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**CADMIUM LEVELS IN THE SHORELINE
SEDIMENTS OF SAN FRANCISCO BAY**

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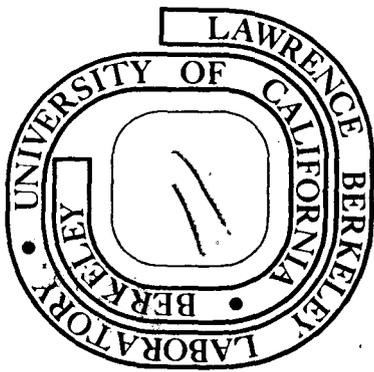
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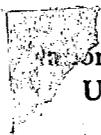
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**CADMIUM LEVELS IN THE SHORELINE
SEDIMENTS OF SAN FRANCISCO BAY**

Brian R. Moyer and Thomas F. Budinger

**Donner Laboratory and Lawrence Berkeley Laboratory
University of California, Berkeley, California**

April 1974

FOREWORD

This study is a part of a broad investigation of the importance of cadmium toxicity in biology and medicine being undertaken by, and supported totally or in part by the Medical Services Department of the Lawrence Berkeley Laboratory. Earlier work in this investigation includes the following:

- Trace-element detection in human tissues by neutron activation analysis without chemical separation (Budinger et al. , 1972a).
- Quantitative neutron activation analysis of human tissues (Budinger et al. , 1972b).
- Epidemiology study of cancer and human kidney tissue cadmium levels (Kolonel, Ph.D.thesis,1972).
- Employee occupational cadmium exposure by correlation to hair, urine, blood levels, and air-filter levels in a cadmium refining plant (Lee, Ph. D. thesis, to be published).
- Biological half-life of cadmium-109 in man and the beagle, and organ distribution over time.
- Investigation of cadmium levels in foods.
- Investigation of the chemistry of cadmium elution from tissues by formalin.
- Monitoring selected employees of this laboratory for possible exposure to cadmium and other metals.

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CADMIUM LEVELS IN THE SHORELINE SEDIMENTS OF SAN FRANCISCO BAY

ABSTRACT

Cadmium levels in the low-tide shoreline sediments of San Francisco Bay were investigated at 68 locations. Sample cores of 5.5 cm diameter and 10 cm depth were separated into top and bottom fractions and analyzed for cadmium by atomic absorption spectrophotometry. A reliable and sensitive ion exchange/organic extraction technique was developed for analysis of cadmium to overcome the interference of iron and other metals that limit the usefulness of the conventional direct acid extraction technique.

The mean values of cadmium content in the top and bottom fractions (in dry soil) were 1.22 ± 0.99 (0.06 to 4.69) $\mu\text{g/g}$ and 0.93 ± 0.74 (0.14 to 3.91) respectively. The mean value for all the 10-cm cores of San Francisco Bay peripheral muds was 1.07 ± 0.89 $\mu\text{g/g}$. The top fraction cadmium content was 1.5 to 2 times more concentrated than the bottom fraction except in the northeast sector of the bay where the surface muds are better mixed; here the average cadmium content is 1.5 times that of the other sectors. This higher cadmium level is associated with the proximity of a lead smelter and several petroleum refineries. Concentrations greater than 2 ppm suggest recent pollution; 13% of the samples were above this level.

INTRODUCTION

This study is part of a broad investigation of the importance of cadmium toxicity in biology and medicine undertaken by the Medical Services Department of the Lawrence Berkeley Laboratory. The biological impact of environmental cadmium must be determined by finding which cadmium compounds are biologically active and to what degree they are prevalent in our surroundings. Here we report the levels of cadmium found in the shoreline sediments of San Francisco Bay.* We have chosen to measure the cadmium levels in tidal shoreline sediments because analysis for cadmium in air or water may often give misleading data on which to base estimates of the gross cadmium levels in an area. Yamagata and Shigematsu (1970) have shown that river waters polluted by cadmium often show low, even undetectable levels, while large concentrations will be found in suspended particles and bottom sediments; especially in waters of neutral or alkaline pH. Piscator found a 4 ppb level in waters downstream from a cadmium plant, but the bottom sediments recorded 80 ppm or a 20,000-fold increase in concentration (Friberg et al., 1971). Thus area pollution assessments can be very much in error unless deposition in soils, dusts and sediments are taken into account.

Our purpose for investigating the San Francisco Bay Area sediments is twofold: (1) to establish background levels to set a base for future environmental monitoring, and (2) to identify the gross soil and environmental characteristics of suspected hot spots. To ensure accurate baseline values for the bay, we developed a separation scheme for cadmium from major soil components and used an atomic absorption analytical technique that provided increased sensitivity over conventional methods used for soils.

*We include San Pablo Bay as part of San Francisco Bay in this study.

Description of San Francisco Bay

The shores of San Francisco Bay have several properties that make them of interest for environmental monitoring. About 40% of California's land mass is drained via the rivers that flow into San Francisco Bay. The southern part of San Francisco Bay on the other hand has a comparatively limited influx of fresh water and thus a potentially more serious pollutant accumulation and disposal problem. (Lager and Tchobanoglous, 1968). Sediment accretion has been continuous and in recent times about one third of the original bay has been taken up by refuse dumping or sanitary land fill.

The generalized rate of estuary sediment accretion of 15 cm per 100 years (1 to 2 mm per year) proposed by Rusnak (1967) therefore is distorted for the San Francisco Bay. The sediment accretion rate in the bay was accelerated between the later half of the 19th century to about 1920 by extensive hydraulic mining. Assuming a maximum accretion of 2 mm per year with no equilibration by tidal washout of the sediment, the naturally accrued level of sediment since 1920 should be around 10 cm.

The bay, with an area of some 400 square miles, occupies a depression formed by tectonic processes (Pritchard, 1967). Most of it is less than 30 feet deep, with the exception of navigation channels dredged to depths of 70 feet. The deeper waters are for the most part found where the scouring action of the heavy tidal currents has prevented deposition. The deepest waters (340 feet) are at the Golden Gate, the 1-2 mile wide strait that forms the only connection between the bay and the Pacific Ocean. Much of the silt that is scoured from the bay ends up on the San Francisco Bar some 10 miles off shore. But the shallow peripheral waters have low current velocities, thus tending to encourage sedimentation. The average rainfall for the San Francisco bay area is 20-30 inches per year and occurs mostly from October through April.

The shores of the bay are never far from either urban concentrations, industrial plants or other sites of heavy human usage. There are numerous petroleum refineries, military and civil airports, shipyards, dock areas, foundries and manufacturing plants, in addition to an urbanized population that is expected to reach six million by 1980.

San Francisco bay mud samples as examined by Pearson et al. (1970) have a wide range in properties. The cation exchange capacity for many north bay samples was a low of 2.3 meq/100 g, while the south bay had a high of 66 meq/100 g. The water of the bay is alkaline (pH 7.2-8.1), and approximately 11 tons per day of gross heavy metals are dumped into the entire bay. Total sulfide levels in the muds range from 0.0 to 2.02 mg S/g dry weight. Lead levels in the bay muds are approximately 20 to 30 $\mu\text{g/g}$ while zinc and iron are generally 14-1800 $\mu\text{g/g}$ and 10,000 $\mu\text{g/g}$ respectively. Levels for cadmium have not been reported.

GEOCHEMISTRY OF CADMIUM

Before inferences of pollution can be made, it is necessary to explore the natural geochemistry of cadmium and determine the background level of the metal. Both Mookerjee (1962) and Greene (1959) give the crustal abundance of cadmium at 0.15 ppm. It seems that natural cadmium concentration is highest in the zinc sulfide ore known as spharilite (Ivanov, 1961, 1964; Marowsky and Wedepohl, 1971; and Mogarovskii and Rosseikin, 1961). The cadmium content of this ore can

reach as high as 4.5% with an average of 0.3%. Cadmium follows the geochemistry of zinc, and both have a high affinity for bonds with sulfur. Cadmium has the higher affinity for sulfur and is precipitated as greenochite (CdS), especially in areas of high reducing capacity such as sulfur-bearing muds. Hanya et al. (1963) have suggested this mechanism for mercury deposition in bottom muds from seawater in Japan.

There are numerous other soil characteristics that affect adsorption and desorption of cadmium (John, 1971). Oxidate sediments such as manganese nodules adsorb significant amounts of cadmium with typical concentrations of 9 ppm being reported (Ahrens, 1967). Both zinc and cadmium are very often considerably enriched in phosphorite deposits of organic origin (Fulkerson and Goeller, 1963; Krauskopf, 1956; Vinogradov, 1959). Segar and Pellenburg (1973), however, found no difference in cadmium concentration in carbonate or organic rich sediments. The South Sea Islands have many areas of sedimentary phosphates, and cadmium levels here have been reported as 100 g/ton (Yamagata and Shigematsu, 1970). Selenium and cadmium also have been shown to precipitate as "cadmoselite" into sediments (Bur'yanova, 1961). This knowledge is relevant to the possible contamination of the environment by increased use of phosphate fertilizers. (Williams and David, 1973)

Environmental Levels

Table 1 gives a worldwide distribution of cadmium for both normal and polluted areas. The table gives some insight into what a background level might be for cadmium. Some high pollution areas are the Jintsu River and Annaka City in Japan and the areas near cadmium smelters in Canada, Kansas, and Colorado. The x-ray fluorescence study by Skei et al. (1972) had poor sensitivity and the accuracy of their results is questionable, though these samples were industrial sediments. John et al. (1972) discuss a depth distribution in an industrial area in Canada (a battery smelter). Lagerwerff et al. (1972) studied soil near a smelter in Kansas and found ~100 ppm of cadmium. Our highest values of ~4000 ppm were from two soil samples taken very close to a cadmium smelter near Denver (Moyer and Budinger, unpublished data). From Table 1 we conclude that nonpolluted surface soil cadmium content is below 2.0 ppm in industrial or areas open to the public.

River beds and estuary sediments, however, are not undisturbed soils. They have a constant influx of solutes from both industrial effluents and dissolved soil components. The desorption of these solutes from chemical precipitation or adsorption will be greater in general than that for dry land soils. The dry land soils receive their cadmium almost exclusively from dustfall, precipitation, and fertilizers.

Sources of Cadmium

To understand the influx of cadmium into marine and estuary environments requires an investigation of sources. Cadmium is not mined outright, but is rather extracted from zinc-lead ore deposits. In 1968 13.3-million pounds of cadmium were consumed in the United States alone (Malin, 1971). About one-half of the total annual consumption of cadmium is for electroplating in a wide variety of industries. The other half of the industrial use of cadmium is in pigments, plastics, batteries, tires, alloys, cosmetics, and other products. Cadmium has been used as an anticorrosive metallic coating for protecting underwater structures (Imperial Smelting Corp., Ltd., 1970). A major problem associated with cadmium control is that only about 5% of refined cadmium is recoverable, while the remainder is dissipated or unaccountable.

Table 1. Global cadmium levels in soils and sediments.

