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Chromium in the San Francisco Bay Estuary: a Study of Cycling, Speciation, and Anthropogenic Inputs

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Abstract

Trace metal inputs to estuarine ecosystems can have substantial impacts on their environmental quality. However, it is imperative to understand background processes which affect trace metal cycling in order to quantify the impacts of human activities. Chromium is an important industrial metal, with known sources surrounding San Francisco Bay. It also has substantial natural sources, being the tenth most abundant element on the planet. Therefore, this research is directed at quantifying the relative magnitude of natural and anthropogenic fluxes of Cr to the San Francisco Bay estuary.

Episodic flushing of a wetlands area, the Yolo Bypass, appears to be the predominant source (up to 980 kg d^{-1}) of dissolved chromium to the San Francisco Bay estuary. Depletion of [Cr]/[Al] in suspended particulate matter within the entrapment zone of the estuary suggests that that chromium is solubilized by weathering of aluminosilicates. Conversely, other processes (e.g., internal inputs, *in-situ* reduction) appear to govern the net flux of chromium within the estuary when the bypass is not being flushed. All of these processes can be demonstrated by examination of ancillary measurements (e.g., hydrographs of freshwater endmembers, nutrient data, other trace metal measurements), which reveal the complexity of the chromium biogeochemical cycle within the hydrologically bifurcated and highly modified estuary.

Sediments located at Green Sands Beach, adjacent to the Mare Island Naval shipyard are known to be impacted by disposal of metal-enriched tailings from sandblasting operations. These

sediments were an order of magnitude enriched compared to the baywide average [Cr]/[Al] ratio. This enrichment showed a gradient leading away from the wetlands above the beach.

Problem Definition

Overview

The estuarine cycling of chromium is relatively complex because of the contrasting geochemistry of its two dominant redox states, Cr(III) and Cr(VI). The hydrolysis species of cationic Cr(III) can be rapidly scavenged within the turbidity maximum zone, whereas the tetrahedral oxydianion, $Cr(VI)O_4^{2-}$, has a very low particle affinity (1). Although Cr(VI) is thermodynamically favored in oxic waters, reduction *in-situ* produces Cr(III) (2,3), which can persist metastably due to its sluggish oxidation kinetics (solution oxidation half-times are days to months). These chemical properties lead to complex spatial distributions of both redox species in estuaries (4,5).

The biogeochemical cycling of chromium in San Francisco Bay is unusually complex because the estuary is hydrologically bifurcated (6). Freshwater discharges into the northern reach of the estuary are normally dominated by seasonal flows from the Sacramento and San Joaquin rivers. In contrast, freshwater discharges in the southern reach are normally dominated by relatively constant wastewater discharges from publicly owned treatment works (7).

The impacts of these contrasting hydrologic regimes have been documented in a previous study (5). It showed that a superposition of geochemical processes leads to complex distribution of chromium redox species within the San Francisco Bay estuary (Abu-Saba & Flegal, 1995). These processes included temporal and spatial variations in fluvial Cr(III) inputs, localized Cr(VI) inputs, and *in-situ* reduction of Cr(VI). However, that study, which was conducted during a prolonged drought, showed no clear evidence for Cr(III) scavenging within the estuary.

Here, we present the results of a more comprehensive study of the seasonal cycling of chromium within the San Francisco Bay estuary, during both normal and drought conditions. The redox speciation of chromium was determined throughout the estuary (Figure 1) over a period of five years, during both high flow and low flow conditions (Figure 2). These conditions are illustrated by the pronounced variability in freshwater discharges to the northern reach of the estuary during the 5 year study period (1992-1996). These discharges include the large episodic flushing of the Yolo Bypass, which also accounts for the seemingly nonconservative distributions of chromium in the estuary during those ephemeral events.

Study area

The cycling of chromium in the San Francisco Bay estuary is controlled by its bathymetry and hydrography. The complete environmental setting of the estuary has been previously described (7, 15, 16). We present here a brief overview in order to relate seasonal flow, shallow bathymetry, and hydrologic bifurcation to the observed chromium distributions.

San Francisco Bay is a very broad, shallow estuary. It's mean depth is 5 m, although much of the bay < 2-3 m deep. Thus, wind and tidal action cause rapid cycling of sediments between the benthos and the water column. This dynamic exchange leads to rapid homogenization of the sediments, as evidenced by the consistent lead isotopic composition of particulate matter throughout the estuary (8). Resuspension, coupled to diagenesis, is also a temporally important source of dissolved nutrients (9,10) and trace elements (11,12,13) in the South Bay.

Freshwater inputs to the northern reach estuary range from 1 to 80 x 10^7 m^3/day. Low-flow inputs are typically ≈3 x 10^6 m^3/day, whereas high-flow inputs are on the order of ≈2 x 10^8 m^3/day. The low-flow period typically occurs during the summer and late fall (June-November), the high flow period is winter and early spring (January-May). In contrast, the southern reach has relatively small natural freshwater inputs, being separated from the north-central California drainage basin by the Diablo Range. The principal sources of freshwater to the South Bay are treated municipal discharge, amounting to ≈0.6 million m^3 d^{-1}. This contrast between the northern and southern reaches defines the hydrologic bifurcation of the San Francisco Bay estuary.

