DGT (Diffusive Gradient in Thinfilm) as a tool to assess sources of bioavailable methylmercury in San Francisco Bay

FINAL REPORT

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Since we were not completely familiar with the specifics of potential areas of concern in the San Francisco Bay area, the design of many aspects of this study, particularly the selection of sites, was arrived at in consultation with Ben Greenfield and Katie Harrold of the San Francisco Estuary Institute. We are grateful for their helpful insights and suggestions.
Ben Greenfield, Katie Harrold, Kat Ridolfi, Darell Slotton and Shaun Ayers did an excellent job managing the logistics and sampling operations for this project.
The data of total Hg concentrations in fish were gathered by the RMP Small Fish project and were generously provided by SFEI for comparative purposes.

Summary

The performance of new DGT sentinels was explored as a monitoring tool to compare levels of methylmercury (MMHg) in the San Francisco Bay area. A small spatial survey conducted in 2008 was followed by a larger survey (44 sites) in 2009.
Samples were collected according to a semi-random protocol originally developed for the Small Fish sampling project. Stations in the spatial survey were sorted into i) open regions, ii) enclosed bays and wetlands, iii) sites with historically elevated mercury or MMHg concentrations, iv) sites with industrial influence, and v) locations downstream of Waste Water Treatment Plants (WWTP). The DGT sentinels identified the open bay regions to be consistently the least exposed to MMHg. In contrast, enclosed bays show greater variability among sites, pointing to important site specific conditions generating higher concentrations of MMHg. Alternatively, the more limited water exchange at enclosed regions allows a higher accumulation of MMHg at these locations. Stations with industrial influence were on average much higher in MMHg compared to open sites. Legacy sites, despite their large variation in MMHg were also significantly elevated. The situation downstream of the Waste Water Treatment Plants is inconclusive. Most (but not all plants) sampled were among the locations with the highest MMHg levels. However, to put the data into perspective, the accumulated mass of MMHg would require an average concentration of 128 ± 32 pg/L (n = 4) of dissolved MMHg, which is presumably associated with dissolved organic material (DOM).
Rather than grouping all sampling stations into categories, when evaluating all data on the spatial scale of the entire Bay area, an intriguing picture emerges. Generally, the highest levels of MMHg were observed in the South Bay, and the highest observations were made in the Alviso area. A clear gradient towards the central Bay follows. Also, the eastern area of Suisun Bay shows a few very high spots of MMHg, potentially indicating influence of Sacramento River discharge. Compared to the other Bay regions, San Pablo Bay was generally much lower in MMHg. A third hot spot was found around Point Isabel in the Central Bay, which was otherwise low in MMHg. This general pattern suggests formation of an enhanced presence of MMHg from historic mining activities, which still export elevated levels of Hg to both ends of the Bay (Guadalupe and Sacramento rivers). In place generated MMHg is subsequently diluted by exchange with ocean water, leading to background levels of MHHg near the Golden Gate Bridge area, which experiences the highest flushing rates.
In both years, MMHg uptake into the DGTs was compared to MMHg concentration in small fish sampled through the Small Fish project. The limited number of sampling sites in 2008 did not allow a meaningful comparison. Nevertheless, sites which have consistently shown high concentrations of MMHg in the past also accumulated the highest amount of MMHg by DGT. This was most evident at the Alviso site, which in both years indicated significantly elevated in MMHg. However, once this location was removed from the comparison group, no correlation was observed between DGT accumulated MMHg and Hg small fish (neither topsmelt nor mississippi silverside). However, the two fish species did not correlate significantly with each other in 2009. This suggests that exposure routes are either very site specific, DGTs as well as different species of small fish access different sources of MMHg, or the significant dilution of local MMHg with open bay water obscures site specific differences, when sampled by non-stationary (bio)sentinels such as small fish.

Introduction

Mercury is a pollutant of concern in San Francisco Bay. However, better knowledge on production and distribution of methylmercury (MMHg) within the bay area is needed to manage mercury more efficiently. To improve the forecasting of impacts of MMHg on endangered species, sport fish and the bay fishery, and to provide feedback to environmental regulators, monitoring of MMHg discharge into San Francisco Bay with sentinels is desirable. Direct analysis of total mercury and MMHg in water, sediment and biota samples using established standard methods do not always produce predictive information. For example, total mercury levels in sediments are consistently about 0.3 μg/g (dw) and do not reflect the levels of MMHg in adjacent biota. Ideally, we should identify and measure those mercury species that are available to biota. Uptake of trace metals is determined by the total concentration of labile species able to cross biological membranes as the first step of biomagnification. Standing pool sizes of MMHg reflect the differences between rapid and competing methylation and demethylation reactions, and are extremely variable in both space and time. Levels of MMHg in punctual samples are so variable that a large number of samples would have to be analyzed to obtain representative estimates of MMHg levels.

Classical biosentinels such as small fish are being developed for monitoring purposes in the Delta region of the Bay. Fish that reside in a spatially limited habitat are optimal and species such as mississippi silverside and topsmelt are explored to serve as indicators for biomagnification of MMHg in food webs. However, in practice the utility of fish sentinels is limited, mostly because of the difficulty to find an appropriate fish, which is present in all the areas that must be studied. As an alternative to biosentinels, passive samplers such as Diffusion Gradient in Thinfilm (DGT) devices are currently being developed as comparable sentinels for mercury and MMHg. Similar contaminant sorption devices have been used to monitor levels of other pollutants including metals (e.g. Denney et al., 1999; Dunn et al., 2003, van Leeuven et al., 2005; Dočekalová and Diviš, 2005). DGT devices accumulate only certain forms of a metal, i.e. mainly the labile metal species able to pass through the diffusion layer and bind with the resin layer. After the DGT device is removed from the sampling site, the mass of metal in the resin layer is determined analytically. The well-defined geometry of the DGT device enables quantitative interpretation of the mass accumulated, either in terms of dissolved concentrations, or remobilization fluxes from sediments to pore waters. In waters that are reasonably well mixed, the interpretation of DGT measured fluxes as labile metal concentrations in solution external to the DGT device is relatively straightforward (Zhang and Davison 1995). In the case of MMHg, methylation of inorganic mercury as a source of MMHg also affects DGT measurements.

In initial studies associated with the HAAF Wetland Restoration Project in San Pablo Bay we have shown that DGT devices are useful to integrate exposures to MMHg. Short-term field incubations indicated that MMHg concentrations in DGTs (ng/L) were strongly correlated with MMHg concentrations in the interstitial water of sediments (ng L^{-1}) determined by conventional techniques over a range of salinities varying from saline to brackish (Best et al. 2007; Clarisse and Hintelmann 2006). Subsequent short-term field incubations formed the basis for strong correlations between MMHg concentrations in DGTs (ng L^{-1}) and net methylation rates (ng g^{-1} DW day^{-1}) in sediments over the same range of salinities (Best et al., 2007). In addition, results of laboratory incubations in which DGTs, clams and fish were exposed to aqueous MMHg and MMHg-spiked food showed correlations between the MMHg mass contained in the DGTs (pg per DGT-device) and the MMHg concentrations (ng g^{-1} DW) in the organisms (Best et al., 2008).

The objectives of the study were to

- determine the performance of DGT sentinels for long-term monitoring of MMHg at relevant field sites
- identify high leverage pathways with high resolution
- identify processes contributing MMHg in the Bay area
- evaluate DGT data as indicative for potential MMHg bioaccumulation in food chains

The goal is to provide the information needed to support water quality management decisions by providing a new (or alternate) method to detect and quantify the bioavailable MMHg species in the Bay area.

Materials and Methods

Preparation and Deployment of DGT Probes

A proprietary reagent for gel formation was purchased from DGT Research, UK. The manufacture of the diffusive and resin gels and the assembly of the probes were performed at Trent University based on a protocol developed in this laboratory (Clarrise and Hintelmann, 2006). DGT probes consisted of a protective nylon filter, a diffusive gel, and a binding resin layer consisting of mercapto-propyl functionalized silica gel embedded in a polyacrylamide gel (Figure 1). The various gel layers are assembled with a specialized plastic piston. The additional bottom support gel ensured the stacked layers did not move once the cover ring was secured.

Water Sampling

Three replicate DGT probes were deployed for each sample location or time and secured in a protective plastic cage (Figure 2). The cage was constructed by clamping two plastic baskets together with nylon cable ties. The three pistons were tied to the inside bottom of one the baskets using braided nylon fishing string. Each cage was engraved with a unique numeric identification and sealed in a large ZipLok bag containing 5 mL of salt water (0.1% w/v) to maintain hydration of the DGT gels.

The cages were placed in a chilled cooler for shipment to the SFEI. A travel blank consisting of a minimum of 3 DGT pistons was sent with each shipment to account for any possible contamination during shipping and storage.

For deployment, the cages were attached to a vinyl coated steel cable with a buoy at one end and weighed down at the other with 1 or 2 cinder blocks. DGT cages were deployed for approximately 28 days whereupon the pistons were removed from the cages, cleaned and rinsed with de-ionized water (DI). Pistons were then placed in Ziplok bags with approximately 1 mL DI then refrigerated for a maximum of one month after which they were shipped to Trent University for analysis. Samples for dissolved organic carbon analysis (using 500 mL PET plastic jars) were taken at deployment and retrieval and refrigerated until analysis. Similarly, in-situ measurements of temperature and salinity were taken for both deployment and retrieval.

Sediment Sampling

For sediment-DGTs the gels were mounted in elongated Perspex-holders designed to be inserted into the sediment with the top 5 cm of the gel exposed to water and the remaining 10 cm exposed to the sediment (Figure 3). The DGT-probes for accumulating MMHg in sediment pore water were constructed in a similar manner as the water probes except that a cellulose nitrate filter was used, the diffusive gel had a thickness of 0.8 mm and no support gel was used. The binding resin gel was the same except that it was cut to fit the elongated holders. After preparation probes were de-aerated and stored under nitrogen until deployment in the field.

Measurement of MMHg and dissolved organic carbon (DOC)

For MMHg analysis, a method modified from Hintelmann and Evans (1997) was used. In the laboratory, the binding resin gel was separated fom the diffusive gel and placed in clean glass vials. The resins were spiked with a known mass of stable isotope internal standard (i.e. ^{201}Hg) and leached using a thiourea/HCl solution (0.005% in 0.1 M HCl). A portion of the resin leachate was added to a reaction vessel containing 100 mL DI water, 0.2 mL of acetate buffer (2 M) and 0.1 mL sodium tetraethylborate (1% w/v). This solution was left at room temperature for 20 min for the tetraethylborate to react and form the volatile organomercury species, ethylmethylmercury. Tenax traps were connected to the reaction vessel and the generated volatile organomercury species were purged from the solution onto the trap using nitrogen (200 mL min-1) . Finally, mercury species were thermally desorbed from the trap (250 °C), separated by gas chromatography, and quantified by isotope dilution inductivey coupled plasma mass spectrometry (ID-ICP/MS, Micromass Platform).
For the 2008 sampling campaign, analysis of the dissolved organic carbon (DOC) was performed on 1:10 dilutions of the filtered water samples using the Shimadzu TOC-V total organic carbon analyzer. For the 2009 campaign, the Shimadzu TOC analyzer was not employed due to the damaging effects of the high salt content on the instrument. An alternative method was developed using UV-visible spectrophotometry (Mattson et al., 1974). The absorbance at 254 nm for filtered water samples was used to quantify the DOC by comparing it to the linear external calibration curve of a DOC reference material (Nordic DOM, IHSS).

Analytical QA/QC

For each batch of samples, a set of QA/QC samples was measured as well, consisting of 3 bubbler blanks, 3 reagent blanks, and 3 travel blanks. The latter was determined from gels, which were prepared and shipped out to SFEI. These blanks were not deployed, but returned and processed together with sample DGTs. Individual reaction yields were determined using the added internal Me^{201}Hg isotope standard. The limit of detection was controlled by the travel blank, which was essentially the procedural blank of the overall method. A typical travel blank was 2.6 ± 0.5 pg per gel (n = 9), resulting in an absolute LOD of 1.5 pg per gel or 10 pg/L calculated dissolved MMHg for an 28 day deployment period, normalized to 20 °C.

Statistical Analysis

Differences in accumulated mass of MMHg between sets of DGTs were determined using one-way analysis of variance (ANOVA) with the null hypothesis being that no differences exist among sites. Analyses were conducted using log-transformed data at a significance level of $P < 0.05$. When comparing categories of sites, the means of each site were used for analysis.

