Time Series of Trace Element Concentrations Calculated from Time Series of Suspended Solids Concentrations and RMP Water Samples

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September 1996

TABLE OF CONTENTS

INTRODUCTION

The supply and fate of trace elements in San Francisco Bay, which are partially dependent upon particulate matter in the Estuary, are important management issues. San Francisco Bay receives many waste water discharges, especially in areas south of the Dumbarton Bridge, that contain trace elements that accumulate in benthic organisms (Luoma *et al.*, 1985; Brown and Luoma, 1995). Trace elements tend to adsorb particulate matter (Kuwabara *et al.*, 1989), so the fate of trace elements is partly determined by the fate of suspended solids. Concentrations of dissolved trace elements are greater in the South Bay than elsewhere in San Francisco Bay, and bottom sediments are believed to be a significant source (Flegal *et al.*, 1991). The concentration of suspended particulate chromium in the Bay appears to be controlled primarily by sediment resuspension (Abu-Saba and Flegal, 1995). Water quality standards for trace elements in the Bay are written in terms of total or near-total trace element concentrations (TEC) (SFEI, 1996a).
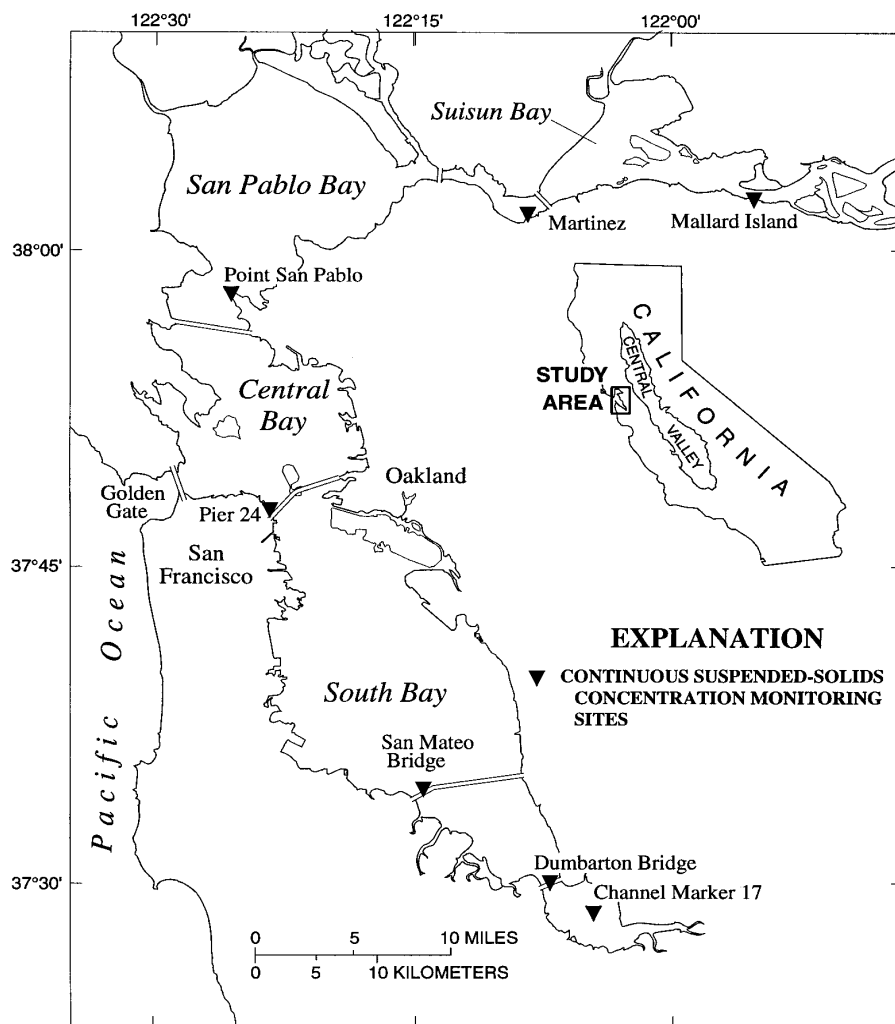
Figure 1. Continuous USGS SSC monitoring sites in San Francisco Bay.