That physical disparity results in mean hydraulic residence times and flushing mechanisms which vary markedly by region and by season. The hydraulic residence times of the northern reach range from 1 to 60 days for low and high flow conditions, respectively (14). The residence time of water in the South Bay is ≈ 120 days during periods of high Delta outflow, with replacement of water occurring by intrusion of Delta-derived low salinity water. During periods of low Delta outflow, water replacement in the South Bay is dominated by tidal currents and wind-induced mixing, resulting in hydraulic residence times of ≈160 days (14).

San Francisco Bay receives from a 163,000-km^2 watershed, which covers 40% of California (15). As previously noted, essentially all of this runoff (>90%) enters the bay through the Sacramento-San Joaquin River Delta during high flow periods in the winter and spring (16). During those peak flow periods, water is diverted through the Yolo bypass to prevent flooding in the Sacramento Valley. The Yolo bypass is a vast (≈200 km^2) wetlands area, surrounded by dikes and levees. Flow from the Yolo Bypass into the Sacramento River above Rio Vista is very episodic. During periods of high delta outflow, the Yolo bypass changes from a drained wetlands into a fluvial system, with flow sporadically exceeding the Sacramento River (Figure 2).

Substantial amounts of the water destined for San Francisco Bay are diverted via an extensive system of canals, and dikes from the Sacramento San-Joaquin River Delta into the California aqueduct to provide water for irrigation in the Central Valley and Southern California municipal use. Median annualized diversions amount to $\approx 10^7$ m^3d^{-1}, while actual monthly diversions are range from -10^8 m^3d^{-1} to 10^8 m^3d^{-1} . Negative diversions reflect the practice of releasing water stored during April-June in the drier months (July-November) (17). Storage of water during high runoff periods has dampened the annual pulse of water which provides a flushing mechanism for the South Bay.

Research objectives

This objectives of this research are 1) to quantify the predominant sources of Cr to the San Francisco Bay Estuary; 2) to evaluate the impact variable seasonal flow on the transport of Cr through the estuary; 3) to identify regional sources of Cr; and 4) to investigate in-situ reduction of Cr(VI).

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Review of Methodology

Samples were collected using trace-metal clean techniques, as previously described (5,6). Total dissolved (<.45 μm) chromium (i.e., Cr[III] + Cr[VI]) concentrations were determined by ferrous hydroxide coprecipitation followed by graphite furnace atomic absorption spectrometry on a Perkin-Elmer 5500 equipped with an HGA-500 furnace (1,5). Those analyses were intercalibrated using inductively coupled plasma mass spectrometry on a Finnegan MAT Element ICP/MS. Dissolved Cr(III) concentrations were determined after ferric hydroxide coprecipitations (1,5). Those coprecipitations were carried out on shipboard within 10 minutes of sample collection for determination of redox speciation during the first four years of the study, while subsequent measurements were made after acidifying samples immediately on shipboard and carrying out only the ferrous hydroxide coprecipitations in the laboratory for determination of total dissolved chromium. Dissolved Cr(VI) was determined as the difference between chromium analyses by ferrous hydroxide coprecipitation and ferric hydroxide coprecipitation. The coprecipitation technique yielded 85 to 100 % recoveries of reference materials (NRC Canada CASS-3 SLRS-2, SLEW-1). The precision of the analyses was 15%, based on replicate extraction's of >100 samples. The process detection limit (3σ) was 0.2 nM, based on daily field blanks processed throughout the 5 year study period.

Concentrations of suspended particulate chromium, aluminum, and manganese were determined by shipboard filtration of particulate matter using 25 mm, 0.45 μm, polycarbonate membrane filters. The particles were digested using concentrated nitric and hydrofluoric acids (trace metal grade). The chromium concentrations of digested particles was measured by GFAAS, whereas the aluminum and manganese concentrations were measured by inductively coupled plasma atomic emission spectrometry. Analysis of reference materials (NRC Canada BCSS-1) showed 83% recovery for chromium, 91% recovery for manganese, and 97% recovery for aluminum.

Dissolved nutrient concentrations (silicate, phosphate, nitrate, ammonium) were determined colorimetrically using established procedures (6). Salinity was determined three ways: (i) on shipboard, using a YSI Model-33 salinity-conductivity-temperature meter; (ii) on shipboard, using a Seabird SBE-19 conductivity/temperature/depth probe; (iii) in the laboratory, using a Guildline Model 8410 Portasal. Dissolved oxygen at the surface was measured using a membrane probe attached to a YSI Model 58 DO meter. Total suspended solids (TSS) concentrations were determined gravimetrically. Other dissolved trace metal concentrations (e.g., Pb, Ag, Cu, Ni, Cd) were determined by GFAAS after chelation and extraction of filtered samples using established procedures (6).

