

CHAPTER 6

Pilot and Special Studies



Estuary Interface Pilot Study

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Introduction

After the first three years of pollutant characterization throughout the Estuary, it became evident that sampling stations at the Estuary margins generally exhibited higher concentrations of trace elements and trace organic pollutants in water and sediment than those in the deeper parts of the Bay. It was not clear which factors were primarily responsible for this phenomenon, and in order to determine what role pollutant inputs from adjacent watersheds are playing, sampling at the interface between the Bay and upland had to be conducted. Initially, one station at the upper end of the tidal prism of Coyote Creek was selected, and in 1997 the sampling was expanded to the mouth of the Guadalupe River, also known as Alviso Slough.

Objectives

The overall goals of the Estuary Interface Pilot Study (EIP) have remained the same as in 1996:

- Link pollutant patterns found in the Estuary with those in adjacent watersheds to test if runoff and sediment taken at the lower end of Coyote Creek and the Guadalupe River differ from each other and from water and sediment in the South Bay, including the Local Effects Monitoring stations maintained by the San Jose-Santa Clara Wastewater Treatment Plant and the Sunnyvale Treatment Plant.
- Explore what kinds of ancillary water quality parameters and watershed characteristics should be measured or described to explain some of the patterns found, improve sampling design, and fine-tune testing methodology.

Specific questions for the second year of sampling included:

1. Is the concentration gradient for certain pollutants that was observed in 1996 for Coyote Creek also applicable for the Guadalupe River?
2. Are there pronounced differences in the pollutant profiles between the two interface stations?
3. Are there pronounced differences between high- and low-flow periods between the interface stations and those in the Estuary?
4. Which factors may influence the findings?

This article describes a two-year data set which should not be interpreted as a definitive assessment of Coyote Creek or Guadalupe River watershed contributions to the Estuary. However, the data will be used in designing a new monitoring component of the RMP that is scheduled to take effect some time in 2001, and that meets the new objective of determining loading pathways of contaminants to the Estuary.

Sampling Plan

In 1997, a second sampling station was selected in the lower reach of the Guadalupe River known as Alviso Slough (BW15). The South Bay Yacht Club graciously provided access to their dock for sampling purposes, and their assistance is gratefully acknowledged. The Coyote Creek sampling station at Standish Dam (BW10) was also occupied in 1997. That station is located very close to Dixon Landing Road and Highway 880 where the city boundaries of Fremont, Milpitas, and San Jose converge (Figure 6.1). Both locations are within the tidal prisms. During the wet season, runoff amounts are large enough to dominate the

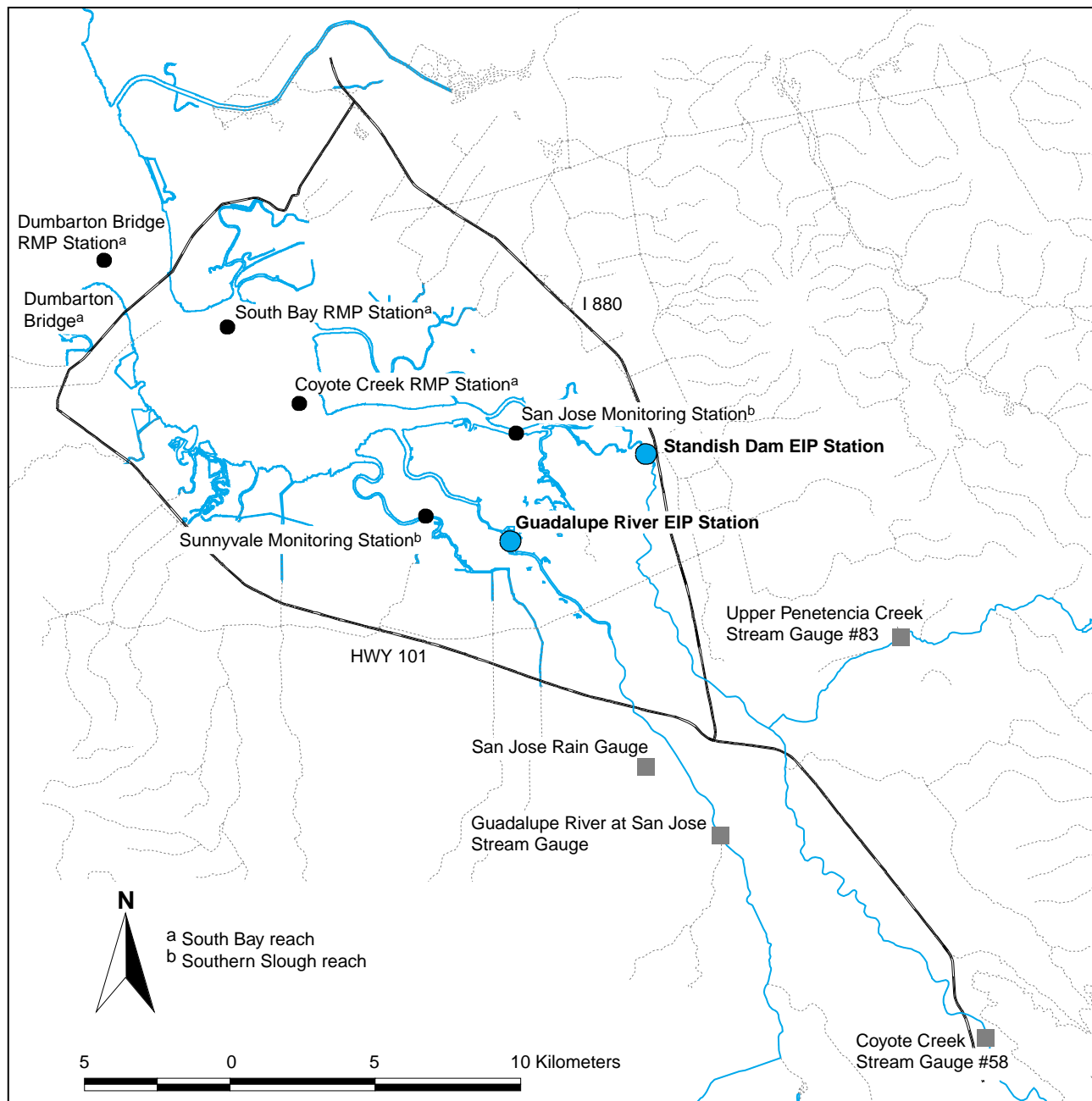


Figure 6.1. Map of Estuary Interface Pilot Study stations.

pollutant signal, while during the dry season, water sampled at both stations was a brackish mix of both freshwater runoff and Bay water. Both sites were selected for their accessibility, location in the brackish transitional zone, and the fact that sediment deposition and accumulation was likely to occur. The winter of 1996/97 was very unusual in that rains produced extremely high runoff during December and January, while very little precipitation occurred during subsequent months.

The same parameters in water and sediment were measured here as in the Estuary at approximately the same times (late February/early March, late April, and early August). The sampling methodology for water was similar to that employed by the RMP. Sediment was sampled from the creek bank at low tide using a Dykon[®]-coated scoop (see *Appendix A: Methods*). Any surface diatom layer was removed before collecting the top five centimeters of an area approxi-

mately the same size as the van Veen grab used at the Estuary stations. Each sample was then homogenized. The homogenate was divided into aliquots for analysis of trace elements, trace organics, conventional sediment parameters such as grain size, total nitrogen, and total organic carbon (TOC), and for archiving. Parameters analyzed in water included trace elements and trace organic contaminants, ammonia, chlorophyll *a*, dissolved organic carbon, hardness, nitrates, nitrites, pH, phaeophytin, phosphate, silicates, and total suspended solids (TSS). Parameters analyzed at the bottom as well as the top of the water column included conductivity, dissolved oxygen (DO), salinity, and temperature.

Flows

Because there are no currently operating stream gauges near the mouth of Coyote Creek, its flow was calculated by combining flow data from the U.S. Geological Survey (USGS) Stream Gauge Station 58 on Coyote Creek at Edenvale and Station 83 on Upper Penetencia Creek, a major tributary to Coyote Creek. This combined value is the best available estimate for Coyote Creek discharge into the South Bay in lieu of a stream gauge closer to the mouth of the creek. A USGS stream gauge currently operates on the Guadalupe River at San Jose approximately 11 km from the Guadalupe River Station, with no major tributaries between it and the station. Values from this stream gauge station were used for stream flow calculations. Rainfall data for both Standish Dam (BW10) and Guadalupe River (BW15) were taken from the San Jose rain gauge, which is the rainfall data source used in the Santa Clara Valley Non-Point Source Pollution Program (SCVNSS, 1991).

Stream and rain gauge locations are found in Figure 6.1. Flows peaked at an estimated 3,500 cubic feet per second (cfs) at Guadalupe River during January floods. The estimated flow on Coyote Creek during the January

flood was approximately 5,300 cfs. Because of the high runoffs, Anderson Reservoir filled to capacity by January 23, began discharging over its spillway to Coyote Creek, and continued to do so throughout the remainder of the month. By February 1 flows had receded to where the reservoir was again below the spillway. Flows during the 1997 sampling were higher than those of 1996 (see Table 6.1). There are four reservoirs which empty directly or indirectly to the Guadalupe River: Calero, Almaden, Guadalupe, and Lexington. Calero Reservoir did not discharge over its spillway during the 1996/97 wet season. Almaden Reservoir spillway discharge occurred from January 1 through February 16, and from May 12 through May 30. Guadalupe Reservoir spillway discharge occurred from January 1 through January 8, and again from January 22 through January 27. Lexington Reservoir spillway discharge occurred from January 3 through January 8, from January 10 through January 31, and from April 1 through April 9. Stream and rain gauge hydrographs for Coyote/Penetencia creeks and Guadalupe River are shown in Figure 6.2.

Results and Analyses

All available data from this Pilot Study have been included in the data tables (see *Appendix C: Data Tables*). Total silver concentrations are not available. Total lead and dissolved silver concentrations are available for the wet season sampling period only. Dissolved lead concentrations are not available for the dry season. No values for silver

Table 6.1. Flows at the gauging stations on the EIP streams and tributaries.

