

CHAPTER 4

Sediment Chemistry



Cover photos

Top left: Bill Power (Retired, left) and Brent Haggin (Biologist II, right) retrieving the tandem Van Veen benthic grab.

Bottom right: A close-up view of sediment collected from the tandem Van Veen benthic grab.

Chapter 4 Sediment Chemistry

INTRODUCTION

The Los Angeles County Sanitation Districts (Sanitation Districts) own and operate the Joint Water Pollution Control Plant (JWPCP), which discharges secondary treated effluent into the Pacific Ocean pursuant to the Waste Discharge Requirements and National Pollutant Discharge Elimination System (NPDES) permit issued by the Los Angeles Regional Water Quality Control Board (LARWQCB; Order No. R4-2017-0180, NPDES No. CA0053813; **Appendix 1.1**). Monitoring and reporting requirements for the NPDES permit are specified in the Monitoring and Reporting Program (MRP) portion of the NPDES permit. The MRP specifies several monitoring elements for the JWPCP, including receiving water (i.e. ocean) monitoring.

Analyzing physical and chemical properties of sediments is an essential element of the JWPCP receiving water monitoring program. Suspended solids in treated wastewater effluents are discharged to an aquatic environment, which typically settle on the bottom and mix with native sediments. The effluent-derived solids are enriched with organic carbon and nitrogen and can cause environmental degradation under certain circumstances. In addition, these particles serve as a conveyance mechanism for trace metals and organic contaminants, including pesticides and pharmaceuticals and personal care products (PPCPs), to enter the marine environment. Native sediments can also serve as a sink for discharged hydrophobic pollutants and can be a significant source of contaminants to the local environment for decades after the discharge of these pollutants has ceased.

The physical and chemical data collected through the Sanitation Districts' ocean monitoring program documents the spatial and historical trends in sediment condition. Inferences can then be drawn regarding the relationship between effluent-derived pollutants and alterations to benthic habitat as well as infaunal (Chapter 5), sediment toxicity (Chapter 6), and epibenthic communities (Chapter 7). Sediment chemistry information is also vital to assess the link between pollutants discharged and seafood consumption health risks for wildlife and humans from the

consumption of exposed prey, such as fish (Chapter 8).

History of sediment monitoring and condition

From 1937 to 1970, the JWPCP discharge off Palos Verdes altered the physical and chemical nature of sediments on the shelf and slope. Suspended solids and the resulting organic matter and contaminant loads to the receiving water increased over time (Figure 1.2) as the Sanitation Districts' service area grew in population and industrialization. By 1970, the discharge had altered the sediment texture (sediments became finer) and polluted the seafloor with organic matter and contaminants (e.g. metals and chlorinated hydrocarbons). Organic loading resulted in sediment hypoxia and formation of free hydrogen sulfide (H_2S) in the porewater of surface sediments. Potentially toxic synthetic organic compounds, most notably DDTs (dichlorodiphenyltrichloroethane and its degradation products) and PCBs (polychlorinated biphenyls), were at levels in the sediments higher than those likely to cause biological effects (Chapter 1). These alterations were severe enough to degrade the sediment-associated biological communities over the entire shelf and slope, particularly near the outfalls.

Since the early 1970s, the Sanitation Districts have monitored benthic biological communities and sediment chemistry quality on the Palos Verdes Shelf (PVS) and slope area. Despite more than 47 years of declining mass emissions of suspended solids and associated industrial contaminants from the JWPCP, there is still a small reservoir of organically enriched and contaminated sediments on the PVS and slope. A series of reports describe the sediments off Palos Verdes in detail (Sediment Dynamics Workshop Group 1987, Lee 1994, Lee and Wiberg 2002, CH2M Hill 2007, Eganhouse and Pontolillo 2008, Ferré et al. 2010, USEPA 2013, LACSD 2014). The deposit contains elevated concentrations of DDT, PCBs, metals, PAH, and organic matter (including effluent-derived materials). The highest concentrations of contaminants are found at the shelf break (between 50 and 70-meter isobaths) buried below 20-50 cm of cleaner

sediment. The effluent-affected shelf break sediments are characterized by a lower density and finer grain size than native sediments.

Both suspended and bedload sediment movement is variable, but the dominant sediment transport direction on the mid-shelf is toward the northwest (Wiberg et al. 2002). The dominance of this northwest sediment transport is evident in the distribution of chemical and sedimentological variables (Stull et al. 1986, Sediment Dynamics Workshop Group 1987, Hampton et al. 2002, Lee et al. 2002, LACSD 2012). Wu et al. (1994) also reported extensive resuspension of sediments near the seafloor. In one example, the resuspended sediment rose up almost 20 m from the bottom, and extended horizontally by at least 4 km.

JWPCP effluent has been historically one of two major sources of sediment to the PVS. The other source is the Portuguese Bend landslide that has contributed rock and sediment to the shelf since at least 1956. Erosion of the land, both past and present, has resulted in an accumulation of slide material on the inner shelf. Slide movement is correlated in part with storms and rainfall that tend to move slide material offshore, and the landslide toe erosion varies with storm-wave energy and direction. The littoral current carries landslide material alongshore to the southeast towards White Point and beyond, including offshore of the Los Angeles Harbor.

By 1988, slide movement was reduced substantially by engineering projects related to stabilization and shoreline protection, including dewatering wells, regrading, better drainage, gabions, and revetments (Kayen et al. 2002). During the 44-year period after initiation of movement (1956-1999), the Portuguese Bend landslide contributed up to 9.4 million metric tons of sediment to the PVS. This is as much as 2.5 times the total mass of particulate discharged from JWPCP during the 50-year period from 1937-1987 (Kayen et al. 2002), of which only a fraction settled on the PVS (Hendricks 1980). The sediment load from the slide has led to significant (>1 m) shoaling on the inshore seafloor east of the slide (Kayen et al. 2002), burying many low-lying rocky reefs in the area (LACSD 2002).

Sediment condition monitoring requirements

The MRP for the JWPCP NPDES permit requires the Sanitation Districts to participate in two sediment condition monitoring programs. A

brief discussion of each monitoring element is described below.

The first is the Local Sediment Chemistry Trends Survey. The Local Sediment Chemistry Trends Survey is conducted at 24 sites annually and at 44 sites once every five-year permit cycle along the Palos Verdes Peninsula (**Figure 4.1**). Over 70 constituents, including organic nitrogen and carbon, trace metals, and organic contaminants are quantified. Grain size distributions are also annually determined at all 44 sites. These physical and chemical datasets are used to assess whether sediment conditions, under the influence of the discharge, are changing over time. Furthermore, the data collected provide context for assessing trends in biological communities (Chapter 5 and Chapter 7), sediment toxicity (Chapter 6), and fish tissue bioaccumulation monitoring programs (Chapter 8) under the NPDES permit.

The second is the Regional Benthic Surveys of sediment conditions. The objective of these surveys is to determine the extent, distribution, magnitude, and trend of ecological change in soft-bottom benthic habitats within the Southern California Bight (SCB). The physical and chemical measurements of the sediment are used to evaluate the relationship between biological responses and exposure to contaminants. Combined with biological and toxicity data results, these studies evaluate the condition of the seafloor environment and the health of the biological resources in the SCB.

These regional studies, termed “Bight” surveys, are conducted every five years under the direction of a steering committee and coordinated by the Southern California Coastal Water Research Project (SCCWRP). When such surveys are scheduled, the Sanitation Districts are required to provide staff and resources for planning, sampling, analyses, and data management associated with the project. The last regional monitoring was conducted during summer of 2018 (SCCWRP 2018). Staff members of the Sanitation Districts served on the Bight '18 Sediment Quality Planning Committee and several associated technical committees. They assisted with this survey through sample collection, sample analysis, quality assurance, quality control, data management support, draft report review, and report production. The most recent publication for the Regional Monitoring can be found at [SCCWRP's website](#).

