TRACE ELEMENT ANOMALIES IN MARINE ORGANISMS OFF SOUTHERN CALIFORNIA *

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ABSTRACT

Large quantities of DDT and trace metals are released annually to the coastal marine ecosystem off southern California via municipal wastewaters discharged through five major submarine outfall systems. Samples of the California seamussel, *Mytilus californianus,* and the Dover sole, *Microstomus pacificus,* were collected from throughout the Southern California Bight to determine if, around these local point sources, contamination of the nearshore biota had occurred. Highest DDT levels in seamussels were observed in specimens collected from the vicinity of a major outfall which, in the past, discharged effluents containing industrial wastes from the manufacture of this pesticide. Copper levels were significantly higher in urban seamussels than in either rural or island control specimens. In contrast, cadmium concentrations were significantly lower in the urban samples. Lead appears to be a wide spread contaminant of the southern California coastal region. Concentrations of chromium were highest in rural seamussels and silver concentration were highest in urban specimens. No significant differences in the nickel and zinc levels were observed between seamussels from any of the three regions. Similarly, no significant enhancements in the trace metal concentrations measured in Dover sole livers were observed despite the close association of the specimens with highly contaminated sediments.

INTRODUCTION

In recent years there has been increasing concern about pollution of coastal marine ecosystems. One aspect of this concern that has received considerable attention is the possibility that trace elements released to this environment through man's actions are being accumulated by organisms to unnatural levels that endanger both their health and their usefulness as seafood. Here we report results of studies into anomalous concentrations of 11 trace elements in two very different marine organisms, an intertidal mollusc, the California seamussel, *Mytilus californianus,* and a nearshore flatfish, the Dover sole, *Microstomus pacificus,* found off the densely populated coastal plain of southern California.

Approximately 11 million persons, or 5% of the Nation's population, inhabits the region between Point Conception and the U.S. Mexico border

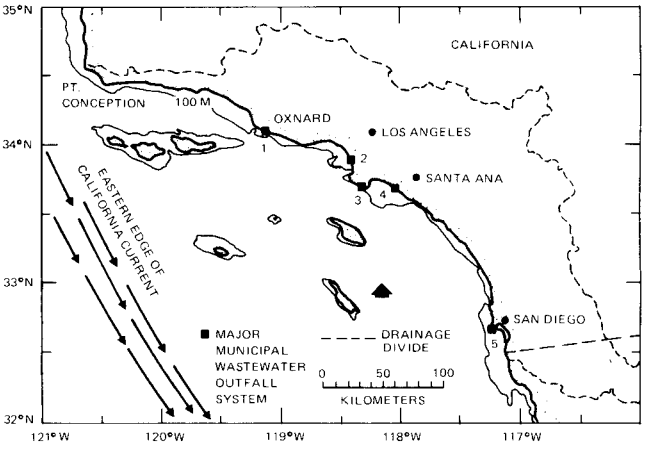

FIGURE 1. The Southern California Bight. Outfall systems are (1) Oxnard City, (2) Hyperion, Los Angeles City, (3) Joint Water Pollution Control Plant (JWPCP), Los Angeles County, (4) Orange County, and (5) San Diego City.

(Figure 1). Most of these people live in the Los Angeles/Orange County Basin * or near San Diego. The municipal wastewaters from these communities in large part are discharged from submarine outfalls a few kilometers offshore, generally at depths shallower than 100 m. Such discharges now total more than 1 billion gallons per day (approximately 1.4×10^{12}l/yr), comparable to the 1941–70 median annual flow of 1×10^{12} liters from surface runoff (United States Geological Survey, 1974). Approximately 95%of this municipal wastewater passes through five major treatment plants, where it generally undergoes only primary settling of solids

* Contribution 39 of the Southern California Coastal Water Research Project.

* Centered around the cities of Los Angeles and Santa Ana.

TABLE 1

Average trace element concentrations (mg/dry kg) in two types of particulates in the Bight *

Trace element	Percent associated with wastewater particulates	Wastewater particulates	Natural nearshore marine sediments
Silver	88	100	1.0
Cadmium	93	130	0.4
Chromium	84	1500	46
Copper	91	1600	16
Mercury	90†	4†	0.04
Nickel	58	350	14
Lead	94	610	8.5
Zinc	92	3000	63

* After Galloway, 1972a and Young et al., 1973.
† Estimates for Joint Water Pollution Control Plant (JWPCP) effluent only.

before release (Southern California Coastal Water Research Project, 1973).