Interpretation of DGT data

Rather than converting the mass of accumulated MMHg into dissolved concentrations, all the following DGT data are expressed initially as the mass of MMHg collected on the DGT resin during time of deployment (unless otherwise noted). We suggest that the accumulated mass of MMHg is more meaningful for risk assessment purposes, since the diffusion of MMHg across a DGT gel is similar to the initial passive uptake of MMHg by primary producers. This initial uptake is often the critical starting point for MMHg bioaccumulation (e.g. Chen et al., 2008; Mason et al., 1996; Pickhardt and Fisher, 2007). Assuming this analogy is correct, accumulation of MMHg in DGTs will be a good proxy for bioavailable MMHg. We will also present estimated concentrations of dissolved MMHg in sea and pore-water by using the mass of MMHg accumulated in the DGT gels. Based on Fick's first law of diffusion, the mass of MMHg accumulated by the resin inside the DGT unit depends on its concentration in solution (C), diffusive coefficient (D) in the polyacrylamide gel, the thickness (Δd = 0.053 cm or 0.08 cm for water and sediment DGTs, respectively) and surface area (A = 3.14 cm^2) of the diffusive gel layer and the deployment time (t) of the DGT device (Clarisse and Hintelmann, 2006):

$$M = (D \times A \times C \times t)/ \Delta d$$

Hence, dissolved MMHg concentration is obtained by:

$$C = (M \times \Delta d)/(D \times A \times t)$$

In this exercise, particular attention needs to be paid to applying the adequate diffusion coefficient for MMHg. From previous experiments, we have shown that the diffusion of MMHg associated with small inorganic ligands is independent of the ligand. However, in the presence of dissolved organic material (DOM) the rate of diffusion slows down considerably, with a D of 0.7×10^{-6} cm^2 sec^{-1} (Clarisse et al., 2009) under conditions were all the MMHg is complexed by DOM. Consequently, we need to know the proportion of MMHg that is associated with DOM at each sampling location. Despite the high chloride concentration in sea water, most researchers predict that MMHg will be associated with either sulfidic ligands in anoxic or brackish waters or with DOM (Han et al., 2007). While there is limited information on MMHg stability constants with freshwater DOM, such data is completely lacking for marine DOM. However, according to the literature (Choe and Gill, 2003; Amirbahman et al., 2002), MMHg in seawater is normally associated with organic matter, either in colloidal form (which would not pass through the DGT gel and hence, is not collected in this study) or bound to dissolved DOM. It was suggested that DOM complexes dominate the marine MMHg speciation at levels > 1 mg/L DOC (Zhong and Wang, 2009). Our sampling locations span a range of salinities, but also have considerable DOM

concentrations, often > 1 mg/L. Hence, we assume that MMHg in this study is entirely bound to DOM and diffuses in the gel in form of MeHg-DOM complexes. Using this approach may overestimate dissolved MMHg in situations, where a considerable fraction is present in form of MeHgCl or MeHgSH, which would both diffuse faster into the gel. Since the diffusion of MMHg through the gel is strongly dependent on the temperature (D changes by approximately 3 % per degree °C) all MMHg concentrations are expressed for diffusion at 20 °C. A diffusive coefficient of 0.7×10^{-6} cm^2 sec^{-1} at 20 °C was used when calculating aqueous MMHg concentrations and the actual value of D was corrected for the respective deployment temperature

Site selection criteria

In 2008, as part of the Regional Monitoring Program (RMP) Mercury Strategy, DGTs were deployed at 20 small fish stations (Figure 4; Table 1). These stations represented a variety of different environments and spanned the types of sites that the Small Fish project is sampling, including long-term sites (annually sampled Small Fish sites, beginning 2005) and potential source sites such as shallow water WWTP discharges, industrial watershed drainages, legacy sediment (identified through Bay Protection Toxic Cleanup Plan and CalFed Sediment Sites), and bay margins (both enclosed and unenclosed regions). However, since DGTs were deployed at no more than 20 sites in 2008, only a small number of each site type was included. After preliminary results from 2008 it was decided to deploy DGTs at every station that is sampled for the Small Fish project in 2009 to increase the spatial coverage in 2009. Additional field tests were conducted to investigate the temporal variability of MMHg accumulation. DGTs were deployed repeatedly over a period of 12 months at the Martin Luther King Regional Shoreline to monitor seasonal changes. This study also included a small scale spatial comparison to test the repeatability of the DGT measurement.

Results

Deployment period

A perennial challenge for any DGT deployment in natural waters is the risk of biofouling, which would potentially clog the membrane preventing unrestricted uptake of dissolved constituents from the surrounding water. This risk has to be balanced with the time necessary to accumulate enough contaminant for an analysis and the desired period, over which the DGT device is supposed to integrate contaminant levels. Especially in the case of MMHg, which is usually present at ultra trace levels in sea water, deployment periods of one week or longer were anticipated for the collection of sufficient mass (i.e. a few pg). To determine the optimum time of deployment, several sets of DGTs were set out for up to 8 weeks at the Martin Luther King Regional Shoreline (MLKRS) and individual sets of three DGTs were retrieved weekly. The accumulation of MMHg over the 8 week period is shown in Figure 5. Uptake was linear at a rate of 0.93 pg per day for the first 5 weeks with relative little variation between individual gels (n = 3). A slight drop was observed in week 6, which may be attributed to clogging of the gel surface due to biofouling. After 6 weeks, reproducibility dropped significantly showing a relative standard deviation (RSD) of 78 % after 8 weeks. However, the variance was caused by single outliers, which interestingly was characterized by an increase of accumulated MMHg, rather than the expected decrease due to membrane clogging and biofilm

growth, which was now very evident upon visual inspection. Possibly, the biofilm on the filter surface of the gel assembly created a microenvironment conducive to mercury methylation. It has been shown before that anoxic micro-habitats such as biofilms are sites of MMHg formation, even in oxic water (Achá et al., 2005; Hintelmann et al., 1993). Likewise, epiphytes from the SFB area exhibited high methylation rates (Best et al., 2005). Hence, we suggest that the inorganic mercury may be actively methylated in the biofilm generating elevated concentrations of MMHg on the surface of the gel assembly, which then readily diffuses into the gels leading to a nonlinear response after 6 weeks of operation. After removal of the outlying data points, a linear relationship was evident over the full 8 week period. Nevertheless, since the risk of unpredictable MMHg formation as well as potential membrane clogging increases with time, shorter deployment periods are desirable. In 2008, a period of one week was chosen and extended to four weeks in 2009 to maximize the concurrent MMHg accumulation by fish and DGTs. Using the accumulated mass of MMHg, we calculated average dissolved MMHg concentrations of 182 ± 53 pg/L and 220 ± 68 pg/L at the MLKRS station for the first 4 and 8 weeks, respectively. Considering the relatively large uncertainties, mean calculated MMHg concentrations obtained after 4 and 8 weeks of deployment are statistically not different from each other.

Spatial survey of MMHg in the Bay area (2008)

The mean masses of MMHg collected on DGTs in the 2008 spatial survey are shown in Figure 6 (Table 2). In 2008, all gels were deployed for one week. The amount of accumulated MMHg varied from below the limit of detection (1 pg per gel for one week deployment) near the SF piers to as much as 16 pg at the Point Isabel marsh. Owing to the small sample size, we do not have sufficient sites within each category to allow a meaningful comparison among site categories. However, a couple of interesting trends emerged. Locations generally elevated with MMHg were identified in the South Bay, particularly near Alviso and the Guadalupe River outflow (up to 14 pg). A second hot spot was found at Point Isabel (16 pg). High levels were also found near Kirker Creek (9 pg) in the easternmost part of Suisun Bay. Samples near wetlands ranged from 1 to 3 pg, which was at the low end of the spectrum. Open regions around the Bay margin were also low in MMHg. Intermediate masses of MMHg were collected from industrial and legacy sites (4 to 5 pg). Water treatment plants contributed varying amounts of MMHg ranging from near detection to 6 pg. This translates into 13.5 to 157 pg/L of MMHg and may demonstrate that individual WWTPs differ in their potential to discharge and/or generate MMHg. Higher MMHg levels may be caused by discharges rich in nutrients and/or organic carbon, which could promote bacterial productivity leading to increasing rates of MMHg formation further downstream or the plant effluents themselves could contain varying levels of MMHg.

MMHg levels in sediment pore water

Previous work has shown that MMHg collected on sediment gels correlates well with sediment in-situ production rates (Best et al., 2007). Sediment-DGTs are therefore thought to provide valuable information on hot spots of MMHg formation in sediments. However, as always, high production rates do not necessarily translate directly into strong sources for the aquatic environment. To be of concern for marine ecosystems, export of the generated MMHg from sediments to water is crucial.

Nevertheless, biota living in the sediment would be directly exposed to higher levels of MMHg present in pore water.
In 2008, DGTs were set out at selected sites for one week and analyzed for MMHg in the layer situated directly above (2 cm) and below (3 cm) the sediment water interface. These two data would provide information regarding in-situ production (sediment exposed section) and potential diffusive fluxes of MMHg from the sediment to the overlying water (water exposed section). As shown if Table 3, highest masses of MMHg were accumulated in Mission Creek and two wetland marshes, China Camp and Benicia State Park. This was not too surprising, since wetland sediments are often sites of high MMHg production. In contrast, the mass of MMHg collected on gels in the water above the sediment interface was relatively low at China Camp, suggesting that although the sediment at this site forms large amounts of MMHg, this MMHg is readily diluted. Previous work has routinely identified China Camp as a location with elevated MMHg in sediments (Best et al. 2005; Best et al., 2008a). Wetland marshes are micobiologically very active. They not only generate high amounts of MMHg but also show high demethylation potential, which counteracts formation, resulting a moderate net MMHg production. This may also explain the modest levels of MMHg (exported) in the overlying water. Low MMHg formation was observed in Petaluma River. Intermediate amounts of MMHg were determined at Kirker Creek and the Guadalupe River. The latter observation is interesting and shows that despite the high inorganic Hg loading (from New Almaden), only a small fraction of this Hg seems to be bioavailable and is converted to MMHg in the sediment.
Comparing the masses of MMHg collected by DGTs pistons ("open water") and sediment DGTs ("sediment interface") shows that without exception more MMHg was found near the sediment surface. This suggest a significant proportion of this MMHg was formed in place in the sediment and mobilized to the overlying water, where it was diluted with less contaminated Bay water. This difference was particularly pronounced at Benicia State Park, Mission and Kirker Creeks.

Comparison of 2008 DGT data with results from the Small Fish sampling project

Due to the limited sample size, the comparison with fish was inconclusive. Correlations between MMHg accumulated on gels and small fish species were statistically insignificant for both topsmelt (TOPS) and mississippi silverside (MISS). On the other hand, the correlation between the two fish species was significant, but driven mostly by the high value measured at Alviso. With this data point removed the correlation ceased to exist ($P < 0.0517$). It is likely that the two (three) sentinels are exposed to different sources of MMHg or that MMHg exposure varied over the duration of the experiment. While DGTs were only deployed for one week, fish were accumulating MMHg for a much longer period. As well, DGTs by their very nature sample MMHg at the point of deployment, while fish move around. Although the chosen species have been shown to be relatively stationary especially topsmelt have the tendency to occasionally retreat to the open ocean and generally span a larger areas than mississippi silverside. It is expected that fish are less likely to experience distinct local signals (either exceptionally strong or weak sources), while DGTs may. This is also supported by the range of MMHg levels measured in fish, which is much more constrained (all concentrations are within a factor of 4.4, 9.4 and 32 for TOPS, MISS and DGT, respectively). MMHg from point sources is diluted in the bay resulting in more uniform MMHg concentrations experienced by fish. To maximize the period over which fish as well as DGTs are accumulating MMHg, the DGT deployment period was extended to four weeks in 2009.

Seasonal variations of MMHg

To assess seasonal variations in MMHg exposure, DGTs were deployed every month for four weeks each at the Martin Luther King Regional Shoreline (MLKRS) from March 2009 to February 2010. As shown in Figure 7 (Table 4), the highest levels of MMHg of up to 35 pg were found in April (normalized to 28 days and 20 °C). Accumulation dropped to 5.9 pg in August, after which MMHg increased again to 26 pg in December. Generally, MMHg levels at MLKRS are elevated in winter/spring and the exposure lowest in mid-summer. A similar pattern was observed for small fish, which can change concentrations rapidly (Eagles-Smith and Ackerman, 2009). An increase in MMHg of 40 % was observed between March and May, followed by a 40 % decrease by July.
To assess the within site variability, two sets of gels were deployed within a few meters side by side in March and April 2009. Considering the variability of MMHg uptake within each set of 3 gels, no significant statistical differences for the mean uptake at two adjacent locations were observed in March and April ($P < 0.375$ and $P < 0.121$, respectively; Figure 7).

Spatial survey of MMHg in the Bay area (2009)

In 2009, the sampling protocol was altered from the 2008 field season. To average over a longer time period, DGTs were deployed for a full 4 weeks. Fish were sampled at time of retrieval to maximize the overlap between MMHg accumulation by DGT and small fish. As well, it was decided to increase the spatial coverage and sample as many as 44 sites in the San Francisco Bay and 4 sites in the Tomales Bay. Sampling locations are shown in Figure 4. Site categories were the same as in 2008, but this year a minimum of three sites per category was sampled. While category assignments were done to characterize its main feature, some sites could fit into more than one category. Table 5 identifies the category that was chosen for the following discussion, which describes results by site category, followed by a general overview across all locations.

