DEPARTMENT OF THE INTERIOR
UNITED STATES GEOLOGICAL SURVEY

PREPARED IN COOPERATION WITH THE
DEPARTMENT OF HOUSING AND URBAN DEVELOPMENT

MISCELLANEOUS FIELD STUDIES
MAP MF – 323

INTRODUCTION

Man is releasing many toxic chemical elements to the ocean environment at increasing rates (Bertine and Goldberg, 1971). In order to distinguish clearly the toxic elements that are potential problems from the elements that can be neglected, considerable information is needed about the temporal and spatial distribution of these elements in the water, sediment, and biota of our coastal marine, estuarine, and river systems. This report, which is a companion to an earlier report on mercury (McCulloch and others, 1971), gives the results of a reconnaissance survey of the elements lead and copper in surface sediment of the San Francisco Bay estuary. Although 30 elements were investigated using a semiquantitative emission-spectrographic method of analysis, in most cases the concentrations of only 15 elements were detectable: Fe, Mg, Ca, Ti, Mn, B, Ba, Co, Cr, Cu, Ni, Pb, Sc, V and Zn (see section on methods). Lead and copper were selected from these 15 elements because both lead and copper apparently indicate the largest relative enrichment in surface sediment as compared with sediment unaffected by the activities of man.

COMPARISON OF LEAD AND COPPER

The analytical results presented in figures 1-5 are from subsamples of the same surface grab samples that were analyzed previously for mercury (McCulloch and others, 1971). In addition, results are included from two near-surface gravity cores and a deep borehole core. Results for the surface sediments will be presented first and then compared with results from the cores (tables 1 and 3).

Surface-sample locations and concentrations (parts per million (ppm) of dry sample weight) are given for lead (fig. 1) and copper (fig. 2). In figure 3, the percentage frequency of the various concentrations of lead and copper is plotted for the entire estuary (top graph); in the lower graphs it is separated into the frequency of the various concentrations from the tributaries and margins and from the channels and shoals. Both lead and copper are more abundant in sediment collected from the tributaries and along the bay margins than in sediment from the shoals and channels of the bay. Lead was not detected (N) or was detected but is less than 10 ppm (L) in 17 percent of the samples; the modal (most commonly measured) concentration is 50 ppm in the tributaries and margins and 30 ppm in the channels and shoals. Copper was detected in all samples and had a modal concentration of 30 ppm in sediment from the tributaries and margins as well as in that from the channels and shoals. The bimodal distribution in the lead and copper concentrations shown in figure 3 may be artificial due to the small ratio of modal concentration to analytical resolution (table 3).

The range of carbon content for various metal concentrations is given in figure 4. In general, the concentrations of both metals increase with increasing concentrations of organic carbon. In addition, the median concentrations of organic carbon relative to the different metals are more similar than the median concentrations of organic carbon relative to the same metal in different environments. This similarity in concentration of lead and copper is also indicated in figure 5. Lead and copper are present in approximately equal abundance, particularly at or below 50 ppm.

To compare the composition of surface sediment with that of sediment uncontaminated by man's activities, the abundance of lead and copper (and other trace elements; see table 3, in section on methods) was examined in one deep and two shallow cores (table 1). Samples from the deep cores are considered uncontaminated by man (prehistoric) because typical rates of sediment accumulation are less than 5 feet per 1,000 years (Kvenvolden, 1962; Story and others, 1966). Results indicate a higher concentration of lead and copper in surface sediments than in prehistoric sediments.

DISCUSSION

The general distribution of lead and copper in San Francisco Bay sediment indicates the effects of sediment grain size, and of local sources thought to reflect the activities of man. The sediment grain size was not determined for this reconnaissance study, but size effects are inferred from the increased element abundance with increasing organic carbon. Enrichments due to local sources are indicated by the increased element abundance in sediment near the bay margins relative to sediment within the bay, and by enrichment in surface sediment relative to deep sediment from cores.

High natural concentrations of trace elements in coastal marine sediment are typically associated with clay minerals and organic matter (Hirst, 1962). While this association with organic matter is generally apparent for lead and copper in San Francisco Bay sediment (fig. 4), effects associated with organic matter are not distinguished from effects associated with clay minerals because both organic matter and clay minerals are commonly more abundant in the fine-grained fraction of sediments (Trask, 1939). If, however, the abundance of organic carbon is an approximate measure of the abundance of fine-grained sediment, then it follows that trace elements should be more abundant in hydraulic environments in San Francisco Bay where fine rather than coarse sediments accumulate. This may explain why relatively coarse-grained sediments in parts of Suisun Bay, containing relatively coarse plant fragments, have a high organic carbon content but a low lead and copper content. (Note the lead and copper concentrations in Suisun Bay in figures 1 and 2, and the organic-carbon range in figure 4.)

