STEINKAMPT

WRI 37-75

PB-251 111

DISTRIBUTION AND MOVEMENT OF ZINC AND OTHER HEAVY METALS IN SOUTH SAN FRANCISCO BAY, CALIFORNIA

Wesley L. Bradford

Geological Survey
Menlo Park, California

February 1976

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

KEEP UP TO DATE

Between the time you ordered this report—which is only one of the hundreds of thousands in the NTIS information collection available to you—and the time you are reading this message, several *new* reports relevant to your interests probably have entered the collection.

Subscribe to the **Weekly Government Abstracts** series that will bring you summaries of new reports *as soon as they are received by NTIS* from the originators of the research. The WGA's are an NTIS weekly newsletter service covering the most recent research findings in 25 areas of industrial, technological, and sociological interest—invaluable information for executives and professionals who must keep up to date.

The executive and professional information service provided by NTIS in the **Weekly Government Abstracts** newsletters will give you thorough and comprehensive coverage of government-conducted or sponsored research activities. And you'll get this important information within two weeks of the time it's released by originating agencies.

WGA newsletters are computer produced and electronically photocomposed to slash the time gap between the release of a report and its availability. You can learn about technical innovations immediately—and use them in the most meaningful and productive ways possible for your organization. Please request NTIS-PR-205/PCW for more information.

The weekly newsletter series will keep you current. But *learn what you have missed in the past* by ordering a computer **NTISearch** of all the research reports in your area of interest, dating as far back as 1964, if you wish. Please request NTIS-PR-186/PCN for more information.

WRITE: Managing Editor
5285 Port Royal Road
Springfield, VA 22161

Keep Up To Date With SRIM

SRIM (Selected Research in Microfiche) provides you with regular, automatic distribution of the complete texts of NTIS research reports *only* in the subject areas you select. SRIM covers almost all Government research reports by subject area and/or the originating Federal or local government agency. You may subscribe by any category or subcategory of our WGA **(Weekly Government Abstracts)** or **Government Reports Announcements and Index** categories, or to the reports issued by a particular agency such as the Department of Defense, Federal Energy Administration, or Environmental Protection Agency. Other options that will give you greater selectivity are available on request.

The cost of SRIM service is only 45¢ domestic (60¢ foreign) for each complete microfiched report. Your SRIM service begins as soon as your order is received and processed and you will receive biweekly shipments thereafter. If you wish, your service will be backdated to furnish you microfiche of reports issued earlier.

Because of contractual arrangements with several Special Technology Groups, not all NTIS reports are distributed in the SRIM program. You will receive a notice in your microfiche shipments identifying the exceptionally priced reports not available through SRIM.

A deposit account with NTIS is required before this service can be initiated. If you have specific questions concerning this service, please call (703) 451-1558, or write NTIS, attention SRIM Product Manager.

This information product distributed by

NTIS U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

BIBLIOGRAPHIC DATA SHEET	1. Report No. USGS/WRD/WRI-76/014	2.	3. Recipient's Accession No.

4. Title and Subtitle

DISTRIBUTION AND MOVEMENT OF ZINC AND OTHER HEAVY METALS IN SOUTH SAN FRANCISCO BAY, CALIFORNIA

5. Report Date
February 1976

6.

7. Author(s)
Wesley L. Bradford

8. Performing Organization Rept. No. USGS/WRI-75-37

9. Performing Organization Name and Address
U.S. Geological Survey, Water Resources Division
345 Middlefield Rd., Bldg. 6
Menlo Park, Calif. 94025

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address
U.S. Geological Survey, Water Resources Division
345 Middlefield Rd., Bldg. 6
Menlo Park, Calif. 94025

13. Type of Report & Period Covered
Final

14.

15. Supplementary Notes

16. Abstracts From September to December 1972, zinc in aqueous solution was discharged into south San Francisco Bay, Calif., the study area, from eight wastewater treatment plants at a net rate of 77 kilograms per day. This newly added zinc moved from the aqueous phase to the bottom sediment at a rate of about 0.026 μg/cm^2/day. Movement in the opposite direction could not be detected. A major fraction of dissolved zinc was being sequestered by organic chelators. The concentrations of extractable Fe, Mn, and Zn in the suspended solids of bay water increased significantly with time but the total mass of zinc in the study area residing in the suspended solids remained constant. Bottom sediments were analyzed for Fe, Mn, Zn, Cu, Co, Ni, and Pb in the 2 mm-20 micron and <20 micron size fractions. Concentrations of all but Ni were higher in the smaller size fraction by factors of 2 to 5. A varimax factor analysis indicated that the concentration of each metal in the sediment is controlled by a separate process, but lead in both size fractions may be controlled by only one process such as automobile emissions.

17. Key Words and Document Analysis. 17a. Descriptors

*Polarographic analysis, *Statistical methods, *Bottom sediments, *California, Colorimetry, Spectrophotometry, Zinc, Copper, Cadmium, Lead, Iron, Manganese, Cobalt, Nickel, Chelation, Sorption, Estuaries, Sewage effluents, Diffusion, Suspended solids.

17b. Identifiers/Open-Ended Terms

*Trace metal budget, *San Francisco Bay, Trace metal movements, Trace metal distribution, Factor analysis, Sediment-water interactions, Sediment size fractionation.

PRICES SUBJECT TO CHANGE

17c. COSATI Field/Group

18. Availability Statement
No restriction on distribution

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page)
UNCLASSIFIED

21. No. of Pages

DISTRIBUTION AND MOVEMENT OF ZINC AND OTHER HEAVY METALS IN SOUTH SAN FRANCISCO BAY, CALIFORNIA

By Wesley L. Bradford

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 37-75

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

February 1976

I

UNITED STATES DEPARTMENT OF THE INTERIOR

Thomas S. Kleppe, Secretary

GEOLOGICAL SURVEY

V. E. McKelvey, Director

For additional information write to:

Regional Research Hydrologist, WRD, WR
U.S. Geological Survey
345 Middlefield Rd.
Menlo Park, Calif. 94025

CONTENTS

ILLUSTRATIONS

TABLES

DISTRIBUTION AND MOVEMENT OF ZINC AND OTHER HEAVY METALS IN SOUTH SAN FRANCISCO BAY, CALIFORNIA

By Wesley L. Bradford

ABSTRACT

From September to December 1972, zinc in aqueous solution was discharged into south San Francisco Bay, Calif., the study area, from eight wastewater treatment plants at a net rate of 77 kilograms per day. This newly added zinc moved from the aqueous phase to the bottom sediment at a rate of about 0.026 $\mu g/cm^2/day$. Movement in the opposite direction could not be detected (the author had previously found in Chesapeake Bay, Md., Va., two mechanisms by which zinc moved out of the sediments). The concentrations of extractable Fe, Mn, and Zn in the suspended solids of bay water increased significantly with time but the total mass of zinc in the study area residing in the suspended solids remained constant. Bottom sediments were analyzed for Fe, Mn, Zn, Cu, Co, Ni, and Pb in the 2 mm-20 micron and <20 micron size fractions. Concentrations of all but Ni were higher in the smaller size fraction by factors of 2 to 5. No variations with either depth or location in total concentration of any metal could be shown. A varimax factor analysis of these data indicated that the concentration of each metal in the sediment is controlled by a separate process. Most of the variance in the lead concentrations in both size fractions is apparently due to the same factor, suggesting a single major source of lead such as automobile emissions.

In water samples after 5 days' settling, Zn and Cu were being sequestered by fast reacting chelators, a fraction of which would not pass a 0.22 μm filter. Zn and Cd were being sequestered by slow reacting chelators. The mean increase in concentration caused by destroying these latter chelators was 0.66 μg/ℓ of Zn and 0.023 μg/ℓ of Cd.

INTRODUCTION

The chemical behavior of major inorganic constituents in many natural water systems can be approximately predicted by equilibrium thermodynamics (Sillen, 1967; Garrels and Christ, 1965) with generally the best predictions being made in systems having long (geologic) time scales in which to reach equilibrium or a steady state approximating equilibrium (e.g., the deep ocean). Biological processes supply free energy to these systems erratically,causing variations in the behavior and distribution of these constituents away from that predicted by thermodynamics. Such variations are short in time scale relative to geologic processes and usually involve transfers of constituents between phases amounting to only a small fraction of the total in each phase (e.g., magnesium, calcium and carbon dioxide movements in the open ocean). By contrast the chemical behavior of the minor metals is not readily predictable from simple equilibrium thermodynamic solubility models as presently understood.

The movements and distribution of trace heavy metals in aquatic systems are usually affected proportionately more by the biogeochemical environment than are the more abundant alkaline and alkaline earth metals. Since trace metals affect the quality of a water resource, the identification and measurement of the processes affecting their movements is most important. But in a review of phosphate and trace metal cycling processes in lakes, Lee (1970) concluded that not enough information is yet available to predict either the net direction or rate of movement under various conditions.

A large number of parameters or processes have been identified. Jenne (1968) suggests that one of the most important is the interaction between the solutes and one of the minor solid phases, the hydrous iron and manganese oxides. Carvajal and Landergren (1969) present a similar argument based upon analyses of deep oceanic sediments. Jenne (1968) also noted that in high organic soils and sediments, the organic fraction can be the most important solid phase interacting with solutes. Many other parameters and processes have been discussed in recent literature. The following are some examples: trace metal sequestering by dissolved organic matter in water (Slowey and Hood, 1971; Cross et al., 1970; Zirino and Healy, 1971; Bradford, 1972), cation exchange desorption from sediments (Forester et al., 1971; Evans and Cutshall, 1972); trace metal sequestering by dissolved organic matter in interstitial water (Brooks et al., 1968; Presley et al., 1972), trace metal movements and diagenesis in variable potential environments (Spencer et al., 1972; Piper, 1971; Gross, 1967), associations of trace metals with high organic layers in sediments (Volkov and Fomina, 1971; Calvert and Price, 1970), and the fixation of dissolved material to biota and movement through the food web (Rice, 1963; Khaylov and Finenko, 1968). There is some feeling among workers that more processes have yet to be identified (Wolfe and Rice, 1972).

The number of ways in which known processes can combine and interact in any given system to create the observed trace metal distribution is astronomical. Thus any system is likely to appear unique from only a cursory examination. The uniqueness problem is often compounded by the observer through his use of inadequate or improper analytical techniques, failure to distinguish between solid and solution phases and inability to determine the chemical speciation of the dissolved trace metal. Models may be formulated in the future that will successfully describe apparently unique systems according to the interaction of a few well recognized processes. At the present time such models do not exist.

In the absence of comprehensive models for trace metal behavior in natural water systems, it is useful to evaluate a few fundamental parameters in any system. Two of these are the direction and rate of movement of at least one trace metal between sediments and water and the chemical conditions associated with this movement. Very few workers have seriously attempted to evaluate these parameters. Exceptions are Rittenberg et al., (1955) and Mortimer (1971). The problem frequently occurring is that the hydrologic data or model necessary to estimate the rate that a metal leaves or enters through the fluid boundaries of the system is usually lacking. South San Francisco Bay seems to be unique in that during the dry season of the area's predominantly Mediterranean climate, the south bay is flushed very slowly (McCulloch et al., 1970) and probably by predominantly dispersive rather than advective processes. Selleck (1968) determined the dispersion coefficients of a conservative constituent at several transects in the south bay area during the dry season. It is possible, using Selleck's (1968) values, to calculate the flux of any constituent across the seaward boundary of the study area if the horizontal concentration gradient is known. In addition to this, during the dry season the only inputs of fresh water and their dissolved constituents are from point sources, namely wastewater treatment facilities, which can be monitored regularly. Based upon these features of the area it seemed possible to determine reasonably accurate figures for the net transport of a trace metal into the system, out of the system and thence between the solid and solution phases.

The primary objective of this study was to determine the net transport of zinc into the study area from the urbanized perimeter, out of the study area across the northern boundary of the study area, and across the sediment-water interface within the study area, all within a limited time period. A secondary objective was to assemble as much data on other trace metals--their concentrations and chemical states in water, suspended solids, sediments and interstitial fluids--as possible within the time and funding constraints of the study in order to describe the existing trace metal conditions in the south bay. Thus the bulk of effort was directed toward evaluating the distribution and movements of zinc, but the data collected on the distribution of other metals is important and is reported here.

The parameters and processes evaluated in this study are listed below in order of priority.

