### Chapter 5

# LEVELS OF SELECT TRACE METALS IN BAY MUSSELS FROM THE SOUTH RICHMOND SHORELINE AREA: THREATENING A VALUABLE RESOURCE?

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# Introduction

The City of Richmond plans to develop part of the South Richmond shoreline as a park in the near future. In addition to bicycling and hiking, one of the projected recreational uses of this area is shellfishing. However, this may not be a viable activity due to elevated concentrations of trace metals in the shellfish. This study will measure levels of select trace metals in shellfish tissue and address trace metal contamination as a potential threat to human health as well as the health of the shellfish resource.

A state-wide mussel quarantine is in effect every year between May 1 and October 31. Although this quarantine is restricted to the coastline, occasionally it is extended to mussels in San Francisco Bay (Clark, 1986, pers. comm.). In addition, the Department of Health Services (DOHS) has posted warnings to potential harvesters at locations where excessive contamination poses a significant human health threat. Shellfishing in beds along the South Richmond shoreline, from Pt. Isabel to the University of California's Richmond Field Station (Figure 1) is presently not recommended by state and county health agencies. Yet despite warnings, people continue to harvest shellfish in this area.

The extent to which recreational harvesting will occur in any area depends, in part, on the accessibility of the shellfish beds. There are no officially-designated access points to the South Richmond shoreline, although people can reach the shorefront via a maintenance trail that runs along the unused railroad tracks owned by the Santa Fe Land Improvement company (Figure 1) (Merrill, 1986, pers. comm.). Consequently, harvesting in this area has been relatively moderate in comparison to an area such as Coyote Point REgional Park in San Mateo County. Nonetheless, there exists the potential for increased access to the South Richmond shoreline as development occurs there. The McAteer-Petris Act, which created the San Francisco Bay Conservation and Development Commission (BCDC), requires that any development code, secs. 66602, 66632.4). In addition, the City of Richmond is currently negotiating with Santa Fe over the rights to the land now occupied by the unused railroad tracks, which run along the length of the shoreline area, in conjunction with the city's Marina Bay Project. The East Bay Regional Park District has plans to remove the railroad tracks in order to establish a hike and bike trail if these negotiations are successful (Anderson, 1986, pers. comm.).

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In view of the present use as well as the prospects for increased human consumption of shellfish from the South Richmond shoreline, the extent of mussel contamination in this area is worthy of investigation. In addition, although trace metal concentrations may not approach levels threatening to human health, they may be responsible for chronic sublethal effects in the mussels themselves, which may have deleterious consequences for the reproductive success of this valuable resource. The purpose of this study is to measure concentrations of copper, cadmium, and zinc in Bay mussels (<u>Mytilus edulis</u>) and to suggest possible sources of metal inputs in the study area.

#### Past Studies

Since the mid 1970's, there has been considerable effort to evaluate and quantify the extent of contamination in shellfish beds throughout San Francisco Bay. One of the first studies measuring levels of contamination in shellfish was by Girvin and others (1975). Since 1976, the State Department of Fish and Game (DFG) has conducted the Mussel Watch Program, a yearly assessment of the geographic and temporal trends of select toxic pollutants in mussels along the California coast (Hayes and Phillips, 1984). The procedures for field sampling and laboratory preparation of mussels specified by the Mussel Watch program were especially useful for this study.

The most extensive studies in the East Bay area have been conducted by the San Francisco Bay Shellfish Program, established by the Regional Water Quality Control Board (RWQCB). The Shellfish Program includes studies of contaminant levels in the tissues of various bivalve mollusks and water (McCleneghan <u>et al.</u>, 1982; Jarvis <u>et al.</u>, July 1981), surveys of existing and potential sources of pollution (Jarvis <u>et al.</u>, March 1981; Rumjahn and Jarvis, 1981) and an evaluation of the size and harvesting potential of Bay shellfish beds (McAllister and Moore, 1982). The Regional Board has also funded several assessments of biological effects, which evaluate possible physiological stresses in mussels. In addition to the studies done by the Shellfish Program, the East Bay Municipal Utilities District (EBMUD) has conducted local effects monitoring programs (LEM), first in 1982 and again in 1985 (Anatec In Kinnetic, 1982; CH2MHill, 1985). Both LEM studies were designed to determine the extent to which receiving water, sediments, and Japanese littleneck clams (<u>Tapes japonica</u>) were affected by overflows from district sewage treatment plants and urban runoff.