Date	Station #58, Coyote Creek at Edenvale cfs	Station #83, Upper Penetencia Creek at Dorel Dr. cfs	Guadalupe River at San Jose cfs	Sample Type
3/4/96	725.00	64.00	567.00	water
3/8/96	813.00	33.00	461.00	sed
4/16/96	44.00	7.50	42.00	water
8/12/96	1.70	0.51	13.00	sed
8/16/96	2.20	0.47	15.00	water
2/7/97	487.00	22.00	253.00	water, sed
4/9/97	11.00	7.00	23.00	water
8/1/97	9.60	0.08	12.00	water
8/6/97	3.20	0.07	13.00	sed

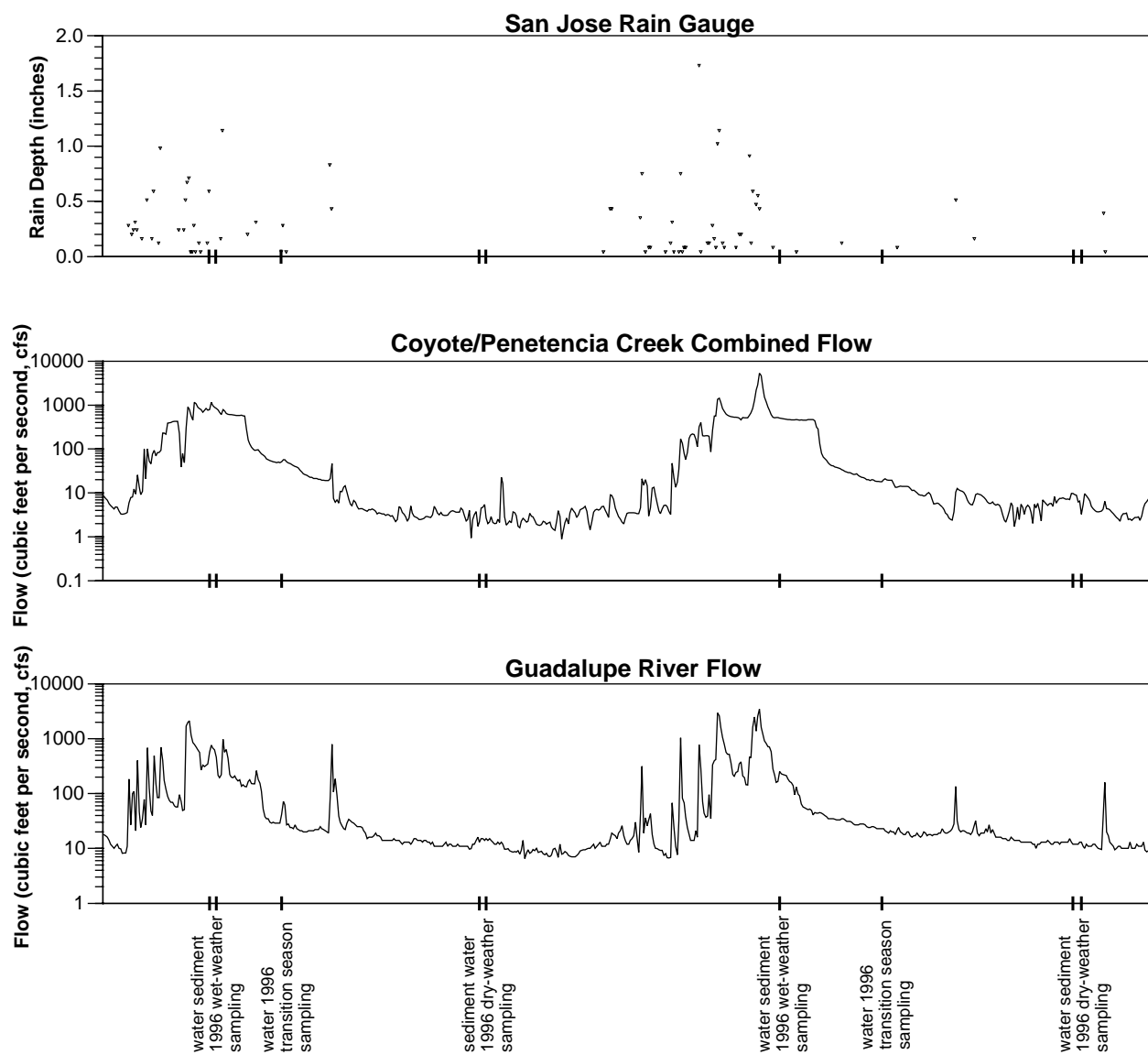


Figure 6.2. Estuary Interface Pilot Study hydrographs.

concentrations in sediment for the sampling event in late summer are reported due to blank contamination. Statistical analyses were performed using SAS (SAS Institute, 1990).

With a second year of data available for the Standish Dam sampling station, as well as a year's worth of data from the Guadalupe River station, additional analyses were performed. Potential seasonal differences between the EIP stations were examined, as were comparisons between years for the Standish Dam station. The mean values of the combined EIP stations (1996-97 Standish Dam and 1997 Guadalupe River) were pooled and compared with those of the other

San Francisco Bay reaches during the same time period. Bay reaches are defined in the *Sediment Introduction*. They are, in addition to the EIP stations, the Southern Sloughs, South Bay, Central Bay, Northern Estuary, and Rivers. Significant difference of means was determined using one-way ANOVA and Tukey-Kramer Honestly Significant Difference (HSD; $p = 0.05$). Stream flow and rainfall data were examined in relation to contaminant concentrations measured in the EIP. Normalizing factors for contaminant concentrations in sediment were determined and used to account for possible variations in concentrations. It should be noted that the observed sediment

concentrations are heavily influenced by flow conditions prior to sampling. During low-flow periods, sediment accumulates in the flat, low-energy reaches of the two creeks and is dominated by small particles in the clay-sized fraction. With the advent of the rainy season, flow velocities increase, thereby scouring the creek beds and banks and carrying smaller-sized particles into the Bay. At the time of the wet-season sampling events in mid-winter, the sediment accumulated during the low-flow periods had likely already been mobilized (see Figure 6.2) for EIP sampling in relation to rainfall and stream flow hydrographs.

Water Metals

Figure 6.3 shows the concentrations of dissolved trace metals in water. The wet season transitional sampling period (April, Cruise 14), showed the highest concentrations of most dissolved metals in the EIP stations, with the exception of mercury from the wet-season sampling (January, Cruise 13). Selenium was consistently higher at the Guadalupe River station for all samples; zinc was higher, and nickel slightly higher, at Standish Dam in the spring sampling. Concentrations of all dissolved trace metals except selenium were higher at Standish Dam in the 1997 sampling year than in 1996. The mean of the pooled reaches was significantly higher for the EIP stations than at any of the other Estuary reaches for selenium and zinc (one-way ANOVA, $p = < 0.0001$).

Figure 6.4 shows the concentrations of total trace metals in water. A similar seasonal pattern was found in the total trace metal concentrations as was found in the dissolved fraction. The wet-season transitional sampling period showed the highest concentrations in both EIP stations with the exception of selenium in both stations, and chromium, copper, and nickel at the Standish Dam station. The Guadalupe River station showed consistently higher concentrations of all total trace metals in the wet season transitional sampling period. Concentrations of all total trace metals were higher at Standish Dam in the 1997 sampling year than in 1996. The pooled mean was significantly higher for the EIP stations for

selenium (one-way ANOVA, $p = < 0.0001$) than at any of the other Estuary reaches. The pooled mean values at the EIP stations for arsenic, mercury, nickel, and zinc were not significantly different from those for the Southern Sloughs, but were significantly higher than those of the other Estuary reaches (one-way ANOVA, $p = < 0.0001$).

Water Organics

Figure 6.5 shows the concentrations of dissolved trace organics in water. Dissolved PAHs and chlorpyrifos were higher in the spring samples at both EIP stations, and for chlordanes the Guadalupe River station concentrations were higher. DDT and dieldrin were higher at the Standish Dam station in the summer. Concentrations of dissolved PCBs, diazinon, and chlordanes were higher in the 1996 sampling year, while dieldrin, chlorpyrifos, and PAHs were higher in the 1997 sampling year at the EIP stations. The mean values of the pooled reaches were significantly higher for the EIP stations than the Estuary reaches for DDTs and chlordanes (one-way ANOVA, $p = < 0.0001$). The pooled mean value at the EIP stations for dieldrin was not statistically different from that of the River reach, but was significantly higher than those of the other Estuary reaches (one-way ANOVA, $p = < 0.0002$). The pooled mean values at the EIP stations for chlorpyrifos and PAHs were not significantly different from those for the Southern Sloughs, but were significantly higher than those of the other Estuary reaches (one-way ANOVA, $p = < 0.0001$).

Figure 6.6 shows the concentrations of total trace organics in water. DDTs, chlordanes, and dieldrin dominated in one or both of the EIP stations. Concentrations of dieldrin and PAHs were higher in the 1996 sampling year at the EIP stations. The mean values of the pooled reaches were significantly higher for the EIP stations than the Estuary reaches for DDTs and chlordanes (one-way ANOVA, $p = < 0.0001$). The pooled mean value for PAHs was not significantly different between the EIP stations and the Southern Sloughs, but was significantly higher than mean values at the other Estuary reaches (one-way ANOVA, $p = < 0.0001$).

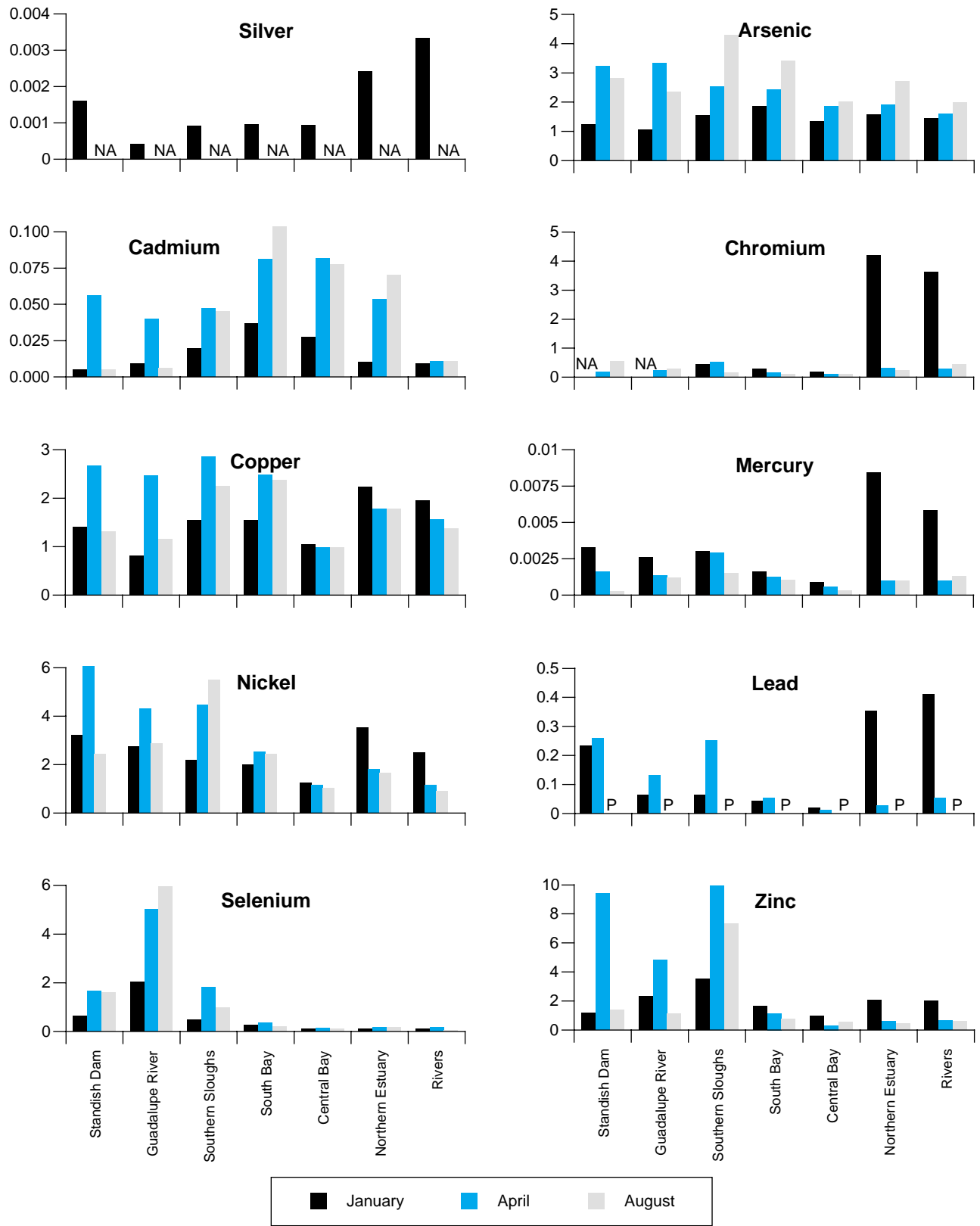


Figure 6.3. Concentrations of dissolved trace elements in water at the EIP sites compared with RMP stations averaged by Bay reach, 1997. NA = not analyzed. P = data pending. All concentrations are in parts per million (ppm).

