TRACE METALS IN SUISUN BAY, CALIFORNIA:
A PRELIMINARY REPORT

By S. N. Luoma, P. V. Cascos, and R. M. Dagovitz

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This report is preliminary and its findings
are not considered to be site specific.

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ABSTRACT

A preliminary study for the period February-July 1983 was completed in Suisun Bay, a shallow embayment of the San Francisco Bay system, California, to determine characteristic heavy metal concentrations present in sediments and organisms (Corbicula clams).

Preliminary results show that the sediments of the study area are typical of other San Francisco Bay study sites. Sediments range from coarse sands to fine silt-clays and are enriched in manganese, with concentrations ranging from 24 to 818 μg/g (micrograms per gram), and are low in total organic carbon, with values ranging from 0.014- to 1.62-percent carbon. Iron is moderately enriched with acid-extractable iron concentrations of 162 to 3,521 μg/g.

Concentrations of silver, zinc, lead, and cadmium measured in sediments between April and July are reported. Other San Francisco Bay studies have shown that pulses of increased concentrations occur during autumn and winter, a sampling period not covered in this data set. Lead concentrations range from 24 to 59 μg/g. Cadmium concentrations range from less than 0.05 to 0.63 μg/g. Acid-extractable copper concentrations range from 1.3 to 32.6 μg/g. Because of the paucity of data to date, interpretations separating physical and chemical influences on concentrations are not yet complete.

Clam-tissue burdens for silver and zinc are similar to those found in Corbicula from pristine areas. Silver concentrations range from 61 to 332 nanograms per gram, and zinc ranges from 110 to 349 μg/g. Copper concentrations range from 41 to 155 μg/g. Cadmium levels range from 0.3 to 5.6 μg/g in Corbicula tissues.

INTRODUCTION

The U.S. Bureau of Reclamation is seeking to obtain a permit from the California State Water Resources Control Board to dispose of agricultural tile drainage water from the San Luis Drain. One of the alternative discharge sites is in Suisun Bay (fig. 1). A possible extension of San Luis Drain would collect and move agricultural tile drainage return water from farm areas around Kettleman City in the south to the upper San Joaquin Valley farms in the north into Suisun Bay for disposal. The possible impacts of the tile drain-water plume would be greatest in the Suisun Bay area and would need to be assessed by the California State Water Resources Control Board prior to issuing a permit.

Benthic sediments and benthic organisms generally function as a repository for trace metals in estuaries. Metals sequestered by sediments and organisms can become available again in the water column unless metal-enriched sediments are removed from the estuary. Present trace-metal concentrations and fluctuations in the Suisun Bay benthic sediments, suspended sediments, and benthic organisms are unknown. In order to assess any future impacts on the bay from the disposal of agricultural drainage water, trace-element concentrations and fluctuations need to be characterized as they currently exist in the drain-water plume area. This preliminary study of Suisun Bay presents the current effort to understand trace-element controlling processes.

PURPOSE

This report, prepared in cooperation with the U.S. Bureau of Reclamation, provides a preliminary baseline of the concentrations of trace metals in sediments and benthic organisms (clams) in San Francisco Bay receiving waters (Suisun Bay). Trace-element concentrations need to be established in Suisun Bay where the drain-water plume would have the greatest impact.

Sediments are repositories of trace metals in estuaries. A study of concentrations and fluctuations of benthic sediments and the clams that feed or reside in and on sediments will help assess the impacts of the drain discharge on the food chain.

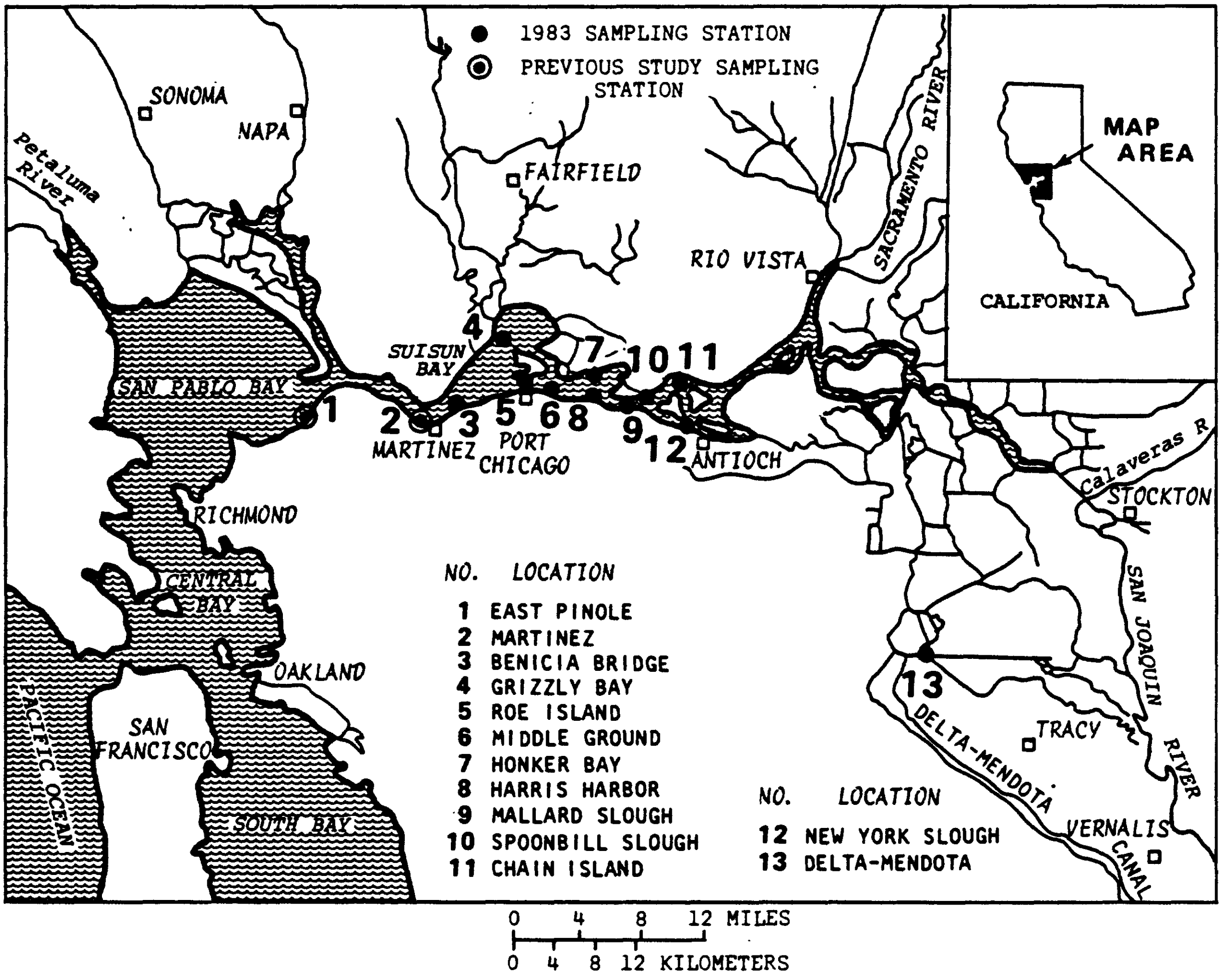

FIGURE 1. -- Location of sampling stations.

SCOPE

The scope of the study includes results of sampling from February to July 1983 in San Francisco Bay receiving waters. Ten sampling stations for sediments and organisms (clams) are located in Suisun Bay, where maximum impacts are expected (fig. 1). An eleventh station is located at the mouth of the Delta Mendota Canal on the San Joaquin River, upstream from the estuary.

Bed sediments were analyzed for total and acid-extractable metal concentrations of copper (Cu), iron (Fe), lead (Pb), manganese (Mn), silver (Ag), and zinc (Zn). *Corbicula* clam tissues, used as an indicator species for benthic organism tissue burdens, were analyzed for Ag, cadmium (Cd), Cu, Pb, and Zn at the sediment station sites.

Preliminary results were compared to prior work at two sites, Martinez and East Pinole (figs. 2 and 3). The annual cycles of metals in Suisun Bay, not addressed in this study because of the limited samples, will be discussed in the final report. The final report will include additional analyses.

A literature review is included in this preliminary report to inform readers of the processes affecting trace-metal distributions in sediments and bioavailability to organisms.

MATERIALS AND METHODS

Sediment Sampling

Sediment samples were collected from 10 stations in the receiving waters of San Francisco Bay and 1 station near the Delta Mendota Canal (table 1). The stations were chosen to give wide spatial coverage of the San Francisco Bay receiving waters (Suisun Bay) where drain irrigation return water could have impacts.

Samples of oxidized sediment were scraped from the surface layers of cored samples approximately 1 to 2 cm (centimeters) deep or taken with a modified rake. These samples, collected by U.S. Bureau of Reclamation personnel with occasional assistance by U.S. Geological Survey personnel, were picked up at the end of the sampling day by Survey personnel for laboratory processing.

Within 24 hours after they were picked up by Survey personnel, samples were processed for the New York Slough, Chain Island, and Delta Mendota Canal stations. Within 48 hours after collection, the remaining station samples were processed (table 1). Laboratory processing began with sieving the samples through 100-μm (micrometer) polyethylene mesh using distilled water to remove particle-size biases caused by large sand grains (DeGroot, 1971). Because particle sizes of sediments from Middle Ground and Roe Island were larger, tests from these stations were run on unsieved material of >100-μm size.

