chapter 4

SEDIMENT GEOCHEMISTRY

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INTRODUCTION

The Orange County Sanitation District's (District) Ocean Monitoring Program (OMP) requires assessments of sediment quality, including the distribution and concentration of chemical contaminants in bottom sediments within the monitoring area. The objectives are to determine the presence, magnitude, and spatial extent of wastewater-related changes to sediment characteristics and their possible relation to the health of biological communities, which are then used to determine compliance with the District's NPDES ocean discharge permit (see box).

Compliance Criteria Pertaining to Sediment Geochemistry Contained in the District's NPDES Ocean Discharge Permit (Order No. R8-2004-0062, Permit No. CAO110604).								
<u>Criteria</u>		Description						
C.3.d	Inert Solids	The deposition of inert solids in marine sediments shall not degrade benthic communities.						
C.4.c	Dissolved Sulfides	Dissolved sulfide concentrations shall not be elevated to concentrations resulting in degradation to biota.						
C.4.d	COP Table B Substances	Substances found in California Ocean Plan Table B shall not cause degradation to biota.						
C.4.e	Organics in Sediments	The concentration of organic material in sediments shall not be increased to levels resulting in degradation of marine life.						
C.5.a	Marine Biological Communities	Marine communities, including invertebrates, fishes, and algae shall not be degraded.						

Both natural and anthropogenic processes affect the physical and chemical properties of sediments. The outfall pipe and the associated ballast rock make one of the largest artificial reefs in southern California. The outfall structure alters current flow and sediment characteristics near the pipe (e.g., grain size and sediment geochemistry). Wastewater discharge is one anthropogenic factor that can affect sediment quality. Discharged effluent contains a variety of organic and inorganic contaminants, including pesticides and metals (Anderson et al. 1993; OCSD 1985, 2003). Changes in the amounts and types of chemical contaminants discharged to the ocean, as well as the proportion of wastewater particles that settle and accumulate on the seafloor, may be reflected in sediments near the outfall. Periodic measurements of the physical, chemical, and toxicological characteristics of sediments are used to assess these changes and can identify temporal and spatial trends.

METHODS

The District collected sediment samples quarterly at ten stations along the 60-meter (m) contour (outfall depth) and annually at an additional 39 stations throughout the monitoring area for physical, chemical and toxicity analysis (Figure 4-1). Three replicate samples were collected at the quarterly stations in July 2007 followed by single samples at those stations in October 2007, and January and April of 2008. The purpose of the quarterly surveys is to determine station differences and long-term trends, while the annual survey is primarily to assess the spatial extent of the influence of the effluent discharge. The annual survey assessment included the first repetition of the quarterly stations collected in July 2007, as well as the 39 annual stations that range in depth from 40 to 303 m (n=49 stations).

Sediments were collected using a paired 0.1 m² Van Veen grab sampler. The top 2 cm of the sample was collected for individual chemical and toxicity analyses using a stainless steel scoop. All sediment chemistry samples (metals. organics, TOC, grain size, and dissolved sulfides) were placed in wet ice on the boat and then transferred to the District's Environmental Sciences Laboratory for analysis.

In addition to the direct measurement of chemical contaminants in the sediments, the District also conducted laboratory sediment toxicity tests as a measure of sediment quality.

Sediment toxicity was tested in January 2008 using whole sediments for the 10-day *Eohaustorius estuarius* amphipod survival test. Amphipods were exposed to test and control sediments and the percent survival in each were determined. Toxicity threshold criteria were selected to be consistent with the Bight'98 Sediment Toxicity Program (Bay et al. 2000). A difference of 20–50% was considered a moderately toxic response, while differences greater than 50% were considered highly toxic.

Metals, chlorinated pesticides, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), and concentrations of organic matter, as measured by total organic carbon (TOC), and dissolved sulfides were measured. Linear alkylbenzenes (LABs), which are commonly found in detergents and serve as useful markers for sewage, were also measured to better distinguish changes in sediment quality attributable to the wastewater discharge. Sediment chemistry and grain size samples were processed and analyzed using performance-based and EPA-recommended methods. Samples for dissolved sulfide were analyzed in accordance with procedures outlined in Schnitker and Green (1974) and Standard Methods 20th Edition (1998).

