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Modeled Trace Element Concentrations and Partitioning in the San Francisco Estuary, Based on Suspended Solids Concentration

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Although trace element (Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn) and methylmercury (MeHg) concentrations have been systematically sampled 1−3 times per year throughout the San Francisco Bay estuary for more than two decades, those collections do not capture episodic events that may govern the biogeochemical cycles of these elements in the Bay and adjacent Pacific coastal waters. Analyses of the partitioning of in situ elemental concentrations between particulate and total dissolved (<0.45 μm) phases coupled with optically based measurements of suspended solids concentration (SSC) showed highly significant ($p < 0.001$) associations between all elemental concentrations and SSC in the Bay. Predictive models were developed to estimate the distribution ratio (D), or partition coefficient (K_d), and total concentration of each element in the water column based solely on SSC measurements. Modeled predictions of total element concentrations and distribution ratios were then coupled with measured SSC to predict the concentrations of dissolved trace elements in the water column. These predicted total and dissolved concentrations of trace elements can provide both better diagnostics of biogeochemical cycling within the estuary and better estimates of fluxes to adjacent coastal waters, overcoming the limitations of the long-running but limited direct measurements of trace elements from existing sampling programs.

Introduction

Total and dissolved trace element concentrations are important to understand when studying complex estuarine ecosystems. Contaminant trace elements can directly affect biological systems in estuaries and are both influenced by and influence anthropogenic usage. Concentrations of several trace elements are high enough to adversely affect biota within San Francisco Bay (*1, 2*), while high levels of mercury in some fish (*3*) exceed criteria for human consumption (*4*). Phillips et al. (*5*) determined that concentrations of silver (Ag), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), and/or zinc (Zn) contributed to the toxicity to bivalve larvae in the northern reach of the Bay. Others (*6, 7*) have associated elevated Ag concentrations with sublethal toxicities in marine invertebrates throughout the estuary, and Se toxicity has been documented in waterfowl within the Bay's drainage basin (*8*).

In response to these issues, trace element concentrations have been extensively monitored throughout the Bay, including both site specific studies and systematic sampling of near total (aqua regia digest) particulate and total dissolved (<0.45 μm) phases of a suite of trace elements (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Zn) and associated parameters (e.g., nutrients, salinity, chlorophyll, suspended particulates). This sampling was initiated over two decades ago (*9*) and has been institutionalized as the San Francisco Estuary Regional Monitoring Program, RMP (*10*). It is the longest running, and perhaps most extensive, monitoring program for trace elements in any estuarine system in the U.S. and elsewhere (*11*). However, even the RMP trace metal data are insufficient, because limited sample collections (1−3 times per year) usually miss extreme or unusual events (e.g., major floods, high wind episodes, algal blooms, atypical tides, or storms) that strongly influence the temporal and spatial distribution of trace elements within the estuary and adjacent oceanic waters (*12*).

Optically derived suspended sediment concentration (SSC) has previously been used to assess water quality for estuarine and coastal waters (*13*−*15*). We investigated the potential for utilizing the relationship between optically derived SSC and trace element concentrations to augment in situ measurements of these elements. The United States Geological Survey (USGS) maintains 13 continuous SSC monitoring stations in San Francisco Bay (*16*), and satellite remote sensing provides synoptic coverage of SSC in the Bay at reduced spatial and temporal scales (e.g., ref *13*). Theoretically, remote sensing has the ability to sample any location in the Bay and adjacent coastal waters at daily temporal resolution. Although this is difficult in reality due to various constraints, time-averaged spatial maps of SSC and associated trace element concentrations could be developed for the San Francisco Bay system to augment existing programs such as the RMP.

That potential was tested with a 10-year triannually collected RMP data set (1993−2003), and a 3-year RMP data set (2004−2006), when samples were collected biannually. A model of the relationship between the distribution ratio and total concentration of a suite of trace elements (Ag, As, Cd, Co, Cr, Cu, Fe, Hg, MeHg, Mn, Ni, Pb, Se, and Zn) with SSC was derived from the 10-year data set. Accuracy of the model was evaluated using the independent 3-year data set, and model outcomes were applied to the 3-year data set to estimate the dissolved concentrations of those trace elements. These estimates were then compared with measured dissolved trace element concentrations to determine the accuracy and bias of the optically based model. These models cannot replace actual measurements but can give snapshot or overview estimations, and can be used to estimate concentrations (with known model error) when in situ data are not available.

Study Area. San Francisco Bay is a turbid, shallow estuary that covers an area of 1240 km^2 (Figure 1), and can be divided into three hydrographic regions. The Sacramento and San Joaquin river system contributes 90% of the Bay's fresh water (*17*) and 83−86% of its fluvial sediment (*18*) into the northern reach of the estuary, which extends from the deltaic confluence of those two rivers (Delta) to San Pablo Bay (*19*).