In addition to a general lead and copper enrichment with increasing organic carbon in sediment (or, as inferred above, with increasing fine-grained particles), lead and copper are more abundant in sediment from the bay margins than in sediment from within the bay (fig. 3). Although the locations, near the margins, of certain samples with relatively high concentrations (figs. 1 and 2) suggest an enrichment from waste outfalls (McCarty and others, 1962); further work is needed to estimate the metal increase associated with particle-size effects and the enrichment resulting from local sources such as industrial and municipal effluents. It is also possible that significant differences exist in background concentrations between Sacramento-San Joaquin River basin soils and local soils. Present data are also inadequate to determine the reason for an apparently higher lead and copper abundance, relative to organic carbon, in sediment from the shoals in comparison to sediment from the bay margins (fig. 4).

The decrease in lead and copper in fine- and coarse-grained sediment with depth in cores (table 1) indicates a near-surface metal enrichment that is apparently not an effect of sediment grain size. Because the number of samples is small, this interpretation is tentative but does agree with a similar decrease in another industrial metal, mercury, that was analyzed by a different method (table 1 and McCulloch and others, 1971). However, because there is a wide natural range in metal concentrations in sediment and soil (table 2), and because the concentrations in most of the San Francisco Bay sediments analyzed fall within that range, a clear distinction cannot be made between natural background concentrations and man's contribution. A much larger differences between natural background concentrations and man's contribution was found in a recent study of sediments on the continental shelf adjacent to New York, where lead and copper were some of the most useful metals for detecting the presence of industrial waste (Gross and others, 1971).

While our data for lead and copper provide only a rough estimate of the abundance of lead and copper in surface sediment, a tentative estimate of the total lead in the upper foot of sediment in San Francisco Bay is 10,000 tons. (See McCulloch and others, 1971; lead is approximately 100 times more abundant than mercury.) This quantity can be brought into perspective if we consider the amount of lead contributed to the environment in urban areas from automotive exhaust and solid sewage waste. The estimated amount of lead in the upper foot of sediment is equivalent to the estimated lead released to the atmosphere by a population of 2 million people within 5 years (Schroeder, 1970), or to that released in sewage sludge by the same population in 10 years (Gross, 1970). It is apparent, therefore, that either is a sufficient source of sediment-associated lead in San Francisco Bay, although the actual contributions of these sources to the metal concentrations found in the bay sediment are unknown. Furthermore, these estimates suggest that the reservoir of sediment-associated lead can account for only a fraction of man's local release of lead to the environment.

METHOD

The surface-sample collecting and handling procedure has been described previously (McCulloch and others, 1971); these surface Van Veen and Shipek samples belong to a depth of about 4 inches. In addition, two surface gravity cores and five deep borehole samples were collected for this study. All sediment samples were air dried and ground to less than 100-micrometer particle diameter using a ceramic ball mill. Sample collection and preparation were conducted so that contamination is not considered a problem. Lead and copper were determined by direct-current arc-emission spectrograph (Grimes and Marrazaino, 1968). This method yields precision that is generally within ± 50 percent variability (repeat values range from 1/2 to 3/2 times the amount first reported). Well-recognized analytical problems, including matrix (sediment) effects and sample heterogeneity, are beyond the scope of this baseline study and are not evaluated in this report. The percentage organic carbon (by dry weight of sediment) was estimated as the difference between total carbon, determined using an induction furnace, and carbonate carbon determined by wet-chemical methods (Gross, 1971).

The semiquantitative spectrochemical method included analyses for 30 elements (table 3). Lead and copper were selected as the elements that were both (1) adequately detected by the analytical method used and (2) sufficiently enriched in modern sediment, relative to prehistoric sediment, to be reasonably explained as having been introduced by man's activities. This selection of lead and copper is discussed below.

Table 3, column 3, lists the modal concentration of the element in each surface sediment. For the 15 elements with a modal concentration in surface sediment at least three times the analytical resolution, an increase in abundance in modern sediments relative to older ones of San Francisco Bay can be examined by comparing their concentration in surface sediment with that in old sediment from deep cores (locations indicated in figures 1 and 2). Such an increase would be indicated by an increased ratio of the modal concentration in surface sediment to the modal concentration in sediment from deep cores (table 2, column 7). When this ratio is less than three, the analytical method has limited application for resolving differences in abundance of that element between surface (modern) and deep (prehistoric) sediment because the analytical error is ± 50 percent. At present only the data for lead and copper, within the group of 15 metals analyzed, are considered significant for the above discussion because they show a greater-than-threefold increase in concentration in surface sediment relative to that in deep sediment (table 2, columns 5, 6, and 7).