Chapter overview

This chapter provides the results of the physical and chemical analyses of surface sediments for the Local Benthic Trends Surveys in 2018 and 2019. Consistent with the objectives

of the monitoring and reporting requirement, the local trends data are analyzed and discussed in terms of spatial and temporal relationships between sediment chemistry condition and proximity to the JWPCP outfall.

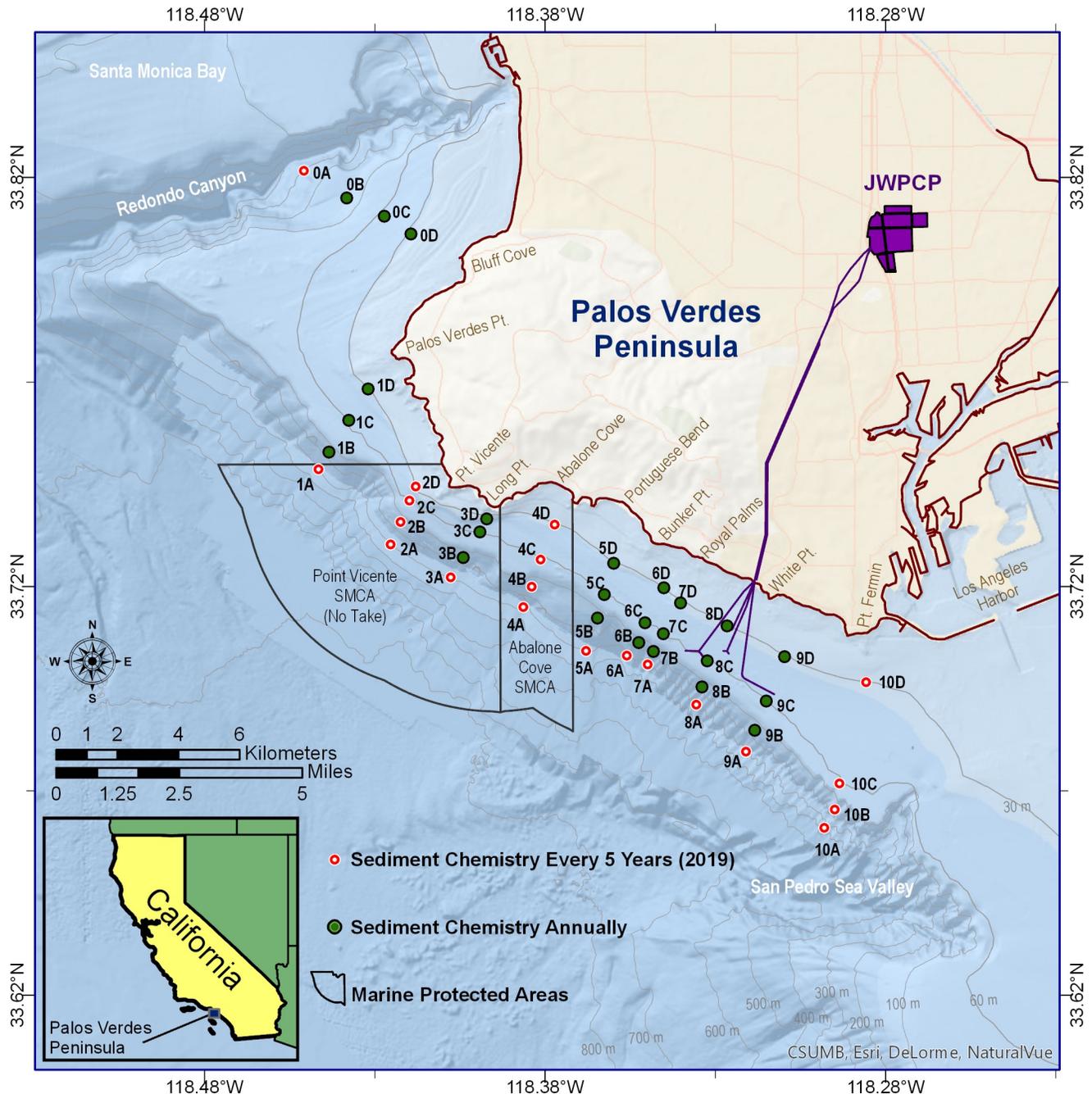


Figure 4.1 Benthic Sediment Monitoring Stations

Map of the sampling sites for physical and chemical analysis of surficial (top two centimeters) sediments. Analyses are performed on all 44 sites (compound circles) every five years with the full survey. A subset of 24 stations (full circles) are sampled and analyzed annually. Total organic carbon, organic nitrogen and grain size are measured at all 44 sites annually as required for the benthic infauna monitoring program (Chapter 5) and are also utilized in this chapter.

This chapter is one component of the JWPCP Biennial Receiving Water Monitoring Report (LACSD 2020a). The complete report includes results and analyses for all JWPCP NPDES receiving water monitoring requirements and associated appendices. Electronic copies of the complete JWPCP Biennial Receiving Water Monitoring Report can be downloaded from the [Sanitation Districts' website](#).

MATERIALS AND METHODS

Field sampling

In the summer of 2018 and 2019, paired sediment samples were collected with a 0.1 m² tandem Van Veen grab at 44 sites (Figure 4.1). At each site, sediment samples were collected for both benthic infauna and physical and chemical analyses. Surficial sediment, defined here as the top two centimeters, was collected from the dedicated sediment grab sample. At the time of sampling, sediment color and type, presence of hydrogen sulfide odor, and temperature were recorded. The field sampling standard operating procedure (SOP) is provided in **Appendix 4.1**.

Sediment analysis

Table 4.1 lists the specific physical and chemical parameters measured in surficial sediments collected for the Local Sediment Chemistry Trends monitoring program. All chemical analyses for sediment samples were performed by the Sanitation Districts' laboratories

and its contract laboratories in accordance with the standard operating procedures (SOPs). The Sanitation Districts' laboratories are certified by the State of California under the Environmental Laboratory Accreditation Program (ELAP, **Appendix 4.2**).

Grain size analysis was performed using a laser particle analyzer (Standard Method 2560D). Total organic carbon (TOC) was quantified using a carbonaceous analyzer (SW-846 Test Method 9060A). Organic nitrogen was measured using the automated titrimetric method (SM4500 NH3 B, C) and dissolved sulfides (i.e. H₂S) were quantified using a sulfide specific electrode (Standard Method 4500S-G). All trace metals, with the exception of mercury, were analyzed using inductively coupled plasma mass spectrometry (ICP-MS; EPA Test Method 6020A). Cold vapor atomic absorption spectroscopy was utilized for mercury quantification (EPA Test Method 7471A). Chlorinated pesticides (DDTs and chlordanes) and PCBs were measured using a gas chromatograph combined with electron capture detectors (GC-ECD; EPA Test Method 608, SW-846 Method 8081A or SW-846 Method 8082).

Data analysis

All results from 2018 and 2019 are presented in summary tables. Interpretation of the physical properties and chemical sediment contamination data is focused on spatial distribution and historical trends primarily as they relate to the proximity of the discharge and treatment period. The treatment periods used for this analysis are: Baseline (1973-1974); Advanced

Table 4.1 Physical and Chemical Sediment Condition Parameters

Required physical and chemical analyses for sediments collected under the Local Benthic Trends Survey.