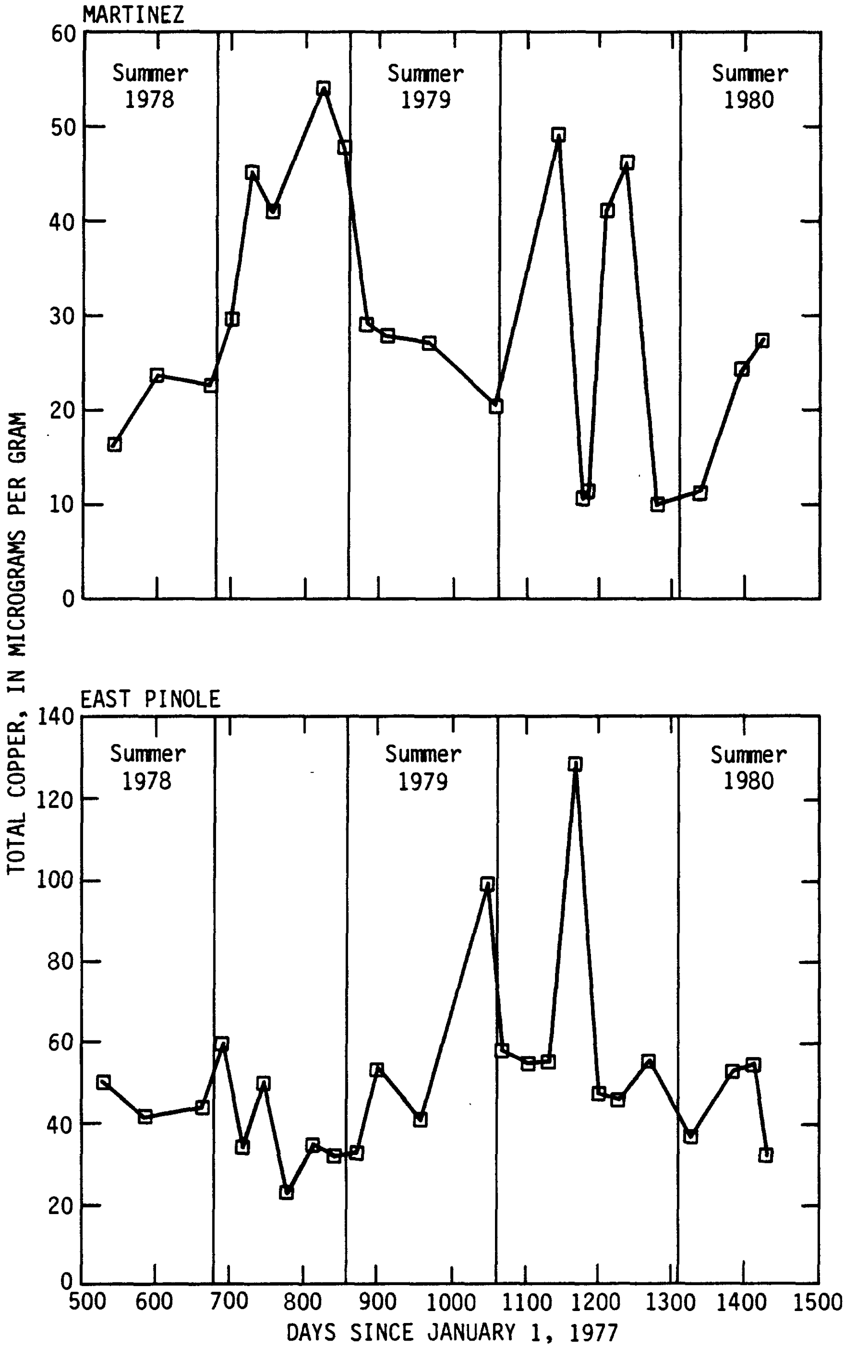

FIGURE 2.—Copper in sediments at Martinez and East Pinole, summer 1978 through summer 1980. (Summer for this study is defined to begin after the last winter day of rainfall and to end the day before the first winter rain. This definition is the cause for the variable length of time shown for each year's "summer").

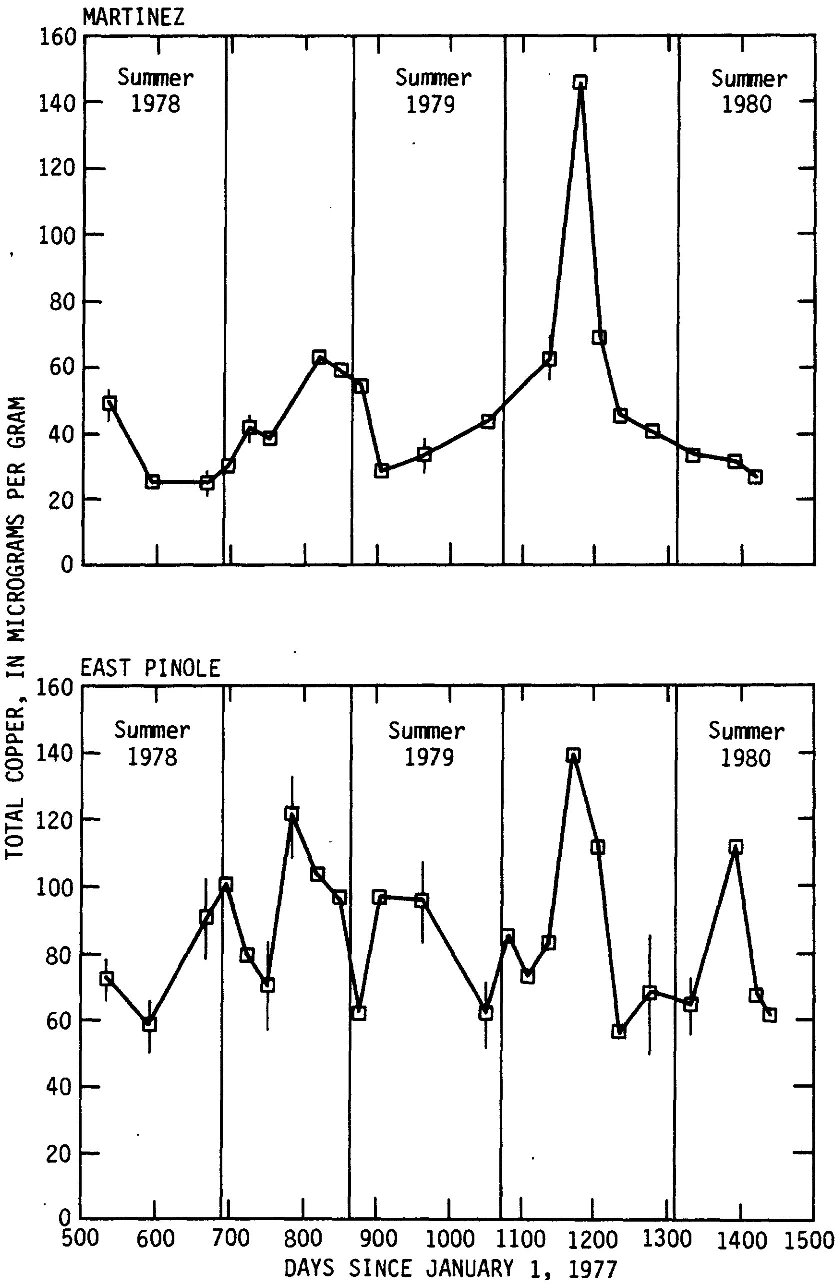

FIGURE 3.—Copper in clam tissues of Macoma balthica at Martinez and East Pinole, summer 1978 through summer 1980. (Summer for this study is defined to begin after the last winter day of rainfall and to end the last day before the first winter rain. This definition is the cause for the variable length of time shown for each year's "summer"). Data point is mean value for all samples. Vertical line through data point represents one standard deviation.

In the interest of developing sediment-characterization schemes for maximum use in correlation with biological variables (Luoma and Bryan, 1978), chemical treatments were kept as simple as possible. Subsamples of wet sediment were collected from a slurry using a pipette sampler while swirling. Each subsample of sediment was treated with a different extractant--that is, samples were not extracted sequentially. Duplicate subsamples were washed with distilled water, then dried at 80°C (degrees Celsius) to obtain salt-free dry weights. Dry weights sampled, ranging from 250 to 550 mg (milligrams), differed by no more than 10 mg between replicates. Extractions were carried out in 20-mL (milliliters) glass scintillation-counting vials, which were shaken at frequent intervals. The extractant was separated from the sediment by filtration under pressure through a 0.45-µm membrane filter. The filtrates were analyzed for Ag, Cd, Cu, Fe, Mn, Pb, and Zn by flame atomic absorption spectrophotometry (AAS). Ag was determined by graphite furnace AAS. Background correction was used in Ag, Cd, and Zn analyses. Because of low Cd concentrations in the sediments, extractions used higher sediment to extractant ratios (2 g (grams) sample to 10 mL extractant).

Sediment Metal Extractions

5-percent hydrochloric acid (HCl). Subsamples of 1-mL wet sediments were extracted for 2 hours with 20 mL of 5-percent HCl. Cd samples were extracted using a ratio of 2 g of dry sediment samples to 10 mL of extractant. Earlier experimental work showed that similar concentrations of metal were extracted from air-dried or wet sediments. As a strong acid, 5-percent HCl extracts metals by destroying carbonates and hydroxides of Fe and Mn and removes metals from organic ligands by exchange with hydrogen ions (Agemian and Chau, 1977).

0.1 N hydroxylamine hydrochloride in 0.01 N nitric acid at pH 2 (Chao, 1972). Subsamples of 1 mL were extracted for 30 minutes in 20 mL of extractant adjusted to a pH of 2. Hydroxylamine was extremely sensitive to the presence of any $CaCO_3$ in sediments (due to the poor buffering capacity of 0.01 N nitric acid). Neutralization dramatically affected extraction of at least Cu, Zn, and Fe. San Francisco Bay sediments were found to have low carbonate concentrations (Luoma and Bryan, 1978). Results for these samples are expected to be a good representation of metal concentrations.