Other research has concentrated on the fluctuations of trace metal concentrations in shellfish due to seasonal and temporal variation in contaminant availability and shellfish physiology (Luoma and Cain, 1979; Luoma <u>et al.</u>, 1985).

Only one of the aforementioned reports (McCleneghan <u>et al</u>., 1982) collected Bay mussel samples in the area covered by this study.

#### Trace Metals: Bioaccumulation and Toxicity

Mussels are indiscriminate filter feeders, absorbing metals both from solution and from ingested phytoplankton and other suspended particles. Studies indicate that fine-grained, oxidized particles

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provide the most important source of available metals for mussels (Bryan <u>et al</u>., 1985). Augmented levels of certain trace metals in mussel tissue can have serious consequences for humans who consume it. Since the entire mussel, including the stomach contents, is usually eaten raw or partially cooked, the human health risks involved can be particularly severe (FDA, 1985).

Although it appears that these metals have a relatively low acute toxicity for the mussels themselves, studies such as those by DFG (Martin <u>et al</u>., 1982) have indicated a statistical correlation between high levels of certain metals and long-term deleterious effects, such as reduced fecundity and reduced oxygen consumption rates.

#### Trace Metals: Anthropogenic Sources

A variety of trace metals occur naturally in the environment; some are harmful to humans at low concentrations and others have been augmented by human activities to levels at which they become harmful. Of the metals examined in this study, cadmium (Cd) is classified as a major toxic metal, whereas copper (Cu) and zinc (Zn) are essential metals, necessary in trace quantities for life.

Found in wastes from electroplating plants, pigment works, textile printing and chemical industries, cadmium is ubiquitous in the urban environment. Human exposure to cadmium occurs mainly through food consumption. Very small doses often lead to severe consequences such as bone and kidney disorders. Exposures to cadmium are particularly problematic because of its tendency to accumulate in the body (Casarett and Doull, 1986).

Anthropogenic sources of copper include corroded copper plumbing, electroplating, and algicides (Cole <u>et al.</u>, 1984). Unlike cadmium, copper contamination in humans usually results from occupational and accidental exposures rather than from environmental accumulation. High copper concentrations have been linked to physiological stress in mussels (Martin et al., 1982).

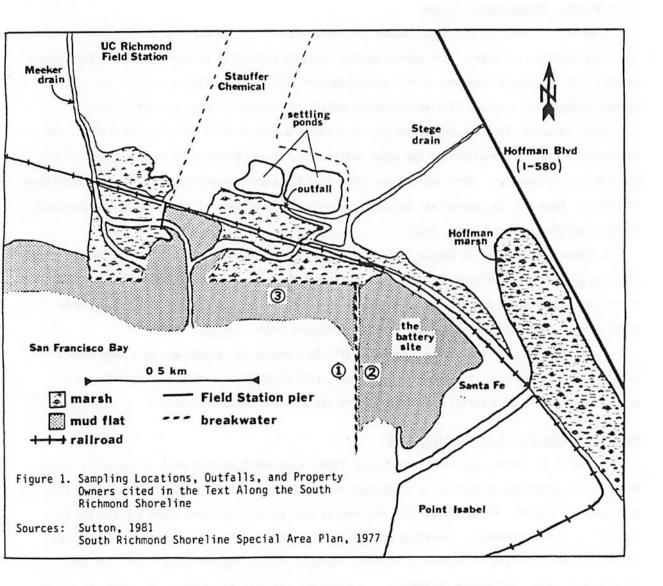
Zinc is introduced into the environment mostly in pigments for paints and as a component of automobile tires (Cole <u>et al.</u>, 1984). Like copper, zinc is toxic to humans only in high-level, acute doses, and is of interest more in regard to its possible effect on mussels.

