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Role of phytoplankton in mercury cycling in the San Francisco Bay estuary

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Abstract

To study the role of phytoplankton in mercury cycling, we measured methylmercury (MeHg) and total mercury (Hg_T) in surface waters during the spring 2003 phytoplankton bloom in San Francisco Bay. Conditions that described the peak of the bloom, the amount of sorbent, and decay of the bloom were summarized by principal component analysis (PCA). Multivariate analyses conducted with the PCA factors demonstrated that the bloom accounted for a significant ($p = 0.03$) decrease in dissolved ($<0.45 \mu m$) MeHg. Dissolved MeHg was depleted to $0.026 \text{ pmol L}^{-1}$ and was unaffected when chlorophyll *a* concentrations nearly tripled, indicating that bloom dilution could occur as a result of a limited amount of MeHg. The calculated algal MeHg concentration was $3\text{--}10 \text{ pmol g}^{-1}$ (dry weight). As the bloom decayed, dissolved MeHg concentrations significantly ($p = 0.04$) increased, likely due to MeHg remineralization from decaying phytoplankton and/or production in sediments. By creating suboxic conditions in surface sediments and stimulating microbial activity, decomposing phytoplankton could bolster MeHg production, a potential side effect of large blooms. Unlike dissolved MeHg, dissolved Hg_T concentrations were not measurably altered by the bloom or decay factors. That difference corroborated previous culture studies in which phytoplankton actively accumulated MeHg, but not Hg_T . As the bloom decayed, $Hg_T K_d$ values significantly ($p = 0.012$) increased, possibly because particles (i.e., phytoplankton) with low Hg_T concentrations were lost from the water column. Based on the relationship between Hg_T particulate concentrations and percent phytoplankton, the calculated algal Hg_T concentration was $\sim 0.5 \text{ nmol g}^{-1}$ (dry weight).

Studies in laboratories (Mason et al. 1996; Moye et al. 2002), mesocosms (Pickhardt et al. 2002), and lakes (Watras and Bloom 1992; Chen and Folt 2005) indicate

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that phytoplankton play a critical role in mercury uptake and bioavailability. For example, culture studies show that phytoplankton actively accumulate methylmercury (MeHg) and concentrate it by a factor of 10^4 to 10^5 (Moye et al. 2002; Pickhardt and Fisher 2007). Because phytoplankton store MeHg in the cytoplasm, where it is readily assimilated by zooplankton, phytoplankton are responsible for the preferential accumulation of MeHg over inorganic forms of mercury in food chains (Mason et al. 1996).

Ultimately, the concentration of MeHg in fish may depend on the abundance of phytoplankton, based on studies that show an inverse correlation between algal abundance and mercury concentrations in zooplankton and fish (Pickhardt et al. 2002; Chen and Folt 2005; Pickhardt et al. 2005). We sought to evaluate the role of phytoplankton in the San Francisco Bay estuary, where mercury concentrations are generally lower than in culture studies and where myriad other processes affect mercury cycling. To capture a change in phytoplankton biomass, we sampled during a predictably occurring spring diatom bloom in the southern reach of San Francisco Bay, or South Bay (Fig. 1).

Sampling during a spring bloom is a strategy that has been previously used in South Bay to study the uptake of other metals (e.g., cadmium [Cd], copper [Cu], manganese [Mn], nickel [Ni], lead [Pb], and zinc [Zn]) by phytoplankton (Luoma et al. 1998; Luengen et al. 2007). The conditions that set up the bloom—calm, stratified water and neap tides (Cloern 1996)—also minimize sediment resuspension and horizontal movement of water. Thus, changes in metal concentrations during a bloom may be attributed to biological activity. Luoma et al. (1998) used the 1994 spring bloom to show that Cd, Ni, and Zn were

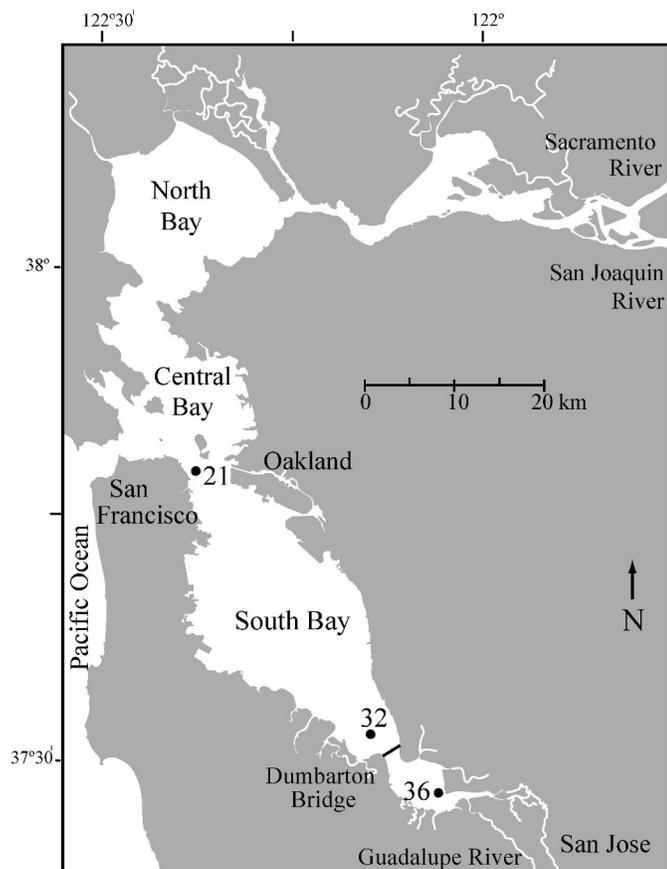


Fig. 1. Samples were collected in the southern reach of San Francisco Bay (South Bay) at three sites. Site 21 (Bay Bridge) was the most oceanic site. Sites 32 (Ravenswood Point) and 36 (Calaveras Point) exchange less water with the Pacific Ocean than does site 21, and these sites also receive mercury inputs from the Guadalupe River and other tributaries that drain the New Almaden mercury mining district.

bioavailable because they were depleted from the water during the bloom, but that dissolved Cu was not depleted and was not bioavailable. Similarly, Luengen et al. (2007) found that concentrations of some metals (e.g., Mn, cobalt [Co], Zn, and Pb) increased as the spring 2003 bloom degraded, demonstrating that decay of the bloom also affected metal cycling. However, neither total Hg (Hg_T), which includes both inorganic and organic forms of mercury, nor MeHg has been previously measured during a South Bay bloom, despite the mercury pollution in the estuary (Thompson et al. 2000; Davis et al. 2003).

Concentrations of Hg_T as high as 440 pmol L^{-1} (Conaway et al. 2003) in unfiltered surface waters are primarily the result of both historic gold and mercury mining in the estuary's watersheds (Ganguli et al. 2000; Domagalski 2001; Thomas et al. 2002). Mercury that enters the northern reach of the estuary via the Sacramento and San Joaquin Rivers was transported to the Sierra Nevada during historic gold mining operations (Hornberger et al. 1999; Domagalski 2001). That mercury was originally mined in the Pacific Coast Ranges, and the now-abandoned Coast Range mines drain into South Bay through the

Guadalupe River and other small tributaries (Cargill et al. 1980; Thomas et al. 2002). The combined mercury inputs from the Sierra Nevada and the Coast Range contribute up to several hundred kilograms of mercury to the estuary every year, far more than inputs from contemporary sources (e.g., atmospheric deposition, wastewater treatment plants, and surface-water runoff) (Domagalski 2001; Thomas et al. 2002; Conaway et al. 2003). Although the cycling of this mercury in the estuary has been previously studied (Choe and Gill 2003; Choe et al. 2003; Conaway et al. 2003), the role of phytoplankton in mercury cycling needs further investigation (Choe et al. 2003).

Data from the northern reach of San Francisco Bay (Choe and Gill 2003; Choe et al. 2003) along with field data from other studies indicate that phytoplankton can affect mercury cycling. For example, Choe et al. (2003) found a relationship between chlorophyll *a* (Chl *a*) and particulate Hg_T in some seasons in North Bay. Those variables were likewise correlated in a study of the Kara Sea, Siberia (Coquery et al. 1995), which the authors attributed to uptake of Hg_T by phytoplankton. Field studies have also found evidence of uptake of MeHg by phytoplankton. For example, in Minnesota lakes, MeHg concentrations increased in net plankton ($\geq 300 \mu\text{m}$) while simultaneously decreasing in water (Monson and Brezonik 1998). Finally, phytoplankton may be involved in Hg^0 formation, based on the correlation between phytoplankton pigments and Hg^0 in the Scheldt estuary, the Netherlands (Baeyens et al. 1998). Our research expands on these field studies by following a specific bloom event across a large range of Chl *a* concentrations and uses principal component analyses (PCA) and general linear models to ascribe changes in mercury concentrations to specific processes.

By closely following the spring bloom, we sought to test in an estuary some of the hypotheses that were developed in mesocosms and lakes. First, we predicted that the bloom would measurably deplete dissolved ($<0.45 \mu\text{m}$) MeHg from the water column, a result that would be consistent with those of previous studies showing that phytoplankton actively (i.e., energy expended) accumulate MeHg (Moye et al. 2002; Pickhardt and Fisher 2007). Second, we looked for evidence that MeHg concentrations in phytoplankton decreased when Chl *a* concentrations were high, which would be evidence of bloom dilution. According to the bloom dilution hypothesis, which has been tested in mesocosms (Pickhardt et al. 2002) and lakes (Chen and Folt 2005), an increase in algal biomass decreases the amount of MeHg per individual phytoplankton and thus the amount of MeHg accumulated in higher trophic levels. If bloom dilution occurs in South Bay, we would expect that the recently observed increase in algal biomass in San Francisco Bay (Cloern et al. 2006) would decrease MeHg availability to the food chain. Third, we calculated the concentration of MeHg and Hg_T in South Bay phytoplankton to provide regulators with site-specific bioaccumulation factors that can be used to model mercury transport in the estuary. Finally, we wanted to determine if the decay of the bloom affected MeHg and Hg_T concentrations or partitioning, as has been observed for some other metals during that period (Luengen et al. 2007).

Based on these studies, we expected that the growth and decay of the bloom would alter mercury cycling in San Francisco Bay and that processes affecting phytoplankton biomass (e.g., eutrophication) could affect mercury bio-availability in estuaries.

Methods

Sampling—Surface-water samples were collected at three sites in the channel of South Bay (Fig. 1) as part of a previously described study focused on the 2003 phytoplankton bloom (Luengen et al. 2007). Sampling began 19 February 2003 and continued at approximately weekly intervals until 01 May 2003, well after the peak of the bloom. A subsequent cruise on 27 August 2003 provided a nonbloom contrast to the spring data at those sites. At least 10% of field samples were taken in duplicate to provide a measure of precision (Lyn et al. 2003). All samples were taken aboard the U.S. Geological Survey (USGS) R/V *Polaris*.