Location	Cadmium Concentration ^a	Method ^b	Sample Description	Reference																										
<u>Canada:</u>																														
	7.9 - 95.4 0.45- 2.5	AAS	Cadmium battery smelter: 15 m from battery smelter 30 m to 300 m from the battery smelter Vertical distribution:	John, et al., 1972																										
			<table border="1"> <thead> <tr> <th>Distance</th> <th>Depth</th> </tr> </thead> <tbody> <tr> <td>44.25</td> <td>15 m 0 - 5 cm</td> </tr> <tr> <td>2.45</td> <td>15 m 5 - 10 cm</td> </tr> <tr> <td>0.67</td> <td>15 m 10 - 15 cm</td> </tr> <tr> <td>0.62</td> <td>15 m 15 - 20 cm</td> </tr> <tr> <td>0.39</td> <td>15 m 20 - 25 cm</td> </tr> <tr> <td>0.32</td> <td>15 m 25 - 30 cm</td> </tr> <tr> <td>0.87</td> <td>30 m 0 - 5 cm</td> </tr> <tr> <td>0.67</td> <td>30 m 5 - 10 cm</td> </tr> <tr> <td>0.64</td> <td>30 m 10 - 15 cm</td> </tr> <tr> <td>0.45</td> <td>90 m 0 - 5 cm</td> </tr> <tr> <td>0.32</td> <td>90 m 5 - 10 cm</td> </tr> <tr> <td>0.88</td> <td>33 agricultural soils (mean)</td> </tr> </tbody> </table>	Distance	Depth	44.25	15 m 0 - 5 cm	2.45	15 m 5 - 10 cm	0.67	15 m 10 - 15 cm	0.62	15 m 15 - 20 cm	0.39	15 m 20 - 25 cm	0.32	15 m 25 - 30 cm	0.87	30 m 0 - 5 cm	0.67	30 m 5 - 10 cm	0.64	30 m 10 - 15 cm	0.45	90 m 0 - 5 cm	0.32	90 m 5 - 10 cm	0.88	33 agricultural soils (mean)	
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<u>Finland:</u>																														
	2 - 30 ppm ash	S	Peat bogs	Salmi, 1950 (from: Yamagata and Shigematsu, 1970)																										
<u>Great Britain:</u>																														
Solway Firth Salton Allonby	n. d. - 2.4 2.4 - 4.0	AAS	Industrial area and controls: 58 controls 10 industrial samples	Perkins et al., 1973																										
Firth of Clyde	n. d. - 4 3 - 7	AAS	Industrial area and controls: 52 controls 27 sludge dump area samples	Mackay et al., 1972																										
Severn Estuary	1.6 - 4.7	AAS	Industrial area: 7 coal and mining samples	Butterworth et al., 1972																										
<u>Japan:</u>																														
		S	Cadmium endemic areas and controls	Kobayashi et al., 1964 (from: Yamagata and Shigematsu, 1970)																										
Yao	0.13 ppm ash		Control																											
Yohono	1.2 ppm ash		Endemic area																											
Shinya	1.4 ppm ash		Water inlet																											
Shinya	0.44 ppm ash		Water outlet																											
Jintsu River	0.16 - 238 ppm ash		Endemic area																											
Kurihara - gun	1.6 - 17.24 ppm ash		Endemic bottom mud																											
Annaka City	26 ppm ash		Endemic bottom mud																											
Tsushima Is.	1.68 - 14.6 ppm ash		Endemic bottom mud																											
Okudake River	4.0 ppm ash		Endemic bottom mud																											
Jintsu River	0.16 - 5.0 ppm ash		Endemic bottom mud																											
Kurihara - gun	1.2 - 12.5 ppm ash		Endemic soils																											
Annaka City	2.6 - 11.6 ppm ash		Endemic soils																											
Tsushima Is.	2.2 - 11.6 ppm ash		Endemic soils																											
Okudake River	1.9 - 24.0 ppm ash		Endemic soils																											
Jintsu River	1 - 7.5 ppm ash		Endemic soils																											
	n. d. - 1.8 ppm ash		Control																											
Rice area	2.2 - 7.2 ppm ash		Agricultural soil																											
	n. d. - trace		Agricultural soil																											

Table 1 (continued)

Location	Cadmium Concentration ^a	Method	Sample Description	Reference
<u>Norway:</u>				
	16 - 850 114	XRF	Industrial sediments (Cd discharge = 30 kg/day) Range Mean of 16 samples	Skei, et al., 1972
<u>Russia:</u>				
40th meridian	0.1 - 0.3 0.1 0.1	NS	Russian plains Plains Granites Basic igneous rocks	Vinogradov, 1959
<u>Nepal:</u>				
Namche Bazar	0.21	AAS	Mount Everest area	Moyer and Budinger, unpublished data
Lukla	0.74			
Everest	0.19			
<u>United States:</u>				
California		AAS	Hills around the San Francisco Bay	Moyer and Budinger, unpublished data
Tamalpais	0.21			
Rodeo	0.88			
Belmont	0.45			
Hayward	0.37			
Colorado	3,700 - 4,500	AAS	Cadmium refinery, surface soil in very close proximity 2 samples	Moyer and Budinger, unpublished data
Kansas		AAS	Smelter soil (N - HCl extractable) 330 m Northeast: Depth 0 - 5 cm 5 - 10 cm 10 - 20 cm 1000 m Northeast: Depth 0 - 5 cm 5 - 10 cm 10 - 20 cm 1670 m Northeast: Depth 0 - 5 cm 5 - 10 cm 10 - 20 cm	Lagerwerff, et al.,
	102			
	48			
	22			
	32.6			
	12.2			
	3.1			
	26.8			
	7.2			
	1.2			
Michigan	0.41 0.57 0.37 0.29	AAS	Land use study 70 residential samples 91 agricultural samples 86 industrial samples 7 airport samples	Klein, 1972
Maryland	0.08 - 0.65 0.2 - 1.45 0.12 - 0.94	AAS	Roadside soils 8 to 32 m from roadside 18 samples of Sassafras sandy loam 18 samples of Collington silt loam	Lagerwerff and Specht, 1970a, 1970b

Table 1 (continued)

Location	Cadmium Concentration ^a	Method	Sample Description	Reference
<u>United States</u> (cont.)				
Missouri	0.51 - 0.90	AAS	Knox silt loam 18 samples	Lagerwerff and Specht, 1970a
Montana	0.11 - 0.56	AAS	Roadways 3 samples 7 to 200 m from roadside	Lagerwerff, 1971
		AAS	Industrial area 1 mi, top 4 in. 6 to 10 in. depth 0.7 mi from stack Railroad tracks area	Miesch and Huffman, 1972
		AAS	Near smelter 69 samples within 4.5 mi	Hindawi and Neely, 1972
		AAS	Roadside soils and silt loam Roadside, 8 - 32 m 18 samples Cincinnati silt loam	Lagerwerff and Specht, 1970a, 1970b
Ohio	0.3 - 1.04 0.18-1.82	AAS	Roadside soils and silt loam Roadside, 8 - 32 m 18 samples Cincinnati silt loam	Lagerwerff and Specht, 1970a, 1970b
Texas	0.1 - 1.9 2 - 130	AAS	Corpus Christi Bay and Harbor 287 samples Bay range Harbor range	Holmes, et al., 1974
			Wisconsin	0.2 - 5.5
<u>World:</u>				
	0.15	NS	Crustal Abundance	Greene, 1959
	0.5		Soil abundance	
	0.13 - 0.18	S and NAA	Basic magma	Mookherjee, 1962
	0.1 - 4.5 %		Spheralite ores	
	9.0	S	Manganese nodules in deep-sea bed	Ahrens, 1967
	0.12 - 0.34	NAA	Rocks	Bilefield and Vincent, 1961
	0.008-0.04	NAA	Meteorites: 7 samples of irons	Schmitt et al., 1963
	0.015-3.3		14 samples of chondrites	
	0.004-1.79		6 samples of achondrites	
	0.33 -0.5		Terrestrial samples: 2 theolitic basalts	
	0.24 -0.26		2 elogitic basalts	

^aConcentrations are in terms of ppm dry sediment or soil unless otherwise stated.

^bAAS, atomic absorption spectrophotometry; C, chemical; NAA, neutron activation analysis; NS, not stated; XRF, X-ray fluorescence; S, spectrographic.

Figure 1 shows in simplified form the contributing sources and sinks for cadmium in the environmental progression to man. The role of soils is primarily as a sink and thus they can serve as important monitoring points for gross cadmium levels from which exposures to the public might be inferred.

Beyond simple industrial effluents, common sewage plays a role in estuary pollution. Berrow and Webber (1972) have written an overview of this problem for cadmium and other trace elements. Van Loon and Lichwa (1973) have extended this to investigate fertilizers as well, since industrial and domestic sewage plant sludges have often been used as plant nutrients in the past (Linnman et al., 1973). Schroeder (1963) also found superphosphate fertilizers to be high in cadmium, and found vegetables grown on this type of fertilizer have excessive cadmium levels. Stones (1959) published a series of articles on the fate of metals during the treatment of sewage. Cadmium was not investigated, but it was found that the efficiency of metal extraction processes including activated sludge treatment, chemical, biological filtration, and sedimentation resulted in a retention of only 60 to 70% of the total zinc. We can assume that cadmium extraction has a similar poor efficiency. However, Linstedt et al. (1974) have examined cadmium removal by such methods as lime precipitation and by activated carbon and found 95 and 99% removal, respectively.

Local Sources of Cadmium. The San Francisco Bay Area has no local sources of cadmium. However, the American Smelting and Refining Co. has operated a lead-slag fuming plant at Selby near the Carquinez Straits for over 60 years. This plant has curtailed operations in the past few years. It has been shown that lead contained in the plume rise had settled in significant amounts in the local area. The lead dispersed from the plant was deemed responsible for the deaths of several horses that had grazed on contaminated grassland. All of these deaths were in the northeast section of the bay near Vallejo (downwind of the plant for the prevailing winds).

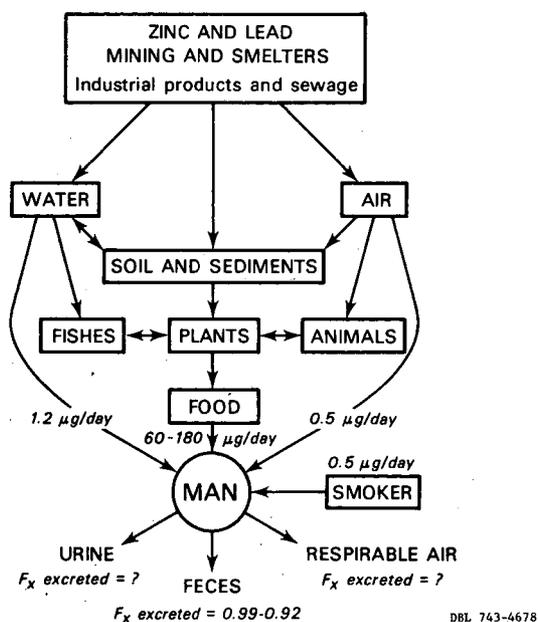


Fig. 1. The cadmium pathway to man (simplified). The diagram describes the various ways which cadmium can eventually reach man. The relative daily intake and excretion levels are incorporated.

Figure 1 shows that cadmium is refined from the tailings of zinc-lead ores. The refining of lead by slag fuming processes consequently refines cadmium as well. The fumes from this process are generally retorted in a large stack to reduce emissions, but significant amounts still escape to the ambient air. Thus higher levels of cadmium would be expected in the sediments of the northeastern section. The net influx of fresh water through Carquinez Straits from the Central Valley rivers passes near the plant and would serve somewhat to reduce sediment cadmium levels and disperse the metal into San Pablo Bay (Fig. 2).

In this northeast section of the bay are numerous petroleum refineries extending from Martinez and Benicia to Richmond on both sides of the slag fuming plant at Selby. Petroleum refining introduces sulfur dioxide into the air and thus possibly indirectly aids in the sediment deposition of cadmium. Sulfur dioxide from the petroleum refineries might play an important role in the precipitation of cadmium sulfide (greenochite) from dissolved cadmium salts in the bay. The extent of this process is discussed later in this paper.

Other possible contributors of cadmium to the waters of the bay might be found in numerous shipbuilding and repair facilities, both civil and military, such as Mare Island N. S., San Francisco N. S. (Hunters Point) the commercial shipyards of Oakland and San Francisco and municipal wastewater and sewage. The reserve (mothball) fleet anchored just east of Benicia in Suisun Bay might introduce cadmium to the bay waters through simple dissolution of protective paints over the years.