Young, Young, and Hlavka (1973) have summarized the importance of these wastewaters as sources of trace metals to the coastal ecosystem. For a number of metals, discharges from these systems contribute either a majority or a significant fraction of the estimated total input from the coastal plain. In collaboration with J. Galloway (University of California, San Diego), we found that most of these metals are associated with filterable particulates, and that the concentrations on such effluent solids are often two orders of magnitude above natural levels for bottom sediments found around the submarine outfalls (Table 1).

DDT AND TRACE METALS IN CALIFORNIA SEAMUSSELS

It has been shown that at least one chemical constituent of municipal wastewater can significantly contaminate the marine biota over a wide area. During summer 1971, we collected intertidal California seamussels, *M. californianus,* from coastal and island stations throughout the Southern California Bight. The whole soft tissues of specimens 4 to 6 cm in length were analyzed for chlorinated hydrocarbons by B. de Lappe and R. Risebrough at Bodega Marine Laboratory. Data on resultant DDT concentrations illustrate the striking effect one outfall system has had on residue levels of this pesticide in an intertidal invertebrate (Figure 2). Values decreased by factors of 50 to 100 in five directions away fromPalos Verdes Peninsula, the site of the outfalls of County Sanitation Districts of Los Angeles County. The source apparently was industrial DDT wastes released in very large quantities from a manufacturer of the pesticide over an undetermined period. During 1971, 20 metric tons of this waste were carried to the sea via effluent discharged from the Joint Water Pollution Control

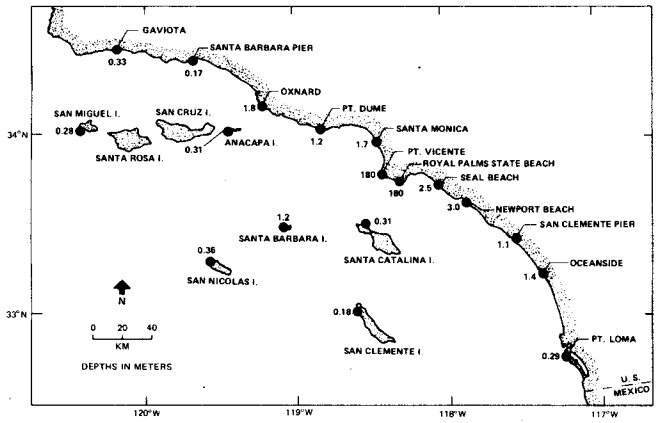

FIGURE 2. Total DDT concentrations (mg/dry kg) in whole soft tissues of California seamussel, *Mytilus californianus,* 1971. Average wet to dry weight ratio for these samples was 4.4 (Analyses by B. de Lappe and R. Risebrough).

Plant, and we found 200 metric tons in the bottom sediments of the Palos Verdes shelf the following year (McDermott, Heesen, and Young, 1974).

To determine if there was corresponding widespread contamination of the nearshore biota from anthropogenic inputs of trace metals, digestive glands of seamussels obtained from the 1971 collection were analyzed by G. Alexander utilizing optical emission spectroscopy at the University of California, Los Angeles. Composites of this tissue from three male and three female specimens were measured, and application of the Wilcoxon signed-rank test revealed no significant effect of sex on the resultant metal concentrations.

The results do not indicate dramatic copper contamination of the intertidal zone off Los Angeles and Orange Counties (Figure 3), despite the fact that we estimate more than 500 metric tons of this metal were discharged during 1971 via municipal