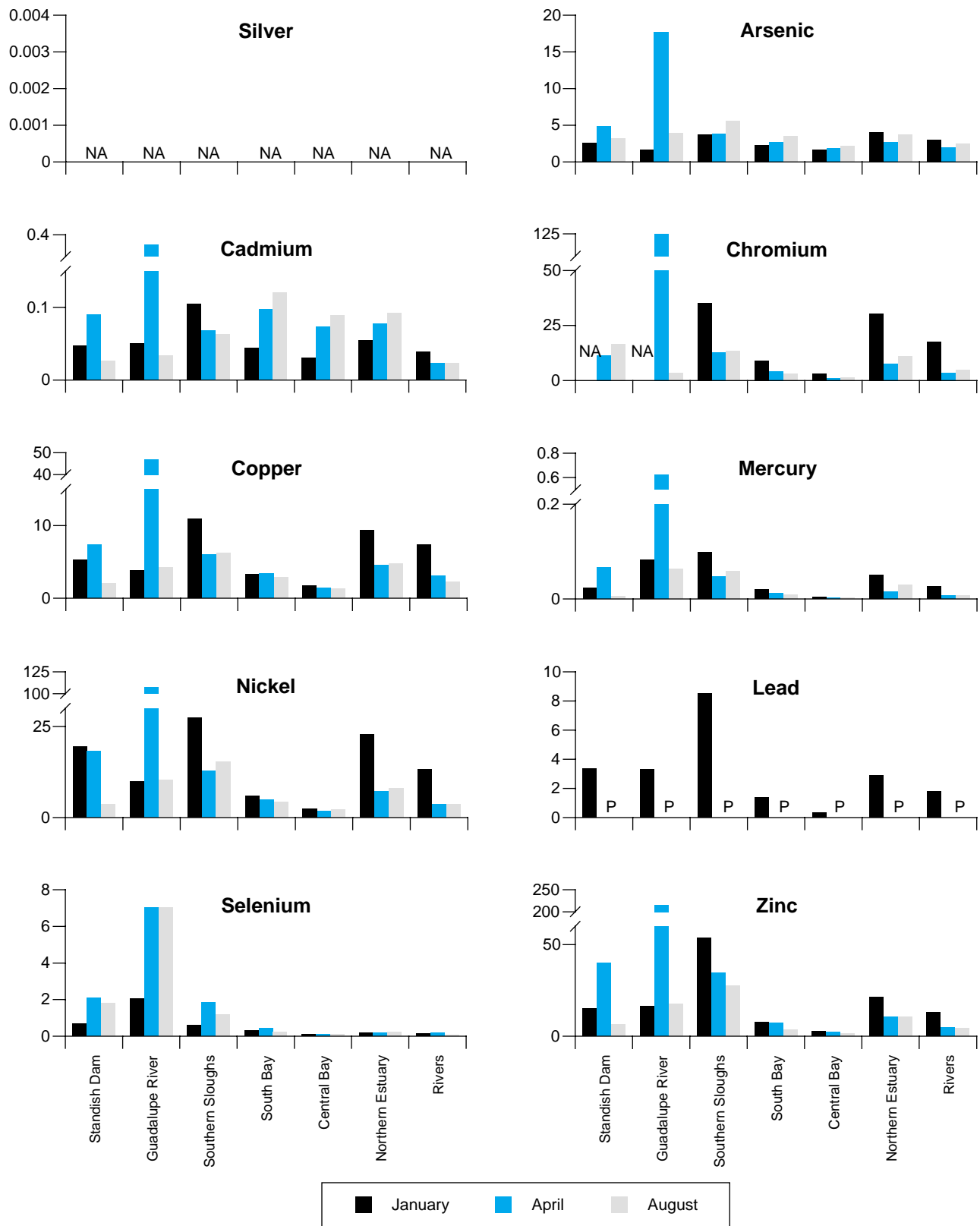


Figure 6.4. Concentrations of total trace elements in water at the EIP sites compared with RMP stations averaged by Bay reach, 1997. NA = not analyzed. P = data pending. All concentrations are in parts per million (ppm).

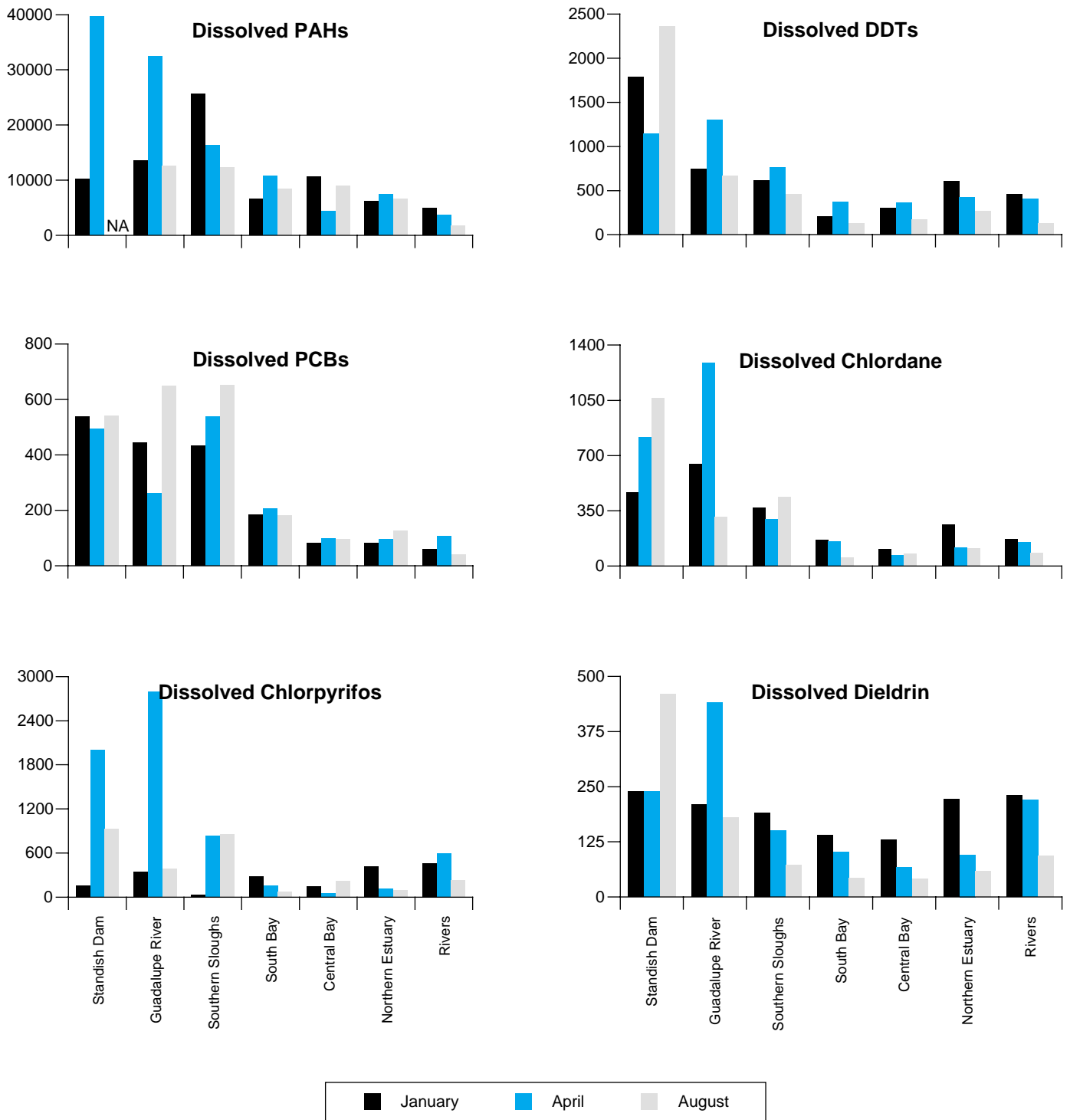


Figure 6.5. Concentrations of dissolved trace organics in water at the EIP sites compared with RMP stations averaged by Bay reach, 1997. NA = not analyzed. All concentrations are in parts per quadrillion (ppq). Concentrations of diazinon were below detections in the dissolved fraction of water at most stations, and therefore not represented.

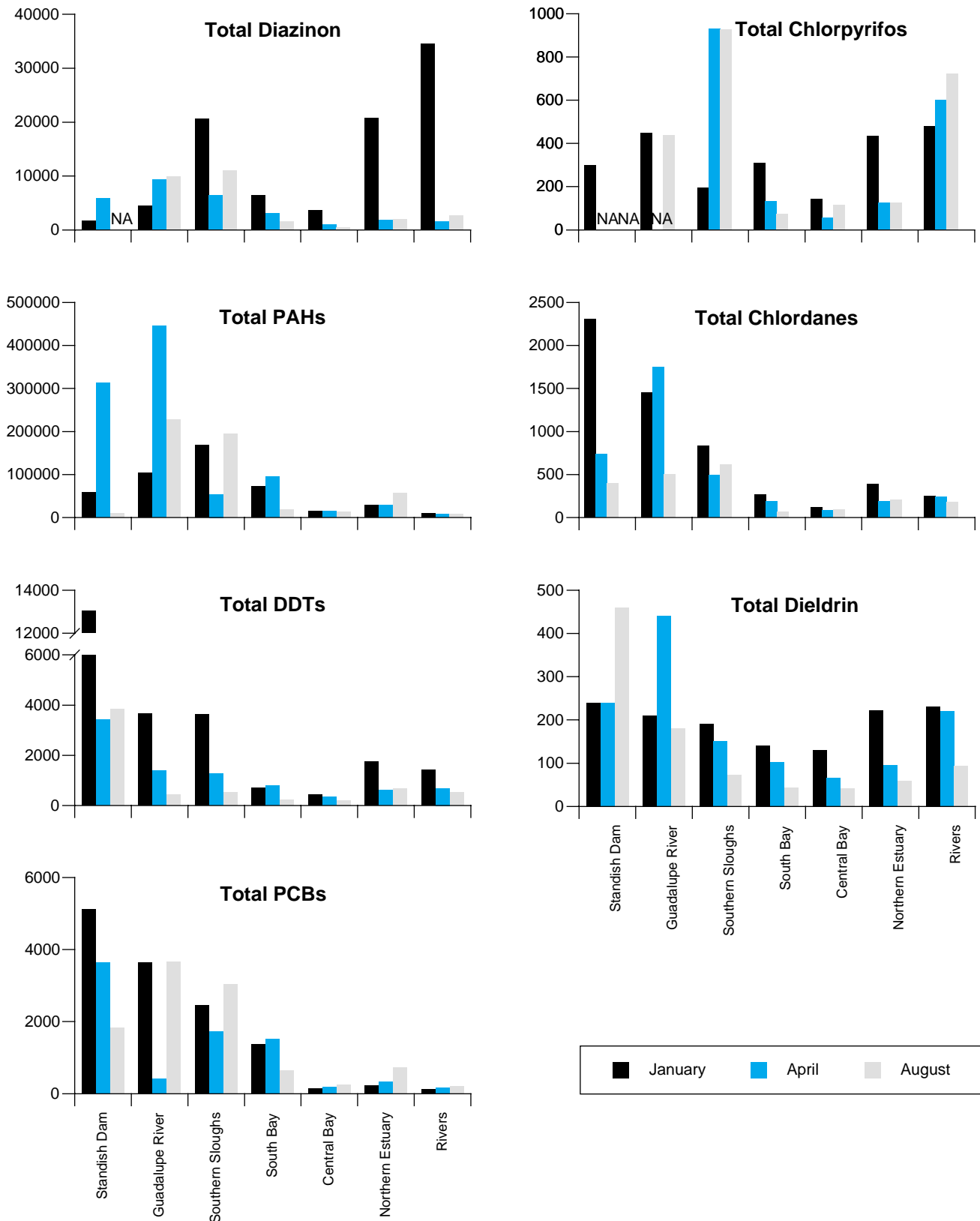


Figure 6.6. Concentrations of total trace organics in water at the EIP sites compared with RMP stations averaged by Bay reach, 1997. NA = not analyzed. All concentrations are in parts per quadrillion (ppq).