#### Sources of Trace Metals in the Study Area

Liquid waste loads enter San Francisco Bay either from point sources or from non-point sources. Point source discharge is that which originates from a definite location, such as industrial and municipal wastewater. Point sources are required to have permits which regulate the quality and quantity of their discharge. Non-point sources have no specific origin and at this time are not subject to the same type of regulation as point sources. Consisting mostly of street and agricultural runoff, non-point source wastewater is a major and unregulated source of pollution to the Bay. Under the recent revision of the Clean Water Act (1987), surface runoff from municipal and industrial sites will be considered a point source inflow and thus subject to regulation and permitting. This redefinition has not yet been implemented by the RWQCB.

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Trace metal contaminants which can potentially affect the mussels along the South Richmond shoreline are derived from several possible sources. One such source is located along the shoreline area owned by Santa Fe (Figure 1). During 1980 and 1981, elevated concentrations of lead and zinc were found here in samples of shellfish tissue and sediments (McCleneghan <u>et al.</u>, 1980; RWQCB Permit, 1987). This contamination was attributed to an illegal dumping of storage battery cases along the shoreline of the property. Recently, contaminated sediments and soils from the battery site were dredged and the spoils, as well as the batteries, were either removed to an approved disposal site or encapsulated in an on-site landfill. The extent to which these corrective procedures have confined lead contamination has yet to be determined.



There are three outfalls in this area, all of which have year-round flow (Figure 1). Meeker drain, north of the UC Berkeley Field Station, consists of surface water inputs from sections of Richmond and El Cerrito (Jarvis <u>et al</u>., March 1981). Stege drain, containing storm runoff from Richmond, flows into the eastern end of the tidal basin. Both of these drains service large areas and thus carry a large volume of runoff, especially during the winter months (Davidson, 1987, pers. comm.). One of Stauffer Chemical Company's discharge outfalls is located east of the UC Berkeley field station. This outfall is described as a storm drain containing ". . . runoff from undeveloped areas in the plant site, and adjoining off-site areas; and copper, zinc and tetracholoroethylene from unknown sources" (RWQCB, 1984), and its flow mixes with discharge from Stege drain before entering the tidal basin. Stauffer has also reported overflows from their chemical drain which have entered into this storm drain (Rumjahn and Jarvis, 1981).

Another potential source of metal contamination in the study area is an inactive landfill containing "acidic, heavy metal, salt cinders" which covers seven acres of Stauffer property (Figure 1) (Rumjahn and Jarvis, 1981, Appendix A). It is uncertain whether the contents of this landfill are being leached into the tidal basin.

# Methods

<u>Field Sampling</u>: Bay mussels (<u>Mytilus edulis</u>) were chosen as the shellfish to be tested for two reasons. First, DFG and DOHS have recommended that <u>Mytilus edulis</u> be used as an indicator species in contamination studies because trace metals and other contaminants accumulate more in mussel tissue than in clam tissue (Jarvis <u>et al</u>., 1983). Secondly, Bay mussels constitute the largest shellfish population along the South Richmond shoreline area since the removal of local <u>Tapes japonica</u> and <u>Mya arenaria</u> beds as part of the Santa Fe battery clean-up.

Two collections were made, one in December 1986 and the other in January 1987. Mussel samples were taken from three locations on the breakwater (Figure 1). All locations were sampled on the same day. At each location a total of 30 mussels was collected from 10 sites spaced at six-meter intervals. No effort was made to sample at the same 10 sites during the first and second collection dates.

Since mussels of different sizes concentrate trace metals and other contaminants differently (Hayes and Phillips, 1984), only mussels of 55-65 mm in length were collected, to reduce size-related variation (Table 1). Average shell lengths were measured using 15 of the 30 mussels collected at each location, selected at random. To minimize contamination during handling and transport, all samples were collected using the trace metal "clean" techniques as outlined in the Mussel Watch Procedural protocol (Hayes and Phillips, 1984). Samples were kept frozen until processing.

<u>Laboratory preparation</u>: Sample preparation and tissue digestion were carried out following the procedures outlined in the State Mussel Watch protocol (Hayes and Phillips, 1984). Gonads were excluded from trace metal tissue analysis in order to reduce variability caused by differential metal

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ncentration between individuals in different stages of spawning.