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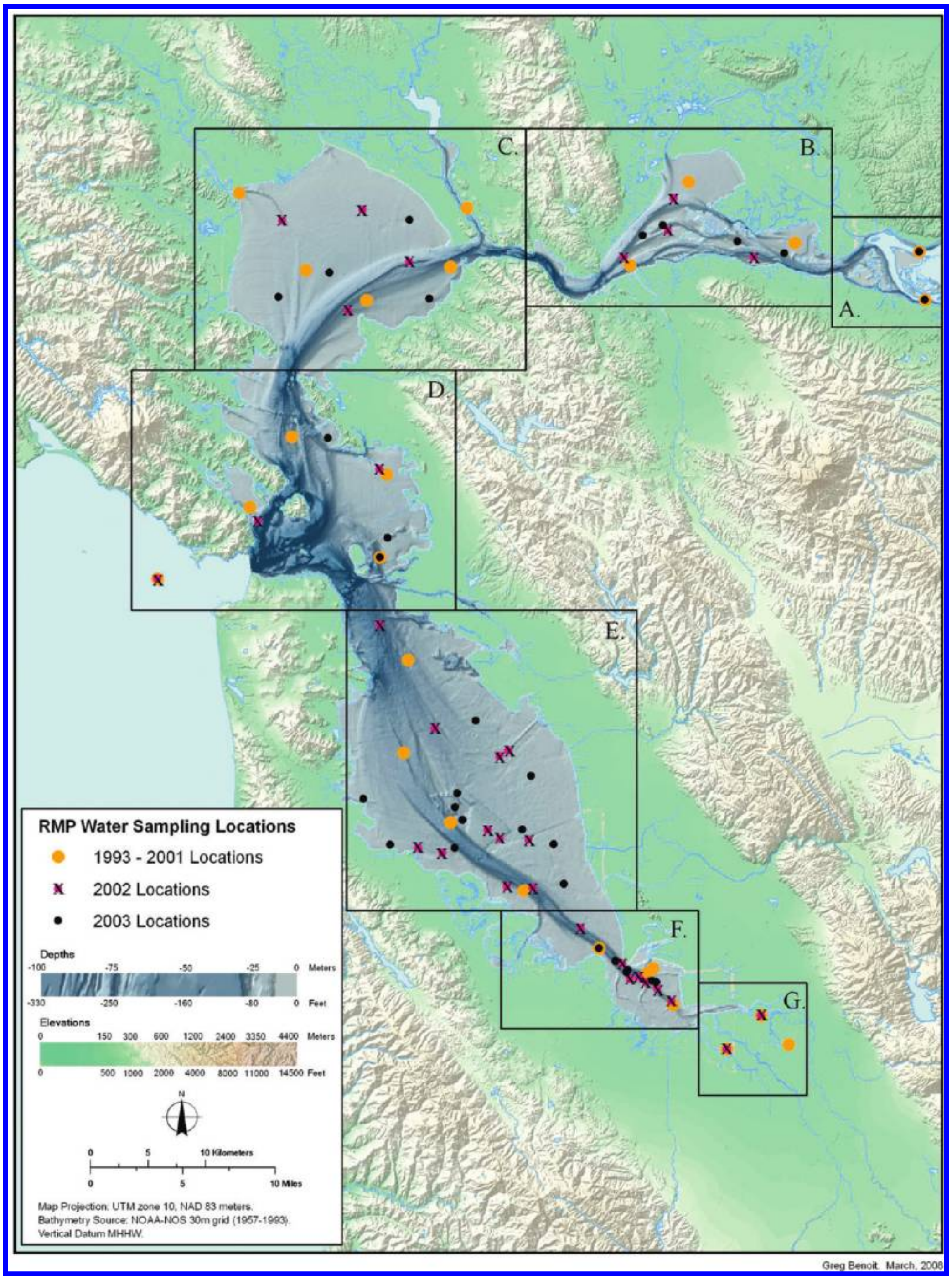

FIGURE 1. San Francisco Estuary sampling station locations; 1993−2001, 2002, and 2003. Boxes indicate discrete Estuary regions described in the text: A. North Bay (delta) (where Sacramento and San Joaquin rivers enter); B. North Bay (east); C. North Bay (west) (San Pablo Bay); D. Central Bay; E. South Bay (north); F. South Bay (south); G. South Bay (input).

Regulated freshwater inputs to the estuary through the region, which primarily occur in winter and spring, range from 1000−10 000 m^3 s^{-1}. Those discharges also flush the southern reach of the Bay (South Bay), which has a seasonal, albeit much smaller, freshwater input (100−1000 m^3 s^{-1}). During low flow periods the primary source of freshwater is wastewater discharges from the surrounding metropolis (*20*), and the South Bay is essentially a high salinity (≥20 psu) lagoon (*21*). The northern and southern reaches are joined by the Central Bay, which connects to the Pacific Ocean through the Golden Gate.

The estuarine system, which is a critical habitat for migratory birds and serves as a nursery ground for local fisheries (*22*), has been adversely impacted by anthropogenic activities (*23*) including urban development, accumulation of hydraulic-mining debris, dike construction, extensive landfill that reduced the Bay's surface area by 37% (*24*), and elevated trace element concentrations in Bay sediments (*25*). Major factors controlling the suspended sediment concentration in this estuary system are fluvial input from the Central Valley watershed, semidiurnal tidal forcing, and wind-wave resuspension in shallow waters (*23, 26*). Consequently, freshwater inflow, tidal forcing, and wind forcing influence the movement of sediment-associated trace element contamination through the system (*27, 28*). Several recent publications have reviewed various aspects of these and other factors on the biogeochemical cycles of trace elements in the Bay (e.g., refs *12, 7, 29−32)*.

Experimental Section

Data. Water column total concentration (WCT) and water column dissolved concentration (WCD) data for the trace elements (Ag, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni Pb, Zn), methylmercury (MeHg), salinity (psu), macronutrients (nitrate+nitrite, phosphate, silicates), chlorophyll-a (Chl-a), and suspended solids concentration (SSC) were obtained from samples collected with trace element clean techniques and analyzed at UCSC using established protocols (*12*), as part of the San Francisco Bay Regional Monitoring Program or RMP (http://www.sfei.org/rmp/). WCT and WCD data for metalloids (As and Se) were collected concurrently and measured with established protocols (*33*). Data for each trace element at each sampling event are reported in WCT and WCD fractions, as described by Flegal et al. (*12*).

SSC was determined using optical backscatter sensor (OBS) profiles, reported in Formazin turbidity units (FTU) and converted to mg/L. Optically derived and directly measured SSC are highly correlated (*34*). For simplicity, the term SSC is used in this report when discussing either SSC or total suspended solids (TSS) measurements as proposed by Gray et al. (*35*).

Both trace element concentrations that were (*1*) error-qualified (had some recorded error associated) but within acceptable limits for the RMP or (*2*) error-qualified and outside acceptable limits for the RMP (*36*), were excluded from the following models. Similar procedures were employed for excluding SSC, salinity, and Chl-a data. This statistical approach was designed to produce models that can be used to predict the distribution ratios and WCT values from a suite of potential predictor variables (see Supporting Information (SI), model development description).

Predictors. Variation in water quality parameters, distribution ratios and WCT, attributed to differing geographic regions of the estuary, seasonality, salinity differences, and level of Chl-a were evaluated using a generalized linear model analysis of variance. The estuary was divided into seven natural subdivisions (*37*) identified in Figure 1. Season-dependent variability was defined as "winter" (January−March), "spring" (April−June), and "summer" (July−September). "Autumn" (November−December) was excluded because no RMP samples were collected during that period. Predictors include the continuous variable SSC and the categorical variables Bay Region (α), Season (ϵ), and the interaction between Region and Season (season-x-region, δ). Model outcomes were applied to the independent 3 year data set to estimate the dissolved concentrations of those trace elements, and these estimates were compared with measured dissolved trace element concentrations to determine the accuracy and bias of the optically based model.