Sediment Metals

All raw trace metal concentrations at the EIP stations, except selenium, were higher in the 1997 sampling year compared to 1996. The mean raw concentrations of trace metals at the EIP stations were not significantly different than those of the other reaches, with the exception of cadmium. The mean raw concentrations of cadmium at EIP and Southern Slough stations were not significantly different from each other but as a group these were significantly higher than concentrations at the other reaches (one-way ANOVA, $p < 0.0001$). The EIP, Southern Sloughs, and South Bay stations were not significantly different from each other, but as a group exhibited significantly higher metals concentrations than the other Bay reaches (one-way ANOVA, $p < 0.0002$).

Sediment Contaminant Normalization

A common practice used to improve the sensitivity of comparing trace element and organic contaminant concentrations in sediments is to normalize them to some sediment constituent which is unaffected by human activities such as contaminant input (Luoma, 1990; Hanson, 1993; Daskalakis and O'Connor, 1995). Some of the constituents commonly used include aluminum, iron, TOC, and grain size (Daskalakis and O'Connor, 1995). Statistically speaking, these are *independent variables*, i.e. their concentrations are independent of the variable being examined, the *dependent variable*. The dependent variable in this case is defined as the organic or trace element contaminant whose concentration is dependent on the concentrations of the independent variable(s) found in the sediment.

Since all four of the independent variables mentioned above were analyzed in this pilot study, the first step in the normalization process was to determine how they were correlated with each other. If there was a high correlation between the four independent variables, it would then be possible to reduce the group to a single representative normalizing analyte. This was indeed the case. A Pearson product-moment pair-wise correlation was used to determine if there was a signifi-

cant linear relationship between the variables. Aluminum was significantly correlated with iron ($r = 0.89$; $p = 0.0001$), with clay ($r = 0.74$; $p = 0.0001$; a surrogate for grain size), and with TOC ($r = 0.66$; $p = 0.0001$). It was, therefore, chosen as the normalizing variable.

The next step was to calculate correlation coefficients for aluminum and the trace elements and organic contaminants. This was done using the Pearson product-moment pair-wise correlation. Chromium, copper, nickel, lead, selenium, and zinc had a correlation value r of at least 0.60 ($p = 0.0001$). Mercury was more closely correlated with TOC than with aluminum ($r = 0.57$; $p = 0.0001$). Silver, cadmium, and total chlordanes, PAHs, PCBs, and DDTs had lower correlations ($r < 0.50$) with both aluminum and TOC. Interestingly, TOC was not significantly correlated with any of the organic contaminants in the data set, which is contrary to what would be expected. All available 1997 RMP observations ($n = 50 \leq 102$, depending on the analyte) were used in the above correlation calculations. The r values are found in Table 6.2.

Table 6.2. Pearson correlation coefficients r .

Pearson correlation coefficient (r) of aluminum and			
	r	n	p
Cu	0.7983	52	0.0001
Cr	0.7598	52	0.0001
Se	0.7391	52	0.0001
Ni	0.6166	52	0.0001
Zn	0.6085	52	0.0001
Pb	0.5927	51	0.0001
Hg	0.5059	52	0.0001
Cd	0.3885	52	0.0044
PAHs	0.2896	51	0.0393
DDTs	0.1212	49	0.4068
PCBs	0.0456	45	0.7662
Ag	-0.0419	50	0.7728
Chlordanes	0.0121	50	0.037
Pearson correlation coefficient (r) of TOC and			
	r	n	p
Cu	0.6977	51	0.0001
Se	0.6935	51	0.0001
Al	0.6645	51	0.0001
Pb	0.6000	50	0.0001
Hg	0.5719	51	0.0001
Ni	0.5451	51	0.0001
Cr	0.5258	51	0.0001
DDTs	0.4373	48	0.0019
Zn	0.3974	51	0.0039
Cd	0.3330	51	0.0169
Ag	0.3166	49	0.0267
PAHs	0.2685	50	0.0593
Chlordanes	0.1954	20	0.4091
PCBs	0.1780	44	0.2476

Now it is possible to calculate an adjusted (i.e., normalized) value which takes into account these independent variables. This value is commonly expressed as a ratio of the contaminant concentration for which there was a significant correlation divided by the concentration of Al (or in the case of Hg with TOC) at each site. Figure 6.7 shows normalized values for the 1997 data compared with the corresponding raw values.

Figure 6.8 shows the concentrations of all available trace metals in sediment. Raw value concentrations at the Standish Dam station were higher in the summer than in the winter for all trace metals. However, when normalized for aluminum, all trace metals at this station except chromium were higher in the winter in relation to summer. Looking at raw value concentrations, there were no predominant seasonal differences at the Guadalupe River station except for mercury, which was higher in the winter. However, when normalized for aluminum, trace metals were higher in the winter sampling period for chromium, copper, nickel, lead, selenium, and zinc. These results are not surprising, since high flows prior to wet-season sampling had removed the finer particle sizes that generally contain greater contaminant mass per unit weight than larger sediment particles. Therefore, the relative concentrations of these contaminants, after normalizing for aluminum, were greater in the winter sampling period with its greater hydrographic activity.

Sediment Organics

Figure 6.9 shows the concentrations of trace organics in sediment. Concentrations of PCBs, DDTs, and chlordanes were higher in wet-season samples compared to those collected during the dry season, but total PAHs were higher in the dry-season samples. Because dieldrin was below the detection limit at most of the stations, it was not included in these analyses. As in 1996, the 1997 sampling year showed that EIP stations had the highest concentrations of DDTs and chlordanes. There was no significant difference in concentrations of PAHs or PCBs at Standish Dam in the 1996 sampling season compared with 1997. Chlordanes were higher, and DDTs slightly higher

in 1997. There was no difference in the mean concentration of PAHs at the Estuary interface stations compared with the other Bay reaches. The mean concentrations of total chlordanes was significantly higher at the EIP stations than the other Bay reaches (one-way ANOVA, $p = < 0.0001$). The mean concentrations of total DDTs at the EIP stations were significantly higher than concentrations at the other reaches (one-way ANOVA, $p = < 0.0001$).

PCB Fingerprinting

Analysis of the congener spectrum of PCBs to discern source, fate, and transport patterns has been undertaken in a number of studies (van Bavel, 1997; Johnson *et al.*, 1998). A congener spectrum of this sort is often called a "fingerprint". PCB fingerprints were generated from samples collected at the EIP stations and representative stations in all reaches of the Bay, for the dissolved and particulate fractions of water and for sediments, for all cruises.

Similar patterns of higher molecular weight congeners dominated in the EIP and South Bay in both the water fractions and the sediments. These patterns were distinctly different from those measured in the rest of the Bay, which consisted of higher percentages of the lower weight congeners, and lower overall concentrations. A concentration gradient can even be seen between the EIP stations, which are higher, and San Jose (C-3-0), the representative South Bay station. This suggests a possible ongoing source load near the EIP stations, and a mixing of the PCB congener signal away from the watersheds. An example of a PCB fingerprint is shown in Figure 6.10.

The concentration gradients found in the water fractions between the EIP stations and South Bay representative station San Jose (C-3-0) were not seen in the sediment samples. On the contrary, the concentrations of PCB congeners at San Jose (C-3-0) were at least as high if not higher, which suggests that this area could be a PCB sink for sediments transported away from the EIP stations. There was, however, a discernible sediment concentration gradient between Coyote Creek (BA10) and the rest of the South

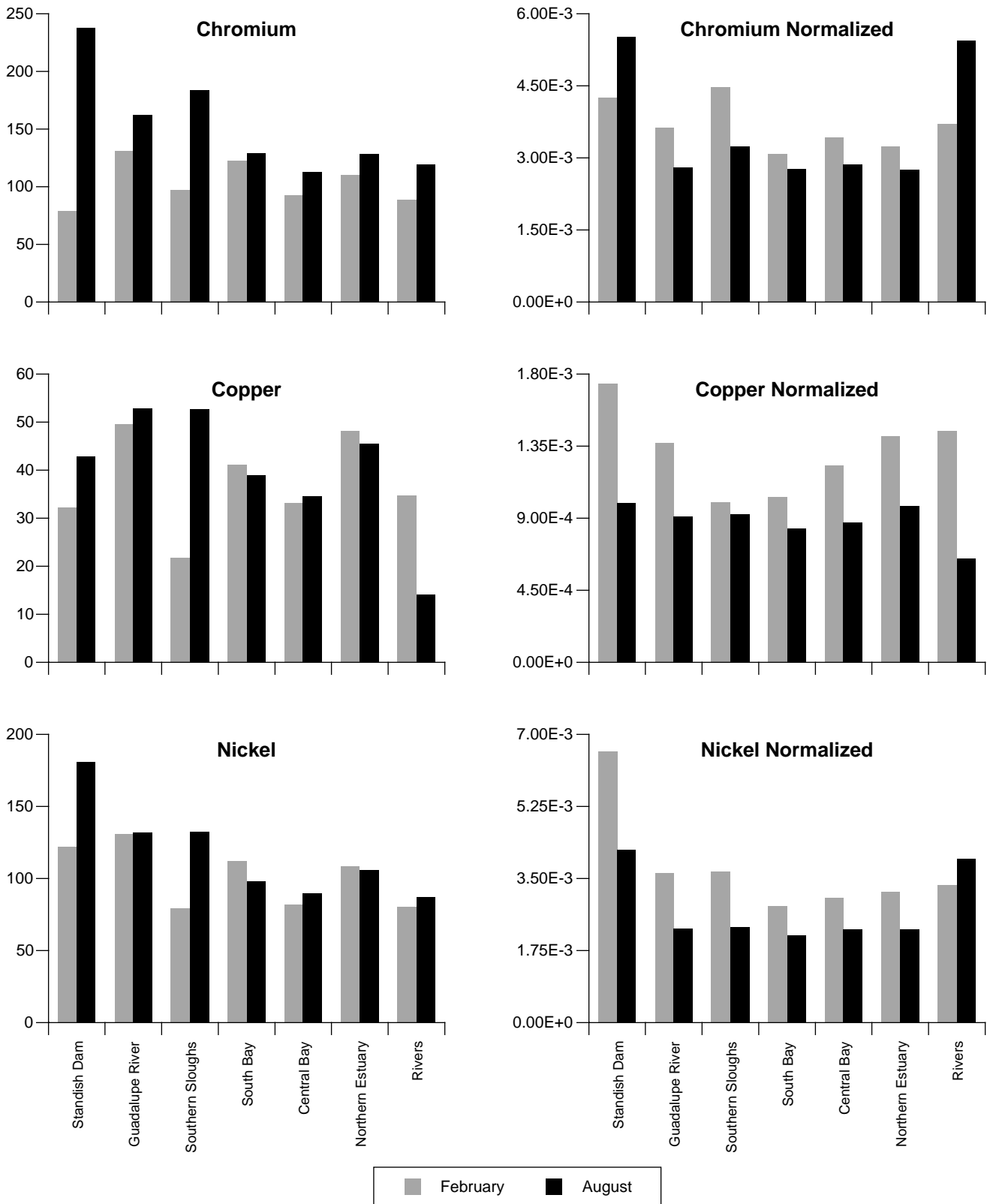


Figure 6.7. Normalized versus non-normalized values. Concentrations of trace elements in sediments for the Standish Dam and Guadalupe River sites compared with RMP stations averaged by Bay reach, 1997. Non-normalized concentrations in parts per million (ppm). Normalize values ratio of trace element concentration/concentration of aluminum.