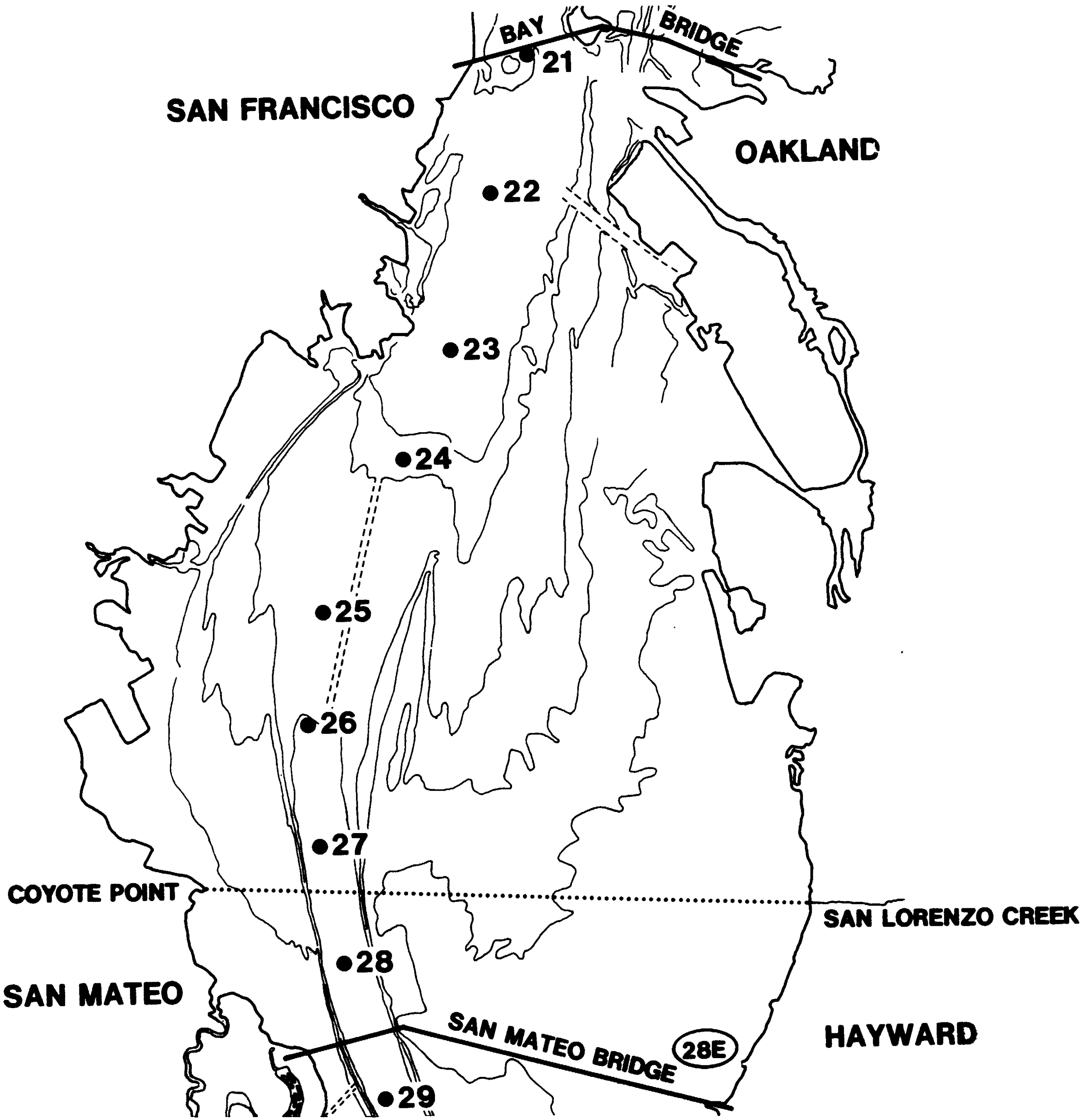
1. The net direction and rate of exchange of zinc across the boundaries of the study area and the sediment-water interface within the study area.
2. The distribution of zinc between organic chelators and the bulk of the solution in the aqueous phase.
3. The concentrations and variations thereof with time of zinc, iron, manganese and copper in suspended solids trapped by an 0.22µm filter.
4. The rate of discharge of dissolved zinc from sediments.
5. The concentrations of iron, manganese, zinc, copper, cobalt, nickel and lead in sediments and interstitial fluids, and the processes controlling these concentrations.

To my knowledge, nothing has been published previously on the concentrations of zinc in water or sediments in San Francisco Bay. At the beginning of this work, the only data available on zinc concentrations in sewage effluent were in periodic reports required by regulatory agencies. These data were largely unacceptable for use in evaluating the zinc loadings from sewage effluent because sampling was infrequent and the analyses were performed on whole samples rather than on separate water and suspended solid phases.

DESCRIPTION OF THE STUDY AREA

The area of San Francisco Bay south of a transect one-half mile north of the San Mateo Bridge was chosen as the study area (Figure 1). McCulloch and others (1970) documented the major features of the circulation in this area of the bay: 1) strong tidal currents and winds generally stir the water column daily so that vertical density stratification and the subsequent condition of low oxygen concentrations over the bottom are rarely observed; 2) the freshwater input during the dry season, May through November, comes almost exclusively from sewage discharges; 3) major flushing action in the area is caused by high flow in the Sacramento and San Joaquin Rivers. Major floods usually occur in late winter.

The period of the study was September to December 1972. The wet season's first rains occurred in October and some major storms occurred in November and December, but these early rains soaked into the soil so that significant stream flow did not develop until later in the season, about mid-January. During storms, sizeable amounts of stormwater drained into the study area from urban developments on the bay, but this flow was not a significant fraction of total freshwater flow into the study area during the period and the zinc discharged in stormwater was a slight fraction of the total.


BAY BRIDGE
●21
SAN FRANCISCO
OAKLAND
●22
●23
●24
●25
●26
●27
COYOTE POINT
SAN LORENZO CREEK
●28
SAN MATEO
SAN MATEO BRIDGE
28E
HAYWARD
●29

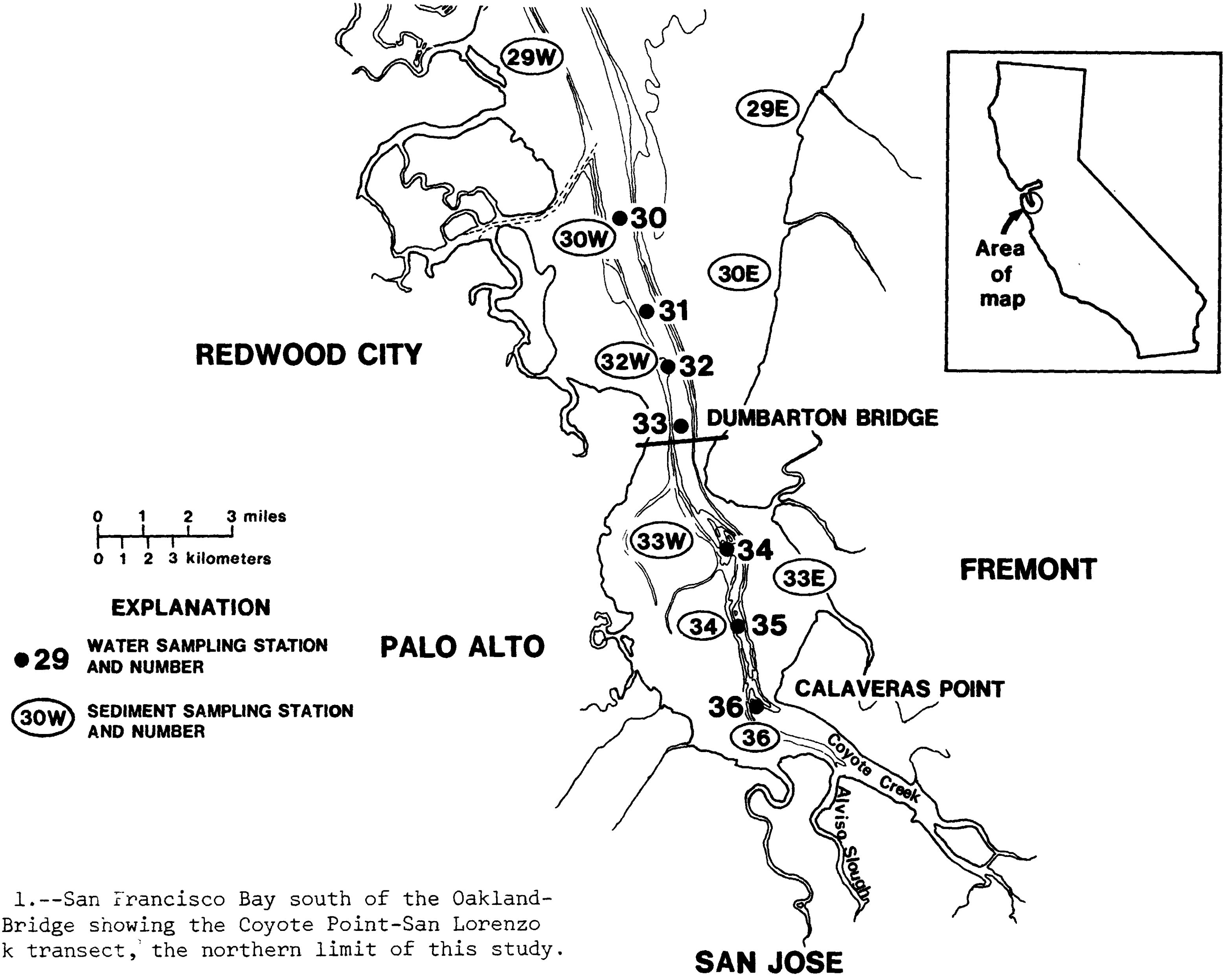


FIGURE 1.--San Francisco Bay south of the Oakland-Bay Bridge showing the Coyote Point-San Lorenzo Creek transect, the northern limit of this study.

The area has an average water depth of about 2.3 metres. The sediment area is about 206 x 10^6 m^2, 53 percent of which is intertidal. The perimeter is marked by several drainage sloughs, creeks and evaporating basins. The sewage from 12 municipalities is discharged into the area following treatments which range in effectiveness from minimal secondary to tertiary. Most stormwater is handled by established storm sewers.

MATERIALS AND METHODS

Sampling stations, equipment and sample handling

Sewage Water Samples. In order to determine the soluble zinc inputs to the area over the study period, discharges containing zinc were first located and then sampled regularly. Several potential sites of zinc loading were selected for preliminary evaluation including 23 sewage plants, creeks and sloughs. Those sites where the zinc concentration in grab samples was less than 20 μg/ℓ at each of three separate samplings in a two-week period were eliminated. The remaining sites, 8 in number and all municipal wastewater treatment facilities, were sampled regularly. These sites are identified by number only. Samples from five of these showed considerable zinc concentration variability from day-to-day so were sampled twice a week. At the other three sites, the sample zinc concentrations were much less variable so these were sampled weekly.

Bay Water Samples. Water and suspended solid samples were collected at stations already established by the U.S. Geological Survey's Office of Marine Geology and the Water Resources Division. Their south bay stations are shown in figure 1. Samples were taken aboard the Survey vessel R/V Polaris. Cruise records are shown in table 1. On cruise B1, samples were taken from station 36 at four increments of distance off the bottom to attempt to find a concentration gradient which would indicate discharge of zinc from the sediment. At subsequent stations on that cruise, a single sample was collected from 10 metres because of limited sample storage space. On subsequent cruises, at station 36, samples were taken at 3 and 5 metres. At all other stations, samples were taken from 5 to 10 metres. The samples were collected when the current was moving and within 5 minutes of anchoring on station to avoid possible contamination from the zinc antielectrolysis plates on the ship's hull.

TABLE 1.--*Records for water sampling cruises*

Cruise number	Date 1972-1973	Stations Sampled
B1	25 September	36, 30, 29, 28, 26
B2	2 November	36, 32, 30, 29, 27, 24
B3	11 December	36, 32, 30, 27, 24, 22
B4	3 January	36, 32, 30, 27, 24, 21

The water sampling device consisted of a peristaltic pump fitted with silastic silicon tubing connected to 12 metres of polyethylene tubing. The polyethylene tubing was taped to nylon line weighted with an epoxy covered 7 kg steel weight. The tubing intake was extended about 30 cm perpendicular to the line to avoid contamination from the line. Two samples were collected in 1-liter high density polyethylene bottles. One was stored immediately unfrozen over ice. The second sample was filtered through a 0.22μm Nucleopore[1/] filter and stored unfrozen over ice. Both samples were later stored in the laboratory at 4°C. Analyses of the filtered samples began in the laboratory soon after returning from the cruise. The unfiltered samples stood for 5 days at 4°C to let heavy solids settle, then the top 800 ml of water was siphoned off for analysis. From this point on, the filtered and unfiltered samples were treated identically. Zinc loss by adsorption to bottle walls was found to be undetectable using Zn^{65}. This finding agrees with that of Robertson (1968).

The filters were dried over silica gel for one month, and reweighed. The reported weight gain from water absorption by Nucleopore filters exposed to water and then dried is <0.05 mg (J. R. Schubel, The Johns Hopkins University, oral communication). No correction for water adsorption was made in determining suspended solids weights.

[1/] The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Sediment Samples. Sediment cores were taken at the stations shown as ovals in figure 1. Sediments were taken closer to shore rather than in the main channel because the channel is impenetrable with simple coring devices and, since it is dredged occasionally, those sediments do not represent the normal sedimentation pattern. The sediments collected consist primarily of silt and clay with some sand and a small amount of shell from G. gemma or broken shell from old oyster beds.

The sediment cores were collected on 7 April 1973 from a small 111 skiff. The coring device was a Wildco K. B. Sampler (Saginaw, Mich.) specially fitted with a lexan core tube and adapter. The top 12 cm of core was extruded immediately under nitrogen into 3 cm sections directly into jars lined with plastic bags. The jars were tightly sealed and stored in an ice chest that was flushed daily with nitrogen. Over the 5- to 10-day storage period, the color of the mud surfaces changed from gray-black to chocolate brown in nearly all cases but the mud inside the outer 5mm layer remained gray-black.