Open regions at bay margins
"Open" stations are characterized as locations which are at the bay margin and in direct water exchange with the Bay proper. They were expected to show low MMHg exposure and could be considered as reference or background locations. Except for one location (71OTH, Honker Bay back inlet) levels were evenly distributed and indeed very low ranging from 0.6 to 6.4 pg (Figure 8). We speculate that some site specific conditions at Honker Bay must contribute to the observed very large MMHg levels. This could include a shallow bay with little water exchange, relatively large runoff from adjacent watersheds, or most likely a strong impact of Hg export from the Sacramento River, which may lead to the much higher than expected MMHg accumulation of 39 pg. A Q-test readily identified this location as an outlier among "open" stations and the data was excluded for the following comparisons. The remaining sites show an average accumulation of 3.8 ± 2.0 pg or 25 ± 14 pg/L of dissolved MMHg.

Enclosed regions at bay margins
The enclosed stations were all locations in confined bays or sub-bays, wetland or marshes that were not in direct exchange with the Bay proper, but connected via discrete outlets. This group of sites showed greater variations from below detection to as high as 20 pg at Point Isabel, which was already identified in 2008 as a hot spot for MMHg. Results were skewed towards higher masses of

MMHg. Clearly, MMHg within this category is controlled by site specific conditions leading to elevated MMHg levels at some locations. The category includes stations which are deemed to be very productive zones of methylation, such as wetlands and marshes. This, combined with limited water exchange with the open Bay, may lead to high MMHg under the proper circumstances. The average accumulation was 8.4 ± 6.7 pg or 53 ± 42 pg/L of dissolved MMHg.

Legacy sites

Like the enclosed stations, the legacy stations are characterized by large variations of MMHg. Accumulation ranges from background levels of 1.4 to the highest value found in this study of 76 pg (Figure 9). Data are skewed by some MMHg hot spots, especially by the very high response found at Alviso. Since many of these stations were potentially impacted by historic Hg from mining activities, the resulting MMHg was high, but not uniformly extreme (except for Alviso). We speculate that some of the legacy mercury may be present in a form, which is not readily available for methylation (e.g. cinnabar). Sites are also very diverse in geochemistry, which contributes a wide range of substrates resulting in varying methylation potentials. Combining the considerable diversity in Hg species available for methylation with a presumably large gradient in biological activity makes the prediction of bioavailable MMHg very difficult and may explain the observed variation among legacy sites. Regardless, this group is near the top of the list of categories in terms of MMHg exposure with an average accumulation (after removal of the Alviso extreme) of 13 ± 8.7 pg or 91 ± 63 pg/L of dissolved MMHg.

Industrial watersheds

The industrial stations show an even distribution of MMHg ranging from 6.1 to 10 pg (Figure 10). However, compared to the open stations, concentrations are significantly higher with an average accumulation of 8.5 ± 2.1 pg or 57 ± 13 pg/L of dissolved MMHg. This suggest that sites within industrial watersheds have typically twice as much MMHg relative to the background. However, they are within the same range as enclosed sites without known industrial influence. This illustrates again that an MMHg risk assessment must include both the concentration of Hg potentially available for methylation (and which is presumably elevated at industrial sites) and the potential for conversion (i.e. microbial activity), which is often enhanced in natural environments such as wetlands and marshes.

Waste Water Treatment Plants

In contrast to 2008, the locations downstream of WWTPs sampled in 2009 showed the highest levels of MMHg accumulation from 16 to 23 pg. On average 19 ± 3.5 pg or 119 ± 31 pg/L of dissolved MMHg were accumulated (Figure 11). This average is slightly higher than the mean found at legacy sites in 2009. It should be noted though, that WWTPs were not directly sampled at the site of discharge, but further downstream. Therefore, levels in the water may be a combination of MMHg directly discharged by the plant or MMHg was formed in the channel, where the samples were collected. It is quite possible that WWTP discharge promotes MMHg formation. Elevated nutrient levels may enhance the general microbial activity in sediments, which in turn leads to higher MMHg formation rates, compared to other sites sampled in 2009. Regardless, it is still a bit puzzling, why WWTPs turn out quite variable from year to year and closer attention needs to be paid to the individual plants, the uniformity of response within this category and potential differences in the type of water treatment, which may help to explain the discrepancy. Still, predicted aqueous MMHg concentrations are moderate and not unreasonable for WWTP effluents.

Tomales Bay

Tomales Bay in northwestern Marine County is impacted by historic mercury mining (Gambonini Mine), which exported mostly cinnabar (HgS) into the Bay, where it is naturally converted to MMHg. An effort is now under way to improve the Bay's ecological health. Four sites within the Bay were sampled by DGT to possibly identify and compare local sources of MMHg. Two sites were located around the mouth of Walker Creek, one was in the Lagunitas and one in the south end of the bay at Eucalyptus Beach.

Between 8.9 and 15 pg of MMHg were collected on DGTs over the 4 week deployment period (Figure 12). Anova testing (after log transformation) revealed significant differences among sites, with the Hamilton site (southern edge of Walker Creek Delta) being significantly higher compared to the other three sites, which were not different from each other. This is consistent with existing data on MMHg in sediment and water in Tomales Bay. For example, a recent study (Ridolfi et al., 2010) found higher MMHg in sediments in the Walker Creek Delta, although some sites in the Lagunitas Creek Delta had also elevated MMHg concentrations. Even more interesting, MMHg in water was lowest at Eucalyptus Beach and Lagunitas and much higher at Hamilton, where DGTs also indicated higher MMHg levels. Dissolved MMHg concentrations at the three similar sites calculated from the accumulated mass on the DGTs were on average 81 ± 29 pg/L, which compares favorably with the reported concentration of 90 ± 30 pg/L measured for unfiltered water. DGTs concentrations are expected to be lower since DGTs only sample the truly dissolved fraction. Compared to SF Bay, DGT-MMHg values in Tomales Bay were comparable to the higher values typically found in the SF South Bay area, indicating elevated MMHg exposure in Tomales Bay.

Spatial overview of MHHG as indicated BY DGT probes in SF Bay in 2009

Another view of the distribution of MMHg in the Bay area as sampled by DGTs is presented in Figure 13, comparing the main regions regardless of site category. This picture reveals a general North to South gradient with generally lower MMHg levels around the Golden Gate Bridge and the Northern Bays, and gradual increases over the Central to the South Bay and the most eastern reaches of Suisun Bay. In particular the South Bay is characterized by a larger number of elevated sites, dominated by the Alviso region in the far south. The situation in the east Bay is complex and seems to be regulated by site specific conditions, with a potential impact of Hg export from the Sacramento River resulting in localized high MMHg levels. A recent small fish study came to similar conclusions (Greenfeld an Jahn). The authors reported highest Hg concentrations in fish for the southernmost stations (nears Alviso), intermediate levels in Central Bay stations and lowest concentrations in the North Bay.

This general pattern can be interpreted as a possible impact of historic mining activity, which exports Hg from the Guadalupe River via the Alviso Slough into the South Bay. While the North Bay also receives Hg inputs from historic mining operations, North Bay sediments may be less productive Hg methylation sites and/or the more efficient flushing leads to stronger source dilution and lower MMHg concentrations, especially in San Pablo Bay.

Comparison of MMHg accumulation in DGT with concentrations in small fish

Results reported so far provide an overview of spatial distribution of (DGT-labile) MMHg in the Bay area indicating that Diffusive Gradient Thinfilm devices are useful as indicators for potential MMHg accumulation at relevant field sites over a range of time periods. MMHg concentrations

calculated from the DGT measurements are deemed to correspond to the concentration of dissolved MMHg complexes. As such, it directly responds to changes in MMHg concentrations in the water body surrounding the stationary sampling device. Conventional biosentinels on the other hand are more or less mobile, depending on the species used for monitoring. Fish are commonly used to assess mercury risk to wildlife and to aquatic systems in general. However, even small fish covering a relatively small area have their own individual life cycle and ecosystem niche, which makes them reasonably useful as a general monitoring device. The Small Fish sampling project is collecting a series of species, including mississippi silverside and topsmelt, which are common in the Bay area.
Silversides are mostly found in shallow water and concentrate near protected areas with sand or gravel bottoms. They usually feed in deeper water on zooplankton, copepods and cladocerans, but are a common prey choice themselves and will quickly return to shallow areas for protection. They grow to 8-10 cm in their first year and most die immediately after spawning in their first or second summer.
Topsmelt are a marine fish found in bays and estuaries, but young-of-the year also frequent fresh or brackish waters. They are omnivores feeding on diatoms, algae, detritus, chironomid midge larvae, and amphipods. Juvenile topsmelt are less benthically focused and have also been found to consume various kinds of zooplankton. They grow up to 8 years old with an average length of 20 cm, but individuals collected in this study were much smaller and presumably only 1 - 2 years old.
Because of their difference in preferred habitats, both species were not captured at all sites.
When all data from all sampling locations are considered, MMHg accumulated on DGTs correlated well with Hg measured in both TOPS and MISS ($P < 0.0009$ and $P < 0.0039$, respectively; Figure 14). The correlation is driven mainly by the strong response to MMHg at the Alviso site. Without this point, the correlation is statistically insignificant. However, if one only compares MISS and TOPS with each other, a similar result is obtained. The correlation between MISS and TOPS is only statistically significant with the inclusion of Alviso ($P < 0.0003$, Figure 15) and vanishes after removal of this location from the correlation analysis ($P < 0.196$). It should be noted that the fish analysis was not the focus of this study and is included for informational purposes only. Although a previous study found a significant effect of length on Hg (Greenfield and Jahn, 2010), length correction was not performed before evaluating spatial patterns.
While not entirely satisfying, this comparison emphasizes that different (bio)sentinels are exposed to different sources of contaminant. Even small fish, which are relatively local, may access MMHg from a variety of sources or forage over different areas leading to slightly different results. Particularly in an area with few extrema (except for Alviso, which always stands out with every sentinel), fish occupy essentially the same ecosystem (SF Bay) and dilution of point sources is significant enough to obscure fine variations among sites. A similar observation was reported by Greenfield and Jahn (2010), who showed that MMHg concentrations decreased with distance from Alviso and exhibit a more uniform range of concentrations away from this hot spot, resulting in only weak correlations between MISS and TOPS.
A major difference between DGTs and small fish is, of course, the vastly different exposure period. DGTs accumulated MMHg for up to 4 weeks, while fish take up MMHg over their entire life span. Even assuming that the size cohorts captured for this study only comprise young-of-the-year fish, they may grow up to 6 months old (assuming spawning in April and capture in October). In situations, where the seasonal variation of the MMHg source strength differs among locations, DGTs and fish integrate different sources of MMHg.

Conclusions

The DGT sentinels used in this study were able to identify high leverage pathways of MMHg to the Bay. Three areas of concern were recognized: 1) the highest MMHg levels were observed emerging from the Guadalupe River inflow in the Alviso area with decreasing trends towards the North; 2) pockets of locally high MMHg were encountered in eastern most part of Suisun Bay; and 3) a strong point source of MMHg was spotted around Point Isabel. The first two hot spots are likely influenced by historical mining activities, exporting high levels of Hg into the Bay. A major fraction of this Hg is possibly in the form of HgS, which is less bioavailable and requires particular conditions to become microbially available before it is transformed into toxic MMHg. This may explain the spottiness of some observations. The south bay shows a consistent gradient towards the golden Gate Bridge, where MMHg levels were consistently lowest. The North Bay (San Pablo Bay) is an area of low MMHg exposure, most likely due to the higher flushing rate and more immediate water exchange with the open sea. This exchange is limited when moving east into Suisun Bay, potentially leading to the locally high areas of MMHg.

DGT sentinels offer the advantage of being able to be deployed almost anywhere. The only constrain is that the gels need to be kept moist at all times, preferably submersed under water. This may limit their use in tidal areas, where careful placement is essential to prevent drying of gels. Exposure periods of up to 4 weeks seems to be the best compromise between, integrating and monitoring MMHg exposure over a reasonable time frame and acceptable temporal resolution, accumulating sufficient MMHg for analysis and avoiding excessive biofouling. The monthly deployment protocol is also valuable in identifying seasonal variations of MMHg exposure at individual locations.

In general, DGT sentinels offer a couple of advantages over conventional collection and analysis of water samples for monitoring purposes:

- the device can be mass produced and is easy to deploy and retrieve; especially, if used at dedicated or permanent monitoring stations
- DGTs concentrates MMHg *in situ*, minimizing problems with sample contamination during collection, transport and storage of water samples
- sample collection by DGT devices is less expensive, as it can be conducted by non-specialists
- DGT samples are amenable to measurement using automated MMHg analysis systems
- it can provide information about the actual MMHg species present in the water by varying the thickness and pore size of the diffusion gel layer (was not part of this study).

Compared to other (bio)sentinels, DGT devices have the advantage that they can be deployed for MMHg assessment at locations where fish or other biomonitors cannot exist. DGTs are usable year round and data are guaranteed, while the same biosentinel is not necessarily present at every location or every time of the year. For a coastal monitoring program, DGTS offer the possibility to use the same tool across a wide range of salinities, which is especially useful in the Bay area consisting of coastal, estuary and riverine environments, and salt ponds. Owing to their pinpoint deployment characteristics, DGTs are able to identify point sources, and can be used to monitor discharge and plumes of MMHg. If deployment stations are carefully chosen, e.g. open areas with sufficiently high flushing rates, DGTs will also integrate over wider spatial area.