Using trace metal-clean techniques previously employed in San Francisco Bay (Flegal et al. 1991), surface water for mercury analyses was collected via two peristaltic pumps equipped with acid-cleaned Teflon tubing. One pump was equipped with an acid-cleaned Osmonics polypropylene filter (Calyx Capsule) to collect dissolved ($<0.45 \mu\text{m}$) samples. The second pump was used to collect total (unfiltered) samples. Samples were immediately frozen on dry ice and were stored frozen until analysis.

In addition to the mercury samples, we considered 15 water chemistry variables: Chl *a*, phaeophytin (Phaeo), Chl *al* (Chl *a* + Phaeo), suspended particulate matter (SPM), salinity, dissolved oxygen, temperature, water density (σ_t), dissolved organic carbon (DOC), dissolved reactive phosphate, dissolved silicate, dissolved inorganic nitrogen, tidal amplitude, and total (unfiltered) iron (Fe) and Mn. Techniques for collecting and analyzing those samples, including the use of a Sea-Bird Electronics underwater unit (SBE-9 plus) to take vertical profiles, are described elsewhere (Luengen et al. 2007).

Analyses of MeHg and Hg_T—Dissolved and total (unfiltered) water samples for MeHg analyses were preserved by addition of 0.02% sulfuric acid (Parker and Bloom 2005). We then analyzed the samples at Studio Geochimica by distillation, aqueous-phase ethylation, volatile organic trapping, and quantification by cold vapor atomic fluorescence spectrophotometry (CVAFS) (Bloom 1989; Horvat et al. 1993; Bloom and Von Der Geest 1995). The detection limit was $0.041 \text{ pmol L}^{-1}$. Because no certified reference material for MeHg in water existed, we analyzed a diluted digestion of a dogfish reference material (DORM-2) from the National Research Council, Canada. Recovery was 86%. Matrix spike recoveries averaged 94%.

Dissolved and total water samples for Hg_T analyses were thawed and oxidized by addition of 0.5% bromine monochloride for at least 2 h. Samples were then pre-reduced with hydroxylamine hydrochloride, reduced with tin chloride, and then analyzed by CVAFS and two-stage

gold amalgamation trapping (Gill and Fitzgerald 1987; Bloom and Fitzgerald 1988).

At the University of California, Santa Cruz (UCSC), we analyzed Hg_T samples with a Tekran 2600, as described in Conaway et al. (2003). The instrument was calibrated using a 5-point curve with an $r^2 > 0.99$ (simple linear regression). We checked accuracy by analyzing a certified reference material from the National Research Council, Canada (ORMS-3), which consisted of river water spiked with inorganic Hg. Its certified value ($\bar{x} \pm$ standard deviation [SD]) was $62.8 \pm 5.5 \text{ pmol L}^{-1}$, and our measured value was $59.6 \pm 4.5 \text{ pmol L}^{-1}$. We also ran matrix spikes with quantitative (82–100%) recoveries. Sample concentrations were above detection limits ($3 \times \text{SD}$ of the blanks), which were 0.43 pmol L^{-1} for dissolved samples and 3.7 pmol L^{-1} for total samples. For dissolved samples, the relative standard deviation (RSD) of laboratory duplicates was 15%, and the RSD of duplicate field samples was 17%. For total samples, the RSD of laboratory replicates was 4%, and the RSD of duplicate field samples was 6.5%.

After analysis of MeHg and Hg_T dissolved and total samples, particulate MeHg and Hg_T concentrations were calculated as the difference between total and dissolved concentrations. Distribution coefficients (K_d) between the particulate and dissolved phases were calculated as the particulate concentration per gram of SPM (mol kg^{-1}) divided by the dissolved concentration (mol L^{-1}) (Stumm and Morgan 1996). The K_d values are, accordingly, in units of L kg^{-1} .

PCA factors—We (Luengen et al. 2007) previously used PCA to reduce the 15 water chemistry variables into three composite factors. The complete details, including data for all of the water chemistry variables, have been previously presented (Luengen et al. 2007). Here, we present a brief synopsis of the rationale behind the analysis and the composition of the resulting PCA factors.

The purpose of PCA was to create new factors that were, by definition, independent (i.e., non-collinear). The new composite factors could then be used in subsequent analyses in place of original variables, many of which were collinear and would therefore violate the assumptions of multivariate analysis. Each composite factor also summarized a broad set of environmental conditions, making it a better descriptor of a biophysical phenomenon (e.g., a bloom) than any single parameter.

For example, the first PCA factor grouped Chl *a* concentrations (+), dissolved oxygen concentrations (+), dissolved inorganic nitrogen concentrations (–), dissolved silicate concentrations (–), salinity (–), and temperature (–) into a single factor, in which the direction of the relationship between the new composite factor and the original variable was given by the sign in parentheses (see Table 1 for component loadings). Grouping these variables was consistent with the biology of the bloom; freshwater stratified the water column, enabling phytoplankton to grow rapidly in surface waters and deplete the nutrients. The bloom developed during the lowest temperatures (Table 2), perhaps reflecting the temperature preference

Table 1. Principal component analysis (PCA) was used to reduce the water chemistry variables into three composite factors. The contribution of each original variable to the new composite factor was given by its component loadings (in parentheses), where +1 would be a perfect positive correlation with all points on the line and -1 would be a perfect negative correlation. As discussed in our previous work (Luengen et al. 2007), only original variables with component loadings of ≥ 0.6 or ≤ -0.6 were interpreted. Based on the loadings, the first composite factor characterized the high chlorophyll *a* (Chl *a*) concentrations and associated water chemistry conditions that occurred at the peak of the bloom. The second factor represented the amount of suspended particulate matter (SPM) and manganese (Mn) and iron (Fe) (hydr)oxides available for metal sorption. The third factor was a composite of particulate and dissolved phases of decay. Dissolved organic carbon (DOC) concentrations were inversely correlated with the decay factor (i.e., decreasing values of the decay factor corresponding with increasing DOC concentrations).*

Bloom factor	Sorbent factor	Decay factor
DO(0.703)	log SPM(0.748)	log DOC(-0.657)
T(-0.622)	σ_t (-0.646)	log Phaeo(0.697)
Salinity(-0.620)	log DRP(0.832)	
DIN(-0.607)	UFFe(0.819)	
DSi(-0.834)	UFMn(0.775)	
log Chl <i>a</i> (0.864)		

* DO, dissolved oxygen; T, temperature; σ_t , water density; Phaeo, phaeophytin; DRP, dissolved reactive phosphate; DIN, dissolved inorganic nitrogen, UFFe, total (unfiltered) Fe; DSi, dissolved silicate; UFMn, total (unfiltered) Mn.

of the diatoms (*Thalassiosira punctigera*) that dominated the bloom (Luengen 2007). Because multiple variables (Fig. 2; Table 2) all described conditions at the peak of the bloom, we grouped them into a bloom factor for subsequent statistical analyses. The bloom factor was well correlated with Chl *a* concentrations (Luengen et al. 2007) and had the highest values on 04 March, when Chl *a* peaked (Figs. 2, 3), but also included the other variables that characterized bloom conditions.

Conducting statistical analyses for the effects of each original variable on dissolved mercury concentrations (e.g., looking for relationships between Chl *a* and mercury, then nutrients and mercury, then salinity and mercury) could have led to the incorrect conclusion that each of these variables was individually important (e.g., mercury depletions were related to low nutrient concentrations), rather than part of the phytoplankton bloom. Moreover, picking some variables over others (e.g., Chl *a* vs. dissolved oxygen, see Fig. 2) would have been arbitrary. Accordingly, the PCA factors were the most appropriate terms to use in later statistical analyses.

The second PCA factor was a composite of SPM (+), unfiltered Fe (+), unfiltered Mn (+), dissolved reactive phosphate (+), and σ_t (-). This PCA factor was positively correlated with the amount of particulate matter, including Fe and Mn (hydr)oxides. Dissolved reactive phosphate, which is particle reactive, also positively contributed to the second PCA factor. Water density was inversely related to the other variables, likely because fluvial inputs contained high particulate concentrations. Based on the contributions

of these variables, the second PCA factor was considered a sorbent factor that represented the amount of material available for metal sorption. Sorption, which is “the partitioning of solutes between the solution and the whole of a particulate phase” (Morel and Hering 1993, p. 556), was the most appropriate term because we did not distinguish between adsorption of metals onto particulate surfaces and absorption of metals incorporated into Fe and Mn hydr(oxides) and organic coatings.

The third factor was a composite of DOC (-) and Phaeo (+). Phaeo concentrations, which are particulate measures of Chl *a* breakdown, peaked during the bloom (Fig. 2). The breakdown of phytoplankton into dissolved carbon did not happen until April, as shown by the DOC concentrations in Fig. 2. As a result of the differences in timing, Phaeo and DOC were inversely related to each other. However, both were indicators of the decomposition of the bloom, making factor 3 a decay factor. As values of the decay factor decreased (Fig. 3), the bloom was broken down into the dissolved phase.

Together, the three PCA factors explained 77% of the variance, with the first factor explaining 31%, the second 27%, and the third 19% (Luengen 2007). Additional composite factors were not meaningful, based on their eigenvalues of < 1 . When eigenvalues are < 1 , composite factors explain less variation than would be expected from an original variable, indicating that meaningful composites have not been generated (Quinn and Keough 2002). Because most of the variance could be explained by just three composites, and because those composites could be interpreted in terms of the biogeochemistry of the bloom, we used the three PCA factors in subsequent multivariate analyses.

Development of multivariate models—The first goal of our statistical analysis was to determine if the composite factors developed by PCA were associated with MeHg concentrations or partitioning. Because most of our MeHg samples were from site 36, our statistical analysis focused only on that site. We began by examining the dissolved MeHg and MeHg K_d data for normality, and we log-transformed the MeHg K_d values to achieve a normal distribution. We then used a general linear model (GLM) routine in Systat (version 10.2.05) to run multiple linear regressions with the dependent variable as either dissolved MeHg concentrations or MeHg K_d values. The composite factors were by definition independent, and we therefore initially included all of them in the analysis. Composite factors with a *p* value of > 0.15 were then successively dropped from the model to develop models that described the dependent variables with the fewest number of factors, an approach that we used previously for other metals (Luengen et al. 2007).