The District's NPDES ocean discharge permit states that the concentrations of substances contained in Table B of the California Ocean Plan (COP) and the concentration of organic substances shall not be increased to levels that would degrade marine life. The COP does not contain numeric sediment quality criteria and there are no numeric sediment contaminant limits in the District's NPDES discharge permit. Sediment contaminant concentrations were evaluated against sediment quality guidelines known as Effects Range-Low (ERL) and Effects Range-Median (ERM) (Long et al. 1995) and the mean ERM quotient (mERMq) method (Long et al. 1998). The ERL/ERM guidelines were developed for the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends Program as non-regulatory benchmarks to aid in the interpretation of sediment chemistry data and to compliment toxicity, bioaccumulation, and benthic community



Figure 4-1. Sediment geochemistry sampling stations for annual (blue) and quarterly (red) surveys, 2007-08.

assessments (Long and MacDonald 1998). The ERL is defined as the 10th percentile concentration of a chemical in sediment below which a toxic effect is unlikely. An ERM is the 50th percentile concentration above which a toxic effect frequently occurs (Long et al. 1995).

Because chemical contaminants tend to co-occur in sediments and toxicity can be related to exposures to multiple contaminants, Long et al. (1998) developed the mean ERM quotient (mERMq) to improve the ability to use contaminant concentrations to predict toxicity. The mERMq is the average of specific compound concentrations divided by their corresponding ERM. Based on the recommendations in Long et al. (1998), the minimum level of significance for mERMq analysis was set at 0.11. A mERMq of 0.1 to 1.0 corresponds to a 32% probability of high sediment toxicity and 16.5% of marginal sediment toxicity, or a 48% likelihood of the sediment exhibiting some degree of toxicity. A mERMq of greater than 1.0 corresponds to a 71% probability of high sediment toxicity and 6% of marginal sediment toxicity, or a 77% likelihood of some degree of sediment toxicity. The mERMq was also employed as an assessment benchmark in this analysis.

Statistically significant differences between quarterly stations for physical parameters and chemical analytes were determined using one-way analysis of variance (One-way ANOVA) followed by a Tukey multiple comparison test. Depth-related gradients were measured using linear regression. Spatial trends were measured using principal components analysis (PCA) techniques. Data was transformed where appropriate. ANOVA and regression analyses were performed using the Minitab® Statistical Software package.

Total DDT represents the summed concentrations of o,p'- and p,p'- [2,4- and 4,4'-] isomers of DDD, DDE, and DDT), total PCB represents the summed concentrations of 45 congeners, and total chlordane represents the sum of alpha- and cis-chlordane and cisand trans-nonachlor. For summed concentrations, undetected components (i.e., concentrations below the analytical detection limits) were treated as zero. When all component concentrations were undetected, the corresponding total concentrations were assumed to be zero. Single analytes not detected during analysis were given the value of one-half the detection limit for statistical analysis.

A more complete summary of methods for the analyses and the indices used in this chapter are presented in Appendix A.

RESULTS AND DISCUSSION

The following is a summary of the annual survey conducted in July 2007 and the four quarterly surveys conducted in July and October 2007, and January and April 2008. Results of the July 2007 annual survey are presented in Tables B-13 (sediment physical characteristics and organic contaminants) and B-14 (sediment metals).

Spatial Analysis

Sediment Grain Size

Grain size distributions typically followed a pattern of larger grain size inshore and downcoast of the diffuser and become finer as you move offshore and into deeper, depositional environments, such as the Newport Canyon. In July 2007, as in previous years, sediment grain size varied considerably in the monitoring area. In particular, changes in the percentage of fine particles (silt + clay = fines) and median grain size (phi) changed with bathymetry and proximity to the outfall (Figure 4-2; note that the greater the median phi the smaller the sediment grain size).