Outlook

Since the 2009 sampling campaign focussed on parallel sampling at the same stations that were also targeted by the Small Fish project, other opportunities to exploit the full potential of the DGT sentinels were missed or not taken full advantage of. One of the strengths of the DGT devices is their utilization for point source identification. The following studies, which are difficult to accomplish with traditional biosentinels such as fish, are suggested for future work. They mainly fall into the area of investigating gradients originating from point sources (plume monitoring) and include:

- tributaries of interest such as the Guadalupe (Alviso area) and Sacramento River (ominous hot spots observed in eastern Suisun Bay)
- Zone 4 Line A
- wetlands and sloughs draining wetlands
- Waste water Treatment plants: is MMHg discharged by WWTPs (which should generated a plume originating at he discharge point) or is the WWPT discharge enhancing in-place production of MMHg resulting in higher MMHg.

Other areas of investigation that can be uniquely pursued by DGT sentinels are the investigation of

- sediment in-situ production of MMHg: use of sediment gels to monitor pore water profiles and to provide estimates of MMHg fluxes to the overlying water
- seasonal variations of MMHg exposure at representative bay sites: important for catching times of concern such as peak breeding periods
- MMHg in salt ponds.

For a regular monitoring program, the installation of dedicated stations (e.g. permanently anchored buoys to attach DGT cages) should be considered to greatly improve the ease of deployment and retrieval.

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Table 1: Stations and their coordinates, selected for DGT deployment in the 2008 spatial survey

Station ID	Category	Name	Time Deployed	Duration, h	Latitude	Longitude
66OTH	Open		10/15/08 14:50	192	37.8036	-122.4007
MTNVW	WWTP	Mountain View	10/1/08 15:05	212	38.0197	-122.0942
61OTH	Open		10/21/08 11:55	191	37.5034	-122.1654
29BIR	Open	Bair	10/21/08 13:40	190	37.5334	-122.2319
226WE	Open	wetland	10/14/08 14:40	213	38.0482	-122.4976
CHINA	Open	China Camp	10/14/08 12:55	214	38.0142	-122.4899
ALVSL	Legacy	Alviso	10/9/08 10:25	169	37.4594	-122.0214
306WE	Enclosed	wetland	10/2/08 12:25	187	38.2089	-122.5789
MISCK	Legacy	Mission Creek	10/15/08 13:35	192	37.7734	-122.3939
BENPK	Open	Benicia State Park	10/1/08 11:05	214	38.0641	-122.1918
4ALVS	Legacy	Alviso	10/8/08 16:06	187	37.4385	-121.9923
04OTH	Enclosed		9/9/08 15:07	160	37.9033	-122.3251
ARROY	Industrial	Arroyo del Hambre	10/3/08 14:05	164	38.0209	-122.1408
SUWTP	WWTP	City of Sunnyvale	10/9/08 11:25	164	37.424	-122.0145
2ALVS	Legacy	Alviso	10/8/08 18:40	185	37.4475	-122.0198
KIRKE	Legacy	Kirker Creek	10/3/08 11:15	169	38.0247	-121.8438
NALMA	Legacy	New Almaden	10/8/08 13:25	190	37.4228	-121.9757
PTISA	Enclosed	Point Isabel	9/9/08 13:00	162	37.9043	-122.3196

Table 2: MMHg accumulated on DGT, calculated dissolved MMHg concentrations, site conditions and total Hg in small fish (TOPS = topsmelt; MISS = mississippi silverside) for the spatial survey conducted in 2008.

	DGT			water			TOPS		MISS	
Station	MMHg	MMHg	RSD	DOC	salinit	T	HgT	RSD	HgT	RSD
	pg	pg/L	%	mg/L	psu	°C	ng/g DW	%	ng/g	%
66OTH	0.0	nd	0	3.3	32.3	15.3	39	2.4		
MTNVW	0.5	13	2	40	1.1	18.9			15	0.9
61OTH	1.0	30	18	3.7	32.1	15.2	42	7.2	98	9.7
29BIR	1.6	42	11	4.0	32.6	17.8	43	2.9		
226WE	1.5	46	28	3.3	27.1	12.9			65	3.3
CHINA	1.7	51	4	2.0	27.0	14.6	46	1.4	92	28
ALVSL	3.0	80	28	4.8	27.1	18.7	62	5.6	203	6.6
306WE	3.0	81	8	12.7	34.2	17.9	52	2.5	86	10
MISCK	3.3	90	21	3.5	32.0	18.1	45	3.0		
BENPK	3.7	98	20	4.5	16.6	19.1	31	4.2	72	3.3
4ALVS	4.7	123	4	8.8	16.5	19.5	172	13	259	25
04OTH	5.1	136	8	4.8	31.9	18.5	60	4.4	80	
ARROY	5.4	148	3	2.4	16.2	17.5	28	1.7	60	6.9
SUWTP	5.8	157	16	10.5	2.8	18.4			108	2.8
2ALVS	8.8	228	16	5.8	21.1	19.6	73	10	148	24
KIRKE	9.4	252	42	2.7	1.8	18.6			33	1.2
NALMA	12.2	334	21	4.3	1.9	17.8			160	9.9
PTISA	16.4	450	16	4.8	31.9	17.7	54	2.0	96	8.3

Table 3: MMHg accumulated on sediment-DGT and calculated dissolved MMHg concentrations in porewater and water just above the sediment water interface.

Station ID	Time Deployed	Duration	MMHg in top sediment		MMHg in water above sediment		T
			MMHg mass	MMHg conc.	MMHg mass	MMHg conc.	
	pg	hours	pg	pg/L	pg	pg/L	°C
306WE	10/2/08 11:45	188	29	140	9.7	59	16.6
61OTH	10/21/08 11:20	192	55	274	6.8	45	15.1
BENPK	10/1/08 11:45	214	610	2707	131	773	18.5
CHINA	10/14/08 11:55	215	286	1450	5.8	39	14.2
KIRKE	10/3/08 11:10	169	124	558	71	427	18.2
MISCK	10/15/08 13:25	192	641	2923	35	213	15.9
NALMA	10/8/08 12:40	191	96	444	30	184	17.3
SUWTP	10/9/08 11:20	164	39	176	17	104	16.2

Table 4: Stations and their coordinates, selected for DGT deployment in the 2009 spatial survey

Station ID	Category	Name	Time Deployed	Duration, h	Latitude	Longitude
ETTIE	Industrial	Ettie Street Pump Stn	8/6/13 11:30	649	37.82993	-122.295
PLMCK	Industrial	Plummer Ck, S Bay	9/10/13 12:45	624	37.51207	-122.0543
SANBD	Industrial	San Bruno D	9/18/13 11:59	696	37.6434	-122.4001
CORTE	Industrial	Corte Madera Creek	10/9/13 12:12	673	37.94189	-122.5182
OAKIH	Legacy	Oakland Inner Harbor	8/6/13 13:00	650	37.79063	-122.264
JOYCE	Legacy	W Montezuma Sl	8/20/13 11:00	627	38.16398	-122.0467
SIBS2	Legacy	S India Basin, SF	9/18/13 13:03	671	37.73382	-122.3729
ISLAI	Legacy	Islais Ck channel, SF	9/18/13 13:24	672	37.74682	-122.3893
CENBI	Legacy	Central Basin Inner	9/18/13 13:51	669	37.76358	-122.3866
RICHH	Legacy	Richmond Harbor	10/2/13 10:15	652	37.90976	-122.3369
SMCRK	Legacy	San Mateo Creek	10/2/13 12:03	599	37.57412	-122.3067
Z4LA	Legacy	Industrial Storm Drain	10/2/13 12:46	601	37.64536	-122.1363
HAYLC	Legacy	Hayward Landing	10/2/13 13:16	601	37.64721	-122.1461
ALVSL	Legacy	Alviso Slough	9/10/13 13:33	646	37.45949	-122.0206
EDENL	Enclosed	Eden Landing	8/13/13 12:30	648	37.59354	-122.1433
NEWSL	Enclosed	Newark Slough	9/10/13 11:54	624	37.50684	-122.0867
PTISA	Enclosed	Point Isabel Marsh	10/2/13 15:25	645	37.90423	-122.3194
08OTH	Enclosed	Mid S Bay	8/13/13 13:40	651	37.5215	-122.2394
09OTH	Enclosed	Suisun, Cross Slough	8/20/13 9:45	625	38.18372	-121.9548
13OTH	Enclosed	Suisun, Tree Slough	8/20/13 12:55	624	38.16368	-121.9916
14OTH	Enclosed	Fagan Slough	9/3/13 11:35	675	38.21377	-122.3021
10OTH	Enclosed	Napa Slough	9/3/13 12:28	673	38.16118	-122.3988
12OTH	Enclosed	Mowry Slough, S Bay	9/10/13 13:07	626	37.4835	-122.023

Station ID	Category	Name	Time Deployed	Duration, h	Latitude	Longitude
18OTH	Enclosed	Petaluma River	9/24/13 12:48	650	38.14909	-122.5335
19OTH	Enclosed	Richardson Bay	10/9/13 11:17	672	37.88931	-122.5016
BIRDI	Open	Bird Island	8/13/13 13:12	650	37.54312	-122.2219
CANDL	Open	Candlestick Park, SF	9/18/13 12:43	694	37.71797	-122.3796
CHINA	Open	China Camp	9/24/13 11:16	649	38.0148	-122.4894
HAMIL	Open	Hamilton old AFB	9/24/13 12:01	650	38.04814	-122.4946
BENPK	Open	Benecia State Park	10/9/13 15:37	621	38.06455	-122.1929
69OTH	Open	Mid S Bay, E side	8/13/13 11:55	648	37.55589	-122.1261
67OTH	Open	San Pablo Bay	9/3/13 12:55	672	38.11025	-122.3144
73OTH	Open	Brisbane Harbor	9/18/13 12:22	695	37.66839	-122.3838
70OTH	Open	SW San Pablo Bay	9/24/13 10:54	648	38.00362	-122.4677
72OTH	Open	Alameda bayshore	10/2/13 14:40	644	37.7679	-122.2766
74OTH	Open	Richmond Bridge	10/9/13 13:15	674	37.92949	-122.398
75OTH	Open	Concord Naval Base	10/9/13 14:59	619	38.0568	-122.0456
71OTH	Open	Honker Bay back inlet	10/9/13 16:25	623	38.07373	-121.9096
EUCBH	Tomales		6/11/13 9:13	458	38.19004	-122.9373
HAMLT	Tomales	Hamilton Bay	6/11/13 9:35	457	38.20276	-122.9248
LAGUN	Tomales	Lagunitas Bay	6/11/13 11:45	456	38.1023	-122.8497
WALKR	Tomales	Walker Creek	6/11/13 12:42	458	38.21119	-122.9416
FSSDW	WWTP	Fairfield-Suisun	8/20/13 12:15	646	38.20944	-122.0569
SVCSD	WWTP	Sonoma Valley	9/3/13 13:44	717	38.23713	-122.4317
PALOA	WWTP	Palo Alto	9/10/13 10:23	647	37.45946	-122.1113

Table 5: MMHg accumulated on DGT, calculated MMHg concentrations, site conditions and total Hg in small fish (TOPS = topsmelt; MISS = mississippi silverside) for the 2009 spatial survey.

	DGT			water			TOPS		MISS	
Station	MMHg	MMHg	RSD	DOC	salinit	T	HgT	RSD	HgT	RSD
	pg	pg/L	%	mg/L	psu	°C	ng/g DW	%	ng/g	%
ETTIE	7.4	47	34	1.5	25.3	20	148	6	514	25
PLMCK	10.0	66	14	3.3	29.2	19	203	17	473	16
SANBD	10.5	70	13	2.0	29.5	19	123	8		
CORTE	6.1	45	34	1.2	24.6	16	98	9	223	14
OAKIH	9.9	59	26	1.6	25.1	23	251	29		
JOYCE	1.4	9	99	3.3	8.9	21			148	19
SIBS2	10.2	69	9	0.9	30.3	18	157	14		
ISLAI	8.6	55	9	1.0	26.0	20	195	6		
CENBI	3.7	26	37	0.7	30.4	17	121	8		
RICHH	23.0	171	68	1.2	22.2	15			673	23
SMCRK	26.2	182	21	2.0	27.3	17	169	29	286	44
Z4LA	14.8	100	21	4.3	0.3	18				
HAYLC	22.1	151	29	2.8	21.7	18	174	11	275	24
ALVSL	76.4	515	54	4.3	26.6	18	461	64	790	42
OMHEA	3.1	19	19	1.1	25.3	22	183	12		
EDENL	5.2	31	30	1.9	29.8	22	197	17	436	16
NEWSL	4.8	32	39	3.5	29.7	18	203	12		
PTISA	19.3	124	21	2.3	26.6	20	216	6		
08OTH	7.7	45	35	3.1	29.8	24	178	13		
09OTH	3.4	21	78	7.4	6.5	21			256	57
13OTH	20.0	122	36	9.6	7.0	22			252	26
14OTH	13.2	84	17	6.1	19.7	20			257	23

