rivers, sediments and mussels in order to determine whether these management practices ultimately reduce POP concentrations in the Sanctuary. The load of POPs from urban runoff into the ocean also is an important data gap that should be filled to provide a more complete picture of contaminant sources and loads into the Sanctuary.

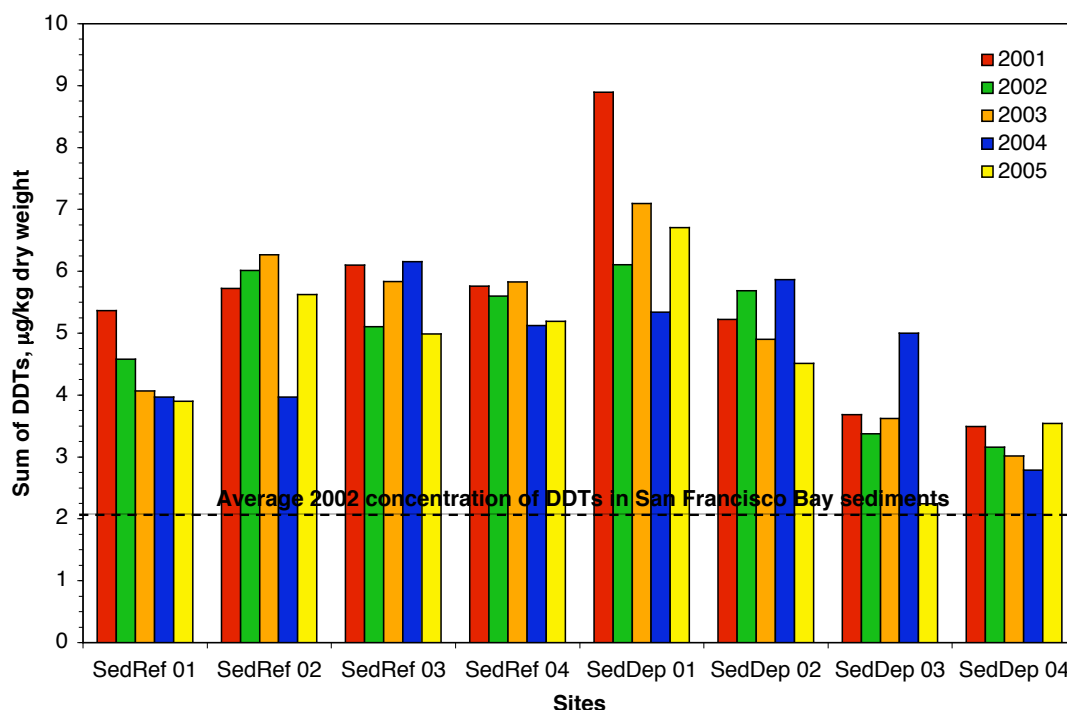


Figure 25. Concentrations of DDTs in sediments at eight CCLEAN sites measured over a five-year period.