INTERSTITIAL WATER EXTRACTION AND SEDIMENT SIZE FRACTIONATION

The interstitial water was extracted from the sediment samples inside a nitrogen filled glove tent using the hydraulic squeezer described by Manheim (1966). The squeezer was rinsed with deionized water before each use. Filter, filter separators and containers were presoaked in 0.1 M HNO_3 and rinsed with distilled water. The maximum pressure applied was 1,000 psi on coarse sediments and 800 psi on fine grained or silty sediments.

The Eh was measured immediately using a combination platinum-calomel electrode. The initial pH was measured on a 7.0 mℓ aliquot using a combination glass electrode. Then to titrate the alkalinity, 0.10 mℓ increments of 0.789 M HCl were added to the aliquot until the pH was in the range 2-3. The alkalinity is calculated by subtracting the excess acid added, as determined from the final pH, from the total acid added. The aliquot with added acid increments was returned to the sample bottle and 0.1 mℓ of 6 M HNO_3 added to the sample.

After squeezing, the semi-dry cake was weighed, and two sections were cut from it using a stainless steel knife. One section was weighed and then air dried to constant weight at 80°C to determine the moisture content, and the other section was weighed and reconstituted with distilled water saturated with chloroform to retard bacteria. After 3 days of soaking, the sediment in slurry form was separated into three size fractions by the method of Jenne et al., (in preparation). Briefly the >2 mm fraction was removed by seiving, and the fractions greater than and less than 20 microns (μm) were separated by decanting and settling. After separating and quantitatively splitting the sample to reduce the volume, the solids were concentrated by filtration through 0.22 μm Nucleopore filter. Half of each filter was used to determine the dry weight of sediment collected, and the other half was analyzed.

METHODS FOR TRACE METAL ANALYSES

Field Analysis for Zinc in Wastewater. Analyses for zinc in wastewater were performed by a variation of Huff's (1948) mixed color dithizone method. The green dithizone reacts with heavy metals in the aqueous phase to form reddish metal dithizonate complexes also soluble in the CCl_4 phase. The mixture of excess unreacted green dithizone and the metal dithizonate ranges in color from greenish blue to bright pink when virtually all of the dithizone is complexed.

Huff's (1948) report noted methods for reducing most analytical interferences but these are not effective for reducing interferences from palladium, cadmium and tin. Concentrations of palladium and cadmium are expected to be small in sewage and can be safely ignored (Teng Wu, Regional Water Quality Control Board, oral communication, August 1972). Since tin is widely used in industry, the interference from Sn(II) was examined further. In acetate buffer, the color from the Sn(II) dithizonate deteriorates in 3 minutes to one-half its original intensity. The initial color intensity ratio relative to zinc is reduced by half by adding thiosulfate (as per Huff, 1948), and the rate of color deterioration is comparable. The Sn(II) interference was effectively eliminated by waiting 3 minutes after mixing before reading the mixed color.

To evaluate the method, 37 samples were analyzed over a period of 4 weeks both by mixed color dithizone and by atomic absorption. In the atomic absorption analysis, the sample was diluted 1:2 with 2 N HCl, and the calibration curve determined by three standard additions. A Student "t" test showed the difference between mean values by each method to be insignificant. A linear regression analysis of the data gave a slope of 1.00, correlation coefficient of 0.966 and intercept less than one standard error from the origin. These analyses suggest that there are no observable systematic differences between the methods. The coefficient of variation on replicate analysis by the colormetric method is 20 percent. The method measures dissolved zinc plus the zinc readily exchangeable from suspended particulate matter.

Analyses for Trace Metals and Chelation Effects in Bay Water. Anodic Stripping Voltammetry (ASV) was used according to methods developed by the author (Bradford, 1972) to analyze for zinc and cadmium and to characterize the extent of metal complexing by organic matter. A coefficient of variation of 4 percent on replicate zinc analyses at the 2.5 μg/ℓ was reported earlier. The practical detection limit for zinc is restricted by the presence of interfering constituents which vary between samples.

The author also developed methods for using ASV as a qualitative indicator of trace metal complexing by organic matter in water. Briefly, if chelators are present, they reduce the signals produced with ASV by a given actual metal concentration. If the chelators are destroyed, the signals increase. In practice, two subsamples of a sample are prepared. One is irradiated with strong ultraviolet light to destroy dissolved organic matter (Armstrong and Tibbitts, 1968), and the two subsamples are analyzed in sequence--the raw subsample followed by the irradiated. An increase in signal sensitivity (the signal increase due to a standard addition) indicates the presence of fast-reacting chelators, thought to be like EDTA and other strong complexing agents. An increase in the apparent metal concentration (basically the initial signal divided by the sensitivity) indicates the presence of slow-reacting chelators, thought to be weak complexers like amino acids. Complete reaction within 15 minutes is considered fast here. In this way information on the complexing of zinc, cadmium, lead and copper may be obtained. In this study, significant complexing of only zinc, cadmium, and copper was observed and reported.

Both filtered and unfiltered samples were analyzed by ASV, and in pairs of raw and irradiated subsamples. Zinc and copper concentrations were also determined by atomic absorption on some samples to check the results by ASV. The APDC-MIBK (amino pyrolidine dithiocarbamate-methyl isobutyl ketone) extraction scheme of Brooks et al., (1967) was used in these analyses.

Extraction and Analysis of Trace Metals in Sediments and Suspended Solids. Trace metals were extracted into 1 M sodium citrate buffer under strong oxidizing conditions followed by strong reducing conditions (Jenne and Ball, in preparation). The range in chemical conditions provided is similar to the extremes encountered in natural water systems. Extraction was carried out in acid cleaned high density polyethylene bottles using reagents precleaned by adding APDC and extracting with three aliquots of MIBK. To reduce and equalize the iron interference in subsequent APDC-MIBK extraction of other metals, the extracts were diluted to a range of iron concentrations of 40-70 mg/ℓ. Iron and manganese were determined directly on the dilutions by atomic absorption. The other metals of interest were concentrated by the APDC-MIBK method of Brooks et al., (1967) using two MIBK aliquots which together recovered 95 percent of each metal. Recovery effectiveness was confirmed by extracting random diluted extracts with additional aliquots of MIBK and determining the amount of additional metal removed.

Each set of sample extracts in sodium citrate was analyzed on two successive working days. Standard curves for iron and manganese were determined each day using standard solutions prepared earlier. Standard curves were determined one day only but in duplicate for the extracts of zinc, copper, cobalt, nickel and lead in sediment fraction samples and for zinc and copper in suspended solid samples. The points, excluding the blanks, were fitted to a second order polynomial by the least squares method and the blanks and the intercept were compared. In all cases the agreement was good, so the coefficients for the curve were recalculated using all the points, and the new intercept was taken as the analytical blank.

The coefficients of variation for the analyses of the sediment extracts are, for the iron and manganese analyses ∿2 percent, and for the zinc, copper, cobalt, nickel and lead analyses ∿5 percent. The overall coefficient of variation on replicate procedures for separation through analysis is estimated as ∿5 percent for iron and manganese, and ∿10 percent for the other metals.

The interstitial water samples were handled in the same way as the sediment and suspended solids samples. Since the volume of sample was small (less than 25 mℓ) most of the analytical values for trace metals were very close to the detection limits.

The detection limits and coefficients of variation for analyses of water for the several analytical methods used in this study are listed in table 2.

TABLE 2.--*Detection limits and coefficients of variation in analytical techniques used for water analyses*

Analysis		Detection Limit	Coefficient of Variation	Level
Wastewater				
Colorimetric	Zn	20 μg/ℓ	20%	60 μg/ℓ
AAS*	Zn	20 μg/ℓ	5%	100 μg/ℓ
Bay Water				
ASV**	Zn	0.1 μg/ℓ	3.7%	2.5 μg/ℓ
	Cd	0.01 μg/ℓ	7%	0.3 μg/ℓ
AAS Ⓦ (Solvent extraction)	Zn	0.3 μg/ℓ	15%	3.9 μg/ℓ
	Cu	0.7 μg/ℓ	7.8%	2.7 μg/ℓ
Interstitial water				
AAS	Fe*	1.0 mg/ℓ	5%	10.0 mg/ℓ
	Mn	0.3 mg/ℓ	5%	3.0 mg/ℓ
AAS Ⓦ (Solvent extraction)	Zn	.01 mg/ℓ	10%	.10 mg/ℓ
	Cu	.01 mg/ℓ	10%	.10 mg/ℓ
	Co	.01 mg/ℓ	10%	.10 mg/ℓ
	Ni	.01 mg/ℓ	10%	.10 mg/ℓ
	Pb	.05 mg/ℓ	10%	.50 mg/ℓ

*AAS - Atomic Absorption Spectrometry
**ASV - Anodic Stripping Voltammetry

RESULTS

Zinc Input from Wastewater Treatment Facilities. The zinc concentrations observed in effluents from the eight wastewater treatment facilities identified as significant contributors to the zinc loading are plotted with time in figure 2. The zinc concentrations varied nearly three orders of magnitude between facilities and concentrations within one facility varied nearly two orders of magnitude.

The cumulative zinc input from wastewater discharges was determined by taking the products of the 5-day average concentrations and the respective discharge rates for the same time period and summing over all eight facilities. The results are shown in figure 3. The linear regression correlation coefficient for the cumulative discharge with time is very close to unity, a surprising result considering the extremities of the variations in zinc concentration in effluents. The rate that soluble zinc is discharged to the study area appears to be remarkably constant at 0.077×10^6 grams per day over the entire study period.

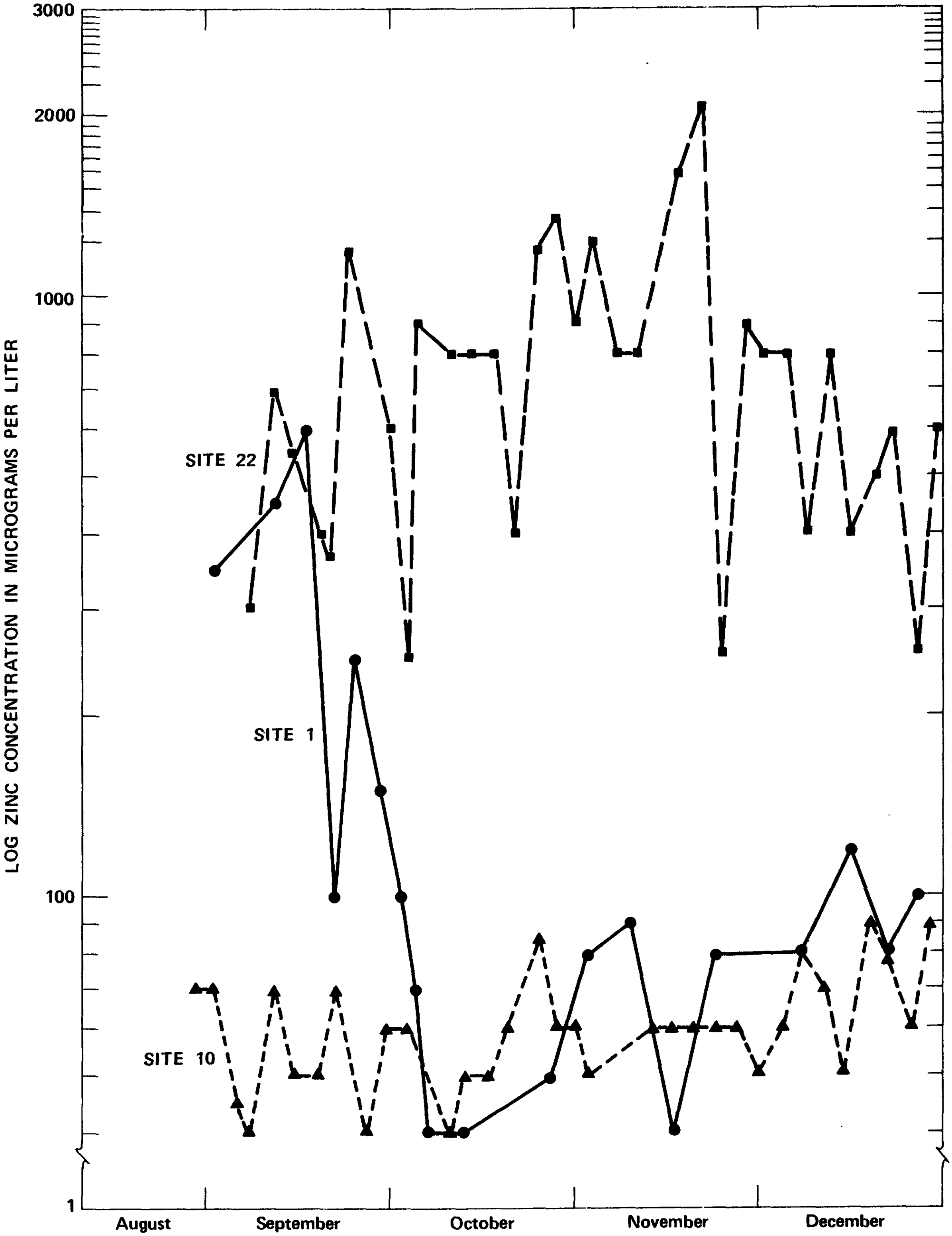


FIGURE 2.--Zinc concentrations in effluent from eight sewage treatment facilities.

