

## TRACE METALS IN NEARSHORE SEAWATER

Municipal wastewaters are a major source of trace metals to the coastal ecosystem. However, our past research has shown that, on the average, approximately 90 percent of most metals in these wastewaters are associated with filter-able particulates. When discharged, most of these particulates settle, resulting in highly contaminated bottom sediments around some outfall systems. In general, metals are believed to be much more toxic in the dissolved state than when bound to particulates. The objective of the research discussed here was to learn if any detectable increases in concentrations of dissolved metals of concern could be observed in the water column near a major sub-marine discharge.

The outfall system selected for the initial test was the JWPCP discharge off Palos Verdes Peninsula. In collaboration with Dr. John Martin (Moss Landing Marine Station), we collected seawater samples at this site aboard the R/V CAYUSE on 24 February 1975. The wastewater plume was first tentatively located using a transmissometer, and its identity confirmed by measuring the level of ammonia-nitrogen in a test water sample. We made the collection using an acid-cleaned polyethylene system that pumped the sample to the surface. Triplicate 2-liter samples from each station were immediately filtered through a 0.4-micron Nuclepore filter under a plastic shield. We then preserved the dissolved ( $<0.4$  micron) and particulate ( $>0.4$  micron) fractions by acidifying the water to a pH of 1.6 with ultrapure nitric acid and freezing the filter pads. We also added standard solutions of the metals of interest to one filtered subsample from each set to monitor ionic recovery. Double-deionized water was used to measure blanks for each collection bottle and to obtain process blanks, beginning with the filtration step. In the laboratory, trace metals in the dissolved fraction were concentrated using the APDC-MIBK organic solvent extraction procedure, which includes internal standardization with previously-extracted seawater. The particulate fraction was digested and concentrated by evaporation. Analyses were conducted with an atomic absorption spectrometer equipped with a graphite furnace.

Our results are presented in Table 1; corresponding station locations are illustrated in Figure 1. Three replicate metal concentrations were obtained for both the dissolved and particulate fractions at the four stations; in each case, we have selected the median value as the representative concentration. Typical process blank values applied to obtain the net dissolved cadmium, chromium, copper, and nickel concentrations listed were 0.02, 0.06, 0.20, and 0.19 p.g/l, respectively; recoveries ranged from 87 to 106 percent. Blanks and losses for the particulate analyses were negligible. Most of the effluent values listed were obtained from monitoring data for 4 February and 11 March 1975. We have separated these metal concentrations into estimated dissolved and particulate fractions, using previously obtained values for the percent of metal particulate in this effluent (95 percent for cadmium, chromium, and copper; 45 percent for nickel). The light attenuation at each station was calculated from the trans-missometer readings; the results were then used to obtain estimated concentrations of suspended solids.

The data in Table 1 indicate that, at Stations 120-122, we did indeed sample the JWPCP wastewater plume. Both light attenuation and ammonia-nitrogen values exceeded values at the control station (Station 123) by more than a factor of ten. The three plume temperatures also agreed within  $0.1^{\circ}\text{C}$  despite the depth range of 16 to 44 meters; the temperature at the control

station at an Intermediate depth of 25 meters was 1°C higher. Furthermore, the concentrations of the four metals measured in the particulate phase were one to two orders of magnitude greater in the plume than at the control station.

Comparison of effluent and seawater concentrations of suspended solids and ammonia-nitrogen suggest dilution factors of 100 to 200 for both the particulate and dissolved fractions of the wastewater at the three plume stations sampled. Somewhat higher estimates (150 to 350) are obtained by comparing total (dissolved plus particulate) concentrations of the metals.