Station	DGT			water			TOPS		MISS	
	MMHg	MMHg	RSD	DOC	salinit	T	HgT	RSD	HgT	RSD
	pg	pg/L	%	mg/L	psu	°C	ng/g DW	%	ng/g	%
10OTH	1.5	10	103	3.6	24.7	18			351	10
12OTH	9.6	64	18	4.5	28.6	18	192	19		
18OTH	(0.2)	(1)		5.6	23.6	19	166	31	255	5
19OTH	7.1	53	23	1.1	27.4	15	216	13		
BIRDI	6.6	39	93	2.1	29.6	22	171	23		
CANDL	6.6	45	14	1.0	30.1	18	110	8		
CHINA	1.3	9	33	2.0	23.3	19	121	16		
HAMIL	2.2	15	19	2.1	22.7	19	159	13	250	19
BENPK	4.2	29	8	1.6	16.2	17	178	16	250	10
69OTH	1.9	12	100	2.0	29.7	21	199	11		
67OTH	0.6	4	148	2.7	23.3	20			308	24
73OTH	6	40	16	1.2	30.0	19	140	29		
70OTH	3.8	25	49	2.2	23.4	19	106	15	335	19
72OTH	3.6	22	18	1.4	26.6	22	166	23	257	80
74OTH	5.2	39	16	0.8	25.9	15	143	26		
75OTH	3.4	24	38	1.9	11.1	17	124	11	212	20
71OTH	39.3	277	2	2.3	6.2	17	152	21	196	11
EUCBH	9.1	65	23	0.3	31.0	16				
HAMLT	18.3	123	23	0.6	34.0	18				
LAGUN	9.3	58	13	4.2	28.3	21				
WALKR	11.8	79	9	0.9	33.8	19	471	17		
FSSDW	17.1	108	14	18.1	4.8	20			197	28
SVCSD	22.8	154	15	14.2	28.2	18			475	22
PALOA	16.5	94	7	5.8	1.9	24			350	27

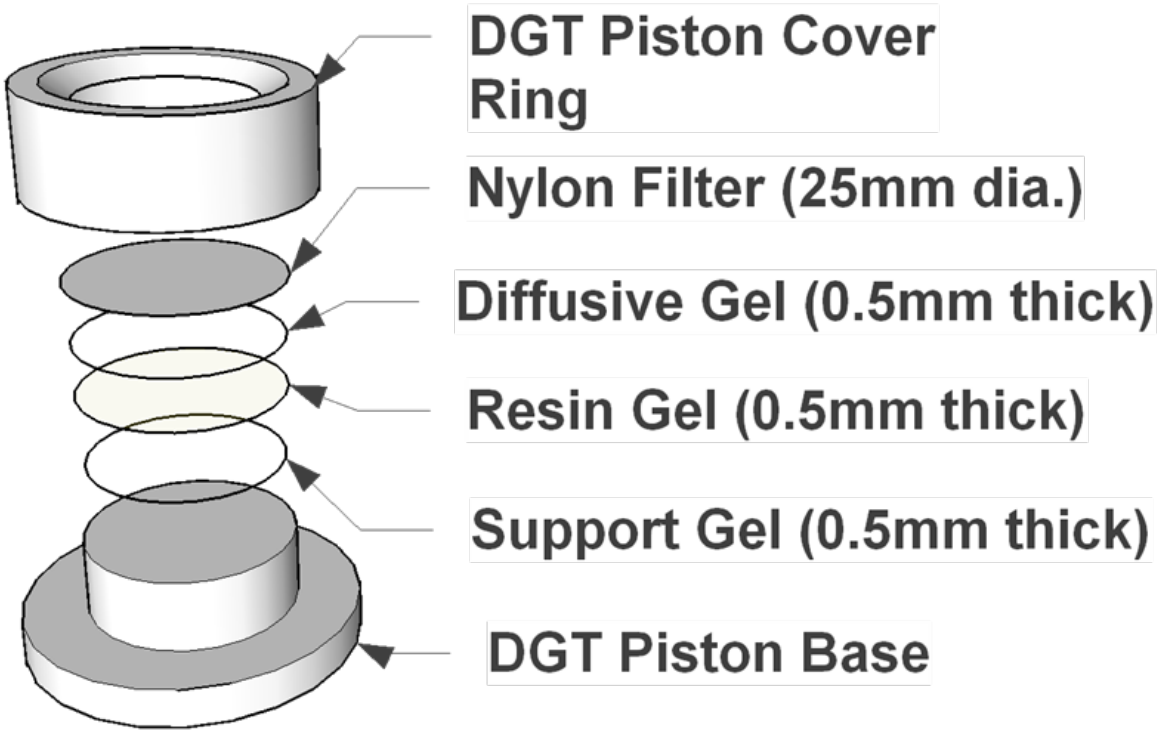

Figure 1: Water-DGT probe assembly

Figure 2: DGT piston configuration in bottom basket and closed DGT cage

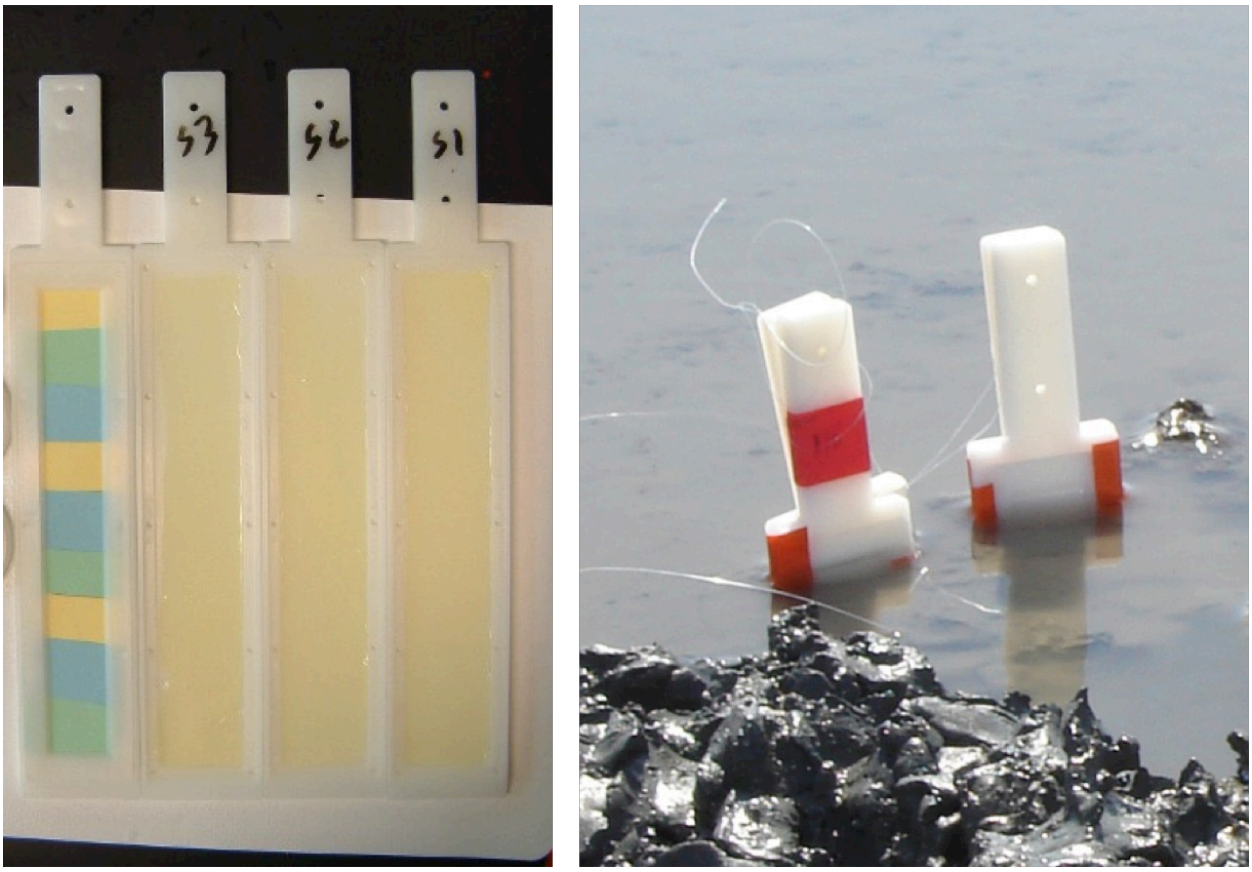

Figure 3: Sediment-DGT probe

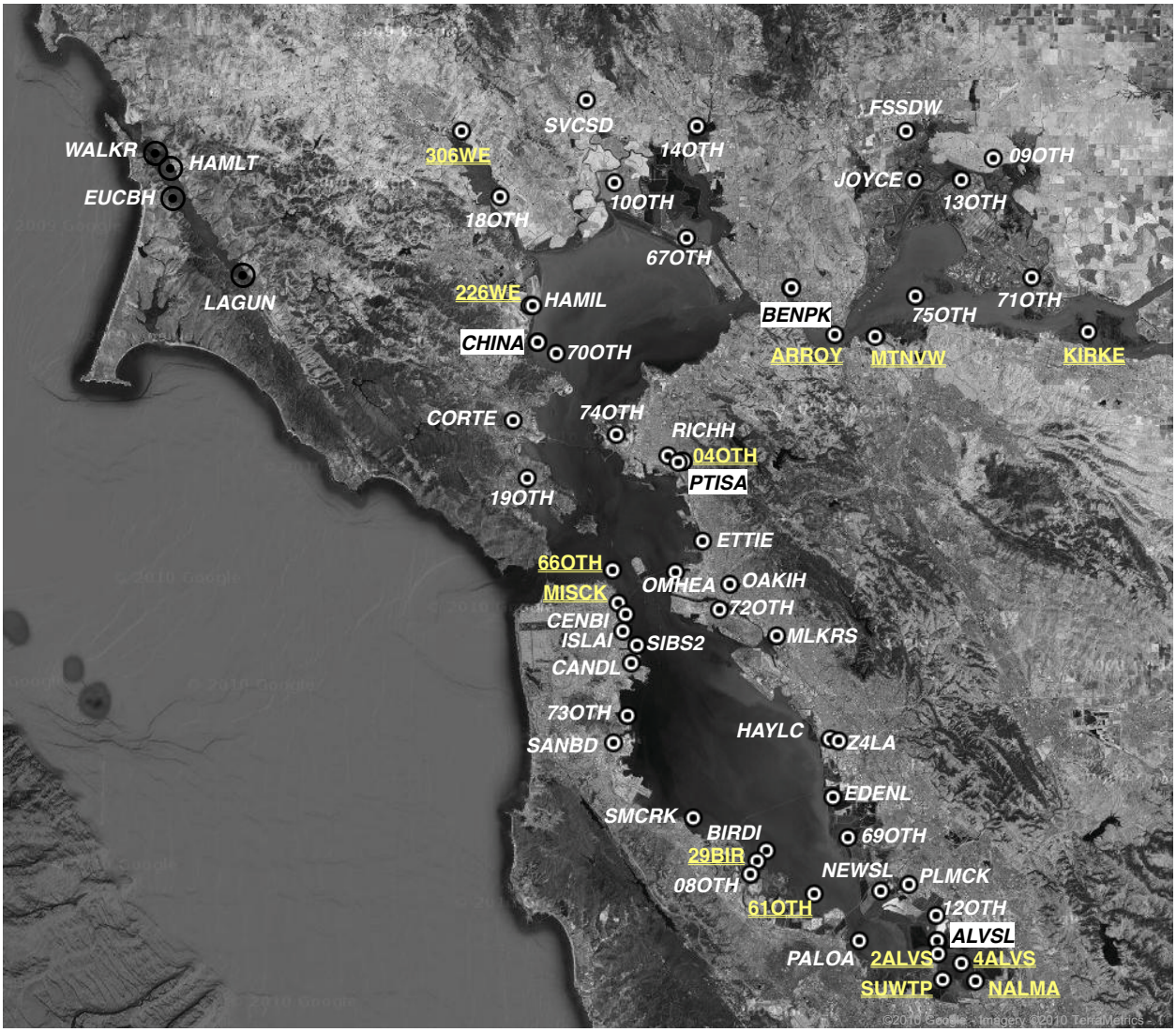

Figure 4: DGT sampling stations in 2008 in yellow letters and 2009 in white letters. Stations sampled in both years are in black letters on white background. Precise location and ancillary information are in Table 1.