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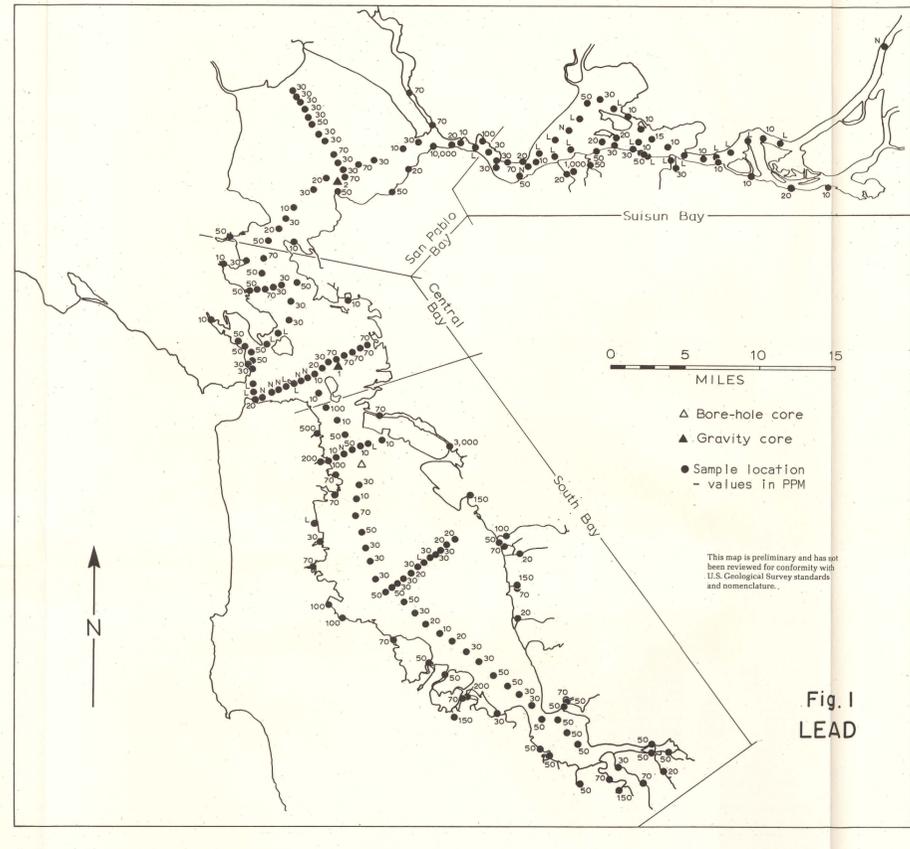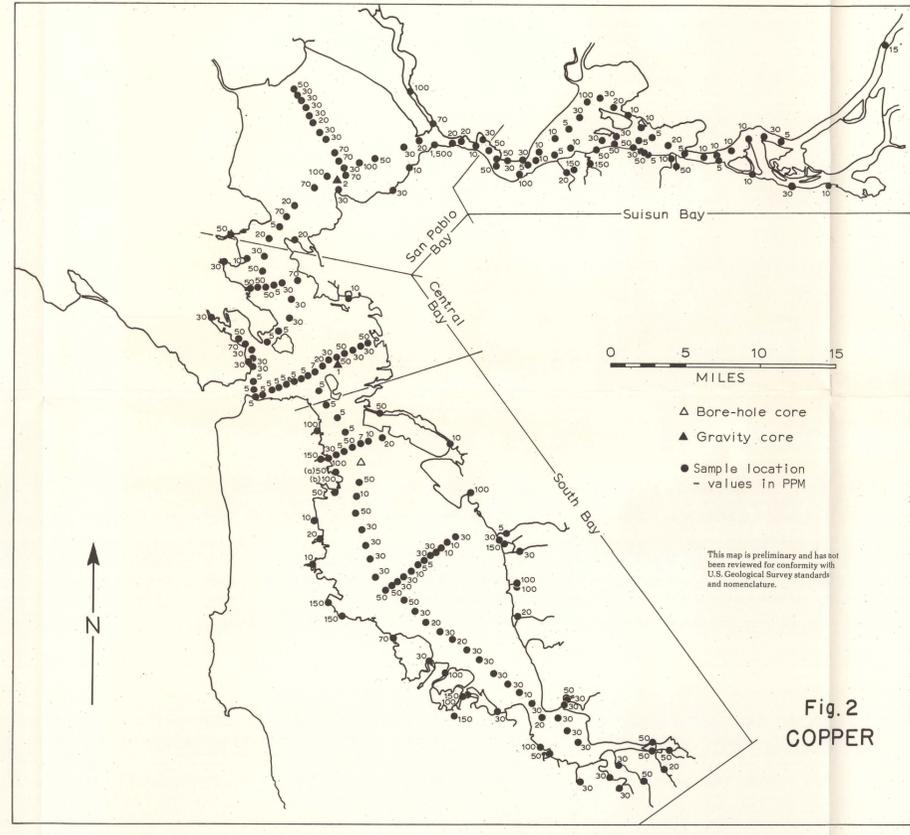
Fig. 1 LEAD