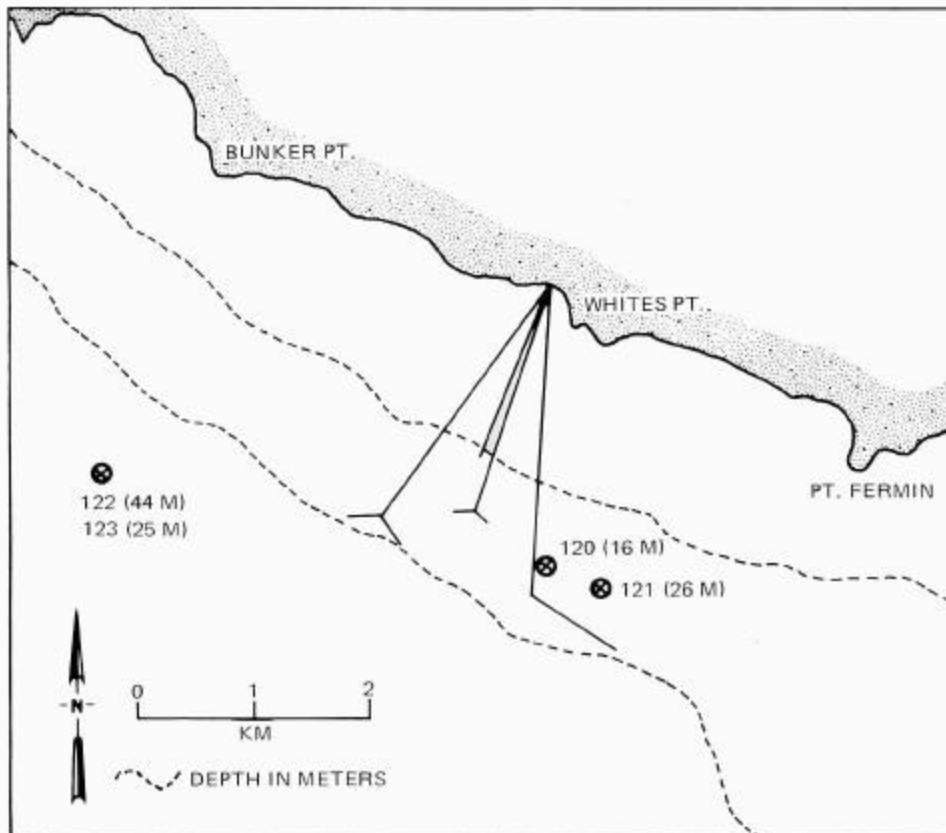
Application of the Mann-Whitney U-test revealed no significant increase in the dissolved levels of cadmium or chromium at the plume stations. For example, although the plume values for particulate chromium were 30 to 50 times higher than the control values, seven of the nine dissolved chromium concentrations measured in the plume fell between 0.18 and 0.26 µg/l, and the three control values ranged from 0.23 to 0.25 µg/l. In contrast, there was a significant increase in dissolved concentrations of copper and nickel—on the average, levels at the plume stations were four times those at the control station. It should be noted that even higher concentrations of dissolved copper and nickel were measured at the mouths of San Pedro, Newport, and San Diego Harbors. As shown earlier in the report, typical concentrations of copper and nickel ranged from 1 to 3 µg/l and from 1 to 2 µg/l, respectively.

These results indicate that, although very large increases in particulate concentrations of metals can occur in the wastewater plume near a major municipal outfall, there are much smaller increases in the dissolved fraction. The largest such concentration measured in the plume was about 1 µg/l for nickel, which is probably the most soluble of any of the trace metals now regulated. Furthermore, although the increases in plume concentrations above control values for dissolved copper and nickel were statistically significant, these levels were less than those measured at the mouths of three major harbors in the Bight. Chromium and cadmium showed only slight increases in the dissolved fraction of the plume; these increases, which did not exceed a factor of 2, were not significant. Chromium levels ranged from 0.2 to 0.5 µg/l; these values are within the range of reported seawater concentrations and also within the range observed in our harbor mouth study.

Thus, as plume dilutions increase several times beyond the factors of 100 to 350 that we found within 2 km of the JWPCP submarine outfalls, levels of dissolved metals from the effluent probably will become indistinguishable from baseline values for the adjacent nearshore waters.

**Table 1. Median concentrations of dissolved (<0.4-micron) and particulate (>0.4-micron) metals (µg/l) in JWPCP municipal wastewater and in seawater collected 24 February 1975 around the Whites Point submarine outfalls.**

	JWPCP Effluent	Outfall Plume			Control Seawater
Station		120	121	122	123
Depth (m)	—	16	26	44	25
Temperature (°C)	24.4	10.60	10.72	10.65	11.70
Attenuation (% per m)	99	67	61	70	5
Suspend Solids (mg/l)	290	2	1.5	2	0.05
NH <sub>3</sub> (mg/l N)	39	0.21	0.33	0.21	0.015
Cadmium					
Dissolved	2	0.06	0.08	—	0.05
Particulate	36	0.17	0.09	0.18	0.07
Chromium					
Dissolved	35	0.50	0.18	0.24	0.23
Particulate	640	2.0	1.3	1.9	0.03
Copper					
Dissolved	25	0.61	0.49	0.26	0.10
Particulate	480	1.2	0.89	1.4	0.02
Nickel					
Dissolved	180	1.2	0.72	1.0	0.29
Particulate	150	0.23	0.18	0.26	0.02



**Figure 1. Locations and depths (m) of wastewater plume Stations 120, 121, and 122, and Local Control Stations 123 around the JWPCP submarine outfalls off Palos Verdes Peninsula. Station 123 is above 122 in the water column.**