Results and Discussion

Prediction of *D* as a Function of SSC. Distribution ratios (*D*; L/kg) for each trace element and methylmercury sampled between 1993 and 2003 (SI Table S1) are plotted in SI Figure S1. While log−log transformed data would potentially be more statistically robust (*38*), we present the data in semilog space to facilitate comparison with previous publications (e.g., ref *39*). The plots show slight decreases in *D* values with increasing SSC for all of the trace elements and MeHg similar to other studies (e.g., refs *37*−*39*). Most of the trace elements (Pb, Ag, Cb, Co, Fe, Hg, Mn, and Zn) are effectively scavenged by SSC throughout the Bay and throughout the sampling period. The relatively lower (<4) log*D* values of the metalloids (Se and As) indicate that they are not as effectively scavenged by suspended solids (*33*).

Mean *D* values increase in the order of Se < As < Cd < Cu < Ni < Mn < Ag < Co < Zn < Hg < Cr < Pb < Fe (ANOVA, $p < 0.001$). This is similar to the rankings reported by Luengen et al. (*40*) for three locations in the central and southern reach of the Bay, although those authors found the *D* for Co was less than that for Mn during their 4 month sampling period. Our reported average log*D* for Ag (5.2, $n = 399$) is remarkably similar to observations in the Bay for a single year (*41*), as are several of the other values compared to previous reports including Sañudo-Wilhelmy et al. (*11*), (Cu, Fe, Ni, Zn, $n = 8$), Luoma et al. (*2*), (Cd, Cu, Ni, Zn, $n = 18$), and Luengen et al. (*40*), (Co, Cu, Ni, Pb, Zn, $n = 18$). Our values are significantly higher than the initial ambient log*D* for Ni (3.65, $n = 6$), Cu (3.88, $n = 6$), and Zn (4.52, $n = 6$) in the southern reach of the Bay compared to Gee and Bruland (*42*) who used a different method to estimate the exchangeable particulate element fraction (c_p); both seasonal and particle concentration effects may have contributed to this disparity.

Our *D* order is also similar to other estuarine waters reported by Benoit et al. (*38*), (Cu < Zn < Ag < Pb), Windom et al. (*43*), (Cu < Cd < Ni < Zn < Co < Pb < Mn < Fe), and Tang et al. (*38*), (Ni < Cu < Cd < Zn < Mn < Pb < Fe). The spatial disparity in partitioning is tentatively attributed to geographic differences in sediment type, grain size, and organic composition, as discussed by Honeyman and Santchi (*44*), and/or differences in processing, as discussed by Tang et al. (*38*).

Influence of Other Variables on *D*. The geographic region of the Bay was found to have a highly significant ($p < 0.001$, ANOVA) affect on *D* values for all trace elements except Ag, Cr, and Se. Similarly, seasonality was found to have highly significant ($p < 0.001$) affects on most trace elements (Ag, Cd, Cr, Fe, Hg, Ni, Pb, Zn, but not Cd, Cu, and Se). The combined effect of region-by-season was also highly significant ($p < 0.001$) for a few trace elements (Cr, Hg, and Pb).

The influence of other variables on the partitioning of trace elements in the Bay was limited. The variation of *D* with salinity was not significant for any of the trace elements except Cd and Cr ($p < 0.001$), consistent with previous studies (*45, 9*). Conversely, the variation in Chl-a did not significantly affect the partitioning of any of the elements in our 10-year data set, in contrast with previous reports for several trace elements (Ag, Co, Cu, Hg, Ni, Pb, and Zn) in the southern reach of the Bay (*46, 40*). Organic carbon content of particles has been shown to impact *D* values when carbon is a principal component of the suspended particulate matter (*42*), while bloom formation and decay has been linked to changes in oxidation state, biological uptake, and sorption (*40*). The lack of correlation in our analysis suggests that the impact of intense algal blooms on the partitioning of trace elements in the Bay had not been captured by the RMP "snapshots" taken over the past decade, or was statistically overwhelmed by nonbloom sampling events.

Modeling *D*. Least squares regression analysis of log*D* versus SSC were used to obtain information needed to predict, with varying levels of accuracy, *D* values of trace elements as a function of SSC in the Bay. We began with the model reported by Benoit et al. (*39*):

$$\mathrm{Log}D_{\mathrm{p}} = \log(K_{\mathrm{d}})_{\mathrm{p}} = m \times \mathrm{SSC} + b \qquad (1)$$

where $\log D_{\mathrm{p}}$ is the predicted distribution ratio, *m* is the slope and *b* the intercept for the log*D* versus SSC regression. We then improved that prediction with the application of a most predictive model (SI, model development description). SSC values were normalized, using the transformation: $\mathrm{SSC}^{.25} = \mathrm{SSC}_{\mathrm{root}}$. Robust least median of squares regression produced slope (m_{o}) and intercept (b_{o}) coefficients (see SI Table S2). Log*D* predictions were then calculated using a modified eq 1:

$$\log D_{\mathrm{p}^*} = \log(K_{\mathrm{d}})_{\mathrm{p}^*} = m_{\mathrm{o}} \times \mathrm{SSC}_{\mathrm{root}} + b_o \qquad (2)$$

Analysis of variance determined the variables that significantly affect *D* values for each trace element in the

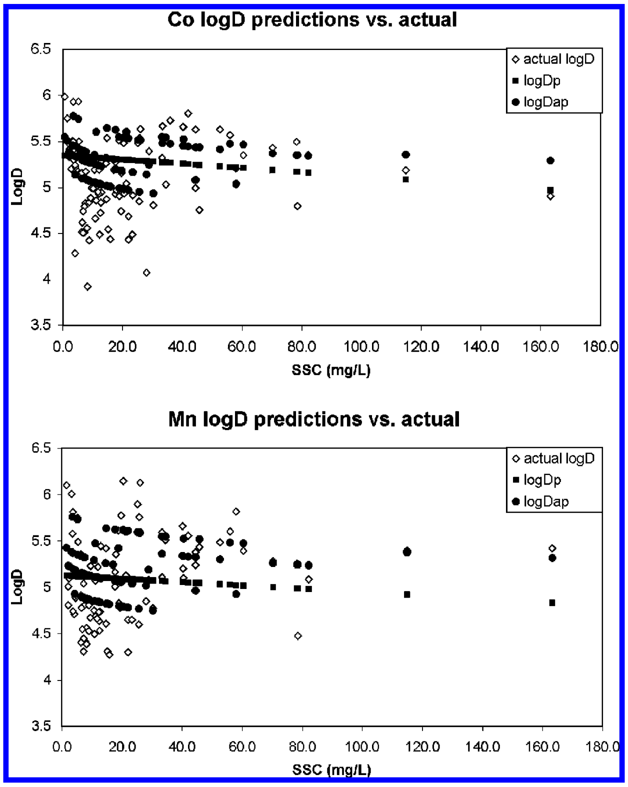

FIGURE 2. Actual log*D* values for Co and Mn are plotted with associated SSC. The simple predicted logD_p, and the prediction output from the most predictive model, logD_{ap}, for each SSC are also plotted. Data are from 2004−2006.

