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Characterization of Sediment Contamination in Central Bay Margin Areas

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Executive Summary

The Bay margins (i.e., mudflats and adjacent shallow areas of the Bay) are important habitats where there is high potential for wildlife to be exposed to contaminants. However, these areas are not routinely sampled due to logistical considerations. In 2015, the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) conducted a survey of margin areas in Central Bay to determine ambient concentrations of contaminants in sediment in these areas. The results generally confirmed the current conceptual model expectation that the margin sediments are often more contaminated than those in the subtidal open bay, with PCBs showing the largest differences. These differences between Central Bay margins and open water areas are likely the largest to be found in San Francisco Bay, as margins in other bay segments generally account for more of the total area and the adjacent land use is less heavily industrial.

The ambient data provide a useful baseline context against which the severity of contamination at specific sites can be compared. The baseline data will also be useful in setting targets and tracking improvements in watershed loads and their nearfield receiving waters, or for appropriate re-use or disposal of dredged sediment. These spatially unbiased data can also improve estimates of mean concentrations and contaminant inventories in margins. For example, based on data from this study, contamination in the margin areas accounts for ~20% of PCBs in Central Bay which is disproportionately high compared to the margin area (5% of Central Bay). Given a large inventory of contaminants in the open bay compared to annual loads, changes may be difficult to see at the bay scale in the short- and mid-term. However, with margins' smaller inventories and greater proximity to likely sources, improvements in margin sediments may be easier to observe.

This ambient sampling effort also identified or verified one expected area of very high PCB concentrations which had not been previously measured. However, the randomized monitoring design used for the Central Bay study was not ideal for identifying "hot spots". Future studies with a goal of detecting hot spots should use deterministic sampling designs.

1. Background

The Bay margins (i.e., mud flats and adjacent shallow areas of the Bay) are important habitats where contaminant exposure is high in some known locations, but that have seldom been sampled by the RMP due to logistical considerations. The RMP Status and Trends efforts have historically focused on deep water locations, starting with a survey primarily in the main channel of the Bay, and limited even after the 2002 redesign to areas accessible by a moderately large boat (~3 foot draft). Aside from the margins' importance as habitats in themselves, it is hypothesized that contamination in margins may contribute to the lack of decreasing trends in biota (e.g., fish tissue) concentrations of PCBs (and other persistent bioaccumulative contaminants), despite evidence of long-term trends of decreasing sediment concentrations in some parts of the open Bay. Locations on the margins generally have a closer linkage with terrestrial sources and therefore a higher potential for showing a positive response to localized management actions aimed at reducing contaminant loads and impairment. Analysis of margins contaminant concentrations in the RMP Margins Conceptual Model Report (Jones et al., 2012) suggested higher and more variable concentrations in margins, but much of the previous sampling was spatially biased to focus on polluted areas in the margins associated with Superfund sites and other known legacy sources, while the characteristics of ambient concentrations of contaminants in the rest of the Bay margins is generally unknown.

1.1. Study objectives

A study of the margins was therefore designed to provide an unbiased, spatially distributed characterization of surface-sediment contamination and ancillary characteristics (grain size, and total organic carbon (TOC)) in shallow Central Bay margin areas, weighted towards urbanized areas (i.e., with fewer sites along the Marin shoreline). According to the RMP Margins Conceptual Model Report (Jones et al., 2012), such ambient data are needed to characterize and model contaminant risk, fate, and trends in the Bay margins. Otherwise, assessments of exposure and risks to margins biota would have to rely on extrapolation from data from deeper, subtidal, open-water areas of the Bay, and/or margin cleanup target areas. Both are likely biased representations of locations in the margins. Further continued deterministic sampling is also still needed to plan and monitor cleanup actions in specific contaminated locations, but is complementary and should be addressed by monitoring schemes specifically designed for those needs.

Although there are broader questions and needs for ambient margins data (addressing ecosystem status and possible trends, paralleling those for the Bay S&T), this initial pilot effort was focused on Central Bay, containing areas adjoining many potential management actions on land. This plan accelerated characterization of ambient Central Bay margins to be able to compare to and complement deterministic sampling at priority margin areas and watersheds that will potentially be managed. It will thus provide a baseline against which to evaluate the effectiveness of management actions, especially with regards to PCBs.

Information needs addressed by these data include:

1. Ambient concentrations of PCBs and other contaminants in sediment in the margin areas. This information facilitates setting achievable targets for restoration and/or load reductions.
2. Mass balance calculations for PCBs and other contaminants in margin areas, which can show the relative importance of watershed loads in maintaining elevated concentrations in the sediments.

This information helps to evaluate whether taking management actions in the watersheds is likely to change the margin concentrations.

3. Effectiveness of on-the-ground watershed management projects at reducing loads or concentrations. Since few major actions have been taken to date, this provides baseline information to show in the future whether the approaches taken are having any impact in the near-field receiving waters.
4. Screening for the existence of additional hotspots in areas that have not been sampled to date. Although areas around many or most expected sources have already been sampled, distributed sampling may provide evidence of major sources not yet accounted for.

It should be noted that the extent of “Central Bay” follows the RMP definition rather than the definition used by the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB). Both definitions share a common northern limit running between Point San Pablo in Richmond and Point San Pedro in San Rafael. For the SFBRWQCB, the southern limit of Central Bay ends at the San Francisco-Oakland Bay Bridge, whereas the RMP definition includes a portion south of the Bay Bridge, extending approximately from San Francisco Airport to Oakland Airport. Many of these margins adjoin some older industrialized areas and thus might be expected to be of interest for legacy pollutants such as PCBs and Hg.

2. Approach

A margin sampling frame was defined in consultation with Josh Collins of the San Francisco Estuary Institute (SFEI) and the SFEI GIS team, minimizing overlap with other monitoring such as CRAM assessed wetland areas (by excluding vegetated areas) and the open water areas already in the RMP Bay S&T (areas below 1 foot below MLLW). In most areas, this is approximately synonymous with mudflat (plus additional shallow subtidal areas).

A GRTS method was used to draw sampling locations (up to 128 per segment) from this frame for the whole Bay in an unbiased, equally-weighted manner through consultation with Don Stevens, who previously helped design the RMP open Bay GRTS sample draw. Although there were sites previously skipped in the Bay S&T sampling (due to water being too shallow for the vessel to access), Don Stevens recommended that these areas (perhaps mischaracterized as deeper open water) not be added to the margins frame, as oversample sites had already been sampled to replace those.

The original draw was allocated based on the total area of margins throughout Central Bay, with fourteen sites around Marin County margins. This was modified by using half (the first seven of fourteen) of the sites from Marin County margins to reduce sample density in that region. Due to the small number of samples left in Marin through this reduction, the seven Marin sites in this initial reduced selection did not include any urbanized areas, so the next seven sites of the original draw in Marin were selected to ensure some representation nearer Marin urban areas. The seven Marin sites which were not sampled were replaced with oversample sites in other parts of Central Bay.

In consultation with a TRC Subcommittee, criteria were identified for rejecting sites and replacing them with oversample locations. If any of the following logistical criteria occurred at the planned site coordinates, they were moved nearby or replaced by oversample sites:

- Access/safety: The site could not be accessed safely; OR

- Substrate: The substrate at the site was too coarse to collect a cohesive sample, was rocky shoreline, was covered with dense aquatic vegetation, or was shell hash; OR
- Upland area: The planned site was in a salt marsh or upland area.

Unsamplable sites were pre-identified through a desktop exercise from aerial imagery, and replaced by the next site in the overdraw list. Figure 1 shows the outcome of that initial desktop exercise, with sample sites skipped in Marin shown as white circles, unsamplable sites in other regions marked with white squares, and the first 40 remaining sample and oversample sites marked as orange squares.

If the field team encountered unsamplable conditions, there was a contingency plan to sample a location with suitable conditions within a 50-meter radius of the target site. To avoid biasing (e.g., always going to the deepest allowed depth) an attempt was made to sample at the expected original depth for the site. Using this contingency plan, all of the planned sites were successfully sampled. Therefore, none of the sites were replaced by oversample sites beyond those changed initially in the desktop exercise.

2.1. Sample Size

The total sample size was 40 sites, with seven of those sites in the margins areas of Marin County. The reduction of sample density in Marin was an effort to pre-stratify within Central Bay to allocate even more sites to areas adjoining urbanized industrial areas. However, given the small number of samples remaining in the (presumed less variable) less urbanized area of Marin, the representativeness of the remaining sites may show some artifacts of the small sample count, noted later in this report.

2.2. Sampling Frequency

This study plan represented a one-year effort in Central Bay to get a characterization of ambient conditions in margins of this highly urbanized segment. Decisions about repeating this study or monitoring margins in other segments will be made through the RMP multi-year planning process.

2.3. Target Analytes

Sediment samples were analyzed for grain size and ancillary parameters, mercury, methylmercury, trace metals, and PCBs (209 congeners). Extra archive samples were collected so that additional parameters could be analyzed in the future. Samples were analyzed by the methods employed for the RMP Status and Trends Program, with the same measurement quality objectives and procedures for data handling and flagging. The raw data are available for download through the CD3 tool on the SFEI website, and are also accessible through CEDEN.



Figure 1. Margin sites in Central Bay (orange symbols). Yellow areas are margins frame sampled. White squares are sites in the original draw that were dropped due to unsuitable habitat.

3. Results

3.1. Ambient Concentrations of Contaminants in Margin Areas of Central Bay

Samples were analyzed for fifteen parameters (or 222, if the 209 PCBs are counted as individual congeners, rather than just as two types of PCB sums) of interest (see Table 3.1.1), as well as total organic carbon (TOC) and grain size, ancillary parameters often used as normalizing factors. All samples had detects for all parameters, with the exception of 2 stations (CB36 and CB46) for cadmium, and one station (CB46) for methyl mercury.

One of the major objectives of the study was to establish ambient concentrations of PCBs and other contaminants in sediment in the margin areas. This information will facilitate setting achievable targets for restoration and/or load reductions. The PCB analytical method on these samples may bias results slightly (~15%) higher than the previous method used for RMP S&T sediments, but is not the primary cause of differences seen versus open bay sediments. More details are in the Appendix (QA summary of reported data).

Table 3.1.1 contains statistics for the distributions of contaminant concentrations in Central Bay margin areas. The distributions are a combination of equally weighted sites in Marin and non-Marin areas, using different weighting factors for each of these areas due to the disproportionately lower allocation of samples to Marin margins. The statistics reported in Table 3.1.1 are reported on an area weighted basis (i.e., each Marin sample represents a greater area, contributing more to the mean or cumulative percentile than a sample from the non-Marin portion of Central Bay).

The distributions are skewed for many of the anthropogenic pollutants (e.g., cadmium, lead, mercury, PCBs), with mean concentrations higher than their medians, suggesting large contributions from a few relatively high concentration results. The contaminants with the largest skewedness are PCBs and methylmercury.

Table 3.1.1 – Range, weighted percentile and weighted means for the distributions of contaminant concentrations in Central Bay margins (rounded from lab results to 3 significant digits)

Parameter	Minimum	1st Quartile	Median	3rd Quartile	Maximum	Mean
Aluminum (mg/kg dw)	2,770	14,200	22,000	25,500	29,700	19,800
Arsenic (mg/kg dw)	2.25	5.99	8.31	9.61	13.5	7.81
Cadmium (mg/kg dw)	0.0207	0.116	0.155	0.24	0.812	0.211
Copper (mg/kg dw)	3.45	24.8	35.9	42	224	37.6
Iron (mg/kg dw)	5,780	20,200	29,600	34,700	40,800	27,600
Lead (mg/kg dw)	3.34	14.9	21	32.2	135	26.7
Manganese (mg/kg dw)	65.7	235	288	381	674	325
Mercury (mg/kg dw)	0.0304	0.172	0.232	0.309	2.65	0.317
Methyl Mercury (µg/kg dw)	0.014	0.139	0.256	0.468	10.3	0.803
Nickel (mg/kg dw)	7.54	40.9	65.4	71.5	99.8	59.6
Selenium (mg/kg dw)	0.043	0.183	0.27	0.345	0.462	0.259
Silver (mg/kg dw)	0.0364	0.145	0.186	0.268	0.469	0.216
Sum of 208 PCBs (µg/kg dw)	0.765	8.9	16.1	41.1	1,590	70
Sum of 40 PCBs (µg/kg dw)	0.616	7.17	12.6	32.2	1,290	56.5
Zinc (mg/kg dw)	19.2	78.1	99.5	117	228	97.5

3.2. Spatial Variability of Contaminants in Margin Areas of Central Bay

The raw concentrations of mercury and PCBs are plotted on a map of Central Bay in Figures 3.2.1 and 3.2.2.

Mercury concentrations were highest in the area around the Oakland inner harbor (Figure 3.2.1), with values below 1.0 µg/kg at all other locations.

Sums of the RMP 40 PCB congeners ranged from 0.616 to 1290 µg/kg dry weight, with the highest concentration found north of Oyster Point, and other high concentration locations in Oakland inner harbor and San Leandro Bay (Figure 3.2.2).

See the appendix for maps of other parameters.

Figure 3.2.1 Mercury Concentrations – Bubble areas are proportional to concentration (mg/kg dw)

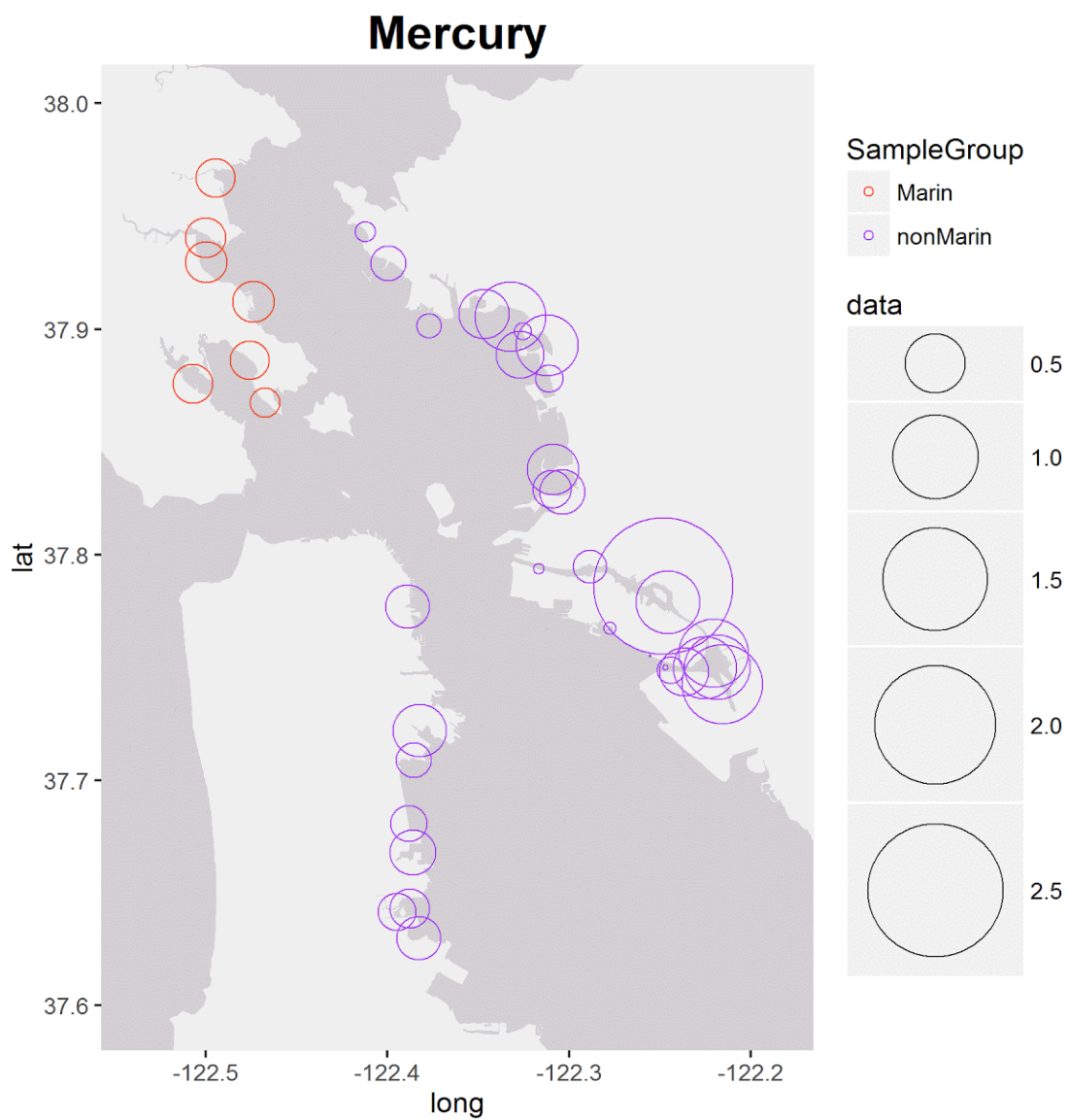
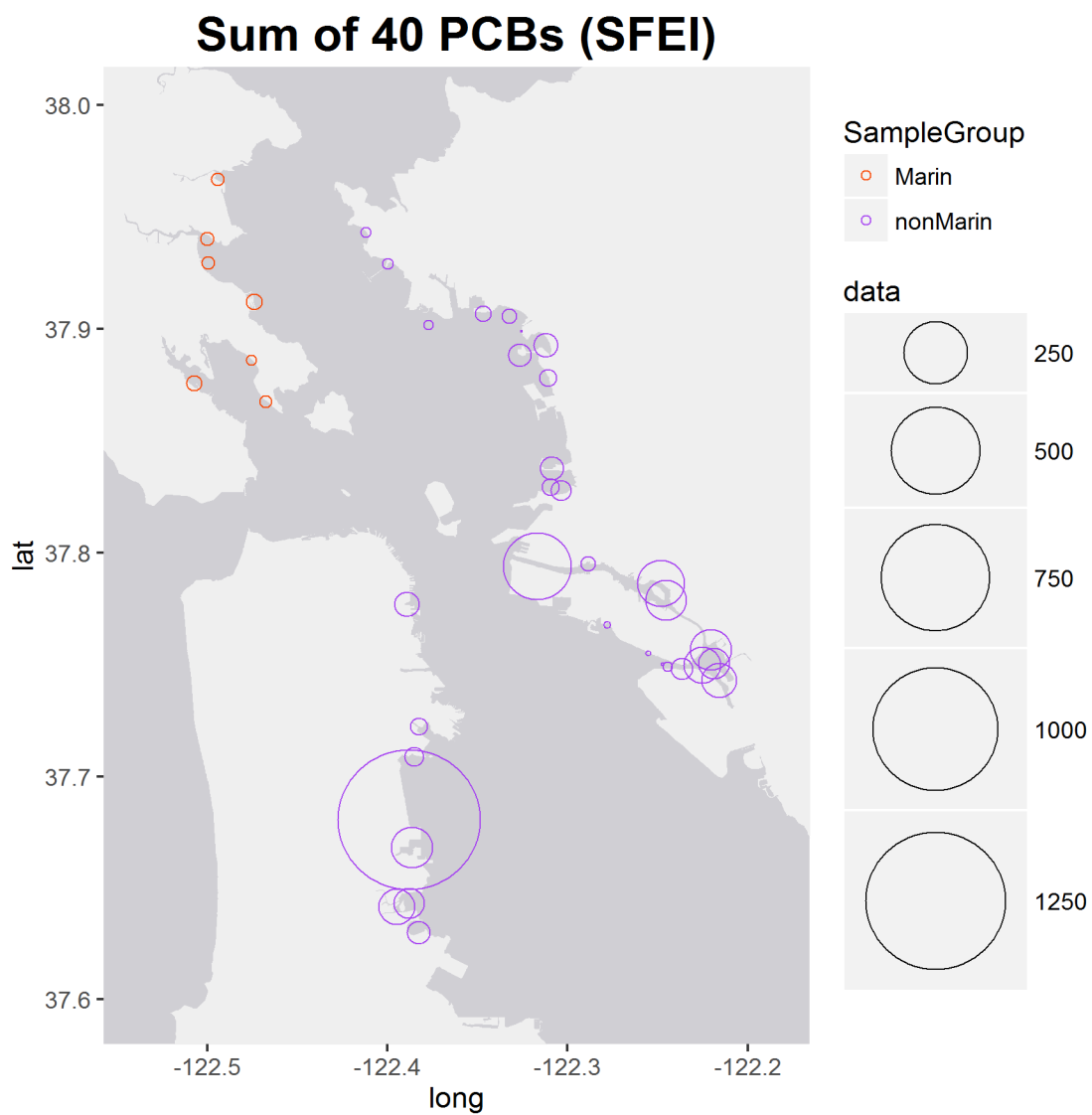