Fig. 2 COPPER

Bore-hole core
Gravity core
Sample location - values in PPM

This map is preliminary and has not been reviewed for conformity with U.S. Geological Survey standards and nomenclature.

DISTRIBUTION OF LEAD AND COPPER IN SURFACE SEDIMENTS IN SAN FRANCISCO BAY ESTUARY, CALIFORNIA
by
D. H. Peterson, D. S. McCulloch, T. J. Conomos, and P. R. Carlson
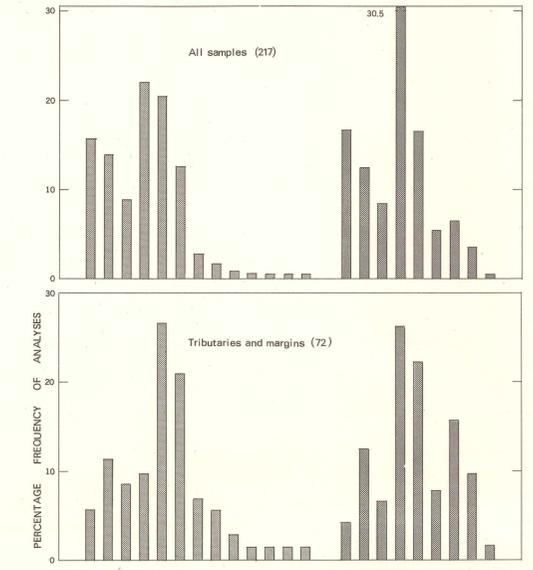## 1972

Figure 3.—Frequency distribution of lead and copper in San Francisco Bay sediment. Explanation: Figures are drawn from six-step spectrographic analyses by the laboratories of the U.S. Geological Survey. The analyses are reported as geometric midpoints (1.0, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1) of geometric brackets having boundaries 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12; see Myers and others, 1961); for Pb, L detected but less than 10 parts per million, N not detected. Analysts G. W. Day, R. N. Babcock and R. T. Hopkins.
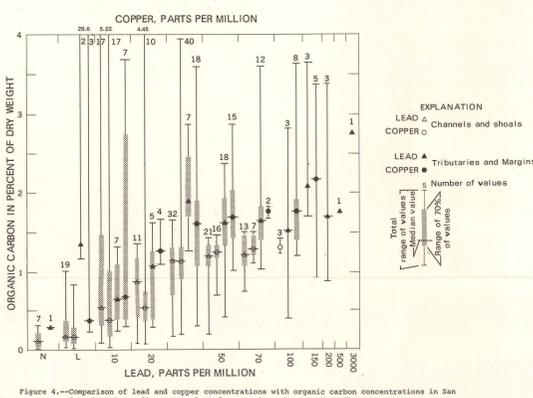

Figure 4.—Comparison of lead and copper concentrations with organic carbon concentrations in San Francisco Bay sediment. Analyst for organic carbon, L. M. McPherson.

Figure 5.—Comparison of lead and copper concentrations in San Francisco Bay sediment.