Pollutant class	Specific Parameters Analyzed in Group
Conventional pollutants	Grain size, total organic carbon (TOC), organic nitrogen, dissolved sulfides (H ₂ S)
Trace metals	Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni), Silver (Ag), Zinc (Zn)
DDTs	4,4'-DDT; 2,4'-DDT; 4,4'-DDE; 2,4'-DDE, 4,4'-DDD, 2,4'-DDD
Total DDTs	Sum of detectable DDTs
PCBs	Aroclor-1016, Aroclor-1221, Aroclor-1232, Aroclor-1242, Aroclor-1248, Aroclor-1254, Aroclor-1260
PCB congeners	PCB congeners 18, 28, 37, 44, 49, 52, 66, 70, 74, 77, 81, 87, 99, 101, 105, 110, 114, 118, 119, 123, 126, 128, 138, 149, 151, 153, 156, 157, 158, 167, 168, 169, 170, 177, 180, 183, 187, 189, 194, 201, 206
Total PCBs	Sum of detectable PCB (Aroclors)

Primary (1974-1983); Partial Secondary (1984/1985-2002); Full Secondary (2003-2017); and Current (2018-2019). The Baseline period represents the first complete sediment chemistry data obtained from the PVS following more than 35 years of primary treated discharge. During the Advanced Primary period, improvements were made to solids removal and processing which greatly reduced the level of suspended solids in the discharge. The Partial Secondary period represents the period when secondary treatment facilities went online in 1984 and provided biological (i.e. secondary) treatment to 60% of the total discharge (the remainder being advanced primary treated). Lastly, the Full Secondary period began with the construction of additional biological, secondary treatment facilities in late 2002. This expanded the treatment capacity to 100% of the wastewater entering the JWPCP, and represents the level of treatment provided in the Full Secondary and Current treatment periods.

The spatial distributions and historical trends of conventional pollutants, trace metals, and total DDTs and PCBs are presented as contour maps, using the average values for each treatment period. To better visualize changes between treatment periods, average values were grouped into pollutant concentration intervals that are based on percentiles of observed values (10th, 50th, and 90th); in some cases, the percentiles were replaced by concentrations based on biological effects or clean-up targets. Due to periodic changes in monitoring frequency, sampling locations, measured parameters, and analytical methods, the specific years and/or number of data points represented varies between constituents.

RESULTS

All NPDES permit-required sediment samples for the 2018 and 2019 survey years were collected and analyzed. Results from 2018-2019 for conventional pollutants, trace metals, and organic contaminants are provided in **Tables 4.2, 4.3 and 4.4**, respectively. Complete data sets for the 2018 and 2019 surveys, including individual constituents within the classes of organic contaminants, were submitted to the LARWQCB electronically in August 2018 (LACSD 2019) and 2019 (LACSD 2020b), respectively.

DISCUSSION

The objectives of the local sediment contamination monitoring requirements in the NPDES permit are to assess trends in sediment pollutant concentrations within the current and historical influence of the discharge. The resulting physical and chemical data are used to make inferences concerning the relationship between effluent-derived habitat alteration and patterns of infaunal (Chapter 5), sediment toxicity (Chapter 6) and epibenthic community structure (Chapter 7). Furthermore, these data are used to assess potential sources of bioaccumulative compounds in fish that may pose a threat to human or wildlife health (Chapter 8). The following discussion provides the spatial distribution and temporal change of sediment condition in relation to the history of effluent quality and proximity to the discharge.

Current condition, 2018-2019

Conventional pollutants

Average surface sediment distribution patterns for conventional pollutants measured during the 2018 and 2019 sampling period are displayed in the last row of contour maps on **Figure 4.2**. The intervals of these contour maps use the 10th, 50th, and 90th percentiles from the results of individual contaminants. During the 2018 and 2019 surveys, grain size analysis was performed with the laser particle analyzer methodology for all 44 stations. Sediments with a smaller particle size (higher phi) were generally distributed in the 305-meter stations and several stations along the 61-meter isobath (e.g.: 4C, 5C and 6C). Sediments with a large particle size (lower phi) were mostly distributed in the 30-meter isobath stations except 5D, which is heavily impacted by the Portuguese Bend landslide. The laser particle analyzer method used to determine grain size distribution is efficient but was determined to be inaccurate for sediment samples where coarser materials were abundant. Consequently, grain size results were not reported for station 2D, where sediment samples contained coarse sand and shell hash. In 2019, the Sanitation Districts conducted an inter-laboratory calibration using the laser particle size analyzer method and the gravimetric method and determined that the gravimetric method is more

Table 4.2 Conventional Pollutants in Palos Verdes Sediments, 2018-2019

Mean grain size (phi size), organic nitrogen (% dry weight), total organic carbon (TOC; % dry weight) and porewater hydrogen sulfide (H₂S; mg/L porewater) in surficial sediments collected from 44 sites except H₂S from 24 sites in 2018 (Figure 4.1) along Palos Verdes. *: Data were determined to be unreliable using the laser method, due to the presence of large grains. ND: Below analytical detection limit. NS= Not sampled. IS: No interstitial water after centrifugation. Min: Minimum, Max: Maximum, SD: Standard Deviation.

DEPTH	SITE	Mean Grain Size		Organic Nitrogen		Total Organic Carbon		Hydrogen Sulfide	
		2018	2019	2018	2019	2018	2019	2018	2019
30 M	0D	3.43	3.43	0.05	0.05	0.43	0.58	ND	ND
	1D	2.54	2.51	0.05	0.03	0.96	0.62	ND	ND
	2D	*	*	0.03	0.02	0.94	0.50	NS	IS
	3D	3.19	3.28	0.05	0.06	0.58	0.30	ND	ND
	4D	3.56	3.59	0.06	0.06	0.64	0.64	NS	ND
	5D	4.54	4.58	0.07	0.05	0.86	0.31	ND	ND
	6D	3.81	3.86	0.04	0.05	0.29	0.63	ND	ND
	7D	3.79	3.72	0.04	0.05	0.79	0.80	ND	ND
	8D	3.44	3.61	0.05	0.06	0.72	0.50	ND	ND
	9D	3.51	3.42	0.04	0.04	0.55	0.52	ND	ND
10D	3.56	3.42	0.06	0.05	0.64	0.58	NS	ND	
60 M	0C	4.35	4.06	0.10	0.09	0.94	0.88	ND	ND
	1C	4.03	3.93	0.08	0.08	0.98	0.87	ND	ND
	2C	3.48	3.70	0.10	0.08	1.10	0.85	NS	ND
	3C	3.95	3.86	0.11	0.10	1.20	1.00	ND	ND
	4C	4.58	4.54	0.11	0.12	1.30	1.30	NS	ND
	5C	4.53	4.23	0.10	0.12	1.50	1.50	ND	ND
	6C	4.16	4.16	0.11	0.11	1.60	1.60	ND	ND
	7C	4.24	3.79	0.07	0.08	1.40	1.00	ND	ND
	8C	3.85	3.68	0.22	0.20	3.10	3.60	ND	0.07
	9C	3.76	3.73	0.06	0.06	0.89	0.63	ND	ND
10C	3.29	3.35	0.04	0.05	0.51	0.56	NS	ND	
152 M	0B	4.46	4.20	0.14	0.14	1.30	1.50	ND	ND
	1B	3.86	3.72	0.09	0.07	1.00	1.10	ND	ND
	2B	3.66	3.68	0.09	0.08	1.00	0.96	NS	ND
	3B	3.76	3.77	0.10	0.11	1.20	1.10	ND	ND
	4B	3.91	3.84	0.19	0.17	2.60	2.10	NS	ND
	5B	3.67	3.88	0.19	0.18	2.80	2.30	ND	ND
	6B	3.84	3.69	0.19	0.21	3.50	2.80	ND	ND
	7B	4.03	3.86	0.15	0.26	2.30	4.00	ND	ND
	8B	3.54	3.63	0.23	0.23	3.50	3.30	ND	ND
	9B	3.75	3.74	0.12	0.12	1.60	2.00	ND	ND
10B	3.80	3.78	0.08	0.07	0.85	0.73	NS	ND	
305 M	0A	5.00	4.76	0.28	0.25	3.10	2.60	NS	ND
	1A	4.32	4.12	0.14	0.14	1.50	1.90	NS	ND
	2A	4.05	4.06	0.11	0.10	1.20	1.10	NS	ND
	3A	4.01	4.02	0.13	0.17	1.40	2.00	NS	ND
	4A	4.44	4.30	0.16	0.18	2.20	2.40	NS	ND
	5A	4.25	4.06	0.13	0.13	1.80	1.90	NS	ND
	6A	3.97	4.30	0.14	0.11	3.10	1.80	NS	ND
	7A	4.08	4.13	0.14	0.09	1.50	1.20	NS	ND
	8A	4.16	4.53	0.21	0.21	2.80	2.50	NS	ND
	9A	4.18	4.34	0.18	0.19	2.20	2.40	NS	ND
10A	4.11	4.06	0.09	0.10	0.95	1.20	NS	ND	
Min		2.54	2.51	0.03	0.02	0.29	0.30	ND	ND
Max		5.00	4.76	0.28	0.26	3.50	4.00	ND	0.07
Mean		3.92	3.88	0.11	0.11	1.48	1.42	ND	ND
SD		0.44	0.41	0.06	0.06	0.88	0.92	-	-

Table 4.3 Trace Metals in Palos Verdes Sediments, 2018-2019

Arsenic, cadmium, total chromium, copper and lead concentrations (mg/kg dry weight) in surficial sediments collected from 44 sites in 2018 and 2019 (Figure 4.1) along Palos Verdes. NS= Not sampled. Min: Minimum, Max: Maximum, SD: Standard Deviation.