This report has two objectives. The first objective is to demonstrate the relationship between suspended solids concentration (SSC) and TEC by developing equations relating SSC to total (or near-total) concentrations of trace elements based on Regional Monitoring Program (RMP) data collected during 1993 and 1994. The second objective is to demonstrate the temporal variability of TEC that are linearly correlated (LCTEC) with SSC by presenting time-series information on LCTEC based on nearly continuous SSC measurements collected during the 1995 water year (October 1, 1994 to September 30, 1995) and the SSC-LCTEC equations.

DATA COLLECTION

During 1993 and 1994, the RMP conducted six sampling trips in San Francisco Bay during which water quality samples were collected and analyzed for many constituents, including SSC and TEC (SFEI, 1994, 1996a). A total of 120 samples were collected at sites within the Bay, outside the Golden Gate, and in natural and waste water tributaries.

The USGS has established several SSC monitoring sites in San Francisco Bay (Figure 1) (Buchanan and Schoellhamer, 1995; Buchanan *et al.*, 1996). At most sites, optical backscatterance (OBS) sensors are positioned at mid-depth and near the bottom. The OBS sensors optically measure the amount of suspended material in the water every 15 minutes, and the output of the sensors is converted to SSC with calibration curves developed from analysis of water samples. The sites are serviced every 1 to 5 weeks to clean the sensors, which are susceptible to biological fouling, and to collect water samples for sensor calibration. About half the data collected are invalid, primarily because of sensor fouling. Continuous SSC data for water year 1995 presented in this report are provisional and subject to change.

RELATIONS BETWEEN RMP SSC AND TEC DATA

Linear regression was used to determine equations relating RMP SSC and TEC data. The equations will be applied to the USGS SSC measurements in Bay waters, so outlying data collected in tributary streams were discarded.

Excellent correlations with SSC were found for seven trace elements—silver, chromium, copper, mercury, nickel, lead, and zinc. The linear regressions are shown in Figure 2 and statistical properties of the regressions are given in Table 1. All regressions are significant at less than the 0.001 level. SSC accounts for approximately 90 percent of the variability in the LCTEC. The validity of the regression equations decreases when SSC is outside of the range used to develop the equations. The May 1993 data for silver were scattered, typically with a high silver concentration, so these data were discarded. Spot checks indicated that the linear regressions for each sampling trip were similar. Better relations might have been found if particulate trace element concentration (total concentration minus dissolved concentration) or other water-quality constituents (salinity, dissolved organic carbon, etc.) were considered, but the goal of this work was to develop a relationship for TEC applicable to the USGS SSC measurements.
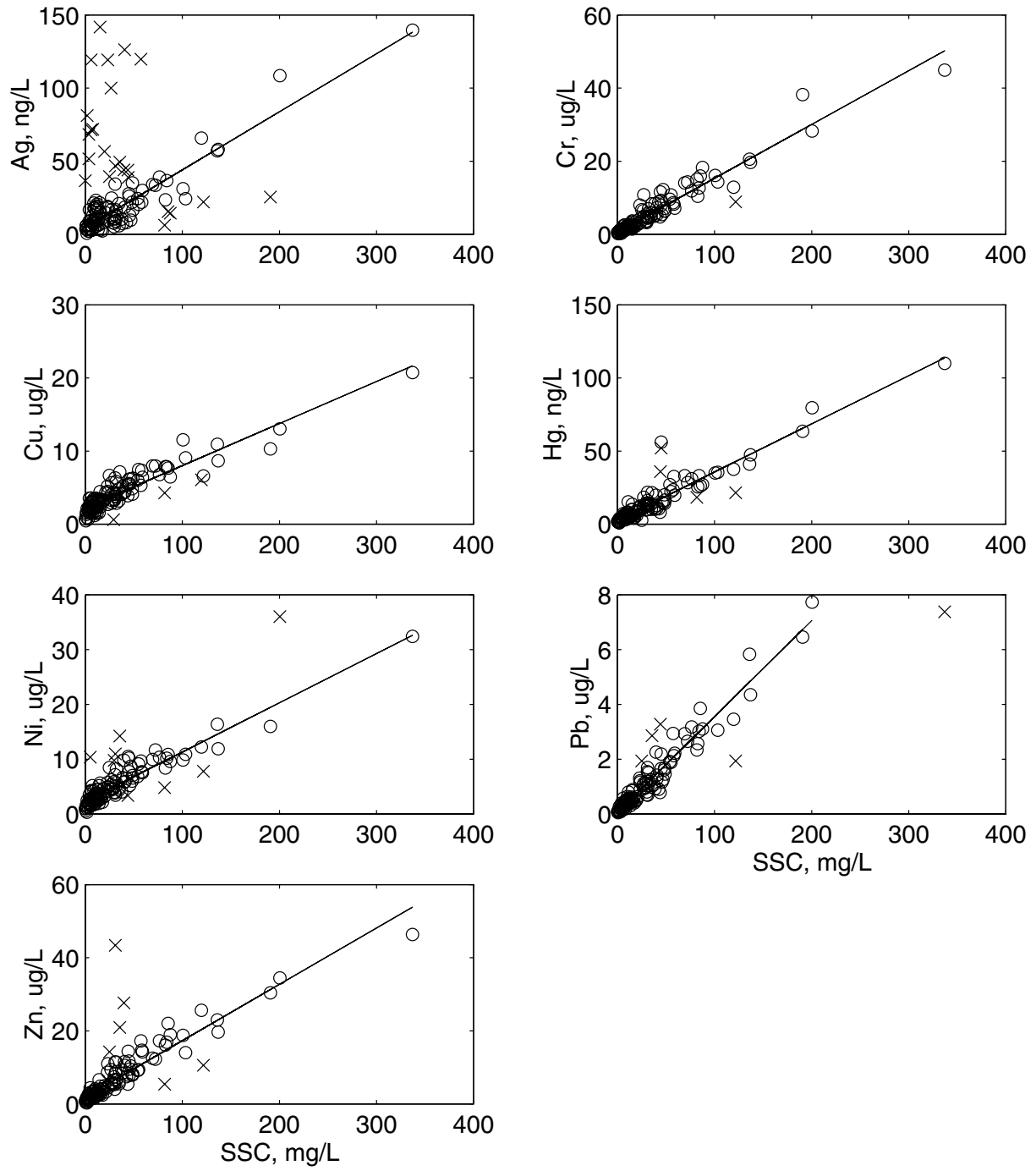
Figure 2. Correlation of SSC and total or near-total concentrations of silver (Ag), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). Outliers from samples taken from influent waters are indicated with an 'x' and were not used to develop the correlations given in Table 1.