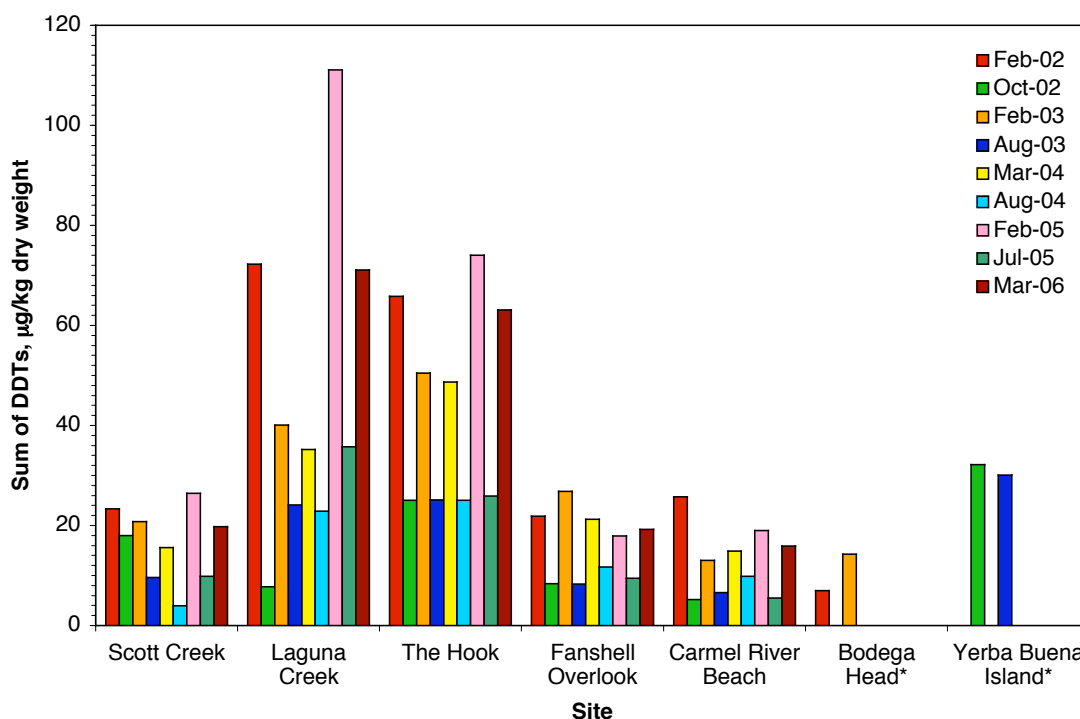


Figure 26. Concentrations of DDTs measured in mussels at five CCLEAN sites over a four-year period compared to a coastal background site and a contaminated estuarine site. * = Bodega Head is an uncontaminated coastal location where mussels are collected for various transplanted-mussel monitoring programs. Yerba Buena Island is in San Francisco Bay.

Long-term contaminant data are a critical element of any attempt to protect the water quality of the Sanctuary. The paucity of long-term contaminant data that became evident through this study suggests a high priority should be placed on supporting ongoing monitoring programs. The relatively high cost involved in measuring POPs at low detection limits makes it difficult to include such sampling and analytical components in the volunteer water quality monitoring programs in the Sanctuary. The two existing programs that continue to provide long-term data on POPs in the Sanctuary are the NS&T program, which analyzes mussels approximately every two years and the CCLEAN program, which measures POPs in mussels, sediments, rivers and wastewater twice per year. Such measurements are essential to tracking the health of the Sanctuary. Moreover, given the precarious nature of the southern sea otter population, sample material from such monitoring programs should be archived to enable future analyses for emerging contaminants of concern, which have not been considered here. Compounds such as PBDEs, fluoropolymers and pharmaceuticals and personal care products are receiving increased scrutiny for their environmental effects (Kannan *et al.*, 2006; She *et al.*, 2002; U.S. Environmental Protection Agency National Exposure Research Laboratory, 2005).

5.0 ACKNOWLEDGEMENTS

This work was supported by a contract from the Monterey Bay Sanctuary Foundation through the Sanctuary Integrated Monitoring Network (SIMoN) program at the Monterey Bay National Marine Sanctuary, National Oceanic and Atmospheric Administration (NOAA). The authors wish to thank Dave Jessup and Melissa Miller for their support and encouragement and for providing comments on a draft of this report. Dave Jessup also provided unpublished data on concentrations of contaminants in sea otter prey from Elkhorn Slough. We also thank Eric Zhang for his crucial assistance with the GIS production of figures.

6.0 LITERATURE CITED

- AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY. (1994). Toxicological Profile for Chlordane, pp. 262. U.S. Department of Health and Human Services Public Health Service, Atlanta, GA.
- AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY. (1995). Toxicological Profile for Polycyclic Aromatic Hydrocarbons, pp. 487. U.S. Department of Health and Human Services Public Health Service, Atlanta, GA.
- AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY. (2000). Toxicological Profile for Polychlorinated Biphenyls (PCBs), pp. 948. U.S. Department of Health and Human Services Public Health Service, Atlanta, GA.
- AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY. (2002a). Toxicological Profile for Aldrin/Dieldrin, pp. 354. U.S. Department of Health and Human Services Public Health Service, Atlanta, GA.
- AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY. (2002b). Toxicological Profile for DDT, DDE, and DDD, pp. 497. U.S. Department of Health and Human Services Public Health Service, Atlanta, GA.