Bay; we chose to consider *p*-values <0.001 to be significant. The geographic region (α) of the Bay was again found to affect *D* values for all trace elements except Ag, Hg, and Se ($p < 0.001$). The season (ϵ) of sampling affected the partitioning of Cd, Cr, Fe, Ni, Pb, Zn ($p < 0.001$). Salinity only affected *D* values for Cd and Cr ($p < 0.001$) individually; the influence of salinity on partitioning is likely coupled with that of seasonality because one major effect of seasonality is freshwater input. The interaction between region and season (δ) only affected the *D* values for Cr and Pb ($p < 0.001$). Finally, variation in Chl-a was not found to significantly affect the *D* values of any of the trace elements assessed.

Generalized linear modeling (GLM) was used to identify additive components from least-squares analysis for the terms associated with each element to calculate a most predictive model using an adjusted predicted partition coefficient (logD_{ap}):

$$\log D_{ap} = \log(K_d)_{ap} = \log(D)_{p^*} + \alpha + \varepsilon + \delta \qquad (3)$$

Although predictions of *D* values for Ag, As, Hg, and Se are not improved by adding α, ϵ, or δ terms, all other elements show improved prediction with one or more of those terms (SI Table S3).

An independent 3-year (2004−2006) data set was used to assess the predictive models by comparison of the measured log*D* result versus the predicted ratio (logD_p) and the adjusted predicted ratio (logD_{ap}), using simple linear least-squares regression. Prediction of the *D* values for Co, Cu, Mn, and Zn, were considerably improved using the most predictive model (Figure 2, SI Table S4) while the r^2 and *p*-value improved for each element.

Prediction of WCT as a Function of SSC. Utilizing the 10-year water quality data set, the dependence of trace element water column total (WCT μg/L) concentration on SSC was evaluated. Ordinary least-squares (OLS) linear regression and robust least median of squares regression were used to relate total element concentration in the water column to the SSC (SI Figure S2).

The values for Co, Cr, and Fe were highly correlated with SSC ($r^2 > 0.9$, *p*-values <0.001). The OLS regression r^2 for Hg in this study was below the same correlation reported by Schoellhamer (*47*), which is attributed to his smaller sample size. The WCT for Ag was not as well correlated with SSC ($r^2 = 0.523$), consistent with previous analyses of RMP data (*41, 47, 48, 7*). However, all regressions were highly significant ($p < 0.001$) using the equation:

$$\mathrm{WCT} = m \times \mathrm{SSC} + b \qquad (4)$$

where the mean relationship between SSC and WCT for each trace element for any region or time inside the estuary is estimated for parameters *m* and *b* (SI Table S5).

Analysis of variance was used to determine the variables that significantly affect WCT values for each trace element. The geographic region was significant ($p < 0.001$) for all trace elements except Co, Fe, and Mn, indicating that these elements are more predominantly distributed in one phase, presumably as ferromanganese oxyhydroxides. Seasonality and salinity only affect As and Cd ($p < 0.001$), most likely related to freshwater input. The effect of season-x-region was highly significant ($p < 0.001$) for As, Cd, and Se, again reflecting the temporally and spatially associated influence of salinity. Chl-a was not found to significantly affect the WCT for any the trace elements tested except Se.

WCT was recalculated using the following equation:

$$\mathrm{WCT} = m \times \mathrm{SSC} + b + \alpha + \varepsilon + \delta \qquad (5)$$

where the slope (m) and intercept (b) terms are from SI Table S5, and general linear regression terms are provided in SI Table S6. The near total concentrations of the trace elements were then predicted using the independent data set from 2004−2006, using concurrently collected trace element samples and optical backscatter for SSC. WCT for most of the trace elements can be estimated with reasonable accuracy (Figure 3). The most predictive model significantly predicted actual WCT in all cases (Table 1, SI Table S7), except for MeHg which has an exceedingly complex biogeochemical cycle within the Bay (*32, 40*).

Application of the most predictive model (eq 5) significantly improved prediction for WCT estimates of As, Cd, and Se. For comparison, using OLS regression results (eq 4) produced: As ($r^2 = 0.008$, $p = 0.496$), Cd ($r^2 = 0.004$, $p = 0.566$), and Se ($r^2 = 0.00$, $p = 0.887$), as compared to As ($r^2 = 0.444$, $p = 0.000$), Cd ($r^2 = 0.125$, $p = 0.000$), and Se ($r^2 = 0.351$, $p = 0.000$) for the most predictive model. The improvement of Se estimation is especially notable because Se is an element of particular toxicity concern in San Francisco Bay (*49*).

Estimation of WCD as a Function of SSC. Employing these most predictive models, it was possible to use an SSC measurement to predict both the WCT concentration and distribution ratio of trace elements in the Bay. WCD estimates for the estuary can similarly be calculated from the 10-year data set (Figure 3, SI Table S8). The same independent data set was used to evaluate the accuracy of the predicted WCD concentrations using directly measured WCD and the equation:

$$[\mathrm{WCD}] = (\mathrm{WCT} \times 10^6)/(D \times \mathrm{SSC} + 10^6) \qquad (6)$$

WCD concentrations for As, Co, Cu, Mn, Ni, Se ($p < 0.001$), Cd, and Zn ($p < 0.05$) were significantly estimated, whereas WCD concentrations for Ag, Fe, Hg, and Pb were not predicted accurately despite the highly accurate predictions of the terms