Figure 3.2.2 Sum of 40 PCBs Concentrations – Bubble areas are proportional to concentration ($\mu\text{g}/\text{kg dw}$)



3.3. Evaluating Ancillary Parameters to Reduce Variability

Concentrations were fitted to a linear model with either proportion of fines in the sample (%fines) or total organic carbon (%TOC). While the correlation was significant in most cases, each ancillary parameter generally accounted for considerably less than 50% of the observed variance (see Table 3.3.1 below). This finding is consistent with the idea that, although there are tendencies of many anthropogenic pollutants to partition to fine particles or TOC, there are other factors that influence the contaminant concentrations locally. For example, there is more limited transport and exchange in the margins, and these areas are thus more heavily influenced by localized sources than is found for sediments in open water subtidal areas of the bay.

Table 3.3.1 Regressions with ancillary parameters - R-squared and p-value from the F-statistic from linear models of unmodified concentrations ~ fines or total organic carbon (as a proportion)

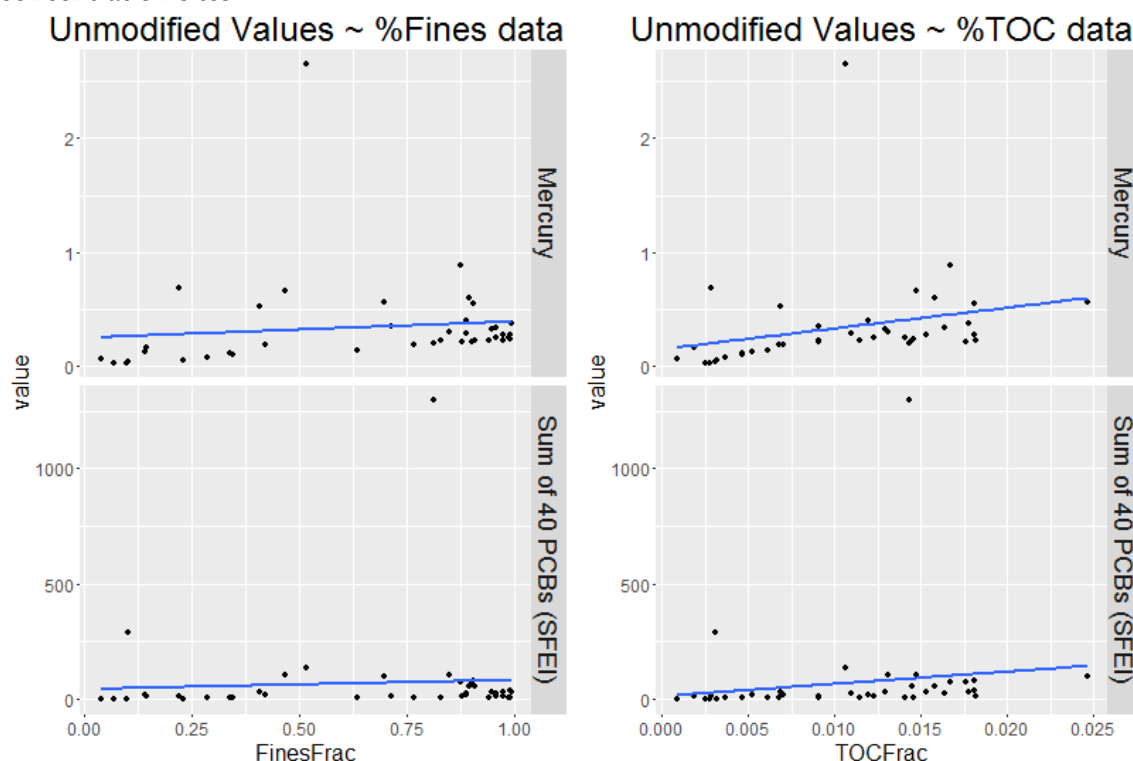
Parameter	R ² %Fines	p-value %Fines	R ² %TOC	p-value %TOC
Aluminum	0.927	3.16E-23	0.664	1.56E-10
Arsenic	0.65	3.43E-10	0.317	0.000156
Cadmium	0.0666	0.108	0.334	9.35E-05
Copper	0.101	0.0462	0.195	0.00439
Iron	0.862	6.10E-18	0.611	2.68E-09
Lead	0.098	0.0492	0.246	0.00115
Manganese	0.499	3.47E-07	0.227	0.00187
Mercury	0.0254	0.332	0.151	0.0145
Methyl Mercury	0.0126	0.49	0.0645	0.114
Nickel	0.648	3.83E-10	0.561	2.75E-08
Selenium	0.752	4.72E-13	0.914	8.07E-22
Silver	0.263	0.000838	0.515	2.72E-07
Sum of 208 PCBs (SFEI)	0.00432	0.687	0.0239	0.341
Sum of 40 PCBs (SFEI)	0.00406	0.696	0.0233	0.347
Zinc	0.423	5.53E-06	0.692	2.88E-11

Figure 3.3.1 shows plots of the mercury and PCB data versus %fines and %TOC. The slopes of the relationships are nearly flat (small compared to the total range of values), indicating that these ancillary variables do not explain much of the variability in the concentrations observed. Notably, the highest concentration points are not correlated with the highest percent fines or TOC for these two priority pollutants.

Although the fits of these regressions would be improved by removing these seeming “outliers” (i.e., with PCBs or Hg much higher than would be expected for their TOC or %fines), such fits would represent a different population than margins as a whole. This sub-population of “outliers” indicates factors separate from widespread non-point urban sources and general partitioning behavior can dominate pollutant distributions in specific locations.

TOC and % fines were moderately co-correlated (R^2 of 0.68).

Figure 3.3.1 – Linear models of mercury and PCB concentrations to %fines and to %TOC (shown as decimal fractions). Although the main body of the margin population suggests correlations to both %fines and %TOC, these factors poorly predict the highest concentration sites



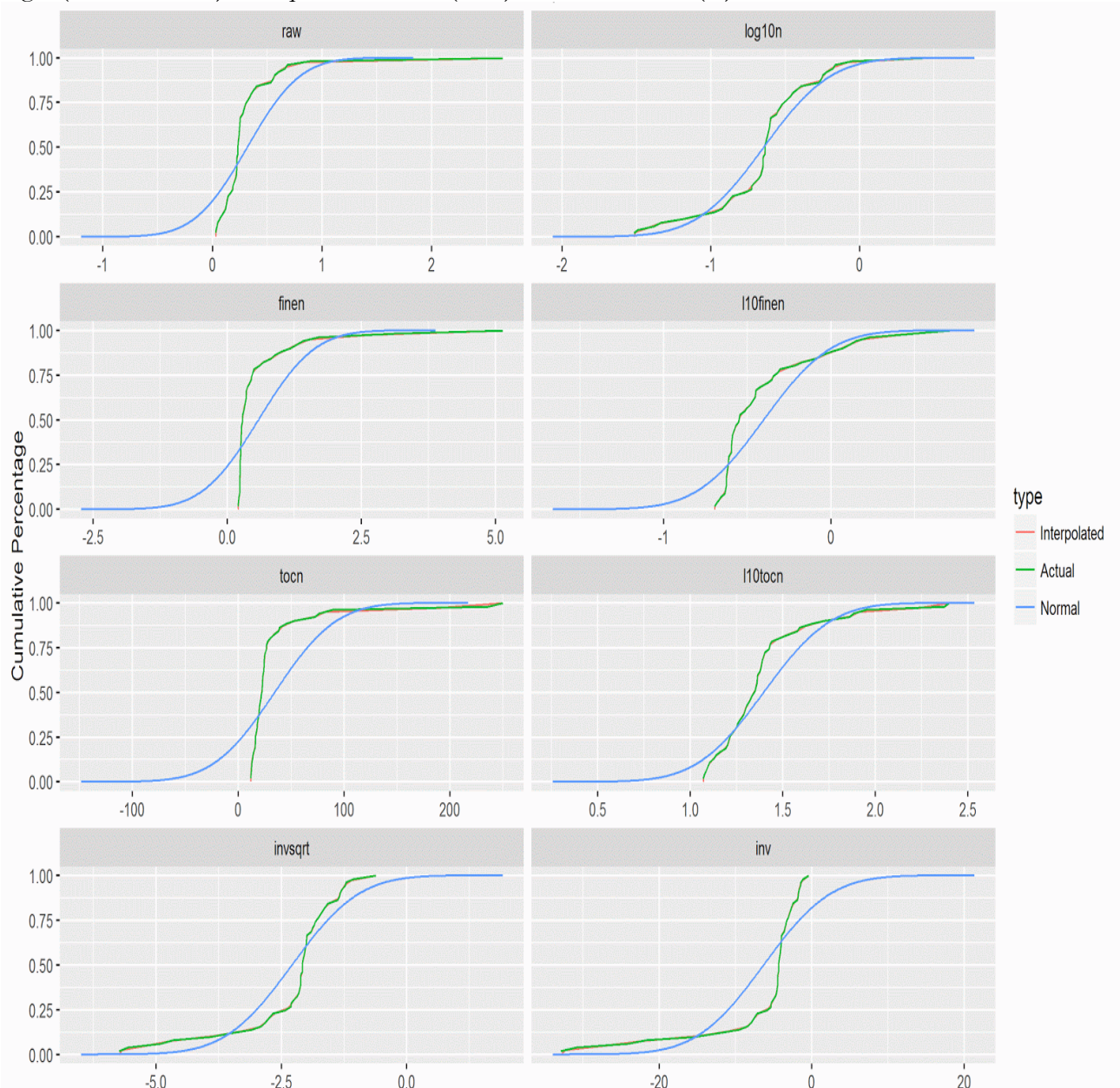
3.4. Evaluation of Contaminant Distributions for Normality

A variety of transformations of the contaminant distributions to meet conditions of Normality were attempted without success. Figure 3.4.1 below shows ECDFs (empirical cumulative distribution functions) of the attempted transformations on the mercury data.

Each transformed value was weighted, then compiled into an interpolated ECDF. Each interpolated ECDF was then compared to a normal distribution (sharing the same transformed mean and variance) using an Anderson- Darling test.

There was no single transformation that produced consistently normally distributed results across parameters (see appendix for table of results of all tests). As a result, attempts to normalize the data were abandoned, and non-parametric tests were adopted for statistical evaluations. However, most figures use Log_{10} values for visual clarity.

Figure 3.4.1 Weighted empirical cumulative distribution functions of mercury concentrations after different transformations (green line) compared to a normal distribution (blue line) – the labeled transformations are as follows: raw = none; log10n = $\log_{10}(\text{value})$; finen = $\text{value}/\% \text{ fines}$; l10finen = $\log_{10}(\text{value}/\% \text{ fines})$; tocn = $\text{value}/\% \text{ TOC}$; l10tocn = $\log_{10}(\text{value}/\% \text{ TOC})$; invsqrt = $-1 * \text{value}^{(-1/2)}$; inv = $-1 * \text{value}^{(-1)}$.



4. Data Analysis

4.1. Comparison of Ambient Concentrations of Contaminants in the Margins and the Open Bay

In Section 3.1, the data from this study were used to characterize the distribution of ambient concentrations of PCBs and other contaminants in sediment in the margin areas. The next question is whether these ambient concentrations are higher than in the open Bay as hypothesized in recent conceptual models (Jones et al., 2012).

The non-normal distribution of the results and the different weighting for sub-areas within the Central Bay margins precluded the use of simple parametric comparisons to test this hypothesis. Therefore, a two-sample Kolmogorov-Smirnov (KS) test was chosen to test whether the distributions of contaminant concentrations in the margins and the open Bay could be from the same population. This test was chosen because it is non-parametric and allows the incorporation of weights depending on the location of each station. Weights for the Marin and non-Marin sub-regions were incorporated by creating a weighted ECDF and then interpolating evenly distributed points on that ECDF equal in number to the original number of sites (i.e., 40). Data for the open Bay consisted of RMP Status and Trends sediment monitoring data in the Central Bay segment from 2002-2014 (excluding 2004 to 2006 data with low biased extraction artifacts, N=56). Results with a p-value <0.05 were considered significantly different distributions. The magnitude of the difference was also evaluated by comparing the 50th and 75th percentile values of the two populations.

Table 4.1.1 outlines the outcomes of the KS test. The highlighted parameters had p-values less than 0.05, indicating low probabilities of open Bay and margin contaminant distributions originating from the same population. The distributions of (sum of 40) PCBs were significantly different. The distribution of PCBs in the margins generally had higher median concentrations than the open Bay (50th percentile concentrations of 12.6 vs 10.8 ug/kg-dw). However, the larger difference between the two populations was at the highest concentrations. The 75th percentile concentration for the margins areas was 32.2 ug/kg-dw compared with 15.8 in the open Bay distribution. In contrast, the distributions of total mercury in the margins and the open Bay were not significantly different. However, there was a difference in the methylmercury concentrations, with open Bay sediments having higher concentrations.

Figures below provides examples of a parameter where the distributions cannot be distinguished (4.1.1.1 for mercury) and of a parameter where they can (4.1.1.2 for Sum of 40 PCBs). The ECDFs are shown for log transformed values, but the log transformation does not affect the outcome of the KS test, and is used just to allow visualization of the separation of the ECDFs throughout their range, and visibility of their 95% confidence interval bounds (of the “actual” underlying CDF from which the ECDF is sampled) (see R code function “cdf.tol.est.fcn” from Stevens, 2011).

The results of the KS test interestingly suggest marginal (non-significant at alpha of 0.05, but a few parameters pass a weaker threshold of 0.10) differences between the Bay and margins for a few of the anthropogenic pollutants (cadmium, selenium, Sum of 208 PCBs). Although higher sample counts might eventually reveal significant differences, the need to prove

significance of a difference is not required. The relatively modest or weak differences seen for these contaminants may suggest lower degrees of concern, as their margins concentrations are not easily distinguished from those in the open bay. Other parameters show significantly different concentrations between the Bay and margins, but lower concentrations in the margins, indicating that a conceptual model of terrestrial sources and/or preferential retention in the margins is inappropriate for these chemicals.