- AISSLABIE, J. M., RICHARDS, N. K. & BOUL, H. L. (1997). Microbial degradation of DDT and its residues—a review. *New Zealand Journal of Agricultural Research* **40**, 269-282.
- ARCTIC MONITORING AND ASSESMENT PROGRAMME. (2004). AMAP ASSESMENT 2002: PERSISTENT ORGANIC POLLUTANTS IN THE ARCTIC, pp. 310 pp. Arctic Monitoring and Assessment Programme, Oslo, Norway.
- BACON, C. E., JARMAN, W. M., ESTES, J. A., SIMON, M. & NORSTROM, R. J. (1999). Comparison of organochlorine contaminants among sea otter (*Enhydra lutris*) populations in California and Alaska. *Environmental Toxicology and Chemistry [Environ. Toxicol. Chem.]* **18**, 452-458.
- BASKIN C.G. (1975). The Golf Course Superintendent's Role in the Economic Squeeze. *USGA Green Section Record*, 19-21.
- BRAY, S. & LANGSTON, W. J. (2006). Tributyltin pollution on a global scale. An overview of relevant and recent research topics: impacts and issues, pp. 54. World Wildlife Fund, Godalming, Surrey, UK.
- BRODBERG, R. K. & POLLOCK, G. A. (1999). PREVALENCE OF SELECTED TARGET CHEMICAL CONTAMINANTS IN SPORT FISH FROM TWO CALIFORNIA LAKES: PUBLIC HEALTH DESIGNED SCREENING STUDY, pp. 28. Office of Environmental Health Hazard Assessment, Sacramento, CA.
- BRUNER, K. A., FISHER, S.W. & LANDRUM, P. F. (1994). The Role of the Zebra Mussel, *Dreissena polymorpha*, In Contaminant Cycling: II. Zebra Mussel Contaminant Accumulation from Algae and Suspended Particles, and Transfer to the Benthic Invertebrate, *Gammarus fasciatus*. *Journal of Great Lakes Research [J. GREAT LAKES RES.]* **20**, 735-750.
- CCLEAN. (2006). Annual Report 2004-2005, pp. 125. Central Coast Long-term Environmental Assessment Network, Santa Cruz, CA.
- CCLEAN. (2007). 2001–2006 Program Overview. Central Coast Long-term Environmental Assessment Network, Santa Cruz, CA.
- ESTES, J. A. (1990). Growth and equilibrium in sea otter populations. *Journal of Animal Ecology [J. ANIM. ECOL.]* **59**, 385-401.
- EXTENSION TOXICOLOGY NETWORK PESTICIDE INFORMATION PROFILES. (1996). Tributyltin (TBT). June 1996. <http://extoxnet.orst.edu/pips/tributyl.htm>.
- HEBERT, C. E. & KEENLEYSIDE, K. A. (1995). To normalize or not to normalize? Fat is the question. *ENVIRONMENTAL TOXICOLOGY AND CHEMISTRY* **14**, 801-807.
- HEINTZ, R. A., RICE, S. D., WERTHEIMER, A. C., BRADSHAW, R. F., THROWER, F. P., JOYCE, J. E. & SHORT, J. W. (2000). Delayed effects on growth and marine survival of pink salmon *Oncorhynchus gorbuscha* after exposure to crude oil during embryonic development. *Marine Ecology Progress Series [Mar. Ecol. Prog. Ser.]* **208**, 205-216.
- HEINTZ, R. A., SHORT, J. W. & RICE, S. D. (1999). Sensitivity of fish embryos to weathered crude oil: Part II. Increased mortality of pink salmon (*Oncorhynchus gorbuscha*) embryos incubating downstream from weathered Exxon Valdez crude oil. *Environmental Toxicology and Chemistry [Environ. Toxicol. Chem.]* **18**, 494-503.
- JURADO, E., LOHMANN, R., MEIJER, S., JONES, K. C. & DACHS, J. (2004). Latitudinal and seasonal capacity of the surface oceans as a reservoir of polychlorinated biphenyls. *Environmental Pollution* **128**, 149-162.