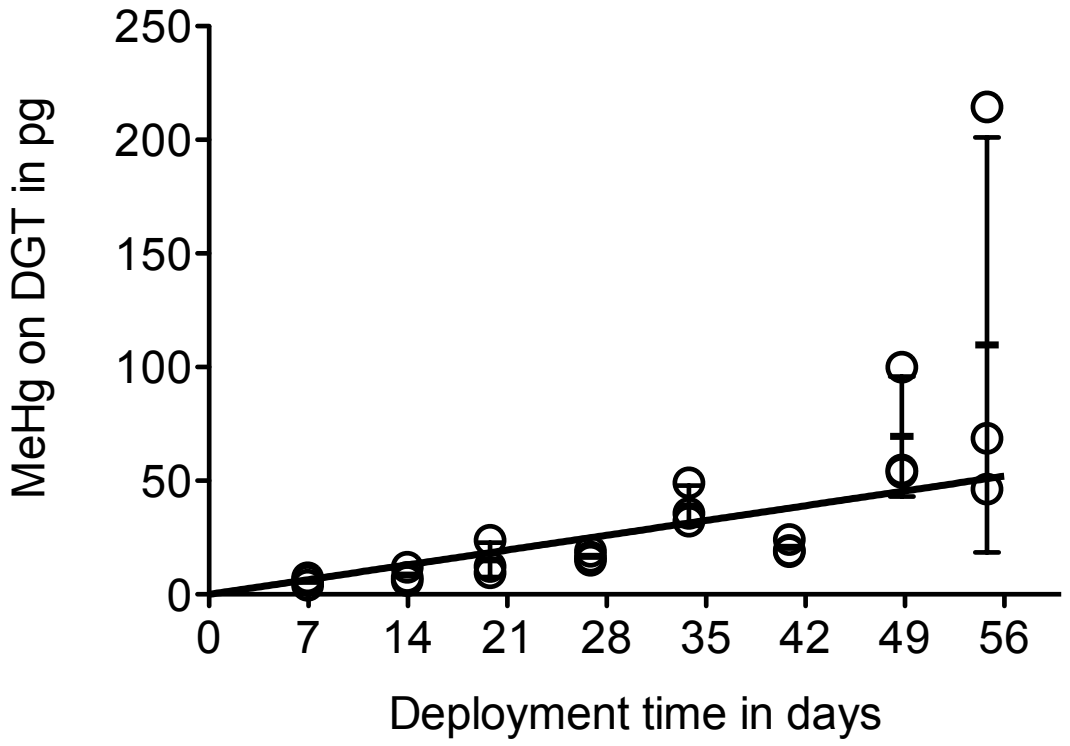

Figure 5: Accumulation of MMHg on DGT devices over an 8 week period. Linear regression shown is based on the entire 8 week period (ignoring the single high outliers observed at 7 and 8 weeks, respectively)

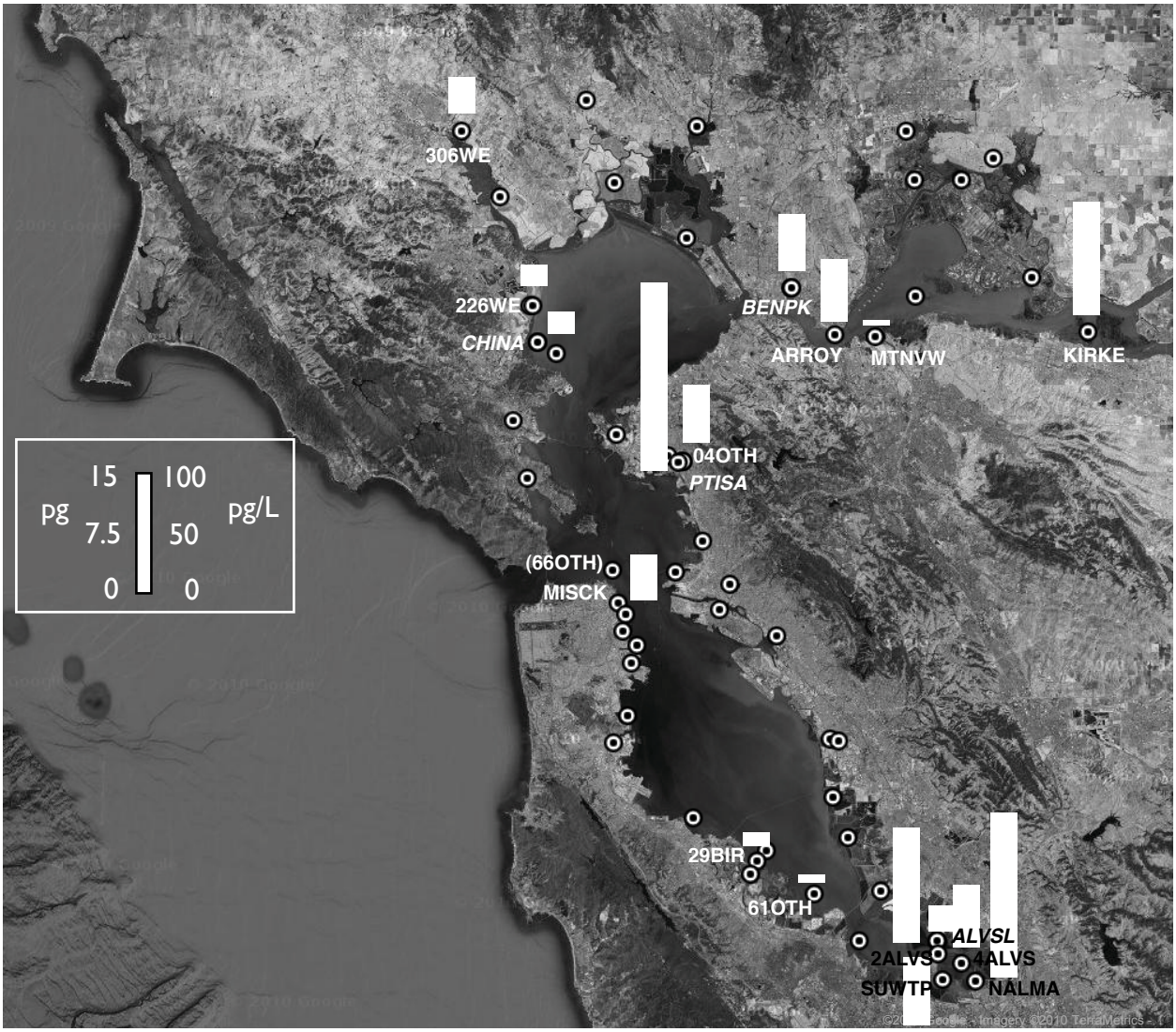

Figure 6: Spatial survey 2008 showing mass of MMHg accumulated on DGTs in the San Francisco Bay area.

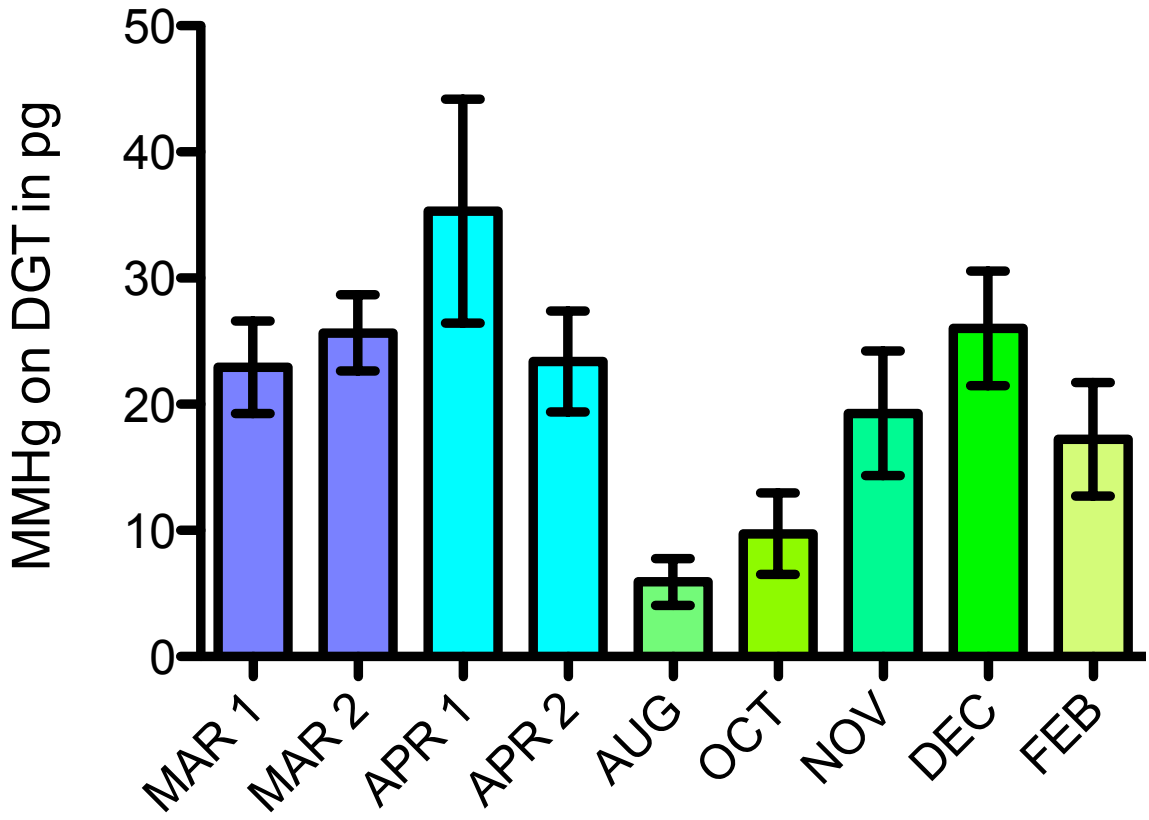

Figure 7: **Seasonal variation of MMHg accumulation on DGTs at the Martin Luther King Regional Shoreline over the period from March 2009 to February 2010. Error bars represent standard deviation of replicate DGTs (n = 3). MAR 1+2 and APR 1+2 are two side-by side replicate deployments of two sets of DGTs, respectively, to evaluate the spatial variability of the DGT measurement at a single station.**

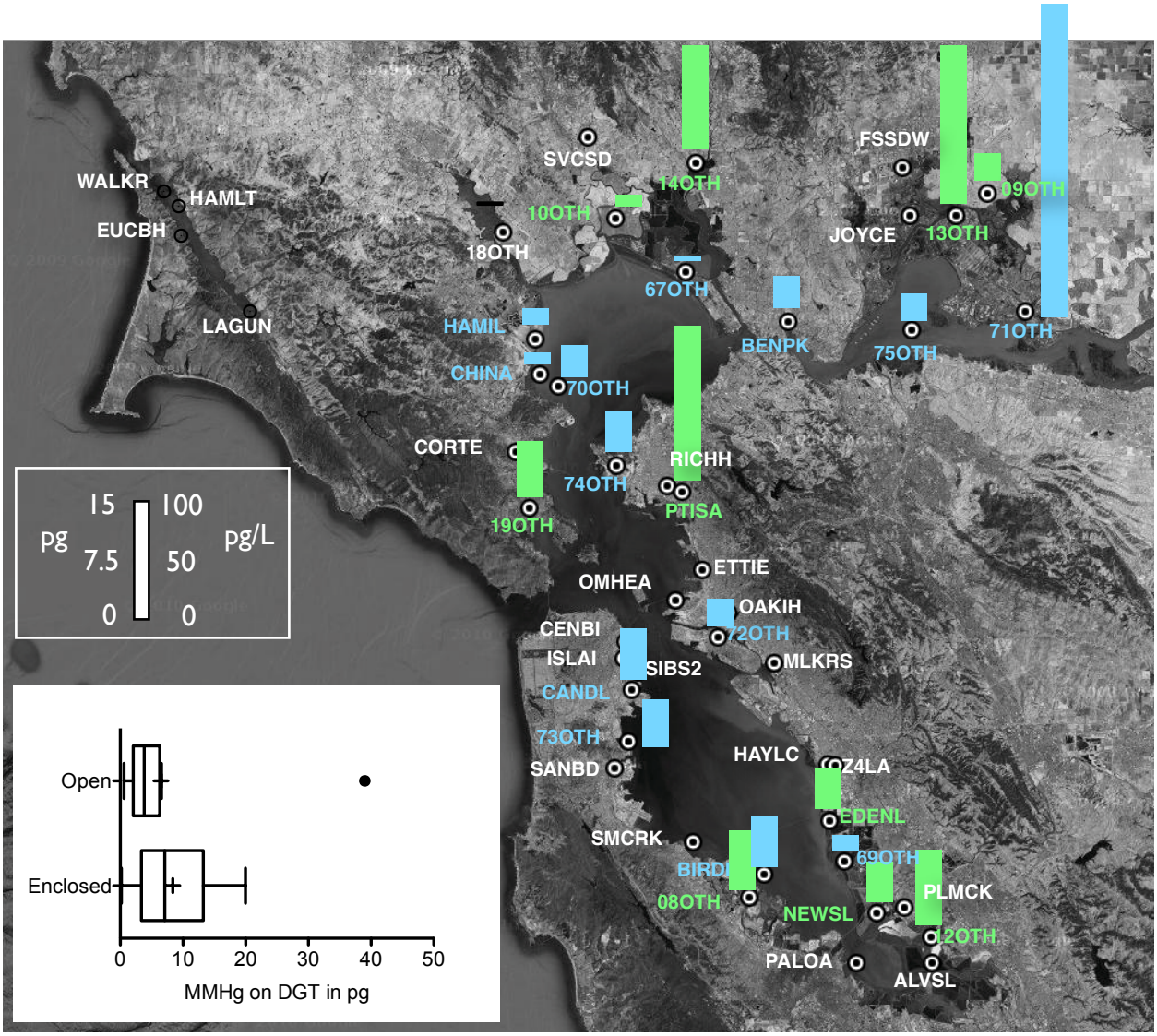

Figure 8: **Mass of MMHg accumulated on DGTs at open (blue) and enclosed (green) regions in the San Francisco Bay area. Box plots show the 25th and 75th percentile of data, and whiskers illustrate the range of all values in each category. The mean is indicated by the vertical line in each box, while the cross represents the mean. The box plot suggests that the "71OTH"-site is an outlier among open region stations.**