Hydroxylamine may complex some metals; it reduces oxides of Mn (Chao, 1972), and it dissolves some amorphous Fe oxide (Luoma and Bryan, 1979). Hydroxylamine also desorbs metal weakly associated with organic ligands in single-phase experimental sediments (Luoma and Jenne, 1976).

1 N ammonium acetate at pH 7. Subsamples at 2 mL of wet sediments in 20 mL of extractant were extracted for 2 hours. The filtrate was preserved for analysis with 25-µL (microliter) concentrated HNO_3. Ammonium acetate desorbs cations from surface exchange sites, may weakly complex some metals, and may reduce some hydrous oxides.

TABLE 1.--Sediment data, 1983

[Total includes surface bound metals (absorbed) plus crystalline metals. HCl extraction includes surface bound metals (adsorbed), which are more chemically active. HA (hydroxylamine) extracts amorphous iron from the most active binding sites. Abbreviations: µg/g, micrograms per gram; µm, micrometers; mg/g, milligrams per gram; ng/g, nanograms per gram]

Sample site and date	Particle size (percent finer than 14 µm)	Organic carbon[1] (percent)	Extractable organics[2] (absorbance units, NaOH)	Silver, total (ng/g)		Lead, total (µg/g)		Copper, total (µg/g)		Copper, HCl (µg/g)	
				Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
New York Slough											
February	68.5	1.321	2.2	186	±13	45.6	±11.1	47.5	±0.9	22.5	±0
April	52.1	1.284	1.3	265	±55	58.8	±1.2	50.7	±5	13	±1
May	50.8	.892	2.1	136	--	48.2	±9.7	46.6	±11.4	18	±1
June	50.8	1.099	3.2	188	±2	50.7	±7.8	49.2	±1.8	20	±1
July	51.0	--	1.3	216	±7.8	36.0	±.6	44.2	±.8	17	±1
Chain Island											
February	27.4	.647	3.3	188	±20	24.2	±4.7	43.7	±.1	24	±2
April	52.3	--	2.7	28	±12.7	24.1	±1.6	31.9	±.6	15	±0
May	43.9	.940	6.3	124	±1	34.3	±1.1	62.0	±1.6	26	±3
June	39.9	.588	4.8	--	--	--	--	--	--	23	±2
July	39.4	.871	10.8	105	±89.1	36.1	±4.7	62.8	±6.7	30	±0
Mallard Slough											
February	71.7	.482	3.1	40	±11.3	26.3	±2.3	41.4	±7	7.3	±1.4
May	31.2	1.349	15.0	304	±42	59.3	±8.3	74.4	±11.4	27.4	±.8
June	43.8	1.165	11.8	128	±84.9	40.3	±5.2	55.8	±1.6	20.2	±1.5
July	40.3	1.254	16.9	197	±8.5	39.1	±.3	59.8	±1.0	25.4	±.9
Harris Harbor											
April	34.4	1.623	9.0	84	±10	35.2	±5.2	46.4	±1.3	16.7	±.7
May	21.5	.790	6.7	256	±46	37.7	±3.2	50.4	±5.7	19.3	±.8
June	35.3	1.165	13.6	51	±29.6	42.0	±10.5	37.1	±1.0	14.7	±.6
July	35.5	1.254	14.7	28	±18.4	37.2	±.6	49.6	±1.5	17.2	±.6
Delta Mendota											
May	29.0	--	5.8	155	±32	39.2	±2.1	41.5	±0	17.2	±0
June	43.9	.912	7.7	247	±10	39.1	±2.2	36.3	±.6	14.6	±1.8
July	--	1.111	9.1	162	±13.4	39.4	±8.8	39.1	±1.1	18.3	±0
Roe Island											
June	0	.014	.13	69.5	±2.1	16.5	±.2	9.6	±.1	1.3	±0
July	2.4	.015	.05	--	--	17.8	--	10.4		2.5	±0
Benicia Bridge											
May	40.5	.921	3.6	112	±16	36.4	±3.0	34.4	±1.8	12.5	±.7
Middle Ground											
June	1.5	.017	.21	104	±1	23.5	±1.7	12.5	±.4	1.7	±1.4
July	0	.017	.05	--	--	13.1	--	10.9		2.7	±.4
Grizzly Bay											
May	59.0	1.131	8.1	152	±18	47.3	±8.3	61.5	±3.5	32.6	±1.4
June	61.0	1.104	11.6	44.5	±2	32.0	±5.4	38.4	±1.8	19.2	±.5
July	70.4	1.263	17.7	389	--	30.9	±1.2	66.3		30.9	±1.6
Honker Bay											
May	43.8	1.033	11.3	140	±16	43.6	±7.2	49.2	±3.3	21.1	±2.8
June	44.0	.808	7.9	125	--	32.6	±6.4	47.2	±8.3	22.1	±1
July	42.0	.792	8.3	117	±50.9	30.9	±1.2	54.4	±.2	23.0	±0

[1] Percentage of carbon in sediments.

[2] Humic substances.

TABLE 1.--Sediment data, 1983--Continued

Sample site and date	Zinc, total (µg/g)		Zinc, HCl (µg/g)		Iron, total (mg/g)		Iron, HA (µg/g)		Manganese, HCl (µg/g)		Cadmium, HCl (µg/g)	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
New York Slough												
February	109.8	±2.6	45	±3	30.4	±1.4	1,363	±186	500	±21	0.25	±0
April	128.0	±1.0	13	±2	34.7	±.42	521	±18	--	--	.23	±0
May	110.2	±23.6	24	±2	31.5	±.68	1,050	±106	281	±19	.23	±.11
June	92.1	±3.3	31	±4	29.4	±1.2	1,294	±72	468	±51	.23	±.04
July	84.6	±1.5	22	±1	27.9	±1.2	--	--	283	±8	.10	±.07
Chain Island												
February	81.1	±.9	44	±4	23.2	±.11	1,487	±8	382	±34	.13	±.18
April	68.1	±8	20	±1	12.7	±.99	714	±51	171	±9	.55	±.11
May	110	±3.8	36	±5	29.1	±0	1,195	±195	344	±44	.63	±.04
June	--	--	36	±2	--	--	379	±10	463	±27	.20	±0
July	97.1	±12	44	±3	28.0	±4.2	--	--	418	±9	.20	±.04
Mallard Slough												
February	54.2	±3.0	11.1	±.2	21.6	±.44	2,835	±33	398	±4	.05	--
May	142.5	±40	56.7	±3.4	37.6	±4.8	3,509	±155	582	±7	.38	±.18
June	90.8	±1.9	32.6	±2.9	29.7	±.33	2,025	±.92	455	±22	.33	±.18
July	93.1	±2.1	48.6	±1.4	27.4	±4.2	--	--	441	±21	.20	±.14
Harris Harbor												
April	263.8	±109	41.9	±2.8	37.7	±1.8	3,343	±14	--	--	.35	±0
May	102.9	±13.7	37.5	±.3	27.6	±3.6	1,191	±224	318.6	±13	.35	±.07
June	66.7	±4.0	32.0	±0	25.3	±1.7	988	±25	368	±3	.08	±.11
July	89.5	±3.1	38.7	±6	28.2	±.70	--	--	448	±1	.20	±0
Delta Mendota												
May	83.2	±3.0	20.2	±.4	28.3	±.035	2,466	±117	818	±13	.05	±0
June	60.2	±0	20.8	±0	28.1	±.09	3,521	±29	652	±87	.08	±.04
July	69.2	±3.1	21.9	±0	26.6	±2.1	--	--	660	±15	.05	±0
Roe Island												
June	36.8	±4.5	29.9	±1.1	14.8	±2.04	162	±14	65.9	±9.5	.03	±.04
July	39.4	--	10.7	±1.8	17.9	--	41.9	±9.4	<.05	--	--	--
Benicia Bridge												
May	76.4	±3.4	23	±1	24.1	±.39	1,288	±25	317	±16	.25	±0
Middle Ground												
June	49.6	±4.1	14.1	±3.6	20.5	±1.3	162	±43	165	±45	.08	±.04
July	32.8	--	6.2	±.6	14.2	--	--	--	24.5	±2.3	<.05	--
Grizzly Bay												
May	99.3	±9.1	46.3	±1.7	29.9	±1.4	839	±34	723	±35	.38	±.11
June	58.6	±2.6	30.2	±.8	20.0	±.04	1,103	±98	448	±18	.13	±.04
July	101.0	--	43.6	±.5	32.0	--	--	--	549	±20	.23	±.04
Honker Bay												
May	91.4	±11.0	35.4	±3	26.2	±.3	696	±61	481	±62	.24	±.07
June	84.4	±10.3	38.4	±1.3	26.2	±2.1	434	±16	553	±23	.20	±.07
July	93.2	±.4	33.2	±0	28.0	±.02	--	--	481	±7	.25	±0

0.1 N sodium hydroxide. Subsamples of 2 mL wet sediment were extracted with 10 mL of extractant for 7 days. The concentrations of Fe, Cu, and humic substance extracted by NaOH increased rapidly with time, reaching a plateau at approximately 3 days with a slight increase in concentrations occurring between the 3d and 7th day.

HNO_3 and H_2SO_4 total digestion. Two mL of wet sediment was digested in 10 mL of extractant. The mixture was placed on a hot plate and evaporated to dryness. The dry sediment then was reconstituted to 20 mL with 25-percent HCl.

Extractable Organics (Humic Substances)

The NaOH extractant is a strong base that will form anionic hydroxide metal complexes, and will dissolve or disperse some types of organic materials (operationally defined as humic substances). It may complex metals directly, and will attack silica and clays.