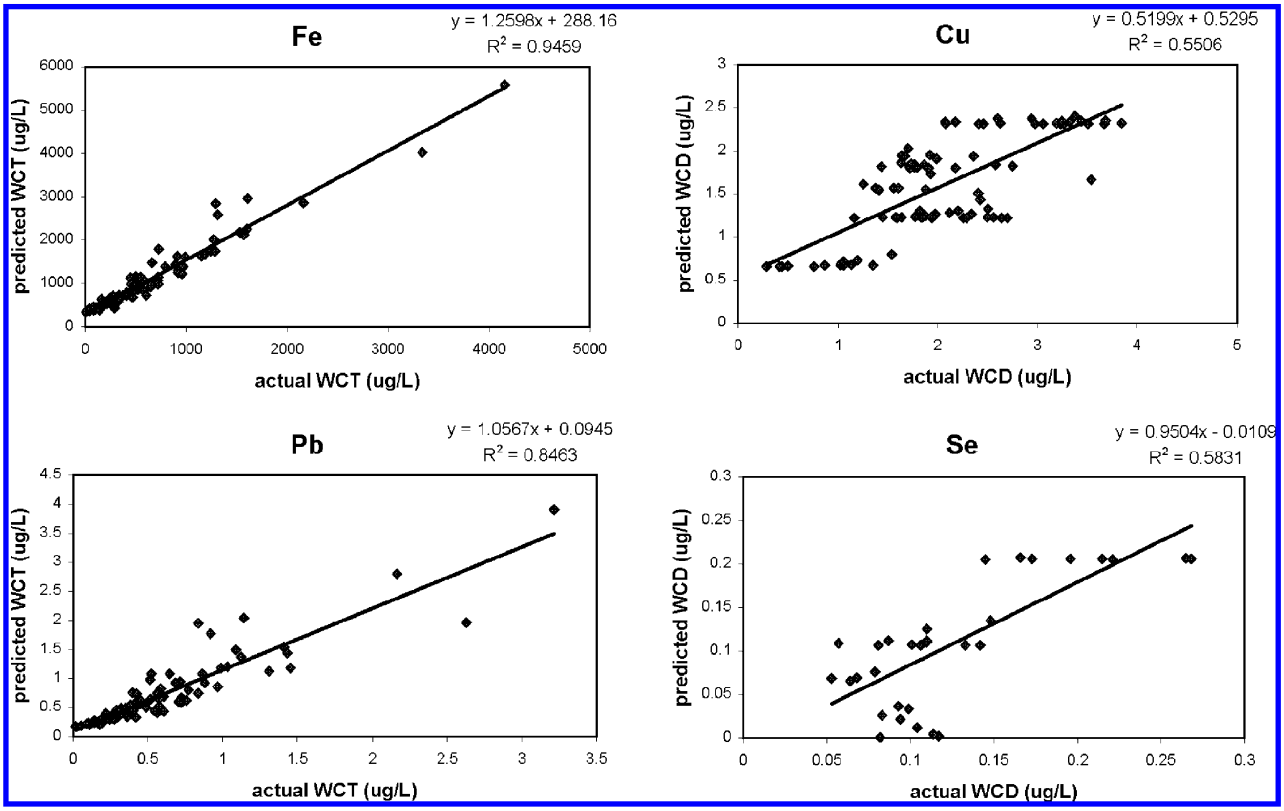

FIGURE 3. Left column: total concentration for the metals Fe and Pb (Water Column Total, WCT; μg/L) are plotted against predictive model WCT estimations based on SSC (mg/L). Right column: Dissolved concentration for Cu and Se (water column dissolved, WCD; μg/L) are plotted against predictive model WCD estimations based on SSC (mg/L). Data from 2004−2006.

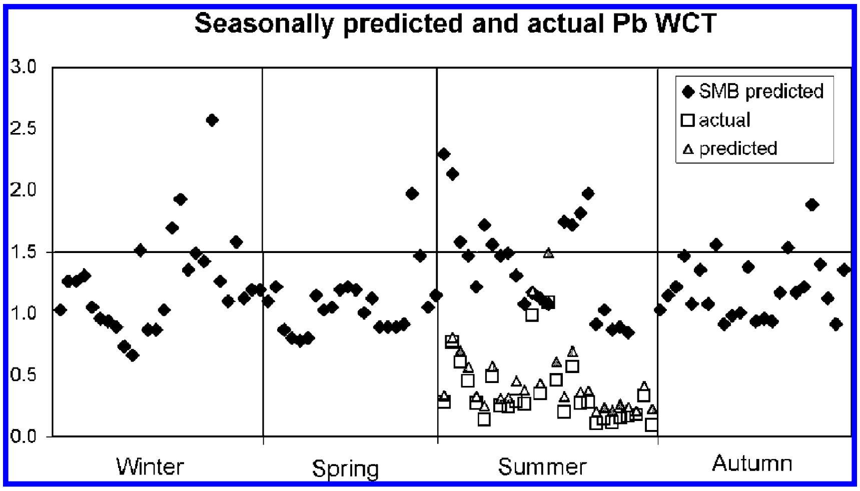

FIGURE 4. Predictions of Pb total concentration in the water column (WCT, μg/L), sorted seasonally for the years 2004−2006 based on the USGS San Mateo Bridge (SMB) (South Bay (north) region) continuous monitoring station SSC data (◆). Pb WCT measurements in this estuary region were measured only during summer, and the measured (actual) Pb WCT values are plotted (□) together with the predicted Pb WCT values based on the in situ measured SSC (△). For presentation purposes, the USGS continuous SSC data were randomly subsampled at a resolution of one day per month for each year, with data from 08:00, 12:00, 15:00, and 18:00 (local time).

used in eq 6 (Table 1, SI Table 9). The estimated SSC (from OBS), WCT (from SSC), and *D* (from SSC) introduce an accumulated error into the WCD prediction (SI Table S9). Regardless, the significant correlations of some elements can be used to obtain rough estimates of WCD of those trace elements when SSC is the only parameter known.

Influence of Algal Blooms on *D*, WCT, and WCD Predictions. The question arises regarding how well the model can be expected to estimate *D*, WCT, and WCD values for trace elements during algal blooms, especially extraordinary bloom events. To test this, trace elements (Co, Cu, Hg, Mn, Ni, Pb, and Zn), methylmercury (MeHg) and ancillary data collected during an algal bloom in the Bay in 2003 (*40*, *48*), were used. These data were obtained from one of the largest algal blooms on record in the San Francisco Bay (*50*).