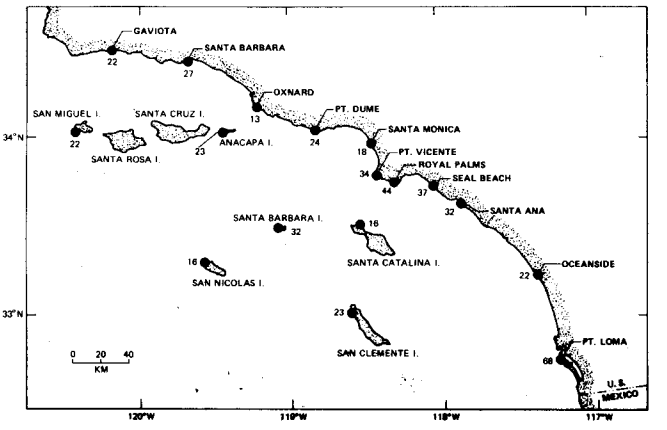

FIGURE 3. Copper concentrations (mg/dry kg) in digestive gland tissue of California seamussel, *Mytilus californianus,* 1971. Average wet to dry weight ratio for these samples was 3.8 (Analyses by G. Alexander).

wastewaters from the three largest submarine outfall systems * of the bight. In contrast, analyses of trace metals in surface runoff conducted in collaboration with J. Morgan, California Institute of Technology, indicated that only about 14 metric tons of copper were carried into the marine environment by storm runoff from these two Counties. While large gradients were not observed, there is a suggestion of somewhat elevated values in mussels collected between Palos Verdes Peninsula and Newport Beach, and off Point Loma in San Diego.

Although these higher concentrations found off the major urban areas might be attributed to municipal wastewater inputs, we recently have reported another potentially important source of copper to the coastal ecosystem (Young, Heesen, McDermott, and Smokler, 1974). Approximately 200 metric tons of this metal in antifouling paints are

* Hyperion Treatment Plant, City of Los Angeles: 340 mgd; JWPCP, County Sanitation District of Los Angeles County: 370 mgd; Orange County Sanitation District: 130 mgd.

applied annually to vessels in the Southern California Bight, with 120 metric tons being used at anchorages between Santa Monica and Newport Beach, and 50 metric tons being used at Mission and San Diego Bays near Point Loma. In contrast, San Diego municipal wastewater introduced only about 20 metric tons of copper off Point Loma during 1971. The highest copper concentrations (average: 68 ppm) found in the 1971 seamussel survey occurred on Point Loma between these two important San Diego anchorages, while the two next highest values (44 and 37 ppm) occurred to the north and south of San Pedro Harbor. Because the copper additives in antifouling paints are designed to effect marine invertebrates, such paints must be considered a candidate along with municipal wastewater as potential sources of the enhanced copper concentrations implied by the distribution found in *M. californianus.*

In addition to municipal wastewater discharges and vessel-related activities, there are other potentially important anthropogenic sources of trace metals to the coastal zone, such as aerial fallout from atmospheric pollutants and direct industrial discharges. Although they have not been adequately quantified to date, the impact of these and other inputs associated principally with major population centers were assessed by evaluating any significant differences in concentration levels of potentially toxic trace elements in the 1971 intertidal mussels collected from three distinct population regions.

We utilized a statistical test developed by Tukey (1953) which allows for multiple comparisons between an unlimited number of groups. The one restriction is that there must be an equal number of sample points per group. Therefore, we separated the intertidal stations into three distinct population groups with five station values for each of the metals analyzed. The urban coastal group included Palos Verdes Peninsula, Santa Monica, Seal Beach, Newport Beach, and Point Loma. The Palos Verdes value was obtained by combining the concentrations from the Royal Palm and Pt. Vicente stations, which are located on the Peninsula near the JWPCP outfalls. The rural coastal group consisted of Gaviota, Santa Barbara, Oxnard, Point Dume, and Oceanside. Island control stations included San Miguel, Anacapa, San Nicolas, Santa Catalina, and San Clemente Islands. Santa Barbara Island was not included because the total DDT concentrations in mussels from this station were approximately five times that of the average for the other islands (Figure 2), suggesting an important influence of the JWPCP outfalls off Palos Verdes Peninsula.

TABLE 2

Average trace element concentrations (mg/dry kg) in digestive glands of the California seamussel, *Mytilus californianus*, showing significant regional differences * off southern California.

Trace element	Urban vs Island	Urban vs Rural	Rural vs Island
Silver	U > I (26) (10)	--	--
Cadmium	U < I (14) (21)	U < R (14) (26)	--
Chromium	--	U < R (5) (15)	R > I (15) (2)
Copper	U > I (38) (20)	U > R (38) (22)	--
Nickel	--	--	--
Lead	U > I (18) (6)	--	R > I (21) (6)
Zinc	--	--	--

* 95% Confidence limit.