There are seven major bridges serving heavy automotive traffic over the bay. Lagerwerff and Specht (1970a) analyzed soils surrounding heavily traveled roads and demonstrated a significant increase in cadmium concentration in surface soil near these roads. The automobile has several wearing components that contain cadmium; these include tires, brake linings, bearings, paints, motor fuels, and lubricants (Fulkerson and Goeller, 1973). The extensive highway network of the bay area utilizes the bay perimeter in every quadrant making automobiles another major source of shoreline cadmium.

Data on the cadmium levels of soils and sediments, the air, and the waters of California, and especially of the Bay Region, are scarce. Silvey (1967) has published the occurrence of cadmium in the waters of California. Analysis was done on spring waters (average Cd 8.2 $\mu\text{g}/\text{liter}$), well water and oil field brine (4 of 82 samples: 71, 5.1, 11, and 7.1 $\mu\text{g}/\text{liter}$), stream water (none detected in 65 samples) and sea water (non detected in 24 samples). Air Cd levels for the Bay Area have been averaging 0.02 $\mu\text{g}/\text{m}^3$. Esvelt, et al. (1972) have reported on the removal of toxic metals from municipal wastewater treatment facilities in the San Francisco Bay region, however, no data on the eventual cadmium distribution in the sediments is presented. The mean primary effluent cadmium concentration reported by Esvelt was 0.01 mg/liter and was reduced 10 to 70 percent by currently used sewage treatment methods.

OVERVIEW OF BIOLOGICAL PROBLEM ASSOCIATED WITH CADMIUM

Zinc-Cadmium Interaction

Zinc and cadmium are members of the same chemical group of the periodic table and thus follow similar chemical pathways. Since the crustal abundance of zinc is 500 to 1000 times that

of cadmium (Mookherjee, 1962), and the two metals have similar chemical properties and appear together in nature, it is said that cadmium geologically "follows" zinc. The same holds true in biological systems. Zinc however is an essential element for life, whereas cadmium is toxic to nearly all forms of life.

Zinc is essential primarily for growth and reproduction in both plants and animals. The human body contains approximately 2.3 grams of zinc with the highest percentages being found in the prostate, bone, muscle, kidney, and liver (ICRP, 1959). Zinc serves as a catalyst for certain essential reactions. It is an essential component in many metal-enzyme complexes. These zinc complexes have been extensively reviewed by Parisi and Vallee (1969). The presence of cadmium can result in inhibited zinc uptake and depression of many zinc-activated or zinc-required systems (Supplee, 1963; Petering et al., 1971). Once in the biosystem, cadmium follows metabolic pathways, deposition, and excretion patterns somewhat unlike those of zinc (Shaikh and Lucis, 1972).

Substitution of cadmium for zinc in zinc-enzyme systems seriously alters their functions (Cotzias et al., 1961). Cadmium will inactivate several sulfhydryl group enzymes (Simon et al., 1947), and is known to interfere with the citric acid cycle (Jacobs et al., 1956), to inhibit ceruloplasmin activity (Murthy et al., 1972), and to inhibit liver alcohol dehydrogenase activity (Druyan and Vallee, 1962). The tobacco mosaic virus (TMV) has also been shown to be inhibited by cadmium (Ulrychova-Zelinkova, 1959). Presence of cadmium causes a diminution of oxygen consumption in mitochondria (Hiltbran, 1971) and in ATPase activity of alveolar macrophages (Cross et al., 1970; Mustafa and Cross, 1971). The partial inhibition of these and other zinc related metabolic pathways can seriously depress or injure normal nutritional and biological balances and lead to metabolic disease states.

The turnover of zinc-65 has been examined in man and animals. Schroeder (1967a) has reported a biological half-life for zinc of about 315 days. But the biological half life of cadmium is uncertain (Friberg et al., 1971). Rahola et al. (1972 and 1973) report an estimate of the biological half life for man as between a few hundred days and infinity. Their results are indefinite since they used very low doses of cadmium-115m which has a physical half life of only 43 days. Burch and Walsh (1959) reported an "exceptionally long half life" for cadmium-115m. Durbin et al. (1957) used cadmium-109 (453 day physical half life) to assess the biological half life in rats and report a 200 day half life. Richmond et al. (1966) found a 200 to 300 day half life, using cadmium-109 in mice. The mode of administration determined the rate of elimination. The qualitative measurements for the half life after ingestion, biological injection, and inhalation have not been determined for man.

Accumulation and Effects in Lower Life Forms

A high percentage of man's exposure to cadmium results from progressive accumulation due to small quantities in food. The cadmium reaches the food chain through soil and ground water. Zinc is an essential element even for such low life-forms as the pondweed, Southern Naiad (*N. quadulepensis*). Cearley and Coleman (1973) exposed this plant to cadmium levels of less than 1 ppm with the roots cut, and the plants clearly demonstrated reductions in chlorophyll, turgor, and stolon development compared to controls. The plants also accumulated over 5000 µg/g of cadmium (as measured in the plant ash) after 21 days of exposure. Aquatic plants pass toxic

quantities of the metal to higher life forms such as fish and waterfowl because plants like the pondweed are major components of their diets.

Trace elements in soils are reflected by levels found in plants (Goodman and Roberts, 1971; Lagerwerff and Specht, 1970a, 1970b; Lagerwerff, 1971; John et al., 1972). Schroeder (1963) found vegetables grown with superphosphate fertilizers had excessive cadmium levels, indicating that extraction from the soil is an important factor, and providing evidence for the important role fertilizers might play in the effects on man's health. Linnman et al. (1973) found elevated cadmium in wheat grown on sewage sludge used as a plant nutrient. The use of such material for this purpose has been suggested frequently since it is generally high in nitrogen compounds and other nutrients. Van Loon and Lichwa (1973) found high cadmium content in fertilizers (< 1-63 ppm) and in domestic sewage sludge samples (5-45 ppm). Berrow and Weber (1972) found 17% of their sewage sludge samples were over 100 ppm cadmium (dry weight basis).

Moritsugu and Kobayashi (1964) studied cadmium in rice grown in Japan; they found that the cadmium content of the rice ash increased rapidly during rice polishing, indicating that cadmium had accumulated in the pulp.

Marine algae, protozoa, porifera, and coelenterates from the Irish Sea where the cadmium-seawater concentration was 0.113 µg/liter (Mullin and Riley, 1954) had concentrations between 0.3 and 0.9 µg/g dry organism indicating a concentration enrichment relative to seawater of between 10^2 and 10^4 (Mullin and Riley, 1956). The protozoa were found to be higher at 2.25 µg/g dry organism or an enrichment factor of 2×10^4 . Porifera and coelenterates were between 1 and 2 µg/g dry organism (10^4 enrichment factor). Preston (1973) showed concentration increases over sea-water for sediment of 10^3 , for plankton of 10^4 , and for seaweed of 10^2 - 10^3 .

Accumulation and Effects in Higher Life Forms

Schroeder (1967a), Mullin and Riley (1956), and Meranger and Somers (1968) found exceptionally high cadmium accumulation in aquatic life forms such as mussels, oysters, echinoderms, other benthic organisms, and anchovies. The soft parts of these organisms had an enrichment factor over seawater of between 10^4 and 10^6 . Enrichment over seawater for molluscs is 10^3 - 10^5 , for crustacea is 10^3 , and for fish is 10^2 (Preston, 1973).

Because oysters have a high metabolic demand for zinc ions (Romeril, 1971), one would expect a similar high biological turnover or possible concentration of cadmium in them. The cadmium level in oyster shells is low (Ferrell, 1973) while the cadmium content of the soft tissues reflects that of the environment (Pringle et al., 1968; Brooks and Rumsby, 1965, 1967; and Bryan, 1971).

Bivalves such as oysters live in and on sediments and their digestive glands pass soil particulates and organisms continually. The cadmium content of the digestive gland can be as much as 0.5% of the soft tissue ash (300,000 X that of seawater). The heavy accumulation in the digestive gland was not decreased even when the animals were allowed to purge the gland with filtered seawater (Mullin and Riley, 1956).

Estuarian teleosts show numerous histological and hematological responses to cadmium (Gardner and Yevitch, 1970). Eisler (1971) examined several marine organisms ranging from the sand shrimp and Hermit crab to the sand worm (Nereis virens) mummichog (Fundulus heteroclitus). The sand shrimp LD₅₀ for 96-hour exposure was 0.320 ppm while the LD₅₀ for Nereis and

Fundulus were 11.0 and 55.0 ppm respectively. Salinity and temperature were important variables. Low salinity (5‰) and higher temperatures (20°C) lowered the tolerance of these organisms. Lallier (1955) detected abnormal development of the sea urchin egg when exposed to cadmium in very small quantities.

Rainbow trout (Ball, 1967) and chinook salmon (Hublou et al., 1954) were found to have higher mortality rates when exposed to cadmium concentrations above 1.0 ppm. Sangalang and O'Halloran (1972) noticed a distinct depression in androgen synthesis in brook trout at levels of only 25 ppb. Testicular damage was also recorded.

Many and possibly all mammals have a detoxification mechanism which also seems responsible for the long biological half life of cadmium. Man and other animals accumulate cadmium in the liver and kidneys; the mechanism for this apparently being a chelation process. A sulfhydryl protein, termed metallothionein, was isolated in equine kidney cortex by Margoshes and Vallee in 1957. Further work by Kagi and Vallee (1960, 1961) revealed the protein to be synthesized in the liver and deposited in the renal cortex. The isolated protein contained as much as 3% cadmium with zinc and copper also being major components. The protein had a low molecular weight (10,000) and appears to be synthesized only when the organism is exposed to cadmium. The production of the protein does not occur immediately after exposure to cadmium, but rather appears between three and six days later (Nordberg et al., 1971). This explains high renal clearance of cadmium immediately after exposure, followed by diminished renal clearance and retention of the remaining cadmium by the organism.

Cadmium binding proteins (Cd-BP) have been isolated from several tissues which include the kidney, liver, and testis (Pulido et al., 1966; Kagi and Vallee, 1961; Chen et al., 1972). Administration of cadmium induces the synthesis of this cadmium binding protein and it has been postulated that this protein (Cd-BP) in the liver, kidney, and testis represents a biological system which protects the organs from the toxic effects of cadmium (Shaikh and Lucis, 1971). Metallothionein, a cadmium binding protein isolated from human and equine renal cortex, show many similarities: 250 nm absorption band characteristic of cadmium mercaptide chromophores, similar rotatory dispersion, large positive Cotton effect due to the asymmetric binding of cadmium to multiple sulfur ligands, and relatively low molecular weights: 10,000-12,000 (Pulido et al., 1966). In the testis this Cd-BP has some similarities to metallothionein found in the liver and kidney. The Cd-BP of the rat testis has been isolated and partially characterized using ^{109}Cd to elucidate the nature of the binding. This protein was isolated by Sephadex gel filtration (G-75 and G-25). Cadmium bound selectively to a low molecular weight protein at pH 7.0 but dissociated at pH 2.0. The molecular weight of this rat testis Cd-BP, determined by gel filtration, was estimated to be 15,000. Disc gel electrophoresis showed one major and two minor bands (Singh et al. 1974).

Health Effects on Man and Other Higher Animals

Several reports in the literature deal with disease states of man and higher animals which are related to cadmium intoxication. Nilsson (1970) provides a fine outline of the aspects of cadmium toxicity to man, especially in terms of industrial exposure. Flick et al. (1971) and Vigliani (1972) provide information of the more subtle effects of cadmium. Gunn, et al. (1963) and Reddy et al. (1973) have related cadmium with interstitial cell tumors in the mouse and rat, respectively. Prostatic cancer in man might be induced by cadmium according to Winkelstein and Kantor (1969), but Levy et al. (1973) found no prostate changes in exposed rats. Nomiya

et al. (1973) described the early signs of cadmium intoxication for the rabbit and Ferm (1971) has explored the teratogenic potential of cadmium for hamsters.