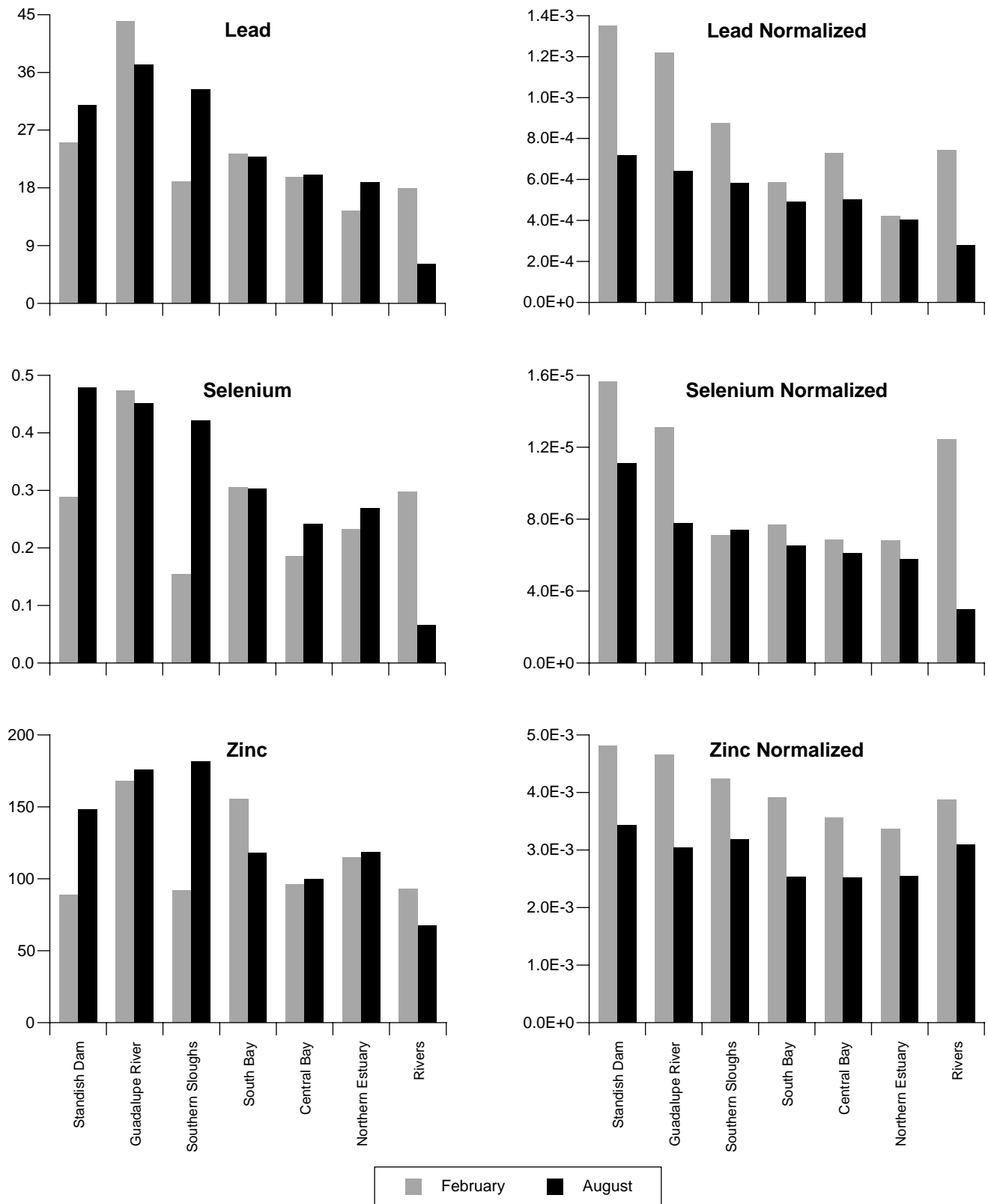


Figure 6.7 (continued). Normalized versus non-normalized values. Concentrations of trace elements in sediments for the Standish Dam and Guadalupe River sites compared with RMP stations averaged by Bay reach, 1997. Non-normalized concentrations in parts per million (ppm). Normalize values ratio of trace element concentration/concentration of aluminum.

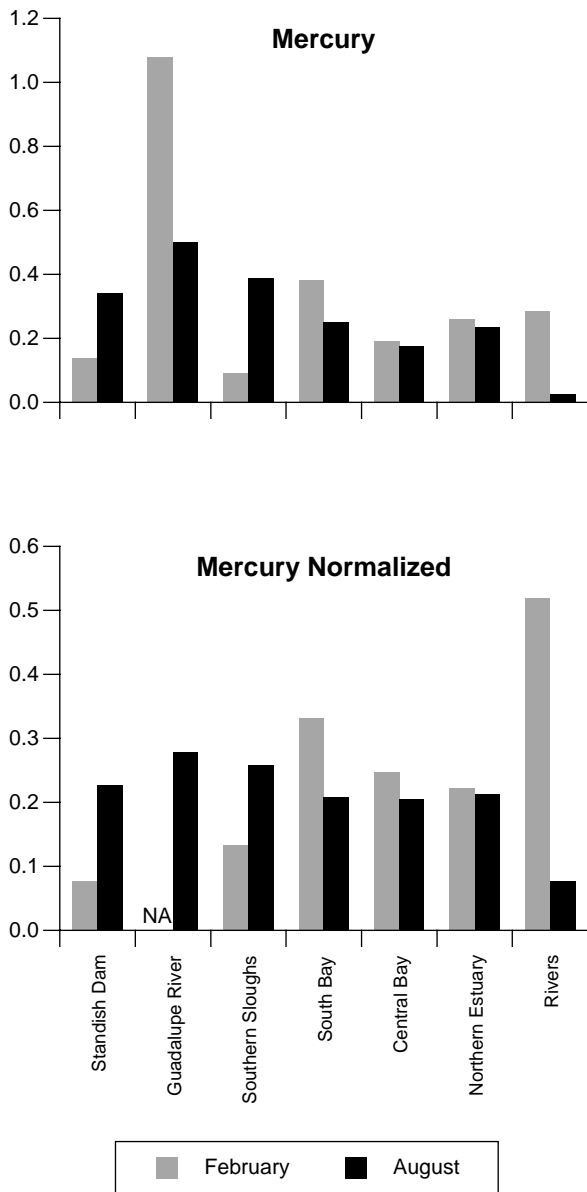


Figure 6.7 (continued). Normalized versus non-normalized values. Concentrations of trace elements in sediments for the Standish Dam and Guadalupe River sites compared with RMP stations averaged by Bay reach, 1997. NA = not analyzed. Non-normalized concentrations in parts per million (ppm). Normalize values ratio of trace element concentration/percent total organic carbon.

Bay stations. Furthermore, the South Bay as a whole exhibits higher PCB concentrations in sediment than do the other Estuary reaches and the EIP stations. Similar gradient patterns are seen in other localized watershed sampling efforts in the Bay. Preliminary data from the San Leandro Bay Project (see Daum and Thompson, 1998) strongly suggest localized inputs of PCBs, as well as PAHs, and some trace metals.

Water Particulates and Sediments

In order to assess whether the Coyote Creek or Guadalupe River watersheds contribute significant sources of trace metal or organic contamination, the concentrations of these contaminants which are on the particulate fraction of the water coming into the Bay must be determined. This was done for three trace metal contaminants of concern: copper, mercury, and nickel. Particulate concentrations for each metal were calculated by subtracting the filtered (dissolved) concentration from the unfiltered (total), with the difference being the particulate fraction. Dividing this value by the total suspended solids (TSS) concentrations gave the normalized water particulate concentration. Each one of these measurements has an associated uncertainty, which can be calculated. The water particulate values from the EIP stations were then compared with the sediment and water particulate values in the Southern Sloughs and South Bay stations to determine if the EIP station concentrations were higher compared to those found in the other stations. Figure 6.11 shows these comparisons for the wet- and dry-season sampling events.

Sampling during the wet season showed roughly the same concentrations of water particulates and sediments for the EIP, Southern Sloughs, and South Bay stations for copper and nickel. The Guadalupe River station showed elevated levels of mercury. Results for the dry weather sampling were striking. Water particulate concentrations were much higher in all three metals and at both Standish Dam and Guadalupe River stations.

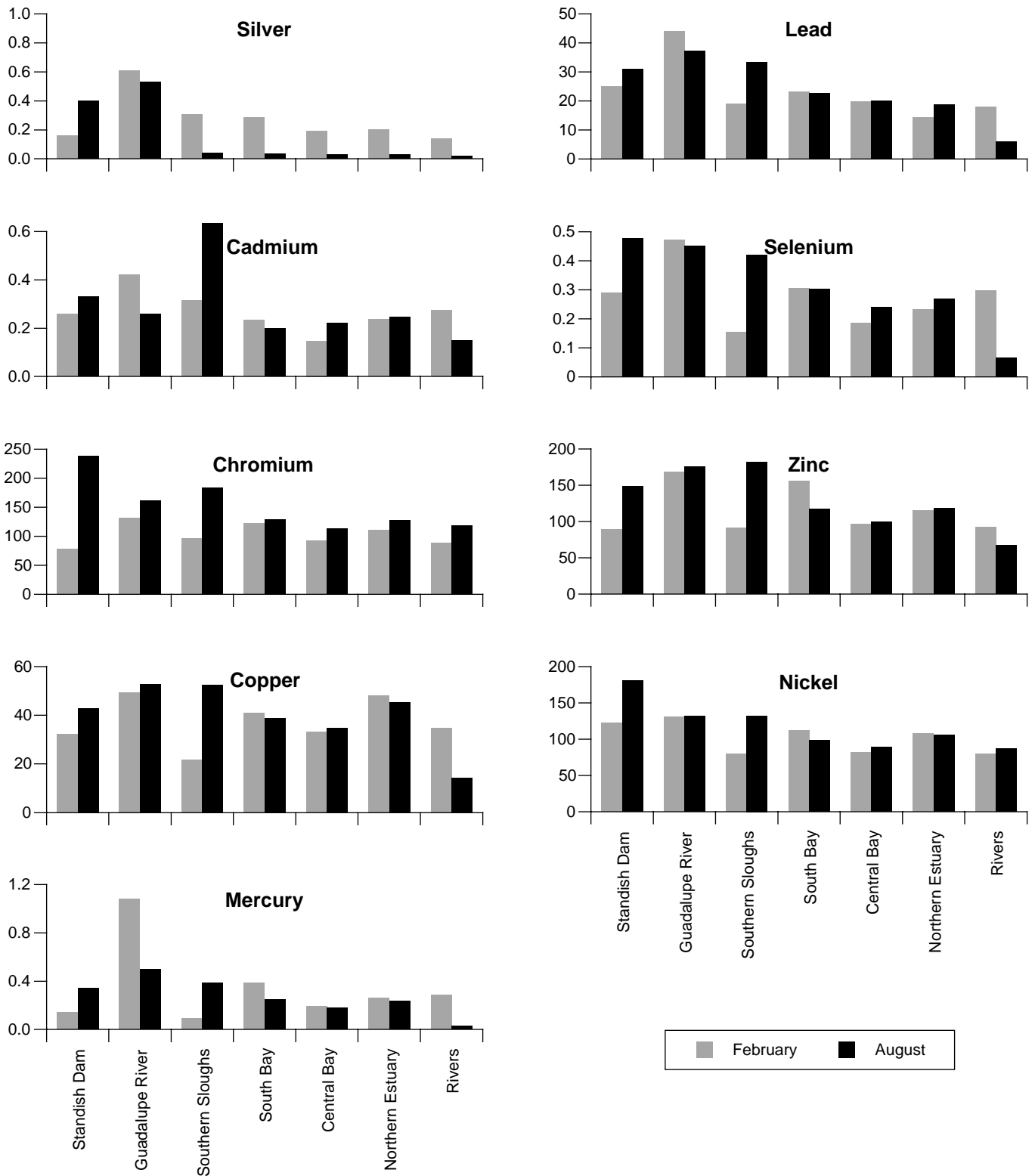


Figure 6.8. Concentrations of trace elements in sediments for the Standish Dam and Guadalupe River sites compared with RMP stations averaged by Bay reach, 1997. All concentrations in parts per million (ppm).