DEPTH	SITE	Arsenic		Cadmium		Total Chromium		Copper		Lead	
		2018	2019	2018	2019	2018	2019	2018	2019	2018	2019
30 M	0D	4.77	4.63	0.80	0.77	34.3	34.7	7.38	15.1	8.99	8.66
	1D	14.7	13.2	4.90	4.80	39.4	33.7	6.57	4.75	8.86	7.07
	2D	NS	8.17	NS	0.69	NS	20.8	NS	3.41	NS	4.83
	3D	7.23	7.45	1.10	0.98	36.8	34.7	11.3	9.94	9.36	8.72
	4D	NS	10.5	NS	1.90	NS	47.3	NS	17.2	NS	12.2
	5D	12.0	10.8	2.20	2.10	45.6	42.6	19.3	15.0	10.8	8.76
	6D	10.5	10.9	1.90	1.80	41.6	40.2	12.9	11.7	10.5	9.36
	7D	10.4	10.9	1.50	1.50	41.0	37.4	11.0	10.1	10.4	9.45
	8D	11.7	11.5	1.30	1.30	45.7	43.6	12.1	12.3	12.2	11.1
	9D	6.30	5.95	0.77	0.72	30.0	29.2	13.6	11.4	8.57	8.43
10D	NS	6.70	NS	0.66	NS	27.5	NS	12.0	NS	9.06	
60 M	0C	6.18	6.28	0.97	0.86	58.5	52.9	20.8	17.8	18.8	15.7
	1C	7.23	6.82	1.60	1.40	75.0	60.2	30.4	23.2	22.4	16.3
	2C	NS	11.2	NS	1.70	NS	80	NS	24.9	NS	20.5
	3C	10.9	10.9	2.40	1.90	90.5	76.6	39.8	30.9	27.1	22.3
	4C	NS	9.11	NS	2.30	NS	89.4	NS	42.9	NS	26.0
	5C	8.74	9.67	2.20	2.90	93.3	100	52.3	56.2	31.4	33.7
	6C	8.69	8.25	2.40	2.30	113	109	62.1	51.2	36.1	31.7
	7C	3.86	6.96	1.20	1.50	46.7	61.5	26.3	32.9	15.4	19.9
	8C	16.7	15.0	7.50	5.80	320	353	197	226	93.9	172
	9C	6.76	6.43	0.96	0.91	53.9	47.1	30.8	23.8	21.3	15.1
10C	NS	7.41	NS	0.38	NS	32.2	NS	17.2	NS	13.9	
152 M	0B	6.75	6.57	1.40	1.30	69.2	66.1	26.7	25.0	20.8	18.8
	1B	8.51	9.58	2.20	2.30	69.7	71.3	23.4	22.9	20.2	19.8
	2B	NS	8.06	NS	1.90	NS	71.8	NS	23.2	NS	19.6
	3B	8.18	8.31	2.50	2.30	81.1	84.7	33.3	32.1	25.2	22.7
	4B	NS	11.2	NS	5.50	NS	204	NS	88.4	NS	53.1
	5B	14.9	15.5	8.10	8.30	221	235	122	124	65.3	70.0
	6B	25.8	18.7	15.3	9.50	374	304	213	160	119	83.6
	7B	18.9	32.9	8.50	22.2	190	370	110	226	74.9	153
	8B	33.6	31.9	23.4	21.6	539	480	303	276	174	159
	9B	11.1	9.98	5.40	4.10	186	168	92.0	78.0	54.5	44.8
10B	NS	7.74	NS	0.60	NS	42.1	NS	26.9	NS	13.5	
305 M	0A	NS	9.87	NS	1.30	NS	95.4	NS	38.2	NS	24.2
	1A	NS	11.3	NS	5.00	NS	148	NS	64.9	NS	39.0
	2A	NS	6.20	NS	1.60	NS	65.5	NS	28.3	NS	15.9
	3A	NS	10.1	NS	4.80	NS	202	NS	73.7	NS	40.7
	4A	NS	13.5	NS	7.10	NS	196	NS	95.2	NS	57.7
	5A	NS	7.41	NS	2.30	NS	124	NS	49.6	NS	29.1
	6A	NS	7.70	NS	1.50	NS	69.4	NS	36.0	NS	17.6
	7A	NS	6.58	NS	1.00	NS	42.5	NS	20.8	NS	8.40
	8A	NS	11.4	NS	2.90	NS	128	NS	56.4	NS	29.4
	9A	NS	11.3	NS	3.50	NS	138	NS	69.6	NS	35.6
10A	NS	8.02	NS	0.85	NS	49.9	NS	30.5	NS	15.4	
Min		3.86	4.63	0.77	0.38	30.0	20.8	6.57	3.41	8.57	4.83
Max		33.6	32.9	23.4	22.2	539	480	303	276	174	172
Mean		11.43	10.51	4.19	3.42	121	109	61.5	52.6	37.5	33.1
SD		6.84	5.60	5.35	4.59	128	103	76.7	61.5	41.3	39.0

Table 4.3 Trace Metals in Palos Verdes Sediments, 2018-2019 (Continued)

Nickel, silver and zinc concentrations (mg/kg dry weight) in surficial sediments collected from 44 sites in 2018 and 2019 (Figure 4.1) along Palos Verdes. Mercury was analyzed in samples from 44 sites in 2018 and 24 sites in 2019; the Los Angeles Regional Water Quality Control Board approved the 2018 data as satisfying the permit requirement to measure mercury at all 44 stations once per permit cycle NS= Not sampled. Min: Minimum, Max: Maximum, SD: Standard Deviation.