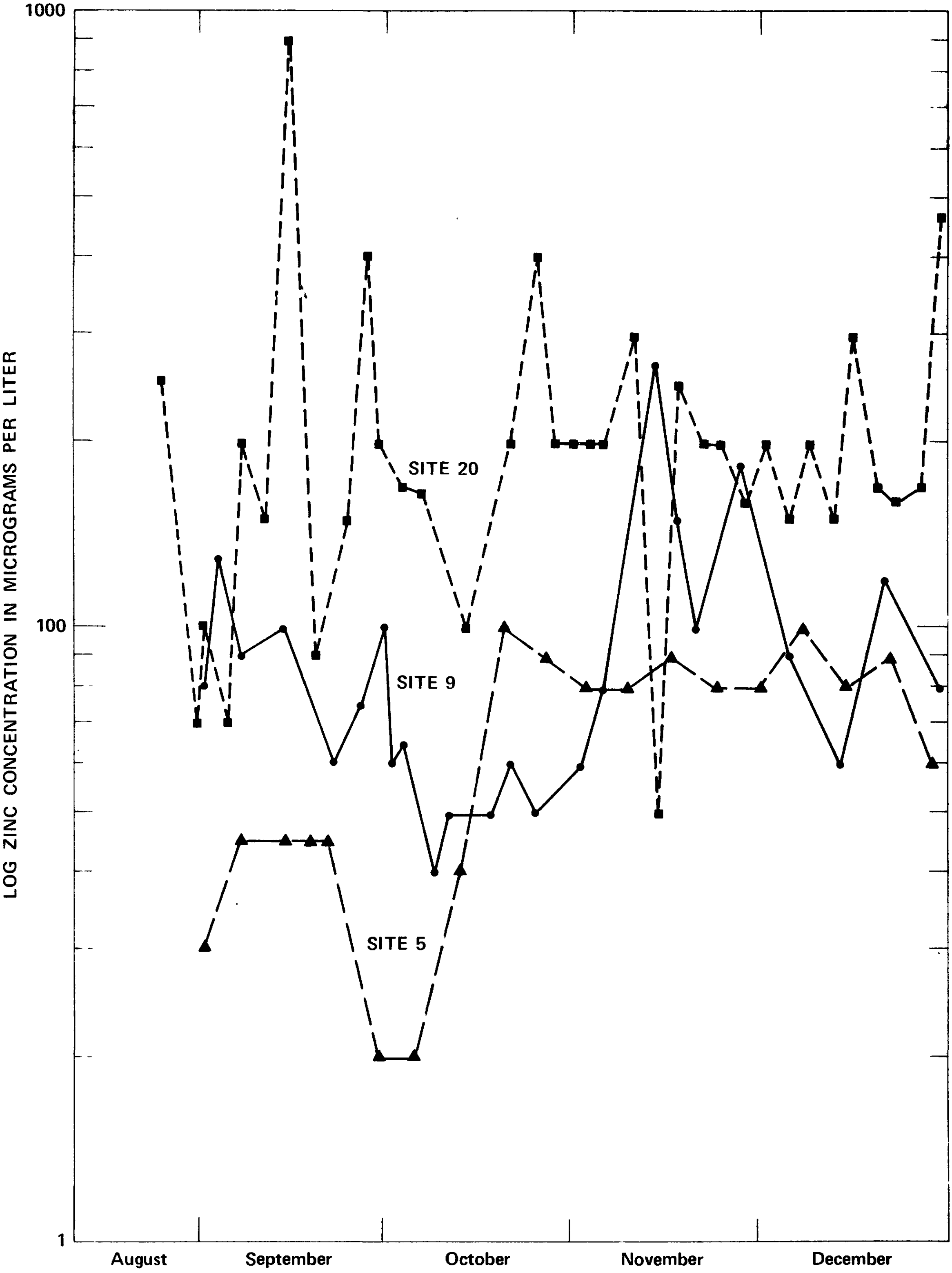


FIGURE 2.--Continued.

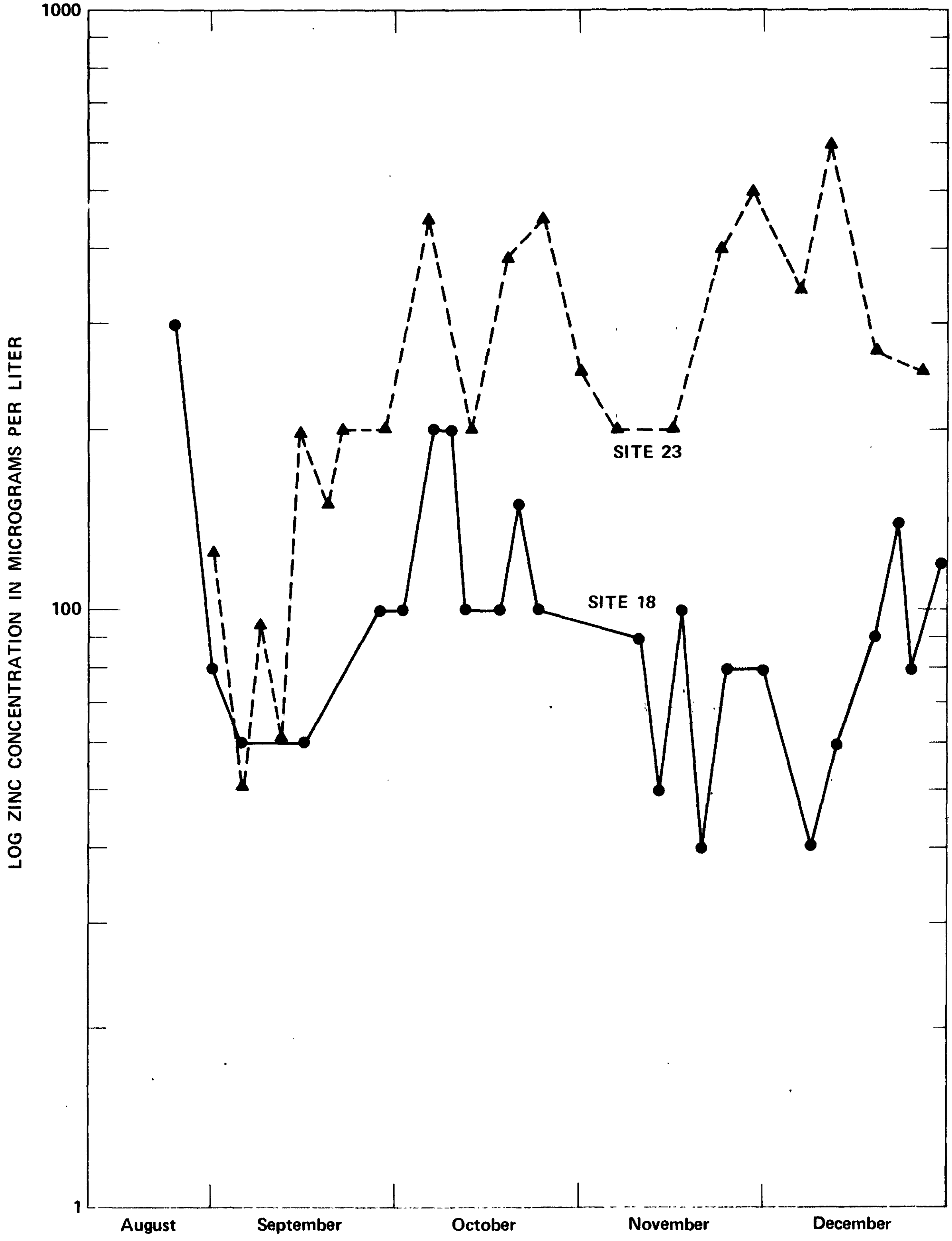


FIGURE 2.--Continued.

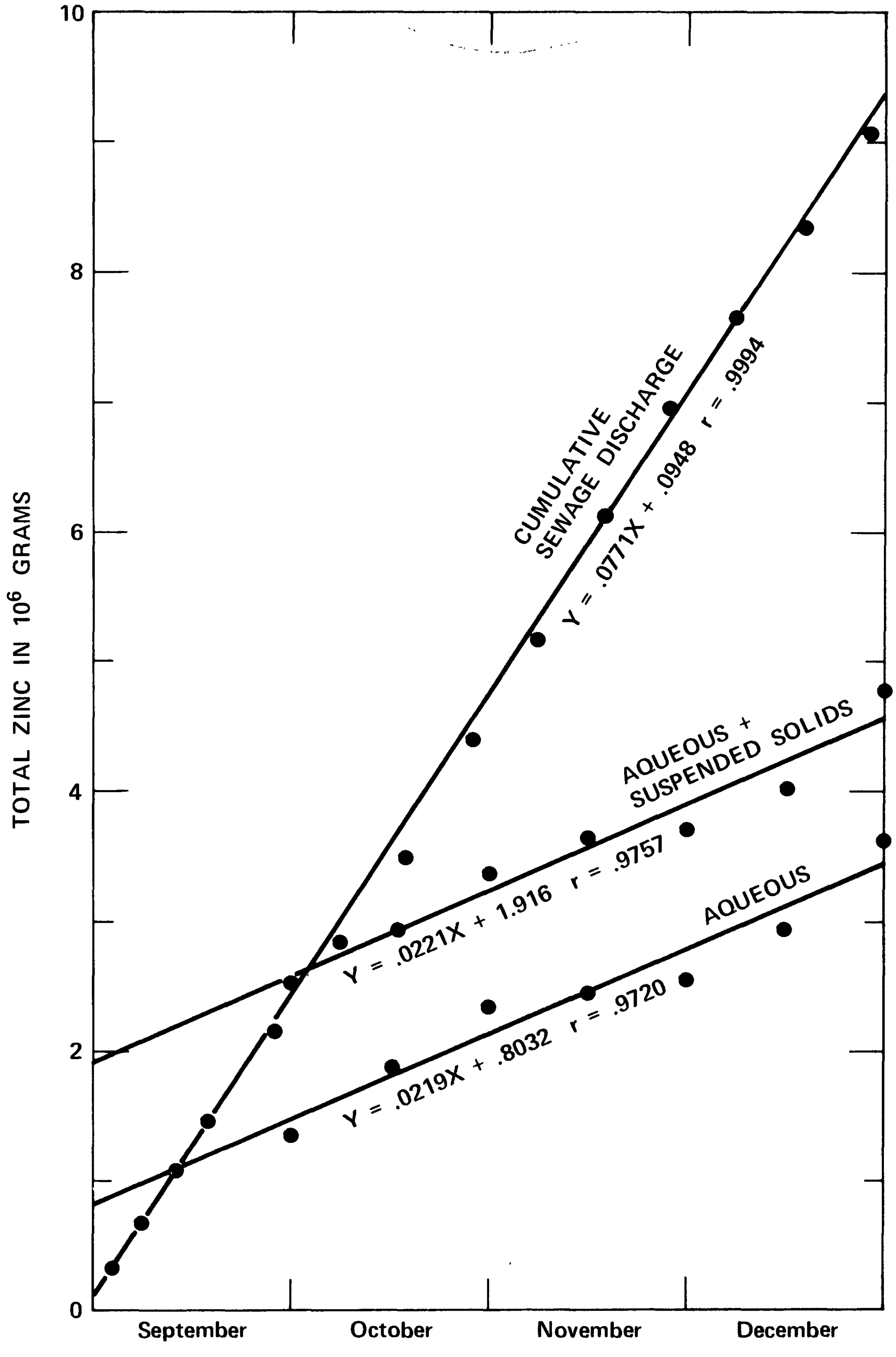


FIGURE 3.--The cumulative discharge of zinc in sewage effluent and the total mass of zinc in the aqueous and combined aqueous and suspended solid phases.

The Quantitative Distribution of Zinc in Bay Water. The fields of figures 4 and 5 depict time-versus-water volume in the study area. On the field of figure 4 are plotted the best estimates of the aqueous zinc concentration, based upon eight to ten separate analyses at each station. Analyses by ASV are usually more precise than those by atomic absorption so when values from both types of analyses were in general agreement, the ASV values are reported. This is the case for the samples from the last two cruises. In samples from the first two cruises, the zinc concentrations were very low and interferences were encountered in the ASV analyses making them less precise than usual. The values obtained by atomic absorption were close to the detection limit. Values reported for the first two cruises are averages of the four values which agreed most closely with each other. The coefficient of variation on these values is estimated at about 30 percent. In figure 5 are plotted the sums of the aqueous zinc concentration and the concentration on the suspended solids expressed as $\mu g/\ell$ in the water. On both figures, the isopleths were drawn with the aid of a 10 point divider.