D values were calculated using the most predictive model (eq 3), and the predicted log*D* was compared to the measured log*D* using OLS regression (SI Table S10). Similarly, WCT and WCD values were predicted using OLS with the most predictive model (eqs 5 and 6). Despite the lack of extreme bloom events in the data used to develop the predictive models, the *D* values for Co, Cu, Ni, and Pb were successfully estimated ($p < 0.05$), whereas estimates

TABLE 1. Summarization of Average Actual WCT and WCD, and Model Prediction Results[a]

	WCT				WCD			
element	avg. (μg/L)	predicted r^2	predicted p	SE	av (ug/L)	predicted r^2	predicted p	prop. err. ± (μg/L)
Ag	0.021	0.592	<0.001	0.005	0.003	0.01	0.521	0.00012 (3.52%)
As	2.7	0.444	<0.001	0.61	2.091	0.47	0.000	0.838 (40.09%)
Cd	0.072	0.125	<0.001	0.033	0.058	0.08	0.014	0.0487 (84.38%)
Co	0.96	0.785	<0.001	0.14	0.189	0.20	0.000	0.0929 (49.22%)
Cr	10.7				0.401			
Cu	4.6	0.552	<0.001	0.83	1.855	0.55	0.000	1.48 (79.70%)
Fe	2024	0.946	<0.001	147	32.191	0.03	0.292	327 (1016.5%)
Hg	0.021	0.547	<0.001	0.003	0.002	0.05	0.224	0.00013 (7.17%)
MeHg	0.13	0.046	0.325	0.021				
Mn	108	0.532	<0.001	18.4	44.75	0.38	0.000	41.7 (93.23%)
Ni	7.7	0.690	<0.001	0.99	2.183	0.45	0.000	1.605 (73.48%)
Pb	1.6	0.846	<0.001	0.20	0.064	0.03	0.079	0.00875 (13.63%)
Se	0.42	0.351	<0.001	0.057	0.379	0.59	0.000	0.0893 (23.57%)
Zn	10.5	0.858	<0.001	0.79	1.654	0.06	0.029	0.4059 (24.55%)

[a] For each of the elements evaluated, the average actual water column total (WCT) and water column dissolved (WCD) are given. Evaluations of the accuracy of WCT (eq 5) and WCD (eq 6) predictions, based solely on SSC, are presented, showing ordinary least squares regression results of predicted-against-actual for the suite of metals and WCT standard errors and WCD propagated errors as both the concentration (μg/L) and percent measured WCD.

for Hg, Mn, and Zn were not statistically significant. The accuracy of WCD estimations for some trace elements also show a response to the bloom conditions, with Hg predictions strongly affected (no longer predictable), while the accuracy of Co and Mn estimations drop from the 99% to 90% confidence interval. The estimation of the WCD for MeHg and Fe were not possible because *D* for MeHg was not modeled, and Fe was not measured by Luengen et al. (*40*). The predictive model for WCT was significant for all elements tested, whereas the MeHg WCT prediction became valid during this bloom.

We conclude that predictions of *D*, WCT, and WCD as a function of SSC for a suite of trace elements, as well as MeHg, in San Francisco Bay is possible. An inherent limitation of this type of statistical model is that it is only robust when applied to similar data sets. However, the large (10-year) data set employed herein yields models that performed reasonably well, even under extreme algal bloom conditions that were not captured during the two decades of sampling.

These indirect measurements may be used as descriptors of the trace element component of water quality and toxicity for a system that is now only sampled annually or biannually. Since predicted and measured Pb WCT is well correlated, it is reasonable to infer that predicted Pb WCT from the San Mateo Bridge SSC data are similarly correlated. Monitoring of contaminant trace elements could therefore be greatly improved by application of these predictive models when direct measurements are not available. While limited, our models provide a good first approximation for the dynamics of trace elements in this complex estuarine system. Use of these predictive models enables extrapolation of trace element distributions to spatial and temporal scales not possible from direct measurements.

These analyses demonstrate that critical water quality parameters in San Francisco Bay can be estimated based on optically derived SSC, as previously proposed (*16, 14, 15*). Remote sensing also provides estimates of Chl-a levels (*51, 52*), enabling analyses of the impact of both trace elements on algal blooms and of algal blooms on trace elements. Finally, these analyses evidence the potential of remote sensing to quantify fluxes of trace elements from the estuary into adjacent northeast Pacific coastal waters, where very few measurements of those elements exist (e.g., refs *53, 54)* while in situ monitoring programs are prohibitively expensive.

Acknowledgments

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Supporting Information Available

Model development description. Figure S1, partition coefficients as a function of suspended solids concentration; Figure S2, total concentrations as a function of suspended solids concentration; Table S1, average distribution ratios and prediction results; Table S2, partition coefficient to suspended solids (SSC) regression results; Table S3, general linear model terms applied to eq 3; Table S4, regression coefficients from direct prediction and modeled D values; Table S5, average water column total concentrations and prediction results; Table S6, general linear model terms applied to eq 5; Table S7, water column total concentrations prediction results; Table S8, average water column dissolved concentrations;Table S9, water column dissolved concentrations prediction results; and Table S10, D, WCT, and WCD predictions during algal bloom conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Luoma, S. N.; Phillips, D. J. H. Distribution, variability, and impacts of trace elements in San Francisco Bay. *Mar. Pollut. Bull.* **1988**, *19*, 413–425.

(2) Luoma, S. N.; van Geen, A.; Lee, B. G.; Cloern, J. E. Metal uptake by phytoplankton during a bloom in South San Francisco Bay: implications for metal cycling in estuaries. *Limnol. Oceanogr.* **1998**, *43* (5), 1007–1016.

(3) Greenfield, B. K.; Davis, J. A.; Fairey, R.; Roberts, C.; Crane, D.; Ichikawa, G. Seasonal, interannual, and long-term variation in sport fish contamination, San Francisco Bay. *Sci. Total Environ.* **2005**, *336* (1−3), 25–43.

(4) Hightower, J. M.; Moore, D. Mercury levels in high-end consumers of fish. *Environ. Health Perspect.* **2003**, *111* (4), 604–608.

(5) Phillips, B. M.; Anderson, B. S.; Hunt, J. W.; Thompson, B.; Lowe, S.; Hoenicke, R.; Tjeerdema, R. Causes of sediment toxicity to *Mytilus galloprovincialis* in San Francisco Bay, California. *Environ. Contam. Toxicol.* **2003**, *45* (4), XXX.