- KANNAN, K., GURUGE, K. S., THOMAS, N. J., TANABE, S. & GIESY, J. P. (1998). Butyltin residues in southern sea otters (*Enhydra lutris nereis*) found dead along California coastal waters. *Environmental Science & Technology [Environ. Sci. Technol.]* **32**, 1169-1175.
- KANNAN, K., KAJIWARA, N., LEBOEUF, B. J. & TANABE, S. (2004). Organochlorine pesticides and polychlorinated biphenyls in California Sea Lions. *Environmental Pollution* **131**, 425-434.
- KANNAN, K., PERROTTA, E. & THOMAS, N. J. (2006). Association between Perfluorinated Compounds and Pathological Conditions in Southern Sea Otters. *Environmental Science & Technology [Environ. Sci. Technol.]* **40**, 4943-4948.
- KATERS, R. (2004). The History of PCB's: When were health problems detected? 1/26/2004. http://foxriverwatch.com/monsanto2a_pcb_pcbs.html.
- LEATHERBARROW, J. E., MCKEE, L. J., SCHOELLHAMER, D. H., GANJU, N. K. & FLEGAL, A. R. (2005). Concentrations and Loads of Organic Contaminants and Mercury associated with Suspended Sediment Discharged to San Francisco Bay from the Sacramento-San Joaquin River Delta, California, pp. 93 pp. San Francisco Estuary Institute, Oakland, CA.
- MCKEE, L. J., ORAM, J., LEATHERBARROW, J., BONNEMA, A., HEIM, W. & STEPHENSON, M. (2006). Concentrations and Loads of Mercury, PCBs and PBDEs in the Lower Guadalupe River, San Jose, California: Water Years 2003, 2004, and 2005, pp. 56 pp. San Francisco Estuary Institute, Oakland, CA.
- MIAMI-DADE COUNTY DEPARTMENT OF ENVIRONMENTAL RESOURCE MANAGEMENT. (2002). Environmental Quality Monitoring at Five Municipal Golf Courses in Miami-Dade County, pp. 159. Miami-Dade County Department of Environmental Resource Management and Florida Department of Agriculture and Consumer Services, Miami.
- NAKATA, H., KANNAN, K., JING, L., THOMAS, N., TANABE, S. & GIESY, J. P. (1998). Accumulation pattern of organochlorine pesticides and polychlorinated biphenyls in southern sea otters (*Enhydra lutris nereis*) found stranded along coastal California, USA. *Environmental Pollution [Environ. Pollut.]* **103**, 45-53.
- NATIONAL TOXICOLOGY PROGRAM. (2000). U.S. National Toxicology Program acute toxicity studies for Dieldrin.
- NORTH, K. D. (2004). Tracking the Fate of Polybrominated Diphenyl Ethers (PBDEs) at the Regional Water Quality Control Plant Palo Alto, California, pp. 15 pp. Environmental Compliance Division, City of Palo Alto, Palo Alto, CA.
- OREGON STATE UNIVERSITY. (1996a). Chlordane. 6/1996. <http://extoxnet.orst.edu/pips/chlordane.html>.
- OREGON STATE UNIVERSITY. (1996b). DDT (dichlorodiphenyltrichloroethane). June 1996. <http://pmep.cce.cornell.edu/profiles/extoxnet/carbaryl-dicrotophos/ddt>.
- PARAMETRIX. (2001). Ecological Screening-Level Risk Assessment of the Lower Ottawa River.
- PARENT, A., RASIER, G., GERARD, A., HEGER, S., ROTH, C., MASTRONARDI, C., JUNG, H., OJEDA, S. & BOURGUIGNON, J. (2005). Early onset of puberty: tracking genetic and environmental factors. *Hormone Research* **64 Supplement**, 41-47.
- PHILLIPS, J. H., HADERLIE, E. E. & LEE, W. L. (1975). An analysis of the dynamics of DDT in marine sediments. Hopkins Mar. Stn., Pacific Grove, CA, USA.
- SHAW, S. B. (1971). Chlorinated hydrocarbon pesticides in California sea otters and harbor seals. *California Fish and Game* **57**, 290-291.

- SHE, J., PETREAS, M., WINKLER, J., VISITA, P., MCKINNEY, M. & KOPEC, D. (2002). PBDEs in the San Francisco Bay Area: Measurements in harbor seal blubber and human breast adipose tissue. *Chemosphere [Chemosphere]* **46**, 697-707.
- STEPHENSON, M. (1992). A report on bioaccumulation of trace metals and organics in bivalves in San Francisco Bay submitted to California Regional Water Quality Control Board San Francisco Region. California Department of Fish and Game.
- STEPHENSON, M., ICHIKAWA, G., GOETZL, J., PAULSON, K., PRANGER, M., FAIREY, R., LAMERDIN, S., TJEERDEMA, R. S., NEWMAN, J., BECKER, J. & STOETLING, M. (1997). Distribution and concentration of selected contaminants in Monterey Bay sediments. In *Southern Monterey Bay Continental Shelf Investigations: Former Fort Ord Restricted Zone*, vol. Open File Report 97-450 (ed. S. L. Eittreim), pp. 76-113. U.S. Geological Survey.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. (1975). DDT Regulatory History: A Brief Survey (to 1975). 02/17/2006. <http://www.epa.gov/history/topics/ddt/02.htm>.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. (2000). National Water Quality Inventory 2000 Report. United States Environmental Protection Agency, Washington, D.C.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. (2006). Polychlorinated Biphenyls (PCB's). 4/18/2006. <http://www.epa.gov/opptintr/pcb/>.
- U.S. ENVIRONMENTAL PROTECTION AGENCY NATIONAL EXPOSURE RESEARCH LABORATORY. (2005). Pharmaceuticals and Personal Care Products (PPCPs) as Environmental Pollutants. December 4th, 2006. <http://www.epa.gov/esd/chemistry/pharma/index.htm>.
- UNITED STATES GEOLOGICAL SURVEY. (2001). Natural Oil and Gas Seeps in California. May 1, 2001. http://seeps.wr.usgs.gov/seeps/ca_seeps.html.
- WANIA, F. & DALY, G. L. (2002). Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCB's. *Atmospheric Environment* **36**, 5581-5593.
- WORLD HEALTH ORGANIZATION. (2006). Concise International Chemical Assessment Document 73, Mono- and Disubstituted Methyltin, Butyltin and Octyltin Compounds, pp. 73. World Health Organization, Geneva, Switzerland.