We also used a model-building approach to look at the effects of the three PCA factors and the categorical variable, site, on dissolved Hg_T concentrations and Hg_T K_d values. Both of those dependent variables were normally distributed. Because this model included a categorical variable (site), we used the GLM routine to run an analysis of covariance (ANCOVA). We first ran a “full” model that included that four-way interaction (factor 1 \times factor 2 \times factor 3 \times site) to test the assumption of

Table 2. Water chemistry variables at three locations in South San Francisco Bay during a spring bloom in 2003.*

Date	Site	Chl <i>a</i> ($\mu\text{g L}^{-1}$)	Phaeo ($\mu\text{g L}^{-1}$)	DOC ($\mu\text{mol L}^{-1}$ C)	NpN ($\mu\text{mol L}^{-1}$)	DRP ($\mu\text{mol L}^{-1}$)	DSi ($\mu\text{mol L}^{-1}$)	NH ₄ ($\mu\text{mol L}^{-1}$)	Temp (°C)	Salinity
19 Feb	21	5.9	2.1		12.24	1.59	71.26	3.36	12.51	25.8
24 Feb	21	28	4.1	310	3.95	1.88	27.08	1.22	13.14	24.3
04 Mar	21	14	3.1	108	12.77	1.49	70.74	2.34	12.87	24.9
12 Mar	21	7.9	0.8	179	5.49	1.11	59.80	0.24	14.10	23.7
27 Mar	21	17	1.7	164	5.95	1.54	37.69	1.17	14.60	25.9
01 Apr	21	12	3.6	285	11.52	1.51	44.12	1.80	13.79	27.4
17 Apr	21	7.2	2.2	170	6.86	2.49	33.72	5.69	14.26	26.8
23 Apr	21	3.5	1.1	843	9.45	2.59	43.71	15.66	14.44	27.1
01 May	21	7.0	2.8	393	10.64	2.65	54.98	8.36	15.05	26.0
27 Aug	21	8.0	4.1	107	20.74	4.32	78.78	6.81	20.91	29.8
19 Feb	32	35	7.4		52.27	6.99	78.71	0.12	12.94	19.9
24 Feb	32	59	8.7		21.56	4.48	35.98	0.68	12.97	21.2
04 Mar	32	84	1.8	277	1.40	2.65	2.06	0.20	14.15	21.6
12 Mar	32	45	3.1	238	0.44	3.62	2.36	0.19	15.15	21.2
27 Mar	32	28	3.4	354	0.37	3.36	3.34	0.07	15.20	23.0
01 Apr	32	16	3.1	604	0.39	3.47	4.45	0.21	16.69	23.4
17 Apr	32	7.8	2.8	428	12.15	4.52	44.43	2.85	14.99	22.7
23 Apr	32	4.3	0.9	609	13.55	5.29	52.70	4.92	15.03	22.6
01 May	32	7.7	2.6	577	17.17	5.18	56.19	2.02	16.13	23.8
27 Aug	32	10	11	217	6.18	10.5	176.31	1.63	23.10	28.5
19 Feb	36	32	19		56.09	9.91	106.23	1.09	13.00	17.2
24 Feb	36	62	5.0	262	31.62	5.60	42.14	0.61	13.01	20.7
04 Mar	36	169	17	283	1.55	3.94	0.85	0.20	14.19	19.2
12 Mar	36	75	4.9	275	2.29	3.84	0.80	0.21	14.94	19.8
27 Mar	36	48	4.7	225	1.81	5.00	1.70	0.14	15.02	21.1
01 Apr	36	16	2.4	383	0.69	4.78	3.63	0.27	17.44	21.6
17 Apr	36	6.1	3.4	289	27.98	6.59	62.90	6.73	15.04	19.6
23 Apr	36	3.8	1.0	520	45.67	8.68	86.60	9.82	14.14	18.8
01 May	36	3.7	1.8	686	34.22	7.39	75.01	5.69	16.42	21.2
27 Aug	36	6.3	5.2	266	30.13	14.2	208.35	3.28	23.41	27.2

* Chl *a*, chlorophyll *a*; Phaeo, phaeophytin; DOC, dissolved organic carbon; NpN, nitrate plus nitrite; DRP, dissolved reactive phosphate; DSi, dissolved silicate; NH₄, dissolved ammonium; Temp, temperature.

homogeneity of complex shapes. If the *p* value was >0.15 , we dropped the interaction term and ran the “reduced” model (Quinn and Keough 2002). As in our approach to the MeHg data, we then dropped factors with $p > 0.15$ to build models that best described dissolved Hg_T concentrations and Hg_T K_d values.

By developing these multivariate models, we were able to account for co-occurring processes, such as decomposition of the bloom and a simultaneous pulse of SPM. This approach was critical to allowing us to work in an estuary in which processes cannot be isolated, as they are in culture studies. To graphically depict these multiple processes, we used partial residual plots, which depict relationships found to be important in the ANCOVA. The partial residual plots show the contribution of a single term by removing it from the model and plotting the residuals against the omitted factor. In the resulting plots, the y-axis shows the number of standard deviations of variation; accordingly, the relative contribution of the different factors can be visualized by comparing the range of the y-axes.

Results

MeHg concentrations—Concentrations of dissolved ($<0.45 \mu\text{m}$) MeHg ranged from below the detection limit

($0.041 \text{ pmol L}^{-1}$) to 0.13 pmol L^{-1} and averaged $0.060 \text{ pmol L}^{-1}$ (Fig. 4). Concentrations of total MeHg varied from 0.12 to 1.3 pmol L^{-1} and averaged 0.45 pmol L^{-1} (Fig. 4). Those concentrations were consistent with the range of dissolved (0.05 – 0.4 pmol L^{-1}) and total (0.10 – 1.2 pmol L^{-1}) MeHg in the only two studies that previously reported MeHg concentrations in South San Francisco Bay waters (Choe and Gill 2003; Conaway et al. 2003).

Most of the MeHg in the water column was bound to particles, as evidenced by high K_d values. MeHg K_d values ranged from $10^{4.8}$ to $10^{5.7} \text{ L kg}^{-1}$ (Table 3). Those values were within the range (10^4 – 10^7 L kg^{-1}) reported for Hg_T in the estuary (Conaway et al. 2003) and also the average ($10^{4.77} \pm 0.39 \text{ L kg}^{-1}$) given for MeHg in the estuary (Choe and Gill 2003). Studies in other regions have found MeHg K_d values of similar magnitude, including $10^{2.9}$ to $10^{5.7} \text{ L kg}^{-1}$ for the Anacostia River in Washington, D.C. (Mason and Sullivan 1998), and $10^{3.7}$ to $10^{5.6} \text{ L kg}^{-1}$ for Offatts Bayou, a subestuary of Galveston Bay, Texas (Han et al. 2007).

MeHg associated with particles comprised 63–96% of the total MeHg in the water column. That percentage was consistent with the results of Choe and Gill (2003), who found that 85% of total MeHg was associated with particles at their site in the extreme South Bay. The

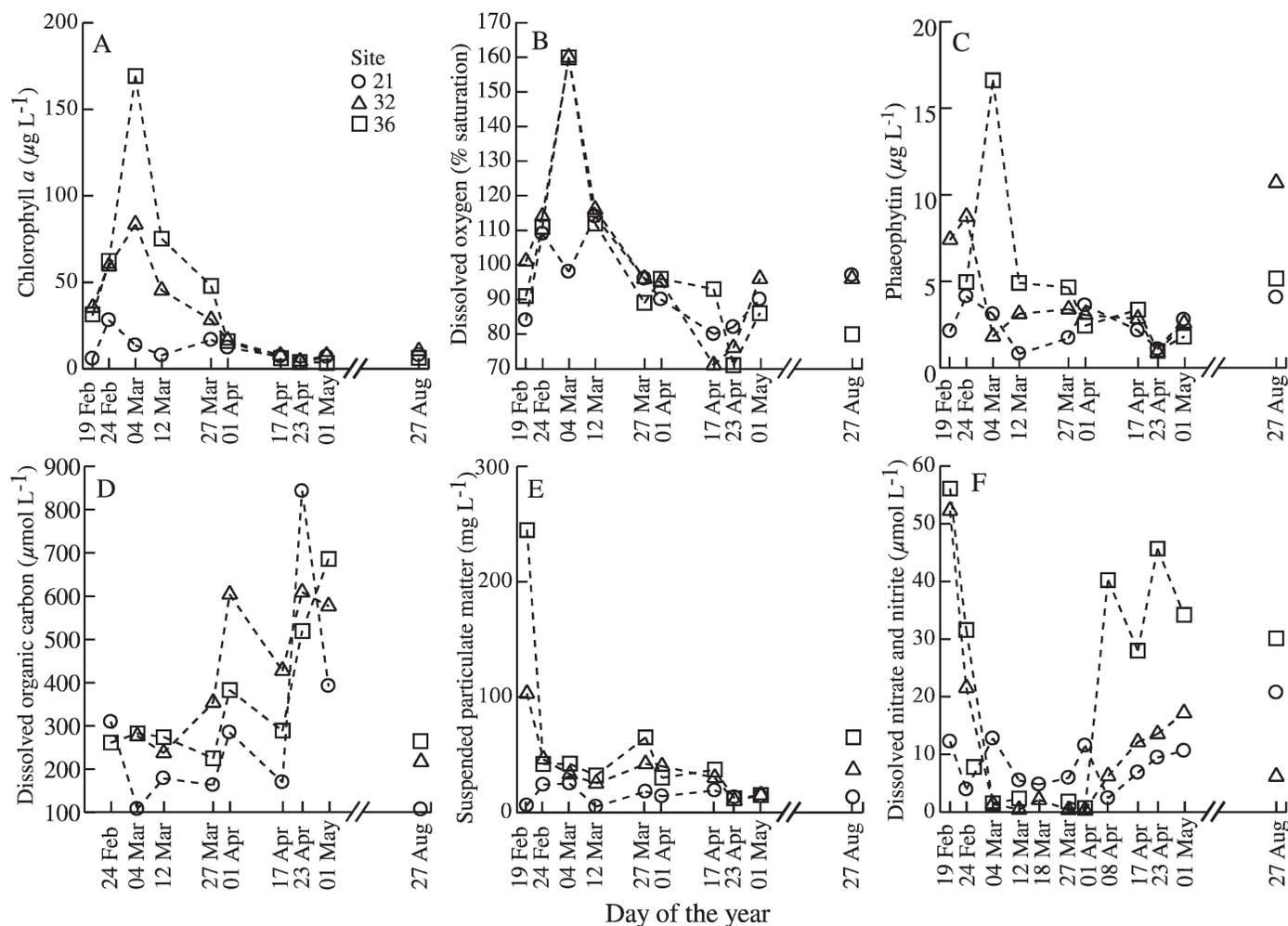


Fig. 2. Descriptive plots of water chemistry variables measured at three sites during the spring 2003 bloom. (A) Chl *a* concentrations were at bloom levels ($>10 \mu\text{g L}^{-1}$) for over a month. (B) Dissolved oxygen became supersaturated as Chl *a* increased. (C) Phaeophytin concentrations, which were particulate measurements of Chl *a* breakdown, were highest in late February and early March, whereas (D) DOC concentrations increased in April. (E) SPM concentrations were highest on 19 February and corresponded with high Hg_T concentrations at site 32, as shown in Fig. 4. (F) Dissolved nitrate and nitrite were rapidly depleted by the bloom, a pattern that was also seen for dissolved silicate and dissolved reactive phosphate (data shown in Table 2).

dominance of the particulate fraction of MeHg is partially due to high rates of resuspension in South Bay from wind-driven mixing and inputs of fine-grained material from channels (Conaway et al. 2007). Our highest value of total MeHg, of 1.3 pmol L^{-1} on 19 February at site 32 (Fig. 4), was associated with a pulse of SPM (Fig. 2), attesting to the importance of MeHg associated with resuspended particles in this system.