(6) Brown, C. L.; Parchaso, F.; Thompson, J. K.; Luoma, S. N. Assessing toxicant effects in a complex estuary: A case study of effects of silver on reproduction in the bivalve, Potamocorbula amurensis, in San Francisco Bay. *Hum. Ecol. Risk Assess.* **2003**, *9* (1), 95–119.

(7) Flegal, A. R.; Brown, C. L.; Squire, S.; Ross, J. R. M.; Scelfo, G. M.; Hibdon, S. Spatial and temporal variations in silver contamination and toxicity in San Francisco Bay. *Environ. Res.* **2007**, *105* (1), 34–52.

(8) Schwarzbach, S.; Adelsbach, T. *Field Assessment of Avian Mercury Exposure in the Bay-Delta Ecosystem*; U.S. Fish and Wildlife Service: Sacramento, CA, 2002.

(9) Flegal, A. R.; Smith, G. J.; Gill, G. A.; Sanudo-Wilhelmy, S.; Anderson, L. C. D. Dissolved trace-element cycles in the San Francisco Bay estuary. *Mar. Chem.* **1991**, *36* (1−4), 329–363.

(10) San Francisco Estuary Institute's Regional Monitoring Program. http://www.sfei.org/rmp (accessed July 7, 2010).

(11) Sanudo-Wilhelmy, S. A.; Tovar-Sanchez, A.; Fisher, N. S.; Flegal, A. R. Examining dissolved toxic metals in U.S. estuaries. *Environ. Sci. Technol.* **2004**, *38* (2), 34A−38A.

(12) Flegal, A. R.; Conaway, C. H.; Scelfo, G. M.; Hibdon, S. A.; Sañudo-Wilhelmy, S. A. Review of factors influencing measurements of decadal variations in metal contamination in San Francisco Bay, CA. *Ecotoxicology.* **2005**, *14*, 1–16.

(13) Ruhl, C. A.; Schoellhamer, D. H.; Stumpf, R. P.; Lindsay, C. L. Combined Use of remote sensing and continuous monitoring to analyze the variability of suspended-sediment concentrations in San Francisco Bay, California. *Estuarine, Coastal Shelf Sci.* **2001**, *53*, 801–812.

(14) Stumpf, R. P.; Pennock, J. R. Calibration of a general optical equation for remote sensing of suspended sediments in a moderately turbid estuary. *J. Geophys. Res., [Oceans]* **1989**, *94* (C10), 14363–14371.

(15) Stumpf, R. P.; Pennock, J. R. Remote estimation of the diffuse attenuation coefficient in a moderately turbid estuary. *Remote Sens. Environ.* **1991**, *38*, 183–191.

(16) Buchanan P. A.; Ganju N. K. Summary of suspended-sediment concentration data in San Francisco Bay, California, water year 2003. *U.S. Geological Survey Data Series*, 2005; Vol. 113 http://pubs.water.usgs.gov/ds113/ (accessed July 7, 2010).

(17) Thompson, B.; Hoenicke, R.; Davis, J. A.; Gunther, A. An overview of contaminant- related issues identified by monitoring in San Francisco Bay. *Environ. Monit. Assess.* **2000**, *64*, 409–419.

(18) Ruhl, C. A.; Schoellhamer, D. H. Spatial and temporal variability of suspended-sediment concentrations in a shallow estuarine environment, San Francisco Estuary and Watershed Science, 2004; Vol. 2, Issue 2, p 1.

(19) Conomos, T. J. Properties and circulation of San Francisco Bay waters. In *San Francisco Bay: The Urbanized Estuary*; Conomos, T. J., Ed.; American Association for the Advancement of Science: San Francisco California, 1979; pp 47−84.

(20) Peterson, D. H.; Cayan, D. R.; Festa, J. F.; Nichols, F. H.; Walters, R. A.; Slack, J. V.; Hager, S. E.; and Schemel, L. E. Climate variability in an estuary: Effects of riverflow on San Francisco Bay. In *Aspects of Climate Variability in the Pacific and the Western Americas*, Geophysical Monograph 55; Peterson, D. H., Ed.; American Geophysical Union: Washington, DC, 1989; pp 419−442.

(21) Cheng R. T.; Gartner J. W. *Tides, Tidal and Residual Currents in San Francisco Bay California. Results of Measurements 1979–1980. Part 1. Description of Data*, Water Resources Investigations Report 84-4339; United States Geological Survey: Washington, DC, 1984.

(22) Warnock, N.; Bishop, M. A.; Takekawa, J.; Williams, T. D. Connecting the spots—Influences on site use b migratory Pacific Flyway shorebirds. *J. Ornithol.* **2006**, *147* (5), 53–53, Suppl. 1.

(23) Nichols, F. H.; Cloern, J. E.; Luoma, S. N.; Peterson, D. H. The modification of an estuary. *Science.* **1986**, *231* (4738), 567–573.

(24) Cheng, R. T.; Casulli, V.; Gartner, J. W. Tidal, residual, intertidal mudflat (TRIM) model and its applications to San Francisco Bay, California. *Estuar. Coast. Shelf Sci.* **1993**, *36* (3), 235–280.

(25) Hornberger, M. I.; Luoma, S. N.; vanGeen, A.; Fuller, C.; Anima, R. Historical trends of metals in the sediments of San Francisco Bay, California. *Mar. Chem.* **1999**, *64* (1−2), 39–55.

(26) McKee, L. J.; Ganju, N. K.; Schoellhamer, D. H. Estimates of suspended sediment entering San Francisco Bay from the Sacramento and San Joaquin Delta, San Francisco Bay, California. *J. Hydrol.* **2006**, *323*, 335–352.

(27) Schoellhamer, D. H. Variability of suspended-sediment concentration at tidal to annual time scales in San Francisco Bay, USA. *Cont. Shelf Res.* **2002**, *22*, 1857–1866.

(28) Leatherbarrow, J. E.; McKee, L. J.; Schoellhamer, D. H.; Ganju, N. K.; Flegal, A. R. *Concentrations and Loads of Organic Contaminants and Mercury associated with Suspended Sediment Discharged to San Francisco Bay from the Sacrament-San Joaquin River Delta*; California RMP Technical Report. SFEI Contribution 405. San Francisco Estuary Institute: Oakland, CA., 2005.