The similar stress responses and disease manifestations which both man and animals exhibit toward cadmium are being explored in such areas as hypertension (Schroeder, 1967b) proteinuria and renal damage from occupational exposure (Friberg, 1957; Lee, to be published; Lauwerys et al., 1974), teratogenic potential (Scanlon, 1972; Chaube, et al., 1973), emphysema (Lane and Campbell, 1954; Bonnell, 1955), cancer (Heath and Daniel, 1964; Haddow et al., 1964; Kolonel, 1972, 1972; Reddy, et al., 1973), diabetes (Wilson, et al., 1941), prostate disorders (Kipling and Waterhouse, 1967), heart disease (Carroll, 1966) and bone disorders (Itokowa, et al., 1973; 1974; The Lancet, 1971; Matsue, et al., 1970).

The underlying mechanism for disease induction is probably through disturbed enzyme systems. However alternate mechanisms such as membrane electrophysical changes, lysosome damage and even chromosome changes are strong candidates that have not yet been investigated.

METHODS

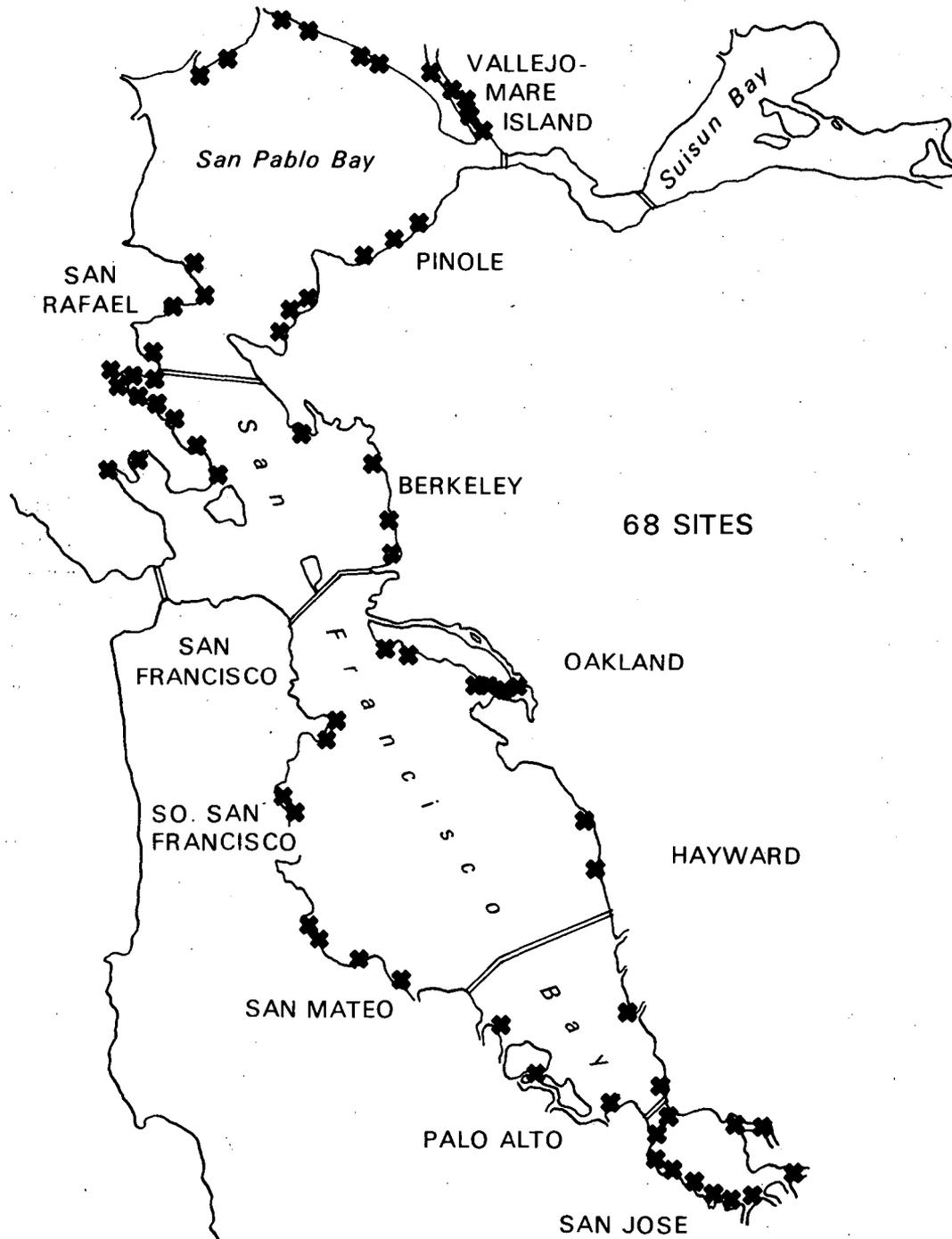
Sample Collection and Preparation

Sixty eight sample collection sites were chosen from Carquinez Straits in the north to San Jose at the southern tip of the bay (see Fig. 2). Sample cores 5.5 cm in diameter and 10 cm deep were obtained at low water. The top-most centimeter of each core was discarded and the remainder divided into top (1 to 7 cm depth) and bottom (7 to 10 cm depth) fractions. Centrally located 2×2×1 cm samples were removed from the top and bottom fractions and dried for 8-10 hr. Following drying, the samples were crushed and passed through a stainless steel screen (2-mm mesh) to remove large rocks and roots. Then they were again crushed and dried for another 4 hr at 110°C. The samples were then cooled for 1 hr and weighed.

Bioexchangeable Cadmium vs Total Cadmium

The presence of a toxic metal in the geological environment does not necessarily infer an ability to enter into a biological system. Insoluble or biologically inert compounds of cadmium do exist in the soil (e.g., bound in silicate lattices). Jones (1973) reports only 60% of the cadmium in the bottom sediments of Cardigan Bay, Wales, were acid soluble. Biological digestive mechanisms do not have the capability to disrupt silicate lattices and free trapped elements such as cadmium, thus total cadmium content measured by neutron activation of rocks (Bilefield and Vincent, 1961) or hydrofluoric acid digestion followed by x-ray fluorescence (Blount et al., 1973) is not truly representative of the fraction of cadmium that is readily exchangeable.

The presence of cadmium in rocks and soils during ingestion does not mean that all of the cadmium will enter a metabolic system. Even when food-borne cadmium is entirely in ionic, metallic or a soluble form, the intestinal tract absorbs only 2 to 9% of it (Schroeder, 1967a; Miller et al., 1968). Bioexchangeable cadmium is that which is in a chemical state that allows it to become incorporated and accumulated in the biological systems of organisms.



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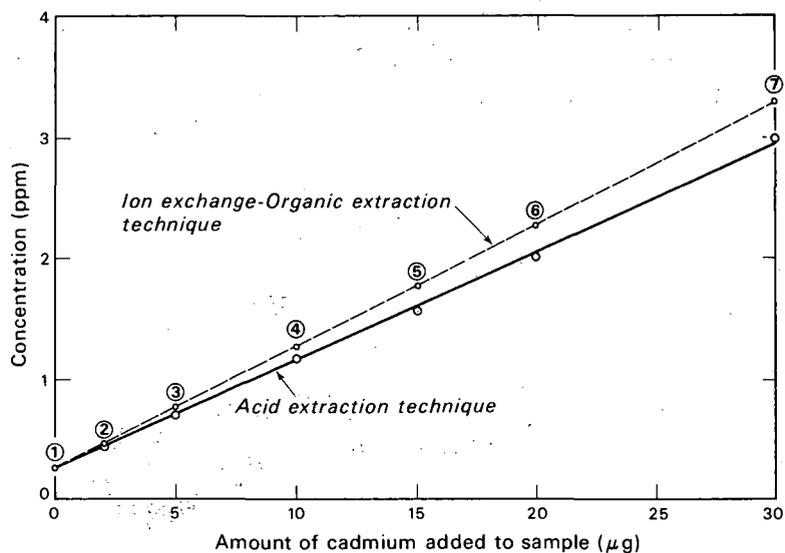
Fig. 2. Approximate locations from which the 68 core samples were taken on the shores of San Francisco Bay.

Procedures for Analysis

Our method consisted of leaching out of the sediment all bioexchangeable cadmium, separating interfering elements, and quantitating by atomic absorption spectrometry. Major divalent and trivalent components such as iron (II), iron (III) and calcium are separated from the cadmium by ion-exchange since preconcentration of the samples allows these components to depress the cadmium ionization in the flame. High ionic strengths also tend to introduce variable aspiration rates for the samples relative to standards.

Following the ion-exchange step, the separated cadmium is chelated into an organo-cadmium complex. This complex is efficiently extracted into an organic solvent from a weakly acidic medium (pH = 3.0). The organo-cadmium complex organic solvent mixture is compared against standards by atomic absorption spectrophotometry.

The method expands on work done by Nakagawa and Harms (1968) and Ward et al. (1969), and incorporates separation procedures and sensitivity improvements from the works of DeVoe (1960), Samuelson (1963); Strelow, (1960); Strelow, et al. (1971); Lehnert (1968), and Nagata, et al. (1970). The Acid Extraction Phase. The widely used acid extraction method of Nakagawa and Harms (1968) proved to be inconsistent for the reproductibility we desired. Figure 3 compares the recovery of added cadmium for the separation procedure presented here to the acid extraction procedure of Nakagawa and Harms. Our cadmium levels were recovered with a reproducible error of approximately $\pm 3\%$ at the 3 ppm level, while the acid extraction curve dips from the correct value by as much as 10%.

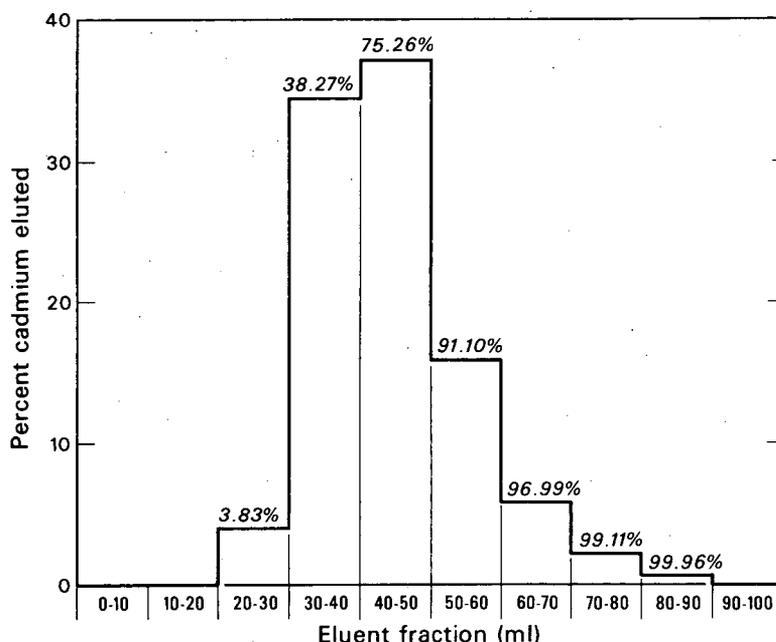


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Fig. 3. Recovery curves for two methods of soil analysis. Various levels of cadmium were added to aliquots of a soil sample. Recovery from the acid-extraction technique was significantly less than the ion-exchange-organic extraction technique.

The sample (~10g) is acid-leached with 20 cc of HNO₃ (conc.), 15 cc HCl(conc.) and 2 cc H₂SO₄ (conc.). A few drops of octyl alcohol is added to prevent frothing. The sample is stirred occasionally on low heat until viscous, then 10 cc of 3 N HCl is added with continuous stirring. The sample is filtered using Whatman No. 1 filter paper and a Buchner funnel attached to a vacuum pump. The undissolved material is washed with 3 N HCl until the filtrate is clear. The pH of the filtrate is adjusted to 1.0 with ammonium hydroxide (concentrated) keeping the temperature at or below 20°C. The volume is adjusted to 100 cc and the sample is ready for direct aspiration (error ≈10 to 15%) if desired.