Statistical models for MeHg—Our statistical approach used multivariate analysis (Table 4) and partial residual plots (Fig. 5) to demonstrate that both the bloom and decay factors significantly ($p < 0.05$) explained dissolved MeHg concentrations. This multivariate approach was necessary because much of our sampling occurred after the peak of the bloom (Fig. 2), when myriad processes co-occurred. For example, Chl *a* concentrations changed while the bloom decayed. By using multivariate analyses to look at the effects of the bloom factor *after* accounting for the

decay factor, and vice versa, we were able to isolate the effects of each factor individually. We then used partial residuals plots (Fig. 5) to illustrate the direction and magnitude (based on the number of SDs on the y-axis) of the effect of each individual factor. Those plots (Fig. 5) showed that high values of the bloom factor (peak of the bloom) corresponded with low dissolved MeHg concentrations. Similarly, decreasing values of the decay factor (decay of the bloom) explained increases in dissolved MeHg concentrations (Fig. 5). Both the bloom and decay factors contributed equally to dissolved MeHg concentrations, based on the comparable t values, which can be used to assess the relative contribution of the terms in the model.

When we used a similar model-building approach to look at the effects of the PCA factors on MeHg K_d values at site 36, we found that the bloom factor was the only factor significantly ($p = 0.021$) associated with MeHg K_d values (Table 5). At the peak of the bloom (high values of the bloom factor), MeHg K_d increased (Fig. 6). That

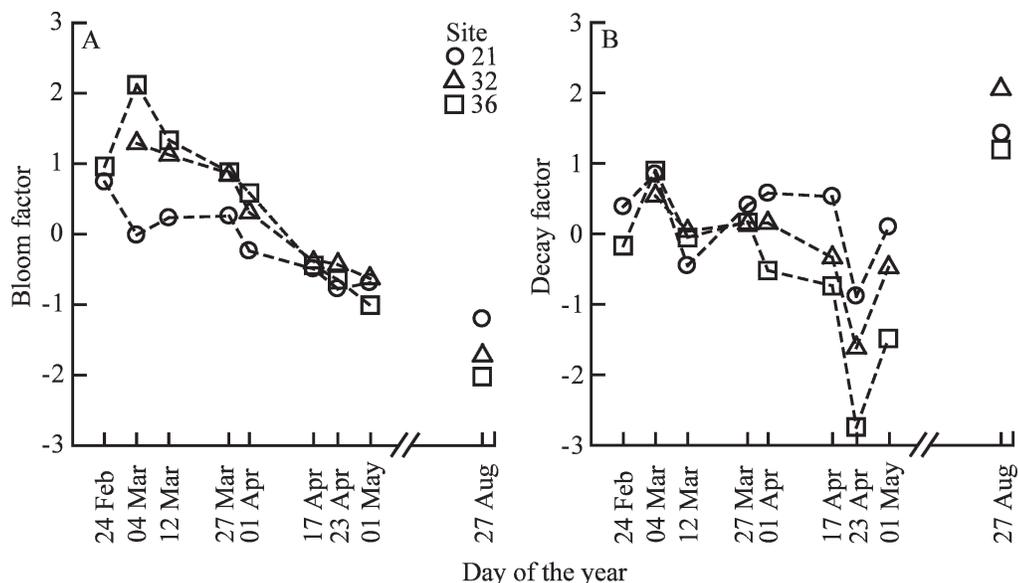


Fig. 3. Descriptive plots showing how the bloom and decay factors, which were composite factors generated by principal component analysis of the water chemistry variables, changed over the course of the spring 2003 bloom. (A) The highest values of the bloom factor corresponded with high values of Chl *a* and dissolved oxygen (Fig. 2). (B) As the bloom decayed, values of the decay factor became more negative. The highest values of the decay factor occurred during nonbloom conditions in August.

increase was likely due to phytoplankton uptake of MeHg, which would have increased MeHg concentrations in the particulate phase.

Hg_T concentrations—Concentrations of dissolved Hg_T in this study ranged from 1.5 to 6.6 pmol L⁻¹ and averaged 3.9 pmol L⁻¹ (Fig. 4), which was consistent with concentrations (2.8–53 pmol L⁻¹) observed in two previous studies in South Bay (Choe et al. 2003; Conaway et al. 2003). Concentrations of unfiltered Hg_T in this study ranged from 8.1 to 150 pmol L⁻¹ and averaged 40 pmol L⁻¹ (Fig. 4), which also agreed with previous measurements (1.8–210 pmol L⁻¹). Our highest value, 150 pmol L⁻¹, was measured at site 32, near the Dumbarton Bridge. Choe et al. (2003) found that their highest concentration of unfiltered Hg_T was in South Bay; they measured 163 pmol L⁻¹ in the extreme South Bay in March 2001. Concentrations at their other two South Bay sites were considerably lower (~20 and ~40 pmol L⁻¹) and were consistent with average values reported by Conaway et al. (2003) for the southern and central regions of the estuary.

Our K_d values for Hg_T ranged from 10^{4.8} to 10^{5.8} L kg⁻¹ (Table 3). Those relatively high values demonstrated that most Hg_T was associated with SPM. Strong particle association was also shown by Conaway et al. (2003), who reported K_d values ranging from 10⁴ to 10⁷ L kg⁻¹ for Hg_T throughout the estuary. Similarly, Choe et al. (2003) found that 88% ± 7% of the unfiltered Hg_T from their sites throughout the estuary was associated with particulates.

Statistical models for Hg_T—In our GLM for dissolved Hg_T, concentrations of Hg_T were significantly (*p* < 0.01) affected only by location (Table 4). Concentrations of dissolved Hg_T were highest at site 36, intermediate at site

32, and lowest at site 21 (Fig. 4). In contrast to dissolved MeHg concentrations, dissolved Hg_T concentrations were not measurably affected by the bloom or decay factors.

After developing a GLM for dissolved Hg_T concentrations, we developed a GLM for Hg_T partitioning. Table 5 shows that the decay factor significantly (*p* = 0.012) affected Hg_T K_d values. As the bloom decayed (decreasing values of the decay factor), Hg_T K_d values increased (Fig. 6), indicating that more Hg_T became associated with SPM over that period. The categorical variable, site, and the sorbent factor also had significant (*p* = 0.048) and marginally significant (*p* = 0.068) effects, respectively, on Hg_T K_d values (Table 5). However, site and the sorbent factor were less important than the decay factor for describing Hg_T K_d values, based on their comparatively lower *p* values and mean-square values (Table 5). The mean-square values provide an estimate of the variance associated with each of the terms and can, therefore, be used to assess the relative contribution of each of the terms to the model fit. Accordingly, we concluded that the most important term explaining Hg_T partitioning in the model was the decay factor.

Discussion

Bloom factor related to dissolved MeHg concentrations—Our multivariate analysis demonstrated that dissolved MeHg concentrations were significantly related to the bloom factor (Fig. 5). The relationship between the bloom factor and the MeHg residuals occurred in samples collected at various stages of the bloom: prior to its peak, at its peak, as it decayed, and in summer nonbloom conditions, indicating that the PCA did an excellent job of separating the effects of bloom factor from other processes, such as decay of the bloom. The decline in dissolved MeHg

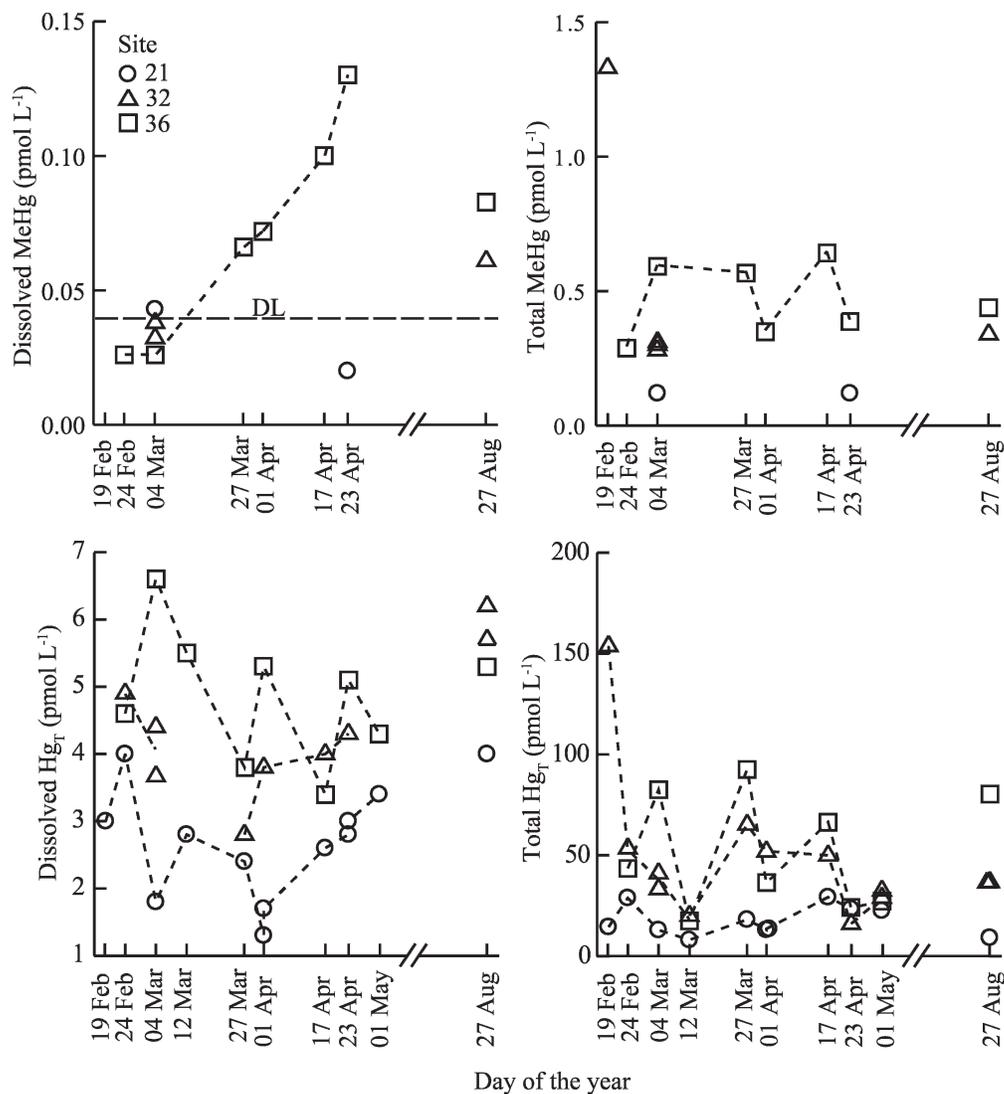


Fig. 4. Descriptive plots of dissolved ($<0.45 \mu\text{m}$) and total (unfiltered) methylmercury (MeHg) and total mercury (Hg_T) concentrations in South Bay in 2003. DL, detection limit. Dissolved MeHg duplicate field samples are shown on 04 March at site 32. Total MeHg duplicate field samples and a distillation replicate are shown for that same site and date. Dissolved Hg_T duplicate field samples are shown on 04 March and 27 August for site 32 and on 01 April and 23 April for site 21. Total Hg_T duplicate field samples are shown on 04 March, 01 May, and 27 August for site 32 and on 01 April for site 21.

concentrations as the bloom factor increased (Fig. 5) was evidence that an algal bloom could deplete dissolved MeHg from the water column. We observed a corresponding increase in MeHg concentrations in the particulate phase (Fig. 6).