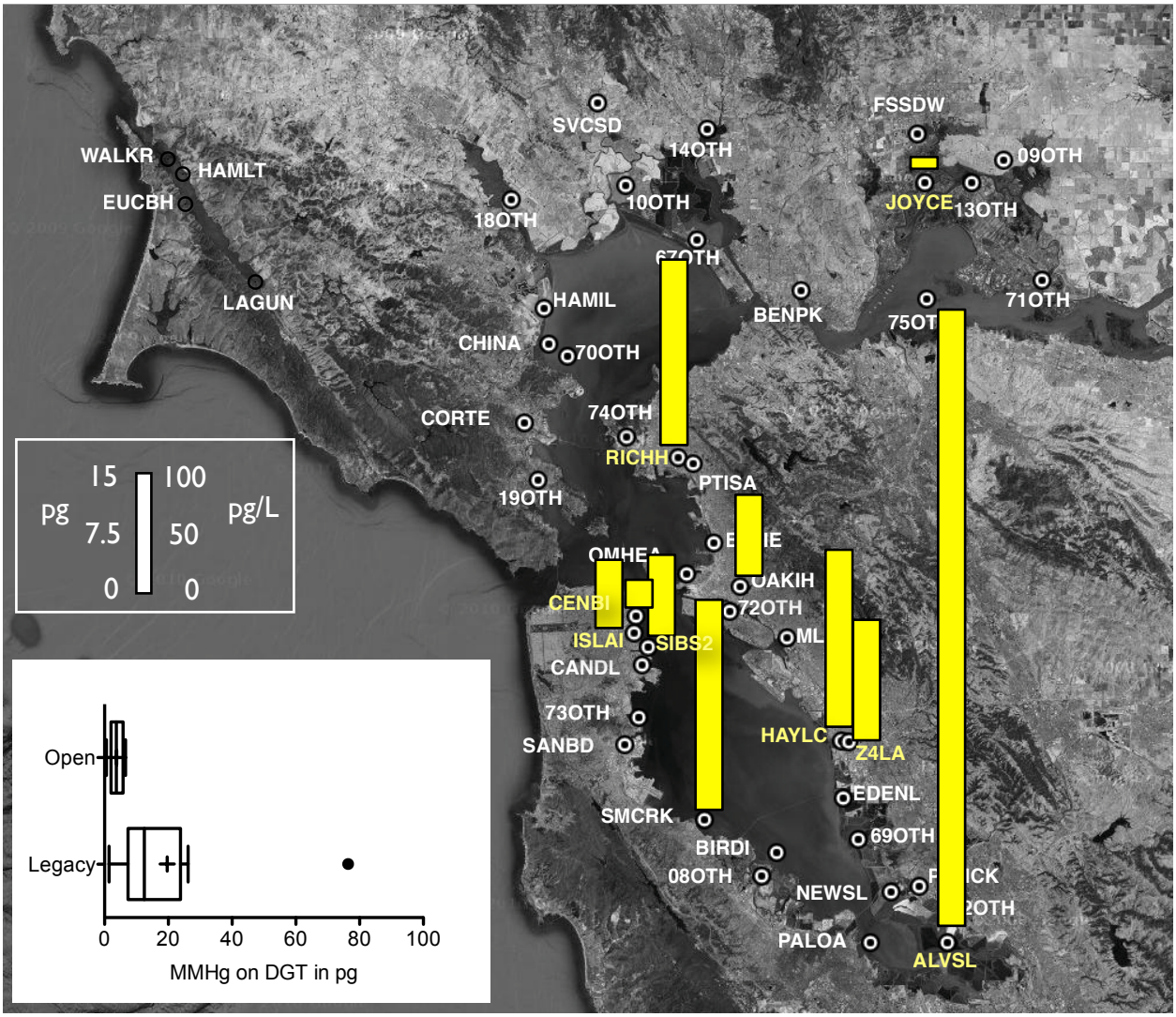

Figure 9: **Mass of MMHg accumulated on DGTs at legacy sites in the San Francisco Bay area. Box plots show the 25th and 75th percentile of data, and whiskers illustrate the range of all values in each category. The mean is indicated by the vertical line in each box, while the cross represents the mean. The box plot suggests that the "ALVSL"-site is an outlier among legacy sites.**

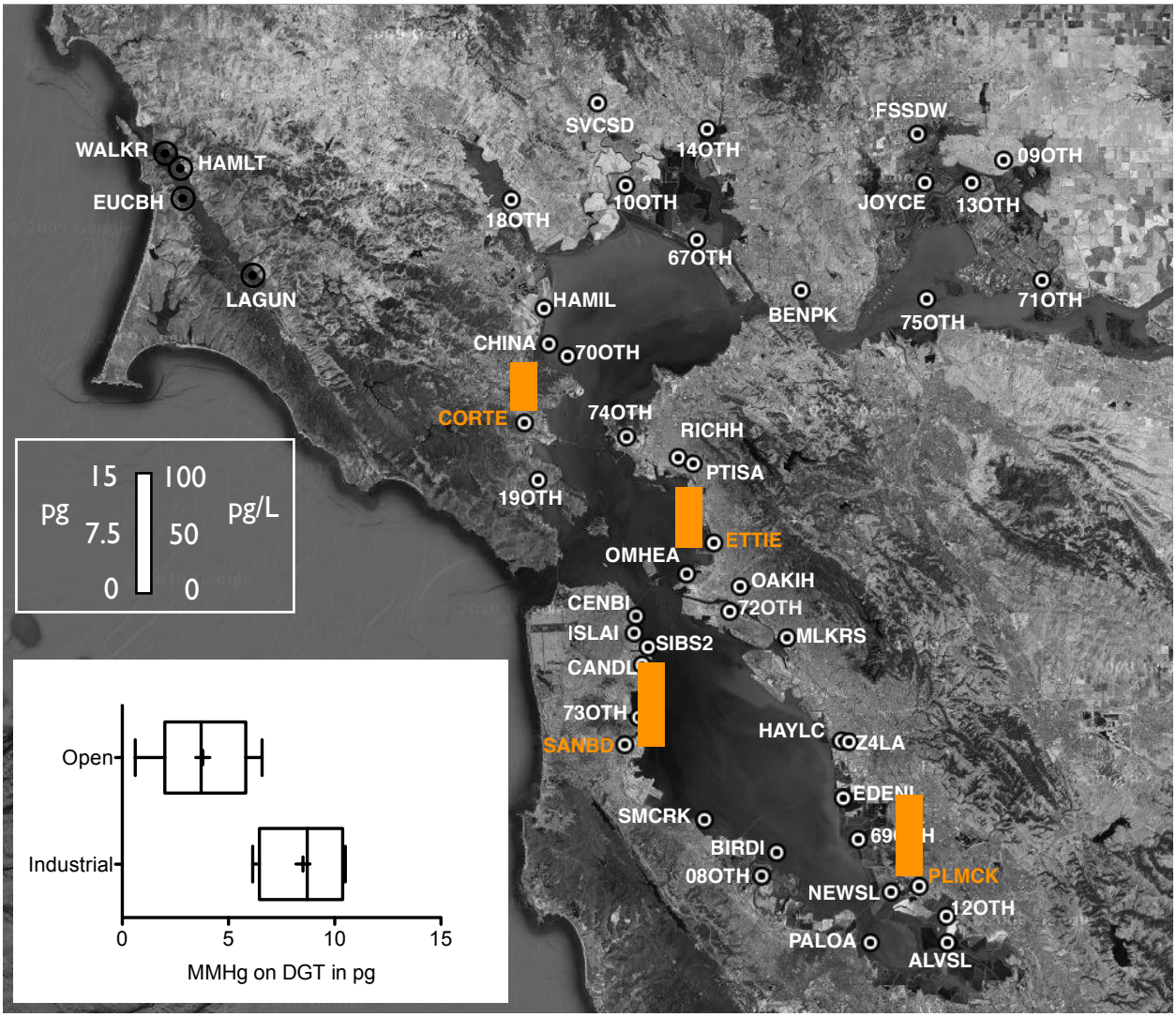

Figure 10: Mass of MMHg accumulated on DGTs in industrial watersheds in theSan Francisco Bay area. Box plots show the 25th and 75th percentile of data, and whiskers illustrate the range of all values in each category. The mean is indicated by the vertical line in each box, while the cross represents the mean.

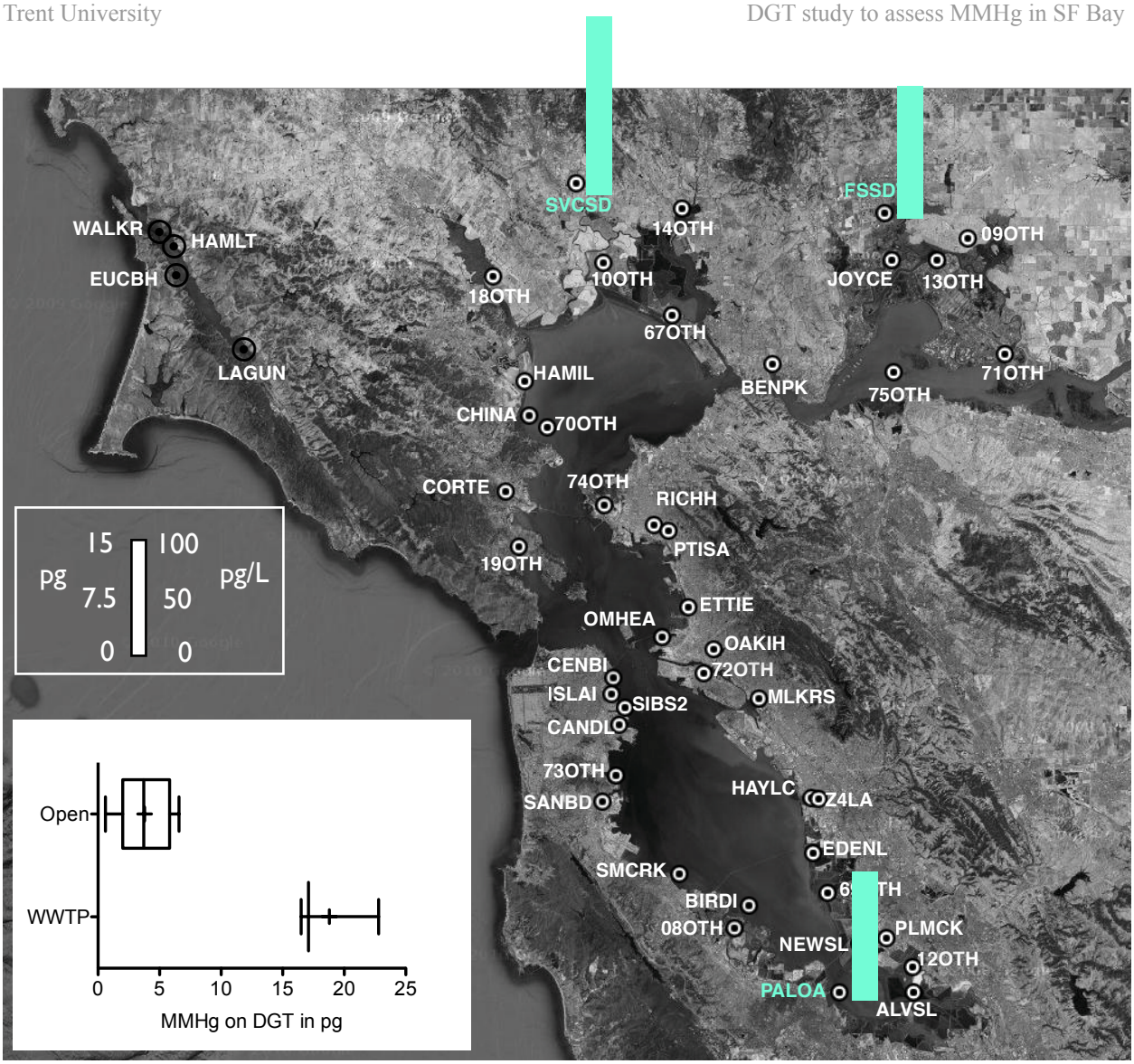

Figure 11: Mass of MMHg accumulated on DGTs downstream of selected waste water treatment plants in the San Francisco Bay area. Box plots show the 25th and 75th percentile of data, and whiskers illustrate the range of all values in each category. The mean is indicated by the vertical line in each box, while the cross represents the mean.