The Ion Exchange/Organic Extraction Phase. The ion exchange step is necessary to prevent possible supersaturation of the chelator which could lead to incomplete cadmium removal. Addition of the chelator before ion exchange also produces a viscous solution which is not always easily accommodated by the organic solvent. Complete separation of the soil components from the cadmium is not necessary; a simple gross separation is sufficient. The procedure is as follows: Remove 30 cc of the sample and adjust the aliquot to a pH of 1.3 with 8 N KOH. Prepare an ion exchange column (Bio-Rad AG 50W-X8; 50-100 mesh) in a slurry with 0.2 N HCl on a 50-cc buret (40 cc of resin bed). Add the sample to the column at a flow rate of approximately 2 cc/min. Once the column has been loaded, wash the column with 25 cc of 0.2 N HCl. Elute the cadmium from the column with 0.8 N HCl (Fig. 4). Collect the first 120 cc of eluent and save. Because of competition for active sites on the column, the cadmium does not come off as a uniform plate and thus a tailing effect is noticeable.



DBL 738-5290

Fig. 4. Ion-exchange elution curve for 30 µg of cadmium in a high iron (50,000-µg) "mock" soil sample.

Adjust the 120 cc of eluant to a pH of 3.0 and transfer to a separatory flask. Add 5 cc of 5% ammonium pyrrolidine dithiocarbamate (APDC; Fisher Scientific) and shake vigorously for 1 min. The efficiency of this chelator is plotted against pH in Fig. 5. It is important to use a pH of 2.5 or greater (a weakly acidic pH is preferable). Add to this organo-metallic complex a known volume of water-saturated methyl isobutyl ketone (MIBK) and shake vigorously again for 1 min. Wait 3 to 5 min. before separating phases and then centrifuge the samples at ~5000 rpm for 5 minutes.

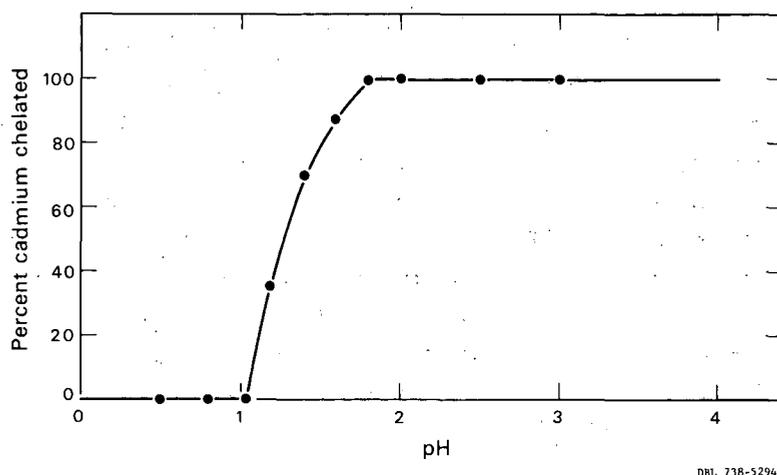


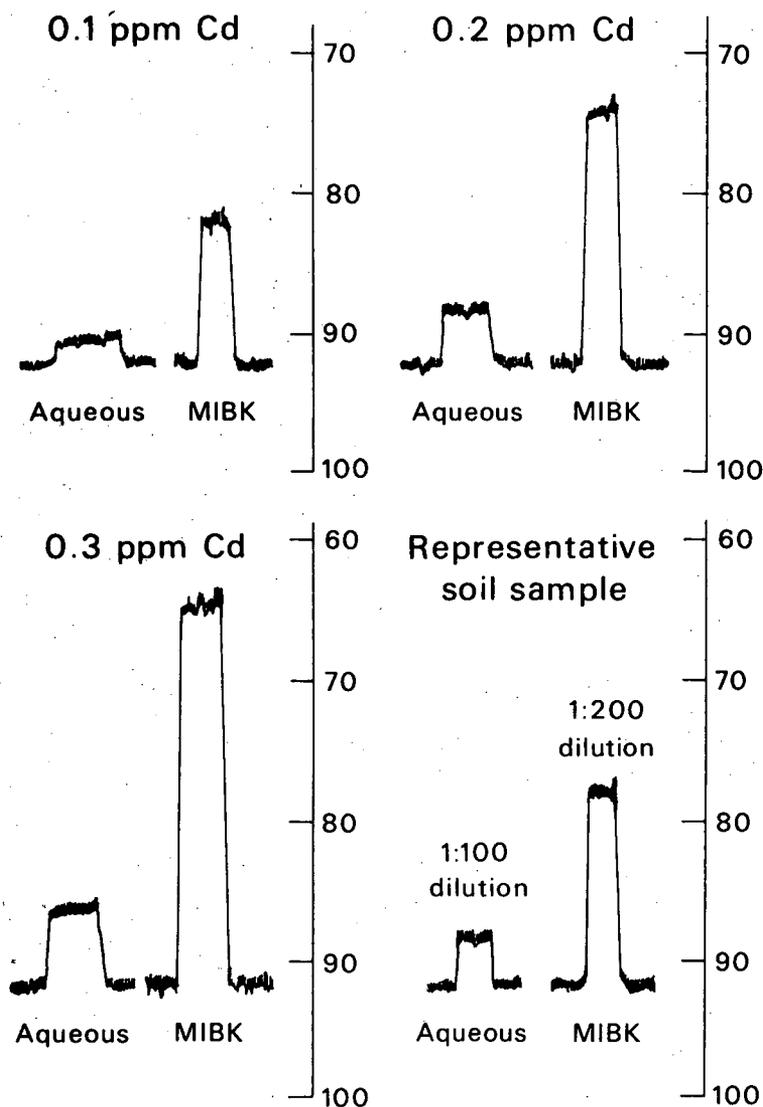
Fig. 5. Efficiency curve for APDC (ammonium-pyrrolidine dithiocarbamate) at various pH.

The Atomic Absorption Phase. The MIBK solvent serves to increase the sensitivity for cadmium analysis. Figure 6 demonstrates the signal intensities of a representative soil sample and standards in both aqueous and organic phases. Figure 7 demonstrates the absorbance differences of standard curves for the aqueous and organic media. The percent error in absorbance is decidedly less for the organic than the aqueous ($\pm 3\%$ = organic phase; $\pm 10\%$ = aqueous phase) at the absorbances which the soils exhibit.

The instrument parameters for the atomic absorption unit are as follows:

Lamp current:	4 mA
Slit Width:	0.15 mm (150 μ m)
Wavelength:	228.8 nm
Air and acetylene gas mixture:	very lean
Single slot burner head:	Jarrell Ash Model JA-82-374

Aspirate the samples into the nebulizer burner assembly, keeping the air and acetylene mixture very lean. Compare the samples against blanks standards prepared from washed and ignited sand (Mallinckrodt). The sand blanks and standards are made by passing each through the entire separation scheme and adjusting the organic volumes for quantitation.



MIBK = Methyl Isobutyl Ketone

DBL 738-5293

Fig. 6. A comparison of atomic absorption signal strength for the aqueous and organic media. A representative soil sample is presented. The aqueous signal of the soil sample gave a percent error twice as high as the MIBK (methyl isobutyl ketone) signal.

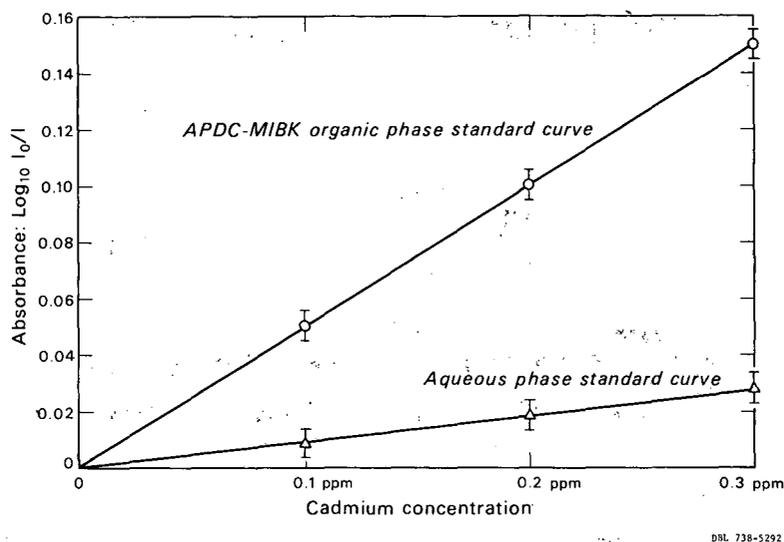


Fig. 7. A standard curve showing the increased sensitivity of the organic extraction method over the aqueous technique.

RESULTS

The distribution of cadmium concentrations for all of the fractions analyzed is given in Table 2 and shown graphically in Fig. 8. The distribution in the bay sediments is Gaussian if the contribution from samples containing >2 ppm is neglected. The first and major mode is 0.6 to 0.79 $\mu\text{g/g}$. Eighteen samples had concentrations greater than 2.0 $\mu\text{g/g}$; we suspect these represent cadmium added above background levels.

To explore this suspicion, we divided the bay into four sectors as shown in Fig. 9. Table 3 then gives the mean values for the top, bottom, and combined-fraction analyses for all of the 68 cores as well as sector values. The mean top fraction for the bay as a whole was 1.22 ± 0.99 $\mu\text{g/g}$ and the bottom fraction mean was 0.93 ± 0.75 $\mu\text{g/g}$. The mean value for all the samples irrespective of core position was 1.07 ± 0.89 $\mu\text{g/g}$.

Considering top versus bottom concentrations, approximately 17.5% (12 of 68) were above the 2.0 $\mu\text{g/g}$ level as opposed to only 8.9% (6 of 68) of the bottom fractions. Figure 9 shows the geographical distribution of cadmium along the bay perimeter with plots of the specific core concentrations at each collection site relative to the means for the bay as a whole. The points of high cadmium accumulation thus stand out relative to the mean values.

Sector Comparisons

Table 4. describes the location of each sample, the cadmium concentrations for both the top and bottom fractions, and a description of major sediment and local environmental characteristics. The table is divided into the same sectors as Fig. 9 and progresses from a northern to a southern area.

Sector I: The Northwest. We collected 19 core samples in this sector ranging from a point on Highway 37 to Richardson Bay. The majority of samples were clay with tan to dark brown coloring. The northwest sector does not include any major industrial center. The samples had a mean top

Table 2. Concentration interval breakdown of soil samples

No.	Concentration interval (ppm)	No. of samples	Percent of samples
1	0.0-0.19	12	8.8
2	0.2-0.39	5	3.6
3	0.4-0.59	14	10.3
4	0.6-0.79	36	26.5
5	0.8-0.99	21	15.4
6	1.0-1.19	14	10.3
7	1.2-1.39	7	5.1
8	1.4-1.59	3	2.2
9	1.6-1.79	4	2.9
10	1.8-1.99	1	<1
11	2.0-2.19	0	0
12	2.2-2.39	1	<1
13	2.4-2.59	2	1.4
14	2.6-2.79	3	2.2
15	2.8-2.99	5	3.6
16	3.0-3.19	1	<1
17	3.2-3.39	2	1.4
18	3.4-3.59	1	<1
19	3.6-3.79	2	1.4
20	3.8-3.99	1	1
21	4.0-4.19	0	0
22	4.2-4.39	0	0
23	4.4-4.59	0	0
24	4.6-4.79	1	<1
25	4.8-4.99	0	0

fraction cadmium content of $1.15 \pm 0.87 \mu\text{g/g}$ and a mean bottom fraction of $0.70 \pm 0.34 \mu\text{g/g}$. Overall this sector was low in cadmium relative to the entire bay mean values.