On suggestion of a reviewer of the draft report (Tony Olsen, USEPA), an alternative method to compare distributions was tested. The Wald statistic (Kincaid 2000) was applied to compare open bay and margins data using the same area weights as we applied for the KS tests. The `cont.cdf.test` function in the `spsurvey` package (Kincaid and Olsen, 2016, from the CRAN R repository) was used to apply this test. The results were similar, but the Wald statistic also indicated significant differences (at $p < 0.05$) for Sum 208 PCBs, selenium, and cadmium, whereas they had only been significant at $0.05 < p < 0.1$ for the KS tests.

Table 4.1.1 Comparison of Margins to Open Bay Concentration Quantiles – Percentiles for Central Bay data are weighted (between Marin and non-Marin) for margins and unweighted for open Bay (since RMP S&T sites are allocated uniformly within each segment). Comparisons were made between the ECDFs for the Margins and Bay strata using the Kolmogorov-Smirnov test. Analytes with significant ($p < 0.05$) differences are shaded, percentiles where the margin values are higher in red bold text. Numbers in parentheses are the 95% confidence interval range for each quantile.

Parameter	p-Value of KS Test	50 th %ile Margins	50 th %ile Open Bay	75 th %ile Margins	75 th %ile Open Bay	90 th %ile Margins	90 th %ile Open Bay
Aluminum (mg/kg dw)	0.00233	22000 (19500-23000)	30100 (23700-30700)	25500 (23200-27500)	31600 (30600-43000)	27800 (26300-29700)	40700 (32600-52700)
Arsenic (mg/kg dw)	0.356	8.31 (7.53-8.76)	8.39 (7.76-9.19)	9.61 (9.24-9.78)	10.4 (9.47-11.5)	10.3 (9.64-13.5)	12.7 (11.3-15.6)
Cadmium (mg/kg dw)	0.0608	0.155 (0.127-0.183)	0.195 (0.17-0.21)	0.24 (0.182-0.345)	0.24 (0.214-0.287)	0.454 (0.34-0.574)	0.312 (0.263-0.444)
Copper (mg/kg dw)	0.63	35.9 (29.5-37.5)	33.6 (29.6-37.6)	42 (37.5-49.3)	41.9 (39-44.6)	55.5 (45.7-184)	45.4 (43.9-47.1)
Iron (mg/kg dw)	0.0105	29700 (29100-32000)	35200 (32700-37700)	34700 (33300-35300)	39200 (38400-40800)	38000 (35200-40800)	41500 (40100-45200)
Lead (mg/kg dw)	0.00479	21.6 (20.2-23.6)	18.3 (17.1-20)	33.3 (28.2-37)	21.5 (20.4-23.1)	41.2 (37.7-58.8)	24.8 (23-30.1)
Manganese (mg/kg dw)	0.000371	293 (275-352)	401 (375-423)	381 (356-451)	491 (436-577)	511 (449-667)	688 (575-828)
Mercury (mg/kg dw)	0.632	0.232 (0.224-0.251)	0.241 (0.224-0.256)	0.321 (0.273-0.397)	0.279 (0.262-0.295)	0.565 (0.401-0.683)	0.342 (0.292-0.42)
Methyl Mercury (µg/kg dw)	0.0273	0.256 (0.17-0.357)	0.418 (0.333-0.498)	0.472 (0.329-1.06)	0.604 (0.535-0.73)	2.08 (1.04-3.83)	1 (0.732-1.74)
Nickel (mg/kg dw)	0.0446	65.4 (61.1-68.2)	72.6 (69-73.7)	71.5 (67.1-79.4)	81.9 (76.8-83)	79.4 (75.6-99.5)	83.9 (82.9-92.1)
Selenium (mg/kg dw)	0.0882	0.281 (0.223-0.317)	0.219 (0.193-0.228)	0.345 (0.292-0.379)	0.28 (0.247-0.301)	0.382 (0.352-0.462)	0.331 (0.289-0.45)
Silver (mg/kg dw)	0.33	0.186 (0.172-0.226)	0.172 (0.154-0.19)	0.269 (0.244-0.331)	0.217 (0.199-0.249)	0.378 (0.329-0.43)	0.274 (0.242-0.377)
Sum of 208 PCBs (µg/kg dw)	0.0586	16.6 (11.6-20.8)	12.3 (11.9-17.6)	41.1 (31.6-77.2)	19.6 (16.3-21.6)	122 (76.2-277)	21.5 (19.7-28.2)
Sum of 40 PCBs (µg/kg dw)	0.0465	12.6 (9.14-16.2)	10.8 (9.45-13.5)	32.2 (26.8-63.1)	15.8 (13.8-17)	98.3 (61.5-228)	17.9 (15.9-37.9)
Zinc (mg/kg dw)	0.347	100 (93.2-105)	93.1 (88.2-102)	117 (104-137)	107 (103-117)	139 (132-146)	119 (116-130)

Figure 4.1.1.1 – ECDF of all sites comparing Mercury in Bay and Margins – Solid lines (Bay in black, Margin in gray) represent the ECDF estimated value (Log_{10} of Hg in mg/kg dw), with the dotted lines (also Bay in black, Margin in gray) indicating their 95% confidence interval lower and upper bounds.

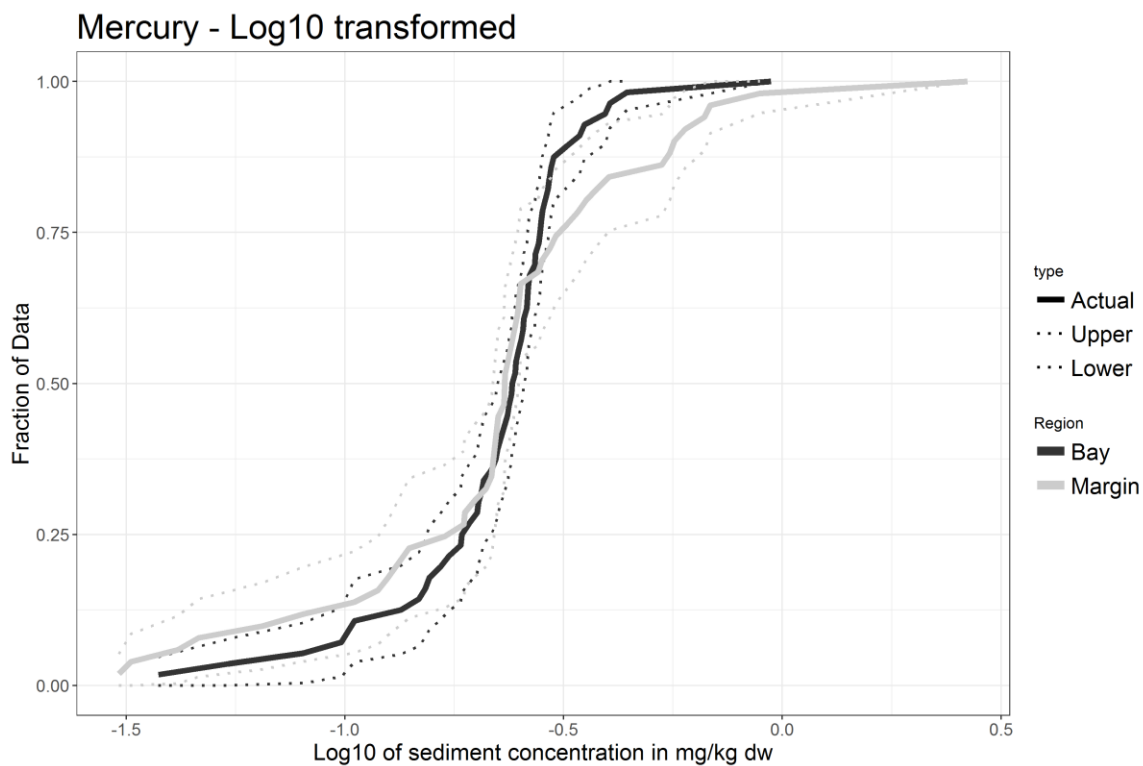
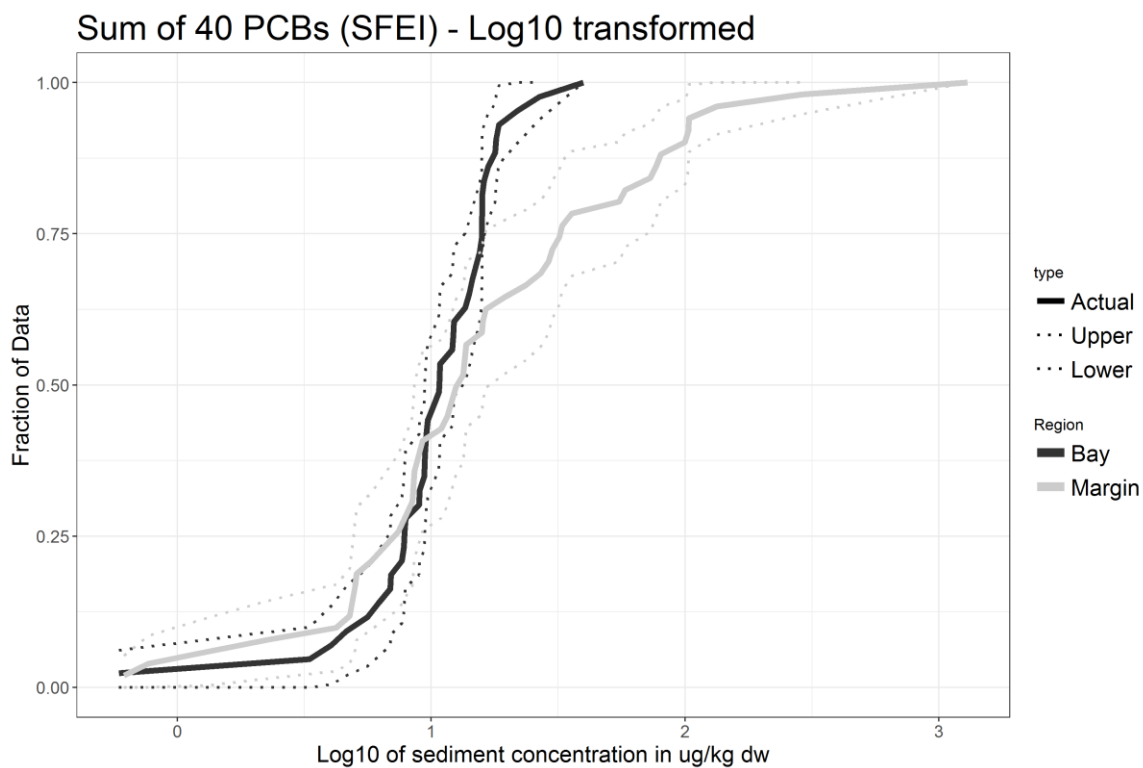


Figure 4.1.1.2 - ECDF of all sites comparing PCBs in Bay and Margins – Solid lines (Bay in black, Margin in gray) represent the ECDF estimated value (Log_{10} of Sum of 40 PCBs in $\mu\text{g}/\text{kg dw}$), with the dotted lines (also Bay in black, Margin in gray) indicating their 95% confidence interval lower and upper bounds.



As a verification of the results from the KS tests on the ECDFs, we also evaluated non-Marine areas in isolation using a different non-parametric test. A Kruskal-Wallis (KW) test by ranks was chosen to compare the contaminant concentrations in margins and open Bay areas, with stations limited to only those outside of Marin County. For the open Bay areas, non-Marine areas were defined as the portion south of a line from the midpoint of the Golden Gate Bridge (-122.47820, 37.81805) to the Northeast corner of Treasure Island (-122.37760, 37.83040), and to the east of lines from Treasure Island, to the middle of the Richmond-San Rafael Bridge (-122.44840, 37.93540), then to the midpoint of the northern bound of the Central Bay segment (-122.43905, 37.97425). The number of open bay results in the non-Marine sub-area was reduced to 48, and the number for margins to 33. The KW test was not used for the previous analysis because it could not accommodate the differential weighting that was introduced when fewer samples were allocated to the Marin portion of Central Bay.

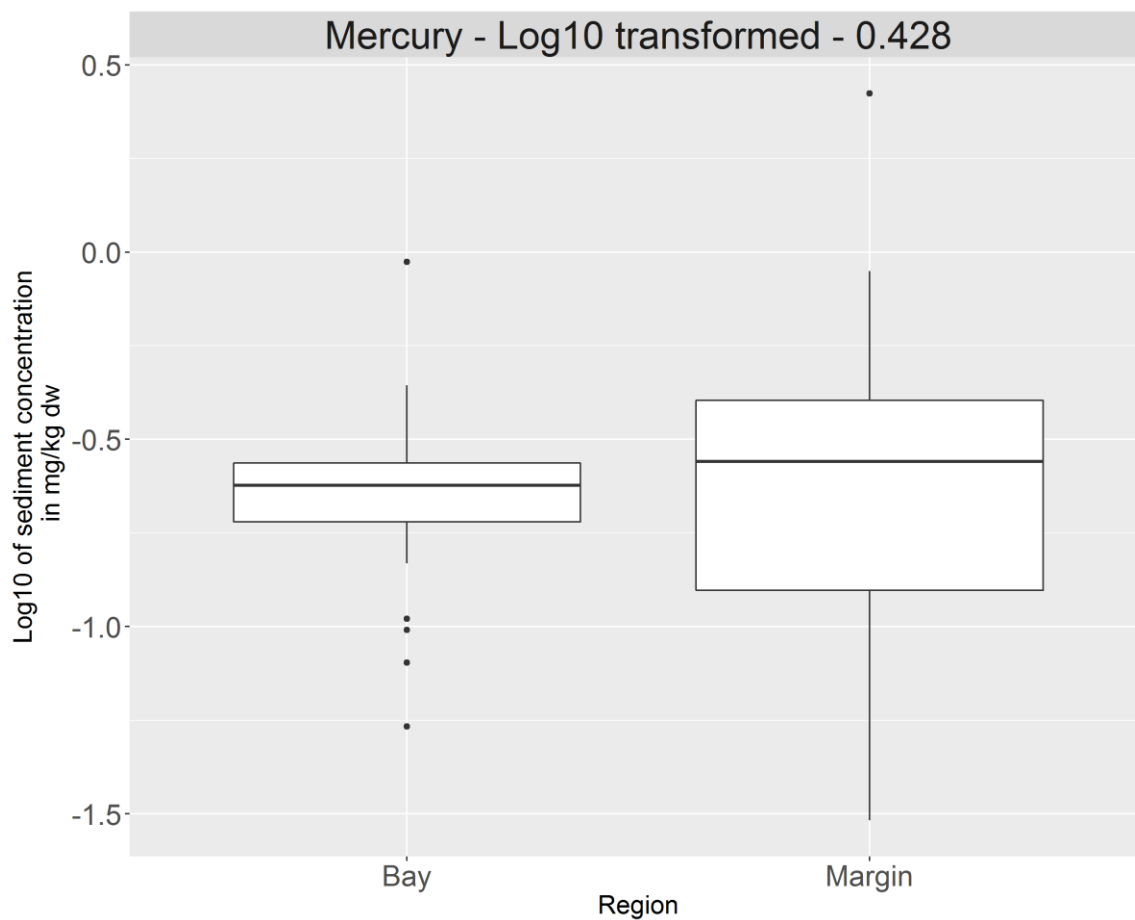
Table 4.1.2 provides a summary of the results of the KW test, with p-values less than 0.05 highlighted. Significance of differences using different statistical tests gives us greater confidence in the robustness of the conclusions, as they test somewhat different characteristics of the empirical distributions. Nine parameters showed significant differences between the margins and the open Bay areas (versus 7 for the previous KS test). However, at a threshold of $p < 0.061$, nine of the Central Bay KS tests would also have been significant. Methylmercury, which was significantly different with the KS test, was not significantly different between habitats with the KW test. Many of the same parameters remained not significantly different between the bay and margins, although a few increased slightly in significance for this comparison of only non-Marine data. Differences were mainly caused by splitting out the sub-regions of Central Bay, rather than the method selected for statistical comparison, as KS tests on the non-Marine data only yielded results more similar to those of the KW test than to the whole Central Bay KS tests.

Figure 4.1.2.1 shows the distribution of mercury concentrations, which remained not significantly different between the bay and margins. Figure 4.1.2.2 for the Sum of 40 PCBs shows an example with a significant difference. Findings of significance in both the KS and KW tests for a given parameter increase our confidence that the results represent a real difference between margin and open bay sediments rather than artifacts of method selection or data set reduction. Interestingly the only analytes consistently significantly different in both the KS and KW tests, and higher in their margins for their means and/or 75th percentiles, were lead and (sum of 40) PCBs. All others were either inconsistently significant between the statistical methods, or higher in the open bay concentrations than in margins.