The larger grain size and a lower percentage of fines near the outfall are due in part to scouring by currents and contributions from coarse-grained shell hash (i.e., the calcareous tubes of worms and mollusk shells). Correlation analyses performed on the relationships of tLAB sediment concentrations to median phi (R = 0.27) and percent fines (R = 0.20) indicate that only a minor percentage of the observed patterns are attributable to the wastewater discharge.

At the quarterly stations, annual mean values for median phi ranged from 3.37 at Station 12 to 3.86 at Station 5, while proportions of percent fines (silt and clay) ranged from 14.2% at Station ZB2 to 39.2% at Station 5 (Table 4-1). Mean grain sizes were smaller upcoast of the outfall diffuser following the pattern seen in the July 2007 annual survey.

Linear Alkylbenzenes (LAB)

In July 2007, concentrations of total LABs (tLAB) were highest within the ZID followed closely by stations in the San Gabriel Submarine Canyon (Figure 4-3). In July 2007, tLAB concentrations ranged from 12 μ g/kg at Station 55 to 737 μ g/kg at Station 0 (Appendix D, Table D-1). This spatial pattern suggests the deposition of wastewater particles since LABs and wastewater are strongly associated (SAIC 2003).

In the quarterly surveys, tLAB concentrations were highest at ZID stations and decreased with increasing distance from the outfall in both directions along the 60 m contour (Table 4-1). Within ZID concentrations were between 2 and 8 times greater than concentrations at Station CON.

Sediment Organic Content

Total Organic Carbon (TOC)

In July 2007, sediment TOC concentrations ranged from 0.25% at Station ZB to 1.87% at Station C5 (Appendix D Table D-1) and generally increased with depth (Figure 4-3). This is expected since sediment organic carbon content tends to increase with decreased grain size and increased percent fines. Correlation analysis found significant relationships of median phi to TOC (r = 0.94) and percent fines to TOC (R = 0.89).

At quarterly stations, sediment percent TOC was higher at Stations 0 (0.425) and ZB2 (0.403) compared to the other quarterly stations (mean = 0.314) (Table 4-1). The infaunal populations at these stations showed evidence of adverse impact from the effluent discharge (see Chapter 5).



Figure 4-2. Spatial distributions of median grain size (phi) and fine sediments (% less than 62 micron diameter) during July 2007.

Orange County Sanitation District, California.

Table 4-1. Average annual concentrations of sediment organic contaminants (µg/kg) compared to Effects Range–Low (ERL) and Effects Range–Median (ERM) values (Long et al. 1995), and measurements of sediment physical characteristics at the District's quarterly stations in 2007-08.

Values greater than the ERL are bolded in red. Quarterly stations n = 4; Total LAB only collected in July 2007.

Station	Depth	Median Phi	Fines (%)	Sulfides (mg/kg)	ТОС (%)	Total DDT (ug/kg)	Total PCB (ug/kg)	Total PAH (mg/kg)	Total LAB (ug/kg)	
0	56	3.47	14.6	7.49	0.425	37.0	23.1	295	644	
1	56	3.69	27.9	3.46	0.365	3.07	9.03	59.9	116	
4	56 3.44 15.1 4.10		4.10	0.287	0.908	0.553	34.1	185		
5	59	3.86	39.2	1.64	0.302	2.61	4.93	75.0	121	
9	59	3.42	17.4	2.47	0.305	1.50	1.39	36.9	134	
12	58	3.37	17.6	5.34	0.302	1.61	2.43	35.5	88.1	
С	56	3.61	27.9	4.07	0.360	3.25	0.990	30.1	88.0	
CON	59	3.66	26.6	1.97	0.347	3.83	0.413	59.3	88.6	
ZB	56	3.53	18.1	5.87	0.243	0.785	1.36	43.6	196	
ZB2	56	3.48	14.2	4.70	0.403	2.31	7.49	153	428	
		SEDIMEN	NT QUALI	TY GUIDELII	NE AND R	EFERENCE	VALUES			
ERL		N/A	N/A	N/A	N/A	1.58	22.7	4,022	N/A	
ERM		N/A	N/A	N/A	N/A	46.1	180	44,792	N/A	
SCBPP Outfall Average		N/A	N/A	N/A	N/A	147	43.0	ND	N/A	
SCBPP Non- Outfall Average		N/A	N/A	N/A	N/A	15.3	8.00	ND	N/A	
Bight'98 Mid-Depth AWM		N/A	N/A	N/A	N/A	54.0	6.50	67.0	N/A	
N/A = Not Applicable, ND = Not Detected, AWM = Area Weighted Mean ¹ Schiff and Gossett (1998)										