The top fractions of two cores, however, were considerably above the others while the bottom fractions of these same cores were strikingly low. The mean top to bottom ratio for these two samples was a very high 8.3. These samples were taken in an intertidal area near Corte Madera and had a particularly foul odor. The bottom fraction of one was light colored.

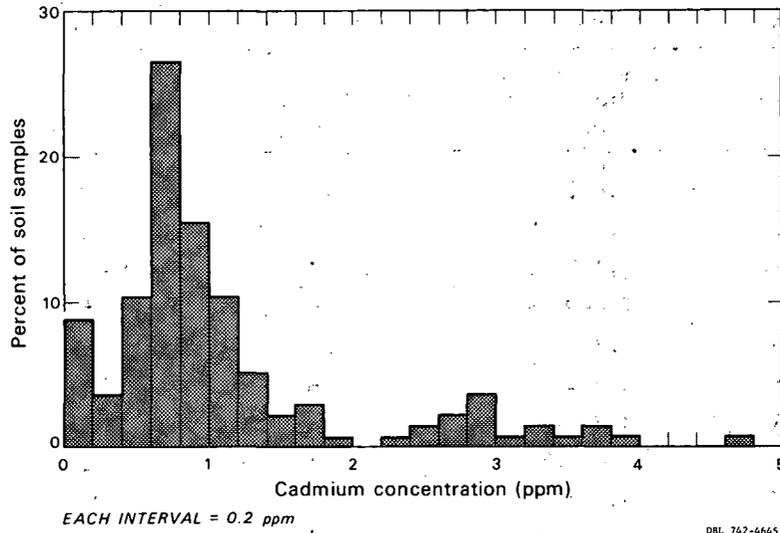


Fig. 8. The concentration distribution of cadmium in the San Francisco Bay sediments. Top and bottom fraction designation was ignored. The diagram is divided into 0.2 ppm intervals.

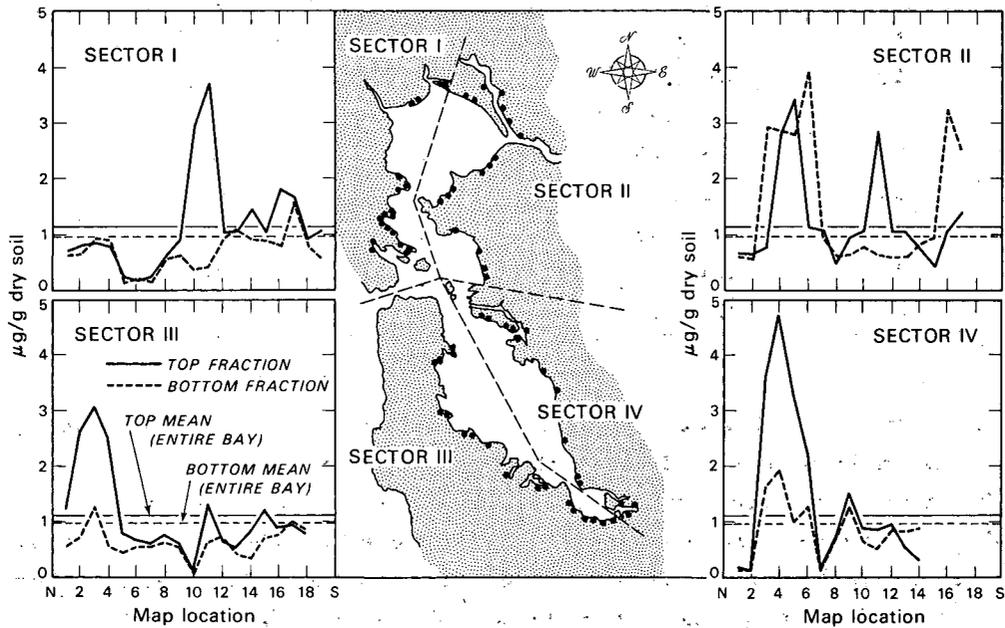


Fig. 9. Sector division of the bay and a point by point display of the cadmium levels found in the top and bottom fractions of each core sample. Each sector display progresses from the northern-most sample to a southern-most sample. The bay top fraction and bottom fraction mean values are overlaid to allow for a point to mean comparison.

Sector II: The Northeast. An interesting characteristic of this sector, shown in Table , is that the bottom fraction mean is almost twice that of the other sectors while the top fraction mean was almost equal to top fraction mean for the whole bay. The mean value for the bottom fractions was

Table 3. Total bay and sector means with standard deviations.

Sector	No. of sample	Fraction	Means and standard deviation
Entire bay (all sectors)	68	Top	1.22 ± 0.99
	68	Bottom	0.93 ± 0.75
	136	Combined	1.07 ± 0.89
Sector I (northwest sector)	19	Top	1.14 ± 0.87
	19	Bottom	0.7 ± 0.34
	38	Combined	0.92 ± 0.70
Sector II (northeast sector)	17	Top	1.25 ± 0.86
	17	Bottom	1.54 ± 1.14
	34	Combined	1.40 ± 1.02
Sector III (southwest sector)	18	Top	1.10 ± 0.78
	18	Bottom	0.65 ± 0.24
	36	Combined	0.88 ± 0.62
Sector IV (southeast sector)	14	Top	1.43 ± 1.41
	14	Bottom	0.85 ± 0.53
	28	Combined	1.14 ± 1.10

1.54 ± 1.14 µg/g, while the top fraction mean was only 1.25 ± 0.8 µg/g. The combined top and bottom mean was the highest of all sectors at 1.40 ± 1.02 µg/g. The incidence of high cadmium was most common in those from the Mare Island N. S. and Emeryville mud flat sites. Both of these areas had exceptionally high cadmium levels in the bottom fractions. Among the samples that were above 2 ppm in Fig. 8 (n = 18), this sector contributed 50% (n = 9).

Sector III: The Southwest. This sector had the lowest combined top and bottom mean value of cadmium content at 0.88 ± 0.62 µg/g. The mean top fraction was 1.10 ± 0.78 µg/g and the mean bottom fraction was 0.65 ± 0.24 µg/g. Compared to the other sectors shown in Fig. 9, this sector had the lowest incidence of cadmium. High top fraction values were found at Hunters Point and South San Francisco. The lowest bay sediment value was also found in this sector at Redwood City.

Sector IV: The Southeast. This sector had a combined top and bottom fraction mean cadmium content of 1.14 ± 1.10 µg/g. The top fractions gave a mean value of 1.43 ± 1.41 µg/g, but this mean value is somewhat distorted because 2 of the 14 samples were exceptionally high. These two samples were from San Leandro Bay and were not significantly offset by the low values found at the Alameda beach sampling stations.

The bottom fractions had a mean of 0.85 ± 0.53 µg/g with no significantly high samples relative to top fractions. San Leandro Bay had the most consistently high top fraction values for any point to point area of the bay. The samples taken at Corte Madera (Sector I), Mare Island (Sector II), and Hunters Point - South San Francisco (Sector III) all had at least one low fraction.

Table 4. Sample locations, fractions, Cd concentrations, and soil characteristics.

Site No.	Location	Sample No. and fraction	µg Cd/g dry sediment	Soil characteristics	
				Description	Physical environment
Sector I: Northwest (19 samples):					
1	Highway 37	1T ^a	0.68	Dark brown, moist clay with moderate vegetation present; continuous top to bottom.	Near roadway and bridge; farmland area, river area.
		1B ^b	0.65		
2	Highway 37	2T	0.77	Dark brown, moist clay, slight vegetation, continuous top to bottom.	Near farmland and roadway, relatively little activity.
		2B	0.67		
3	Black Point	1T	0.83	Dark black, moist ooze with some moderate vegetation. Veg. roots extended to bottom fraction.	Near freeway and boat landings, bridge area and large waterway.
		1B	0.97		
4	Black Point	2T	0.78	Black to gray, moist ooze, some brown clay in bottom fraction, vegetation present.	Approximately 50 ft from Site No. 3, upstream.
		2B	0.88		
5	San Rafael (No.)	1T	0.24	Brown clay and sand, some vegetation and rocks present in area--none in sample.	No land development; lightly traveled road 50 ft away.
		1B	0.14		
6	San Rafael	2T	0.15	All sand, beach area, light tan to white sand (moist).	Park area on tip of peninsula.
		2B	0.20		
7	San Rafael (So.)	3T	0.18	Dark sand with large pebbles, some white sand present.	Sand-fill area with cement pilings and blocks.
		3B	0.18		
8	Pt. San Quentin	1T	0.63	Dark sand with some shells present, no vegetation.	Near freeway and boat-house.
		1B	0.61		
9	Corte Madera	1T	0.89	Dark, moist clay with low vegetation, foul odor.	Open water area, some refuse in muds.
		1B	0.69		
10	Corte Madera	2T	2.94	Dark, moist, organic ooze foul odor with some light material in bottom fractions.	Near roadway and rock quarry operation.
		2B	0.39		
11	Corte Madera	3T	3.72	Dark ooze (organic), bottom fractions relatively drier with sand.	25 ft from Site No. 10.
		3B	0.41		
12	Corte Madera	4T	1.00	Brown sand, uniform consistency, some vegetation.	Open area with shellfish in the area.
		4B	0.99		
13	Larkspur	1T	1.04	Moist sand with some dark streaks, uniform texture.	Open flat land, no noticeable industry or land use nearby.
		1B	1.05		

Table 4. (continued)

14	Larkspur	2T 2B	1.43 0.81	Sand and clay mixture, brown with shells present.	Open flat land, no noticeable industry or land use nearby.
15	Tiburon	1T 1B	1.77 0.78	Clay with black color in bottom fraction, high shell content.	Boating and residential area, clean fill and breakwater.
16	Tiburon	2T 2B	1.67 1.56	Clay with some sand, denser in bottom frac- tion.	Recreation area.
17	Tiburon	3T 3B	1.03 0.89	Clay with black streaks in top fraction only, stones.	Home area with homes built near water, high vegetation.
18	Richardson Bay	1T 1B	0.93 0.74	Brown and gray color, uniform texture.	Eastern side of bay with very little activity, home area, high vege- tation.
19	Richardson Bay	2T 2B	1.03 0.59	Brown and gray color, uniform throughout.	Near heliport and free- way, high vegetation area.
Sector II: Northeast (17 samples)					
1	Highway 37	3T 3B	0.66 0.61	Dark tan color, uniform clay texture.	Flat area with scrub brush and other vege- tation.
2	Highway 37	4T 4B	0.62 0.61	Same as Site No. 1.	Close to highway area, water inlet area.
3	Mare Island	1T 1B	0.74 2.93	Dark tan to dark red- brown clay at bottom.	North of naval ship- yard.
4	Mare Island	2T 2B	2.74 2.86	Dark clay, uniform con- sistency with some roots.	Across from naval shipyard, rapid water movement, high vege- tation area.
5	Mare Island	3T 3B	3.44 2.74	Uniform dark-brown clay with root structure holding sample together.	Across from naval shipyard, high vege- tation and rapid water movement.
6	Mare Island	4T 4B	1.11 3.91	Rocky surface and dark clay under surface.	Down toward bay from shipyard activity.
7	Vallejo (Carquinez)	1T 1B	1.08 0.92	Tan clay at bottom frac- tion, black to brown mixture.	Near major bridge and high traffic area.
8	Pinole (No.)	1T 1B	0.48 0.68	Black throughout sample, some roots.	Refineries nearby, water areas insect-laden.
9	Pinole	2T 2B	0.96 0.64	Tan to gray coloring, bottom fraction mostly gray.	Near steel industry, peninsular area.
10	Pinole (So.)	3T 3B	1.04 0.76	Tan to gray-brown mix- ture, sand prevalent com- ponent.	Sandy beach area south of peninsula, slow water motion.