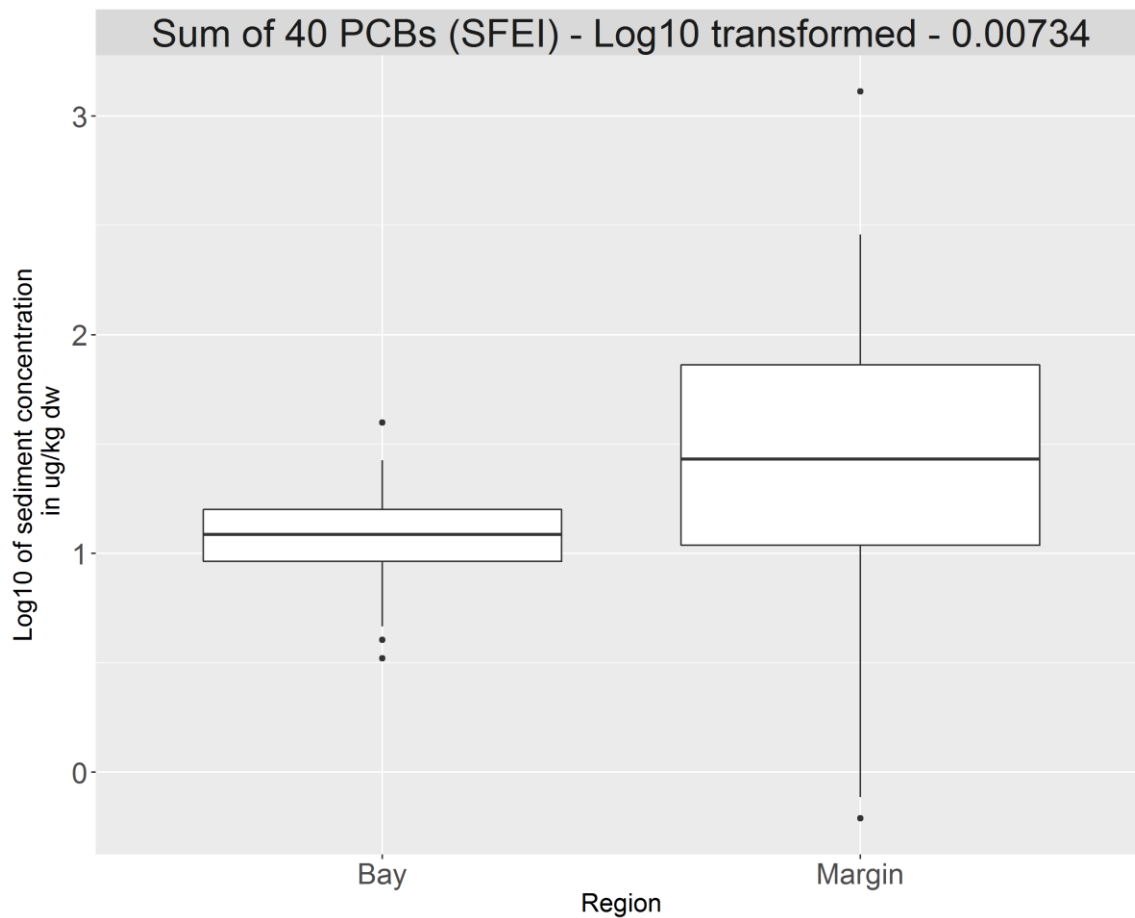
Table 4.1.2 Comparison of Margins to Open Bay Concentration Quantiles, Non-Marin – Percentiles within the Non-Marin sub-region of Central Bay are unweighted for both margins and open Bay data, allowing comparisons using the Kruskal-Wallis test (of ranks). Analytes with differences are shaded, percentiles where the margin values are higher in bold. Numbers in parentheses are the 95% confidence interval range for each quantile.

Parameter	p-Value of KW Test	50 th %ile Margins	50 th %ile Open Bay	75 th %ile Margins	75 th %ile Open Bay	90 th %ile Margins	90 th %ile Open Bay
Aluminum (mg/kg dw)	8.79E-05	18600 (12400-21900)	29700 (23900-30600)	23100 (21800-24500)	31000 (30500-40200)	27000 (23900-28900)	39700 (31200-52700)
Arsenic (mg/kg dw)	0.0106	6.64 (5.99-7.41)	7.83 (7.57-8.5)	8.65 (7.52-9.44)	9.95 (8.77-11.5)	9.56 (9.24-12)	12.2 (10.8-14)
Cadmium (mg/kg dw)	0.96	0.182 (0.154-0.234)	0.195 (0.169-0.211)	0.27 (0.238-0.471)	0.24 (0.212-0.295)	0.535 (0.372-0.774)	0.322 (0.255-0.512)
Copper (mg/kg dw)	0.788	32.7 (27.6-39.7)	32 (29.4-36.3)	44.4 (39.8-49.1)	40.9 (37.2-44.6)	54.4 (46.5-178)	45.2 (42.6-47.2)
Iron (mg/kg dw)	0.000246	28200 (20600-30600)	34900 (30600-37600)	32600 (30800-34800)	39000 (37600-40900)	36500 (34400-40000)	41400 (39800-46500)
Lead (mg/kg dw)	0.0106	28.6 (21.9-33.3)	18.3 (16.8-19.9)	38.6 (33.4-45.2)	21.5 (20-23.1)	50.4 (40.3-113)	25.6 (22.9-30.3)
Manganese (mg/kg dw)	4.77E-08	268 (232-294)	391 (374-422)	353 (330-373)	456 (425-546)	380 (362-408)	592 (497-791)
Mercury (mg/kg dw)	0.428	0.274 (0.188-0.328)	0.237 (0.218-0.253)	0.396 (0.326-0.575)	0.272 (0.259-0.294)	0.644 (0.545-2.2)	0.341 (0.283-0.436)
Methyl Mercury (µg/kg dw)	0.198	0.327 (0.166-0.454)	0.418 (0.332-0.494)	0.7 (0.484-1.27)	0.593 (0.519-0.728)	3.7 (1.26-6.52)	0.997 (0.716-1.84)
Nickel (mg/kg dw)	9.15E-05	60.1 (41-64.3)	72.6 (69.2-73.5)	66.1 (64.3-74.9)	80.6 (76.2-82.9)	75 (68.2-94.5)	84 (82.7-93.3)
Selenium (mg/kg dw)	0.111	0.229 (0.188-0.32)	0.214 (0.19-0.225)	0.342 (0.32-0.373)	0.273 (0.226-0.298)	0.385 (0.358-0.462)	0.331 (0.288-0.361)
Silver (mg/kg dw)	0.0365	0.247 (0.168-0.299)	0.171 (0.153-0.185)	0.333 (0.299-0.379)	0.225 (0.2-0.266)	0.398 (0.353-0.469)	0.281 (0.25-0.378)
Sum of 208 PCBs (µg/kg dw)	0.0211	32.3 (20.4-41.3)	16.5 (12.1-19.7)	85.1 (41.3-126)	20 (17.7-23.2)	129 (96.6-1450)	22 (20.4-28.2)
Sum of 40 PCBs (µg/kg dw)	0.00734	26.8 (15.9-32.7)	12.2 (9.66-14.6)	69.1 (32.6-102)	15.9 (14.4-18)	103 (78.7-1170)	18.2 (16.5-39.4)
Zinc (mg/kg dw)	0.672	98.5 (82.1-115)	91.6 (86.6-101)	132 (116-139)	107 (103-117)	143 (138-212)	120 (114-131)

Figures 4.1.2.1 Boxplots of non-Marin Mercury – Number in header is p-value of KW test. Y-axis is Log_{10} of mercury (in mg/kg dw). Boxes indicate interquartile ranges, and whiskers the 95th percentile range (dots are individual results outside those ranges). Mercury data are not significantly different between Central Bay margins and open bay areas.



Figures 4.1.2.2 Boxplot of non-Marin Sum of 40 PCBs – Number in header is p-value of KW test. Y-axis is Log_{10} of Sum of 40 PCBs (in $\mu\text{g}/\text{kg dw}$). Boxes indicate interquartile ranges, and whiskers the 95th percentile range (dots are individual results outside those ranges). Despite overlapping interquartile ranges, differences between Central Bay margins and open bay PCB results are significant.



4.2. Mass balance contaminant inventory

One application of the data from this study is to estimate the inventory of priority contaminants in the margin, to evaluate their potential role in the long-term contaminant mass balance. The area defined as being in the margin constitutes a small portion (around 5%) of the total Central Bay segment, only 22 km² compared to 402 km² for the subtidal (deeper than 1 ft below MLLW) portion.

Table 4.2 shows the spatially averaged sediment concentrations of the reported contaminants in CB margins, compared to the average of open Bay sediments from RMP Status and Trends monitoring. Pollutant inventories in Central Bay were calculated based on these average concentrations, and the relative areas of margin and subtidal habitats, assuming equivalent sediment mixed layer depths for both. For most of the contaminants, the margin average is modestly higher than the open Bay average. PCBs are the exception with mean concentrations in the margins that were 4-5 times higher than the open Bay.

The mass in the margin never represents a majority of the total inventory for any contaminant, but for several contaminants, such as PCBs and lead (and perhaps mercury, albeit less significantly), higher average concentrations indicate an influence of the CB margin disproportionate to its total area. PCBs show the greatest enrichment in the margins. Approximately 20% of the mass of PCBs in Central Bay is in the margin areas, compared to 4-7% for other contaminants.

These differences in average concentrations between the margin and open bay sediments may be compounded by greater productivity and rates of exchange and bio-uptake from the sediment to the water in margin areas. However we do not currently have sufficiently representative measurements of these processes in the different bay habitats to adequately estimate their net impacts.

Table 4.2 Contribution of Margin Sediment to Pollutant Mass in Central Bay Segment – Margins account for ~5% of Central Bay area, so contaminants with higher mass percentages in margins are likely to originate from terrestrial or nearshore sources

Parameter	CB Subtidal Mean	CB Margin Mean	% Mass in Margin
Aluminum (mg/kg dw)	29200	19800	4%
Arsenic (mg/kg dw)	9.07	7.81	4%
Cadmium (mg/kg dw)	0.205	0.211	5%
Copper (mg/kg dw)	33.5	37.6	6%
Iron (mg/kg dw)	34200	27600	4%
Lead (mg/kg dw)	18.7	26.7	7%
Manganese (mg/kg dw)	448	325	4%
Nickel (mg/kg dw)	70.1	59.6	4%
Selenium (mg/kg dw)	0.219	0.259	6%
Silver (mg/kg dw)	0.177	0.217	6%
Zinc (mg/kg dw)	94.2	97.5	5%
Mercury (mg/kg dw)	0.245	0.317	7%
Methyl Mercury (ug/kg dw)	0.538	0.809	7%
Sum of 40 PCBs (ug/kg dw)	12.2	56.5	20%
Sum of 208 PCBs (ug/kg dw)	14.5	70	21%

4.3. Management effectiveness

Although this survey of CB margin sediments was not specifically designed or optimized to evaluate potential trends or changes in contaminant concentrations, it at least establishes a baseline of the current contaminant distribution for comparison to future regional or localized (e.g., individual site) data. Due to their proximity to terrestrial contaminant sources and pathways, margin areas are more likely than open bay subtidal areas to show any possible impacts of management actions to reduce contaminant loads. The heterogeneity in concentrations over small distances often seen in past studies of contaminated sites suggest that only very large temporal changes may be easily detected in margins. However, open bay areas are even less likely to show detectable changes, due to their larger (but lower concentration) contaminant inventories, greater distances from source areas and potential management actions, and complexities of influences from numerous interacting sources, pathways, and processes. Thus, aside from tracking or tallying net benefit or change right at the location of management action, monitoring of conditions in the margins in the nearfield of specific sites or sub-regionally may represent another means of assessing net benefit of management (perhaps in conjunction with biological monitoring) that might be measurable within a reasonable (i.e., less than lifetime) time frame.

4.4. Screening for highly contaminated areas

There was some hope that this survey of margin areas might reveal previously unknown sources. However, aside from serendipity, for numerous reasons (especially small-scale spatial heterogeneity often seen in sediment contamination) noted previously, only the largest of sources might be expected to be found via a random survey. Some of the previously known most severe and widespread contaminated areas, i.e., Oakland Harbor and San Leandro Bay, were confirmed in this study. One suspected area, on the Brisbane shoreline next to a large landfill and in the nearfield receiving water of an older industrial watershed, was also found or confirmed to be highly contaminated. However, such finds should be considered low-probability (e.g., 1 in 40 in this case) chance side-benefits of random surveys, whose primary objectives are to characterize the distribution of a population.

5. Summary and Future Directions

This survey of Central Bay margins sediment has largely been successful in achieving its primary goals and made a start towards potential applications.

In its first goal of characterizing the ambient concentrations of contaminants these shallow and intertidal margin habitats, the results generally confirmed current conceptual model expectations, i.e., that the margin sediments are often more contaminated than those in the subtidal open bay. For a few contaminants, the concentrations in the margins were significantly higher than those in sediments from the subtidal areas of Central Bay. PCBs had the largest (about 4 to 5-fold) difference between the average concentrations in the margins versus the open Bay.

The Central Bay margin areas probably represents as extreme a difference as we are likely to see in San Francisco Bay, as the Central Bay has both the highest density of population and industrial activity historically or currently (i.e. the largest pollutant sources), and the most exchange with the open ocean (the cleanest receiving water). To the north and south, margins generally account for more of the total area, and the population and potential pollutant sources are reduced, so we may expect more similar concentrations between margins and the subtidal bay.

With a spatially unbiased sample, we are also able to make an estimate of mean concentrations, and thus estimate the mass or inventory of contaminants in margins to compare to the quantity in the open bay. The extent and degree of contamination in the margins is not sufficient to account for a majority of mass of any pollutant in Central Bay, but for example with an average PCB concentration 4 to 5 times that in the open water sediments, margins are likely to have an influence on long term PCB fate disproportionate to their (small in Central Bay) area. After accounting for likely differences in biological productivity, contaminant exchange, transport, and uptake processes as compared to the subtidal bay, the influence of the margins on contaminant impacts may even be larger.

Although there has been little in the way of management action aside from decades old bans or past reductions in usage (and thus currently perhaps only asymptotically decreasing concentrations), the ambient characterization of margins may be useful in the future for evaluating changing loads of specific watersheds or sets of watersheds. The inventory of contaminants in the open bay is huge compared to annual loads, so changes in the inventory of contaminants in subtidal sediments may be difficult to see in the short- and mid-term. However, given the proximity to likely sources, the current characterization of margin sediments may be a useful baseline against which to compare progress at different locations and scales.

Characterizing the baseline distribution of contaminant concentrations in margins is also helpful for evaluating and prioritizing areas for management actions. The first four “priority margin units” being studied for possible management action have PCB concentrations far above ambient (subtidal) bay concentrations, and in the top quartile of margin concentrations. However, identifying the next tier of areas to focus on, and determining

what degree of contamination defines a “priority” area, would benefit from the unbiased information on the distribution of PCBs and other contaminants in margins. Similarly, a sense of the background distribution for margins would be useful in setting possible targets for watershed loads and their nearfield receiving waters, or for appropriate re-use or disposal of dredged sediment.

Finally, although the yield rate is very low, ambient surveys can fill spatial holes in previous efforts, and occasionally identify or verify sources that would otherwise not have been characterized. In this study, one contaminated “hot spot” site was identified in Brisbane, near a landfill, and in the receiving water of a watershed already being studied to evaluate expected PCB loads. Despite the results of this site confirming our expectations, studies focused on finding and characterizing contaminated areas are generally best designed to be sampled deterministically, in the extreme near-field of known/expected sources. At other known contaminated sites in San Francisco Bay (Davis et al., 2016(draft)), concentrations are highly variable, and often drop to near ambient (regional) background concentrations within several hundred meters. The odds of finding highly contaminated spots are thus very low using random sampling schemes, with sites often spaced 1 km or more apart, often too far to observe any elevated gradient around a source.

5.1. Recommendations for Future Studies

In future studies of margin areas, we recommend use of simple area-proportional weighting for the probabilistic design. Dividing the sample frame into small substrata may compromise or greatly complicate the post-hoc analysis of the data. For this study, the design was modified in an attempt to detect more “hot spots” by undersampling Marin areas and oversampling the more urbanized areas of Central Bay. One hot spot (out of 40 stations) was found, but that site would have been included in the original design, and only one result in the top decile of concentrations for PCBs was among the seven reallocated samples. The weighting imposed some additional constraints on the data analysis, as some statistical comparisons were not possible or not easily done with differential sample weights. Also, variable weighting can create some artifacts, such as the artificial compression of the apparent variance of concentrations in Marin (i.e., a lower maximum, but also a higher minimum) due to the low sample count in this stratum (N=7).

Unless the sample size of future studies are greatly increased (e.g., doubled or quadrupled), reallocation of samples to different strata of a random draw should be avoided. Reallocation of stations between strata is not likely to reduce sample spacing enough to observe any gradients or detect hot spots. Deterministic sampling designs at points of interest would be more efficient to achieve that objective.

6. References

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7. Appendix

Table A-1. Coordinates of 33 planned non-Marin Central Bay sample sites, with additional potential oversample sites. Dropped sites marked in strikethrough text.