Table 1. Statistical properties of the linear regressions between SSC and LCTEC

Trace element	Number of data points	Squared correlation coefficient	Slope	Intercept	Root-mean-squared error
Silver	94	0.85	0.40 ng/mg	4.3 ng/L	7.6 ng/L
Chromium	118	0.93	0.15 µg/mg	0.64 µg/L	1.9 µg/L
Copper	114	0.85	0.058 µg/mg	2.3 µg/L	1.1 µg/L
Mercury	115	0.90	0.33 ng/mg	2.7 ng/L	5.0 ng/L
Nickel	111	0.89	0.090 µg/mg	2.3 µg/L	1.4 µg/L
Lead	113	0.94	0.035 µg/mg	0.058 µg/L	0.31 µg/L
Zinc	113	0.91	0.15 µg/mg	1.9 µg/L	2.2 µg/L

One assumption of linear regression is that residuals (differences between observations and predictions) are independent. Plots of residuals along the axis of the Bay (not shown) indicate that residuals for silver, mercury, and lead decrease from the South Bay to Suisun Bay (Kendall's tau test of mean station residuals, significance level less than 0.01). Residuals for copper, nickel, and zinc decrease from the South Bay to the Central Bay, and residuals for copper and zinc have local maxima in the North Bay. Because the assumption that residuals are independent is sometimes violated, confidence intervals and hypotheses tests, including significance levels, may be incorrect (Helsel and Hirsch, 1992). Increasing the size of the data set and spatially subdividing the data would alleviate this problem.

Outlying data from tributaries had either low or high LCTEC compared to the predicted values based on SSC ('x' symbols in Figure 2). These data probably reflect the influent waters, not Bay waters, and therefore were discarded. For example, influent from waste water treatment plants sometimes had a greater ratio of LCTEC to SSC than Bay waters, and influent from natural rivers sometimes had a smaller ratio of LCTEC to SSC than Bay waters (Table 2). Not all data collected at the tributary sites are outliers because Bay waters may be present at the sites (during flood tides for example), the tributary discharge may be small, or the ratio of LCTEC to SSC of the influent water may be close to that of Bay waters.