The results of the analysis for the seven trace metals considered show that relatively constant values of about 20 mg/dry kg (ppm) lead were observed in both the urban and rural coastal zones, and that this level was significantly higher than the island mean of 6 ppm (Table 2). Only those differences between digestive gland concentrations which are statistically significant at the 95 percent confidence level are listed. This distribution may be a result, in part, of the large quantity (approximately 7000 tons) of tetraethyl lead burned annually in internal combustion engines and introduced via automotive exhaust to the coastal plain (Huntzicker, Friedlander, and Davidson, 1975).

Of the remaining six metals, the mean urban copper concentration (38 ppm) was significantly higher than both the rural and island means (22 and 20 ppm, respectively). For silver the urban mean (26 ppm) was significantly higher than the island mean (10 ppm), but not the rural mean (12 ppm). In the case of cadium, the urban mean (14 ppm) was significantly lower than both the rural and island means (26 and 21 ppm, respectively). For chromium, the rural mean (15 ppm) was significantly higher than both the urban and island means (5 and 2 ppm, respectively). In the case of nickel and zinc, no significant differences between groups were observed; bight-wide averages for these two metals were 8 and 76 ppm, respectively.

Although individual results for these seven potential pollutants are quite varied, a general conclusion which may be drawn from this comparison is that there does not appear to be a pattern of dramatic urban enhancements of the trace metals analyzed in this intertidal invertebrate. Urban depressions as well as enhancements are observed, and regional group means generally agree within a factor of two or three. The biological implications of such variations are not yet well understood.

TRACE METALS IN DOVER SOLE

Following this regional survey, we conducted an intensive investigation into trace element

contamination of a benthic flatfish commonly found around local submarine outfalls. The Dover sole, *M. pacificus,* was initially selected because of its high incidence of fin erosion disease with increased proximity of trawling location to an urban source of contamination. This source, the JWPCP submarine outfall system, discharged on the average more than 50% of the trace metals, under consideration here, which were released via municipal waste in 1971. Similarly, over 90% of the total amount of DDT released to the local marine environment during 1971–72 was discharged via this outfall. Enhanced muscle tissue concentrations of DDT compounds in fish collected around this discharge indicated that specimens trawled from the Palos Verdes shelf have resided there for an extended period of time. This apparent localization of the species makes it a viable choice for studying regional differences.

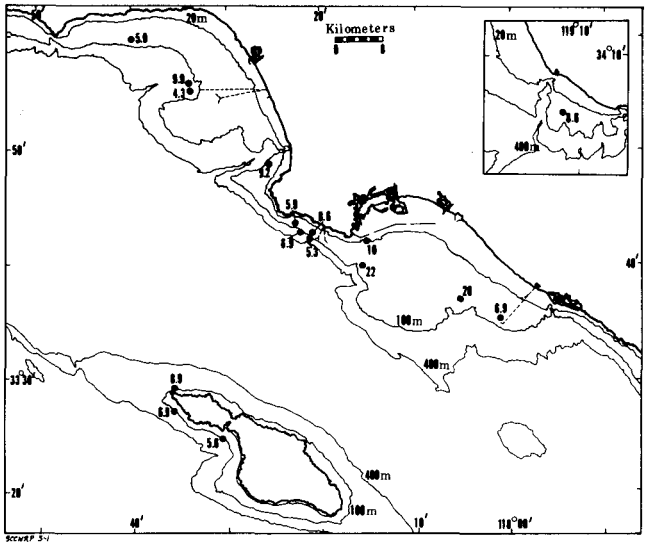

FIGURE 4. Copper concentrations (mg/dry kg) in liver tissue of Dover sole, *Microstomus pacificus,* 1970–71. Average wet to dry weight ratio for these samples was 3.3 (Analyses by J. de Goeij and V. Guinn).

In collaboration with V. Guinn and J. de Goeij (University of California at Irvine), liver tissue of Dover sole collected during 1971–72 from around the three largest discharges of municipal wastewater in the bight (and control stations off Catalina Island) were analyzed by neutron activation analysis. Median body lengths for the outfall and control specimens were 242 and 180 mm, respectively. The distribution observed for copper in this flatfish (Figure 4) does not indicate any enhancement of liver tissue concentrations of this metal in Dover sole trawled from the discharge regions of the three large outfall systems off Santa Monica, Palos Verdes Peninsula, and Newport Beach; concentrations around these outfalls, and those of the Catalina Island control stations, all averaged about 7 mg/dry kg (ppm). The two highest values measured (22 and 20 ppm) occurred to the south of San Pedro Harbor, the largest anchorage in the bight. This again suggests the possible importance of copper in vessel antifouling paints as a significant source of this contaminant to coastal marine organisms.