Orange County Sanitation District, California

² Noblet et al. (2002)



Figure 4-3. Spatial distributions of total organic carbon (TOC, %) and total linear alkyl benzenes (tLAB) during July 2007.

Orange County Sanitation District, California.

Dissolved Sulfides

In the annual survey, sediment sulfide concentrations ranged from not detected at Stations 18 and 55 to 51.5 mg/kg at Station C2 and showed no discharge related patterns beyond the near ZID stations (Appendix D Table D-1). Sulfide concentrations were generally higher in the Newport Canyon and offshore slope areas, which is expected for these depositional environments. Dissolved sulfide concentrations were elevated within the ZID compared to shelf stations located near and upcoast of the diffuser, which were fairly uniform (Figure 4-4). However, several stations located downcoast of the diffuser had concentrations comparable to ZID stations. For example, Station 33 had sediment sulfide concentrations 3–7 times higher than ZID stations. However, invertebrate community analysis indicated a normal community exists at that station (see Chapter 5).

In the quarterly surveys, sediment sulfide concentrations were elevated at the ZID stations compared to Station CON (Table 4-1). However, only Station 5 had a mean concentration lower than Station CON and the concentration at Station 12 exceeded ZID Stations 4 and ZB2.

Organic Contaminants

Polycyclic Aromatic Hydrocarbons (PAH)

In July 2007, sediment total PAH (tPAH) concentrations were highest in the ZID, Newport Submarine Canyon, and offshore slope areas (Figure 4-4). Concentrations ranged from 3 μ g/kg at Station 37 to 404 μ g/kg at Station 0 (Appendix D Table D-1). Correlation analysis showed a significant relationship of tPAH with tLAB (R = 0.80). All tPAH concentrations in the monitoring area were well below the ERL value, indicating a low probability of sediment toxicity due to PAHs.

Total PAH concentrations at quarterly stations ranged from 30.1 μ g/kg at Station C to 295 μ g/kg at Station 0 (Table 4-1). Only Stations 0 and ZB2 had tPAH concentrations greater than 75 mg/kg, while the other quarterly stations ranged between 30.1 and 75.0 mg/kg. All concentrations were well below the ERL.

Chlorinated Pesticides

Total DDT (tDDT) continued to the dominant pesticide detected in the sediments. While the use of DDT has been banned since the 1970's, it is still present in the sediments in the Districts monitoring area due to the long half-life of the compound and its breakdown products. DDT tends to adhere to fine particles (i.e., grain size, which generally decreases with increasing depth), so these contaminants tend to be found in deeper, depositional areas (e.g., San Gabriel Canyon).

In July 2007, tDDT concentrations generally increased with depth, with no outfall pattern indicated (Figure 4-5). All of the annual stations, except Stations 4, 9, 12, 55, and ZB, exceeded the ERL; none exceeded the ERM (Appendix D Table D-1). Total DDT concentrations ranged from 0.74 μ g/kg at Station ZB to 30.2 μ g/kg at Station 58. All concentrations were below the ERM value of 46.1 μ g/kg as well as the Southern California Bight Pilot Project (SCBPP) outfall averages and the Bight'98 mid-depth area weighted mean (Appendix D Table D-1). This was consistent with previous monitoring years and within the range of background values reported by regional monitoring studies (Schiff and Gossett 1998, Noblet et al. 2002).



Figure 4-4. Spatial distributions of dissolved sulfides concentrations (mg/kg) and total polycyclic aromatic hydrocarbons (tPAH) concentrations (ug/kg) during July 2007.