Poor correlations with SSC were found for the other three trace elements measured by the RMP—arsenic, cadmium, and selenium. The squared correlation coefficients were 0.27, 0.077, and 0.000 for arsenic, cadmium, and selenium, respectively, for 119 samples.

USGS SSC DATA

The statistical properties of the SSC data collected at the USGS monitoring sites (Figure 1) during water year 1995 are presented graphically as boxplots in Figure 3. SSC is not normally distributed, so a logarithmic scale is used to better visualize the boxplots. SSC is greater near the bottom of the Bay, which is expected because of the negative buoyancy of sediment particles. In the South Bay, there was a gradient of increasing SSC south of the San Mateo Bridge. The root-mean-squared error of the calibration of the OBS sensors and the percent of valid data collected at each site are given in Table 3.

Table 2. Ratio of observed and predicted total concentrations for the outlying data in Figure 2.

Trace element	Date	Site	Ratio of observed and predicted LCTEC
Silver	3/93	Pacheco Creek	0.17
	5/93	Al1	-
	2/94	San Jose	2.8
	2/94	Sunnyvale	2.2
	4/94	Coyote Creek	2.8
	4/94	Napa River	1.8
	4/94	San Jose	2.7
	4/94	Sunnyvale	4.4
	8/94	Napa River	.42
Chromium	8/94	Napa River	.48
Copper	3/93	Pacheco Creek	.61
	2/94	Coyote Creek	.66
	2/94	Napa River	.15
Mercury	3/93	Pacheco Creek	.62
	4/94	Napa River	2.1
	8/94	Napa River	.50
	8/94	Sunnyvale	3.0
Nickel	3/93	Napa River	2.0
	3/93	Pacheco Creek	.50
	3/93	Redwood Creek	3.7
	5/93	San Joaquin River	.54
	2/94	San Jose	2.1
	4/94	San Jose	2.6
	8/94	Napa River	.59
	8/94	San Jose	1.8
Lead	4/94	Coyote Creek	2.1
	4/94	Napa River	2.0
	4/94	Petaluma River	.62
	4/94	San Jose	2.2
	8/94	Napa River	.45
Zinc	3/93	Pacheco Creek	.37
	2/94	San Jose	6.5
	2/94	Sunnyvale	3.4
	4/94	San Jose	2.8
	4/94	Coyote Creek	2.5
	8/94	Napa River	.51

Table 3. Root-mean-squared error of OBS sensor calibrations and percent valid data for the SSC monitoring sites, water year 1995.