Depletion of dissolved MeHg from the water column would be consistent with studies showing that algal blooms have depleted other metals. For example, in our previous study of this bloom (Luengen et al. 2007), we found that concentrations of dissolved Mn, Ni, and Pb declined as the bloom factor increased. Similarly, Luoma et al. (1998) found that the spring 1994 in South Bay depleted dissolved Cd, Ni, and Zn. Depletion of some metals during phytoplankton blooms has also been observed in other bays, including dissolved Cd and Zn in the Scheldt estuary, the Netherlands (Zwolsman and van Eck 1999), and truly

dissolved ($<1 \text{ kDa}$) aluminum (Al), Co, Cu, Mn, and Ni in Ekhagen Bay, Baltic Sea (Ingri et al. 2004).

Calculated concentration of MeHg in phytoplankton—To evaluate the role of phytoplankton in mercury cycling, we supplemented our statistical approach by calculating algal MeHg concentrations, using both our own data and values from the literature. During a bloom, algal MeHg concentrations can be calculated by dividing an increase in algal biomass between any two dates by the change in dissolved MeHg concentrations in the water column. This approach (Luoma et al. 1998; Luengen et al. 2007) is only possible during bloom conditions, during which algal biomass increases rapidly and metals are simultaneously depleted from the dissolved phase. In the highly turbid San Francisco Bay, these calculations are the best way to

Table 3. Particulate concentrations and distribution coefficients (K_d values) for methylmercury (MeHg) and total mercury (Hg_T) at three locations in South San Francisco Bay during a spring bloom in 2003. Particulate concentrations were calculated as the difference between the total (unfiltered) and dissolved ($<0.45 \mu m$) fractions.*

Date	Site	Particulate MeHg (pmol g ⁻¹ SPM)	Particulate Hg_T (nmol g ⁻¹ SPM)	Log Hg_T K_d (L kg ⁻¹)	Log MeHg K_d (L kg ⁻¹)	SPM (mg L ⁻¹ dry weight)	% of bloom-derived material in SPM
19 Feb	21		1.9	5.8		6	16
24 Feb	21		1.0	5.4		24	16
04 Mar	21	2.9	0.45	5.4	4.8	25	8
12 Mar	21		1.1	5.6		5	20
27 Mar	21		0.88	5.6		18	12
01 Apr	21		0.85	5.8		14	13
17 Apr	21		1.4	5.7		19	6
23 Apr	21	7.2	1.6	5.7	5.5	13	4
01 May	21		1.4	5.6		14	8
27 Aug	21		0.40	5.0		13	11
19 Feb	32		1.5			103	5
24 Feb	32		1.1	5.3		46	17
04 Mar	32	7.9	1.0	5.4	5.4	33	30
12 Mar	32		0.8			25	23
27 Mar	32		1.5	5.7		42	9
01 Apr	32		1.2	5.5		40	6
17 Apr	32		1.5	5.6		30	4
23 Apr	32		1.2	5.4		10	6
01 May	32		2.1			15	8
27 Aug	32	7.6	0.83	5.1	5.1	37	7
19 Feb	36					245	2
24 Feb	36		0.93	5.3	5.4	42	19
04 Mar	36	14	1.8	5.4	5.7	42	52
12 Mar	36		0.38	4.8		32	29
27 Mar	36	7.7	1.4	5.6	5.1	65	9
01 Apr	36	9.4	1.0	5.3	5.1	30	7
17 Apr	36	15	1.7	5.7	5.2	37	3
23 Apr	36	21	1.6	5.5	5.2	12	5
01 May	36		1.5	5.5		15	4
27 Aug	36	5.5	1.2	5.3	4.8	65	2

* SPM, suspended particulate matter.

evaluate algal concentrations, because high concentrations of suspended sediments make it impossible to collect pure phytoplankton samples. Because of limited data from the other sites, we focused our calculations on site 36.

To determine how much MeHg was depleted between prebloom conditions and the beginning of the bloom on 24 February, we used literature values to help establish a winter prebloom dissolved MeHg concentration. Conaway

Table 4. Best-fit models relating the factors that primarily describe concentrations of dissolved methylmercury (MeHg) and total mercury (Hg_T) in our study of the 2003 spring diatom bloom in San Francisco Bay. The bloom and decay factors are composite variables, formed by principal component analysis of the water chemistry data, which describe the conditions surrounding the peak and decomposition of the bloom. The categorical variable, site, is the location at which the samples were collected.*

Best-fit model for dissolved MeHg, adjusted $r^2=0.77$						
Effect	Coefficient	SE	Std coef	Tolerance	t	p (two-tailed)
Constant	0.0708	0.00708	0		10.0	<0.01
Decay factor	-0.0170	0.00570	-0.587	0.97	-2.99	0.040
Bloom factor	-0.0174	0.00549	-0.624	0.97	-3.18	0.034

Best-fit model for dissolved Hg_T , $r^2=0.51$					
Source	Sum of squares	df	Mean square	F -ratio	p
Site	20.7	2	10.4	12.2	<0.01
Error	19.6	23	0.852		

* SE, standard error; Std coef, standard coefficient.

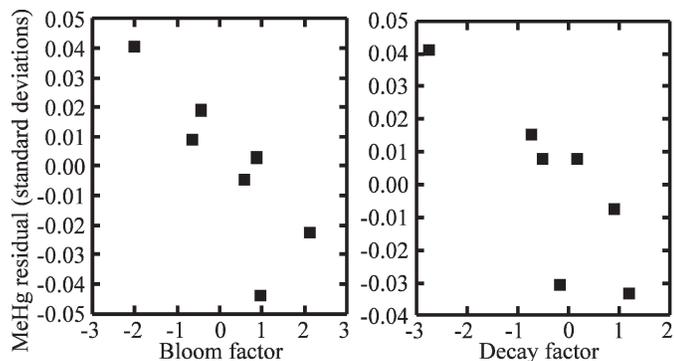


Fig. 5. Partial (studentized) residual plots showing the effects of the bloom and decay factors on dissolved methylmercury (MeHg) concentrations in the extreme South Bay (site 36). Values are the residuals (standardized by dividing by the standard deviation), when the model was run without the factor on the x-axis, plotted against the omitted factor.

et al. (2003) previously measured a dissolved MeHg concentration of $0.085 \text{ pmol L}^{-1}$ under nonbloom conditions ($\text{Chl } a = 4.9 \text{ } \mu\text{g L}^{-1}$ and $\text{Phaeo} = 1.4 \text{ } \mu\text{g L}^{-1}$) in February 2000 at a site (37.47°N , 122.06°W) located less than 300 m from our site 36. Their reported value was in excellent agreement with our nonbloom ($\text{Chl } a = 6.3 \text{ } \mu\text{g L}^{-1}$ and $\text{Phaeo} = 5.2 \text{ } \mu\text{g L}^{-1}$) summer concentration of dissolved MeHg of $0.083 \text{ pmol L}^{-1}$ at site 36. A slightly higher concentration of 0.11 pmol L^{-1} of dissolved MeHg was measured by Choe and Gill (2003) under low- $\text{Chl } a$ ($4.09 \text{ } \mu\text{g L}^{-1}$) conditions in March 2001 at their site (37.47°N , 122.06°W) in South Bay. We used the average of those three values, which was $0.093 \text{ pmol L}^{-1}$, as our best estimate of the prebloom concentration of dissolved MeHg at site 36. The corresponding $\text{Chl } a + \text{Phaeo}$ concentration was $8.9 \text{ } \mu\text{g L}^{-1}$, which was the average from Conaway et al. (2003) and our 27 August sampling, in which both $\text{Chl } a$ and Phaeo were reported.

We then calculated that the phytoplankton assimilated $0.067 \text{ pmol L}^{-1}$ of MeHg as the bloom developed between early February and 24 February. That value was the difference between the prebloom concentration (0.093 pmol

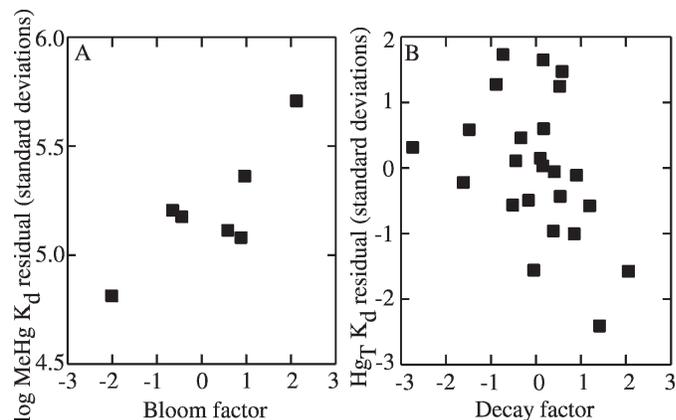


Fig. 6. Partial (studentized) residual plots showing that distribution coefficients (K_d) for (A) MeHg at site 36 were associated with the bloom factor, whereas K_d values for (B) Hg_T at all sites were associated with the decay factor. (A) At the peak of the bloom (high values of the bloom factor), more MeHg was associated with particles. (B) During decay, which was indicated by decreasing values of that factor, $\text{Hg}_T K_d$ increased at all sites.