(29) Buck, K. N.; Ross, J. R. M.; Flegal, A. R.; Bruland, K. W. A review of total dissolved copper and its chemical speciation in San Francisco Bay, California. *Environ. Res.* **2006**, *105*, 5–19.

(30) Conaway, C. H.; Ross, J. R. M.; Looker, R.; Mason, R. P.; Flegal, A. R. Decadal mercury trends in San Francisco Estuary sediments. *Environ. Res.* **2007**, *105*, 53–66.

(31) Doblin, M. A.; Baines, S. B.; Cutter, L. S.; Cutter, G. A. Sources and biogeochemical cycling of particulate selenium in the San Francisco Bay estuary. *Estuarine Coast. Shelf Sci.* **2006**, *67* (2), 681–694.

(32) Conaway, C. H.; Black, F. J.; Grieb, T. M.; Roy, S.; Flegal, A. R. Mercury in the San Francisco estuary. *Rev. Environ. Contam. Toxicol.* **2008**, *194*, 29–54.

(33) Cutter, G. A.; Cutter, L. S. Selenium biogeochemistry in the San Francisco Bay estuary: changes in water column behavior. *Estuarine Coastal Shelf Sci.* **2004**, *61*, 463–476.

(34) Fishman, M. J.; Malo, B. A.; Boyle, D. K. A standard-reference water-suspended sediment sample for total recoverable metals. *J. Test. Eval.* **1984**, *12* (3), 182–186.

(35) Gray J.; Glysson D.; Turcios L.; Schwarz, G. Comparability of Suspended-Sediment Concentration and Total Suspended Solids Data, USGS WRIR 00-4191; U.S. Department of the Interior: Washington, DC, 2000.

(36) Lowe S.; Hoeniche R.; Davis J.; Scelfo G. *1999 Quality Assurance Project Plan Regional Monitoring Program for Trace Substances*, San Francisco Estuary Regional Monitoring Program. May 1999. http://www.sfei.org/documents/2840 (accessed July 7, 2010).

(37) David N.; Bell D.; Gold J. *Field Sampling manual for the Regional Monitoring Program for Trace Substances* San Francisco Estuary Institute, 2001. http://www.sfei.org/sfeireports.htm (accessed July 7, 2010).

(38) Tang, D.; Warnken, K. W.; Santschi, P. W. Distribution and partitioning of trace metals (Cd, Cu, Ni, Pb, Zn) in Galveston Bay waters. *Mar. Chem.* **2002**, *78*, 29–45.

(39) Benoit, G.; Oktay-Marshall, S. D.; Cantu, A.; Hood, E. M.; Coleman, C. H.; Corapcioglu, M. O.; Santschi, P. H. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Mar. Chem.* **1994**, *45*, 307–336.

(40) Luengen, A. C.; Raimondi, P. T.; Flegal, A. R. Contrasting biogeochemistry of six trace metals during the rise and decay of a spring phytoplankton bloom in San Francisco Bay. *Limnol. Oceanogr.* **2007**, *52* (3), 1112–1130.

(41) Smith, J. S.; Flegal, A. R. Silver in San Francisco Bay Estuarine Waters. *Estuaries.* **1993**, *16* (3A), 547–558.

(42) Gee, A. K.; Bruland, K. W. Tracing Ni, Cu, and Zn kinetics and equilibrium partitioning between dissolved and particulate phases in South San Francisco Bay, California, using stable isotopes and high-resolution inductively coupled plasma mass spectrometry. *Geochim. Cosmochim. Acta* **2002**, *66* (17), 3063–3083.

(43) Windom, H. L.; Schropp, S. J.; Calder, F. D. Natural Trace-metal concentrations in estuarine and coastal marine-sediments of the Southeastern United States. *Environ. Sci. Technol.* **1989**, *23* (3), 314–320.

(44) Honeyman, B. D.; Santchi, P. H. Metals in aquatic systems. *Environ. Sci. Technol.* **1988**, *22* (8), 862–871.

(45) Abu-Saba, K. E.; Flegal, A. R. Chromium in San Francisco Bay: superposition of geochemical processes causes complex spatial distributions of redox species. *Mar. Chem.* **1995**, *49*, 189–19.

(46) Ndung'u, K.; Ranville, M. A.; Franks, R. P.; Flegal, A. R. On-line determination of silver in natural waters by inductively-coupled plasma mass spectrometry: Influence of organic matter. *Mar. Chem.* **2006**, *98*, 109.

(47) Schoellhamer, D. H. *Time Series of Trace Element Concentrations Calculated from Time Series of Suspended Solids Concentrations and RMP Water Samples: Summary and Conclusions*, Regional Monitoring Program 1995 Annual Report; San Francisco Estuary Institute: Richmond, CA, 1997; p 53.

(48) Squire, S.; Scelfo, G. M.; Revenaugh, J.; Flegal, A. R. Decadal trends of silver and lead contamination in San Francisco Bay surface waters. *Environ. Sci. Technol.* **2002**, *36* (11), 2379–2386.

(49) Purkerson, D. G.; Doblin, M. A.; Bollens, S. M.; Luoma, S. N.; Cutter, G. A. Selenium in San Francisco Bay zooplankton: Potential effects of hydrodynamics and food web interactions. *Estuaries* **2003**, *26* (4A), 956–969.

(50) Cloern, J. E. Phytoplankton bloom dynamics in coastal ecosystems: A review with some general lessons from sustained investigation of San Francisco Bay, CA. *Rev. Geophys.* **1996**, *34* (2), 127–168.

(51) Kudela, R. M.; Chavez, F. P. The impact of coastal runoff on ocean color during an El Nino year in Central California. *Deep-Sea Res., Part II* **2004**, *51* (10−11), 1173–1185.

(52) Lee, Z. P.; Carder, K. L. Absorption spectrum of phytoplankton pigments derived from hyperspectral remote-sensing reflectance. *Remote Sens. Environ.* **2004**, *89* (3), 361–369.

(53) Van Geen, A.; Luoma, S. N. Trace Metals (Cd, Cu, Ni, and Zn) and nutrients in coastal waters adjacent to San Francisco Bay, California. *Estuaries.* **1993**, *16* (3A), 559–566.

(54) Hurst, M. P.; Bruland, K. W. The effects of the San Francisco Bay plume on trace metal and nutrient distributions in the Gulf of the Farallons. *Geochim. Cosmochim. Acta* **2007**, *72*, 395–411.

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