Orange County Sanitation District, California.



Figure 4-5. Spatial distributions of total DDT (tDDT) and total PCB (tPCB) concentrations (ug/kg) during July 2007.

Orange County Sanitation District, California.

Quarterly station means for tDDT ranged from 0.908 µg/kg at Station 4 to 37.0 µg/kg at Station 0 (Table 4-1). No outfall pattern was indicated as both the highest and lowest concentrations occurred within the ZID and Station CON had the second highest concentration among the quarterly stations. Historically, tDDT has been found to be highly variable between years (OCSD 2003). The lack of outfall influence is consistent with results from previous years and the legacy contaminant properties of DDT.

The majority of the other chlorinated pesticides were not detected and the distribution of the summed constituents of these pesticides did not follow any particular pattern relative to the outfall.

Polychlorinated Biphenyls (PCB)

In July 2007, sediment concentrations of total PCB (tPCB) ranged from 0.090 µg/kg at Stations 12 to 50.8 µg/kg at Station 0 (Appendix D Table D-1). Concentrations of tPCB were higher in sediments at and upcoast from the outfall diffuser (Stations 0, ZB2, and 1, respectively) and within portions of the San Gabriel and Newport Submarine Canyons (Stations 57, 62, and C2, respectively) (Figure 4-5). This pattern is consistent with previous monitoring years (OCSD 2007). All tPCB concentrations at annual stations were below the ERL values and the SCBPP outfall average, while most were below the SCBPP non-outfall average and Bight'98 area weighted mean.

Quarterly station mean tPCB concentrations ranged from 0.413 μ g/kg at Station CON to 23.1 μ g/kg at Station 0 (Table 4-1). Mean concentrations were higher at ZID stations and the two closest upcoast stations (1 and 5), suggesting an outfall influence. Station 0 had mean tPCB concentrations above the ERL, but not above the ERM (Table 4-1).

<u>Metals</u>

In July 2007, as in previous years, two basic patterns were observed in sediment metal concentrations: 1) those showing grain size/depth-related increases with no clear outfall effect indicated (Group A metals), and 2) those showing some degree of outfall influence (Group B metals). Figure 4-6 presents contour plots of the spatial distribution of one representative Group A and Group B metals (copper and cadmium, respectively). In July 2007, Group A metals included arsenic, beryllium, chromium, copper, lead, mercury, nickel, selenium, and silver. Group B included only cadmium and zinc. This is in contrast to previous years where Group B metals generally included copper, mercury and silver (OCSD 2007). In July 2007, copper and nickel concentrations exceeded their respective ERLs at several stations, generally those located within the canyons and slope areas, with no outfall effect indicated. Figures B-22 and B-23 present contour plots for all metals not presented in Figure 4-6.

In the quarterly surveys, no metal exceeded its ERL value in 2007-08 (Table 4-2). Cadmium and zinc showed elevated outfall concentrations compared to the other 60 m stations, but the concentrations were well below the ERL.

Sediment Toxicity

Whole-sediment toxicity testing was conducted on sediments collected during the January 2008 survey. No significant toxicity was found. The percent difference in amphipod



Figure 4-6. Spatial distributions of copper (mg/kg) and cadmium (mg/kg) during July 2007.