7.0 APPENDIX 1: RELEVANT CITATIONS

- ANDERLINI, V. (1974). The distribution of heavy metals in the red abalone, *Haliotis rufescens*, on the California coast. Arch. Environ. Contam. Toxicol. 2, 253-265.
- *ANDERSON, B. S., HUNT, J. W., PHILLIPS, B. M., NICELY, P. A., DE VLAMING, V., CONNOR, V., RICHARD, N. & TJEERDEMA, R. S. (2003). Integrated assessment of the impacts of agricultural drainwater in the Salinas River (California, USA). Environmental Pollution [Environ. Pollut.]. 124, 523-532.
- BACON, C. E., JARMAN, W. M. & COSTA, D. P. (1992). Organochlorine and polychlorinated biphenyl levels in pinniped milk from the Arctic, the Antarctic, California and Australia. Chemosphere 24, 779-791.
- BACON, C. E., JARMAN, W. M., ESTES, J. A., SIMON, M. & NORSTROM, R. J. (1999). Comparison of organochlorine contaminants among sea otter (*Enhydra lutris*) populations in California and Alaska. Environmental Toxicology and Chemistry [Environ. Toxicol. Chem.]. 18, 452-458.
- *BASKARAN, M., HONG, G. H., DAYTON, S., BODKIN, J. L. & KELLEY, J. J. (2003). Temporal variations of natural and anthropogenic radionuclides in sea otter skull tissue in the North Pacific Ocean. Journal of Environmental Radioactivity [J. Environ. Radioact.]. 64, 1-18.
- BECKMEN, K. B., LOWENSTINE, L. J., NEWMAN, J., HILL, J., HANNI, K. & GERBER, J. (1997). Clinical and pathological characterization of northern elephant seal skin disease. Journal of Wildlife Diseases [J. WILDL. DIS.]. 33, 438-449.
- BENDER, J. A. (1975). Trace Metal Levels in Beach Dipterans and Amphipods. Bulletin of environmental contamination and toxicology 14, 187-192.
- *BROWN, D. W., MCCAIN, B. B., HORNESS, B. H., SLOAN, C. A., TILBURY, K. L., PIERCE, S. M., BURROWS, D. G., CHAN, S.-L., LANDAHL, J. T. & KRAHN, M. M. (1999). Status, correlations and temporal trends of chemical contaminants in fish and sediment from selected sites on the Pacific coast of the USA. Marine Pollution Bulletin [Mar. Pollut. Bull.]. 37, 1-2.
- *BUHLER, D. R., CLAEYS, R. R. & MATE, B. R. (1975). Heavy Metal and Chlorinated Hydrocarbon Residues in California Sea Lions (*Zalophus californianus californianus*). Journal of the Fisheries Research Board of Canada 32, 2391-2397.
- *BUHLER, D. R. & MATE, B. R. (1973). Mercury Levels in California Sea Lions. In Mercury in the Western Environment, pp. 97-102. OREGON STATE UNIV., CORVALLIS. ENVIRONMENTAL HEALTH SCIENCES CENTER, Corvallis, OR (USA).
- BURNETT, R. (1971). DDT Residues: Distribution of Concentrations in *Emerita analoga* (Stimpson) Along Coastal California. Science 174, 606-608.
- COX, J. L. (1970). DDT Residues in Marine Phytoplankton: Increase from 1955 to 1969. Science 170, 71-73.
- COX, J. L. (1971). DDT Residues in Coastal Marine Phytoplankton and Their Transfer in Pelagic Food Chains. Ph.D. thesis, Stanford University.
- *CULLEN, J. T. & SHERRELL, R. M. (1999). Techniques for determination of trace metals in small samples of size-fractionated particulate matter: phytoplankton metals off central California. Marine Chemistry [Mar. Chem.]. 67, 233-247.
- *DELONG, R. L., GILMARTIN, W. G. & SIMPSON, J. G. (1973). Premature births in