One-week extractions with 0.1 N sodium hydroxide were chosen in order to optimize the extraction of the humic substance and of Cu, the metal most soluble in the basic extracts. All sediments were extracted wet, and the dilution factor was kept as near 5:1 as possible.

Concentrations of humic substances extracted by NaOH were measured by light absorbance (480 nm (nanometers)) in 1-cm cells containing the filtered extract.

Total Organic Carbon

Total organic carbon was determined on a carbon analyzer, as the difference between total carbon and inorganic carbon. Inorganic carbon was determined after conversion of carbonates to CO_2 by digestion in hot concentrated phosphoric acid, 85-percent pure.

Particle Size

Particle-size approximation for each site was measured by the settling rate of 20 mL of sieved sediment (100-µm mesh) in distilled H_2O (using Andreason pipette) for 15 minutes. Calculations from Stokes' law indicates that particles greater than 14 µm settle in 15 minutes. Particle-size analysis was performed without sieving when the sediment was uniformly greater than 100 µm, as found at two stations--Middle Ground and Roe Island.

Clam Sampling

The clam Corbicula was sampled simultaneously with the sediment samples (tables 2 and 3). The stations were chosen at sites where Corbicula were abundant enough to maintain a long-term sampling program. Drain water carrying heavy metals could have impacts upon organisms, especially benthic organisms. Corbicula was chosen as a biological indicator species for monitoring heavy-metal tissue burdens in the bay receiving waters.

Corbicula clams are surficial sediment feeders with the top of their shells buried a few millimeters below the sediment surface. Using an iron rake with a stainless steel basket modified to sample the upper 4 cm of sediment, clams were collected and were transported in plastic bags chilled on ice to the U.S. Geological Survey laboratory in Menlo Park, Calif. The specimens were placed in clean water of a similar salinity as the ambient water they were sampled from and left to depurate (starve) for 3 days. Depuration allows the elimination of food and sediments from the digestive tract which, if not removed, can erroneously elevate tissue-burden concentrations.

Size groupings were determined for individual sample sites and dates by measuring all the sampled clam shell lengths and dividing the clams into five to eight groups of similar shell length. This method of grouping or pooling clams of similar size assures that clams in the same state of growth, an important factor in estimating metal tissue burdens, are pooled together. Larger clams have higher tissue burdens per unit weight than small, younger, fast-growing clams. Fast growth in young clams tends to "dilute" trace-metal tissue burdens per unit weight.

TABLE 2.--1983 station sites and sampling dates for sediments and clams

[c, clams only sampled; s, sediment only sampled; x, sediment and clams sampled. Analytical data from the samples are tabulated in tables 1 and 3]

Station	1983				
	February	April	May	June	July
New York Slough---------	x	x	x	x	x
Chain Island------------	x	x	x	x	x
Mallard Slough----------	x		x	x	x
Harris Harbor-----------		x	x	x	x
Roe Island--------------			c	x	x
Benicia Bridge----------			s		
Middle Ground-----------			c	x	x
Grizzly Bay-------------			s	s	s
Honker Bay--------------			s	s	s
Spoonbill Slough--------			c		
Delta Mendota-----------			x	x	x

TABLE 3.--Corbicula clam data, 1983

[Sample size varies from one to seven subsamples of pooled clams]

Sample site and date	Copper (micrograms per gram)		Silver (nanograms per gram)		Zinc (micrograms per gram)		Cadmium (micrograms per gram)	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
New York Slough								
February	95	±68	123	±39	198	±81	---	---
April	110	±29	126	±44	183	±21	1.9	±0.6
May	108	±33	202	±38	180	±61	2.6	±.9
June	109	±45	116	±41	168	±14	2.3	±.7
July	94	±38	150	±100	300	±184	2.4	±1.1
Chain Island								
February	123	±58	217	±67	253	±96	4.2	±1.4
April	143	±16	169	±31	191	±24	2.6	±.5
May	103	±29	98	±23	160	±16	1.9	±.9
June	87	±24	61	±22	152	±32	2.5	±.6
July	101	±29	90	±38	---	---	3.4	±.9
Mallard Slough								
February	74	±16	136	±36	349	±183	2.7	±.2
May	89	±19	121	±54	177	±51	2.7	±.7
June	87	±16	90	±43	163	±19	2.3	±.5
July	77	±12	123	±41	153	±33	2.5	±.3
Harris Harbor								
April	77	±14	166	±40	258	±72	1.6	±.3
May	70	±17	95	±21	154	±15	1.7	±1.0
June	64	±14	79	±58	198	±73	1.3	±.5
July	67	±24	76	±35	137	±32	1.5	±.8
Delta Mendota								
June	41	±5	94	±14	110	±19	.3	±.1
July	42	±11	122	±64	122	±33	.3	±.1
Roe Island								
May	94	±42	127	±40	129	±17	3.2	±.8
June	100	±30	71	±9	171	±39	3.4	±.8
July	94	±44	115	±40	154	±19	2.5	±.8
Middle Ground								
May	65	±21	83	±35	136	±24	1.9	±.7
June	107	±66	218	±88	218	±88	4.3	±2.6
July	155	±74	233	±66	157	±40	5.6	±2.7
Spoonbill Slough								
May	97	±38	130	±56	146	±7	3.0	±1.1

The number of samples of clam data is the number of pooled clam-tissue groups. The number of animals pooled by size class varies by body size and the number of animals available in each size class taken on a specific sampling date. *Corbicula* metal concentrations are reported as means and standard deviations (table 3) and could be biased by size effects. A more extensive analysis of size effects will be included in the final report.

Metal Extractions

Pooled clam tissues were dissected, dried in an oven at 70°C, and subsequently weighed. Dried tissues were refluxed with HNO_3, evaporated, and then reconstituted with 25-percent HCl to dissolve the organic material. When material such as fats did not dissolve, the sample was filtered to remove the insoluble fraction. Dissolved samples then were measured for trace-metal concentrations using an atomic absorption (flame-mode) spectrophotometer.

RESULTS

Data Limitations

This preliminary report is limited by the partial completion of sampling and the presentation of partial data results. The most critical limitation of partial data sets is the omission of time-dependent relationships. High winter riverflows and low summer riverflows into the San Francisco Bay are the governing forces for metal inputs into the Suisun Bay receiving waters from riverine sources. The change from summer low-flow conditions to winter high-flow conditions is abrupt and affects trace metals in the estuary. Riverflow affects sediment-size characteristics, sediment-distribution patterns in the estuary, the relative location of the null current zone, and biological productivity in the water column. Metal-sediment interactions, physicochemical states of metals, and clam-tissue burdens change with the abrupt change in the inflow to Suisun Bay. The annual cycle of trace-metal concentrations in both sediments and clam tissues will be examined in the final report when data sampling is complete for one annual cycle.

As occurs in the initial phases of scientific study, most of the preliminary work involved coordination and establishing sampling and analytical procedures. Thus, the number of samples differs among stations and among parameters (tables 1 and 3). Most data were collected during spring and summer. Previous work suggests that large changes in metal inputs occur in late autumn and winter (S. N. Luoma and E. A. Thomson, U.S. Geological Survey, written commun., 1984).

Sediment Data

In general, the sediment data agree with earlier studies showing sediments enriched in Mn compared to other estuaries (Luoma and Bryan, 1981). Mean Mn concentrations ranged from 24 to 818 µg/g with most values lying between 300 to 600 µg/g (fig. 4). Sediments generally were low in organic carbon compared to many other estuaries (table 1). Mean total organic carbon ranged from 0.014- to 1.623-percent carbon in sediments. Fe is moderately enriched in bay sediments. Mean total Fe ranged from 13 to 32 mg/g (milligrams per gram). Mean amorphous Fe, extractable with hydroxylamine hydrochloride, had a range of values from 162 to 3,521 µg/g, ranging over an order of magnitude (table 1).

Some enrichment of Pb may occur at New York Slough relative to other stations. Mean concentrations of Pb range from 24 to 59 µg/g. Mean Cd values range from less than 0.05 to 0.63 µg/g (table 1 and fig. 4). However, previous experience indicates pulses of higher concentrations can occur in autumn and winter in North Bay (Martinez and East Pinole).

The influence of sediment characteristics on metal concentrations in sediments is shown in figure 5. Data from the current study and previous studies show a strong relation between total Cu in sediment and total organic carbon. Positive deviations from the apparent relation are indicative of metal enrichment (anthropogenic metal input). The Cu data collected thus far in this study fit on the general correlation observed for East Pinole and Martinez stations, suggesting general similarity of Cu input throughout the area (fig. 5). There is some indication of a few periods of higher concentrations at some stations (most consistently at Chain Island), relative to the other stations. Interestingly, slight Cu enrichment (table 3) is found in Corbicula at Chain Island; however, additional data are needed to confirm this result. In general, sediment Cu levels appear typical for the area. As more data are accumulated, such "within system" comparisons will be possible with other metals.