Table 4. (continued)

11	Pt. San Pablo (No.)	1T 1B	2.86 0.68	Black surface gradually turning gray at bottom.	Foul area with large sediment accumulation.
12	Pt. San Pablo	2T 2B	1.03 0.58	Brown to red-brown, mottled texture, some pebbles.	Near foul area.
13	Pt. San Pablo (So.)	3T 3B	1.04 0.61	Black surface and brown to brown-red bottom frac- tion.	Inlet area, intertidal with obvious erosion.
14	Richmond	1T 1B	0.70 0.88	Light tan clay with uni- form consistency, low water content.	Water inlet to bay, some foul odors.
15	Albany	1T 1B	0.41 0.99	Sand and pebbles of many colors on top with some clay in bottom fractions.	Open to bay proper, near bay fill areas.
16	Emeryville	1T 1B	1.02 3.22	Black ooze, poor ability to hold form, very gummy and organic (oily).	High industry and high freeway traffic, very foul.
17	Emeryville	2T 2B	1.39 2.55	Dark, oily ooze, gummy texture throughout.	Industrial area, very foul odor, high freeway traffic, intertidal area.
Sector III: Southwest (18 samples):					
1	Hunter's Point	1T 1B	1.24 0.56	Black to gray-black. Dark sand in bottom frac- tion.	Shipyard area, high in- sect population, stagnant pools.
2	Hunter's Point	2T 2B	2.62 0.73	Black to gray-black. Dark sand in bottom frac- tion.	Shipyard area. Same as No. 1 about 50 ft away.
3	So. San Francisco	1T 1B	3.10 1.26	Dark black top fraction.	Water inlet and stream.
4	So. San Francisco	2T 2B	2.46 0.58	Dark brown to red-brown top to bottom gradual change.	Industrial area, new industry, foul area, high insect population.
5	Millbrae	1T 1B	0.80 0.47	Brown clay with continuous consistency.	Near major airport and water inlet (drainage).
6	Millbrae	2T 2B	0.68 0.56	Brown clay, uniform tex- ture.	Near major airport, open to bay proper.
7	San Mateo	1T 1B	0.60 0.56	Loose gravely high-water content sand with numerous red-colored stones and shells.	Peninsula area, recrea- tion area with some boating.
8	Belmont	1T 1B	0.60 0.56	Dark clay, solid texture, some stones in bottom levels.	Dense hard-pack soil, cliff-like bay water interface, moderate vegetation.
9	Belmont	2T 2B	0.75 0.64	Dark, high-water con- tent, sand-clay mixture.	Arid area, samples taken in water.

Table 4. (continued)

10	Redwood City	1T 1B	0.06 0.15	Red soil, many pebbles present, somewhat dry texture.	Poor bay access, delta region, dry land and water passageways.
11	Palo Alto	1T 1B	1.30 0.63	Black, very wet clay, uniform in top fraction, mottled in bottom.	Near airport and roadway.
12	Palo Alto	2T 2B	0.65 0.75	Black top fraction, dark-brown bottom fraction.	High vegetation in area, use of boats and airports.
13	Mountain View	1T 1B	0.53 0.48	Dark brown clay, tan colored blotches in bottom fraction, roots present.	Intertidal area, low physical activity, high vegetation.
14	Mountain View	2T 2B	0.78 0.36	Dark brown to tan clay with numerous roots, sandy bottom fraction.	Intertidal area.
15	San Jose	1T 1B	1.23 0.72	Algae-laden soil, brown to dark brown loose structure.	Waterway area, intertidal area near boating.
16	San Jose	2T 2B	0.76 0.76	Black, sandy soil with pebbles, uniform throughout.	Waterway area, some low vegetation.
17	San Jose	3T 3B	0.94 1.00	Brown to red soil with poor holding capacity, dry texture.	Waterway area.
18	San Jose	4T 4B	0.78 0.86	Brown to black (top to bottom) coloring, some shells present.	Waterway area.
<u>Sector IV: Southeast (14 samples):</u>					
1	Alameda	1T 1B	0.19 0.16	Sandy, very wet composition, lower fraction shell-laden.	Beach area.
2	Alameda	2T 2B	0.13 0.15	Sandy, very wet composition, lower fraction shell-laden.	Approx. 100-200 yards away from Site No. 1.
3	San Leandro Bay	1T 1B	3.64 1.68	Brown clay with roots not progressing to bottom fraction.	High vegetation area, some air traffic, minor road traffic.
4	San Leandro Bay	2T 2B	4.69 1.93	Black, foul clay with moderate water content.	Possible landfill area in past, moderate vegetation.
5	San Leandro Bay	3T 3B	3.25 1.03	Gummy, foul, black clay, some sand.	Near air service area, poor water composition.
6	San Leandro Bay	4T 4B	2.21 1.27	Brown to dark-brown color, fairly uniform texture.	Landfill area east of airport.

Table 4. (continued)

7	San Leandro Marina	1T 1B	0.14 0.14	Foul odor, black and oily color texture.	Near marina with boating, land drainage area.
8	San Lorenzo	1T 1B	0.75 0.72	Tan color with generous dispersion of black particles.	City dump area, land fill.
9	Union City-Fremont	1T 1B	1.49 1.27	Dark-brown to tan color, compact matrix.	Farmland area nearby.
10	Newark	1T 1B	0.90 0.68	Brown to light-tan clay bottom.	Intertidal area with low vegetation, insects.
11	Newark	2T 2B	0.86 0.52	Brown and tan mottled consistency, many roots.	Near industries and matted land from dead vegetation.
12	Milpitas	1T 1B	0.94 0.86	Algae mixed with dark black-brown spongy soil.	Delta region.
13	Milpitas	2T 2B	0.94 0.72	Algae mixed with dark-brown and black spotted materials.	Delta region with much vegetation.
14	Milpitas	3T 3B	0.28 0.83	Brown, loose soil, sandy upper layer.	Delta terrain with numerous intertidal areas and pockets.

^aT = top fraction

^bB = bottom fraction

Sector Top to Bottom Ratios

The ratios of each sector's top mean values to the bottom mean values were surprisingly consistent for three of the sectors. Sector I had a top mean to bottom mean ratio of 1.61 and this compared very well with Sectors III and IV which were 1.71 and 1.66, respectively. Sector II showed a reversal with a bottom fraction mean higher than the top fraction mean (top/bottom ratio = 0.88).

DISCUSSION

Sediment examination appears to be a valid technique to explore trace element buildup from sources of environmental pollution. Monitoring the geochemistry of estuary sediments and investigating the tidal and current flow can lead to more accurate accounting of trace metal pollution than air and/or water measurements.

We designed this study to give analytically accurate shoreline measurements and to identify localized high cadmium concentrations. We chose to investigate bioexchangeable cadmium as being more meaningful as a contaminant of the environment rather than total cadmium, which neutron activation or X-ray fluorescence analysis would have uncovered. The analytical procedure used in this study enhanced our sensitivity over current acid extraction techniques and brought virtually all of our samples to within a $\pm 3\%$ error in absorbance.

It is difficult to compare our results to samples that have been published as "ppm ash" since there is a strong likelihood for cadmium loss by both evaporation of low boiling point cadmium compounds or by fusion into insoluble forms of silicates. Our samples are measured as $\mu\text{g/g}$ dry sediment to avoid doubt concerning loss of the metal.

The shoreline sediments of San Francisco Bay have cadmium concentrations which are similar to levels found in nonpolluted or marginally polluted areas of the world as presented in Table 1.

A "global mean value" for sediment abundance of cadmium can be estimated from Table 1 and is approximately 0.5 $\mu\text{g/g}$. The Gaussian peak of Fig. 8 is at the 0.6 to 0.79 $\mu\text{g/g}$ interval, indicating that bay sediment values are very close to background. Those samples above 2.0 $\mu\text{g/g}$ (the upper limit in this case for a uniform Gaussian distribution) represent possible areas of elevated environmental cadmium.

The top fraction range was 0.06 to 4.96 $\mu\text{g/g}$ while the bottom range was 0.93 to 3.91 $\mu\text{g/g}$. The range of values found in our study is comparable to the work of Perkins (1973), Mullin and Riley (1956), Lagerwerff and Specht (1970a), Klein (1972), Iskandar and Keeney, 1974 and

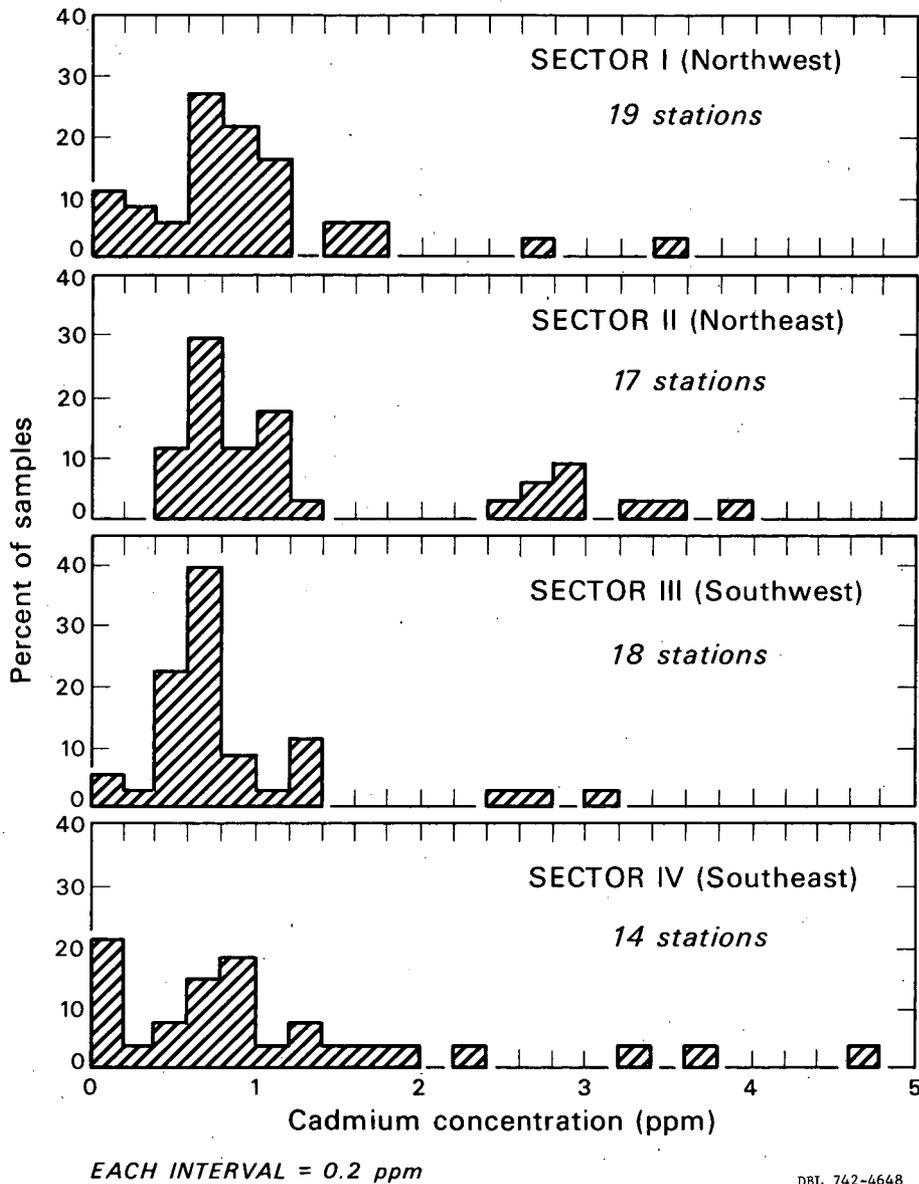


Fig. 10. The cadmium concentration distributions in each sector. Top and bottom fractions designation was ignored to give a further breakdown of Fig. 8.