- California sea lions: association with high organochlorine pollutant residue levels. *Science* 181, 1168-1170.
- DRAPER, W. M. & KOSZDIN, S. (1991). Speciation and Quantitation of Aroclors Based on PCB Congener Data: Application to California Mussels and White Croaker. *Journal of Agricultural and Food Chemistry* 39, 1457-1467.
- *FERNANDEZ, L. M. (1991). Demonstration of pesticide best management practices for controlling nonpoint source pollution in the Monterey Bay watershed. In 7th Symposium on Coastal and Ocean Management, vol. 4, pp. 3056-3067. ASCE, NEW YORK, NY, (UAS), Long Beach, CA, USA.
- *FLEGAL, A. R., ROSMAN, K. J. R. & STEPHENSON, M. D. (1987). Isotope systematics of contaminant leads in Monterey Bay. *Environmental Science and Technology* 21, 1075-1079.
- FROESCHEIS, O., LOOSER, R., CAILLIET, G. M., JARMAN, W. M. & BALLSCHMITER, K. (2000). The deep-sea as a final global sink of semivolatile persistent organic pollutants? Part I: PCBs in surface and deep-sea dwelling fish of the North and South Atlantic and the Monterey Bay Canyon (California). *Chemosphere [Chemosphere]*. no. 6, 651-660.
- *GOLDBERG, E. D., KOIDE, M., HODGE, V., FLEGAL, A. R. & MARTIN, J. (1983). U.S. Mussel Watch: 1977-1978 Results on Trace Metals and Radionuclides.
- *GUINN, V. P. & KISHORE, R. (1974). Results from Multi-Trace-Element Neutron Activation Analyses of Marine Biological Specimens. *Journal of radioanalytical chemistry* 19, 367-371.
- HADERLIE, E. C. (1970). Influence of Pesticide Run-Off in Monterey Bay. *Marine pollution bulletin* 1, 42-43.
- *HALL, A. S., TEENY, F. M. & GAUGLITZ, E. J., JR. (1976). Mercury in fish and shellfish of the Northeast Pacific. 2. Sablefish, *Anoplopoma fimbria*. *Fish. Bull. NMFS/NOAA* 74, 791-797.
- *HOTHEM, R. L. & POWELL, A. N. (2000). Contaminants in Eggs of Western Snowy Plovers and California Least Terns: Is There a Link to Population Decline? *Bulletin of Environmental Contamination and Toxicology [Bull. Environ. Contam. Toxicol.]*. 65, 42-50.
- *HOWARD, E. B., ESRA, G. N. & YOUNG, D. (1977). Acute foodborne pesticide toxicity in cormorants (*Phalacrocorax sp.*) and seagulls (*Larus californicus*). In Symposium on Pathobiology of Environmental Pollutants: Animal Models and Wildlife as Monitors, pp. 290-296, Storrs, CT (USA).
- *HUNT, J.W., B.S. ANDERSON, B.M. PHILLIPS, P.A. NICELY, R. TJEERDEMA, H.M. PUCKETT, M. STEPHENSON, K. WORCESTER, and V. DE VLAMING. 2002. Ambient toxicity due to chlorpyrifos and diazinon in central California watershed. *Environ. Monit. Assess.* 82:83-112.
- *HUNT, J. W., ANDERSON, B. S., PHILLIPS, B. M., TJEERDEMA, R. S., PUCKETT, H. M. & DE VLAMING, V. (1999). Patterns of aquatic toxicity in an agriculturally dominated coastal watershed in California. *Agriculture, Ecosystems & Environment [Agric., Ecosyst. Environ.]*. no.
- JARMAN, W. M., HOBSON, K. A., SYDEMAN, W. J., BACON, C. E. & MCLAREN, E. B. (1996). Influence of trophic position and feeding location on contaminant levels in the Gulf of the Farallones food web revealed by stable isotope analysis. *Environmental Science and Technology [ENVIRON. SCI. TECHNOL.]*. 30, 654-660.