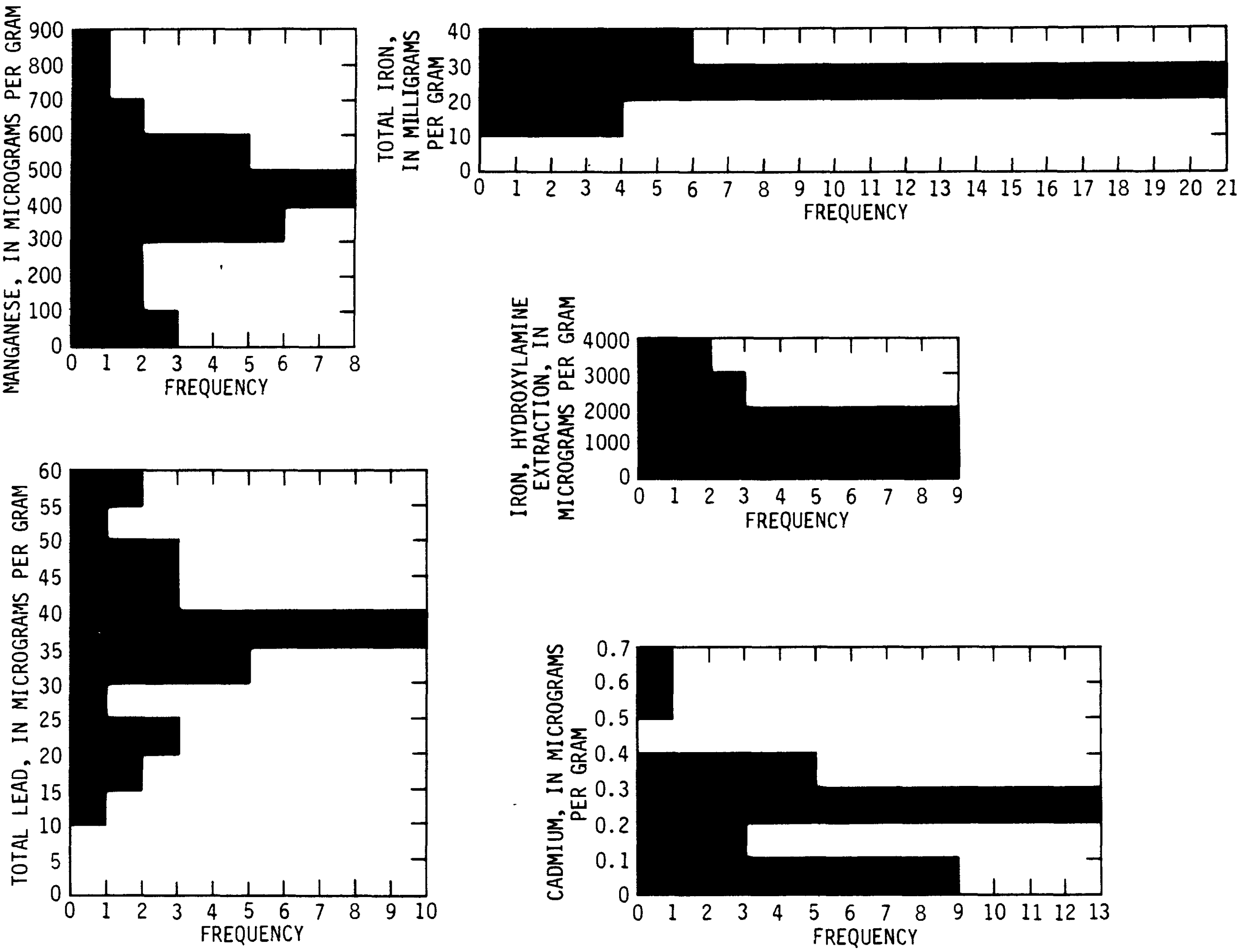

FIGURE 4.—Frequency distributions of mean trace-metal concentrations in sediments.

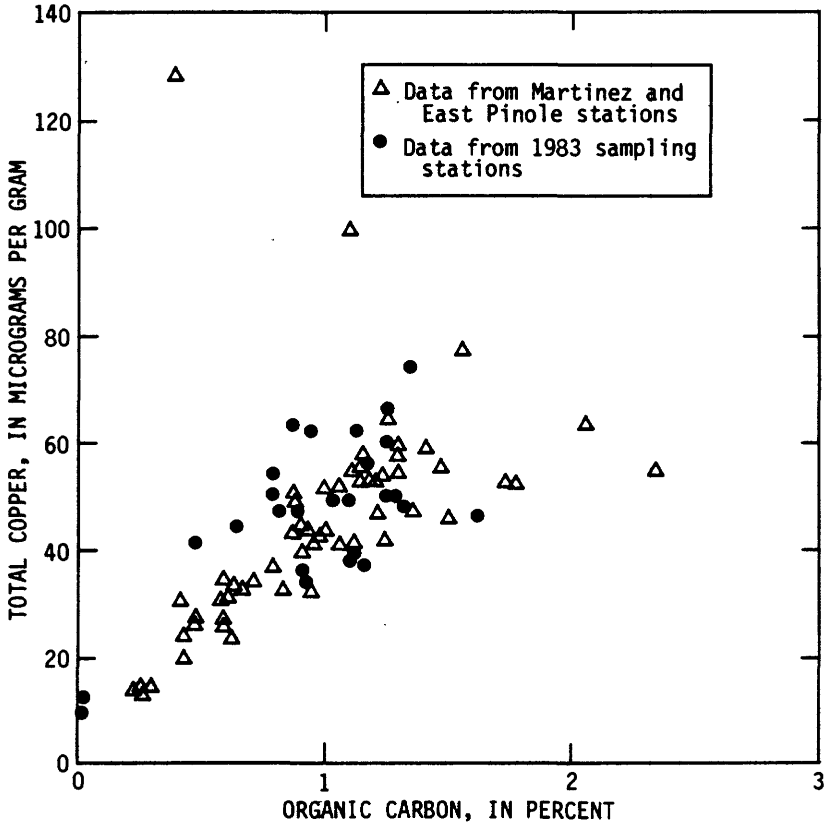

FIGURE 5.—Correlation of copper and total organic carbon.

Clam-Tissue Burdens

The metals analyses of clam-tissue burdens for Cu, Ag, Zn, and Cd for the 3 to 5 months of samples are shown in table 3. In *Corbicula*, most concentrations of Ag and Zn appear to be near levels found in ecologically similar freshwater organisms (and the few *Corbicula* data found) in pristine areas. Mean Ag concentrations range from 61 to 233 ng/g. Mean Zn concentrations range from 110 to 349 μg/g (fig. 6).

The mean Cu concentrations in tissues range from 41 to 155 μg/g (fig. 6 and table 1), and concentrations at the Chain Island and Middle Ground stations are definitely higher than concentrations at the Delta Mendota station. Cu concentrations in *Corbicula*, a surficial sediment feeder, are, in general, 5 to 10 times higher than in filter-feeding freshwater bivalves from pristine systems. The relatively high levels of Cu in clam tissues at Roe Island and Middle Ground stations, where Cu is very low in sediments because of the very sandy nature of the sediment, also are very interesting.

Concentrations of Cd in *Corbicula* also are elevated at all stations compared to the Delta Mendota station. Both Cd and Cu vary with size in *Corbicula*. A much more definitive interpretation of the data will be possible when the size factor is incorporated into the analysis in the final report.

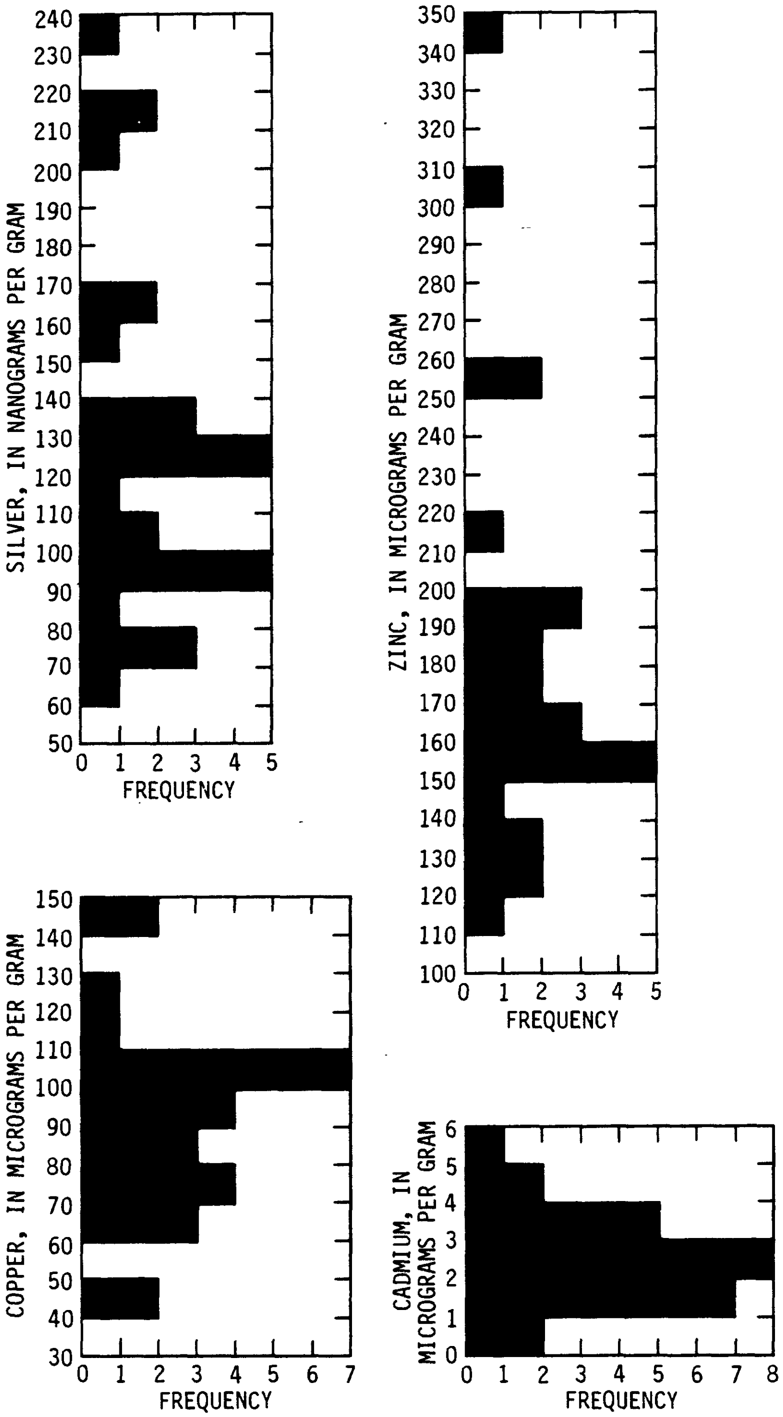

FIGURE 6.—Frequency distributions of mean trace-metal concentrations in Corbicula clam tissues.