L^{-1}) and the 24 February concentration ($0.026 \text{ pmol L}^{-1}$), when $\text{Chl } a$ concentrations were $62 \text{ } \mu\text{g L}^{-1}$ (Fig. 2). Under those rapid growth conditions, dissolved MeHg concentrations were depleted below our analytical detection limit of $0.041 \text{ pmol L}^{-1}$. Accordingly, a value of half the detection limit (0.02 pmol L^{-1}) would also have been a reasonable value for our calculation, but would have resulted in an assimilation of the same magnitude.

Although our calculated assimilation of $0.067 \text{ pmol L}^{-1}$ of MeHg was small, it was above the background noise, based on our detection limit and our precision from duplicate field samples. If we used the detection limit of $0.041 \text{ pmol L}^{-1}$ as an indicator of the amount of change that we could measure, $0.067 \text{ pmol L}^{-1}$ was above that threshold. Our precision from duplicate field samples was even lower; our dissolved field duplicates at site 32 on 04 March differed by only $0.006 \text{ pmol L}^{-1}$ (Fig. 4).

Table 5. Best-fit models relating the factors that primarily describe distribution coefficients (K_d) for methylmercury (MeHg) and total mercury (Hg_T) during the 2003 spring diatom bloom in San Francisco Bay. K_d is calculated as the following: (concentration of particulate metal per gram of SPM)/(concentration of dissolved metal). For MeHg, only site 36 was included in the analysis.

Best-fit model for log MeHg K_d , adjusted $r^2=0.63$						
Effect	Coefficient	SE	Std coef	Tolerance	t	p (two-tailed)
Constant	5.17	0.0645	0		80.2	<0.01
Bloom factor	0.170	0.0509	0.830	1	3.33	0.021
Best-fit model for $\text{Hg}_T K_d$, $r^2=0.37$						
Source	Sum of squares	df	Mean square	F -ratio	p	
Site	1.09×10^{11}	2	5.46×10^{10}	3.57	0.048	
Sorbent factor	5.73×10^{10}	1	5.73×10^{10}	3.75	0.068	
Decay factor	1.18×10^{11}	1	1.18×10^{11}	7.73	0.012	
Error	2.90×10^{11}	19	1.53×10^{10}			

* SE, standard error; Std coef, standard coefficient.

Table 6. Mercury concentrations in phytoplankton (dry weight) from various waterbodies. We selected studies that minimized nonphytoplankton particulates. For example, Kuwabara et al. (2005) found no detritus when they examined their samples microscopically. Laurier et al. (2003) used nets to collect a size fraction (150 μm –1-mm fraction) that favored large biological material. Other studies focused on lakes with low suspended particulate matter (SPM) (Watras and Bloom 1992; Kainz and Mazumder 2005). Results from Back et al. (2003) are shown as the range from four size fractions of seston (<35, 35–63, 63–112, and >112 μm) sieved from Lake Superior in spring and summer.*

System	MeHg (pmol g ⁻¹)	Hg _T (nmol g ⁻¹)	Reference
Culture studies of coastal diatom	5–30	0.3–0.5	Mason et al. (1996); Kim et al. (2004)
Wisconsin lake	200	1.5	Watras and Bloom (1992)
Lake Superior	10–80	—	Back et al. (2003)
Vancouver Island, Canada lakes	35±15	—	Kainz and Mazumder (2005)
Vancouver Island, Canada reservoirs	95±100	—	Kainz and Mazumder (2005)
Guadalupe Reservoir, California	<7.5	0.86	Kuwabara et al. (2005)
Seine estuary, France	23±17	0.37±0.11	Laurier et al. (2003)
Monterey Bay diatom bloom	—	0.98±0.4	Martin and Knauer (1973)
San Francisco Bay, California	—	0.5–1.5	Flegal (1977)
South San Francisco Bay, California	3–10	0.47	Present study

* MeHg, methylmercury; Hg_T, total mercury.

Accordingly, we calculated the MeHg concentration in phytoplankton by dividing the MeHg assimilation (0.067 pmol L⁻¹) by the corresponding increase in bloom-derived material from prebloom conditions to 24 February. Then, we converted the increase in bloom-derived material (58 $\mu\text{g L}^{-1}$ of Chl *a* and Phaeo) to grams (dry weight) of phytoplankton, following ratios previously used for South Bay (Cloern et al. 1995; Luoma et al. 1998; Luengen et al. 2007):

$$\left(\frac{58 \mu\text{g Chl } a}{\text{L}}\right) \left(\frac{35 \mu\text{g C}}{\mu\text{g Chl } a}\right) \bigg/ \frac{0.3 \mu\text{g C}}{\mu\text{g phytoplankton}} = \frac{6.8 \text{ mg phytoplankton}}{\text{L}}$$

Division of 0.067 pmol L⁻¹ of MeHg by 6.8 mg phytoplankton L⁻¹ yielded a MeHg concentration in phytoplankton on 24 February of 10 pmol g⁻¹ (dry weight). That result was consistent with previously reported concentrations in the estuary and elsewhere (Table 6).

We repeated the process to calculate the concentration of MeHg in phytoplankton from prebloom conditions to 04 March. On 04 March, dissolved MeHg concentrations were the same as on 24 February (Fig. 4), so we used the same value for the amount of MeHg depleted: 0.067 pmol L⁻¹. From prebloom conditions to 04 March, Chl *a* + Phaeo concentrations increased by 177 $\mu\text{g L}^{-1}$, or 21 mg (dry weight) phytoplankton. Division of 0.067 pmol L⁻¹ MeHg by 21 mg of phytoplankton yielded a concentration of 3.2 pmol g⁻¹ phytoplankton. That 04 March algal value was lower than the 24 February value because Chl *a* concentrations nearly tripled between 24 February and 04 March (Fig. 2), while dissolved MeHg concentrations remained the same (Fig. 4). Thus, our calculated ~30% decrease in phytoplankton MeHg concentrations was the result of a finite amount of MeHg as the bloom grew between 24 February and 04 March.

One limitation to this study is that we used an estimated value (0.093 pmol L⁻¹) rather than a measured value for the water column MeHg concentration prior to the start of

the bloom. A revision of this estimated value would affect our calculated concentration of MeHg in phytoplankton, but it would not affect our conclusion that there was a decline in algal MeHg concentrations between 24 February and 04 March. This decline occurred because algal abundance tripled as the dissolved MeHg concentrations remained at 0.026 pmol L⁻¹. Even if dissolved MeHg concentrations had been depleted to 0 pmol L⁻¹ on 04 March, we still would have seen a drop in algal MeHg concentrations, corresponding to a limited amount of MeHg. However, it is likely that there is a lower bound on the amount of MeHg that can be removed by the phytoplankton.

The drop in MeHg algal concentrations from 10 to 3.2 pmol g⁻¹ (dry weight) was consistent with bloom dilution. Bloom dilution has been previously observed in experiments in which researchers varied nutrient concentrations in different mesocosms to create a range of bloom intensities (Pickhardt et al. 2002). The researchers then added different stable isotopes (CH₃²⁰⁰Hg⁺ and ²⁰¹Hg²⁺) of MeHg and inorganic Hg to the water and found that when Chl *a* concentrations were high, concentrations of MeHg in phytoplankton and zooplankton decreased. However, in those mesocosm studies, no corresponding drop in dissolved concentrations was observed (Pickhardt et al. 2002), perhaps owing to the relatively high concentrations of MeHg used.

Our results indicate that in South Bay bloom dilution may occur as a result of a limited amount of MeHg. One implication is that an increase or decrease in dissolved MeHg concentrations in the water column could affect the amount of MeHg accumulated by phytoplankton during blooms. In South Bay, there is potential to both increase dissolved MeHg from wetland restorations (Davis et al. 2003) and to decrease it through regulatory actions, such as development of a Total Maximum Daily Load to restrict mercury loadings to the estuary (Conaway et al. 2008). Accordingly, the link between dissolved concentrations and algal concentrations warrants further investigation.

As previously noted, one limitation to this field study is that it was not possible to measure MeHg or Hg_T

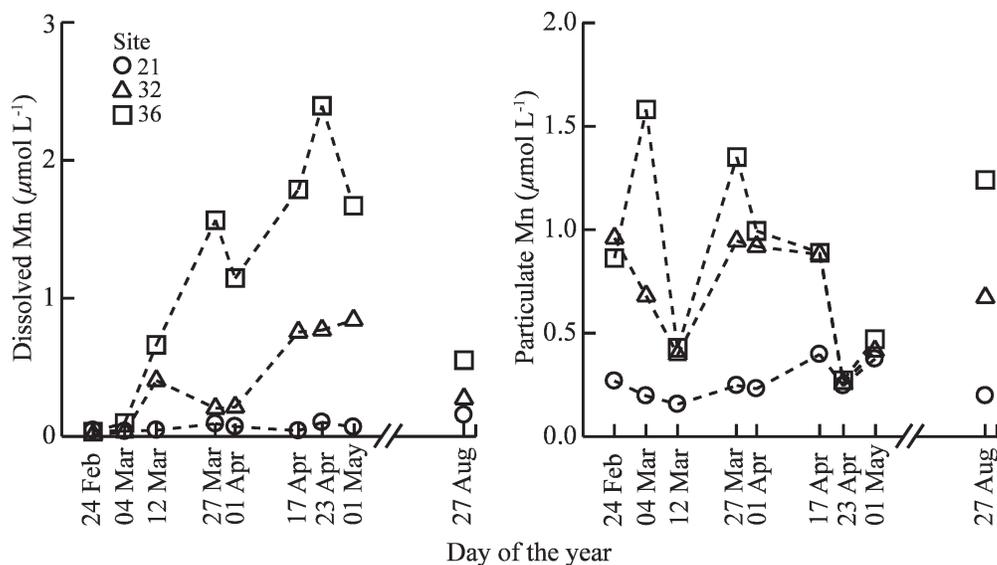


Fig. 7. Dissolved Mn increased by two orders of magnitude in the extreme South Bay (site 36) as the bloom decayed. That increase was indicative of a change to reducing conditions in surface sediments, caused by the sinking and decomposition of the bloom material. In suboxic conditions, bacteria can use particulate Mn(IV) as an electron receptor, reducing it to soluble Mn(II).

concentrations directly in phytoplankton. Although our calculations indicated that algal MeHg concentrations decreased during the bloom, if phytoplankton rapidly assimilated MeHg from another source (e.g., production in sediments or desorption from the particulate phase), the algal MeHg concentration could have remained constant during the bloom. However, we think that desorption from the particulate phase was negligible, based on mesocosm experiments on tidal resuspension that showed that dissolved MeHg and Hg_T concentrations did not increase as a result of sediment resuspension (Kim et al. 2004). Furthermore, stratification of the water column would have limited the flux of dissolved MeHg to the surface water that we sampled. During the calm conditions surrounding the bloom, the South Bay would have resembled the mesocosm conditions in previous bloom dilution experiments (Pickhardt et al. 2002) more closely than it would have at any other time of year. Accordingly, our results are consistent with bloom dilution and demonstrate for the first time that bloom dilution could be an important process in an estuary. However, bloom dilution was a transient event, and as we discuss in the next section, decay may have a larger effect on mercury cycling within the estuary because of the potential for MeHg production during bloom decay.