DEPTH	SITE	Mercury		Nickel		Silver		Zinc	
		2018	2019	2018	2019	2018	2019	2018	2019
30 M	0D	0.06	0.05	13.8	14.1	0.20	0.18	40.4	41.5
	1D	0.04	0.03	10.4	8.98	0.19	0.16	49.7	42.2
	2D	0.01	NS	NS	6.42	NS	ND	NS	21.4
	3D	0.05	0.05	11.3	11.1	0.20	0.16	45.5	44.7
	4D	0.07	NS	NS	22.3	NS	0.25	NS	68.3
	5D	0.08	0.05	24.1	19.9	0.25	0.26	67.0	59.6
	6D	0.06	0.05	16.0	16.2	0.25	0.18	58.7	69.2
	7D	0.05	0.05	13.2	14.0	0.18	0.16	52.0	58.0
	8D	0.06	0.06	13.8	14.7	0.22	0.21	77	75.8
	9D	0.06	0.10	12.1	11.8	0.16	0.16	44.8	56.2
10D	0.08	NS	NS	12.5	NS	0.13	NS	51.0	
60 M	0C	0.17	0.14	19.9	18.8	0.72	0.62	65.6	59.8
	1C	0.19	0.15	19.6	17.4	0.77	0.61	81.8	70.2
	2C	0.16	NS	NS	21.1	NS	0.62	NS	99.0
	3C	0.25	0.20	25.2	23.7	1.02	0.81	129	123
	4C	0.23	NS	NS	27.8	NS	1.05	NS	132
	5C	0.29	0.32	25.7	26.2	1.24	1.49	126	145
	6C	0.33	0.31	25.2	23.2	1.39	1.35	137	137
	7C	0.37	0.17	11.5	17.1	0.61	0.77	63.3	88.1
	8C	0.91	0.57	37.4	31.3	3.55	3.60	427	404
	9C	0.15	0.14	17.3	16.3	0.52	0.46	81.0	83.4
10C	0.07	NS	NS	12.0	NS	0.19	NS	59.7	
152 M	0B	0.23	0.21	21.9	21.4	0.97	0.96	78.1	77.7
	1B	0.14	0.16	18.8	18.8	0.54	0.63	90.7	93.8
	2B	0.40	NS	NS	18.5	NS	0.54	NS	92.2
	3B	0.22	0.21	20.2	19.1	0.74	0.86	114	115
	4B	0.97	NS	NS	26.8	NS	2.46	NS	217
	5B	0.52	0.78	30.6	31.3	3.29	3.59	272	277
	6B	1.10	1.06	39.9	32.4	6.04	4.29	473	326
	7B	0.71	1.37	29.8	42.2	2.98	7.17	284	597
	8B	1.00	1.24	45.4	41.9	7.96	7.51	736	719
	9B	0.45	0.42	27.1	24.3	2.53	2.06	207	204
10B	0.11	NS	NS	17.8	NS	0.30	NS	73.5	
305 M	0A	0.44	NS	NS	29.5	NS	1.56	NS	96.8
	1A	0.22	NS	NS	25.7	NS	1.92	NS	179
	2A	0.14	NS	NS	21.2	NS	0.61	NS	84.6
	3A	0.24	NS	NS	27.6	NS	1.99	NS	240
	4A	0.34	NS	NS	31.3	NS	2.85	NS	259
	5A	0.30	NS	NS	23.9	NS	1.31	NS	141
	6A	0.66	NS	NS	23.1	NS	0.72	NS	118
	7A	0.19	NS	NS	21.6	NS	0.26	NS	86.3
	8A	0.50	NS	NS	28.3	NS	1.58	NS	159
	9A	0.54	NS	NS	27.3	NS	1.80	NS	166
10A	0.14	NS	NS	21.3	NS	0.43	NS	88.4	
Min		0.01	0.03	10.4	6.42	0.16	0.13	40.4	21.4
Max		1.10	1.37	45.4	42.2	7.96	7.51	736	719
Mean		0.30	0.33	22.1	21.9	1.52	1.37	158	145
SD		0.28	0.39	9.45	7.79	1.99	1.69	170	140

Table 4.4 Organic Contaminants in Palos Verdes Sediments, 2018-2019

Total DDTs (mg/kg dry weight), total PCBs (mg/kg dry weight) and total PCB Congeners in surficial sediments collected from 24 sites in 2018 and 44 sites in 2019 (Figure 4.1) along Palos Verdes. Total concentrations represent the sum of all detectable compounds within the class as defined in Table 4.1. ND indicates that none of the targeted compounds within the class were detected. Median is calculated instead of mean for parameters with result of ND. NS= Not sampled. Min: Minimum, Max: Maximum, SD: Standard Deviation.

DEPTH	SITE	Total Detectable DDT		Total Detectable PCB		Total PCB Congeners	
		2018	2019	2018	2019	2018	2019
30 M	0D	0.15	0.13	ND	ND	ND	ND
	1D	0.16	0.14	ND	ND	ND	ND
	2D	NS	0.06	NS	ND	NS	ND
	3D	0.17	0.15	ND	ND	ND	ND
	4D	NS	0.27	NS	ND	NS	0.02
	5D	0.32	0.12	ND	ND	ND	ND
	6D	0.20	0.17	ND	ND	ND	ND
	7D	0.21	0.19	ND	ND	ND	ND
	8D	1.30	0.20	ND	ND	ND	ND
	9D	0.18	0.15	ND	ND	ND	ND
	10D	NS	0.20	NS	ND	NS	ND
60 M	0C	0.58	0.36	ND	ND	0.01	0.01
	1C	1.31	0.77	0.19	0.16	0.09	0.09
	2C	NS	0.75	NS	0.16	NS	0.09
	3C	1.40	1.12	0.20	0.33	0.12	0.15
	4C	NS	1.01	NS	0.29	NS	0.15
	5C	1.98	1.77	0.25	0.24	0.17	0.19
	6C	3.27	2.20	0.28	0.51	0.24	0.26
	7C	2.58	1.32	0.32	0.16	0.25	0.13
	8C	18.9	43.1	1.25	0.75	1.46	1.44
	9C	1.39	1.06	0.14	ND	0.15	0.04
	10C	NS	0.33	NS	ND	NS	ND
152 M	0B	0.52	0.45	ND	ND	0.01	0.02
	1B	1.06	0.69	0.12	0.11	0.05	0.06
	2B	NS	0.76	NS	0.15	NS	0.05
	3B	1.52	1.46	0.17	0.32	0.13	0.19
	4B	NS	4.53	NS	1.39	NS	1.00
	5B	5.04	1.03	1.12	0.92	0.77	0.56
	6B	7.40	4.28	1.91	1.39	1.30	0.77
	7B	6.85	15.8	1.79	3.56	1.08	2.52
	8B	7.79	6.71	2.27	1.67	1.74	1.80
	9B	2.84	3.25	0.45	0.41	0.36	0.45
	10B	NS	0.36	NS	ND	NS	ND
305 M	0A	NS	0.39	NS	ND	NS	0.01
	1A	NS	2.82	NS	0.86	NS	0.44
	2A	NS	1.02	NS	0.40	NS	0.09
	3A	NS	2.03	NS	0.59	NS	0.30
	4A	NS	3.59	NS	0.94	NS	0.56
	5A	NS	6.47	NS	0.54	NS	0.31
	6A	NS	0.92	NS	ND	NS	0.11
	7A	NS	0.75	NS	0.10	NS	0.01
	8A	NS	1.23	NS	0.29	NS	0.09
	9A	NS	1.82	NS	0.41	NS	0.20
	10A	NS	0.40	NS	ND	NS	ND
Min		0.15	0.06	0.12	0.10	0.01	0.01
Max		18.9	43.1	2.27	3.56	1.74	2.52
Mean		2.80	2.64	0.30*	0.41*	0.21*	0.15*
SD		4.16	6.80	0.76	0.74	0.58	0.58