DISCUSSION

Monitoring Trace-Metal Concentrations

Both sediments and organisms have been used to monitor or identify trends in trace-metal contamination and sources of contamination in aquatic environments. Both methods are very useful, but both also have limitations. Sediments integrate metal discharges through time and are the most concentrated physical reservoir of metals in aquatic systems. However, in attempting to identify sources of contamination of sediment, consideration must be given to physicochemical characteristics that may control trace-metal concentrations. As discussed in the literature review, these characteristics include grain size, iron concentration, and concentrations of organic carbon, all of which may be interrelated (Bradford and Luoma, 1980). Furthermore, total metal concentrations in sediments do not necessarily reflect concentrations that are available to biota.

Organisms have been used in comparative monitoring of pollutants in different systems (Bryan, 1979; Goldberg and others, 1978), and to locate sources of contaminants (Young and Jan, 1979; Widdows and others, 1981; Popham and others, 1980; Jensen and others, 1981).

This sentinel organism approach involves analysis of contaminant concentrations in individuals of a single species of organism comparing a number of environments or sampling through time. Organisms occurring naturally or organisms transplanted from another environment may be employed in a monitoring scheme, but all comparisons must be made of individuals of the same species. Organisms integrate short-term temporal fluctuations in contaminant concentrations and can be indicators of longer term trends; they concentrate contaminants to levels that provide much less analytical difficulty than do, for example, solute concentrations; and they help resolve unknowns in contaminant behavior. For example, the interactions which control contaminant bioavailability, and thus effects on biota, are poorly known. However, by definition, organisms respond only to biologically available contaminants rather than to total contaminant loads.

The sentinel organism approach also has limitations. Size or age of the animal is important, as are a number of ecological characteristics. Some organisms are better sentinels for specific contaminants or specific purposes than are others, so the objectives of the program must play a role in choosing a sentinel. Contaminant bioaccumulation also may be affected by environmental processes other than the level of contaminant exposure (temperature, salinity, competing cations, and geochemical factors affecting bioavailability). Bioaccumulation may differ among genetic subgroups of a species, although the importance of this factor is not well understood. Concentrations of a chemical in a sentinel organism are not simply related to effects either on that organism or on other species. Finally, the sentinel organism approach does not resolve the analytical problem that hundreds of chemicals are potential problems in modern society. All these limitations are relatively well understood, however, and reasonable programs can be designed around them. Sentinel organisms have been widely and successfully used in detecting point sources of anthropogenic contaminant input and in assessing overall water quality (the latter with less success than the former). Volumes have been written describing the successes and failures of these programs (Phillips and Gregory, 1979). Widely successful monitoring programs have been established in many areas of the world using the common mussel, *Mytilus edulis*, or its close relatives to monitor chemical contamination in marine and estuarine environments (Goldberg and others, 1978, described initial results from a nationwide "Mussel Watch" program). Metal uptake by organisms remains the only method available for estimating biologically available metal concentrations in natural systems. "In situ" monitoring of organisms is the only method that takes into account all changes in the receiving water quality that may have effects upon biological communities.

This preliminary study of trace metals in the vicinity of a possible San Luis Drain outfall includes both sediments and a benthic, filter-feeding clam *Corbicula fluminea*. The sediment samples consider fine-grained oxidized materials at the sediment-water interface, and the analyses include assessment of physicochemical sediment characteristics (so as to facilitate estimates of present anthropogenic input and bioavailability). Interpretations of both sediment and animal data will provide a model for data collection and data interpretation if the drain is built.

Samples also are being collected intensively in time. The physicochemical characteristics of north San Francisco Bay change dramatically with time--both within and among years. Previous studies indicate these changes strongly affect metal concentrations in sediment and biota. Concentrations of metals in sediment in Carquinez Strait (Martinez) and San Pablo Bay (East Pinole) vary as much as sixfold within a year (fig. 2), as do characteristics of sediments, which influence metal concentrations and metal availability to biota (table 4). Obviously, interpretations of metal-enrichment effects from the drain could not be accomplished with any sensitivity from samples lacking a temporal perspective. Most fluctuations of metal concentrations appear to be related to changes in the hydrologic regime (S. N. Luoma and E. A. Thomson, U.S. Geological Survey, written commun., 1984).

TABLE 4.--Strong metal sorption factors

[Derived from data supplied in Callahan and others, 1979]

Metals	Clays and inorganics	Iron, oxide or hydrous	Nonoxide	Metal oxides	Organics
Arsenic---	x	x			x
Cadmium---	x	x	x		x strongly[1]
Chromium[2]-	x				x
Copper----	x	x	x		x strongly[1]
Lead------	x	x	x		x
Mercury---					x
Selenium--	x weakly			x	x weakly
Silver----	x	x	x		x
Zinc------	x			x	x

[1] Strongly sorbed in polluted sites.
[2] Chromium is weakly sorbed for all factors checked.

Temporal Perspectives

Interpretations of metal-enrichment effects from the drain could not be accomplished with any sensitivity from samples lacking a temporal perspective. Most fluctuations of metal concentrations appear to be driven by changes in the hydrologic regime, as indicated by previous work (S. N. Luoma and E. A. Thomson, U.S. Geological Survey, written commun., 1984). An 18-month complete study of the station sites, combined with the available information from previous studies, could provide an adequate data set to approximate the metal concentrations at any station at most times of year under given hydrologic conditions--especially when riverflows differ between years. Examination of a longer period of record could be made to estimate annual variability in trace-metal concentrations because previous experience indicates pulses of high concentrations can occur in autumn and winter in the area.

Metal concentrations in bivalve molluscs (that is, clam *Macoma balthica*) fluctuate temporally (fig. 3). Establishing the pattern of such fluctuation in *Corbicula*, which occurs under present conditions, is essential to anticipating or detecting effects of metal discharges from the drain on such biota.

Metal Enrichments

Extreme trace-metal enrichments of sediments or clam tissues have not been identified during the sampling period. Cu concentrations in clam tissues may be high at Chain Island relative to other sites, but further results are necessary to corroborate the preliminary results. Cu and Cd in Corbicula tissues both appear to be higher at all stations relative to the Delta Mendota station.

With the planned data collection through late 1984, it might be possible to approximate the degree of sediment enrichment of metals such as Ag, Cd, Cu, Pb, and perhaps mercury (Hg) near the drain. Speculation also will be possible about the potential for biological problems with specific metals, based upon experiences elsewhere in the bay and in other estuaries.

LITERATURE REVIEW

Introduction

Estuaries act as sediment traps (McLusky, 1981). The interaction of currents, winds, and tides control sediment-distribution patterns over space and time (Postma, 1967; McLusky, 1981). Sediment-distribution patterns are an important feature because most metals inputs into estuaries are removed from the water column by processes which incorporate metals into sediments. When dissolved metals are complexed or adsorbed onto suspended or bed sediments, they become less available to organisms. However, the metals in sediments become a repository within the estuary for potential future release into the water column and may be readily available to benthic organisms that filter, ingest, or burrow in sediments.

Sediment Removal of Metals

A number of processes can affect the efficiency of metal removal from solution to sediments in estuaries. pH, ionic strength, Eh, the concentration, size, and characteristics of suspended material, dissolved-oxygen concentrations, and residence time can differ greatly through space and time within an estuary, and all factors may have effects.

Sediment-Metal Binding Capacities

The physical and chemical characteristics of suspended and sedimentary particles also are important. The binding of a metal, M, to any component, j, of a particle may be defined as

$$[MS_j] \rightleftarrows [M_f]\ [S_j], \tag{1}$$

where MS_j is bound metal, M_f is unbound metal, and S_j is binding sites not occupied by the metal.

The binding constant in the reaction may be defined by analogy with an equilibrium constant (Luoma and Davis, 1983) as

$$K_j = [MS_j]/[M_f]\ [S_j]. \tag{2}$$

The concentration of metal bound to the component is thus

$$[MS_j] = K_j\ [M_f]\ [S_j]. \tag{3}$$

The number of sites may be defined per unit weight of sediment, $W_{sed.}$ as:

$$S_j/W_{sed.} = [S_j/W_j]\ [W_j/W_{sed.}], \tag{4}$$

where W_j is the weight of the component. Thus, changes in the overall binding constant of the particle, changes in concentrations of unbound metal (an enriched metal input to the system), changes in the number of sites available for metal binding per unit mass of sediment (increases in concentrations of fine particles or of a sediment component such as organic carbon or iron oxide), or changes in the number of available binding sites per unit mass of a component (a decline in binding site density as iron oxides crystallize) all may change the ability of a particle to sequester metals in an estuary.

Binding constants for trace metals may differ by orders of magnitude among components of estuarine particles such as Fe oxides, Mn oxides, or organic materials (Luoma and Jenne, 1977). The overall binding constant of a particle is a function of the mix of components. The relative abundance of particle components also may differ greatly among estuaries and within an estuary through time. For example, estuarine suspended material may be composed of as little as 3-percent or as much as 30-percent phytoplankton in the turbidity maximum of San Francisco Bay (Peterson and others, 1975). In southwest England, organic materials have the largest potential metal-binding capacities in the surficial sediments of some estuaries; Fe oxides dominate others, and Fe oxides, Mn oxides, and organic materials have similar potential in still others (Luoma and Davis, 1983). The term S_j in equation 3 also may be quite variable. Characteristically, some estuarine sediments have few binding sites (sandy sediments), and others are much richer in sites which might bind metals. The overall abundance of sites is often determined simply by physical differences among sediments in grain-size distributions, which is often a function of hydrologic processes. Thus, as conditions change in time, the efficiency of the estuary in "filtering" metals could change. Any study regarding metal concentrations in sediments must consider these "internal" processes which affect metal concentrations, if interpretations concerning external processes (anthropogenic input) are to be realistic (table 4).