| Site	Depth	Root-mean-squared error (mg/L)	Percent valid data
Mallard Island	Near-surface	5.8	54
	Near-bottom	5.0	83
Martinez	Near-surface	9.0	67
Point San Pablo	Mid-depth	16	78
	Near-bottom	27	83
Pier 24	Mid-depth	12	45
	Near-bottom	16	72
San Mateo Bridge	Mid-depth	6.3	41
	Near-bottom	5.0	26
Dumbarton Bridge	Mid-depth	13	24
	Near-bottom	36	56
Channel marker 17	Mid-depth	22	74
	Near-bottom	21	63
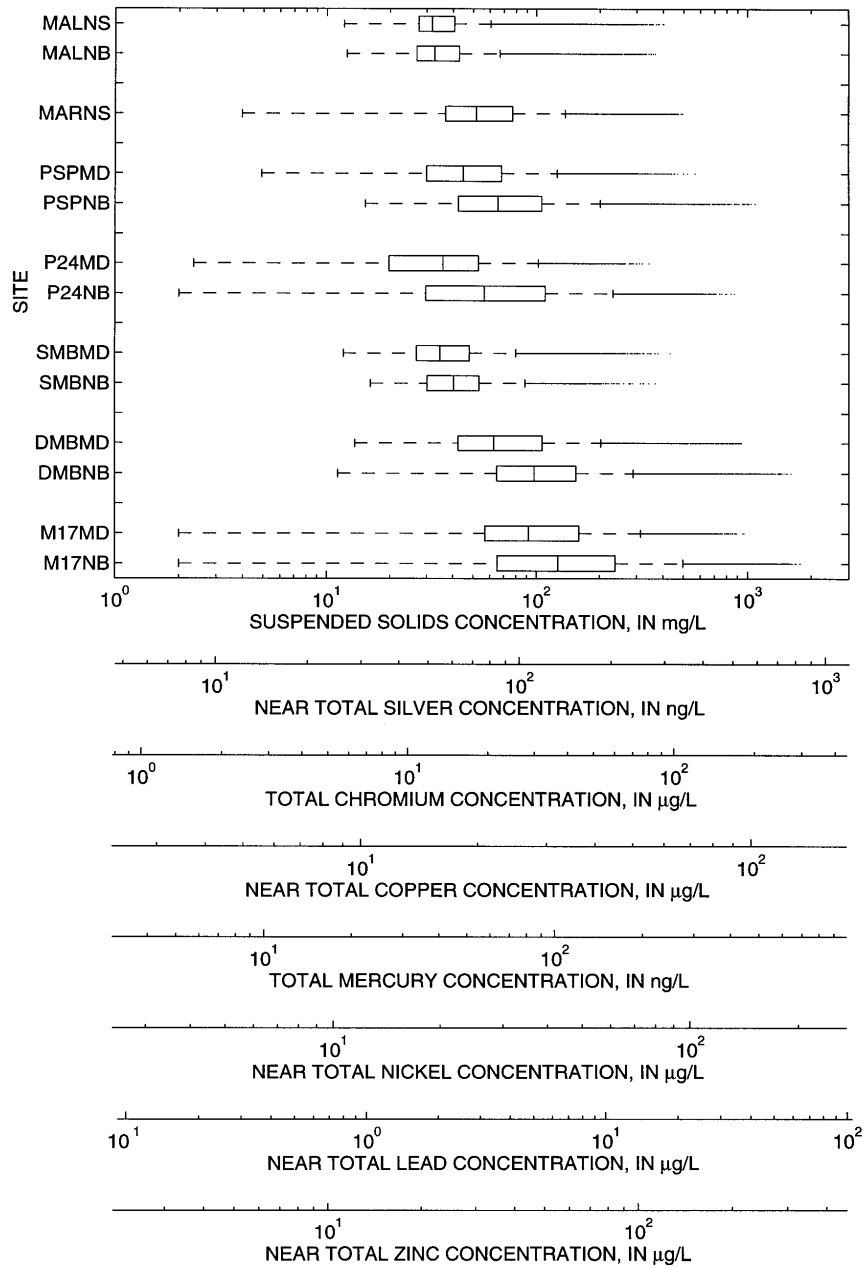
Figure 3. Boxplots of measured SSC and calculated LCTEC for water year 1995. SSC monitoring sites are located at Mallard Island (MAL), Martinez (MAR), Point San Pablo (PSP), San Francisco Pier 24 (P24), San Mateo Bridge (SMB), Dumbarton Bridge (DMB), and Channel Marker 17 (M17). Measurements are taken near the water surface (NS), at mid-depth (MD), and near the bottom (NB). Each box indicates the upper and lower quartiles and the line in each box is the median value. The dashed whiskers extend beyond the box 1.5 times the interquartile range or to the most extreme data point, whichever is closer to the box. Data outside the limits defined by the whiskers are shown individually as a small dot, which often appears as a line due to the large number of data points (about 9,000 to 29,000 per box).