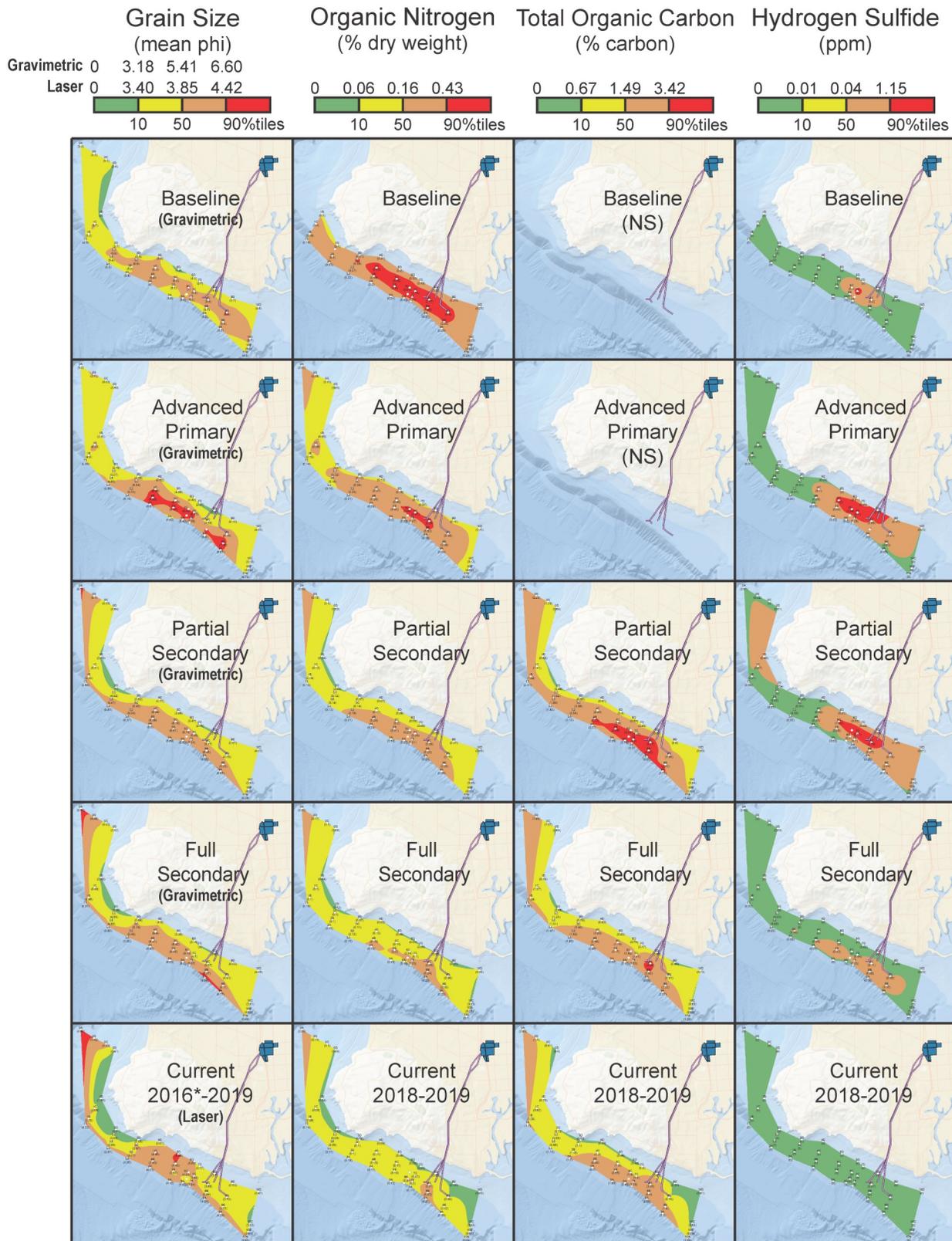


Figure 4.2 Spatial and Historical trends of Conventional Pollutants

Spatial and historical trends in average sediment concentrations over the treatment periods for mean grain size, organic nitrogen, total organic carbon and hydrogen sulfide. NS: Total organic carbon was not measured from 1972 to 1983. *Analytical method for grain size changed from sieving to laser in 2016.

accurate when particle sizes exceed 1000 μm (**Appendix 4.3**). For future grain size analysis, the gravimetric method will be the default for station 2D; laboratory staff will also track grain size at other stations to determine whether the particle sizes warrant the use of the gravimetric method.

Generally, mean grain size varied with testing depth; coarser sediments found nearshore became finer with increasing depth. This distribution is driven by a gradient of physical disturbance, which is greatest in the nearshore due to wave energy and land-based runoff. Contrary to this pattern, a patchy zone of finer grained silt and clay was found adjacent to and northwest of the outfalls, particularly at shelf depth (Figure 4.2, Appendix 4.3). This fine-grained material is assumed to be remnant particulate matter discharged from the outfall, mostly prior to implementation of full secondary treatment in 2002 that reduced the mass emission of suspended solids to very low levels (Figure 1.2). Another area of fine sediment was identified to the extreme northwest of the sampling grid (stations 0A and 0B) within the Redondo submarine canyon. Submarine canyons are natural collection areas for finer sediments and organic matter. Detailed assessment of grain size distributions and spatial patterns for percent clay, gravel, sand, and silt are provided in **Appendix 4.4**.

Elevated concentrations of organic nitrogen and TOC have also been detected in surficial sediment samples in the vicinity of the outfall since 1973 (Figure 4.2). This finding further supports the hypothesis that the origin of fine grain sediments near the outfall is remnant particulate matter associated with the discharge. During the 2018 and 2019 surveys, higher TOC results were measured at stations 6B, 7B, 8B and 8C. Lower TOC results were measured along the 30 m isobath stations (Table 4.2).

Hydrogen sulfide is generated by sulfate-reducing bacteria that converts free sulfate ions (SO_4^{2-}) to H_2S under anaerobic conditions. Anaerobic conditions often exist in organically rich sediments where oxidizing-bacteria have depleted the available oxygen in the sediments. Most porewater H_2S concentrations in 2018 and 2019 were below the detection limit (<0.03 mg/L), except for one measurement in 2019 at station 8C (0.07 mg/L). The resulting spatial pattern of H_2S is consistent with sediments enriched with

historically discharged organic material. Given the extremely low concentrations of suspended solids in the current JWPCP discharge (Figure 1.2), it is unlikely that sufficient organic matter to induce H_2S generation is currently being deposited to the seafloor by the discharge.

Trace metals and organic contaminants

Nine trace metals and two classes of organic contaminants (Table 4.1) were measured in Palos Verdes sediments at 24 sites in 2018 and 44 sites in 2019; the exception was mercury, which was measured at 44 stations in 2018 and 24 stations in 2019. Results for all trace metals and organic contaminants during the 2018-2019 sampling period are listed in Table 4.3 and 4.4, respectively. Representative trace metals (Cd, Cu, Pb, and Hg) from the averaged results of 2018 and 2019 are presented as a contour map in the bottom row of **Figure 4.3**, while the summed totals for DDTs, PCBs and PCB congeners are displayed in the bottom row of **Figure 4.4**. Isobath-related spatial profiles of all measured trace metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Ag and Zn) are provided in **Appendix 4.5**. Contour maps for As, Ni, Cr, Ag, and Zn are provided in **Appendix 4.6**. The intervals of these contour maps use the contaminant's Effects Range-Low (ERL), Effects Range-Median (ERM) developed by National Oceanic and Atmospheric Administration's (NOAA) Sediment Quality Guidelines (Long et al., 1998), and the 90th percentiles from the results of individual contaminant. In general, trace metals and organic contaminants share the same spatial distribution within the monitoring area. Specifically, the highest concentrations are measured proximal to and offshore of the outfalls. Concentrations typically decline rapidly to the southeast and more gradually to the northwest of the outfall.

This pattern is consistent with that observed for conventional pollutants and indicates that the past JWPCP discharge was a significant source of these contaminants to the sediments along Palos Verdes. However, concentrations of these contaminants in the current effluent discharge have greatly declined since the early 1970s. Effluent concentrations of nickel (Ni) have declined by more than 50% and the remaining monitored trace metals (Cd, Cr, Cu, Pb, Hg, Ni, Ag, and Zn) declined by more than 80% since 1972 when the Advanced Primary treatment