Bioavailability

Assessments of the impacts of metals sequestered in sediments upon biota are relevant only if they consider the types of sediments to which biota are exposed. The major flow of energy from primary production to consumer organisms in most estuaries is through the detrital food web (through deposit-feeding and suspension-feeding organisms (Odum and De La Cruz, 1967; Odum, 1980)). These animals directly ingest metal-enriched particles and may transfer any available metal from such particles to higher trophic levels.

Detritus

Although exceptions occur, detritus feeders are most commonly exposed to oxidized sedimentary particles. Suspended particles are oxidized in all but the most eutrophic estuaries. In the sediment bed, an oxidized layer of sediment usually separates anoxic subsurface sediments from the water column. This oxidized interface, operationally definable as a brown layer of sediment with a positive redox potential, is the most important zone of contact between the detritus-based food web and metals bound to the bed sediments (Johnson, 1974). Many deposit feeders, which reside deep in the sediment, use their siphons to ingest particles from the sediment surface. Others have tubes or burrows which cycle oxidized water and particles from the surface. Meiofauna, small benthic invertebrates, live almost exclusively above the redox interface (Coull, 1979). Epifauna are exposed directly to interfacial conditions, and many benthic predators obtain their prey from at, or near, the sediment-water interface, simultaneously ingesting oxidized surface particles.

Some detritus feeders (neredid polychaetes, Goerke, 1981) may selectively choose only specific organic particles when feeding. However, most feed "nonselectively," mechanically separating particles on the basis of particle size or, perhaps, specific gravity (Newell, 1965; Bubnova, 1974; Whitlatch, 1974; Self and Jumars, 1978). Since the objective of such sorting often is to maximize ingestion of adsorbed bacteria and surface organic coatings, the smaller available particles are most commonly preferentially ingested (Tahgon and others, 1978). Differences are found among species in preferred mean particle size, but maximizing energy intake by maximizing ingestion of particle surface area is the relatively generalized strategy of detritus feeding.

One reason that chemical selection of particles is rare among detritus feeders is that few fine particles in estuaries are found as single, discrete minerals. Nearly all silt-clay particles in bed sediments, for example, are organic-mineral aggregates (Johnson, 1974). The end result is that most detritus feeders are exposed to all the organic and inorganic components that may bind metals in sediments. Thus, the chemical processes controlling metal partitioning in sediments play an important role in controlling biological exposures to metals.

From these generalizations it may be concluded, that, with some exceptions, the metal-particle reactions biologically most important in estuaries are those that affect metal distributions among the organic and inorganic components of fine-grained, oxidized sediments.

Oxidation States

The trace-metal chemistry of oxidized sediments such as those at the sediment surface is more complex than that of anoxic sediments. Sulfides dominate the processes controlling metal form in reducing sediments (Morel and others, 1975). However, in oxidized sediments, organic materials, carbonates, and hydrous oxides of both Fe and Mn, all may compete for the binding of trace metals. (For the purposes of this discussion, we will assume the term binding encompasses adsorption, complexation, coprecipitation, and ion exchange.) Clays and other silicate mineral surfaces also have some capacity for binding metals. However, the strength of metal association with clay surfaces is weak relative to metal association with substrates that would compete for binding in oxidized sediments. Thus, the most likely role of the clays in such sediments is that of a carrier for the substrates that bind metals more strongly (Jenne, 1977).

The binding substrates themselves occur in a variety of forms; the forms of the substrates in any given sediment greatly influence the strength of metal-substrate binding processess. In estuarine sediments, major classes of organic materials include humic substances, bacteria, bacterial metabolites, and refractory, nonviable organic material (cellulose and lignins). Oxides of Fe exist in layers on particle surfaces or as particles of mineralogic Fe. The crystallinity of the Fe oxides varies over a continuum from highly amorphous to highly crystalline. Mn may occur as Mn oxides of varying structure or Mn carbonate. In turn, both Fe and Mn also may be found associated with each other or with other binding sites.

Mathematical Models

Mathematical models may be the most realistic approach to predicting metal partitioning in sediments of varying character (analogous to models of metal speciation in solution). Partitioning models would require constants describing the strength of metal-substrate binding and values for the relative abundances of the different forms of the different substrates present in natural sediments. Extraction of sediments with established geochemical techniques may provide information useful in such modeling efforts. Extractions could be used to describe the abundances of operationally defined forms of substrates in different sediments. Statistical relations between trace-metal concentration and the different substrate forms defined by the extractants also may indicate which substrate forms to employ in models (or the developement of constants for the models). Most recent studies employing chemical extractions have attempted to directly define metal partitioning, often implying a degree of specificity for extracting metals from single substrates which probably cannot be obtained with most procedures. Studies with chemically well-defined sediments suggest that extractants which selectively remove metals from a single substrate (much less from a given form of a substrate) are the exception rather than the rule (Luoma and Jenne, 1976; Guy and others, 1978). The useful information provided by the direct extraction of trace metals may be limited to determining a general, operationally defined "extractable phase" of the metals, to providing information about the biological availability of bound metals (Luoma and Bryan, 1978; 1979), and to assessing concentrations of components important in metal partitioning.

Metal Bioavailability

Whether sediments are a permanent repository for bound metals or are a reservoir for metal cycling in the biosphere will be determined by the bioavailability of the sediment-bound metals. Detritus-feeding organisms are exposed directly to sediment-bound metals and are useful for studying metal availability from sediments.

Many trace metals are required by organisms (as enzyme cofactors) (Welch, 1980; Dugdale, 1967). However, there is a window of metal requirement and tolerance for organisms. Metal concentrations beyond a tolerance produce toxic effects which can be lethal. Some species concentrate metals in their tissues which are passed on to their predators (Callahan and others, 1979; McLusky, 1981). Sublethal concentrations of a pollutant can affect growth, reproduction, feeding, respiration, and disease resistance in a species (McLusky, 1981). Such stressful conditions reduce the complexity of an ecosystem by selecting for smaller, more adaptable species. Where sublethal, long-term contamination by trace metals exists, selection may occur for more metal-tolerant species and races of those species. The presence of a toxicant-resistant population indicates long-term, high-toxic loadings (Luoma, 1977).

Metal Uptake from Particles

Organism-tissue burdens are not necessarily linearly related to metal concentrations in the environment. The biological availability of metals to organisms is determined by several factors. The specific physicochemical forms of trace elements in both water and sediments are of major importance. Physicochemical forms refer to adsorbed, organic, reducible, or residual geochemical phases (Hart, 1982). Although benthic organisms assimilate metals much more slowly from sediments than from solute water column forms, the much higher metal concentrations in the sediments make sediment-bound forms important in determining bioavailability (Luoma, 1977; Luoma and Bryan, 1978).

Within sediments the specific components to which a metal is bound can be very important in determining the bioavailability of the metal. In studies with deposit-feeding clams, Luoma and Jenne (1976; 1977) separated uptake from solution and direct uptake from sediment of ^{100}Ag, ^{109}Cd, ^{60}Co, and ^{65}Zn by enclosing some of the experimental animals in dialysis bags. Nuclide concentrations in enclosed animals were subtracted from those in feeding animals to obtain an estimate of uptake from ingestion alone. The contribution of undigested sediment was estimated from uptake kinetics, and the animals were fed individual, well-defined components of sediment for 13 days. Metals bound to Fe oxides, Mn oxides, organic materials, and carbonates were considered in different experiments. Although uptake from solution occurred more rapidly than uptake from sediment, significant bioaccumulation was observed from ingestion alone. Furthermore, uptake from ingestion alone differed among sediment types by as much as 1,000-fold. Differences in availability among sediment types differed among metals. Because experiments with all metals were conducted simultaneously, a common biological control (feeding rate) could not explain the differences. The biological availability of the metals was obviously influenced by binding to different substrates. The differences among sediments in uptake from ingestion correlated significantly with equilibrium sediment-water distribution coefficients for Ag, cobalt (Co), and Zn. This suggested the strength of metal binding to different substrates controlled the availability of metals to organisms ingesting those sedimentary components.

Laboratory experiments show that some direct uptake of metals from sedimentary particles to organisms is possible, and that factors other than concentration (the distribution of metals among substrates) may affect metal uptake from particles. Field studies are necesssary to determine the relative importance of particles as a direct vector of metal uptake, however.

Sediment Source Metal Exposure

If exposures to sediment control metal bioaccumulation by benthos, then metal concentrations in organisms in nature might correlate with concentrations in sediments. Strong correlations most commonly are not observed, however. Poor correlations between marine or estuarine benthic organisms and their sedimentary habitat have been reported by Cross and others (1970), Halcrow and others (1973), Valiela and others (1974), Huggett and others (1975), Luoma (1977b), and Schell and Nevessi (1977). The poor correlations between metal concentrations in benthic organisms and sediments could mean that metals in benthos are not derived from sediments or from sources coupled to sediments. However, they also could result from statistical problems in the comparison or from an influence of variables other than metal concentrations in sediment upon metal bioavailability.