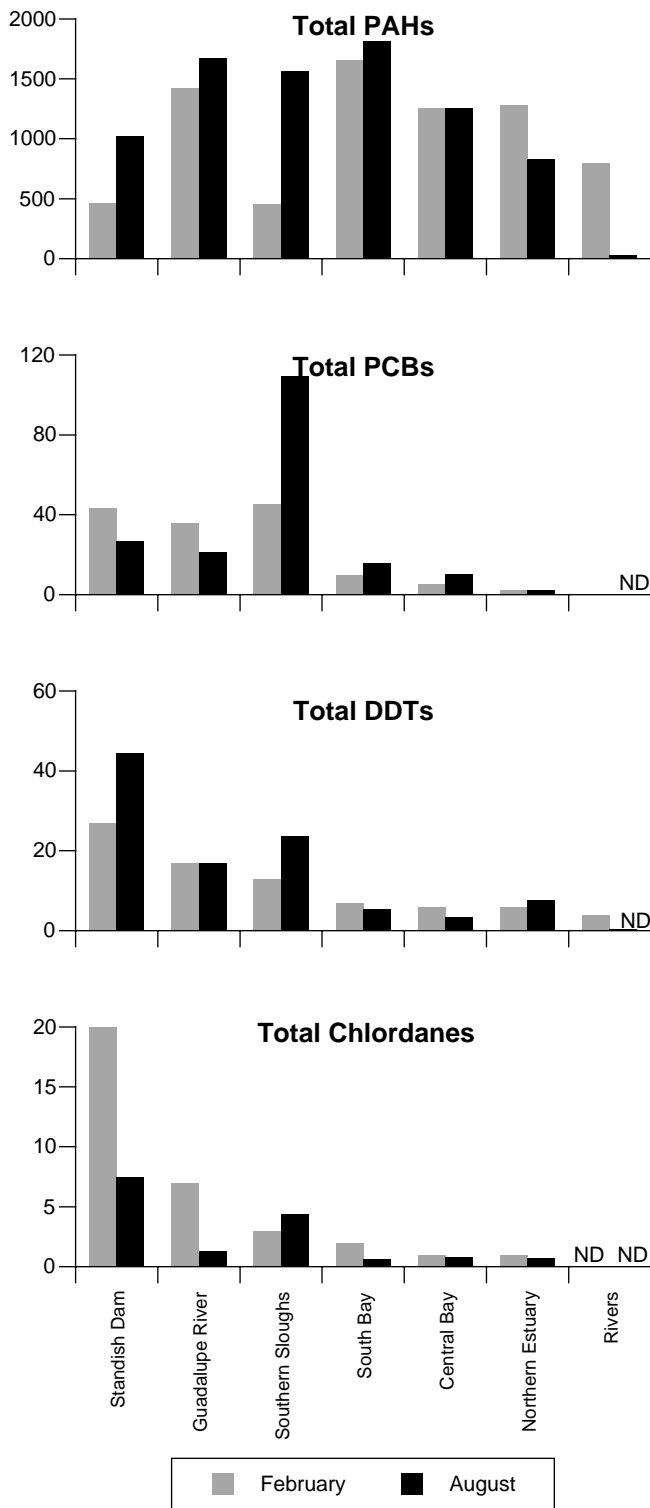


Figure 6.9. Concentrations of trace organics in sediments for the Standish Dam and Guadalupe River sites compared with RMP stations averaged by Bay reach, 1997. All concentrations in parts per billion (ppb). ND = below detection limit. Because dieldrin was below the detection limit at most stations, it was not included.

Conclusions

The second year of the Estuary Interface Pilot Study showed some definite patterns emerging. Although only two years of data have been analyzed, some conclusions can be made. There appear to be similarities in the concentration gradients in both of the EIP stations for many of the contaminants in both the water and sediment fractions. The particulate fraction of water entering the Estuary from the Guadalupe River in the dry season have concentrations of copper, mercury, and nickel which are greatly elevated compared to the respective sediment concentrations of these metals in the Southern Sloughs and South Bay. Hornberger *et al.* (1998) found background levels (i.e., not enriched by human activity) in Grizzly Bay and San Pablo Bay for mercury to be 0.06 ppb +/- 0.01; nickel 82–110 ppb; and copper 23–41 ppb. If the natural background levels in the Coyote Creek and Guadalupe River watersheds are comparable to Grizzly and San Pablo bays, then the incoming particulate metals' concentrations are indeed enriched. More study is needed to determine if this is the case.

It is also probable that copper, lead, and nickel are enriched over background levels in creek sediment, after normalizing for aluminum. The elevated mercury concentrations are probably due to the New Almaden Mine which is located in the Guadalupe River watershed. Results from the Santa Clara Valley Urban Runoff Pollution Prevention Program have indicated that suspended stream sediments are enriched compared to suspended sediments in the South Bay for copper, lead, and nickel among others, which might be contributors to the elevated sediment levels noted here. And formerly widespread use of pesticides, including chlordanes, occurred in both watersheds prior to use restrictions and have been found in urban runoff (BASMAA, 1996; SFEI, 1998).

Specific events such as tidal or storm-influenced shifting water masses, with the resulting pulses of TSS loading, can skew the calculated particulate concentrations for metals and organics. This may explain some of the observed concentration peaks as being artifacts of these events, which are especially acute at the EIP stations. The

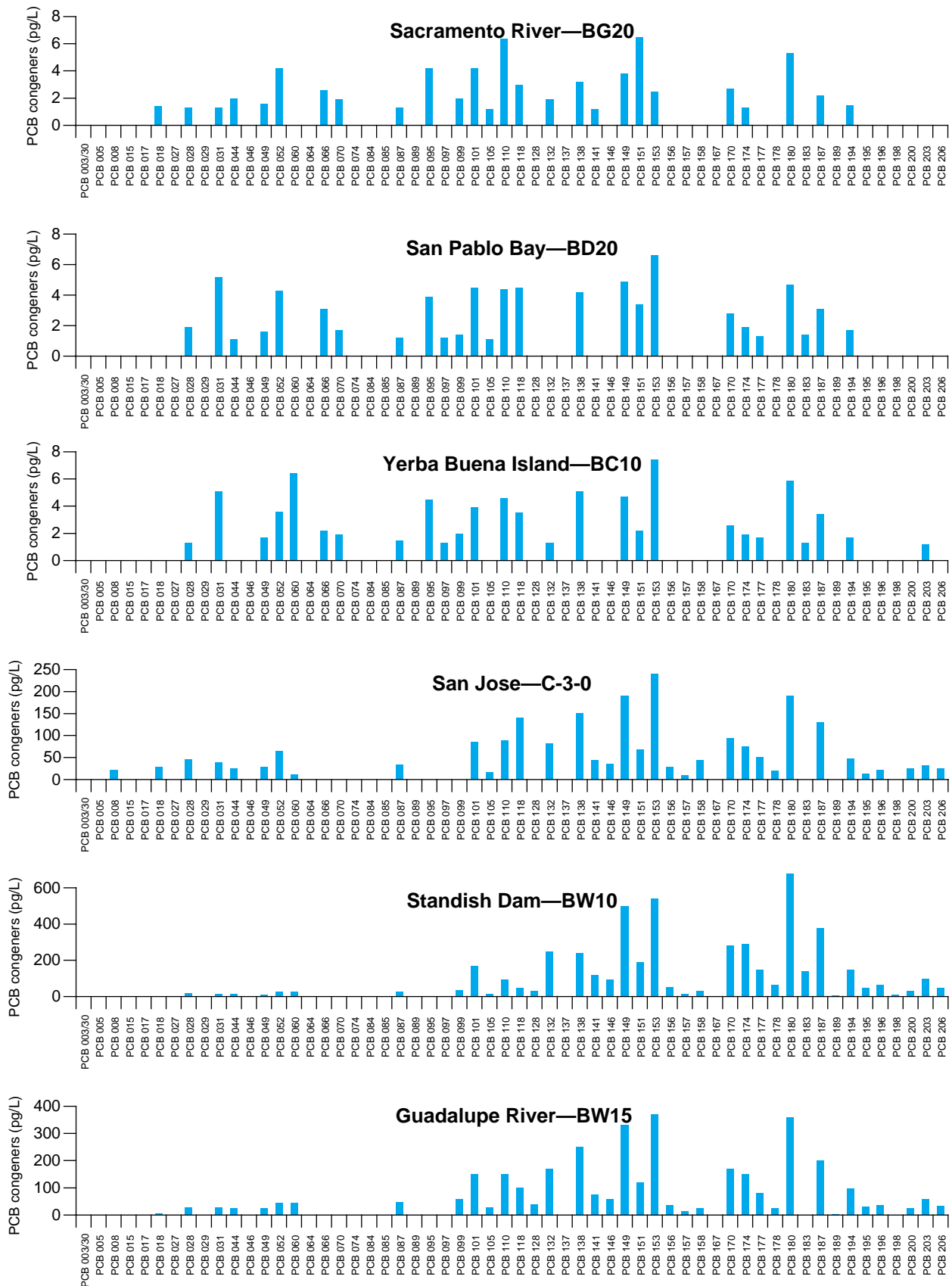


Figure 6.10. PCB fingerprint of the water particulate fraction from the wet season cruise for the Estuary Interface Pilot Program stations and a representative station from each of the reaches.