An example time series of measured SSC data from mid-depth at Point San Pablo is shown in Figure 4. The high frequency variations are caused by tidal advection and tidal resuspension of suspended solids. The fortnightly variation is caused by the spring-neap cycle. About one-half the variance of SSC is caused by the spring-neap cycle, and SSC lags the spring-neap cycle by about 2 days (Schoellhamer, 1996). The relatively short duration of slack water limits the duration of deposition of suspended solids and consolidation of newly deposited bed sediment during the tidal cycle, so suspended solids accumulate in the water column as a spring tide is approached and slowly deposit as a neap tide is approached. High concentrations in January and March were the result of runoff from the Central Valley, which transported suspended sediments to the Bay. Stronger winds during spring and summer increase sediment resuspension in shallow water and thus increase SSC throughout the Bay.
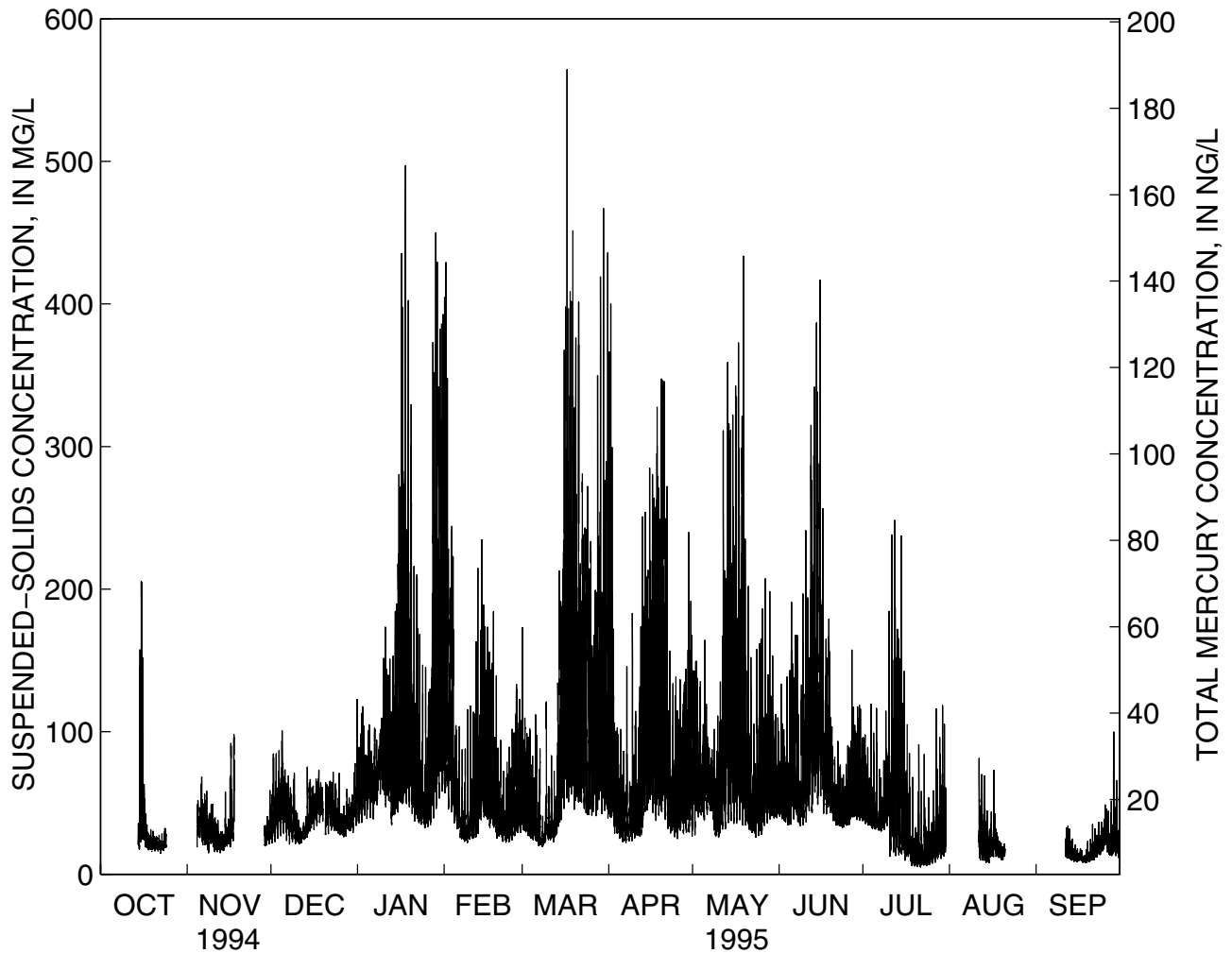

Figure 4. Time series of mid-depth SSC (measured) and total mercury concentration (calculated) at Point San Pablo, water year 1995.

CALCULATED LCTEC DURING WATER YEAR 1995

Because SSC and LCTEC are linearly related, the boxplots in Figure 3 are applicable to the LCTEC when a different horizontal scale is used. Vertical and horizontal spatial gradients that are present in the SSC data will also be present in the calculated LCTEC data because they are linearly related.