Decay increases dissolved MeHg concentrations—During decay of the bloom, which was indicated by decreasing values of the decay factor, dissolved MeHg increased (Fig. 5). We attributed that increase to a combination of remineralization of phytoplankton and production of MeHg in suboxic sediments. Previous research has demonstrated that MeHg is produced in San Francisco Bay sediments (Olson and Cooper 1974; Marvin-DiPasquale

and Agee 2003), presumably as a result of methylation of inorganic Hg by bacteria that reduce sulfate and/or Fe (Benoit et al. 2003; Kerin et al. 2006). As the bloom decayed, conditions would have been favorable for mercury methylation because the decomposing algae likely depleted dissolved oxygen in sediments, as was seen following the South Bay bloom in 1996 (Grenz et al. 2000).

Although this study did not include any benthic sampling, our observed increase in both dissolved ammonium (Table 2) and dissolved Mn (Fig. 7) was indicative of a change to reducing conditions in surface sediments (Stumm and Morgan 1996). As shown in Fig. 7, as the bloom decayed, dissolved Mn increased by more than two orders of magnitude at site 36. That change was not caused by desorption from the particulate phase because particulate concentrations remained relatively constant (Fig. 7) or by remineralization of phytoplankton, which accounted for only 0.1% of the observed increase in dissolved Mn concentrations (Luengen et al. 2007). Instead, we attributed the increase in dissolved Mn to reductive dissolution of Mn and Fe (hydr)oxides, which can occur under suboxic conditions when bacteria reduce particulate Mn(IV) to soluble Mn(II) (Beck and Bruland 2000; Roitz et al. 2002; Luengen et al. 2007). Previous studies in South Bay have attributed increases in dissolved Mn (Roitz et al. 2002; Luengen et al. 2007) and other metals (Co, Mn, Zn, and Pb) to release from sediments during suboxic conditions following a spring bloom (Luengen et al. 2007). In South Bay, sediments are the major mercury reservoir (Conaway et al. 2007, 2008), and a change to reducing conditions following the bloom could have favored mercury methylation and caused an increase in dissolved MeHg concentrations.

Low oxygen conditions in surface sediments would have facilitated the transfer of MeHg to the water column, based

on a study that showed that MeHg fluxes to the water column increased when dissolved oxygen concentrations dropped at night in Lavaca Bay, Texas (Gill et al. 1999). A flux of MeHg from sediments to water under hypoxic conditions was also demonstrated in laboratory incubations of sediments from Baltimore Harbor (Mason et al. 2006). In that study, MeHg and sulfide co-occurred in the overlying water, indicating that sulfate reduction was producing MeHg. Mason et al. (2006) concluded that production of MeHg at the sediment–water interface could be an important, yet overlooked, source of MeHg to the water column. Consistent with these studies, our observed increases in both dissolved Mn and dissolved MeHg indicated that suboxic conditions occurred and facilitated release of MeHg to the water column.

In addition to creating suboxic conditions, decaying algal material could contribute to MeHg production in sediments by providing a readily available source of DOC to sulfate-reducing bacteria. As the bloom decayed, DOC concentrations increased by $>400 \mu\text{mol L}^{-1}$ (Fig. 2). Such algal-derived DOC is a labile source of organic matter (Valiela 1995) that can rapidly increase microbial activity and thus MeHg production, as has been observed in systems in which high DOC concentrations have been linked to high rates of methylation (Benoit et al. 2003). Accordingly, a pulse of bloom-derived DOC could be an important driver of MeHg production in South Bay sediments.

Factors affecting dissolved Hg_T concentrations—Concentrations of dissolved Hg_T increased from our most oceanic site (site 21) to our site in the extreme South Bay (site 36), as shown in Fig. 4. We attributed that distribution to diagenetic remobilization of mercury from historically contaminated sediments within the estuary and ongoing mercury inputs to the extreme South Bay from abandoned mercury mines in the watershed (Thomas et al. 2002; Conaway et al. 2003). When compared to other regions of the estuary, the extreme South Bay also has proportionately long residence times and seasonally high concentrations of many metals as a result of its limited hydraulic flushing (Flegal et al. 1991). These results further indicate that the concentrations of dissolved Hg_T in the estuary are primarily controlled by physical processes, such as inputs and mixing.

Unlike dissolved MeHg, dissolved Hg_T was not significantly ($p = 0.16$; Table 4) depleted by the phytoplankton bloom, consistent with active uptake and internalization of MeHg vs. passive sorption of Hg_T onto cell surfaces. Because most (90%) inorganic Hg sorbs onto cell surfaces (Mason et al. 1996; Pickhardt and Fisher 2007), the phytoplankton bloom may have had a limited capacity to deplete inorganic Hg. In contrast, phytoplankton actively (i.e., energy expended) uptake MeHg, although the mechanism is not understood (Moye et al. 2002; Pickhardt and Fisher 2007). That active uptake of MeHg could have explained why it was depleted from the water, similar to dissolved nutrients (Luengen et al. 2007). Furthermore, the phytoplankton presumably provided a new sink for MeHg because a large fraction ($\sim 60\%$) of MeHg is accumulated

in algal cytoplasm (Mason et al. 1996; Pickhardt and Fisher 2007). Because of these differences in uptake, volume concentration factors for MeHg in phytoplankton can be roughly an order of magnitude higher than those of inorganic Hg (Pickhardt and Fisher 2007). Accordingly, our observed depletion of dissolved MeHg, but not dissolved Hg_T , may be due to active uptake of dissolved MeHg into the algal cytoplasm.

The magnitude of any Hg_T depletion should have been large enough for us to detect based on algal Hg:carbon (C) ratios. A bloom of $65 \mu\text{g L}^{-1}$ Chl *a* (average Chl *a* increase at sites 32 and 36 between 24 February and 04 March) would have produced $0.19 \text{ mmol C L}^{-1}$, given Chl *a*:C ratios used previously (Cloern et al. 1995; Luoma et al. 1998; Luengen et al. 2007):

$$\left(\frac{65 \mu\text{g Chl } a}{\text{L}}\right) \left(\frac{35 \mu\text{g C}}{\mu\text{g Chl } a}\right) \left(\frac{1 \text{ mol C}}{12 \text{ g C}}\right) = \frac{0.19 \text{ mmol C}}{\text{L}}$$

Multiplying $0.19 \text{ mmol C L}^{-1}$ by a Hg:C ratio of $0.037 \mu\text{mol mol}^{-1}$ (Martin and Knauer 1973) gave a potential depletion of 7 pmol Hg L^{-1} , which was well within the precision of our samples (Fig. 4). Accordingly, the lack of a measurable depletion was not an analytical artifact.

We had expected that because Hg_T is surface reactive (see K_d values in Table 3), it would be depleted by sorption onto phytoplankton during growth of the bloom, as we previously observed for dissolved Pb during this bloom (Luengen et al. 2007). However, dissolved Hg_T behaved similarly to dissolved Cu, which was not measurably affected by the growth or decay of the bloom (Luengen et al. 2007). While dissolved Cu was presumably bound to strong organic ligands, dissolved Hg_T may have preferentially sorbed to nonbloom particles. As we will discuss later, nonbloom particles have higher Hg_T concentrations than phytoplankton. Furthermore, mesocosm experiments have shown that Hg_T partitioning is likely controlled by its association with nonliving particles, whereas MeHg partitioning is influenced by phytoplankton (Kim et al. 2004). This study indicates that growth of a phytoplankton bloom does not measurably alter dissolved Hg_T concentrations, unlike dissolved MeHg concentrations.

Cycling of dissolved Hg_T also differed from that of MeHg because dissolved Hg_T concentrations did not increase as the bloom decomposed (Table 4). Previous studies attributed increases in dissolved trace metal concentrations during decay to release of metals associated with Mn and Fe (hydr)oxides, which were presumably reduced during the suboxic conditions created by decomposing organic matter (Flegal et al. 1991; Roitz et al. 2002; Luengen et al. 2007). In those studies, algal remineralization accounted for only a small amount (e.g., $<1\%$ for Mn) of the increase in dissolved trace metals, indicating that release from sediments was the main source of the metals during decay. Thus, the increase in other trace metals, but not Hg_T , indicated that Hg_T was not strongly associated with Mn and Fe (hydr)oxides. Lack of association between Hg_T and Mn and Fe (hydr)oxides was previously demonstrated in laboratory incubations that quantified the flux of

metals from Baltimore Harbor sediments to overlying waters (Mason et al. 2006). In the Baltimore Harbor sediment incubations, fluxes of Mn and Fe to the overlying waters were not related to Hg_T fluxes, indicating that dissolution of Mn and Fe (hydr)oxides did not release Hg_T .

Hg_T partitioning— Hg_T K_d values were only marginally (Table 5) affected by the sorbent factor, which was a factor partially derived from concentrations of SPM and unfiltered Mn and Fe. That result indicated that SPM was not a driving predictor of Hg_T K_d values, unlike the results provided by previous studies (Stordal et al. 1996; Choe et al. 2003) that found a negative correlation between SPM and Hg_T K_d values (the particle concentration effect). The particle concentration effect occurs when proportional increases in both SPM and colloidal material are associated with additional metals in both phases but the colloidal bound metals pass through a $0.45\text{-}\mu\text{m}$ filter and are thus counted in the dissolved fraction (Benoit 1995). One of the assumptions of the particle concentration effect is that changes in SPM concentrations are proportional to changes in colloidal material (Benoit and Rozan 1999), an assumption that may not have been true during a bloom in which growing algae rapidly increase the amount of particulates. In our study, the composition of the SPM changed, whereas previous studies on the particle concentration effect focused on a change in SPM concentrations (Benoit 1995; Benoit and Rozan 1999). As a result, our study was not well-suited for observing the particle concentration effect, and different processes likely governed Hg_T partitioning in our study.

In this study, Hg_T K_d values were explained primarily by the decay factor (Table 5), which was a composite factor that characterized DOC and Phaeo concentrations. As the bloom decayed and DOC increased, Hg_T partitioning onto particles increased (Fig. 6). In the paragraphs to follow, we explore three potential causes of the increase in Hg_T K_d values during decay: (1) an increase in the surface area available for metal sorption as a result of increased particulate surface area during the decay of the bloom; (2) sorption of Hg_T to organically coated clay particles; and (3) a change in composition of the SPM.