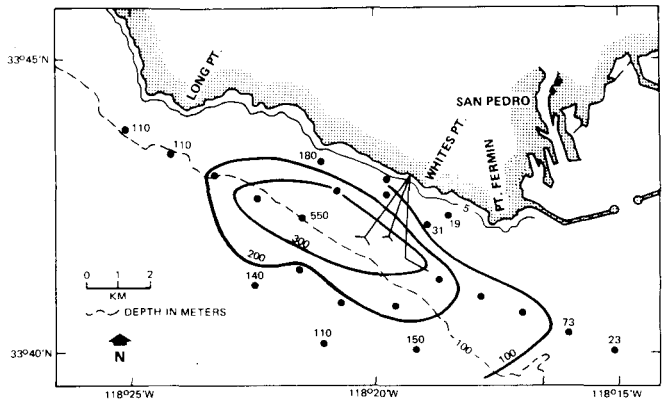

FIGURE 5. Copper concentrations (mg/dry kg) in surface sediments around the Joint Water Pollution Control Plant (JWPCP) outfall system, May 1970 (Analyses by J. Galloway).

Eight of the trace elements detected in these samples had previously been shown to be highly concentrated in bottom sediments around the JWPCP outfalls (Galloway, 1972b; Southern California Coastal Water Research Project, 1973). The contamination patterns for these elements (Figure 5) generally follow those illustrated for copper. From these data, we have estimated typical contamination factors (relative to natural sediment concentrations) for the sediments from which the Palos Verdes outfall specimens were trawled (Table 3). With the exception of silver, these elements are seen to contaminate the surface sediments in this region by average factors of 13 to 160 above estimated natural concentrations.

TABLE 3

Average trace element concentrations (mg/dry kg) in liver tissue from Dover sole, *Microstomos pacificus,* trawled from the Palos Verdes Peninsula outfall region and from a control region off Santa Catalina Island, 1970–72.*

Trace element	Sediments† Outfall‡: Control	Dover sole livers	
		Outfall	Control
Silver	3.0	5.9	7.3
Arsenic	15	4.3	10
Cadmium	160	0.63	1.9
Copper	23	6.6	7.3
Mercury	85	0.36	0.36
Antimony	13	0.010	0.012
Selenium	14	2.1	4.0
Zinc	17	86	89

* After deGoeij *et al.,* 1974.
† Typical trace element contamination factors in surface sediments off Palos Verdes Peninsula.
‡ Specimens from the region termed "very high contamination" by de Goeij *et al.* (1974), within 2 km to the northwest of the Joint Water Pollution Control Plant (JWPCP) submarine outfalls.

In contrast, when compared with control specimens, Dover sole, known by their high DDT concentration and eroded fins to have inhabited the contaminated Palos Verdes outfall sediments, did not exhibit a corresponding enhancement in the concentration of the eight trace elements measured in their liver tissue. The comparison between levels found in the outfall and island control specimens indicate the outfall fish liver concentrations in all cases were slightly lower than the control concentrations, and that the average silver, copper, mercury, antimony, and zinc values generally agreed within 10% of the mean for this flatfish from the two regions. However, for arsenic, cadmium, and selenium, the outfall specimens had significantly lower concentrations, at the 95% confidence level, than the controls. These relative depression were within a factor of two to three. Such depressions are of considerable biological interest, and we are now attempting to learn more about them and their ecological significance.

In summary, these investigations have not revealed any dramatic regional or local enhancement of trace element concentrations in the nearshore biota off southern California, although man has introduced significant quantities of such contaminants to this coastal ecosystem. Both statistically significant enhancements and depressions have been observed for various elements in the mussel and flatfish analyzed; however, such concentrations generally agree with control values within a factor of two or three. Our studies into levels of these and other important trace elements in marine organisms from the Southern California Bight are continuing.

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