SiteCode	Longitude	Latitude	Comments
CB01	-122.382351	37.722188	
CB03	-122.310862	37.878131	
CB04	-122.277808	37.767614	
CB05	-122.38605	37.668048	Oyster Pt Marina - find an undredged spot?
CB08	-122.273028	37.762812	Drop site, Alameda sandy shore
CB10	-122.346692	37.906718	Richmond, Shimada Friendship Park, move shallower
CB12	-122.244206	37.748919	70m from shore, avoid channel
CB14	-122.326734	37.888461	
CB15	-122.303561	37.827887	
CB16	-122.218611	37.750283	San Leandro Bay open water, check depth
CB17	-122.385233	37.708896	
CB20	-122.24553	37.778948	
CB21	-122.387888	37.643081	
CB24	-122.248067	37.786283	
CB26	-122.399457	37.929034	Shoreline near long Chevron Pier
CB27	-122.308601	37.83772	Emeryville Marina, go shoreward either S/SE
CB28	-122.236739	37.74807	
CB30	-122.312071	37.892829	
CB31	-122.288496	37.794937	Oakland Inner Harbor. Shore ~30m away
CB32	-122.220437	37.756571	

CB33	-122.388045	37.680658	
CB35	-122.421463	37.809089	Drop site, Boat dock, shore too far
CB36	-122.255425	37.755244	Alameda coast - sandy beach?
CB37	-122.394541	37.641418	
CB38	-122.377097	37.901622	Bird Island breakwall?
CB40	-122.284968	37.792394	Drop site, Oakland harbor tugboat dock
CB42	-122.332335	37.905501	replacement site
CB43	-122.309408	37.829205	replacement site
CB44	-122.225184	37.749936	replacement site
CB45	-122.411946	37.943148	replacement site
CB46	-122.325568	37.899036	replacement site
CB47	-122.316663	37.793778	replacement site
CB48	-122.21561	37.742746	replacement site
CB49	-122.388918	37.776982	replacement site
CB52	-122.247018	37.750125	replacement site
CB53	-122.382614	37.62998	replacement site
CB54	-122.355094	37.907329	First oversample site for NON-Marin only
CB56	-122.29881	37.834659	
CB58	-122.330989	37.906875	
CB59	-122.303904	37.828478	
CB60	-122.220433	37.749028	
CB62	-122.308229	37.863738	
CB63	-122.327595	37.800313	
CB64	-122.214651	37.751254	

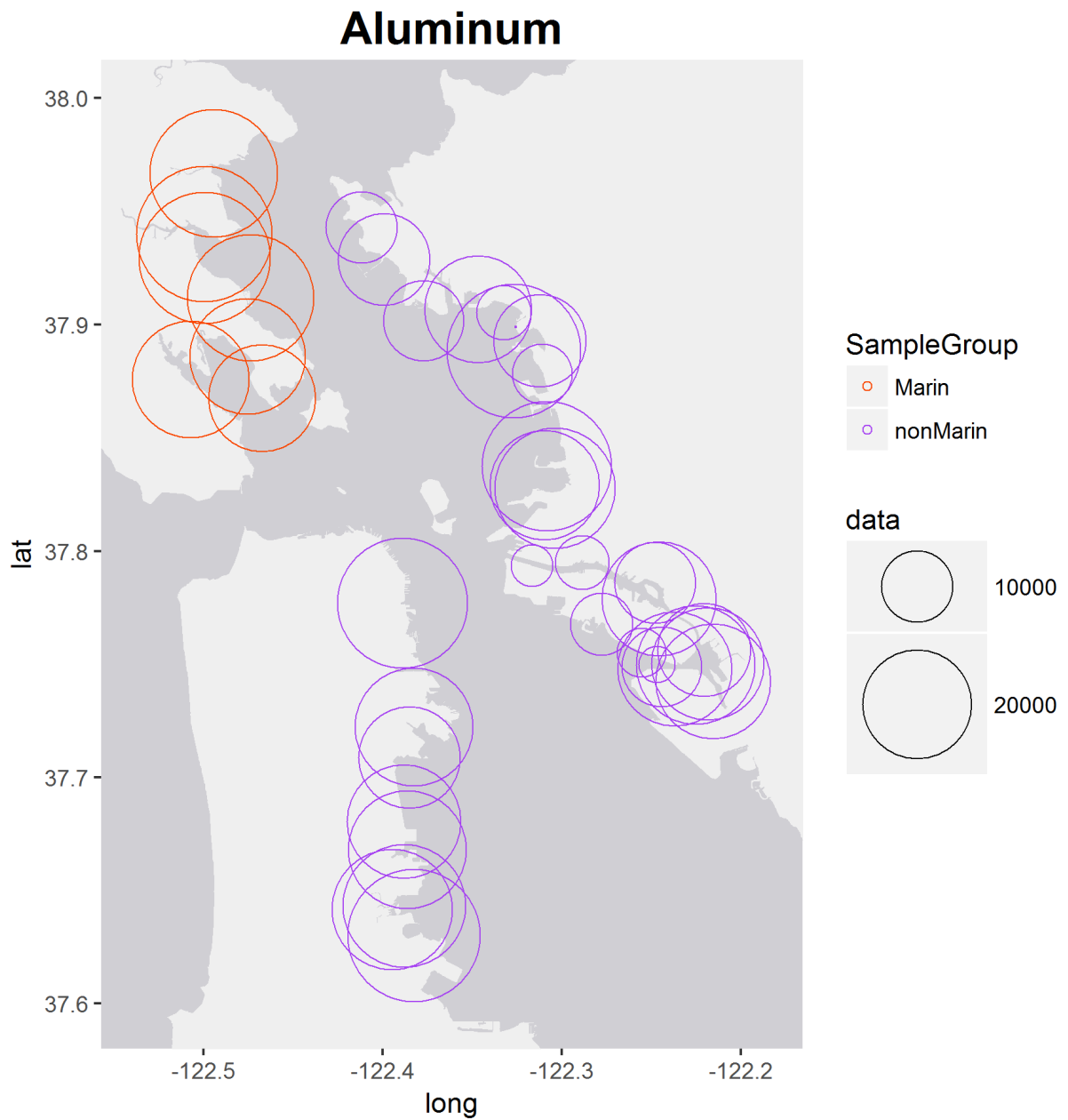
Table A-2. Coordinates of 7 planned Marin Central Bay sample sites, with additional potential Marin oversample sites. Dropped sites marked in strikethrough text.

SiteCode	Longitude	Latitude	Comments
CB02	-122.469677	37.964118	Marin first 7 sites dropped
CB06	-122.50429	37.937035	Marin first 7 sites dropped
CB07	-122.520554	37.885843	Marin first 7 sites dropped
CB09	-122.501168	37.932339	Marin first 7 sites dropped
CB11	-122.500579	37.890492	Marin first 7 sites dropped
CB13	-122.477658	37.917642	Marin first 7 sites dropped
CB18	-122.473296	37.976462	Marin first 7 sites dropped
CB19	-122.467395	37.867506	Marin
CB22	-122.499832	37.940228	Marin
CB23	-122.475494	37.886034	Marin
CB25	-122.499415	37.929527	Marin
CB29	-122.473718	37.91195	Marin Paradise Cay look for shoal?
CB34	-122.494303	37.966809	Marin
CB39	-122.507246	37.875809	Marin City houseboat dock? 100m from shore
CB41	-122.49279	37.925963	First oversample site for Marin only
CB50	-122.490542	37.966632	
CB51	-122.511609	37.887021	
CB55	-122.51132	37.883362	
CB57	-122.492512	37.92215	
CB61	-122.467885	37.984082	

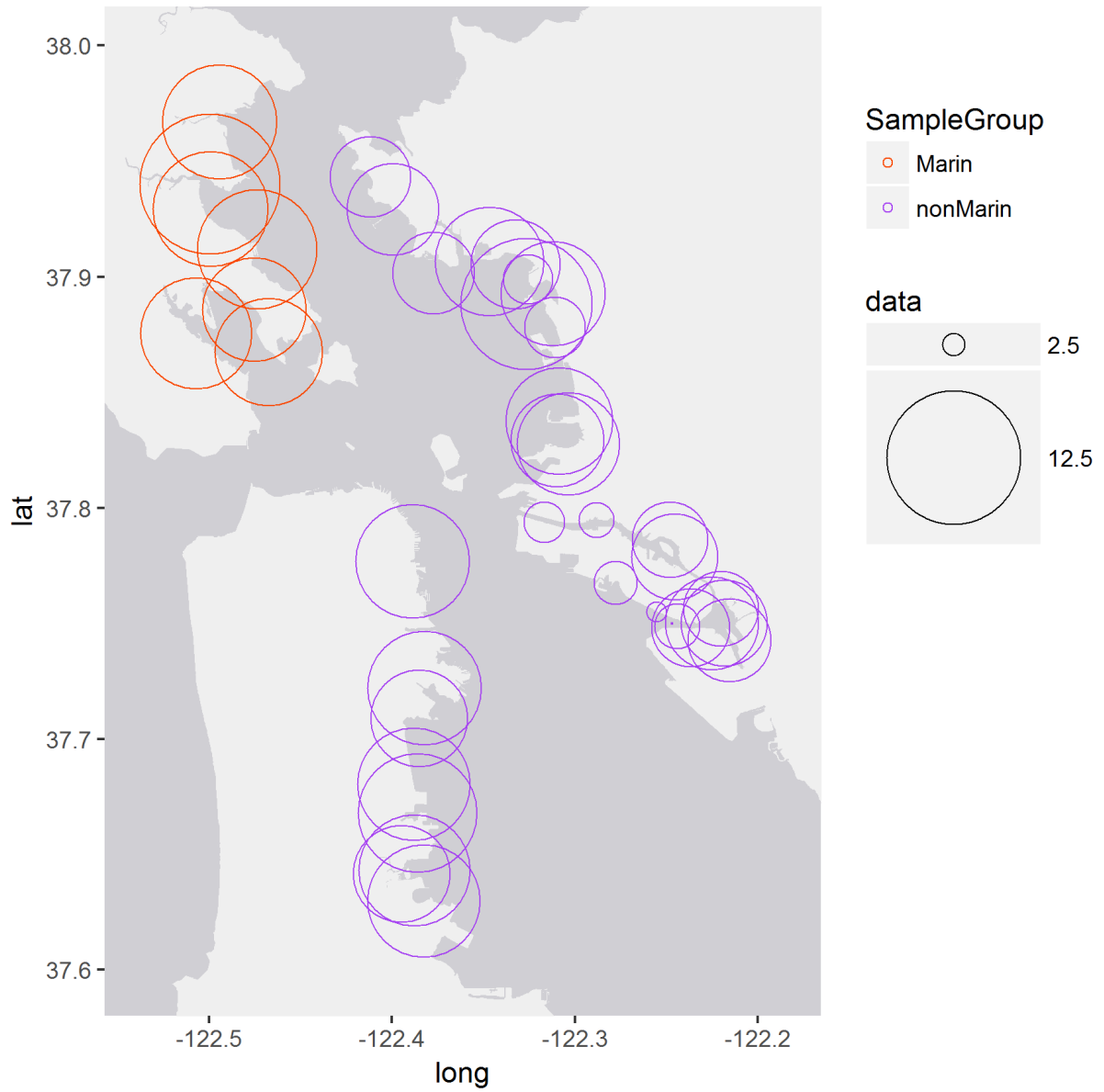
Table A-3.3.1 – p-values from Anderson Darling tests - For all attempted transformations, weighted ECDFs

Transformation	Value/ %Fines	Value/ %TOC	-1/sqrt(x)	-1/x	Log ₁₀ (value)	Log ₁₀ (value/ %Fines)	Log ₁₀ (value/ %TOC)	Raw Value
Aluminum	9.75E-11	0.674	1.12E-11	1.29E-15	2.65E-08	4.70E-06	0.223	0.000905
Arsenic	8.02E-16	1.04E-07	5.59E-08	5.51E-11	2.58E-05	0.000019	0.18	0.0604
Cadmium	5.06E-10	0.000709	1.65E-06	7.62E-15	0.0516	0.0431	0.301	1.53E-07
Copper	6.81E-18	7.14E-21	3.41E-10	1.02E-16	5.81E-05	0.000108	3.53E-08	5.61E-10
Iron	4.81E-12	0.0285	2.18E-11	2.23E-14	1.22E-08	1.60E-06	0.621	0.000176
Lead	2.20E-15	4.11E-12	5.48E-06	1.78E-12	0.04	2.59E-05	0.000539	3.83E-07
Manganese	1.35E-11	0.0201	1.35E-05	1.36E-10	0.0306	0.000274	0.255	0.415
Mercury	2.01E-19	2.37E-20	5.53E-08	7.58E-15	0.00263	1.04E-08	6.43E-06	3.16E-14
Methyl Mercury	3.09E-20	3.68E-18	1.48E-08	1.73E-19	0.0644	0.0334	0.0552	2.86E-21
Nickel	7.74E-10	3.24E-05	2.05E-12	7.44E-17	9.11E-09	3.75E-06	0.244	0.000597
Selenium	1.93E-09	0.000927	6.97E-08	2.09E-12	0.000255	0.00235	0.107	0.444
Silver	3.65E-17	1.42E-12	2.98E-05	2.69E-10	0.0684	0.0139	0.00616	0.0888
Sum of 208 PCBs (SFEEI)	3.70E-24	3.70E-24	7.00E-08	3.48E-20	0.189	0.000281	0.00405	3.70E-24
Sum of 40 PCBs (SFEEI)	3.70E-24	3.70E-24	7.00E-08	3.42E-20	0.163	0.000266	0.00427	3.70E-24
Zinc	3.72E-10	6.64E-07	8.82E-10	4.73E-14	6.35E-06	0.000845	0.00618	0.098

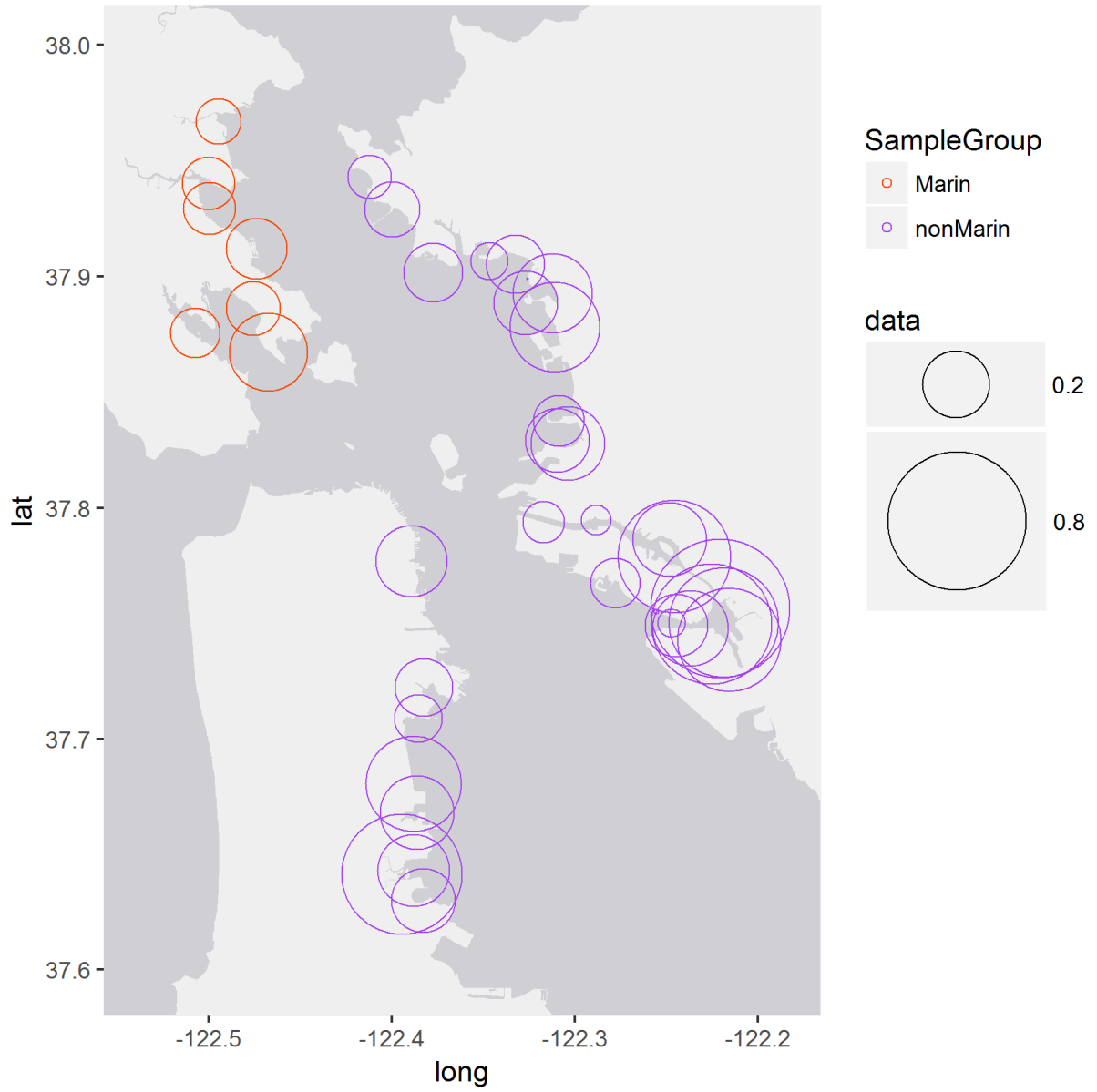
Figures A-3.1.1-15 – Bubble plots of raw concentration (mg/kg dw, except methyl mercury, $\mu\text{g/kg dw}$)