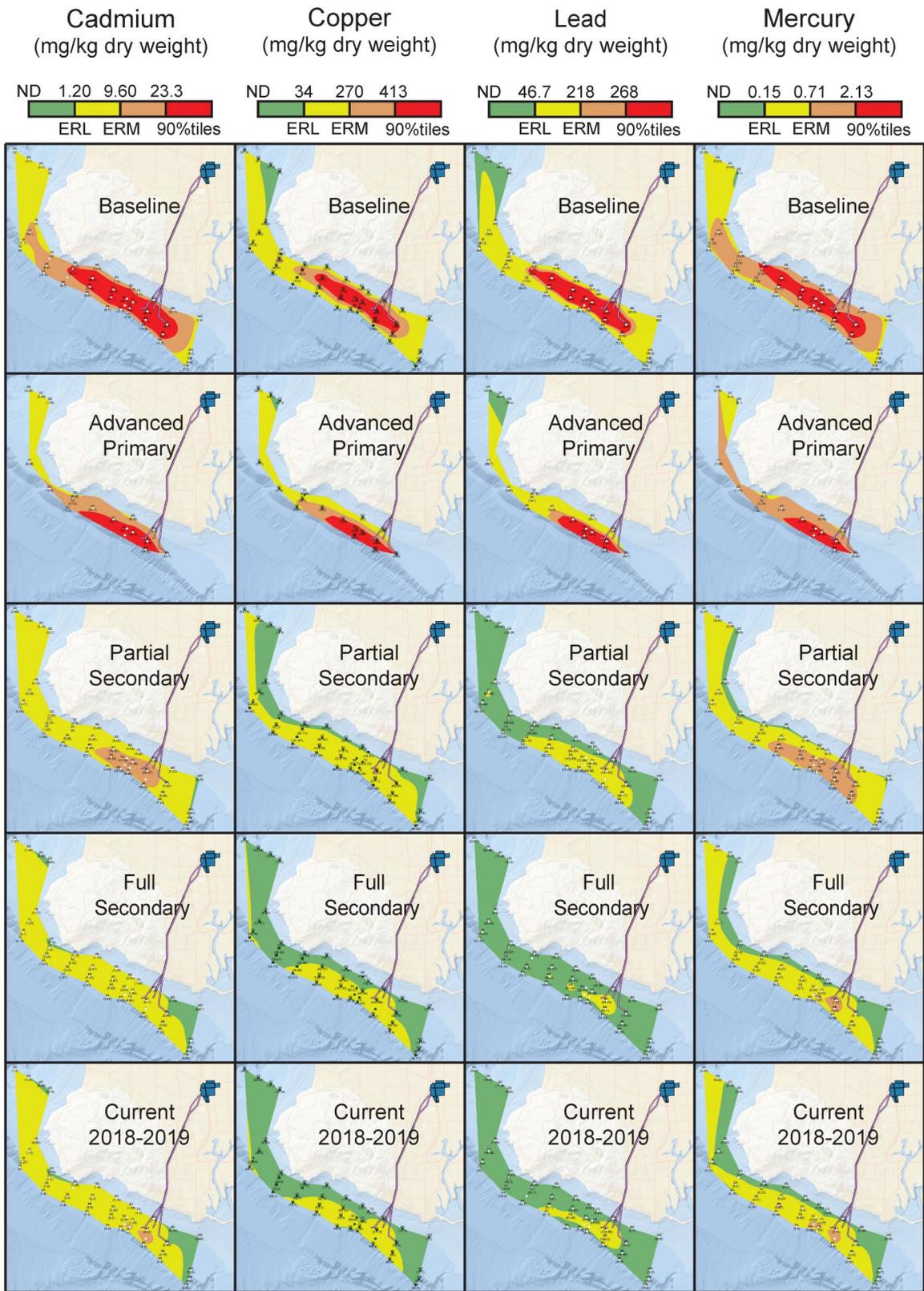


Figure 4.3 Spatial and Historical trends of Trace Metals

Spatial and historical trends in average sediment concentrations over the treatment periods of representative trace metals in Palos Verdes surficial sediments (top two centimeters). Effect Range Low (ERL), Effect Range Median (ERM) and 90percentiles values are used for binning. ND= Below detection level.

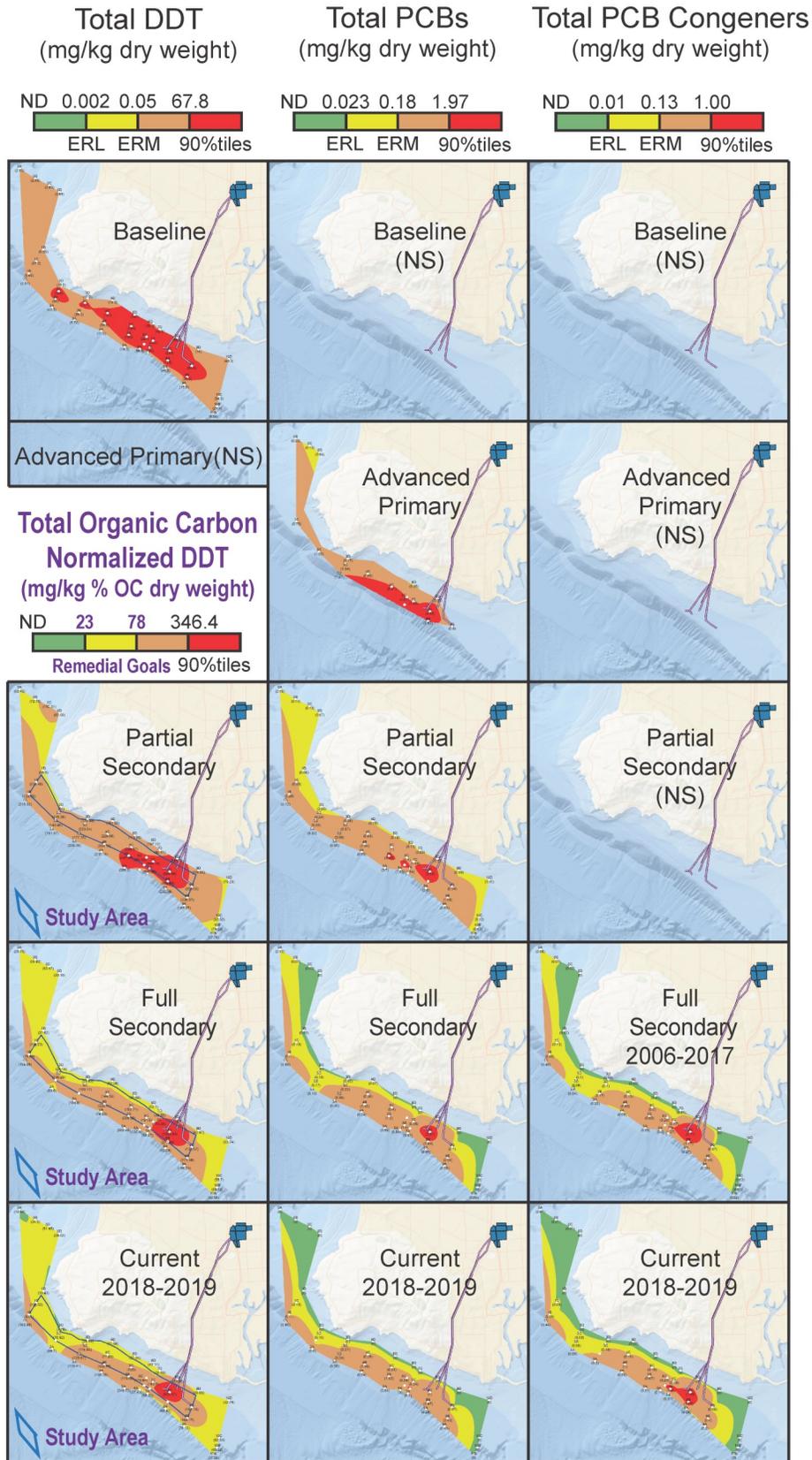


Figure 4.4 Spatial and Historical trends of DDTs and PCBs

Spatial and historical trends in average sediment concentrations over the treatment periods of total DDTs, PCBs and PCB congeners in Palos Verdes surficial sediments (top two centimeters). Effect Range Low (ERL), Effect Range Median (ERM) and 90 percentiles values are used for binning except total DDTs since the Partial Secondary treatment period. Instead, EPA's Palos Verdes Shelf Superfund Site Remedial Goals are used. Contour maps represent samples were collected at 44 stations. NS= Not sampled. ND= Below detection level.

began (Figure 1.3). Compliance monitoring for total PCBs as Aroclors in JWPCP effluent samples (Figure 1.4) was below analytical detection limits in 2018 and 2019 (Table 4.4; LACSD 2019, LACSD 2020b). Furthermore, the 95% reduction in suspended solids in the discharge (compared to 1971) has minimized the potential for these pollutants to adhere to particulate matter and be delivered to the seafloor in the immediate vicinity of the outfalls. Therefore, the contaminants found in surficial sediments are primarily a legacy of historical discharges prior to the implementation of full secondary treatment in 2002.