Table 4	Table 4-2. Average annual concentrations of sediment metals (mg/kg) at the District's quarterly stations in 2007-08 compared with Effects Range–Low (ERL) and Effects Range–Median (ERM) values (Long et al. 1995). NA = Not applicable. Values greater than the ERL are bolded in red. Quarterly stations n = 4. Orange County Sanitation District, California.										
Station	Arsenic	Beryllium	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc
0	3.23	0.229	0.774	21.9	15.8	5.90	0.038	9.14	0.867	0.370	58.6
1	2.78	0.243	0.386	20.9	13.6	6.02	0.031	9.34	0.787	0.298	44.7
4	2.89	0.247	0.269	19.0	9.34	4.62	0.019	8.38	0.751	0.169	40.0
5	3.08	0.269	0.342	23.7	13.4	6.37	0.039	10.6	0.977	0.292	46.9
9	2.53	0.244	0.228	19.1	9.19	4.68	0.021	8.69	0.765	0.175	39.1
12	2.61	0.224	0.200	17.9	8.29	4.60	0.021	8.42	0.798	0.144	37.5
С	3.26	0.245	0.243	20.7	9.96	6.05	0.023	10.2	0.755	0.159	44.8
CON	3.08	0.269	0.208	21.8	9.90	5.82	0.035	10.6	0.744	0.154	44.2
ZB	2.55	0.249	0.435	18.5	9.17	4.06	0.023	8.74	0.687	0.162	43.7
ZB2	3.11	0.228	0.687	20.8	14.8	6.40	0.035	9.15	0.722	0.315	52.2
				SEDIMENT	QUALITY	GUIDELI	NES				
ERL	8.20	NA	1.20	81.0	34.0	46.7	0.15	20.9	NA	1.00	150
ERM	70.0	NA	9.60	370	270	218	0.70	51.6	NA	3.70	410

survival between station and control sediment was less than 9% for all stations, indicating very low toxicity (Table 4-3). Mean ERMq values ranged from 0.02 to 0.07, indicating a low potential for sediment toxicity (Table 4-4).

Long-term (Temporal) Trend Analysis

Trends over time in physical characteristics and chemical concentrations in sediment collected at the 10 quarterly stations was made using grouped data to increase the sample size at each station, which decreases the variability of each data point on the graph. The quarterly stations were divided into five stations groups based on their proximity to the outfall diffuser (MEC 1997): farfield upcoast (FFU = Stations CON and C); nearfield upcoast (NFU = Stations 1 and 5); nearfield downcoast (NFD = Station 9 and 12); within ZID upcoast (WZU = Stations 0 and ZB2); and within ZID downcoast (WZD = Station 4 and ZB). Figure 4-7 presents graphically the long-term trends in sediment measures. Each measure is represented as a line graph, which shows the inter-annual variability, and as a best-fit line to show the overall direction of change (increasing/decreasing).

Sediment Grain Size

The best-fit line in Figure 4-7 shows median phi is increasing over time at NFU and NFD, and decreasing at the other station groups. However, this may be misleading. The increase in NFU appears to be driven by an unusually low value in 2001-02 and an unusually high value in 2002-03, while the remaining values range from about 3.60 to 3.80 consistently. Similarly, median phi at NFD is consistently about 3.45, except for 1999-00, which was down at about 3.25, making the best-fit line show an overall increase over time. Conversely, median phi for WZU, WZD, and FFU is about 3.50 consistently for all three groups, except for 1999-00, which was about 3.60. This resulted in a best-fit line that

Table 4-3. Sediment toxicity test results for January 2008. Whole-sediment (amphipod) test results given as test sediment percent difference from home sediment.

Negative value represent values greater than 100% from control.

Dete	Station											
Date	0	1	4	5	9	12	С	CON	ZB	ZB2		
January 2008	3	3	4	3	-1	-3	9	0	-2	3		
October 2006*	-1.15	-4.60	2.30	1.15	1.15	2.30	5.75	-5.75	3.45	-4.60		
2005-06 Mean	2.53	-0.51	5.55	0.510	-0.510	1.52	0.510	1.52	3.53	0.510		
2004-05 Mean	6.00	7.00	5.00	5.00	1.00	1.00	3.00	1.00	-1.00	6.00		
2003-04 Mean	5.00	4.00	5.00	5.00	4.00	3.00	10.0	3.00	8.00	5.00		
2002-03 Mean	5.33	3.67	5.00	5.00	4.00	3.33	10.3	2.67	8.00	5.33		

Orange County Sanitation District, California.

Amphipod Test: >20% difference and significantly different (p<0.05) from the control = toxic response (Bay et al. 2000) Home Sediment = Control

*Results prior to July 2006 are means based on quarterly testing. Beginning in the 2006-07 monitoring year, only one quarter per year is tested. The quarter to be tested is chosen at random with the provision that a quarter will not be tested in consecutive years.