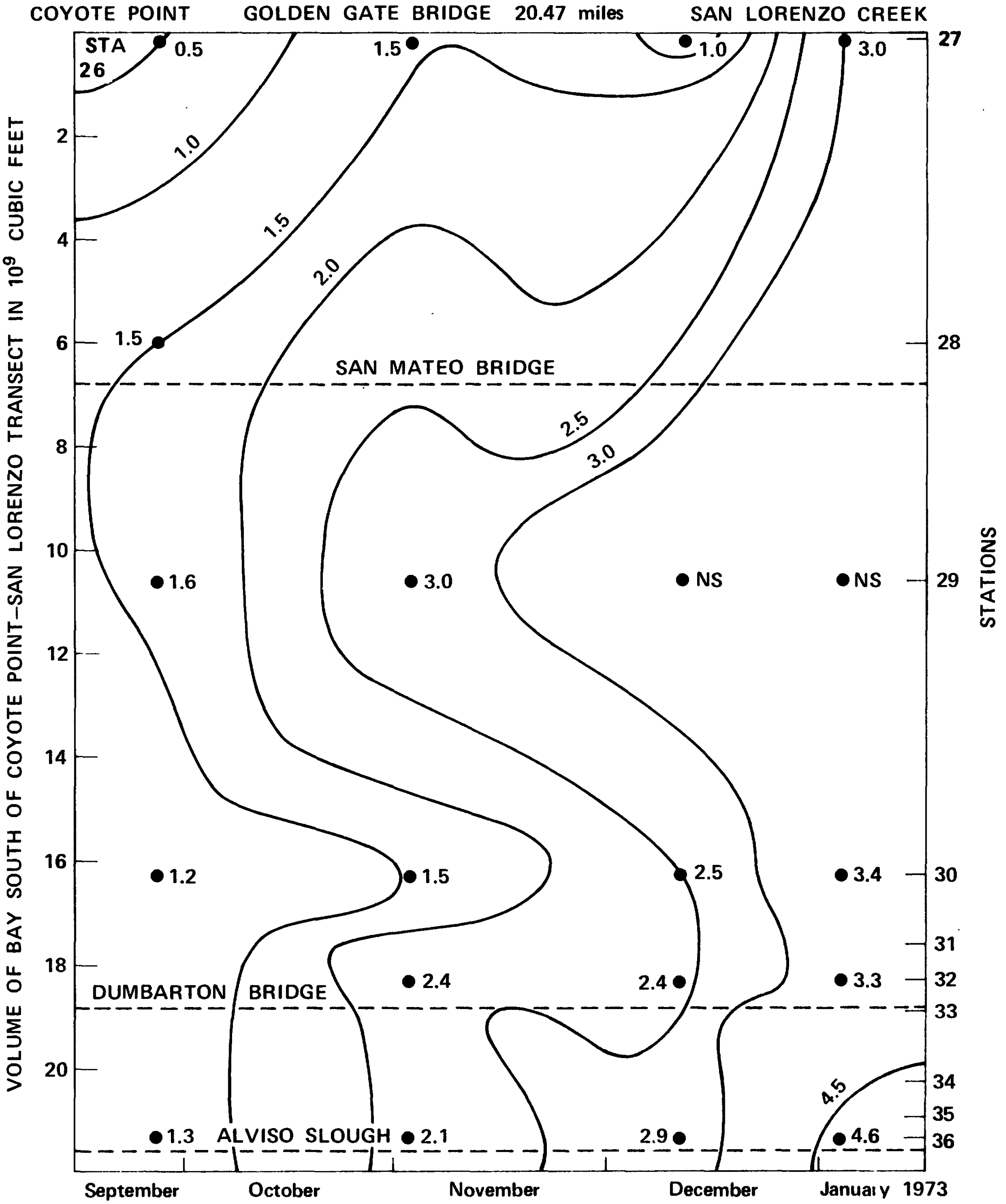


FIGURE 4.--The distribution of the aqueous zinc concentration on a time versus volume field.

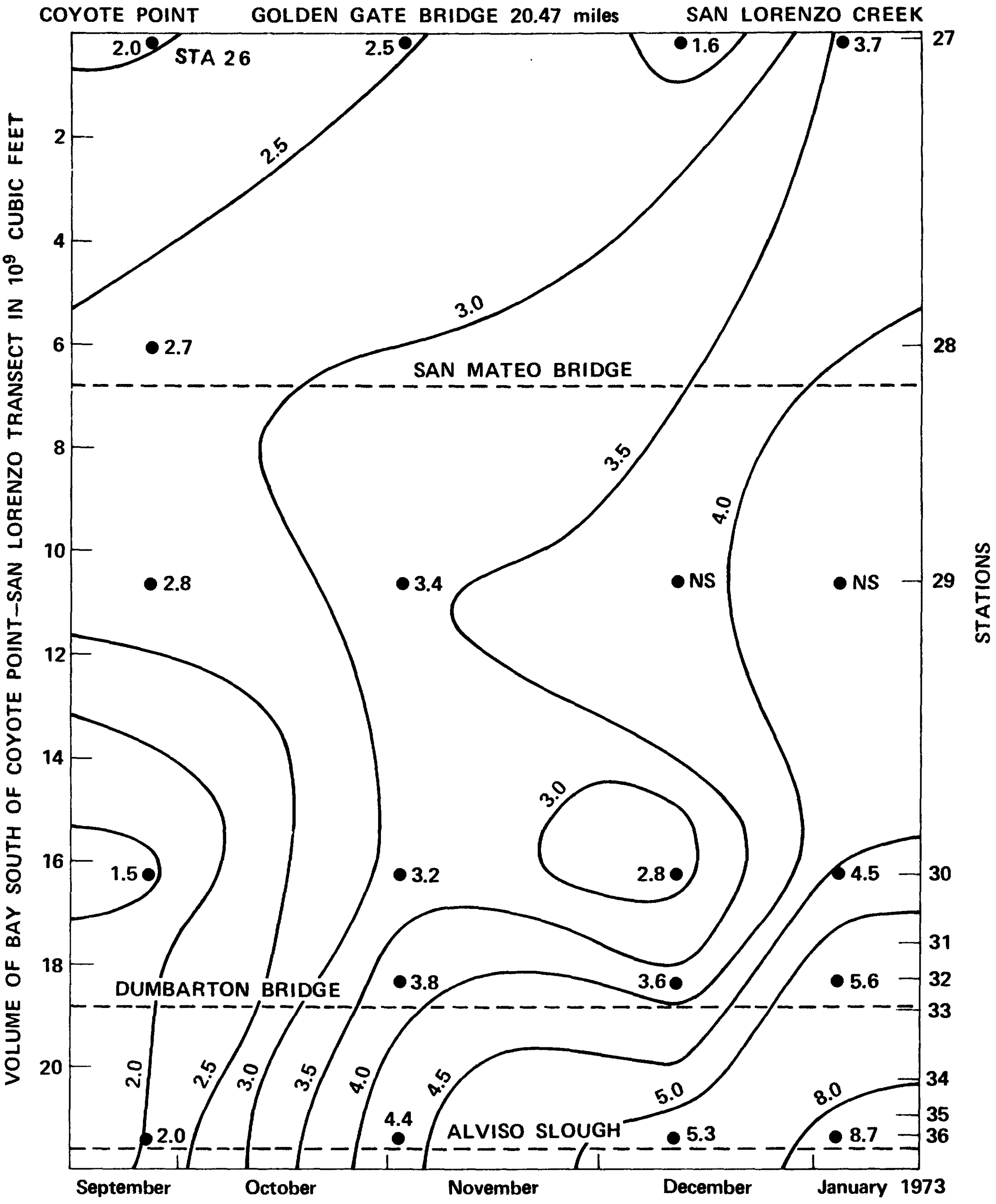


FIGURE 5.--The distribution of the zinc concentration in the combined aqueous and suspended solids phases on a time versus volume field.

The mass of zinc present in the water was estimated at six dates by summing the product of the volume and the concentration over 20 volume increments. These calculated values appear in figure 3. There is a slight upward trend with time in the mass of zinc present in both the aqueous phase and the combined aqueous and suspended solid phases. The difference between the linear regression coefficients of these two sets of points suggests that the mass of zinc present in the suspended solids is fairly constant at 1.1×10^6 grams. The apparent rate of increase in the mass of zinc in the aqueous phase of bay water is 0.021×10^6 grams/day. The difference between this rate and the rate of loading from sewage effluent is 0.055×10^6 grams/day which represents the combined losses due to the flux into the sediments and dispersion out of the study area.

The Chelation of Zinc, Copper and Cadmium. Figure 6 shows the zinc concentrations determined by ASV in raw and irradiated pairs of unfiltered samples, and the percent increase in the zinc and copper sensitivity which accompanied the irradiation. Figure 7 is an identical plot for the filtered water samples. In general, the pairs of analyses and the sensitivity bar graphs together indicate that 1) substantial amounts of zinc are sequestered by slowly reacting chelators, 2) fast reacting chelators are also strongly affecting both zinc and copper and 3) there appear to be no systematic differences in the results between filtered and unfiltered samples. It should be noted that the unfiltered samples are, nevertheless, settled and decanted thus removing particles with Stokes' diameters greater than 0.1μm (Bradford, 1972).

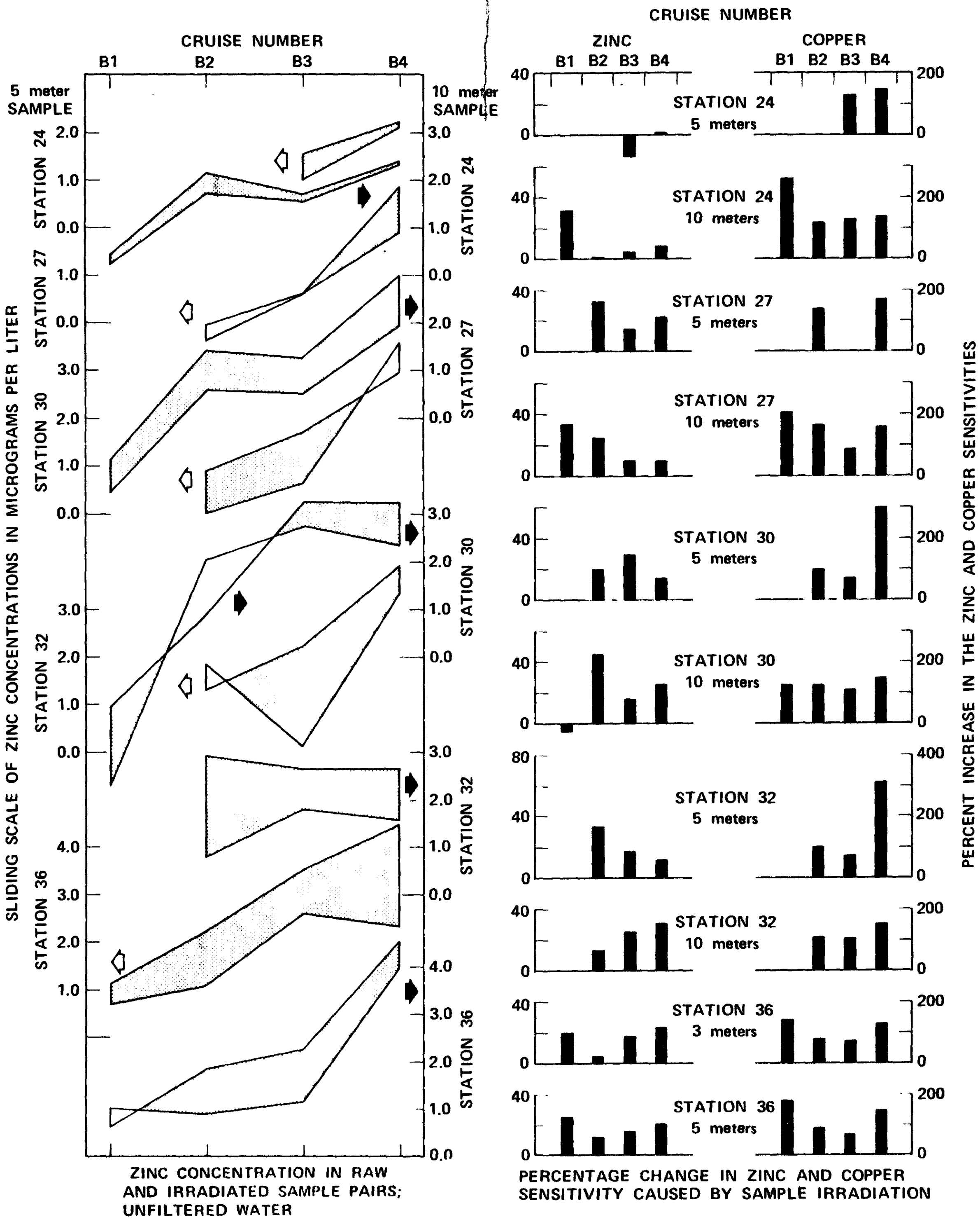


FIGURE 6.--The effects of irradiation with ultraviolet light on the apparent zinc concentration and on the zinc and copper sensitivity in *unfiltered* samples analyzed by anodic stripping voltammetry. Gray--increase in concentration with irradiation. White--decrease in concentration with irradiation.