For example, many correlation studies have included only narrow concentration gradients in the comparisons. Comparisons that have considered wider data ranges have shown some significant correlations between metal concentrations in deposit feeders and concentrations in sediment. Bryan (1974) found that concentrations of Cu, Pb, and Cd in the polychaete *Nereis diversicolor* correlated strongly with concentrations in sediments from the sediment-water interface when data were collected from several estuaries. Packer and others (1980) found that Cd and Zn concentrations in the polychaete *Arenicola marina* followed Cd and Zn in sediments from 24 stations on the coast of Wales. Significant correlations were not observed for Pb, Cu, and Mn, however. In an extensive survey, Luoma and Bryan (1978; 1979; 1981) compared concentrations of Ag, Cd, Co, Cu, Pb, and Zn in two deposit feeders, the burrowing clam *Scrobicularia plana* and the polychaete *Nereis diversicolor*, to concentrations in sediments over a wide range of conditions among 50 stations in 17 estuaries. The data range for all metals was two to three orders of magnitude. Statistically significant (but weak) correlations between total metals in sediments and the tissues of *Scrobicularia plana* were observed for Pb and for all other metals except Cu. Stronger correlations were observed between sediments and *Nereis diversicolor* for Cu and Pb. However, over the broader data set, these correlations were not as strong as those observed by Bryan (1974). In general, the data suggested that total concentrations in sediment contributed to metal concentrations in the deposit feeders, but that an understanding of other contributing variables would be necessary to predict metal concentrations in organisms from concentration in the environment.

Nonsediment Source Metal Exposure

Sediments need not be the only sources of metal exposure for benthic organisms. Deviations in correlations between organisms and sediments could result from uptake from solution. However, even where the source of exposure that controls both the food and solute vectors is well defined, deviations of bioaccumulation from dependence upon exposure alone are evident. For example, Bryan and Hummerstone (1977) observed differences in Ag and Cu concentrations in *Scrobicularia plana* from two estuaries that could not be explained by Ag and Cu either in water or in sediment. In San Francisco Bay, spatial variations in Cu concentration indicated a sewage outfall was the primary source of the metal for the burrowing clam *Macoma balthica*. Cu concentrations in the clams were consistently highest near the outfall and declined in both directions away from the outfalls (Thomson and others, 1983). Sediment analyses also showed Cu enrichment of particles, per unit surface area, near the outfall. Temporal trends in Cu concentrations in surface sediments near the plant outfall followed temporal trends in Cu discharge determined from analyses of plant effluent. This indicated that Cu concentrations in surface sediments were an accurate indicator of Cu discharge from the plant. Comparisons of 5 years of near-monthly analyses of sediments and clams from this site showed that, although Cu levels in *Macoma balthica* were occasionally coupled to exposure, large fluctuations in Cu concentrations occurred in the clams, which could not be explained by changes in exposure. Again, a general dependence upon exposure was evident, but other variables also were obviously important in controlling bioaccumulation.

Multiple-Regression Exposure Models

Employing the broad data set described earlier, Luoma and Bryan (1978; 1979; 1981) used multiple regression to identify the relative importance of several possible causes of spatial variation in concentrations of Ag, Cd, Co, Cu, Pb, and Zn in the two deposit feeders, *Scrobicularia plana* and *Nereis diversicolor*. Variables tested included: (1) Total metal concentrations in surface sediments; (2) the influence of physicochemical form on metal availability; (3) uptake from the solute vector; and (4) the effect of intermetal competitive inhibition or enhancement. The influence of physicochemical form was tested in two ways. First, sediments were extracted with six different extractants. Previous laboratory work with model sediments and deposit-feeding clams (Luoma and Jenne, 1976) had indicated that extractable fractions of some trace metals might correlate with the availability of those metals. Soil scientists also have employed extractants to test the bioavailability of soil-bound metals to crop plants (reviewed by Sterritt and Lester, 1980). Various extractable fractions of metals in aquatic sediments have been described as biologically available (Loring, 1976), although without empirical information.

Second, concentrations of substrates (Fe, Mn, total organic carbon, carbonates, and humic substances) in sediments were included as independent variables in regression calculations. Statistical studies of sediments alone indicated metal partitioning shifted among such substrates as substrate concentrations changed (Luoma and Bryan, 1981). It was assumed that if changes in partitioning affected metal bioavailability (as suggested by Luoma and Jenne, 1977), then metal concentrations in organisms might show some correlation with the substrate concentrations that controlled partitioning.

Uptake from the solute vector was assessed using metal concentrations in the seaweed *Fucus vesiculosus* as an indicator of biologically available metal in solution. Concentrations of Cu in *Fucus vesiculosus* correlated strongly with Cu in sediments; thus this technique could not be used to test uptake of biologically available Cu from solution. Because the data range for all variables was broad, few autocorrelations occurred among independent variables.

The multiple-regression calculations showed that 70 to 80 percent of the variation in all metals in the organisms (except Cu in *Scrobicularia plana*) could be explained by two to five of the independent variables. The solute vector was quite important in Cd uptake by both species and also affected Co and Zn uptake. No effect of uptake from solution was evident for Ag or Pb. Extraction of sediments improved prediction of metal availability from sediment (compared to predictions from total metal concentrations) for Ag, Cd, Co, and Zn. The best correlations were obtained with 1 N ammonium acetate for Zn, as reported in many soil studies (Stearitt and Lester, 1980) and 1N HCl for the other metals. The availability of Pb followed total concentrations in sediment as closely as extractable concentrations. The same was true of Cu in correlations with *Nereis diversicolor*. With the exception of Cd, metal concentrations in sediment (extractable or total) explained 37 to 72 percent of the variation in the deposit feeders.

Concentrations of binding substrates in sediments explained 8 to 49 percent of the variation in metal concentrations in *Scrobicularia plana* and *Nereis diversicolor*. Concentrations of Pb in *Scrobicularia plana* were very closely correlated ($R^2 = 0.89$) with the Pb/Fe ratio in sediments (where Fe was measured by HCl extraction).

Luoma and Bryan (1978) suggested that the availability of Pb was enhanced at low concentrations of Fe in sediment because less Pb was strongly bound to iron oxides as the Pb/Fe ratio in sediments increased. Whatever the cause, the Pb/Fe ratio in sediments was an accurate predictor of Pb in *Scrobicularia plana* in estuaries not included in the original regression calculations.

The substrates that correlated with concentrations of Ag, Cd, Co, and Zn in *Scrobicularia plana* and *Nereis diversicolor* differed among metals, but were usually similar for the two deposit feeders. In all cases, more than one substrate correlated significantly, and the predictive capabilities of the regressions were not as strong as observed with Pb. Nevertheless, the statistical importance of partial extractions and correlation with substrate concentrations in sediments suggested the physicochemical partitioning of metals in sediments provided an important control on metal availability to deposit feeders.

Other Physicochemical Conditions

Physicochemical conditions other than those statistically tested by Luoma and Bryan (1978; 1979; 1981) also appear to influence metal bioavailability from sediment. Increased pH appears to increase the availability of Hg (perhaps by stimulating conversion of Hg^{+2} to Hg^{0}), but not Cu and Pb to marsh plants (Gambrell and others, 1977). Strong reducing conditions cause a substantial decline in the availability of Cd to marsh plants (Gambrell and others, 1977). Unpublished data from the study of Luoma and Bryan also suggest Cd was of lower availabilty in highly anoxic mudflats (inner Poole Harbor). The availability of Cu to the polychaete *Neanthes arenaceodentata* also is less from subsurface than from surface sediments (Pesch, 1979), presumably due to differences in redox potential. In contrast, certain types of reducing conditions enhanced the bioavailability of Cu to the clams *Scrobicularia plana* and *Macoma balthica* (Luoma and Bryan, 1982). Exceptionally high concentrations of Cu were observed in these animals in seven anoxic mudflats and during an unusual period of anoxia on one mudflat. Greater enhancements of Cu availability generally accompanied lower concentrations of Fe in sediments, but the precise cause of the enhancement was not identified.

Some other processes that affect bioavailability include ionic strength (affects stability constants), turbidity (affects rate of photo-oxidation of metal complexes), and environmental history (such as past exposure).

Summary

In a recent review, Bryan (in press) summarized the processes which control metal availability from sediments to aquatic organisms for a number of trace metals. He emphasized that the results were speculative; they sometimes differed among species, and definitive studies have been conducted only with a few species and mostly in estuarine environments. He concluded: (1) High concentrations of organic matter or Fe (probably as amorphous Fe oxide) inhibit the availability of Hg, Pb, arsenic (As), Zn, and possibly Ag and Cu. Sediments high in total organic carbon or extractable Fe may contain high concentrations of trace metals, but the metals do not appear to pass on to most biota. (2) Under some circumstances or for some species, the solute vector of uptake is an especially important source of Cd, Zn, and possibly As and Ag. (3) Total concentrations in sediments control Cu availability to polychaetes, but the controls on Cu availability to molluscs are not clear. Anoxia may enhance Cu availability to molluscs under some circumstances. (4) Zn availability is controlled by readily exchangeable Zn in sediment, by uptake from the solute vector, and by a negative influence of organic carbon. (5) Most metals (especially Hg, Pb, Zn, As, Cu, and Ag) would be expected to be of high bioavailability in coarser grained sediments enriched by anthropogenic metal input and in wastes (smelter wastes or mine wastes) low in organic material or Fe. (This is consistent with the hypothesis of Luoma and Davis, 1983, that the availability of some metals may be inversely related to total metal-binding capacity in sediments.) Some unknown attribute of sewage sludge enhances the availability of Ag and possibly Cd. Anoxic conditions reduce the availability of most metals (especially Cd), but may enhance the availability of Cu.

Although deciphering the most important controls on metal bioavailability in nature will necessitate a multivariable approach, it may be a manageable problem, despite the many complexities involved. Broad-based statistical approaches will not prove cause and effect, but they may be essential in narrowing the focus to more specific studies of the processes with controlling influences.

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