<u>Trace metals analysis</u>: All elemental analyses were made by direct aspiration (air-acetylene) ing a Perkins-Elmer Model 2280 atomic absorption spectrophotometer. Procedures used for the metals alysis are specified in <u>Methods for Chemical Analysis of Water and Wastes</u> (EPA, 1983). Three analytical plicates of ten individuals were run per location per sampling date except where indicated (Table 1). e reading for each replicate corresponds to an average of six readings made over 12 seconds.

All trace metal data are reported on a dry weight basis. The mean dry weight of the samples ranged rom 0.043-0.050 g (Table 1). To enable conversion of the data to wet weight values, the ratios of ry weight to wet weight are given in Table 1.

ocation	Date	<pre># individ in sample</pre>	av. dry wt (g)	Dry/Wet ratio	Length av.	/Individual std. dev.	(mm) range	Metal Conce Cd	entration (u Cu	ng/g) dry wt Zn
		In bampie								
1	12/13/86	5 30	0.45	0.14	58.4	2.72	55-64	4.5(0.78)	7.7(0.95)	164.8(42.67)
	1/31/87		0.43	0.13	59.0	2.70	54-63	5.0(1.05)	7.6(1.17)	208.7(27.41)
2	12/13/80	5 30	0.50	0.16	59.6	3.87	54-66	3.8(1.27)	6.6(0.82)	124.3(41.30)
	1/31/87		0.45	0.15	57.3	2.69	52-62	4.6(0.78)	7.8(0.97)	165.9(19.98)
3	12/13/86	5 29	0.45	0.14	56.2	3.53	53-64	5.5(0.81)	9.5(0.43)	231.2(38.21)
	1/31/87		0.45	0.14	57.9	3.13	54-63	4.9(0.40)	8.7(0.38)	189.0(43.43)
verage								4.7	8.0	180.0

Table 1. Bay Mussel Sampling Data.

Standard deviations in parenthesis

A t-test was used to compare measurements of metal concentrations between different sites and dates. In most biological studies a 95% or greater confidence level is an acceptable measure of statistical ignificance.

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Concentrations of cadmium from the locations tested ranged from 3.8-5.5 ug/g (ppm) and averaged .7 ppm. At the December sampling, mean cadmium concentrations were highest at location 3; in January ne highest levels were at location 1. However, statistical analysis indicates that the means of the amples from all of the locations on both sampling dates were statistically different only at the 80% confidence level.

Concentrations of copper ranged from 6.6-9.5 ppm and averaged 8.0 ppm. Mean copper concentrations ere highest at location 3 on both dates. The means of the samples from locations 1 and 2 were staistically different from that at location 3 at the 95% confidence level for the December sampling only. here was no significant difference in mean copper concentrations between locations 1 and 2 for December.

Zinc concentrations ranged from 124.3-231.2 ppm and averaged 180 ppm. Location 3 had the highest ean zinc concentrations for the December sampling, whereas location 2 had the lowest mean concentrations or both samplings.

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The mean concentration for December sampling at location 3 was statistically different from that at location 2 at the 97% confidence level, whereas there was no significant difference between locations 1 and 3 or 1 and 2. Location 1 had the highest mean zinc concentration for the January sampling date, but this is only statistically different from the mean concentrations at locations 2 and 3 at the 90% confidence level.

Analysis of differences between metal concentrations by location on the two sampling dates showed statistically significant differences only at the 80% confidence level.

# Comparison with FDA Alert Levels

Although the Food and Drug Administration (FDA) has not established maximum concentration levels for heavy metals in human food (except for mercury), it has set alert levels for five metals found in shellfish meat, including cadmium, copper and zinc (Table 2). These levels are meant to be used as indicators of potential human health hazards and do not necessarily correspond to poisonous levels in the shellfish. Although alert levels are directed at metals in soft-shell clams, they are also applicable to mussels.