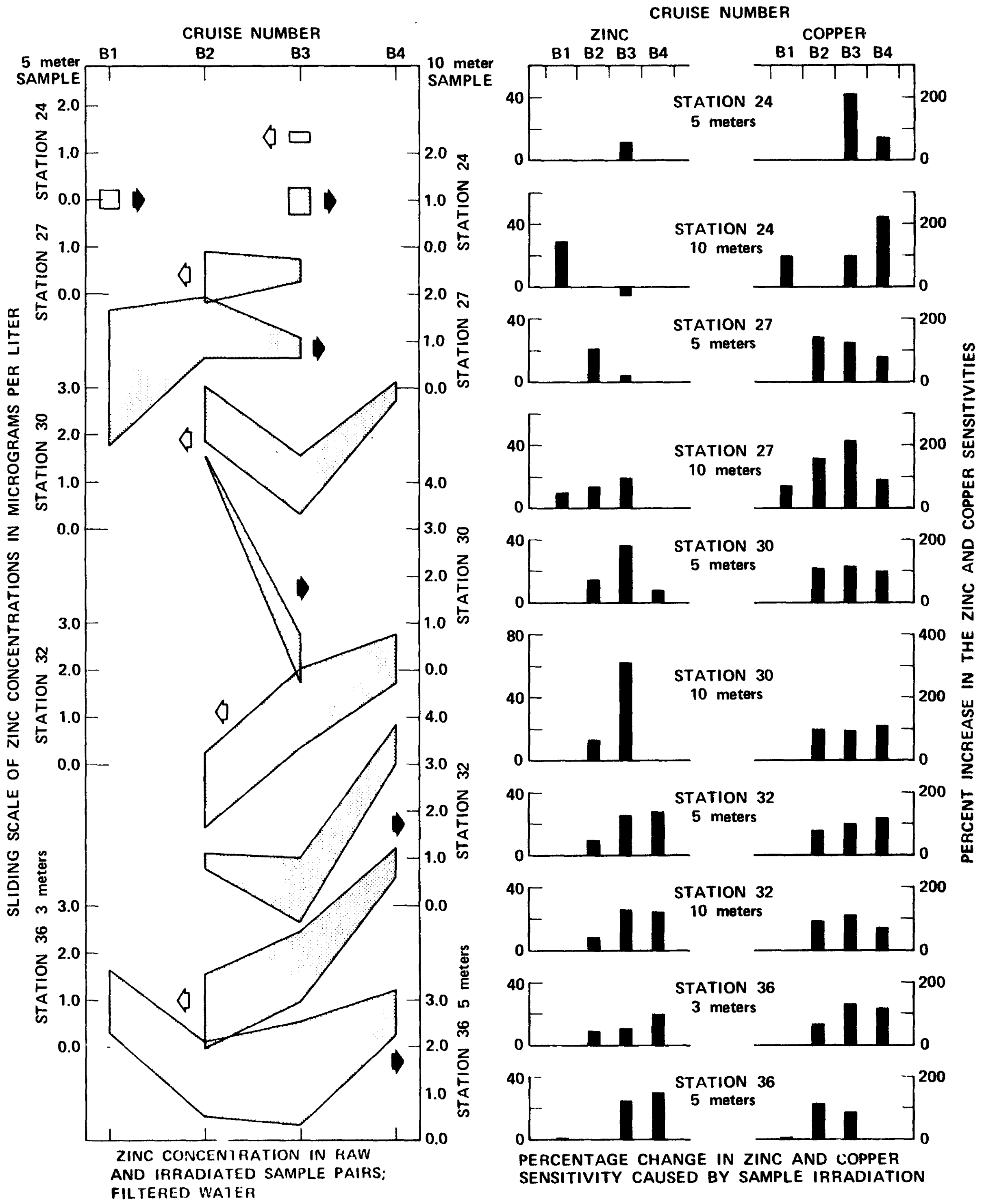


FIGURE 7.--The effects of irradiation with ultraviolet light on the apparent zinc concentration and on the zinc and copper sensitivity in *filtered* samples analyzed by anodic stripping voltammetry.

To determine whether the various methods of sample handling had a significant effect upon the analytical results, differences between pairs of analyses (e.g., the filtered sample zinc concentration minus the unfiltered sample zinc concentration) were summed over all the measurements and the Student "t" test applied to the Null Hypothesis that the mean of the differences is not significantly different from zero. The results are shown in table 3.

From rows 1 and 3, irradiation caused a significant increase in the apparent zinc concentration averaging 0.63 μg/ℓ in unfiltered samples and 1.00 μg/ℓ in filtered samples; the probability that the filtered and unfiltered sample zinc analyses are <u>not</u> different populations is 0.09 (not shown). From rows 2 and 4, filtration caused no significant change in the zinc concentration in irradiated samples, and only a 9 percent probability of a difference in the raw samples. From rows 5 and 6, irradiation caused significant increases in the sensitivity for both zinc and copper; the increases were identical for zinc between filtered and unfiltered samples but, from row 7, the increase in copper sensitivity was significantly larger in the unfiltered samples. The basic statistics for cadmium concentrations in raw and irradiated samples are present in table 4.

TABLE 3.--*Mean* ($\overline{X}$), *standard deviation* (S), *and probability* (P) *that the mean of the differences in concentrations and sensitivities caused by filtration and* UV[†] *irradiation in* N *water samples is not different from zero*[*]

Summation over N of	Zinc				Copper			
	$\overline{X}$	S	N	P	$\overline{X}$	S	N	P
1. (Raw unfiltered) - (UV unfiltered)	- .63	.83	44	<.001				
2. (Raw unfiltered) - (Raw filtered)	.45	1.42	29	.09				
3. (Raw filtered) - (UV filtered)	- 1.00	.78	30	<.001				
4. (UV unfiltered) - (UV filtered)	.087	1.47	30	.73				
5. ([UV sensitivity - Raw sensitivity] ÷ Raw sensitivity) unfiltered (%)	16.3	14.5	44	<.001	143	58.2	40	<.001
6. ([UV sensitivity - Raw sensitivity] ÷ Raw sensitivity) filtered (%)	16.3	13.7	30	<.001	112	47.5	32	<.001
7. Difference ([Row 5] - [Row 6])					30.7	54.3	72	.025

[*] The description in parentheses is the sample analytical value substituted.

[†] UV, ultraviolet light.

TABLE 4.--*The range, mean, and standard deviation of cadmium analyses in raw and irradiated bay water* (μg/ℓ)*

	$\overline{X}$ μg/ℓ	S	N
Raw Cd	.176	.0608	81
UV Cd	.199	.0699	79

* $\overline{X}$ Mean of analyses

S Standard deviation

N Number of samples analyzed

The mean cadmium values in raw and irradiated samples are significantly different at the 0.1 percent confidence level. Thus it appears that irradiation released an average of 0.023 μg/ℓ of cadmium from slow reacting chelators, or approximately 12 percent of the total cadmium present. There also appeared to be a trend toward lower cadmium values going northward. Values ranged from approximately 0.3 μg/ℓ at station 36 to approximately 0.1 μg/ℓ at station 21. No concentration differences due to filtration were apparent.

Trace Metals in Suspended Solids. The concentrations of suspended solids and the concentrations of four trace metals in those solids are shown in table 5. In a preliminary analysis of the data, no significant differences with depth or station were found suggesting that the distribution of suspended solids and trace metals in those solids is spatially homogeneous. The mean values between cruises were found to be different, however. The statistical probabilities of the Null Hypothesis that no differences exist are shown in table 6.

TABLE 5.--*Suspended-solids concentration and the concentrations of* Fe, Mn, Zn, *and* Cu *in the solids**

Cruise	Station	Depth meters	Solids mg/l	Fe mg/g	Mn µg/g	Zn µg/g	Cu µg/g	Cruise	Station	Depth Meters	Solids mg/l	Fe mg/g	Mn µg/g	Zn µg/g	Cu µg/g
B1	36	5.5	11.9	16.7	741	109	44	B2	36	3	10.5	26.1	821	164	48
	36	5	11.2	11.1	326	38	17		36	5	12.9	21.7	671	228	68
	36	4	9.2	13.9	725	40	23		32	5	9.4	27.1	998	193	48
	36	3	12.6	8.4	252	16	9		32	10	14.3	30.3	1,140	66	28
	36	5.5	11.2	26.9	811	106	30		30	5	13.8	32.0	1,150	96	75
	36	5	12.2	15.2	646	75	17		30	10	22.1	33.3	1,300	93	33
	36	4	9.6	20.8	588	90	26		29	5	18.4	29.2	765	24	11
	36	3	9.4	15.3	594	71	28		29	10	20.2	32.4	1,040	19	29
	29	10	22.2	19.6	893	156	60		27	5	13.9	30.3	551	54	29
	28	10	12.3	16.5	780	90	29		27	10	12.7	29.5	645	101	34
	26	10	16.4	14.8	711	92	36		22	10	16.9	35.7	936	70	36
	Mean	$\bar{X}$	12.7	16.3	642	80	29		Mean	$\bar{X}$	15	29.8	910	101	40
	Standard deviation	S	3.8	5	147	39	14		Standard deviation	S	4	3.8	238	68	19
B3	36	3	17.1	30.8	661	116	45	B4	36	3	29.0	40.4	1,390	164	32
	36	5	21.1	32.4	893	128	52		36	5	20.6	39.7	1,430	167	16
	32	5	12.7	29.9	548	91	35		32	5	20.6	38.6	1,360	138	20
	32	10	13.5	30.2	647	90	59		32	10	14.2	34.6	1,330	118	6
	30	5	7.7	27.4	717	30	16		30	5	13.7	34.5	1,060	124	20
	30	10	7.7	29.5	620	58	25		30	10	4.4	37.9	1,500	124	<10
	27	5	4.9	27.3	399	229	28		27	5	8.0	37.8	962	118	8
	27	10	4.8	24.7	1,310	28	<12		27	10	4.9	43.5	1,080	84	<9
	24	5	9.9	40.8	1,010	151	51		24	10	11.0	36.6	867	102	4
	24	10	13.4	39.0	1,050	122	87		24	5	21.0	39.1	895	162	26
	22	5	7.1	35.4	919	182	87		21	5	16.2	37.3	748	157	20
	Mean	$\bar{X}$	10.9	31.6	797	111	45		Mean	$\bar{X}$	14.9	38.2	1,147	133	16
	Standard deviation	S	5.2	5	263	62	26		Standard deviation	S	7.6	2.6	262	27	9

*Mean and standard deviation values in some cases are shown with an additional significant figure to avoid rounding error in subsequent statistical tests.

TABLE 6.--*The probabilities that no significant differences exist between the means of suspended-solids data**

Iron	B1	B2	B3	B4	Manganese
B1		.012	.13	<.001	B1
B2	<.001		.33	.025	B2
B3	<.001	.40		.0016	B3
B4	<.001	<.001	.003		B4

Zinc	B1	B2	B3	B4	Copper
B1		.19	.13	.014	B1
B2	.43		.64	.0014	B2
B3	.22	.74		.0017	B3
B4	.006	.20	.33		B4

*To save space two tables are combined in each square with the diagonal as the dividing line. The number in each row and column block is the probability that no difference exists in the concentration means of the listed constituent between the row cruise and the column cruise.

The following trends are observed: 1) the mean iron and manganese concentrations increase with time except between B2 and B3 where the difference is not significant, 2) the mean zinc concentration increases with time but only the difference between B1 and B4 is significant, and 3) the mean copper concentration in B4 is lower than all the others for an unknown reason.

Interstitial Water. Because of the small sample size, the analyses for copper, zinc, cobalt, nickel and lead were close to the detection limits and are generally unfit for detailed interpretation. There were no trends apparent in the Eh, pH or alkalinity values which would suggest grouping this data for other statistical analyses. Both iron and manganese appeared to be more concentrated in surficial samples: the range in surficial layers was 10.5 - 40.5 µg/ℓ for iron and 5.0 - 30.4 µg/ℓ for manganese as opposed to the ranges in the 9 - 12 cm layers of 4.8 - 19.6 µg/ℓ for iron and 0.8 - 11.3 µg/ℓ for manganese. Iron and manganese were positively correlated with a correlation coefficient of 0.640. A basic statistical summary of these data is presented in table 7.

TABLE 7.--*Statistical summary for the parameters measured in 32 samples of interstitial water*

	Eh, mν vs. Calomel	pH	Alkalinity meq/1 *	Metal concentrations in mg/ℓ						
				Fe	Mn	Zn	Cu	Co	Ni	Pb
Mean	-83	7.07	25.3	13.6	8.42					
Range	-177 - + 13	6.42 - 7.71	15.0 - 39.1	4.8 - 40.5	0.8 - 32.2	0 - .10	0 - .07	0 - .06	0 - .10	0 - .06
Standard Deviation	40	0.37	6.9	8.6	8.3					
Detection Limit				1.0	0.3	.01	.01	.01	.01	.05

* meg/ℓ milliequivalents of alkalinity per liter.

Bed Sediment. The results of the analyses for seven heavy metals in two size fractions of bay sediments are given in table 8. The average concentration of these trace metals in shale is included for reference. The means of all metal concentrations except nickel are significantly different between the two size fractions. Metal concentrations are higher in the <20 µm fraction over the 20 µm-2 mm fraction by a factor of 2 in iron, manganese and cobalt, a factor of 3 in copper and a factor of 5 in lead.

Some trends are apparent by inspection only: 1) manganese is slightly more concentrated in the surficial layers in both size fractions; 2) zinc is slightly more concentrated in both fractions the closer one approaches the south end of the bay; 3) lead is more concentrated in the <20 µm fraction only in the two samples closest to the San Mateo Bridge (28E and 29W) but is more concentrated in the larger fraction only in the two southernmost samples; 4) in most samples, the nickel concentration is larger in the <20 µm fraction, but in the three samples just south of the Dumbarton Bridge (33W, 33E, and 34) it is larger in the larger size fraction.