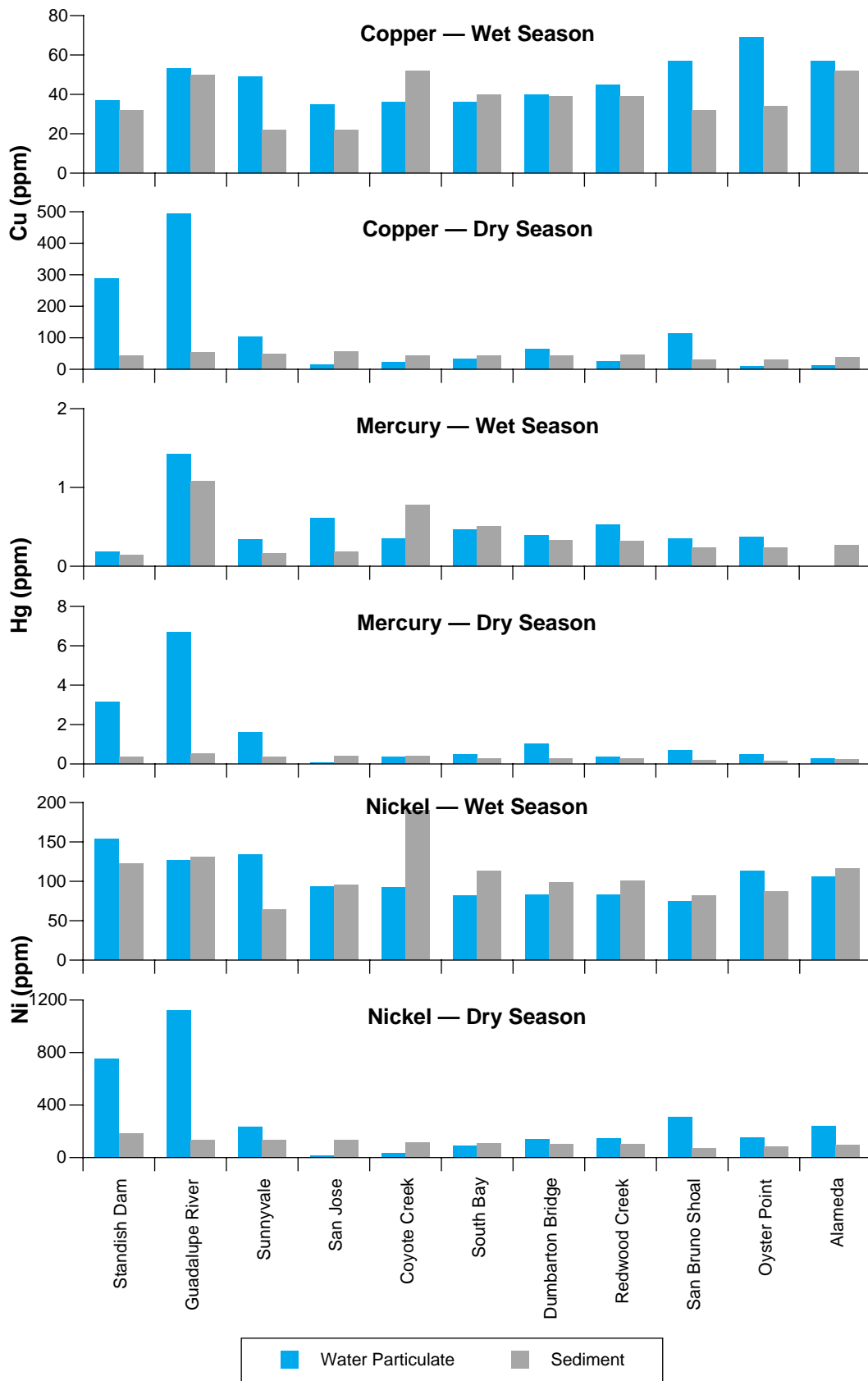


Figure 6.11. Concentrations of trace elements on water particulates and sediments at the Estuary Interface stations compared with the Southern Sloughs and South Bay stations.

RMP Base Program sampling effort is not frequent enough to incorporate these specific conditions, nor is it meant to be. Event-driven sampling, perhaps examining a limited suite of contaminants, could be undertaken to incorporate these conditions. Conversely, avoiding these conditions in the Base Program sampling may enable the collection of more truly representative ambient or background data.

Acknowledgments

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Contaminant Concentrations in Fish from San Francisco Bay, 1997: Summary¹

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Introduction

In 1994 the Bay Protection and Toxic Cleanup Program (BPTCP) performed a pilot study to measure concentrations of contaminants in fish in San Francisco Bay (SFBRWQCB *et al.*, 1995, Fairey *et al.*, 1997). Screening values to identify chemicals of potential human health concern were calculated for the study based on U.S. EPA guidance (U.S. EPA, 1993). The study indicated that there were six chemicals or chemical groups that were of potential human health concern for people consuming Bay-caught fish: PCBs, mercury, DDT, dieldrin, chlordane, and dioxins.

As a result of this pilot study the Office of Environmental Health Hazard Assessment (OEHHA) issued an interim health advisory for people consuming fish from San Francisco Bay (OEHHA, 1994). The advisory states that:

1. Adults should limit consumption of Bay sport fish to, at most, two meals per month.
2. Adults should not eat any striped bass over 35 inches (89 cm).
3. Pregnant women or women that may become pregnant or are breast-feeding, and children under 6 should not eat more than one meal per month, and should not eat any meals of shark over 24 inches (61 cm) or striped bass over 27 inches (69 cm).

The advisory does not apply to salmon, anchovies, herring, and smelt caught in the Bay, other ocean-caught sport fish, or commercial fish. The advice was issued due to concern over human exposure to residues of methylmercury, PCBs, dioxins, and organochlorine pesticides in Bay-caught fish.

As a followup to the 1994 pilot study, an RMP Fish Contamination Committee, including representatives from government agencies, dischargers, and environmental groups, was set up to design a RMP component to measure fish contamination. The RMP Fish Contamination Committee developed two main objectives for the RMP fish contamination monitoring component:

1. To produce the information needed for updating human health advisories and conducting human health risk assessments.
2. To measure contaminant levels in fish species over time to track trends and to evaluate the effectiveness of management efforts.

A five-year workplan for the RMP fish contamination monitoring component was developed in 1997 and included: 1) a core monitoring program that is intended to be conducted every three years, 2) special studies, which are designed to answer questions that were brought up in the pilot study and will lead to a more scientifically sound and

¹This is a shortened version of a report "Contaminant Concentrations in Fish from San Francisco Bay, 1997". The full report is available in hardcopy from SFEI, and on the internet at <http://www.sfei.org>.

cost-effective monitoring program in the future, and 3) development of a study design and survey instruments to measure the rates at which people consume fish caught in San Francisco Bay. This article describes results for the fish tissue core monitoring program and special studies conducted in 1997. The fish consumption study is currently in progress and results will be presented in a technical report in mid-1999.

The core monitoring program targeted seven species that are frequently caught and eaten by Bay fishers and seven popular fishing areas in the Bay (see methods for more details). Special studies included in the 1997 sampling were: 1) collecting and analyzing samples to determine variance among individual fish to assist in the future development of a more cost-effective study design; and 2) a study to determine the difference in contaminant concentrations of fillets of white croaker with and without skin. The second study was designed to determine whether removing the skin from muscle fillets could significantly reduce exposure to organic contaminants. This information should be valuable to public information efforts. Due to space limitations, results of analyses of variance among individual fish (#1 above) are not discussed in this article, but will be included in deliberations concerning design of the sampling to be performed in 2000.

Although the main focus of this study is on human health, it is important to note that the chemicals discussed in this article accumulate in the Bay food web and may also have an effect on other species at higher trophic levels. Studies of piscivorous birds and marine mammals in the Bay have found concentrations of persistent contaminants that appear to be high enough to impair the health of these species (Davis *et al.*, 1997; Davis, 1997; Young *et al.*, 1998).

Methods

The species and fishing locations in the Bay were selected for sampling based on available information on frequencies of catch and consumption by Bay fishers, continuity with the 1994 pilot study, and to provide a broad geographic coverage of the

Bay. The locations sampled are shown in Figure 6.12. Sampling details are provided in Table 6.3.

Fish were collected between May 27, 1997 and July 25, 1997. Special efforts to collect sturgeon only occurred on several days in both March 1997 and October 1997. A complete description of the sampling methods and a detailed cruise report are available from the San Francisco Estuary Institute.

U.S. EPA (1995) defines screening values as concentrations of target analytes in fish or shellfish tissue that are of potential public health concern. Exceedance of screening values should be taken as an indication that more intensive site-specific monitoring and/or evaluation of human health risk should be conducted. Screening values were calculated following U.S. EPA (1995a) guidance. Details about this approach are described in SFBRWQCB *et al.* (1995). A consumption rate of 30 g fish/day that applies to recreational fishers was used in calculating screening values. The only changes in screening values from the pilot study were for mercury and PCBs. A screening value of 0.233 $\mu\text{g/g}$ wet for mercury was applied to the 1997 data based on an updated reference dose (U.S. EPA, 1995b). The mercury screening value applied to the 1994 data was 0.140 $\mu\text{g/g}$ wet (SFBRWQCB *et al.*, 1995). A screening value of 23 ng/g wet for PCBs was applied to the 1997 data based on an updated cancer slope factor (U.S. EPA, 1998). The PCB screening value applied to the 1994 data was 3 ng/g wet (SFBRWQCB *et al.*, 1995).

Summary and Conclusions

Comparisons to Screening Values

As found in the 1994 pilot study (SFBRWQCB *et al.*, 1995, Fairey *et al.*, 1997), persistent toxic chemicals in Bay fish were found at concentrations of potential human health concern in 1997 RMP sampling (Tables 6.4 and 6.5).

Mercury exceeded the screening value in 44 of 84 samples. All collected samples of leopard shark and striped bass exceeded the mercury screening value. For some species, including leopard shark and striped bass, the older and larger fish accumulated higher mercury concentrations. Adjust-

Table 6.3. Fish contamination core monitoring program sampling design. Empty boxes were targeted but fish could not be collected.

Species	White Croaker	Shiner Surfperch	Jacksmelt	Leopard Shark	Striped Bass	California Halibut	White Sturgeon
Target # size classes	1	1	1	3	3	2	2
Target # fish per composite	5	20	5	3	3	3	3
Target size range (cm)	20-30	10-15	21-30	Small: 90-105 Medium: 106-140 Large: >140	Small: 45-59 Medium: 60-82 Large: >82		Small: 117-133 Medium: 134-183
# Size classes caught	1	1	1	2 (small and medium)	2 (small and medium)	1	2 (small and medium)
# Fish per composite	5	20	5	3*	3*	1	3*
Size range (cm)	20-30	10-15	20-30	Small: 91-102 Medium: 108-135	Small: 45-59 Medium: 60-82	55-92	Small: 117-128 Medium: 135-149
Tissue sampled	muscle with skin	muscle with skin	muscle with skin	muscle without skin	muscle without skin	muscle without skin	muscle without skin
South Bay Bridges		3 composites Hg+OCs X 3		2 small 1 medium Hg+OCs X 3	1 small 1 medium (2 fish) 8 individuals OCs X 2 Hg X 10	1 small Hg+OCs X 1	1 small 1 medium (2 fish) 1 individual Hg+OCs X 2 Se X 6
Oakland Harbor	4 composites Hg+OCs X 4 Dioxins X 1	3 composites Hg+OCs X 3	3 composites Hg+OCs X 3				
San Francisco Water Front	3 composites Hg+OCs X 3 Dioxins X 1	3 composites Hg+OCs X 3	3 composites Hg+OCs X 3				
Berkeley	4 composites Hg+OCs X 3 Dioxins X 1	3 composites Hg+OCs X 3	3 composites Hg+OCs X 3	2 small Hg+OCs X 2	1 small 1 medium (2 fish) Hg+OCs X 2	3 small 1 large Hg+OCs X 4	
San Pablo Bay	3 composites Hg+OCs X 3 Dioxins X 3	3 composites Hg+OCs X 3	3 composites Hg+OCs X 3	2 small 1 medium (1 fish) Hg+OCs X 3	2 small (one 12 fish megasample) 1 medium Hg+OCs X 3 Dioxins X 1	1 small 2 large Hg+OCs X 3	1 small 1 medium 1 individual Hg+OCs X 2 Se X 7
Davis Point**					2 small 1 medium 10 individuals OCs X 3 Hg X 13		
Suisun Bay					1 small Hg+OCs X 1		