Table 1.—Lead, copper and mercury concentrations in sediments from shallow and deep cores, San Francisco Bay, California

Sampling method[1]	Sediment depth[2]	Sediment type	Pb (ppm)	Cu (ppm)	Hg (ppm)
	(inches)				
Gravity core 1	.5	Mud	30	50	0.85
	1.5	Mud	70	50	1.10
	2.5	Mud	70	100	1.30
	4.5	Sandy mud	100	150	.85
	5.5	Sandy mud	30	50	.11
	8.5	Sandy mud	30	50	.10
	12.5	Sandy mud	15	50	.15
	14.5	Sandy mud	30	30	.23
	(inches)				
Gravity core 2	0.5	Mud	70	70	.70
	1	Mud	50	70	.65
	2	Mud	70	70	.42
	4	Mud	30	50	.34
	8	Mud	30	50	.34
	16	Mud	30	50	.34
	20	Mud	20	50	.25
	(feet)				
Bore-hole core	205	Mud	15	50	.36
	216	Sand	L	20	.16
	245	Silt	L	20	.32
	350	Mud	10	L	.28
	425	Sand	N	15	.06

[1] For core locations, see figures 1 or 2.
[2] Depth beneath sediment-water interface.
[3] Analysts for Pb and Cu, K. J. Curry and R. T. Hopkins; analyst for Hg, K. Leong (for method see McCulloch and others, 1971).

Table 2.—Abundance of lead and copper in selected materials

Material	Lead Median (ppm)	Lead Range (ppm)	Copper Median (ppm)	Copper Range (ppm)	Reference
Sediment:					
San Francisco Bay, surface	30	N-10,000	30	5-1,500	This report
Nearshore Marine[1]	9-34		13-120		Gross, 1967
Soil	16	<10-700	18	<1-300	Shacklette and others, 1971
Urban sewage sludge	500	150-1,100	1,000	400-4,500	Gross, 1970
Urban atmosphere[2]		0.1-2.3		0.01-0.51	Schroeder, 1970

[1] Natural distributions of lead and copper in pelagic sediment have been investigated in detail (Goldberg and Arrhenius, 1958; Chow and Patterson, 1962).
[2] Concentration is weight of metal in μg per cubic meter air; note the difference in relative concentration of lead and copper in sewage waste and urban atmosphere.

Table 3.—Comparison of resolution of analytic technique with observed trace metal concentrations in San Francisco Bay

Element	Analytic Resolution (ppm)	Modal concentration in surface sediment Mode (ppm)	Range (ppm)	Ratio of modal concentration in surface sediment to resolution	Concentration in deep sediment cores Mode (ppm)	Range (ppm)	Concentration in surface sediment cores Mode (ppm)	Range (ppm)	Ratio of modal concentration in sediment from surface to modal concentration in deep sediment cores
Fe	500	50,000	5,000-150,000	100	30,000	20,000-70,000	30,000	20,000-50,000	1
Mg	200	10,000	1,000-20,000	500	10,000	7,000-20,000	15,000	5,000-20,000	1.5
Ca	500	10,000	1,000-200,000	200	7,000	3,000-20,000	7,000	1,000-5,000	1
Mn	10	3,000	1,000-7,000	150	3,000	3,000	700	500-1,500	1.4
Ti	20	700	1,500			300-700			
Ag	0.5	N-20			N	N	N	N-0.7	N
As	200	N-700							
Au	10	N							
B	10	70	N-100	7	30	20-30	50	20-70	1.5
Ba	20	300	N-700	15	300-700	300-700	300	300-500	1,0,4
Be	1	N-3			L	L-1.5	L	L-1	?1
Bi	10	N							
Cd	20	N-100			N	N	N	N	N
Co	5	30	N-70	6	15	15-30	20	15-30	1.3
Cr	10	150	70-2,000	15	150	150-300	150	70-300	1
Cu	5	30	N-1,500	6	15	15-50	50	5-150	3.3
La	20	20	N-100	1	L	N-L	L	L-L	L/N,L/L
Mo	5	N			L	N-L	L	L	L/N
Nb	10	N-150			N	N	N	N	N
Ni	5	150	N-300	30	70	70-150	100	70-150	1.4
Pb	10	N-10,000		3	15	N-15	30	20-100	3
Sb	100	N-700			N	N	N	N	N
Sc	5	15	20-70	3	15	7-20	15	7-20	1
Sn	10	N-700			L	N-L	L	L	L/N
Sr	100	100	1,500	1	150	150	150	100-700	1
V	10	100	20-300	10	70	70-150	150	30-150	2.1
W	50	N-200			N	N	N	N	N
Y	10	15	N-70	1.5	15	7-15	15	7-15	1.5
Zn	200	L-10,000			20	10-20	15	10-15	1.5

(2) Semiquantitative spectrographic analysis (see Myers and others, 1961; and Grimes and Marrazaino, 1968).
(3) Surface grab samples (reported in McCulloch and others, 1971).
(4) Bore-hole samples are located in Figure 1 or 2 and sample depths are in Table 1.
(5) Gravity core samples are located in Figure 1 or 2 and sample depths are in Table 1.
N Not detected.
L Detected but less than minimum analytic resolution (column 2).