TABLE 8.--*The distribution of three size fractions and the concentrations*

[Values are reported to one additional significant figure to

			Dry Sample Fractionation			
Station Number	Core Depth(cm)	Moisture Fraction	Fraction >2mm	Fraction 20μm-2mm	Fraction <20μm	Percent Recovery
28E	0-3	0.44	0.0	0.53	0.47	103
28E	3-6	.43	.009	.54	.45	98
28E	6-9	.35	.012	.75	.24	107
28E	9-12	.34	.007	.70	.29	98
29W	0-3	.54	.022	.68	.30	104
29W	3-6	.52	.0	.71	.29	94
29W	6-9	.52	.0	.70	.30	100
29W	9-12	.56	.0	.58	.42	105
29E	0-3	.26	.015	.86	.12	88
29E	3-6	.27	.0	.91	.09	85
29E	6-9	.29	.0	.75	.25	96
29E	9-12	.32	.0	.64	.36	88
30W	0-3	.49	.020	.62	.36	101
30W	3-6	.42	.011	.60	.38	105
30W	6-9	.40	.016	.69	.30	96
30W	9-12	.42	.014	.58	.40	102
30E	0-3	.53	.0	.33	.67	113
30E	3-6	-	.0	.26	.74	86
30E	6-9	.46	.0	.50	.50	108
30E	9-12	.38	.0	.59	.41	90
32W	0-3	.48	.068	.47	.46	97
32W	3-6	.48	.002	.29	.71	100
32W	6-9	.51	.003	.37	.62	94
32W	9-12	- - - - -	- - - - -	- - -No Sample-	- - - - -	- - - -
33W	0-3	.52	.0	.33	.67	105
33W	3-6	.49	.009	.35	.64	107
33W	6-9	.50	.0	.38	.62	104
33W	9-12	.48	.011	.36	.63	104
33E	0-3	-	.0	.21	.79	108
33E	3-6	.51	.0	.23	.77	98
33E	6-9	.54	.010	.34	.65	106
33E	9-12	.54	.017	.29	.69	100
34	0-3	.52	.004	.36	.64	105
34	3-6	.51	.0	.32	.68	105
34	6-9	.51	.005	.28	.72	103
34	9-12	.50	.006	.26	.73	114
36	0-3	.51	.025	.34	.63	110
36	3-6	-	.018	.35	.63	105
36	6-9	.47	.0	.30	.70	100
36	9-12	.50	.007	.28	.72	109

Sample mean

Standard deviation

Average shale†

†Average shale composition from Krauskopf [1967]. These values are obtained by total digestion.

of heavy metals in two size fractions of sediments from San Francisco Bay

avoid rounding error in the proceeding statistical treatment]

WITHIN THE 20 MICRON - 2 MM SOLIDS FRACTION							
FE (mg/g)	MN (μg/g)	ZN (μg/g)	CU (μg/g)	CO (μg/g)	NI (μg/g)	PB (μg/g)	Station Number
13.8	201	38.2	8.7	1.9	12.0	2.0	28E
12.4	159	32.1	7.3	2.7	10.7	2.0	28E
10.5	111	22.6	5.7	1.6	7.7	0.8	28E
13.2	143	18.3	2.6	1.4	8.1	0.3	28E
21.3	248	35.9	15.9	2.2	13.3	4.3	29W
26.4	164	42.3	19.1	2.3	16.8	5.2	29W
28.3	170	45.1	21.4	2.5	16.3	4.9	29W
25.5	154	80.6	18.6	2.3	15.1	5.0	29W
14.3	245	29.5	5.2	3.5	14.4	1.0	29E
16.0	190	31.1	5.5	2.5	14.6	0.4	29E
14.4	134	20.9	4.1	2.1	13.6	0.0	29E
18.9	200	35.8	4.9	2.8	17.3	0.0	29E
18.9	185	40.7	11.8	1.8	25.1	0.9	30W
17.8	139	29.0	11.4	2.1	25.4	1.1	30W
20.0	137	26.5	11.6	2.0	26.2	0.3	30W
23.1	159	22.1	9.0	2.0	23.5	0.0	30W
25.9	173	38.1	12.8	2.8	33.0	3.5	30E
25.3	289	50.8	14.0	3.6	46.7	2.7	30E
21.2	248	27.0	6.8	2.0	25.9	2.1	30E
20.7	189	41.5	5.1	2.5	29.1	0.8	30E
32.8	212	76.9	23.8	1.3	26.0	0.0	32W
57.5	306	59.8	19.6	2.6	24.1	0.8	32W
52.3	318	80.6	30.9	3.7	28.8	4.2	32W
- - - -							32W
26.0	290	62.3	26.2	2.3	40.0	3.2	33W
13.2	79	26.1	9.1	1.3	17.6	1.1	33W
11.8	75	27.3	11.5	1.4	18.3	1.1	33W
25.7	167	70.6	20.7	2.7	38.5	1.8	33W
38.5	493	109.8	36.9	4.7	58.3	4.9	33E
36.6	569	99.0	29.1	4.8	48.3	1.4	33E
35.2	350	80.9	25.6	0.6	42.5	1.5	33E
32.6	278	59.0	19.9	4.3	35.5	0.4	33E
27.2	184	50.3	28.8	3.0	31.4	0.9	34
23.2	129	38.8	22.0	2.8	30.5	2.5	34
21.3	300	62.5	13.5	6.6	23.5	12.1	34
20.2	330	61.9	11.6	5.3	20.1	12.7	34
17.5	591	50.2	8.0	4.3	14.9	12.3	36
16.6	277	50.3	7.9	4.3	14.5	8.5	36
19.0	225	68.8	19.5	8.9	40.8	9.1	36
19.1	272	61.2	16.0	8.2	39.3	7.6	36
23.42	232.9	48.8	14.9	3.1	25.3	3.2	
10.20	116.7	22.4	8.6	1.8	12.2	3.6	
47.0	850	80	57	20	95	20	

TABLE 8.--*The distribution of three size fractions and the concentrations of heavy metals in two size fractions of sediments from San Francisco Bay*--Continued

Station Number	WITHIN THE LESS THAN 20 MICRON SOLIDS FRACTION						
	FE (mg/g)	MN (µg/g)	ZN (µg/g)	CU (µg/g)	CO (µg/g)	NI (µg/g)	PB (µg/g)
28E	42.4	502	86.0	40.3	7.3	38.6	47.3
28E	45.1	543	86.0	40.4	7.5	29.3	25.5
28E	49.1	430	115.0	44.5	12.4	33.0	34.0
28E	46.1	490	82.7	324.4	10.2	54.1	19.5
29W	44.8	616	94.8	42.7	9.7	23.4	35.1
29W	41.9	259	119.1	39.7	14.6	16.2	32.4
29W	43.7	279	100.0	39.4	16.1	25.8	48.5
29W	41.4	308	91.6	41.6	9.4	47.7	29.9
29E	58.7	807	84.1	39.0	22.5	51.1	10.2
29E	45.8	458	57.6	32.8	11.8	41.6	16.8
29E	50.2	402	58.6	35.7	12.1	23.2	14.1
29E	43.8	384	45.8	27.1	9.2	32.9	4.5
30W	42.3	378	77.1	30.0	8.3	25.7	22.9
30W	20.7	154	30.4	13.6	2.7	21.5	8.5
30W	47.6	336	81.1	28.3	5.5	34.9	14.2
30W	44.9	354	63.6	27.2	4.1	29.3	6.4
30E	36.9	643	64.7	20.5	7.1	34.5	16.1
30E	71.3	1508	155.2	54.1	12.5	99.6	36.5
30E	54.2	776	77.4	22.5	7.0	39.4	18.6
30E	49.9	476	101.2	21.5	7.5	32.5	16.3
32W	48.7	439	74.3	17.1	4.8	42.7	11.9
32W	44.6	382	48.9	12.0	3.4	27.0	3.9
32W	43.2	333	71.3	18.0	6.9	24.7	1.3
32W							
33W	48.9	532	59.2	32.1	7.4	11.7	20.1
33W	47.0	355	95.3	26.9	6.2	7.0	20.6
33W	50.9	404	95.2	27.2	7.5	10.6	20.1
33W	53.4	441	95.8	33.3	7.6	16.3	21.9
33E	50.1	326	110.5	37.6	7.7	14.7	30.5
33E	47.6	719	96.8	26.5	6.6	20.4	20.8
33E	54.2	614	95.7	30.4	7.8	22.7	19.6
33E	51.8	561	92.3	32.3	7.6	19.3	13.8
34	47.6	407	93.4	47.5	9.0	14.2	15.7
34	50.2	404	118.3	46.2	10.4	16.4	17.8
34	52.3	439	104.3	37.9	9.0	18.8	16.7
34	47.9	444	90.1	33.0	7.7	21.1	14.8
36	42.7	620	99.2	29.2	8.1	18.9	17.0
36	47.4	376	192.8	60.3	11.9	62.9	14.9
36	53.1	433	164.5	52.5	9.4	69.0	10.8
36	47.4	401	166.3	42.8	8.2	52.0	8.1
	47.43	480.4	93.2	41.2	8.8	31.4	19.4
	7.24	218.1	33.2	47.8	3.6	18.4	10.8
	47.0	850	80	57	20	95	20

Interrelationships between the heavy metal concentrations in the sediments were examined by two separate multivariate statistical procedures; factor analysis and multiple regression. Factor analysis with the varimax rotation solution was used by Dawdy and Feth (1967) and thoroughly discussed by Hitchon et al., (1971). In this procedure, the relationships between a number of variables are described by a fewer number of factors that represent common processes affecting the variance of the variables in the data set but can be identified only by considering known information about the variables. The fraction of each variable's total variance accounted by each factor equals the square of the factor loading. A variable's communality, representing the fraction of the variable's total variance accounted by all the factors together, equals the sum of the squares of each variable's factor loadings. In this analysis, the communality is unity when the total variance is completely accounted by all the factors. The variance of the entire data set accounted by each factor is represented by an eigenvalue.

To identify the minimum number of factors required to account for most of the variance in the data set, a principal component analysis was performed in which the maximum variance accounted by each successive factor was extracted from the data set. The less significant factors were then successively rejected until the communality of any variable, initially unity, decreased to below 0.95, indicating that a significant factor had been rejected. The varimax solution was then performed redistributing the variance to maximize that accounted by each factor to produce the rotated factor matrix.

In the principal component matrix only five factors were required to explain 96 percent of the sample variance in the 2 mm-20 μm fraction, but six factors were required to explain 97 percent of the variance in the <20 μm fraction.Elimination of the sixth factor here caused the communalities of both iron and nickel to decrease to 0.7. The rotated factor matrix loadings are shown in tables 9 and 10. The principal component matrices are not shown but have a similar appearance with loadings heavily weighed on the first factors. To make the tables more readable all loadings less than 0.3 (9 percent of the variance) are deleted.

TABLE 9.--*Factor loadings for the constituents of the 2 mm-20 µm size fraction**

Variable	Factor					Communalities
	1	2	3	4	5	
Fe	.888		.383			.989
Mn				.888		.991
Zn	.393	.307	.728	.361		.914
Cu	.494		.831			.953
Co		.551			.788	.979
Ni			.828		.409	.962
Pb		.929				.959

Principal component eigenvalues

1	2	3	4	5
3.776	1.658	.594	.443	.277

Principal component cumulative % of variance explained

1	2	3	4	5
53.9	77.6	86.1	92.4	96.4

Rotated factor matrix eigenvalues

1	2	3	4	5
1.246	1.383	2.150	1.104	.864

Rotated factor matrix cumulative % of variance explained

1	2	3	4	5
17.8	37.6	68.3	84.0	96.4

*Factors with eigenvalues <.2 were rejected before rotation. Loading <.3 are omitted from the table.

TABLE 10.--*Factor loadings for the constituents of the <20 µm size fraction**

Variable	Factor						Communalities
	1	2	3	4	5	6	
Fe	.886			.343			.953
Mn	.841					.443	.941
Zn				.934			.979
Cu			.987				.999
Co					.951		.997
Ni						.895	.973
Pb		.975					.992

Principal component eigenvalues

2.789	1.123	1.019	0.755	0.638	0.509

Principal component % of cumulative variance

39.9	55.9	70.5	81.2	90.4	97.6

Rotated factor matrix eigenvalues

1.609	1.030	1.016	1.092	1.017	1.071

Rotated factor matrix cumulative % variance

23.0	37.7	52.2	67.8	82.3	97.6

*Factors with eigenvalues <.2 were rejected before rotation. Loadings <.3 are omitted from the table.

In both matrices, the eigenvalues for each factor are nearly identical suggesting that no single factor plays a dominant role. There are, however, major differences in the distribution of factor loadings between the size fractions. In the <20 μm fraction, each factor tends to dominate a single variable while in the larger fraction, the factor loadings are more evenly distributed among the variables. The variance in the iron and manganese data are caused by the same factor in the <20 μm size fraction but by different factors in the larger size fraction. The iron and zinc variance are partially controlled by the same factor in both size fractions. Lead is heavily loaded in factor 2 in both size fractions suggesting that this factor is the same process in both cases.

The data were also analyzed by multiple linear regression techniques that formulate a first order equation in the independent variables and compute a multiple correlation coefficient between the calculated and observed dependent variables. The results of this analysis confirm those of the factor analysis that the metal concentrations are largely uncorrelated with each other.

DISCUSSION AND CONCLUSIONS

Zinc Transport in South San Francisco Bay. During the period September through December, 1972, eight municipal wastewater treatment facilities, accounting for nearly all of the water discharged to the study area, added soluble and readily exchangeable zinc at a rate of 77 kg/day. Simultaneously the total mass of dissolved zinc in the study area increased at a rate of 22 kg/day. The difference, 55 kg/day, must be accounted for by dispersion seaward and sediment uptake.