* Except as noted

** Davis Point not included in original design

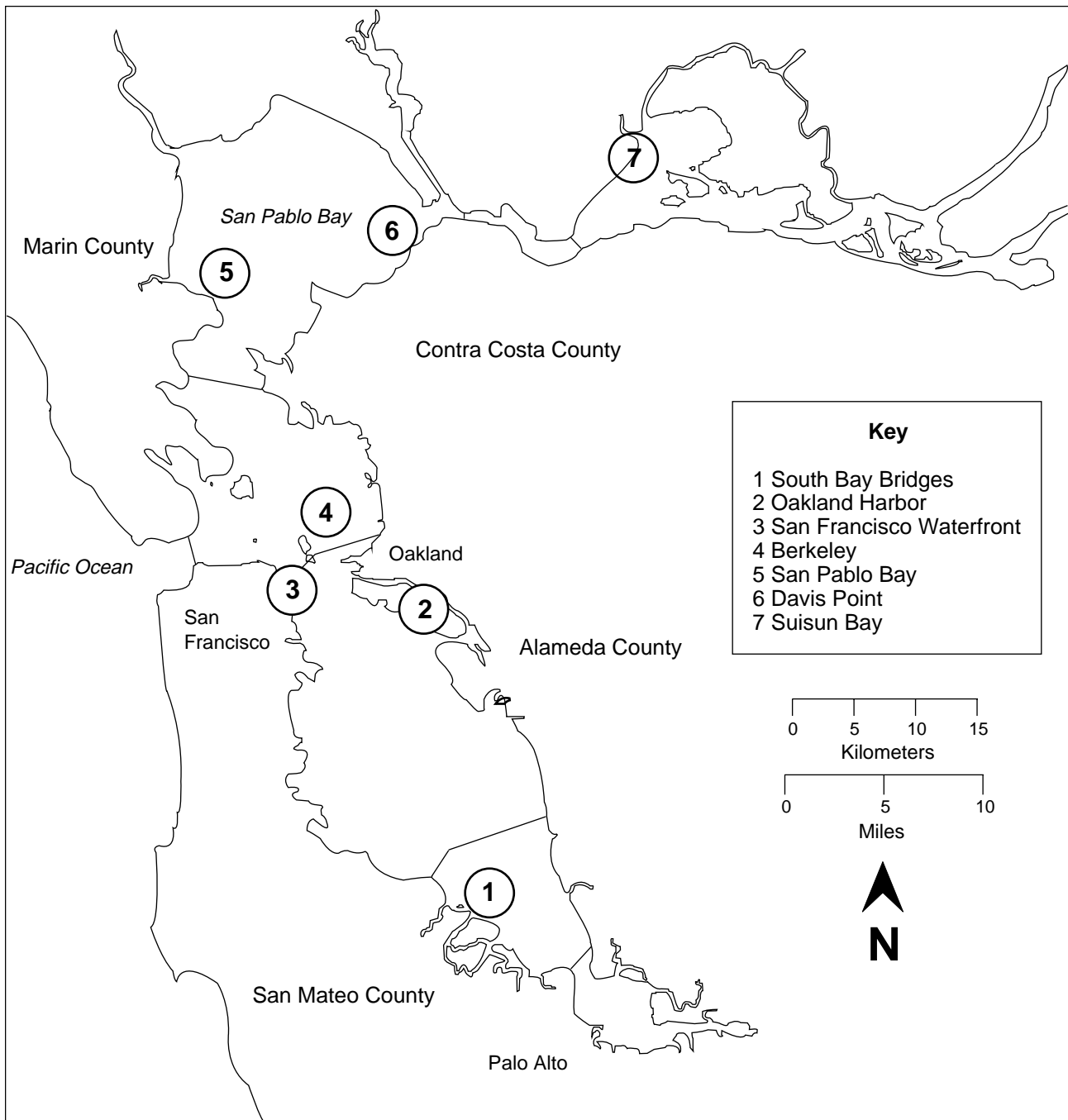


Figure 6.12. Sampling locations for 1997 RMP fish contamination monitoring.

ment of the data for variation in length was useful in evaluation of trends in mercury concentrations in space and time. Data obtained for individual striped bass suggest the existence of two groups of striped bass in the Bay, one with higher mercury concentrations than the other. The reason that striped bass of similar size might display this sort of variability is unknown at this time.

Concentrations of trace organics were highest in white croaker and shiner surfperch. Overall, PCBs exceeded the screening value in 51 of 72 samples. All of the white croaker and shiner surfperch samples exceeded the screening value for PCBs. Other trace organics had lower numbers of samples above screening values: 27 of 72 for dieldrin (including all 14 white croaker samples),

Table 6.4. Summary statistics by species for mercury and organochlorines. Data are medians.

	Number of Composites Analyzed	Number in Composite	Length (cm)	Mercury ($\mu\text{g}/\text{kg}$ wet)	Lipid %	Sum of Aroclors (ng/g)	Sum of PCB Congeners (ng/g wet)	Sum of DDTs (ng/g wet)	Sum of Chlordanes (ng/g wet)	Dieldrin (ng/g wet)
Halibut	8	1	71	0.27	0.34	ND	14	6.6	1.6	0.2
Jacksmelt	12	5	26	0.09	1.85	45	37	34	3.4	0.8
Leopard Shark	8	3	101	0.88	0.24	13	11	5.3	1.1	0.2
Shiner Surfperch	15	20	12	0.11	2.52	179	134	54	8.8	1.7
Striped Bass	11	3	57	0.42*	0.82	34	27	16	3.0	0.8
Sturgeon	4	3	132	0.27	1.30	33	35	17	4.1	1.0
White Croaker	14	5	25	0.19	7.04	306	237	85	18	4.5

Table 6.5. Summary of concentrations above screening values for each species. Numerator indicates the number above the screening value, denominator indicates the number of samples analyzed.

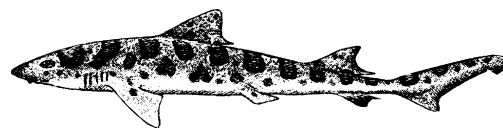
	Mercury ($\mu\text{g}/\text{g}$ wet)	Sum of Aroclors (ng/g wet)	Sum of DDTs (ng/g wet)	Sum of Chlordanes (ng/g wet)	Dieldrin (ng/g wet)	ITEQs (pg/g wet)
Screening value	0.233	23	69	18	1.5	0.15
Halibut	5/8	1/8	0/8	0/8	0/8	
Jacksmelt	1/12	10/12	0/12	0/12	1/12	
Leopard Shark	8/8	1/8	0/8	0/8	0/8	
Shiner Surfperch	0/15	15/15	4/15	3/15	9/15	
Striped Bass	23/23	7/11	0/11	0/11	2/11	1/1
Sturgeon	3/4	3/4	0/4	0/4	1/4	
White Croaker	4/14	14/14	12/14	8/14	14/14	6/6
All Species	44/84	51/72	16/72	11/72	27/72	7/7

16 of 72 for DDTs, and 11 of 72 for chlordanes. Species with low lipid content in their muscle tissue, such as halibut and leopard shark, had the lowest concentrations of trace organics.

Dibenzodioxins and dibenzofurans were measured in six samples of white croaker and one sample of striped bass. ITEQs (dioxin toxic equivalents due to dibenzodioxins and dibenzofurans) in these samples were all above the screening value of 0.15 pg/g wet weight. Total TEQs (including the contributions of dioxin-like dibenzodioxins, dibenzofurans, and PCBs) in these seven samples averaged 9.7 pg/g wet weight, with a minimum of 3.7 pg/g and a maximum of 19.7 pg/g. Dioxin-like PCBs accounted for 83% of total TEQs. Dibenzofurans and dibenzodioxins accounted for 10% and 7%, respectively, of total TEQs.

Spatial Patterns

Significant variation in contaminant concentrations among locations was observed in the three



Leopard Shark

species (white croaker, shiner surfperch, and jacksmelt) employed to evaluate spatial patterns. Spatial variation in wet-weight concentrations was observed, indicating variation in potential human exposure to contaminants of concern. Oakland Harbor had significantly elevated wet-weight concentrations of mercury (in shiner surfperch and jacksmelt), PCBs (shiner surfperch, white croaker, and jacksmelt), DDTs (shiner surfperch), and chlordanes (shiner surfperch, white croaker, and jacksmelt).

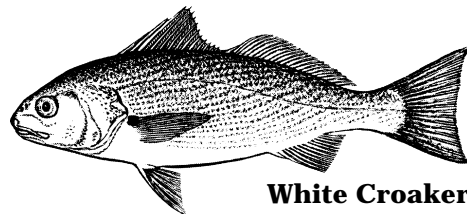
Spatial variation was also evaluated by adjusting the data for the important factors length and lipid content. These adjusted data may provide a better indication of spatial and temporal variation in contamination of the Bay. Length-adjusted mercury concentrations were relatively

high at Oakland Harbor and San Francisco Waterfront (in jacksmelt). Lipid normalized concentrations of PCBs (in jacksmelt and shiner surfperch), DDTs (shiner surfperch), chlordanes (jacksmelt and shiner surfperch), and dieldrin (shiner surfperch) were elevated at Oakland Harbor. Lipid normalized PCB concentrations at Oakland Harbor were 11 times higher than at the sampling location with the lowest PCB concentration. The observation of similar spatial patterns in multiple species support the conclusion that the Oakland Harbor location exhibits elevated concentrations of multiple contaminants. These findings are consistent with observations of high concentrations of PCBs and organochlorine pesticides in sediment at this location (Hunt *et al.*, 1999). Overall, the results of the sampling for spatial patterns suggest that shiner surfperch and jacksmelt are useful indicators of spatial variation in contamination in the Bay.

Temporal Trends

Mercury concentrations in 1997 were not significantly different from concentrations in 1994. In 1997 lipid-normalized concentrations of PCBs were significantly lower than in 1994 in shiner surfperch, white croaker, and striped bass, suggesting a possible general decline in PCBs in the Bay. Significantly lower concentrations were also observed for lipid-normalized DDTs (striped bass), chlordanes (striped bass and white croaker), and dieldrin (striped bass and shiner surfperch). Decreasing concentrations of these synthetic chemicals would be consistent with restrictions on their use that have been in place for many years. Lipid-normalized dioxin ITEQs were also significantly lower in 1997 than in 1994.

Continued monitoring will be required to establish whether the apparent decreases observed for PCBs, organochlorine pesticides, and



White Croaker

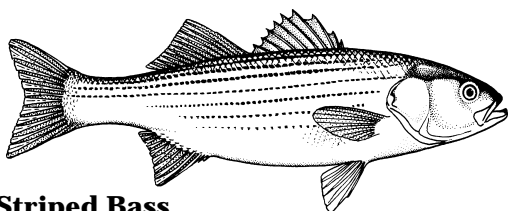
dioxin ITEQs are real indications of declining masses of contaminants in the Bay. Other possible causes of these apparent declines include variation in the physiology or behavior of the fish sampled, changes in the structure of the Bay's food web, variation in analytical methods, or simply short-term fluctuation that is not indicative of a persistent long-term trend. The reason for the large differences in lipid concentrations observed in 1994 and 1997 are not understood and further emphasize the need for continued monitoring to determine trends over time. Continued fish tissue monitoring will also allow detection of changes that have not yet been indicated by results from just two sampling events (1994 and 1997).

Other Conclusions

The use of multiple species for evaluating spatial and temporal trends proved to be valuable. Consistent trends were observed for multiple species, lending greater confidence to conclusions about spatial and temporal variation. The use of multiple species also offers the advantage of increasing the likelihood of obtaining target species, whose distribution in the Bay varies considerably.

Fish size (or age) and lipid content were identified as important factors influencing accumulation of persistent contaminants. Trophic level is probably also an important factor accounting for some of the variation in these results, but the trophic levels of the species sampled in the Bay are not well characterized. Understanding and accounting for these factors is essential to evaluation of spatial and temporal trends in contaminant concentrations.

Substantially lower concentrations of trace organics were measured in white croaker fillets with the skin removed. Concentrations of PCBs, DDTs, chlordanes, dieldrin, and dioxin ITEQs were reduced by 30–50%. These reductions were



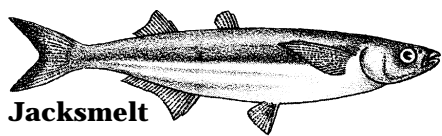
Striped Bass

associated with lipid concentrations that were 33% lower in the fillets without skin. For some samples, skin removal resulted in reduction of chlordane and DDT concentrations to below screening values.

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Alyce Ujihara, California Department of Health Services
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Jacksmelt

Adrienne Yang and Nicole David worked on formatting the report and graphics. Jung Yoon and Samir Arora managed the data. Gabriele Marek assisted with contract management.

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