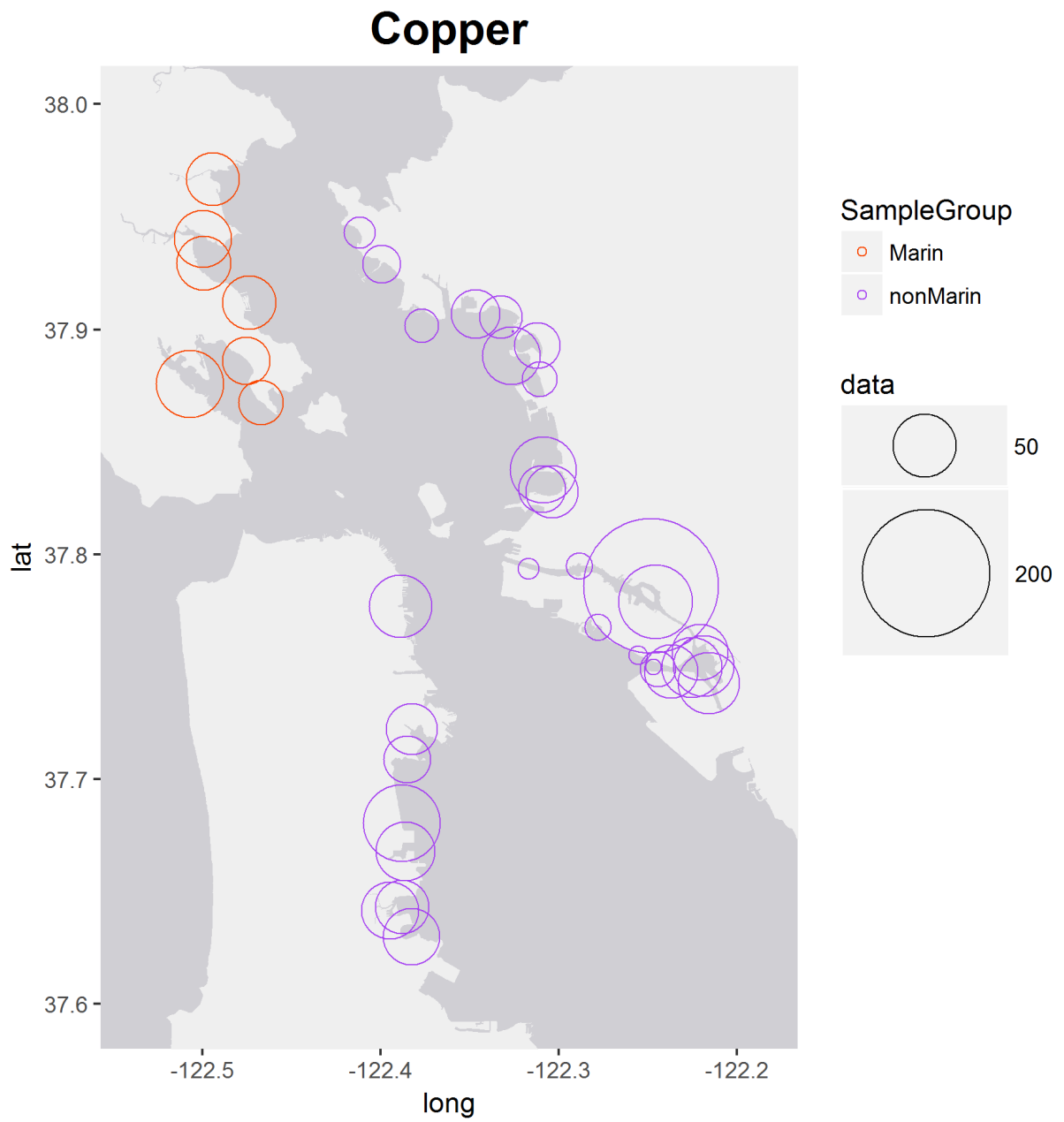


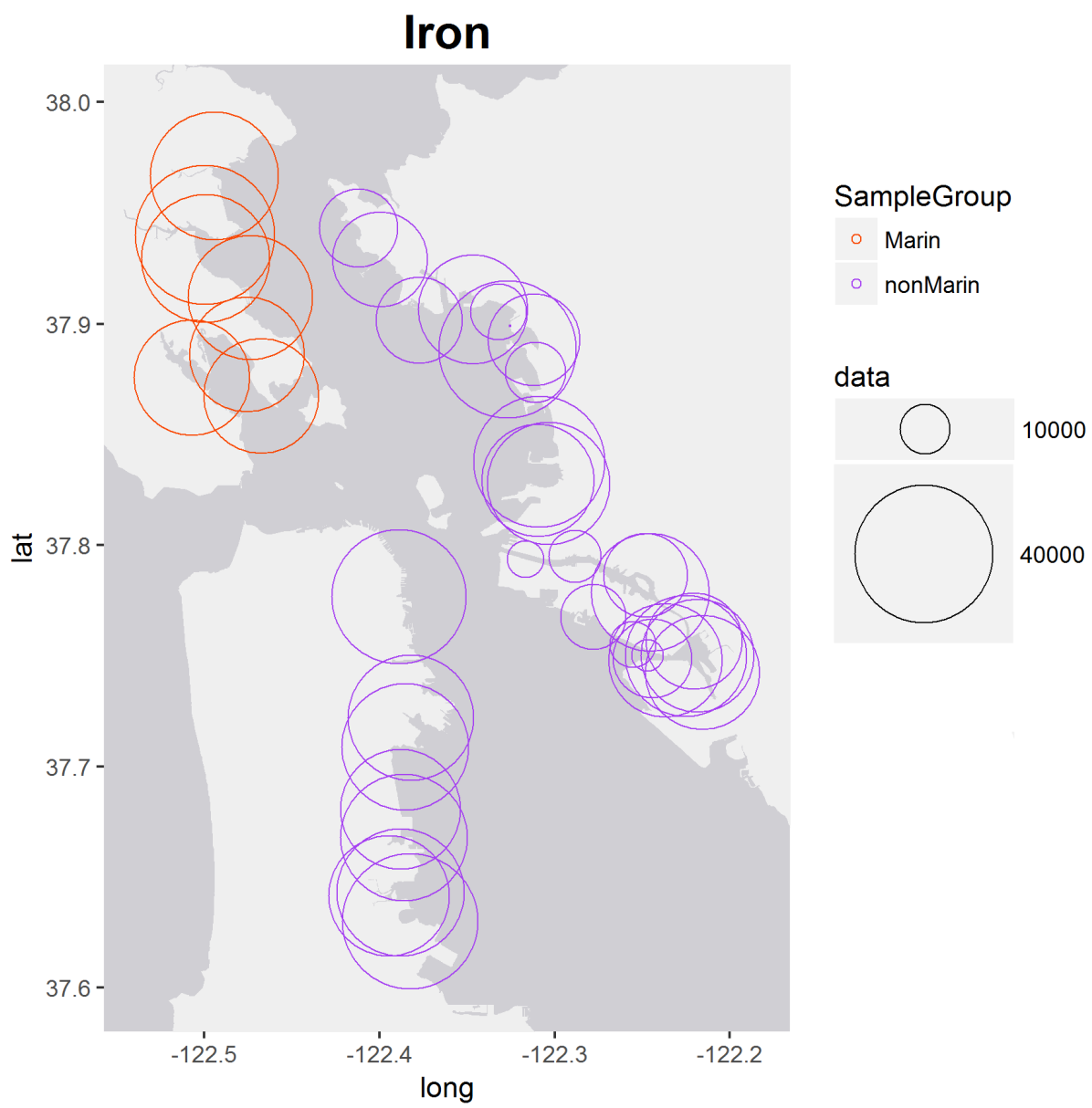
Arsenic



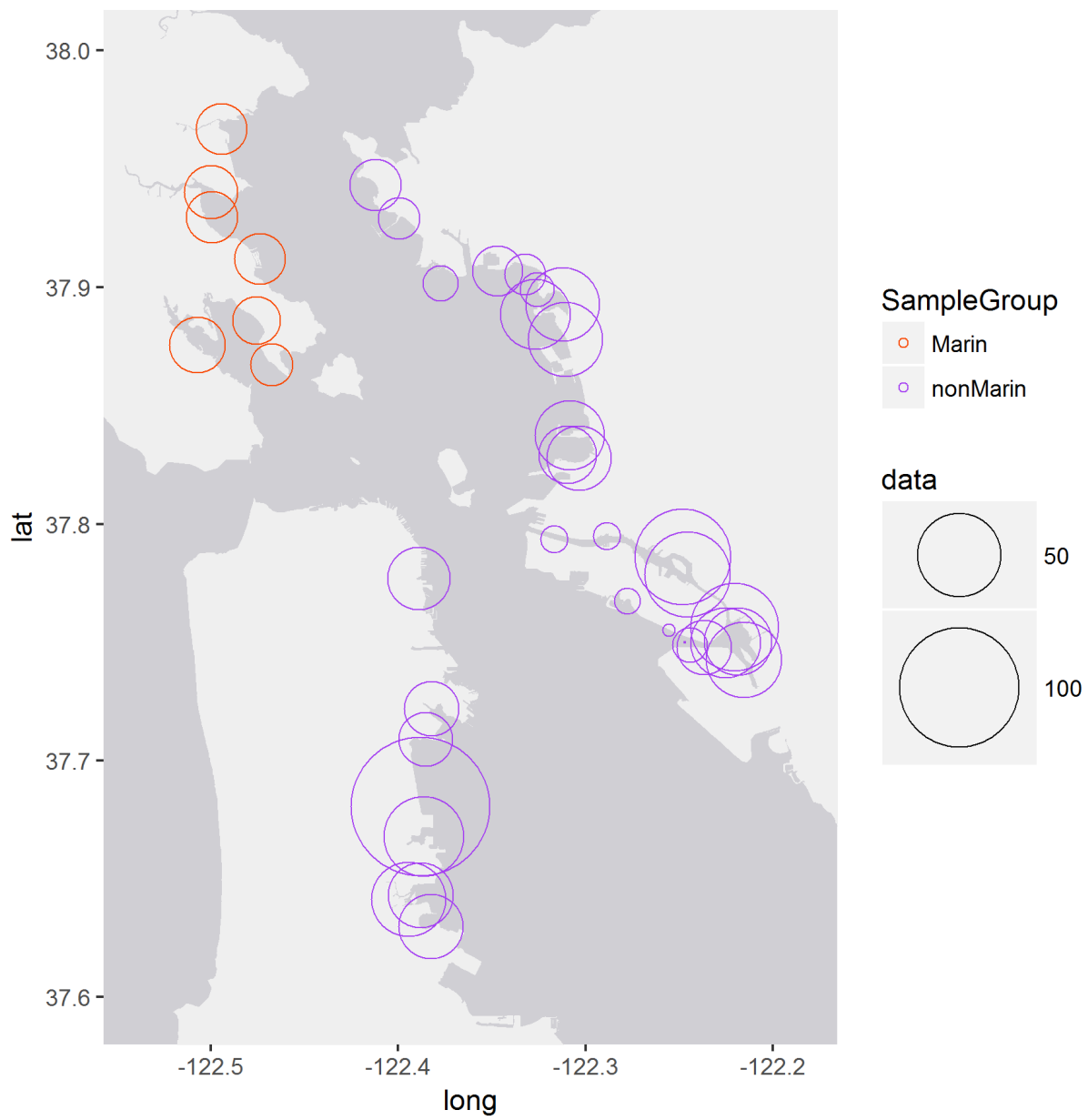
Cadmium



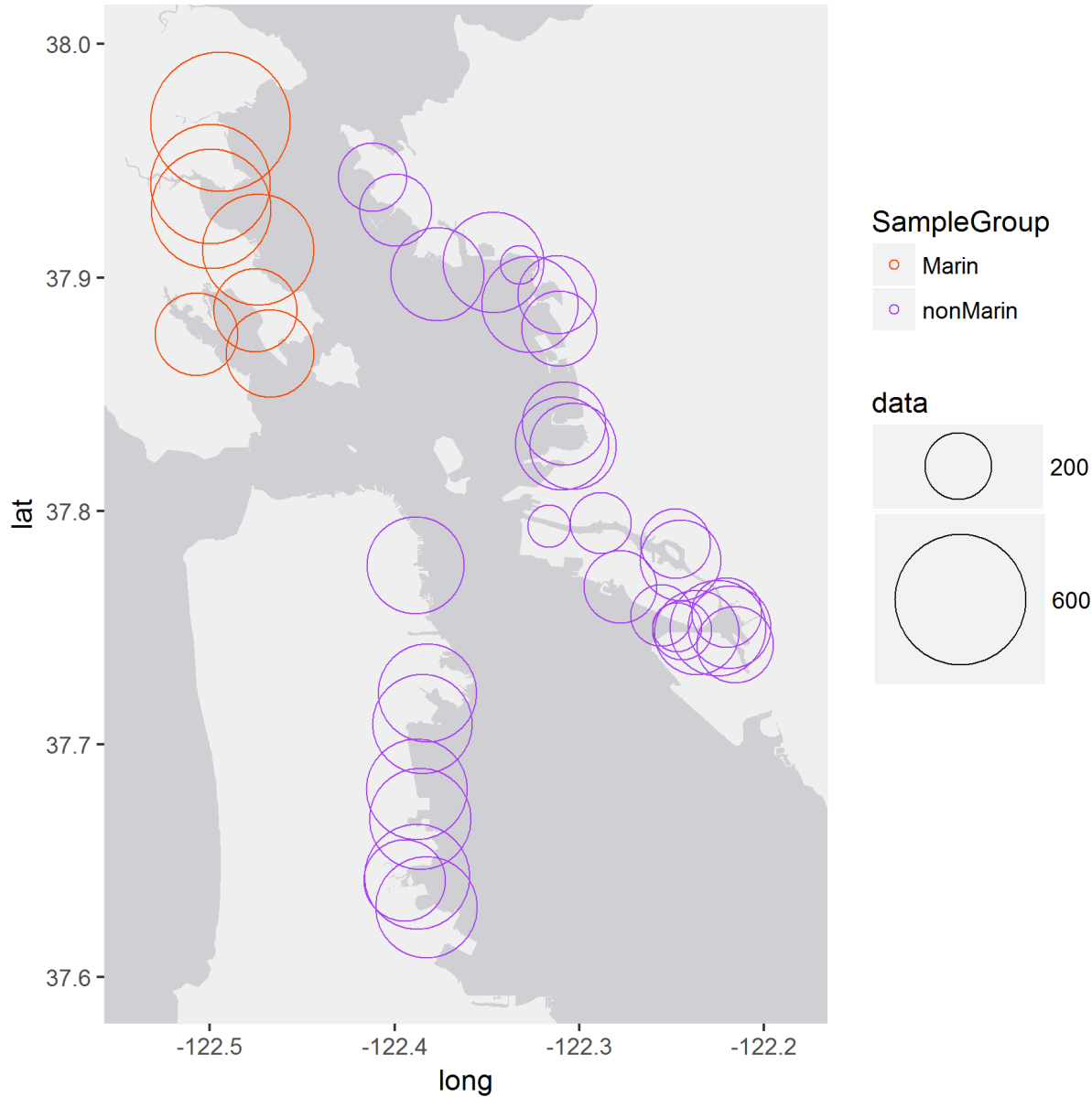




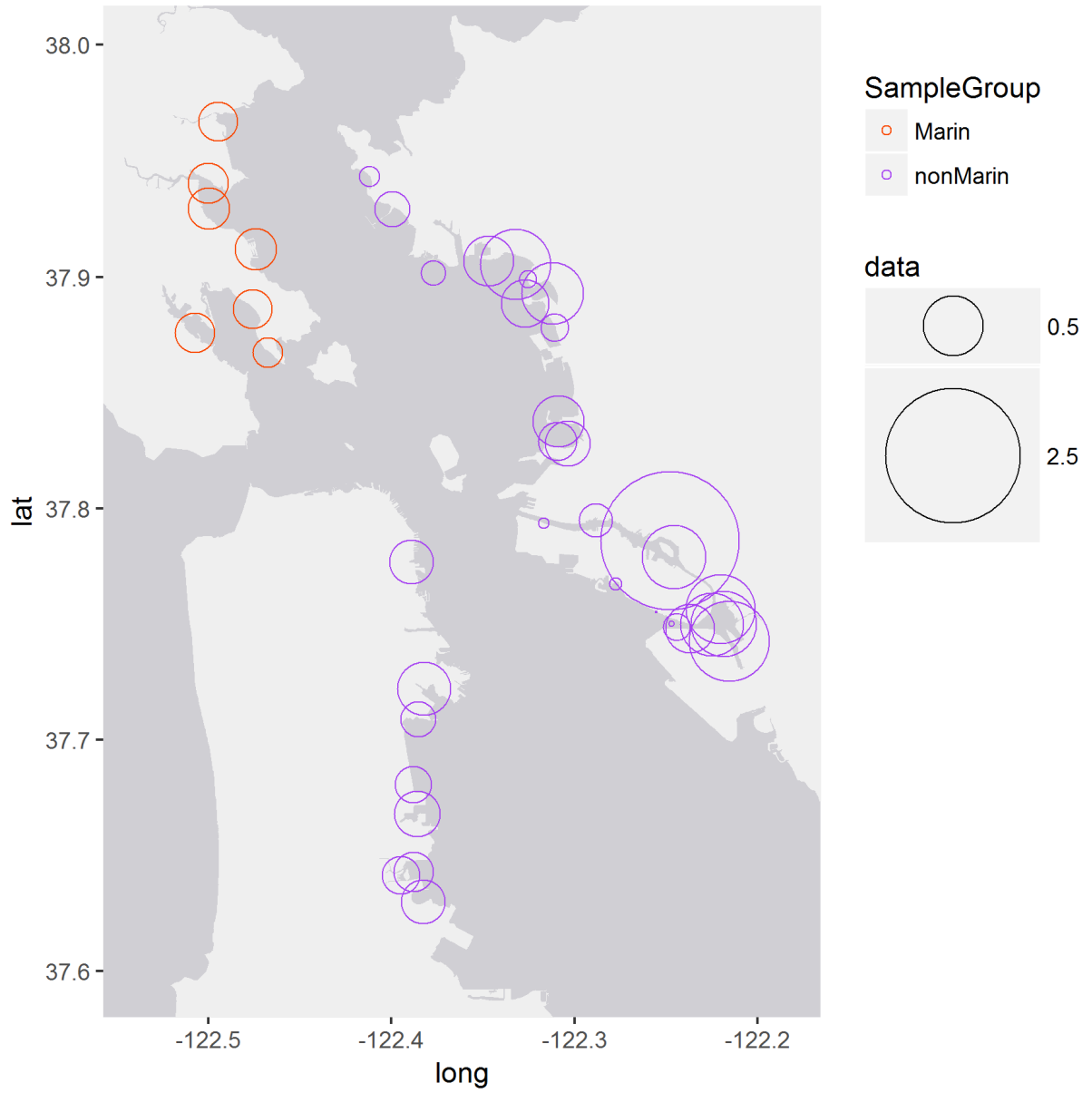