The dispersion transport component may be approximated employing Selleck's (1968) dispersion coefficients and the zinc concentration gradient across the seaward border of the area. Selleck's dispersion coefficients for this area and season range 5.6 - 9.3×10^5 cm^2/sec with a rough average of 7.4×10^5 cm^2/sec. The zinc concentration gradient was difficult to determine. Concentration differences between Stations 24 and 27 were consistently small and variable in sign. A summary of values obtained in unfiltered, irradiated samples collected at these stations is shown in table 11. Apparently the gradient shifts from month-to-month but the mean gradient is zero. Data from the atomic absorption analyses used for backup indicate a mean difference of about 0.2 μg/ℓ. Therefore, the flux estimate to be conservative will be presented as a range of values. Using a linear concentration-dependent dispersion equation:

$$\text{Transport} = \text{Flux} \times \text{Area} = -k \frac{dc}{dx} (A)$$

where $k = 7.4\text{x}10^{5}\text{cm}^{2}/\text{sec}$ (Selleck, 1968)

$dc/dx = (0.0\text{-}0.2\ \mu g/\ell) \div 10\ \text{km}$

$A = 3.9\text{x}10^{8}\text{cm}^{2}$ (cross-sectional area of bay at the transect)

Transport = 0.0 - 5.0 kg/day seaward

The zinc transport into the sediments is 50-55 kg/day. Using a figure of $206\text{x}10^{6}\text{m}^{2}$ for the sediment surface area, the average flux was 0.025-0.027 $\mu g/cm^{2}/day$.

This estimate accounts only for the zinc input from sewage and is certainly lower than the real value. Additional zinc sources not accounted in this work are dry fallout, rainfall and urban runoff. New data from J. D. Hem (oral communication, 1972) suggest that zinc loadings from rainfall and dry fallout were about $0.61\text{x}10^{6}$ and $0.27\text{x}10^{6}$ grams respectively over the study period thus accounting for an additional 9 percent of zinc loading. The amount derived from urban runoff was probably small but could not be evaluated.

No systematic differences in the zinc concentration were observed with depth in the water column, and no concentration gradient was observed close to the sediment-water interface at Station 36. Zinc is not moving out of the sediments fast enough to create an observable concentration gradient close to the bottom. I have observed such gradients in Chesapeake Bay (Bradford, 1972). Further work and new techniques are needed to measure transport of zinc from sediment to water.

TABLE 11.--*Zinc concentrations in unfiltered, irradiated water by ASV at stations 24 and 27 from figures 6 and 7 (in μg/ℓ)*

Cruise/Depth	5 metres		Δ	10 metres		Δ
Station	24	27		24	27	
B1				1.2*	1.7*	-.5
B2				2.2	1.5	+.7
B3	1.6	0.7	+0.9	1.7	1.2	+.5
B4	2.2	2.9	-0.7	2.3	2.9	-.6

*Filtered sample

$\bar{\Delta} = +.05$ $S = 0.73$

Observations on the Chemistry of Trace Metals in the South Bay Water. Both zinc and copper are sequestered by fast reacting organic chelators in both filtered and unfiltered samples. The percent increase in the ASV copper sensitivity caused by irradiating the sample is significantly lower in filtered than in unfiltered samples suggesting that a fraction of these fast reacting chelators are not molecular but colloidal or particulate in size. An analogous difference in the zinc sensitivity was not observed. Williams (1969) also suggested that some copper chelators in seawater were in particulate form.

The zinc and cadmium concentrations determined by ASV are larger in irradiated samples than in raw samples by an average of 0.66 μg/ℓ and 0.023 μg/ℓ, respectively. No significant differences in concentration were observed between filtered and unfiltered water samples, however.

The mean concentrations of zinc in the aqueous phase, and of iron, manganese and zinc in the suspended solids increased with time between September and January suggesting functional relationships between the concentrations and the season or another parameter related to season such as temperature or solar radiation.

Iron is less concentrated in suspended solids than in the sediments while manganese is more concentrated in the suspended solids. Presuming that suspended solids eventually deposit in the sediments, it is possible that, once deposited, the manganese tends to mobilize from the solids more so than iron leaving iron behind to constitute an increasing fraction of the sediments. Zinc and copper concentrations are nearly identical in both the suspended solids and the <20μ fraction of bed sediments.

Observations of Trace Metals in Sediments and Interstitial Fluids.

Iron and manganese concentrations in the interstitial water are large compared to those reported by Presley et al., (1972) for an anoxic fjord but within the same order of magnitude as values reported by O. P. Bricker at the Johns Hopkins University (oral communication, 1972) in interstitial waters in Chesapeake Bay. Iron and manganese concentrations are slightly higher in interstitial fluid from surficial sediments than the fluids from deeper layers, suggesting that these metals mobilize and move upward with ongoing sedimentation.

The extractable concentrations of seven trace metals in the sediments approach the average concentrations in shale. The concentrations of all but nickel are significantly higher in the <20 μm fraction than in the 20 μm-2 mm fraction. Iron, manganese, zinc and cobalt are higher by a factor of two, copper by a factor of three and lead by a factor of five.

A varimax factor analysis of the trace metal concentrations in two size fractions of bottom sediments indicates that the variance in the concentration of each metal is affected most by separate and independent processes. If Jenne's (1968) iron-manganese hydrous oxide model were operating exclusively in the south bay, factor loadings for all the metals would occur together with very few factors (ideally only one) accounting for 95 percent of the data variance. Apparently either the processes are not operating exclusively in this system or this type of statistical analysis is not the proper method by which these processes can be identified.

The variance in the lead concentrations in both sediment size fractions is largely explained by the same factor suggesting that this factor is a single dominating process such as emissions in automobile exhaust. By inspection of table 8, it appears that lead concentrations in the <20μ fraction of sediments are highest at stations 28E, 29W, 33W, and 33E which are close to the two bridges crossing the bay.

ACKNOWLEDGMENTS

Several people have been of invaluable service to me in performing this work. I would like to thank especially Everett Jenne, James Ball, and Jo Burchard without whose well-tested analytical techniques, clean laboratory and abundant advice this work would have been impossible; Vance Kennedy, David Dawdy and Yousif Kharaka for their help with analytical, statistical and computer techniques; and T. John Conomos, David McCulloch and the scientists and crew of the R/V Polaris for their help and cooperation in planning and executing the bay water sampling program.

This work was supported by a post-doctoral research fellowship administered through the National Research Council to the U.S. Geological Survey.

REFERENCES CITED

Armstrong, F. A. J., and Tibbitts, S., 1968, Photochemical combustion of organic matter in seawater for nitrogen, phosphorous and carbon determinations: Jour. Marine Biol. Assoc., U.K., 48:143-152.

Bradford, W. L., 1972, A study of the chemical behavior of zinc in Chesapeake Bay water using anodic stripping voltammetry: Chesapeake Bay Institute, The Johns Hopkins University Tech. Rept. 76, Ref. 72-7.

Brooks, R. R., Presley, B. J., and Kaplan, I. R., 1967, APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic absorption spectroscopy: Talanta, 14:809-820.

_____1968, Trace elements in the interstitial waters of marine sediments: Geochim. et Cosmochim. Acta, 32:397-414.

Calvert, S. E., and Price, N. B., 1970, Minor element contents of recent organic-rich sediments off southwest Africa: Nature, 227 (5258): 593-595.

Carvajal, M. C., and Landergren, S., 1969, Marine sedimentation processes: the interrelationships of manganese, cobalt and nickel: Stockholm, Contributions in Geology, 18(4):99-122.

Cross, F. A., Duke, T. W., and Willis, J. N., 1970, Biogeochemistry of trace elements in a coastal plain estuary. Distribution of manganese, iron and zinc in sediments, water and polychaetous worms: Chesapeake Sci., 11(4):221-234.

Dawdy, D. R., and Feth, J. H., 1967, Applications of factor analysis in study of chemistry of groundwater quality, Mojave River Valley, California: U.S. Geol. Survey Water Resources Research, 3(2): 505-510.

Evans, D. W., and Cutshall, N. H., 1972, Effects of ocean water on the soluble-suspended distribution of Columbia River radionuclides: Preprint from the Symposium on the Interaction of Radioactive Contaminants with the Constituents of the Marine Environments sponsored by IAEA in Seattle, USA.

Forster, W. O., Wolfe, D. A., and Lowman, F. G., 1971, Trace element interactions between river water and sea water: in Third National Symposium on Radioecology Proc., CONF 710501-32, Oak Ridge, Tenn.

Garrels, R. M., and Christ, C. L., 1965, Solutions, minerals and equilibria: New York, Harper & Row Publ. Inc.

Gross, M. G., 1967, Concentrations of minor elements in diatomaceous sediments of a stagnant fjord: in Estuaries ed. by G. H. Lauff, p. 273-282, AAAS Pub. no. 83.

Hitchon, B., Billings, G. K., and Klovan, J. E., 1971, Geochemistry and origin of formation waters in the western Canada sedimentary basin - III. Factors controlling chemical composition: Geochim. et Cosmochim. Acta, 35:567-598.

Huff, L. C., 1948, A sensitive field test for heavy metals in water: Econ. Geology, 43(9):675-684.

Jenne, E. A., 1968, Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides: _in_ Trace Inorganics in Water ed. by R. F. Gould, p. 337-389, Advances in Chemistry Series No. 73, ACS, Washington, D. C.

Jenne, E. A., and Ball, J. W., (In Prep.), The extraction of bio-diagenetically available trace elements from sediments and soils.

Jenne, E. A., Kennedy, V. C., Burchard, J. M., and Ball, J. W., (In Prep.), Sediment collection and processing for trace element analysis.

Khaylov, K. M., and Finenko, Z. Z., 1968, The interaction of detritus with high molecular weight components of dissolved organic matter in sea water: Oceanology, 8(6):980-991.

Krauskopf, K. B., 1967, Introduction to Geochemistry: New York, McGraw-Hill.

Lee, G. F., 1970, Factors affecting the transfer of materials between water and sediments: Univ. Wisconsin, Madison, Water Res. Center, Eutrophication Infor. Prog., Lit. Rev. No. 1.

Manheim, F. T., 1966, A hydraulic squeezer for obtaining interstitial water from consolidated and unconsolidated sediments: U.S. Geol. Survey Prof. Paper 550-C.

McCulloch, D. S., Peterson, D. H., Carlson, P. R., and Conomos, T. J., 1970, A preliminary study of the effects of water circulation in the San Francisco Bay Estuary, I. Some effects of freshwater on the flushing of South San Francisco Bay: U.S. Geol. Survey Circ. 637A.

Mortimer, C. H., 1971, Chemical exchanges between sediments and water in the Great Lakes--speculation on probable regulatory mechanisms: Limnol. Oceanogr.. 16(2):387-404.

Piper, D. Z., 1971, The distribution of Co, Cr, Cu, Fe, Mn, Ni, and Zn in Framvaren, a Norwegian anoxic fjord: Geochim. et Cosmochim. Acta, 35(6):531-550.

Presley, B. J., Kolodny, Y., Nissenbaum, A., and Kaplan, I. R., 1972, Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - II. Trace element distribution in interstitial water and sediments: Geochim. et Cosmochim. Acta, 36:1073-1090.

Rice, T. R., 1963, Review of zinc in ecology in Radioecology ed. by V. Schutz and A. W. Klement, p. 619-631: Proc. First National Symposium on Radioecology, Reinhold Publ. Corp. and The Am. Inst. Biol. Sciences, Washington, D.C.

Rittenberg, S. C., Emery, K. O., and Orr, W. L., 1955, Regeneration of nutrients in sediments of marine basins: Deep-Sea Res., 3:23-45.

Robertson, D. E., 1968, The adsorption of trace elements in sea water on various container surfaces: Anal. Chim. Acta, 42:533-537.

Selleck, R. A., 1968, A model of mixing and dispersion in San Francisco Bay: Jour. Water Poll. Contr. Fed., 40(11)Pt 1:1873-1886.

Sillen, L. G., 1967, Gibbs phase rule and marine sediments in Equilibrium Concepts in Natural Water Systems ed. by W. Stumm, p. 57-70: Adv. in Chemistry Series No. 67, ACS, Washington, D.C.

Slowey, J. F., and Hood, D. W., 1971, Copper, manganese and zinc concentrations in Gulf of Mexico waters: Geochim. et Cosmochim. Acta, 35(2):121-138.

Spencer, D. W., Brewer, P. G., and Sachs, P. L., 1972, Aspects of the distribution and trace element composition of suspended matter in the Black Sea: Geochim. et Cosmochim. Acta, 36:71-86.

Volkov, I. I., and Fomina, L. S., 1971, Trace elements in Black Sea sapropel muds and their interaction with organic matter: Litol. Polez. Iskop., 6:3-15.

Williams, P. M., 1969, The association of copper with dissolved organic matter in seawater: Limnol. Oceanogr., 14(1):156-158.

Wolfe, D. A., and Rice, T. R., 1972, Cycling of elements in estuaries: Fisheries Bull., 70(3):959-972.

Zirino, A., and Healy, M. L., 1971, Voltammetric measurement of zinc in the northeastern tropical Pacific Ocean: Limnol. Oceanogr., 16(5):773-778.

☆GPO 690-314-1976