LCTEC and SSC vary similarly in time because they are linearly related. An example calculated LCTEC time series for mercury at mid-depth at Point San Pablo is shown in Figure 4. SSC for only 0.2 percent of the data points in Figure 4 exceeds the maximum SSC used to calculate the regression equation for SSC and total mercury concentration. Total mercury concentration varies because of tidal advection and tidal resuspension of suspended solids and associated mercury, the fortnightly spring-neap cycle, and the seasonally stronger summer winds. The high inflow during January and March increased SSC and, assuming that the relationship between SSC and total mercury concentration was unchanged at Point San Pablo, increased total mercury concentration. RMP data collected in February and April of 1995 in the Northern (SFEI, 1996b) indicate that the relationship was virtually unchanged in the open Bay waters. As with SSC, about one-half the variance of LCTEC is caused by the spring-neap cycle.

DISCUSSION AND CONCLUSIONS

Seven TEC are well correlated with SSC for Bay waters. Influent waters from waste water treatment plants sometimes had a greater TEC to SSC ratio than Bay waters, and natural tributaries sometimes had a smaller ratio than Bay waters. Linear equations relating LCTEC and SSC can be applied to the nearly continuous time series of SSC collected by the USGS to produce similar time series of LCTEC. Biofouling of the OBS sensors is the primary reason why the SSC and calculated LCTEC are not continuous. The two primary sources of error are the conversion of OBS sensor output voltage to SSC and the conversion of SSC to LCTEC, both of which are achieved with linear regression.

Because of their relationship with SSC, LCTEC vary with time because of tides, the spring-neap cycle, seasonal winds, and watershed runoff. Frequent sampling, on the order of minutes, is required to observe these variations, but such a TEC sampling program would be prohibitively expensive. The combination of the existing RMP sampling data and USGS SSC data produces computed LCTEC every 15 minutes at the USGS SSC monitoring sites. These computed LCTEC can be used to monitor temporal variations in LCTEC that the RMP sampling program can not observe and thus enhance the existing direct RMP TEC measurements by helping to place them in a proper context.

ACKNOWLEDGMENTS

REFERENCES

Abu-Saba, K.E., and A.R. Flegal. 1995. Chromium in San Francisco Bay: Superposition of geochemical processes causes complex spatial distributions of redox species. Marine Chemistry, v. 49, p. 189–199.

Brown, C.L., and S.N. Luoma. 1995 Use of the euryhaline bivalve *Potamocorbula amurensis* as a biosentinel species to assess trace metal contamination in San Francisco Bay. Marine Ecology Progress Series, v. 124, p. 129–142.

Buchanan, P.A., and D.H. Schoellhamer. 1995. Summary of suspended-solids concentration data in Central and South San Francisco Bays, California, water years 1992 and 1993. US Geological Survey Open File Report 94-543, 15 p.

Buchanan, P.A., D.H. Schoellhamer, and R.C. Sheipline. 1996. Summary of suspended-solids concentration data, San Francisco Bay, California, water year 1994. US Geological Survey Open-File Report 95-776, 48 p.

Flegal, A.R., G.J. Smith, G.A. Gill, S. Sanudo-Wilhelmy, and L.C.D. Anderson. 1991. Dissolved trace element cycles in the San Francisco Bay Estuary. Marine Chemistry, v. 36, p. 329–363.

Helsel, D.R., and R.M. Hirsch. 1992. Statistical Methods in Water Resources. Elsevier, New York, 522 p.

Kuwabara, J.S., C.C.Y. Chang, J.E. Cloern, T.L. Fries, J.A. Davis, and S.N. Luoma. 1989. Trace metal associations in the water column of South San Francisco Bay, California. Estuarine, Coastal and Shelf Science, v. 28, p. 307–325.

Luoma, S.N., D. Cain, and C. Johansson. 1985. Temporal fluctuations of silver, copper, and zinc in the bivalve *Macoma balthica* at five stations in South San Francisco Bay. Hydrobiologia, v. 129, p. 109–120.

SFEI. 1994. 1993 Annual Report, San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.

SFEI. 1996a. 1994 Annual Report, San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.

SFEI. 1996b. 1995 Annual Report, San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.

Schoellhamer, D.H. 1996. Factors affecting suspended-solids concentrations in South San Francisco Bay, California. Journal of Geophysical Research, v. 101, no. C5, p. 12087–12095.