Contaminant concentrations in sediments collected from the 2013 Regional Monitoring Survey stations were summarized in the Bight '13 Sediment Chemistry report (Dodder et al. 2016). Although the concentration of the class of flame-retardant chemicals known as Polybrominated Diphenyl Ethers (PBDEs) has dropped by 92% in Southern California Bight embayments over a five-year period, and by 50% offshore, the concentrations of legacy contaminants such as DDTs, PCBs and metals remain largely unchanged. The Santa Monica Bay National Estuary Program (SMBNEP) also examined the soft-bottom habitat conditions for DDT, PCBs, and mercury throughout the Santa Monica Bay and PVS, and concluded that the structure and ecological disturbance is fair and that the conditions for DDT, PCBs, and mercury are improving (Bay et al., 2015).

Historical trends, 1973-2019

In the early 1970s, the Sanitation Districts began to monitor sediment condition with selected parameters and sampling sites. Data gaps occurred in the early years (e.g., Transect 0 was not sampled until 1973; the first surveys for total DDT and metals were 1973 and 1974, respectively). However, significant improvement in sediment chemistry quality was observed due to improved wastewater treatment practices during the past four decades (Chapter 1). Depending on data availability, the discussion of historical trends is categorized by Baseline (1973/1974), Advanced Primary Treatment (1974-1983), Partial Secondary Treatment (1984/1985-2002), Full Secondary Treatment (2003–2017), and Current years (2018-2019). Results for individual parameters

are presented in Figure 4.2, Figure 4.3, and Figure 4.4.

Conventional pollutants

Surface sediment concentrations of conventional pollutants are much lower than they were four decades ago, confined to a much smaller area, and increasingly focused on the outfall termini. Figure 4.2 illustrates the sequence of changes in concentration and spatial patterns of surface sediment organic nitrogen, TOC, and H₂S between 1973 and 2019. This trend indicates that organically enriched particulate matter historically deposited in surface sediments along the majority of the Palos Verdes shelf and slope has largely been remediated. This reduction is primarily due to the combination of reduced mass emissions of organically enriched suspended solids and decomposition of organic matter by microbes, invertebrates, and fish. Burial and downcurrent transport of surface sediments, as a result of sediment resuspension (at varying rates by wave action or storms) has also played a significant role in these reductions.

Grain size analysis was performed gravimetrically using a combination of sieve and pipette analyses from 1973 to 2015. However, the gravimetric method was extraordinarily labor-intensive, and the majority of the other local Public Owned Treatment Works (POTWs) and the Regional Survey “Bight” program discontinued this method of analysis. Since 2016, grain size samples have been analyzed using a laser particle size analyzer. Historically, even the very coarse relict red sands near station 2D were inundated with finer particulate matter, presumably from the JWPCP discharge. However, the pattern has changed through the Partial Secondary and Full Secondary period. Depth, which is inversely proportional to physical disturbance, became the primary determinant of mean grain size, except in the immediate vicinity of the outfall.

Since 1973, the concentration of organic nitrogen in Palos Verdes surface sediments has decreased substantially until there is only a remnant of slightly enriched sediment in the immediate area offshore and downcurrent of the discharge. Although TOC was not measured

from 1972 to 1983, a similar trend can be observed in the TOC time series data. The concentration and spatial extent of H₂S in sediments also declined considerably since the mid-1980s. Hydrogen sulfide observed sporadically in low concentration in recent years is most likely derived from historic deposits of discharged organic matter.

Trace metals and organic contaminants

Historical monitoring of trace metals and organic contaminants has been less consistent than conventional pollutants due to changing permit requirements. Consequently, the specific years available to evaluate historical trends are much more variable and occasionally limited, particularly for the organic contaminants. Despite these limitations, a general trend very similar to that displayed by the conventional pollutants is clearly evident.

Elevated concentrations of trace metals in surface sediments were widespread throughout the monitoring area in the Baseline period (Figure 4.3; Appendix 4.6). Contour maps with 24 stations for the years of the Advanced Primary period (1974-1983) represented high concentrations of the metals at the stations along the 61-meter and 152-meter isobaths. By the Partial Secondary period (1984/1985-2002), concentrations began to decline in shallow water and with distance from the outfall in deeper water. The concentration gradient in sediments to the southeast (upcurrent) of the outfall declined rapidly with distance while to the northwest (downcurrent), the gradient in sediments was more gradual. This pattern of decline continued through the Full Secondary period (2003-2017) until the Current period (2018-2019), where elevated concentrations of trace metals are generally restricted to the immediate vicinity of the outfall. Possibly due to the heterogeneity of historical data at station 8C, the averaged total PCB concentration during the 2018 and 2019 surveys (1.00 mg/kg, dry weight) was less than half its previous 15-year average concentration (3.81 mg/kg, dry weight). Concentrations of the total PCB congeners declined during the Full Secondary period (2003-2017) and Current period (2018-2019). Although sampling efforts varied for DDTs, PCBs, and PCB congeners during the Baseline and Advance Primary treatment periods, similar temporal responses were observed for

these organic pollutants (Figure 4.4). The Palos Verdes Shelf Superfund Site is currently under a remedial process led by the United States Environmental Protection Agency (EPA), which has set interim and final remedial goals for DDT (EPA 2009). Three contour maps plotted using TOC-normalized DDT concentrations in the lower left column of Figure 4.4 demonstrate the temporal distribution and spatial pattern of DDT contamination gradients with the final remedial goal (23 mg/kg OC), interim remedial goal (78 mg/kg OC), and the 90th percentiles of the TOC-normalized DDT concentration. Elevated TOC-normalized DDT concentration is close to the vicinity of outfall discharge and is consistent with EPA's most recent survey conducted from 2013 to 2016 (EPA 2018).

The NPDES permit has required the Sanitation Districts to analyze 41 PCB congeners since 2006 (Table 4.1). Spatial distributions for total PCBs and total PCB congeners are similar during the Full Secondary treatment period (Figure 4.4).

The primary processes responsible for the reductions in surface sediment contamination over time are identical to those identified for conventional pollutants. The greatly reduced mass emissions of suspended solids since 1972 (Figure 1.2) combined with the Sanitation Districts' comprehensive industrial waste pretreatment program (Chapter 1) have significantly reduced the loading of these trace metals and organic compounds to the sediments. Besides the loading decrease, decomposition of organic matter in the sediments by bacteria and other fauna resulted in varying degrees of biodegradation of organic contaminants and/or assimilation into the biota, which has removed these constituents from the area (Eganhouse and Pontolillo 2008). Burial and downcurrent transports of surface sediments due to re-suspension and re-deposition by wave action or storms were also factors in the redistribution of legacy toxicants within the monitoring area.

CONCLUSIONS

For over 81 years, the Sanitation Districts have discharged treated wastewater to the Palos Verdes shelf. By the early 1970s, the effluent inputs of suspended solids and trace constituents, such as organics and metals, had created a zone of fine-grained sediments highly enriched in organic

matter and contaminants. The highest concentration of contaminants was found near the discharge, with an outfall-centered gradient of sediment chemistry quality.

As a result of treatment upgrades initiated in the early 1970s, the final effluent quality has improved dramatically (Chapter 1). This resulted in great improvements in surface sediment chemistry quality across the Palos Verdes shelf and slope. In addition, the magnitude and geographic extent of elevated organic nitrogen, trace contaminants, fine-grained sediments, and porewater hydrogen sulfide has decreased. These changes first occurred on the more physically energetic inner shelf, followed by gradual reductions in sediment organic matter and trace contaminants on the outer shelf and on the slope.

In the 2018 and 2019 surveys, Palos Verdes sediments near, northwest, and offshore of the outfall system were marginally enriched with organic nitrogen and total organic carbon compared to reference sediments. This region also contains the highest levels of chemical contamination. Porewater hydrogen sulfide levels were generally very low and spatially confined to small areas. Although the relative contributions of historic and contemporary wastewater discharge to surface sediment chemistry quality are not easily separated, the extremely low concentrations of pollutants in the current JWPCP effluent discharge suggest that legacy discharges, preserved in a partially buried sediment reservoir, caused the slight residual pollutant enrichment near the outfall.

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