Lead



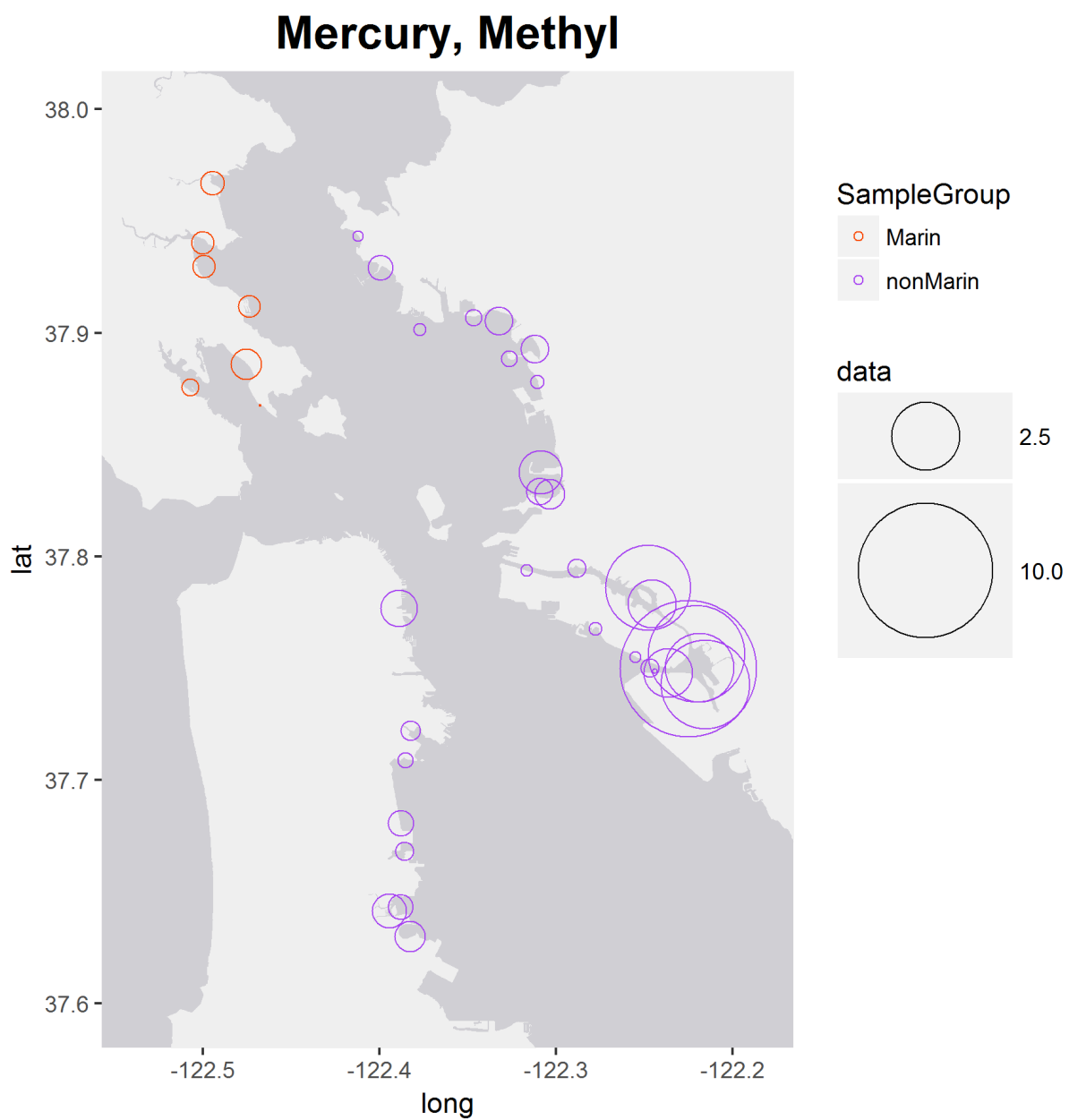
Manganese



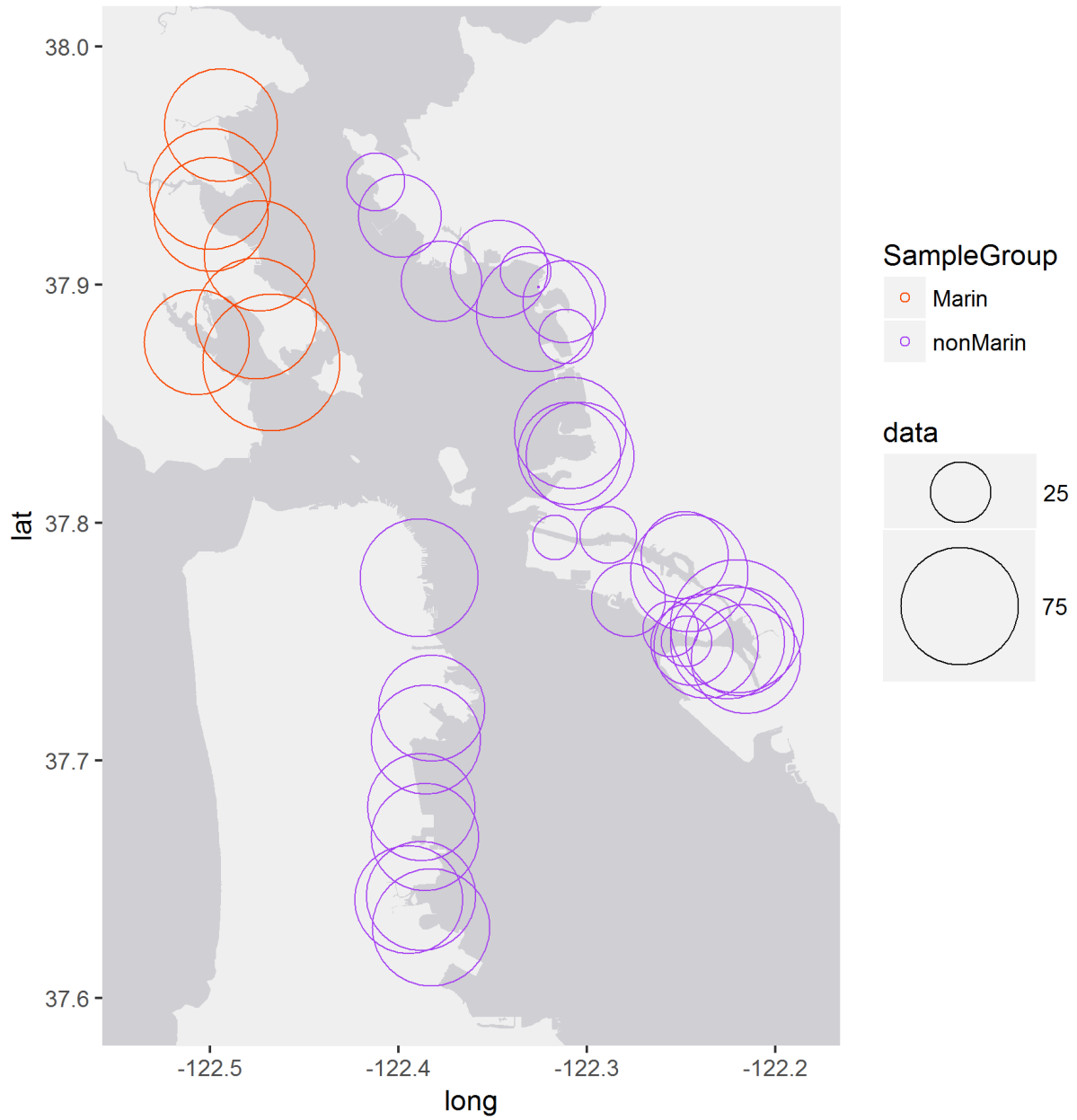
Mercury



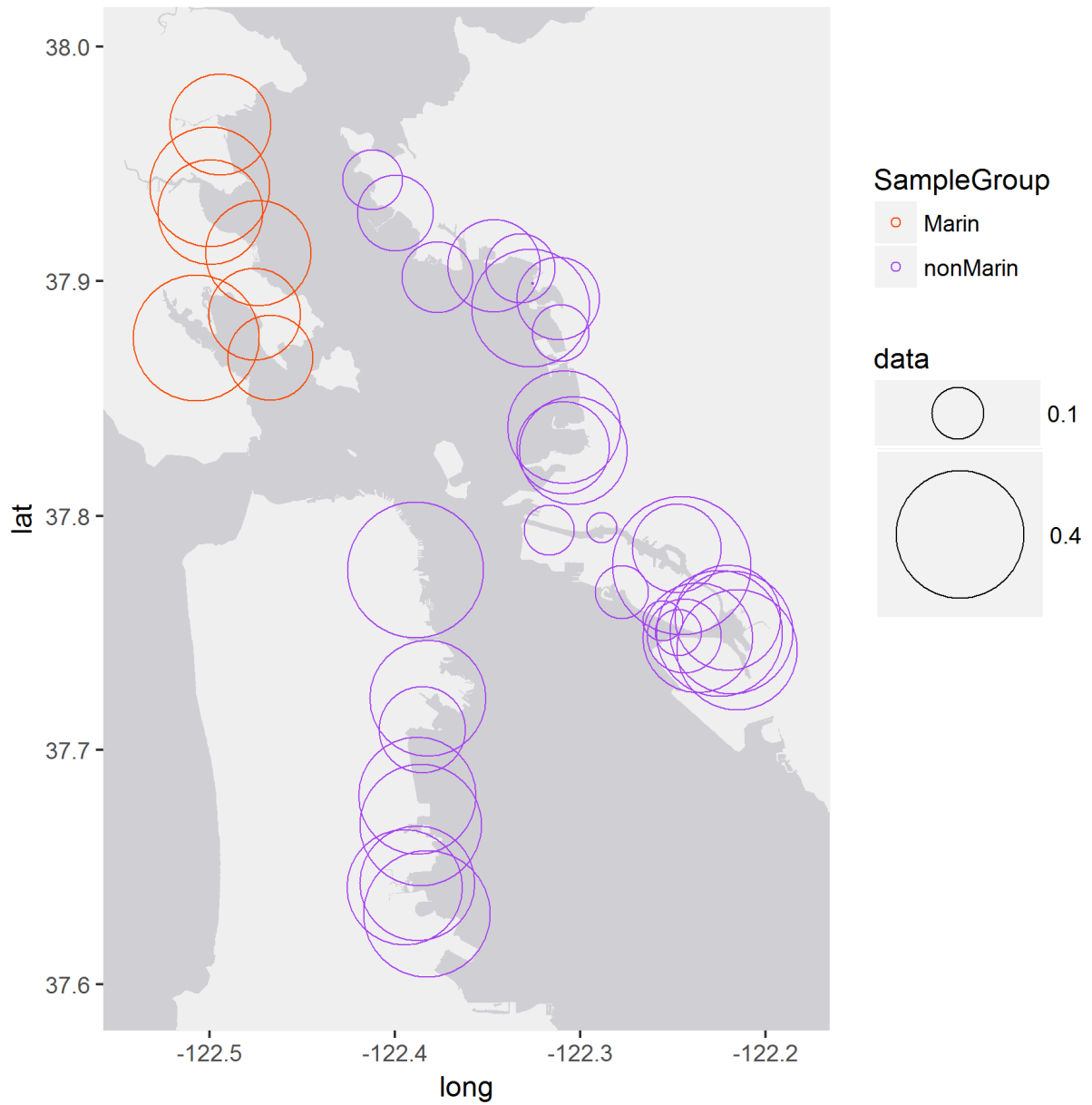
(Note: Units of $\mu\text{g}/\text{kg dw}$ for Methyl Mercury only)