Table 4-4. Mean ERMq values for sediment contaminant concentrations, 2007-08. Values less than or equal to 0.10 indicate a low potential for toxicity.

Orange County Sanitation District, California.

Survey	Stations										
Survey	0	1	4	5	9	12	С	CON	ZB	ZB2	
July 2007	0.07	0.04	0.02	0.04	0.03	0.02	0.03	0.03	0.03	0.04	
October 2007	0.05	0.04	0.02	0.04	0.02	0.02	0.03	0.03	0.03	0.05	
January 2008	0.05	0.04	0.03	0.04	0.02	0.02	0.03	0.03	0.03	0.04	
April 2008	0.06	0.04	0.03	0.04	0.03	0.02	0.03	0.03	0.03	0.05	
2007-08 Mean	0.06	0.04	0.03	0.04	0.03	0.02	0.03	0.03	0.03	0.05	
2006-07 Mean	0.07	0.04	0.02	0.04	0.02	0.02	0.03	0.02	0.03	0.05	

0.0-0.10 = low potential for toxicity

0.11-1.0 =moderate potential for toxicity

>1.0 = high potential for toxicity

(Long et al. 1998)



Figure 4-7. Changes Over Time of RMANOVA Values for total DDT, total PCB, total PAH, median phi, % fines, sulfides¹, total organic carbon,arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc in sediments at the 60 m shelf station groups during 1998 - 2008.

¹Sulfides analysis performed as Acid Volatile Sulfides from 1997 through 2006 and as Dissolved Sulfides for 2007 and 2008.



Figure 4-7 Continued.



Figure 4-7 Continued.



Figure 4-7 Continued.



Figure 4-7 Continued.



Figure 4-7 Continued.

showed a decreasing trend. When these few aberrant results are removed, there appears to be no significant trend at any station group over time.

The trends in percent fines are small in magnitude and showed a similar pattern to median phi. NFU and NFD are increasing, WZU and WZD decreasing slightly, and FFU shows no notable change over time. NFU has the greatest rate of change at about a 5% increase over time, which appears to be only slightly higher than natural variability based on the trend at FFU.

Sediment Organic Content

Sulfide is decreasing in all station groups with the greatest rate of decline occurring at WZU. The large decrease at WZU is due to an extremely high value in the 1999-00 monitoring year. When that value is removed as an outlier, WZU, like the other station groups, shows consistently low concentrations with no temporal trend evident.

Percent TOC is increasing over time at all station groups except the WZU group. The decrease in WZU is due to a single high value in 1997-98. When this value is removed, all five station groups show a similar increase over time of about 0.2 to 0.4%. Since all station groups show essentially the same pattern, a regional, rather than an outfall, influence is indicated.

Organic Contaminants

The three main organic contaminants (DDT, PCB, and PAH) serially show decreasing trends over time. Total DDT is decreasing at all station groups. The decreases at NFU and NFD appear to be driven by large values in 2000-01, while the decreasing trends at WZU and FFU are influenced by higher tDDT concentrations in 1997-98, 1998-99, and 1999-00. WZD shows only a slight decrease over time. Total PCB is very low at all station groups in all years except 1998-99, which results in the decreasing trend in the best-fit line. No significant temporal trend is evident for tPCB. A decreasing trend in total PAH is found for WZU, which also shows the highest variability of the station groups. The decrease is due mainly to higher than average concentrations in 1997-98 and 2000-01. The decreasing trend at FFU is due to a single high concentration in 1998-99, which when removed results in no discernable trend over time. NFU, NFD, and WZD show no trends over time.

<u>Metals</u>

Arsenic is increasing over time at WZD and to a lesser degree at NFD and NFU. WZU is decreasing slightly, while FFU remains relatively unchanged. Inter-annual variability is evident and similar among station groups except for NFU, which was significantly greater.

Beryllium shows little change over time in all stations groups. The trend is consistently flat with the exception of the current year (2007-08), which showed a marked increase throughout the monitoring area, suggesting an area-wide influence.