First, Hg_T K_d values could have increased during the decay as a result of increased surface area from the growth of bacteria. As the cells degraded, the release of organic matter presumably stimulated microbial activity, as has been observed following the addition of glucose or arginine during phytoplankton growth and decay experiments with Chesapeake Bay waters (Miller et al. 1997). That additional surface area could have accounted for the increase in Hg_T K_d values observed in this experiment.

Second, K_d values could have increased if material from decaying cells sorbed onto clay surfaces, creating an organic coating that favored Hg_T binding. The cellular material would have tended to sorb onto clays because clays have a net negative surface charge that attracts organic matter (Stumm and Morgan 1996). In studies in which fulvic acid was added to inorganic particles, creation of an organic coating enhanced $Hg(II)$ sorption (Xu and Allard 1991; Gagnon and Fisher 1997). Studies that

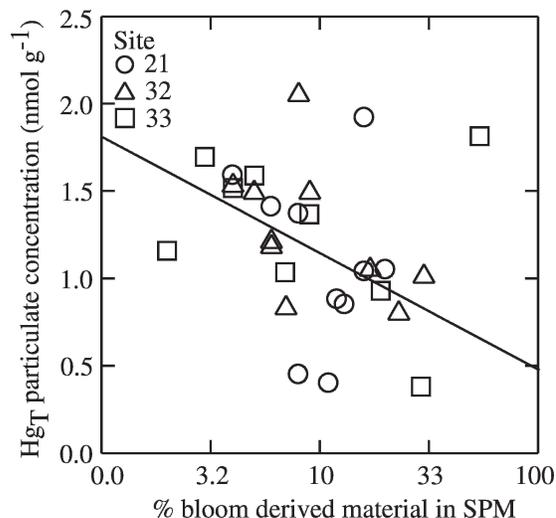


Fig. 8. Particulate total mercury (Hg_T) concentrations (normalized to SPM) were significantly ($p = 0.011$, $F = 7.5$; linear regression) correlated with amount of bloom-derived material in the SPM when the datum with $> 50\%$ phytoplankton in the extreme South Bay (site 36) was excluded from the data set. The relationship indicates that phytoplankton have relatively low Hg_T concentrations compared to other types of suspended particles.

removed organic matter, instead of adding it, found that less (up to two orders of magnitude) $Hg(II)$ sorbed to sediments and calcite after digestion with H_2O_2 and ultraviolet irradiation, respectively (Bilinski et al. 1991; Turner et al. 2001). Sorption of Hg_T to organic coatings may also explain why Hg_T K_d values changed during the decay of the bloom but $MeHg$ K_d values did not; more $Hg(II)$ than $MeHg$ binds to material from broken cells (Mason et al. 1996).

Third, Hg_T K_d values could have increased during decay if the phytoplankton that was lost from the water column had lower Hg_T concentrations than the remaining particles. Figure 8 supports that hypothesis by showing that Hg_T particulate concentrations were highest when most of the material in suspension was not bloom derived. The percentage of bloom-derived material was calculated by converting $Chl\ a + Phaeo$ to dry weight carbon and then dividing by the amount of SPM (Table 3). When an ANCOVA was run to look at the effects of site and percent phytoplankton (log-transformed to normalize the data) on particulate Hg_T concentrations, site was not significant ($p > 0.05$), even when the datum with $> 50\%$ bloom material was excluded. We then dropped the categorical variable, site, from the model to run a linear regression and to obtain a y-intercept (Fig. 8). After excluding the datum with $> 50\%$ bloom material, we found a significant ($p = 0.011$, $F = 7.5$) negative relationship between particulate Hg_T concentrations and percent bloom material (log-transformed).

Although there are not many studies on Hg_T partitioning to different types of particles, a few studies do indicate that algal material may bind less Hg_T than other types of particles. In a comparison of $Hg(II)$ K_d values from different sites, Hammerschmidt et al. (2008) found that $Hg(II)$ K_d values for the Long Island Sound and the

continental shelf were lower ($\sim 10\times$) than for the New York/New Jersey Harbor, possibly because algal material from the sound and shelf did not bind Hg(II) as well as terrigenous vascular plant material from the harbor. Hammerschmidt et al. (2008) also suggested that in the harbor, organic ligands from sewage discharge may increase Hg(II) binding to sediments. As in the New York/New Jersey Harbor, Hg(II) in South Bay may be strongly bound to sediments and other nonalgal particles, and less Hg(II) may be associated with phytoplankton.

Two field studies from estuaries in France (Laurier et al. 2003; Schäfer et al. 2006) also indicate that phytoplankton blooms can suppress Hg_T K_d values. In the Lot-Garonne Estuary, France, Hg_T particulate concentrations (1.0–2.4 nmol g⁻¹) were lower during an intense algal bloom than were concentrations (>2.5 nmol g⁻¹) during nonbloom conditions (Schäfer et al. 2006). In the Seine estuary (Laurier et al. 2003), Hg_T concentrations in particles leaving the high-turbidity zone were diluted in summer by phytoplankton with low mercury concentrations (0.2–0.8 nmol g⁻¹ dry weight in net-collected plankton from four size classes). Laurier et al. (2003) suggested that living phytoplankton had fewer functional groups available to bind Hg_T than did degraded organic material. Consequently, a decrease in phytoplankton biomass and a change to degraded material during the decay of our bloom could have accounted for the observed increase in Hg_T K_d values. Dilution of SPM by phytoplankton has also been previously observed for other metals (e.g., Al, Co, chromium) in the Scheldt estuary, the Netherlands (Zwolsman and van Eck 1999).

Hg_T in particles and phytoplankton—Based on the values from our linear regression (Fig. 8), Hg_T concentrations in nonbloom particles were ~ 1.8 nmol g⁻¹ (dry weight), and Hg_T concentrations in pure phytoplankton were 0.47 nmol g⁻¹ (dry weight). Those values agreed with literature values. For example, Conaway et al. (2003) found that suspended particles collected throughout the estuary under generally low Chl *a* conditions (median Chl *a* of 3 $\mu\text{g L}^{-1}$) had an average Hg_T concentration of 1.8 ± 0.6 nmol g⁻¹.

For phytoplankton, previously reported Hg_T concentrations ranged from 0.2 to 1.5 nmol g⁻¹ (dry weight) (Table 6). Kim et al. (2004) calculated a concentration of Hg_T in phytoplankton of 0.3 to 0.5 nmol g⁻¹ (dry weight), using equations derived from culture studies by Mason et al. (1996). Two field studies in California bays also indicated that Hg_T concentrations in phytoplankton were in that range, although both had contamination from suspended sediments. Martin and Knauer (1973) measured concentrations of Hg_T in phytoplankton collected under bloom conditions in Monterey Bay. To minimize contamination by suspended sediments, we selected data from that study with low Al concentrations (as per Bruland et al. 1991). Accordingly, the best estimate of Hg_T concentrations in phytoplankton from that study was 0.98 ± 0.4 nmol g⁻¹ (dry weight). Finally, Flegal (1977) calculated that phytoplankton from San Francisco Bay contained 0.5 to 1.5 nmol Hg_T g⁻¹ (dry weight) by performing regression analyses and simultaneous equations on seston samples from the estuary.

Our calculated algal Hg_T concentration of 0.47 nmol g⁻¹ (dry weight) agreed well with these previous studies.

Implications of an increase in phytoplankton biomass—Recent research in San Francisco Bay (Cloern et al. 2006) indicates that within the last decade, phytoplankton biomass, as measured by Chl *a*, has increased within all regions of the estuary (i.e., North, Central, and South Bays). That increase has manifested itself in higher baseline Chl *a* concentrations, greater magnitude of the annual spring bloom, and addition of a new fall bloom (Cloern and Dufford 2005; Cloern et al. 2006). Although the estuary has relatively high nutrient concentrations, primarily from wastewater treatment plant inputs (Smith and Hollibaugh 2006), the additional phytoplankton biomass is not related to nutrient concentrations, which have remained constant or slightly decreased (Cloern et al. 2006). The exact cause of the phytoplankton increase is uncertain, but it may be due to a variety of factors, including greater water clarity (Cloern et al. 2006).

That increase in algal abundance is a concern because of the potential for algae to transfer MeHg to the food chain, thus exacerbating the existing mercury impairment in the estuary. Currently, high mercury concentrations (>1.1 nmol g⁻¹ wet weight) in fish are responsible for consumption advisories in the estuary (Thompson et al. 2000). Mercury pollution also threatens wildlife, particularly the reproductive success of the endangered California Clapper Rail, *Rallus longirostris obsoletus* (Schwarzbach et al. 2006). To protect fish and wildlife from mercury exposure, we need to understand the relationship between Chl *a* concentrations and MeHg concentrations in phytoplankton and subsequent trophic levels.

In this study, our calculated algal MeHg concentrations were lowest during the peak of a phytoplankton bloom. This result indicates that bloom dilution can occur in the estuary, as has been previously reported for freshwater mesocosms (Pickhardt et al. 2002, 2005). In this study, bloom dilution resulted from depletion of dissolved MeHg from the water column, indicating that the concentration of MeHg is an important variable in this system. One potential consequence of bloom dilution, observed in lakes, is lower concentrations of Hg_T in fish (Chen and Folt 2005). In addition to bloom dilution, there is potential for growth dilution to occur, if zooplankton feeding on highly nutritious phytoplankton gain biomass without a proportionate increase in MeHg concentrations (Karimi et al. 2007).

However, it is currently unclear if bloom dilution could reduce MeHg bioaccumulation in San Francisco Bay, partially because much of the bloom material is consumed by benthic organisms (Thompson and Nichols 1988), a pathway in which bloom dilution needs further study. It is possible that the additional food consumed by the benthos could counteract any beneficial effects of bloom dilution. The effect on higher trophic levels may also be limited because bloom dilution is transient. Thus, additional studies are needed to determine how a phytoplankton bloom affects MeHg bioaccumulation in South Bay.

Mercury cycling in the estuary may also be altered by the decay of the bloom. Bloom decay is a component of high

algal biomass that has received relatively little attention. Our maximum concentrations of dissolved and particulate MeHg occurred when the bloom was almost completely decayed, on 23 April (Table 3; Fig. 4). The MeHg associated with that decayed material is bioavailable to at least some organisms, based on experiments showing that amphipods can assimilate MeHg from phytoplankton cells that are highly decayed (Lawson and Mason 1998). Moreover, the increase in dissolved MeHg in the water column (Fig. 3) was likely the result of MeHg production in the sediments, through creation of anoxic conditions and increased microbial activity. If decaying algal material boosts MeHg production, the increase in algal abundance could lead to higher MeHg water column concentrations. Finally, we observed an increase in Hg_T partitioning onto particles during the decay of the bloom, which could serve to entrain Hg_T in the estuary, where it may be eventually methylated. In conclusion, although both the growth and decay of the bloom have the potential to alter mercury cycling, the most readily observable and long-lasting effects of an increase in algal abundance may occur when that material decays.

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