John et al. (1972) which are studies of agricultural soils, lake sediments and several other soil types (generally non-industrial). The work of Butterworth, et al. (1972) at the Severn Estuary in Britian, a light industrial area, compares well with the levels we found in San Francisco Bay sediments. The effects of light industry and mining on the sediments of the Severn Estuary are apparently very close to those of the San Francisco Bay.

Figure 10 combines top and bottom fractions for each sector (a further elaboration of Fig. 8). Figures 11 and 12 are the distributions of top and bottom fractions, respectively, for each sector.

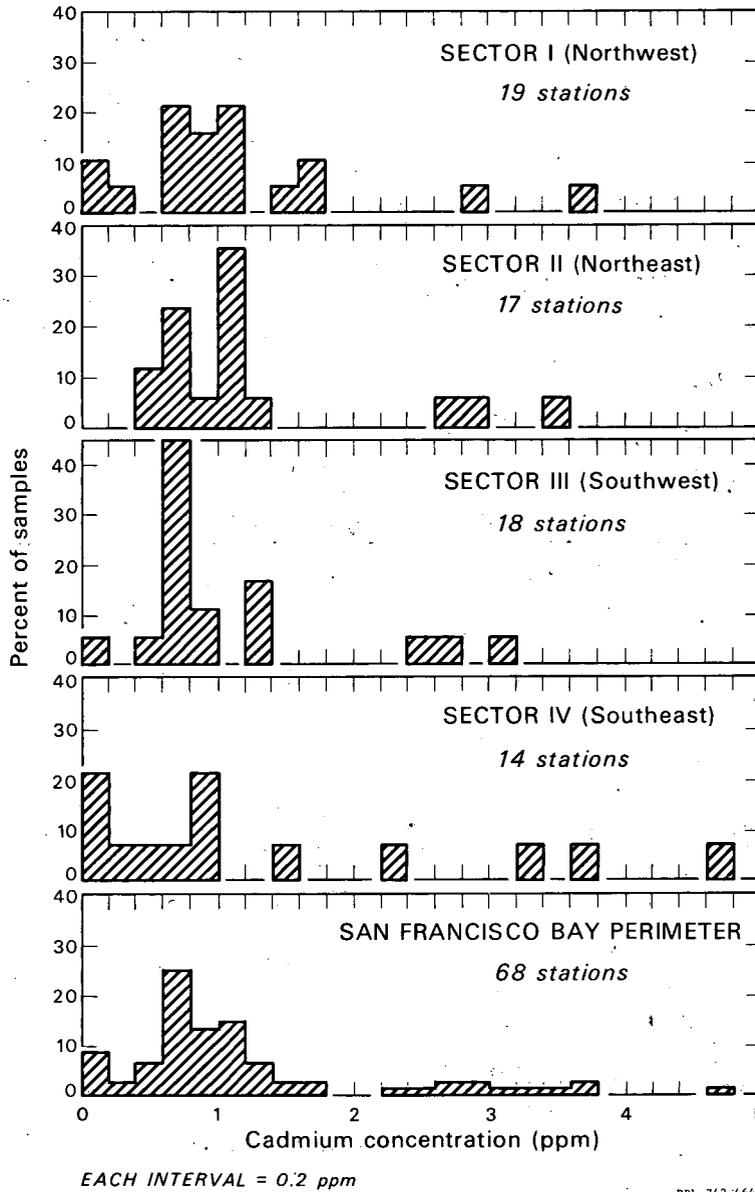


Fig. 11. Cadmium concentration distributions in each sector's top fraction. A combination of all top fractions (n = 68) is portrayed as the San Francisco Bay Perimeter sediments.

The diagrams of the regional distribution of cadmium in top and bottom fractions (Figs. 10, 11, 12) reveal that the major contribution to the variance is from the top fractions (Fig. 11).

Sector II, which includes the lead slag fuming plant at Selby, was the only sector to have bottom fraction cadmium levels above 2.0 ppm. Approximately 35% (6 of 17) of the bottom samples from this sector were above 2.0 ppm. These elevated bottom fractions were primarily found at Mare Island and Emeryville, and are probably due to past slag fuming operations at Selby, shipyard work at Mare Island, the petroleum refining plants between Martinez and Richmond, and the chemical industries, steel works, and sewage treatment facilities in the Emeryville area.

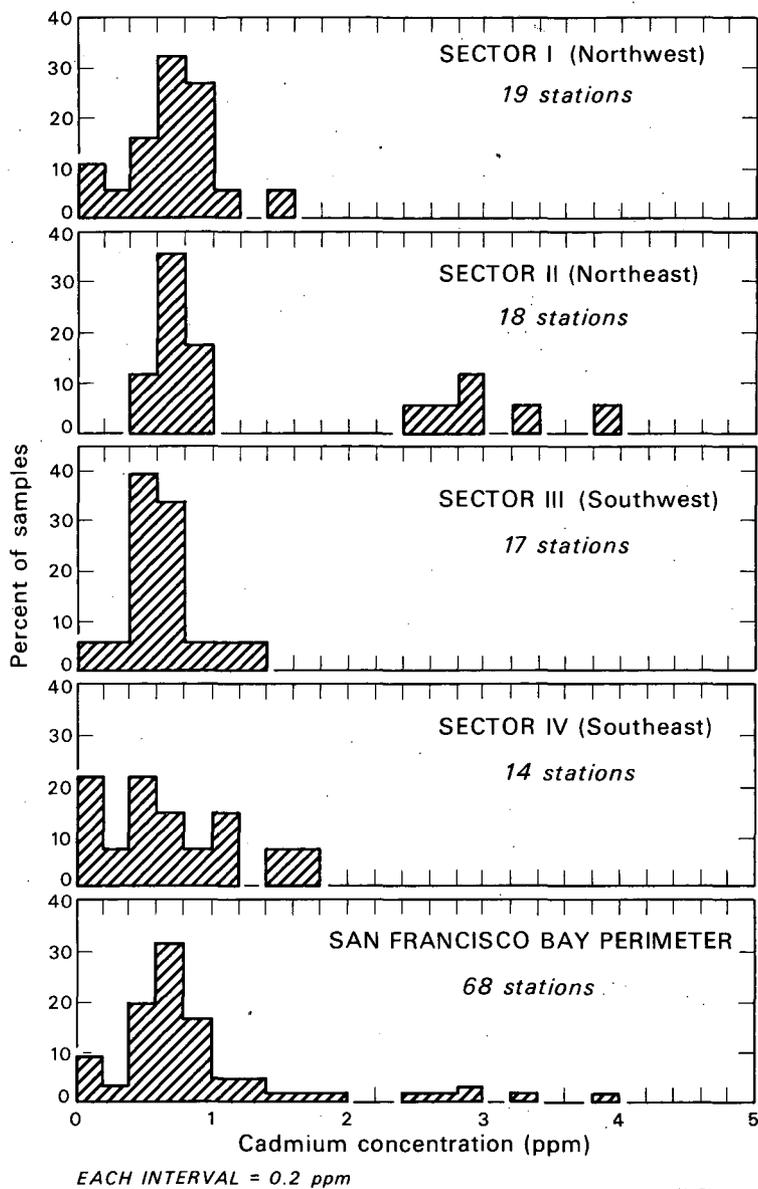


Fig. 12. Same as Fig. 11, but for bottom fractions (n = 68).

Nearly 40% of the California land mass drainage passes through the bay near the shoreline of Sector II. The shallow water environment of interaction of tidal currents and fresh-water runoff leads to semipermanent eddy areas and intertidal areas, and thus pockets of potentially high sediment accumulation adjacent to low accumulation areas. Also the ion-exchange capability of sediments is greatly reduced if the functional groups are washed away. The closing down of operations at the Selby plant may well have allowed much of the top fraction cadmium to be dissipated.

Cadmium is rapidly precipitated by sulfur. The presence of sulfur in sediments is an important factor in the metallic adsorptive and ion-exchange properties of sediments. It is conceivable that the Selby plant operations and the shipyard activities at Mare Island in Sector II have introduced limited cadmium into the water flow of the bay. Once in the bay waters it is precipitated by the air-borne sulfur (from the petroleum refining plants), which continually settles on the surface of the bay and is taken into solution. This hypothesis should be tested and correlated to wind direction, SO₂ dispersion and deposition patterns, current and tidal directions, and sediment accumulation of cadmium. In addition, the different chemical forms of cadmium found in the sediments should be identified.

Table 3 presents the data sample by sample, with soil and environmental characteristics to allow for pollution evaluations. These characteristics are valuable in assessing contributory factors that may explain elevated cadmium levels. From the table, for instance, sandy soils overall exhibit low cadmium levels. Sand possesses a low adsorptive capacity (John, 1972). This agrees well with our findings that low vegetation areas (generally sandy areas), beach areas, and land-fill areas (turned earth or other clean fill) had very low cadmium levels.

Samples taken near developments or industries or samples possessing a dark (black) color and gummy or oily composition and frequently a foul odor (indicating organic enrichment) tended to have elevated cadmium. Almost 75% of the samples above 2.0 ppm (Fig. 8) had these characteristics. Light tan to gray colorings, loose composition or the presence of shells did not correlate well with elevated cadmium. Clay soils in areas of moderate vegetation generally were between 0.5 and 1.5 ppm, and were a sizable majority of the bay samples.

SUMMARY

Bioexchangeable cadmium in the shoreline sediments of San Francisco Bay is currently at acceptable levels. Known endemic areas of the world have sediment cadmium levels 100 to 1000 times higher than the highest levels found in the bay. Those areas of elevated cadmium in the San Francisco Bay include Mare Island, Emeryville, San Leandro Bay, Hunters Point, South San Francisco, and Corte Madera. Levels above 2 µg/g are considered evidence of industrial contamination.

Samples from the eastern shoreline (Sectors II and IV) had the highest and most consistent elevation of both top and bottom fractions. Samples with elevated cadmium from the western shoreline (Sectors I and III) generally showed a marked increase in the top fraction alone. The Mare Island, Emeryville and San Leandro Bay samples were 2 to 5 times greater than the entire bay mean of 1.07 µg/g. Elevated cadmium samples from the west side of the bay were 2 to 3 times greater than the mean. The Mare Island and Emeryville samples had bottom fraction levels in excess of the top fraction. Cadmium enrichment in the top fraction alone was best seen in two of the Corte Madera sampling locations on the northwestern shoreline. These samples were

8.3 times higher in the top fraction relative to the bottom. This finding may be indicative of tidal or current dissemination of cadmium from the northeastern sector.

Numerous chemical-related industries, including slag fuming, shipbuilding, pharmaceuticals, steel, petroleum, etc., exist or have existed in the northeast bay region (Sector II). Many of these industries probably have introduced cadmium into the bay. However, it is the petroleum refineries of this area that may indirectly aid in the deposition of cadmium into the bay sediments. During the refinement of petroleum, gaseous sulfur dioxide escapes into the atmosphere, disperses over the bay and settles in the water, where it rapidly precipitates dissolved metals, especially free or ionic cadmium.

Monitoring of the bay hot spots (i. e., $>2.0\mu\text{g/g}$) can be carried out on a regular basis. The correlation between SO_2 wind dispersion patterns, current and tidal flow patterns, and areas of the bay which have sediments containing elevated cadmium has not been made. Accumulation of cadmium in bivalves and other aquatic life forms in the bay should be examined in areas of elevated cadmium.

ACKNOWLEDGEMENTS

This work was done under the auspices of the Atomic Energy Commission. The authors wish to thank Mr. Anthony Marzan for his assistance in collection and analysis. The technical assistance of Ms. Marcy Wales and Mr. John Flambard is gratefully acknowledged.

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