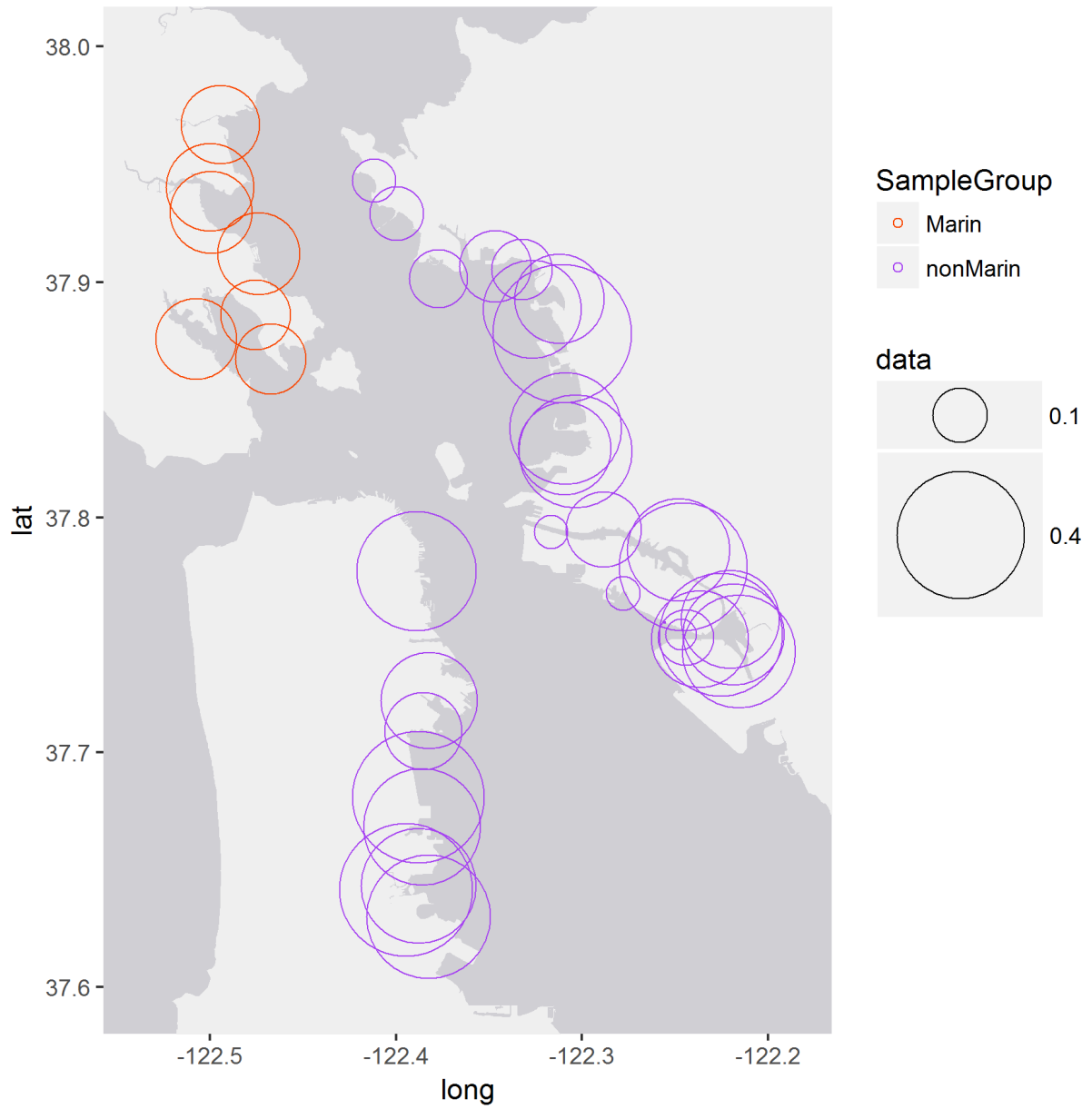
Nickel

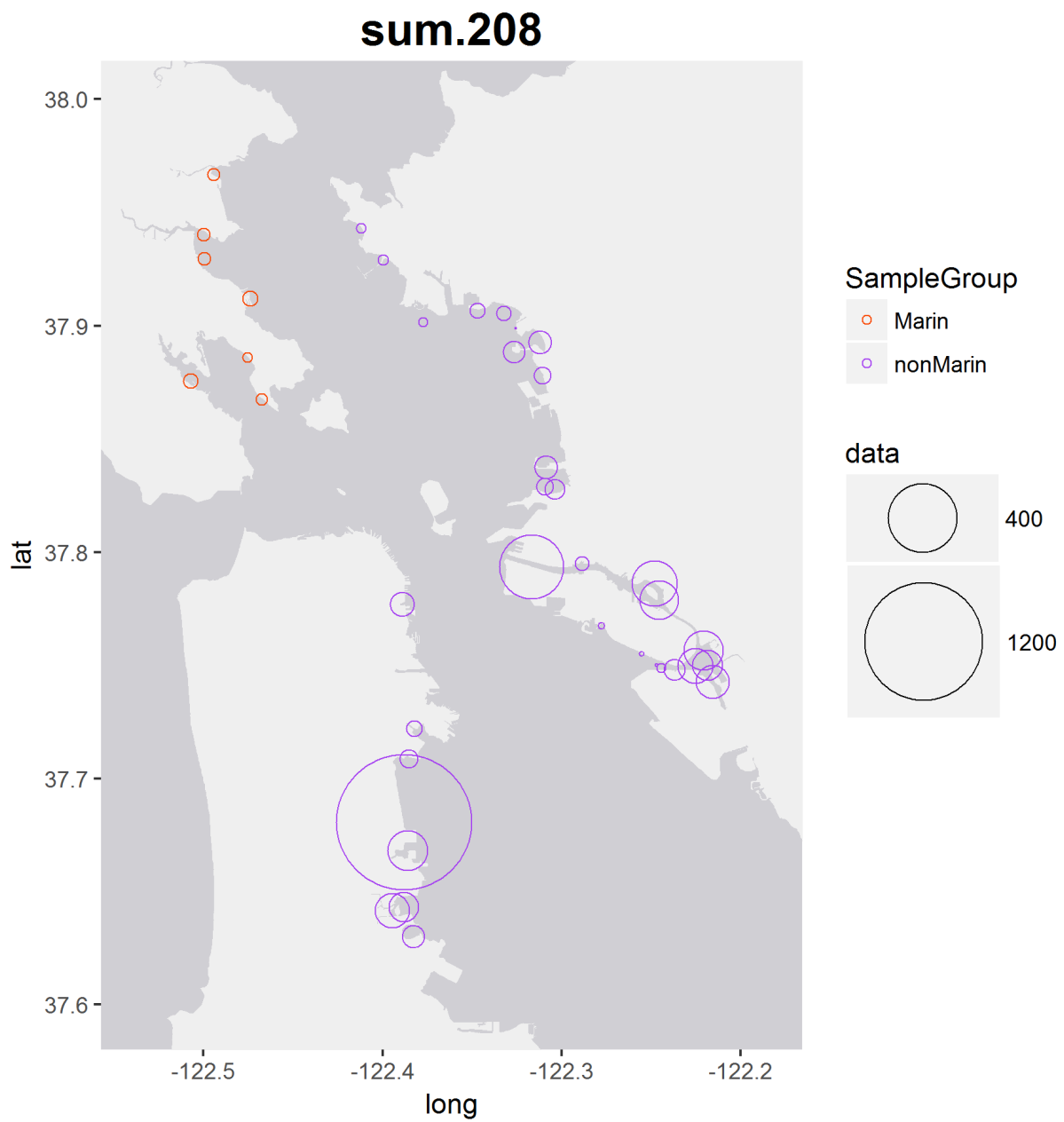


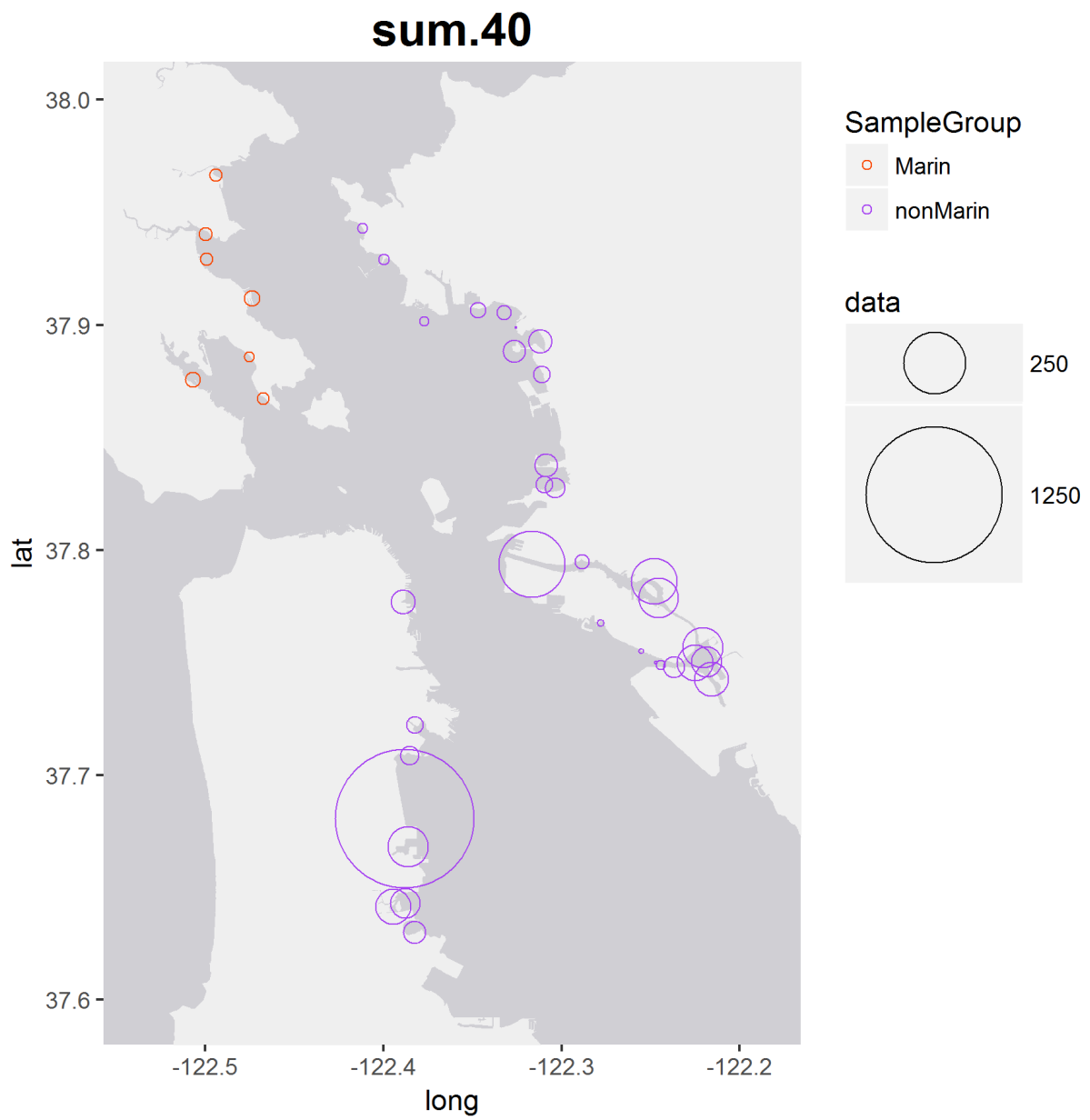
Selenium



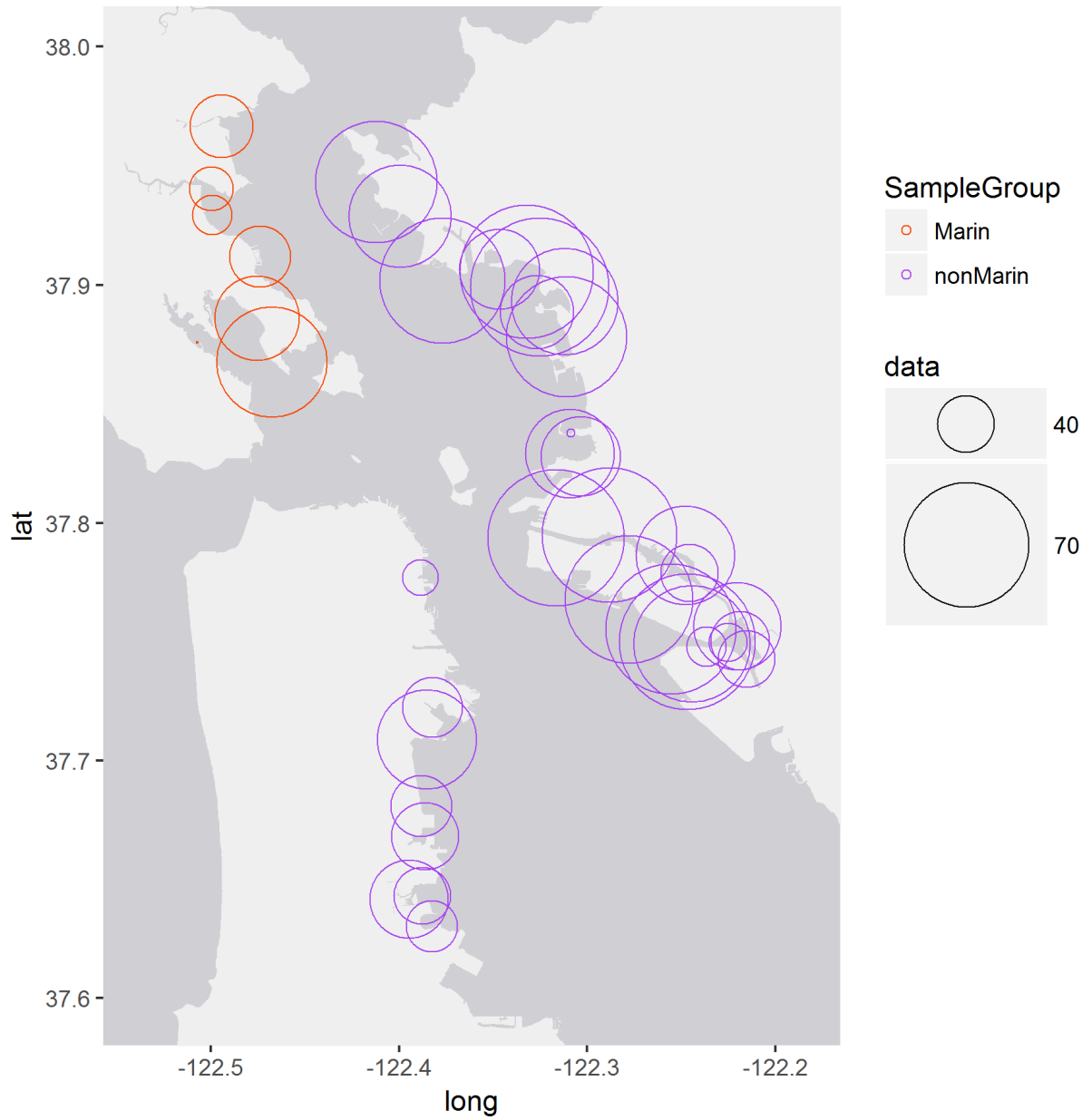
Silver



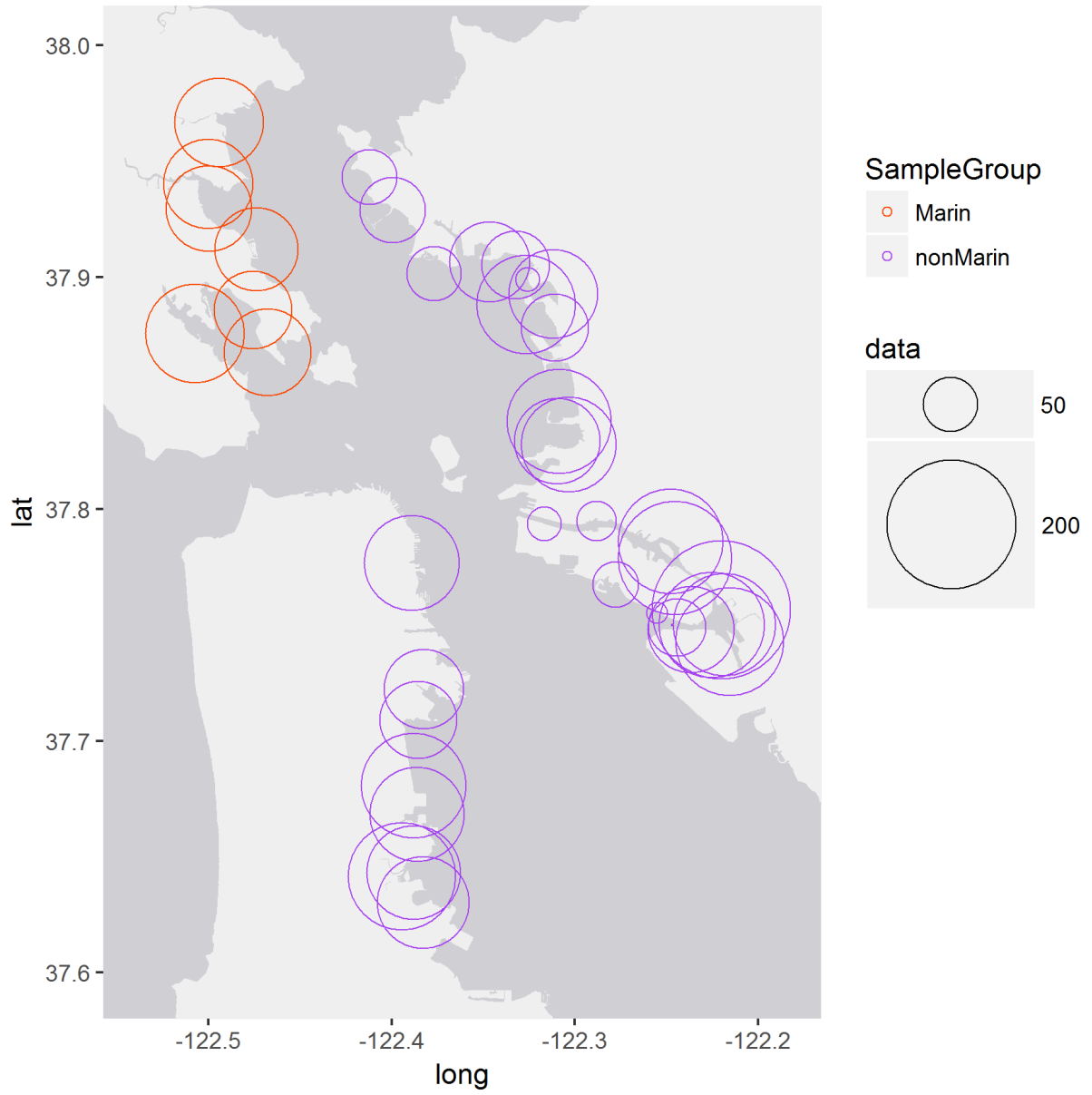




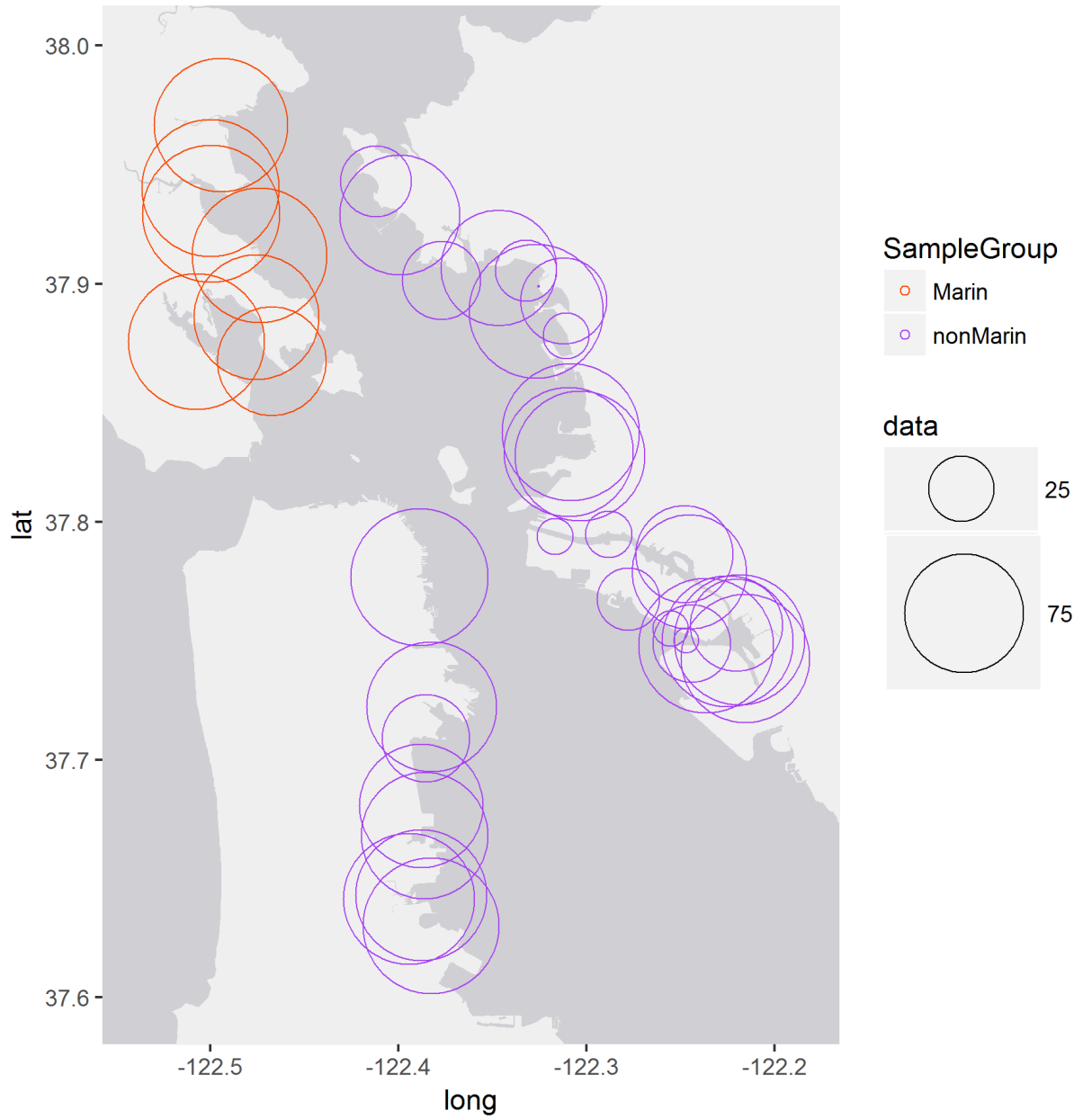
Total.Solids



Zinc



Fine



Total.Organic.Carbon