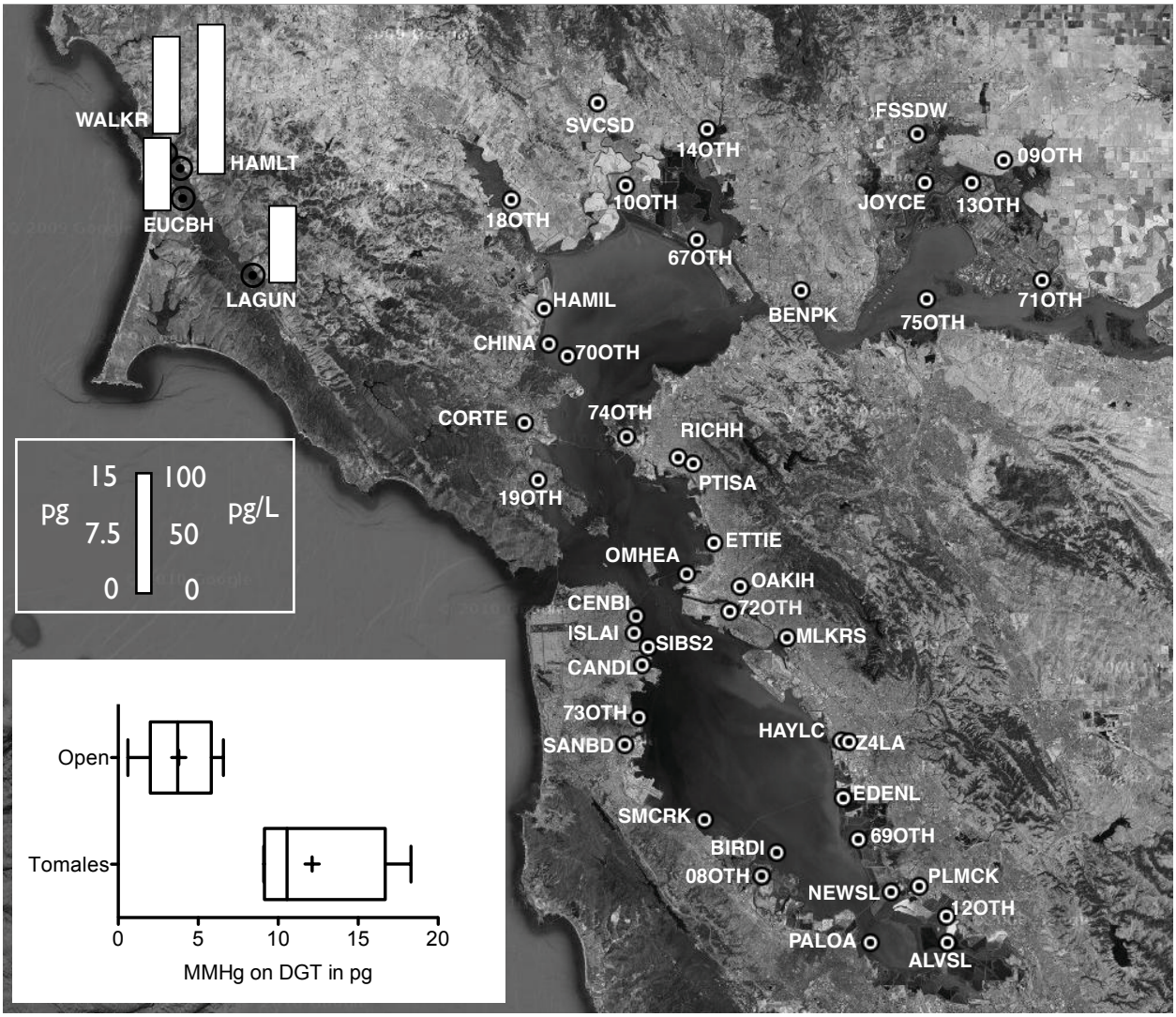

Figure 12: Mass of MMHg accumulated on DGTs in Tomales Bay. Box plots show the 25th and 75th percentile of data, and whiskers illustrate the range of all values in each category. The mean is indicated by the vertical line in each box, while the cross represents the mean.

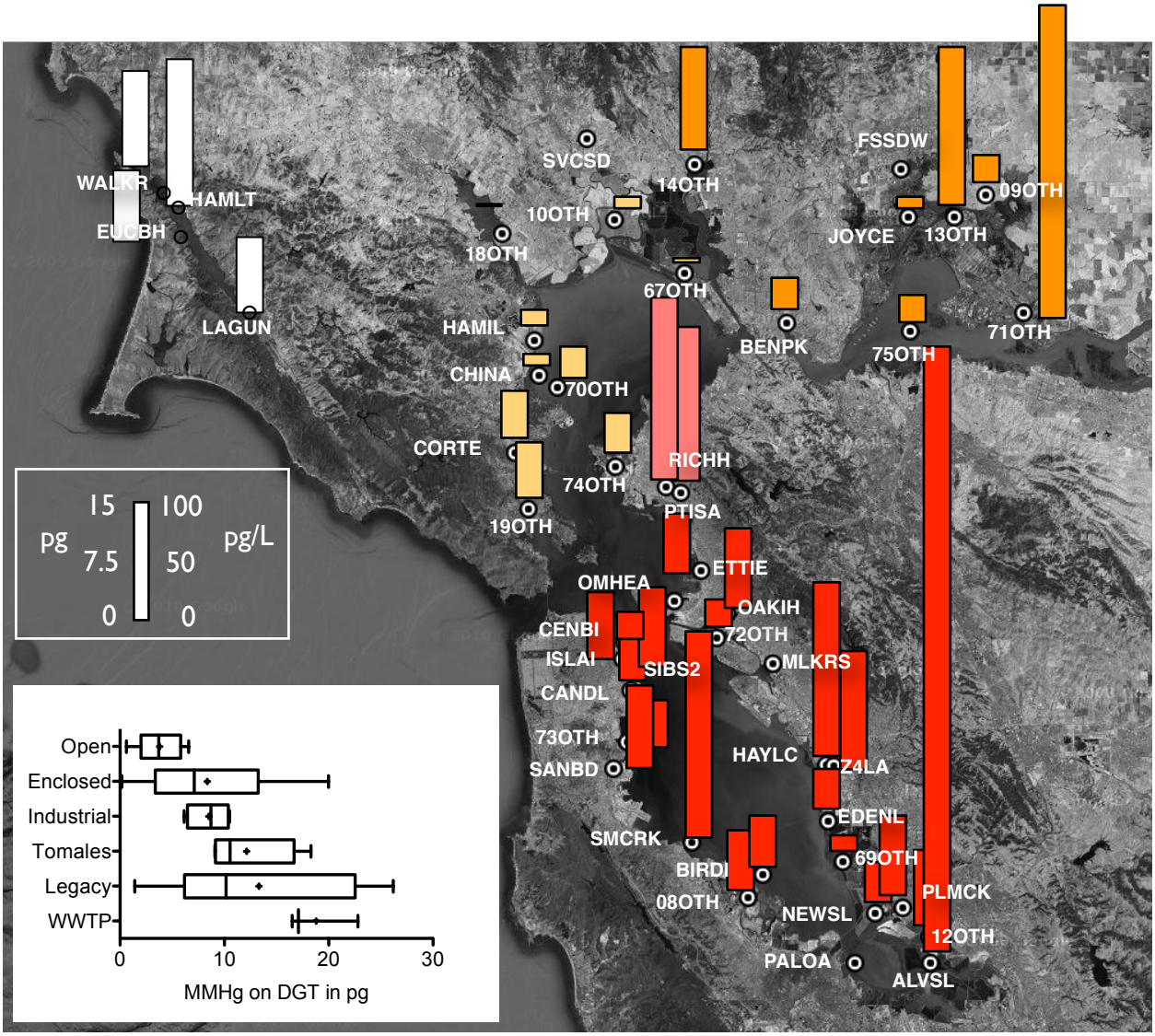

Figure 13: Spatial overview of DGT measurements in the San Francisco Bay area and Tomales Bay. Box plots compare all categories (with outlying values removed) showing the 25th and 75th percentile of data, and whiskers illustrate the range of all values in each category. The mean is indicated by the vertical line in each box, while the cross represents the mean.

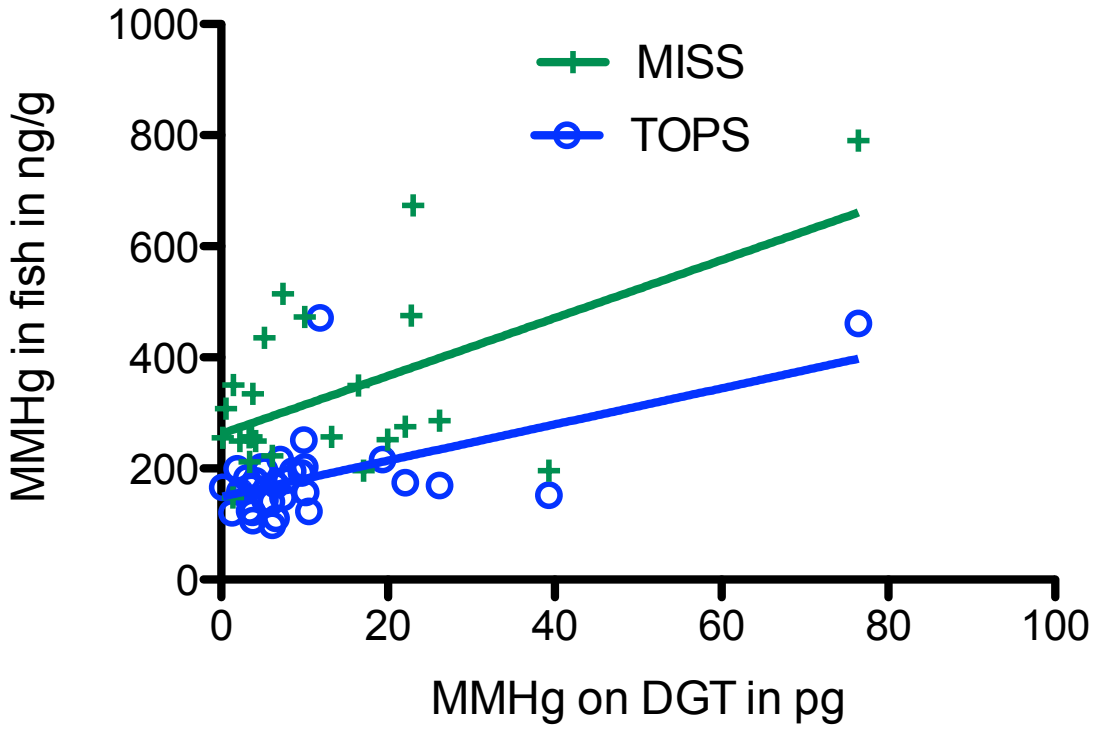

Figure 14: Relationship between MMHg accumulated on DGT after 4 week deployment and Hg concentration of two small fish species, mississippi silverside (MISS) and topsmelt (TOPS). Data are from the 2009 spatial survey.

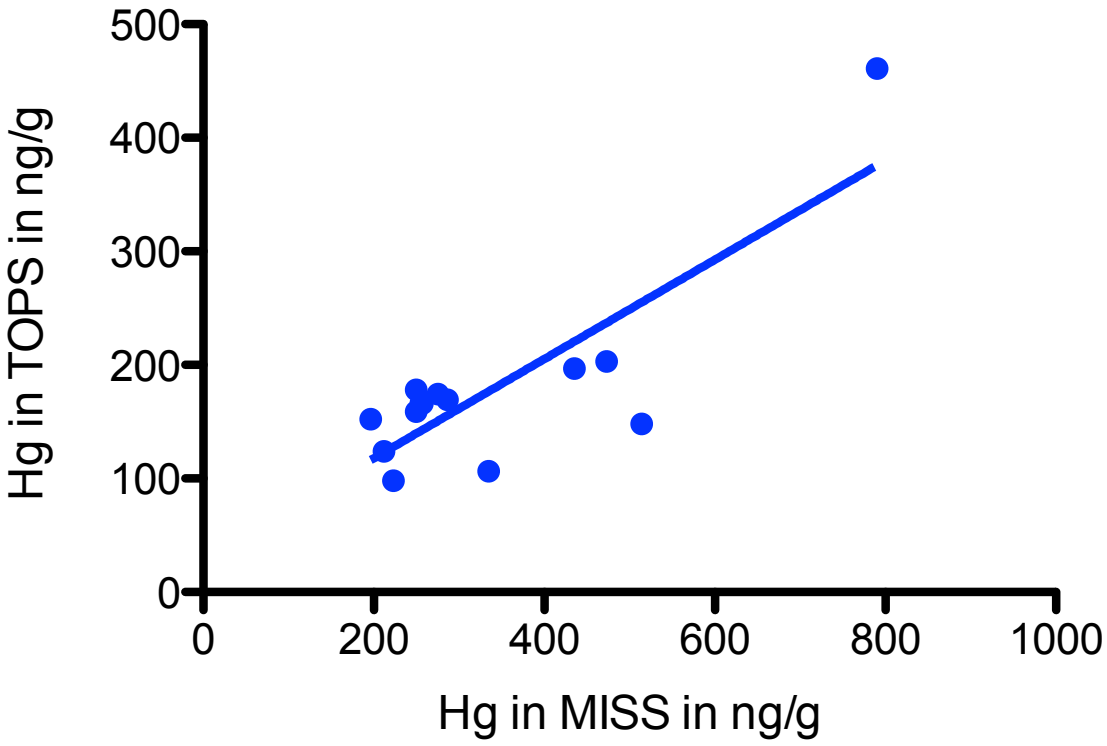

Figure 15: Hg in two small fish species collected at same stations in SF Bay. TOPS = topsmelt, MISS = mississippi silverside. Data are from the 2009 spatial survey.