Location	Source	Date(s)	Hetal Concentration ug/g (ppm) dry weight			
			Cd	Cu	Zn	
S. Rich. Shoreline	This report	12/86, 1/87	3.8-5.5	6.6-9.5	124.3-231.2	
Pt. Isabel	(1)	2/11-15/80	4.1-5.5	6.2-8.2	256.8-367.8	
Pt. Isabel	(1)	7/25-31/80	5.1	5.8	179.5	
Pt. Rich.	(1)	2/11-15/80	4.1	6.2	145.8	
Albany Hill	(2)	4/17/75	2.6	8.4	138.0	
FDA Alert Levels	(3)	-	3.0	148.0	178.0	

Table 2. Comparison of Cadmium, Copper, and Zinc Concentrations in South Richmond Shoreline Mussels With Previously Reported Concentrations and FDA Standards.

Sources: (1) McCleneghan <u>et al.</u>, 1982. (2) Girvin <u>et al.</u>, 1975. (3) Jones and Stokes, 1977.

Concentrations of cadmium in all the samples were above the Alert levels, whereas concentrations of copper in all the samples were below. However, because these cadmium concentrations were not substantially higher than the Alert levels, they probably do not constitute a human health hazard. Alert levels for zinc were exceeded by half of the samples. Because zinc is harmful to humans only in large, acute doses, it is unlikely the concentrations measured in this study would constitute a threat to human health.

#### Possible Effects on Mussels

Although monitoring of metal concentrations in mussels has been the focus of many studies, it is not yet clear how the concentrations of metals in tissue relates to the health of a mussel. One major obstacle in this field of research has been establishing a standard measure of "health" that is acceptable to the scientific community. The "scope for growth index" (Warren and Davis, 1967) is one of the more widely used indices of physiological stress. It is a measurement of the amount of food energy used for the body growth and gamete production of an individual. One shortcoming of the scope for growth index is its inability to distinguish between causative agents.

Martin and others (1982) found a significant negative correlation between copper and zinc tissue concentrations and the health (as measured by the scope for growth index) of the mussels they tested. Since the levels of copper and zinc at which Martin and others (1982) observed negative effects are similar to those reported in this study, it is possible that elevated metal concentrations could be responsible for as-yet-undetected chronic sublethal damage to the mussel population in this area.

#### Comparisons with Data from Other Studies

Metal concentrations from several earlier studies using Bay mussels were compared to the concentrations found at the South Richmond shoreline (Table 2).

McCleneghan and others (1982) (Table 2) conducted the only other study which has measured heavy metal concentrations in Bay mussels from the South Richmond shoreline area. All their samples were taken before the Santa Fe battery site clean-up. The dry-season zinc concentration reported by McCleneghan and others (1982) for the battery site is comparable to that reported in this study, whereas the 1982 wet-season concentrations are somewhat higher. The dry-season copper concentration reported in 1982 was slightly lower than that found in both the 1982 wet season and in this study. Both cadmium concentrations reported in 1982 were similar to those found in this study.

It is likely that zinc concentrations in mussels were higher in the 1982 winter samples than in the summer samples because of increased leaching of metals from the battery cases during the wet season. In addition, the 1982 winter samples were pooled from several spatially-distant locations around Pt. Isabel, whereas summer samples were analyzed individually for each location.

Zinc and cadmium concentrations found in Bay mussels from areas near to the study site (Albany Hill, Girvin <u>et al.</u>, 1975, and Pt. Richmond, McCleneghan <u>et al.</u>, 1982) appear to be lower than those from the South Richmond shoreline (Table 2). If Albany Hill, Pt. Richmond and the South Richmond shoreline area are all subject to similar imputs from non-local sources, then it is possible that local conditions along the South Richmond shoreline have elevated concentrations of these metals to levels

higher than in nearby areas. Only concurrent measurements made at various central Bay locations can determine whether there are significant differences between these areas.

It is important to note that differences in results may reflect differences in sample preparation and analysis rather than actual differences between sites. For example, the sample preparation procedure used by Girvin and others (1975)included a three-day purging of the mussels in clean water, which might have reduced the metal concentrations in the tissues analyzed. In addition, neither Girvin and others (1975) nor McCleneghan and others (1980) removed the gonads from the mussels before analysis, as was done in this study. To what extent these procedural differences account for the differences between results is difficult to determine.