- *JARMAN, W. M., JOHNSON, G. W., BACON, C. E., DAVIS, J. A., RISEBROUGH, R. W. & RAMER, R. (1997). Levels and patterns of polychlorinated biphenyls in water collected from the San Francisco Bay and Estuary, 1993-95. *Fresenius' Journal of Analytical Chemistry* [FRESENIUS J. ANAL. CHEM.]. 359, 254-260.
- JARMAN, W. M., NORSTROM, R. J., MUIR, D. C. G., ROSENBERG, B., SIMON, M. & BAIRD, R. W. (1996). Levels of organochlorine compounds, including PCDDS and PCDFS, in the blubber of cetaceans from west coast of North America. *Marine Pollution Bulletin* 32, 426-436.
- KAJIWARA, N., KANNAN, K., MURAOKA, M., WATANABE, M., TAKAHASHI, S., GULLAND, F., OLSEN, H., BLANKENSHIP, A. L., JONES, P. D., TANABE, S. & GIESY, J. P. (2001). Organochlorine Pesticides, Polychlorinated Biphenyls, and Butyltin Compounds in Blubber and Livers of Stranded California Sea Lions, Elephant Seals, and Harbor Seals from Coastal California, USA. *Archives of Environmental Contamination and Toxicology* [Arch. Environ. Contam. Toxicol.]. 41, 90-99.
- KANNAN, K., GURUGE, K. S., THOMAS, N. J., TANABE, S. & GIESY, J. P. (1998). Butyltin residues in southern sea otters (*Enhydra lutris nereis*) found dead along California coastal waters. *Environmental Science & Technology* [Environ. Sci. Technol.]. 32, 1169-1175.
- *KLAPOW, L. A. & LEWIS, R. H. (1979). Analysis of toxicity data for California marine water quality standards. *J. Water Pollut. Control Fed.* 51, 2054-2070.
- KNAUER, G. A. & MARTIN, J. H. (1972). Mercury in a Marine Pelagic Food Chain. *Limnology and oceanography* 17, 868-876.
- *KONAR, B. & STEPHENSON, M. D. (1995). Gradients of subsurface water toxicity to oyster larvae in bays and harbors in California and their relation to mussel watch bioaccumulation data. *Chemosphere* 30, 165-172.
- KVENVOLDEN, K. A., HOSTETTLER, F. D., ROSENBAUER, R. W., LORENSON, T. D., CASTLE, W. T. & SUGARMAN, S. (2002). Hydrocarbons in recent sediment of the Monterey Bay National Marine Sanctuary. *Marine Geology* [Mar. Geol.]. 181, 1-3.
- *LAUENSTEIN, G. G. & DASKALAKIS, K. D. (1999). U.S. long-term coastal contaminant temporal trends determined from mollusk monitoring programs, 1965-1993. *Marine Pollution Bulletin* [Mar. Pollut. Bull.]. 37, 1-2.
- *LEFEBVRE, K., POWELL, C., DOUCETTE, G., SILVER, J., MILLER, P., HUGHES, P., SILVER, M. & TJEERDEMA, R. (2000). Domoic acid-producing diatoms: probable cause of neuroexcitotoxicity in California sea lions. *Marine Environmental Research* [Mar. Environ. Res.]. 50, 1-5.
- *LEWIS, L. W. (1972). Characterization of Gelbstoffe in Monterey Bay by Nylon Adsorption, Uv, and Paper Chromatography. M Sc thesis, Naval Postgraduate School.
- LORENSON, T. D., KVENVOLDEN, K. A., HOSTETTLER, F. D., ROSENBAUER, R. J., ORANGE, D. L. & MARTIN, J. B. (2002). Hydrocarbon geochemistry of cold seeps in the Monterey Bay National Marine Sanctuary. *Marine Geology* [Mar. Geol.]. 181, 1-3.
- MACLELLAN, D., BRANCATO, M. S. & CARDWELL, R. (2000). Assessment of risks on US Pacific Coast otters feeding on bivalves and associated tributyltin. *Marine Environmental Research* [Mar. Environ. Res.]. 50, 1-5.
- *MADSEN, E. L., MANN, C. L. & BILOTTA, S. E. (1996). Oxygen limitations and aging as explanations for the field persistence of naphthalene in coal tar-contaminated surface sediments. *Environmental Toxicology and Chemistry* 15, 1876-1882.

- *MARTIN, M. (1985). State Mussel Watch: Toxics Surveillance in California. *Marine Pollution Bulletin* 16, 140-146.
- *MARTIN, M. & CASTLE, W. (1984). Petrowatch: Petroleum Hydrocarbons, Synthetic Organic Compounds, and Heavy Metals in Mussels from the Monterey Bay Area of Central California.
- *MCCLOSKEY, L. R. & DEUBERT, K. H. (1973). Polychlorinated biphenyls in the seastar *Acanthaster planci*. *Bulletin of Environmental Contamination and Toxicology* [Bull. Environ. Contam. Toxicol.]. 10, 261-264.
- MODIN, J. C. (1969). Chlorinated Hydrocarbon Pesticides in California Bays and Estuaries. *Pesticide monitoring journal* 3, 1-7.
- NAKATA, H., KANNAN, K., JING, L., THOMAS, N., TANABE, S. & GIESY, J. P. (1998). Accumulation pattern of organochlorine pesticides and polychlorinated biphenyls in southern sea otters (*Enhydra lutris nereis*) found stranded along coastal California, USA. *Environmental Pollution* [Environ. Pollut.]. 103, 45-53.
- NEWMAN, J. W., VEDDER, J. M., JARMAN, W. M. & CHANG, R. R. (1994). A method for the determination of environmental contaminants in living marine mammals using microscale samples of blubber and blood. *Chemosphere* 29, 671-681.
- *O'SHEA, T. J., CLARK, D. R., GAY, M. L., LAMONT, T. G., BROWNELL, R. L. & WALKER, W. A. (1980). Organochlorine Pollutants in Small Cetaceans from the Pacific and South Atlantic Oceans, November 1968-June 1976. *Pest. Monitor. J.* 14, 35-46.
- *PATTERSON, C., SETTLE, D. & GLOVER, B. (1976). Analysis of Lead in Polluted Coastal Seawater. *Marine Chemistry* 4, 305-319.
- PAULL, C. K., GREENE, H. G., USSLER, W. & MITTS, P. J. (2002). Pesticides as tracers of sediment transport through Monterey Canyon. *Geo Marine Letters* [Geo Mar. Lett.]. 22, 121-126.
- PHILLIPS, J. H., HADERLIE, E. E. & LEE, W. L. (1974). An Analysis of the Dynamics of DDT and Its Derivatives, DDD and DDE, in Marine Sediments, pp. 97. National Technical Information Service, Springfield, VA (USA).
- PHILLIPS, J. H., HADERLIE, E. E. & LEE, W. L. (1975). An Analysis of the Dynamics of DDT in Marine Sediments, pp. 98. National Technical Information Service, Springfield, VA (USA).
- RICE, D. W., SELTENRICH, C. P., KELLER, M. L., SPIES, R. B. & FELTON, J. S. (1994). Mixed-function oxidase-specific activity in wild and caged speckled sanddabs *Citharichthys stigmaeus* in Elkhorn Slough, Moss Landing Harbor and nearshore Monterey Bay, California. *Environmental Pollution* 84, 179-188.
- RICE, D. W., SELTENRICH, C. P., SPIES, R. B. & KELLER, M. L. (1993). Seasonal and annual distribution of organic contaminants in marine sediments from Elkhorn Slough, Moss Landing Harbor and nearshore Monterey Bay, California. *Environmental Pollution* 82, 79-91.
- *RISEBROUGH, R. W. (1989). Accumulation patterns of heavy metals and chlorinated hydrocarbons by sea otters, *Enhydra lutris*, in California. California Univ., Santa Cruz (USA).
- *RISEBROUGH, R. W., LAPPE BROCK, W. & SCHMIDT, T. T. (1976). Bioaccumulation factors of chlorinated hydrocarbons between mussels and seawater. *Mar. Pollut. Bull.* 7, 225-228.
- *ROSSI, S. S., ROMMEL, G. W. & BENSON, A. A. (1977). Hydrocarbons in sand crabs