Cadmium shows a slight decrease in all station groups. The rate of decrease and variability is similar for the station groups except WZU, which has greater variability and noticeably higher concentrations.

Chromium is increasing in all station groups except WZU, which is decreasing slightly. All groups follow a similar inter-annual pattern except NFU. The rate of increase and variability is highest in NFU.

Copper concentrations are increasing slightly at NFU and FFU, and show no significant trend at WZU, WZD, and NFD. Variability was highest at WZU.

Lead showed an overall decrease at all station groups until this year when all groups experienced an almost uniform magnitude increase of between 2 to 3 mg/kg. Annual mean concentrations show a similar pattern among station groups except for WZU and FFU, which have notable variability.

Mercury shows a trend of increasing concentrations at WZU, NFU, and FFU, and a decreasing trend at WZD and NFD. Mercury concentrations at WZU were highly variable over time; NFU mercury concentrations were also variable, though less so than WZU. Though the overall trend at WZU is increasing, the concentrations in 2007-08 are much less than in the previous two years and are comparable to values found from 1999-00 to 2004-05. The trend seen at NFU is largely driven by a single high concentration in 2005-06. Beginning in July 2005, sediment mercury concentrations near the outfall began increasing over time reaching a mean concentration of 0.17 mg/kg in the 2005-06 monitoring year (OCSD 2006). The mean concentration decreased slightly in the 2006-07 monitoring year (OCSD 2007) and again this year. What caused the increase in mercury concentrations is not known as no correlations were found to effluent discharges, plant process changes, or oceanographic conditions. A study conducted by the District's Environmental Sciences Laboratory found that sediment mercury concentrations showed high variability in samples from individual stations between years, seasons, sample repetitions, and even split samples. Further study found that by increasing the amount of sediment digested and analyzed from 0.5 g to 5.0 g significantly decreased the variability in test results. This change is within the analytical protocol and was used in this year's monitoring.

Nickel is increasing at a comparable rate at all station groups suggesting an area-wide influence and not an outfall effect. The pattern over time is similar among the station groups except for NFU, which showed high variability. Similar to beryllium and lead, sediment nickel concentrations increased about 1 mg/kg at all station groups this year.

Selenium is decreasing at all station groups and shows a similar inter-annual pattern of concentrations suggesting an area-wide, rather than an outfall effect. The exception is WZU, which was higher in 1999-00 and lower in 2000-01 than the other groups. The District began accepting de-watering flows from the San Diego Creek with increased selenium in about 2003, but there is no evidence of an increase in sediment selenium concentrations in the monitoring area.

Silver is decreasing in all station groups with WZU showing the greatest rate of decrease and variability.

Zinc is decreasing at WZU and WZD, though it has increased the last two years in WZU and this year at WZD. Zinc is increasing at NFU, NFD, and FFU. All station groups show. The variability at WZD, NFD, and FFU is small in comparison to WZU and NFU, which

have a maximum range of about 5 mg/kg. The range of concentrations at WZU and NFU is 12 and 15 mg/kg, respectively.

CONCLUSIONS

The results from the 2007-08 monitoring year were generally consistent with those of previous years and generally showed good sediment quality in the monitoring area. The increase in grain size downcoast of the outfall is a change from previous years, the cause of which is not apparent. There are mostly decreasing trends over time in organic chemical constituents, with most concentrations below the ERL and ERM thresholds. Most metals show decreasing concentrations over time at within ZID stations and all were below their respective ERLs. The mERMq analysis indicated a low probability of sediment toxicity in the monitoring area. Results suggested that there were some minor effects to sediment quality, but they are mainly localized near the outfall. As discussed in Chapter 5 (Invertebrate Communities) and Chapter 6 (Trawl Communities), biological communities were not degraded outside the ZID. Therefore, while some wastewater discharge effects are indicated, the magnitude of these effects was not sufficient to adversely affect biological communities in the District's monitoring area and all permit compliance criteria were met (see Chapter 2).

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