# Sources of Heavy Metals

If continued seepage from the battery site were the primary source of zinc in the mussels, we would expect to see spatial variation in tissue concentrations, with higher values at location 2 than at locations 1 or 3 (Figure 1). Likewise, if Meeker drain, Stege drain and Stauffer Chemical were the major contributors of zinc, cadmium and copper, the concentrations of these metals at location 3 should be higher than at location 1 or 2. In fact, the only significant differences in metal concentrations between locations were in the zinc concentrations at location 3 and 2 in December. However, it is not possible to discern any spatial patterns of zinc distribution from these data because there were no significant differences in concentrations between locations 1 and 3 or 1 and 2. A gradient in copper concentration occurred in the December sampling, where both locations 1 and 2 had significantly lower concentrations than location 3. However, these differences were not replicated in January. Therefore, the data collected in this study do not point conclusively to any one major contributor of metals to the South Richmond shoreline area. It is possible that Meeker and Stege drains, Stauffer outfall and the battery clean-up site are all major sources of metal input. Their relative contributions will be difficult to distinguish without long-term extensive water and tissue sampling.

In national studies, cadmium, copper, and zinc were identified as among the most prevalent constituents of urban runoff (Cole <u>et al</u>., 1984). Since Meeker drain, Stege drain and Stauffer Chemical's outfall receive surface runoff water, they are likely contributors of trace metals to the area. Concentrations of zinc and copper from Stauffer's untreated discharge are monitored by Stauffer as part of their permit requirements, although Stauffer's permit does not require that they treat this runoff water. Reported levels of these metals for winter 1986 equalled and occasionally exceeded effluent limitations suggested by the RWQCB in the revised Basin Plan (RWQCB, 1986). It is, however, likely that Stauffer's contribution is minor compared to that from Meeker or Stege drains because the total area drained by its outfall is smaller. It appears, then, that Meeker drain and Stege drain are the most significant local inputs of trace metals to the study area.

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# It is also possible that non-local sources of metal loading could be affecting the South Richmond shoreline area. Trace metals adsorbed to fine particles can be transported by currents for considerable distances until they are eventually (re)incorporated into the bottom sediment. The oxidation state, sulfide and organic content and sand-silt-clay composition of the sediments influence the release and bioavailability of associated trace metals (Girvin <u>et al</u>., 1975). Because they are a continual source of trace metals, resuspended sediments may obscure direct relationships between metal concentrations and nearby sources.

## Conclusions

The data obtained during this short-term study suggest that elevated levels of zinc and cadmium occur in Bay mussels from the South Richmond shoreline and that these concentrations are in excess of FDA alert levels. Furthermore, it appears that untreated runoff from non-point sources might be a major contributor of bioavailable zinc and cadmium.

In order to test these conclusions, several areas of investigation should be pussued. Long-term studies coordinating water, sediment and tissue sampling during wet and dry seasons will help to determine the degree to which non-point source runoff is a significant contributor of trace metals to the shellfish in the South Richmond shoreline area. Because there are no published studies that have measured heavy metals in both receiving water and Bay mussel tissue, it is difficult to know the extent to which point and non-point source outfalls might influence bioaccumulation in this species. Previous studies which examined other species of shellfish are not useful for comparison due to significant interspecies variation in the ability to bioconcentrate certain heavy metals. Measurements of the mass loading, chemical nature, and fate of the trace metal inputs from Stege and Meeker drains would also aid in determining the influence of local storm runoff. As part of their sediment and shellfish monitoring program for the battery site clean-up, Santa Fe could determine the chemical partitioning of zinc and lead in the sediments in order to determine the bioavailable concentrations residing there. Finally, additional studies should be conducted to determine the implications of observed levels of metal contamination for human health as well as the fitness of the mussel population.

It will be difficult to determine the extent to which non-point sources of runoff contribute to trace metal concentrations in shellfish tissue. Yet if the South Richmond shoreline is to be developed as a park area with shellfishing as one of its beneficial uses, the problem of metal contamination must be addressed by the appropriate agencies. The South Richmond shoreline is one of the many areas in the San Francisco Bay ecosystem which would benefit from further study and control of non-point source runoff.

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