- (*Emerita analoga*) and giant kelp (*Macrocystis pyrifera*) from southern California. *Cibcasio Trans.* 3, 35-43.
- ROUTH, J. D. (1972). DDT Residues in Salinas River Sediments. *Bulletin of environmental contamination and toxicology* 7, 168-176.
- *SCHMIDT, T. T., RISEBROUGH, R. W. & GROSS, F. (1971). Input of polychlorinated biphenyls into California coastal waters from urban sewage outfalls. *Bull. Environ. Contam. Toxicol.* 6, 235-243.
- SHAW, S. B. (1971). Chlorinated hydrocarbon pesticides in California sea otters and harbour seals. *Calif. Fish. Game.* 57, 290-294.
- SHAW, S. B. (1972). DDT Residues in Eight California Marine Fishes. *California Fish and Game* 58, 22-26.
- *SPIES, R. B., FELTON, J. S. & DILLARD, L. (1982). Hepatic mixed-function oxidases in California flatfishes are increased in contaminated environments and by oil and PCB ingestion. *Marine biology*, Heidelberg 70, 117-127.
- STEDING, D. J. & FLEGAL, A. R. (2002). Mercury concentrations in coastal California precipitation: Evidence of local and trans-Pacific fluxes of mercury to North America. *Journal of Geophysical Research. D. Atmospheres [J. Geophys. Res.]* 107.
- *STEPHENSON, M. D., MARTIN, M. & TJEERDEMA, R. S. (1995). Long-term trends in DDT, polychlorinated biphenyls, and chlordane in California mussels. *Archives of Environmental Contamination and Toxicology* 28, 443-450.
- *STOUT, V. F. & BEEZHOLD, F. L. (1981). Chlorinated Hydrocarbon Levels in Fishes and Shellfishes of The Northeastern Pacific Ocean, Including The Hawaiian Islands. *Marine Fisheries Review* 43, 1-12.
- VARANASI, U., CHAN, S. L., MCCAIN, B. B., SCHIEWE, M. H. & CLARK, R. C. (1988). National Benthic Surveillance Project: Pacific Coast. Part I: Summary and Overview of the Results for Cycles I to III (1984-86), pp. 64. National Technical Information Service, Springfield, VA (USA).
- VARANASI, U., CHAN, S. L., MCCAIN, B. B., SCHIEWE, M. H. & CLARK, R. C. (1989). National Benthic Surveillance Project: Pacific Coast. Part II: Technical Presentation of the Results for Cycles I to III (1984-86), pp. 248. National Technical Information Service, Springfield, VA (USA).
- *VETTER, W. (2002). Environmental occurrence of Q1, a C_{sub}(9)H_{sub}(3)Cl_{sub}(7)N_{sub}(2) compound, that has been identified as a natural bioaccumulative organochlorine. *Chemosphere [Chemosphere]* 46, 1483.
- *WOODARD, D. W. (1980). Selected vertebrate endangered species of the seacoast of the United States - brown pelican - eastern and California subspecies (ed. D. W. Linzey), pp. 17. Fish and Wildlife Serv., Slidell, LA (USA). Natl. Coastal Ecosystems Team., Slidell, LA (USA).
- *YANG, J. S. (1989). Determination of Palladium and Platinum in Seaweed. *Journal of the Oceanographical Society of Japan* 45, 369-374.
- * Data from reference were not put into the database due to redundancy with other sources or lack of numerical values.