Sediment samples were collected by Dana Katofsky, an undergraduate researcher, from Green Sands Beach, near the former site of Mare Island Naval Shipyard. Those sediment samples were extracted by leaching in 0.5 N HCl for 24 hours. The filtered leachates were analyzed for trace metals (e.g., Cr, Ni, Cu, Pb, Zn, and Al) by ICP/AES.

The dilute acid leach provides a measure of the bio-available fraction of sediment-bound metals (18). It solubilizes metals which are bound to metal oxyhydroxide surfaces and carbonate phases, while leaving aluminosilicate lattices essentially intact. Thus, this extraction also indicates the metal fraction which is more geochemically labile than lattice-bound metal.

Results and Their Significance

Seasonality and speciation of chromium fluxes to the estuary

Dissolved chromium concentrations within the estuary showed marked spatial and seasonal gradients during the five year study period (Figure 3). Relatively large (>10 nM) concentrations are found in the northern reach of the estuary during the winter and spring periods of high Delta outflow. Episodic increases (30-60 nM) also occurred in the sloughs of the South Bay. During the summers, and throughout the year in the higher salinity regions of the Central Bay, the 2-3 nM dissolved chromium concentrations observed in the estuary were comparable to oceanic surface waters (1,4,19,20).

Inputs of dissolved chromium to the estuary throughout the study were essentially all as the reduced species, Cr(III) (Figure 4). The intercept of 2.0 nM (Figure 4) shows the baywide average Cr(VI) concentration. This concentration is consistent with previously published values for Cr(VI) in estuarine (4) and coastal (19) waters. Throughout the study period, Cr(VI) concentrations were 2.0 ± 0.6 nM (x ± SD), showing that there were minimal inputs of Cr(VI), and some losses due to in-situ reduction (5).

Resolution of time variability and complex estuarine circulation during high-flow periods

The complex spatial distribution of dissolved chromium observed in March, 1993 (Figure 5-A), illustrates the challenge of evaluating long-term mixing and transport processes in a complex estuary with a time-variable freshwater endmember. Others have discussed rigorous methods to resolve that complexity (21, 22). However, we have determined that a simple evaluation of dissolved silicate distributions (Figure 5-B) and the endmember hydrograph (Figure 5-C) is sufficient to resolve the primary time-variable inputs and scavenging processes of Cr(III) within the San Francisco Bay estuary.

This resolution is based on parallels in episodic pulses of dissolved chromium with those of dissolved silicate and freshwater releases from the Yolo Bypass. Just prior to the sampling cruise of March 4-7, 1993, a prolonged drought in California ended, which resulted in massive increases in the freshwater flow to the San Francisco Bay estuary. On January 21, 1993, the Sacramento Weir (USGS gauging station 11453000) was overtopped for the first time in seven years, diverting water into the Yolo Bypass. During the week of February 20-28, 1993, a series of storms resulted in another large pulse of freshwater flow to the estuary (Figure 5-C) which markedly shifted the freshwater composition of the northern reach. The ratio of river flow passing through the Yolo Bypass to that passing through the Sacramento River at Freeport shifted from <5% to 33% in a matter of days, peaking on February 24 (Figure 5-C). This shift in endmember composition sent a pulse of chemically distinct water into the estuary, as demonstrated by the plot of silicate vs. salinity for that cruise (Figure 5-B), which we attribute to the release of water derived in part from the Yolo Bypass.

Compositional changes at the mouth of the Sacramento River dominate the chemistry of freshwater flowing into the estuary. When the Yolo Bypass shifted from <5% to 33% of Sacramento River flow in February, 1993, the San Joaquin River was still <5% of the Sacramento River flow. Since the San Joaquin River is the next largest source of freshwater to the Delta, relative flow rates implicate discharge from the Yolo Bypass as the predominant source of episodic chromium inputs to the estuary.

This proposed cycling reveals areas of the estuary where compositional changes are relatively stable compared to mixing and transport processes. For example, transport processes are essentially fluvial during high-flow periods in Suisun Bay, east of the Carquinez Straits (23). Conversely, in San Pablo Bay, west of the Carquinez Straits, tidal mixing and wind-driven transport become more significant (24). Since the silicate concentrations are conservatively mixed in the 5-25 salinity region (Figure 5-C), chromium : salinity relations may be used to calculate chromium scavenging rates in the northern reach of the estuary, from San Pablo Bay to the Golden Gate.

The convoluted circulation patterns of the San Francisco Bay estuary present an additional complication. Residual eulerian current is affected by bathymetry (24), which elevates flows in channel areas compared to shoals. Therefore, water samples collected from shoal areas are likely "older" than water collected from channel areas, where there is less time for geochemical scavenging of Cr(III).

Consequently, the complex spatial distribution of dissolved chromium (Figure 5-A) can be resolved by analysis of the time-variability and circulation of the estuary. The sudden chromium concentration increase from the Carquinez straits to the head of the estuary is attributed to the pulse of water from the Yolo Bypass, as in the case of silicate. The two San Pablo Bay stations with the lowest dissolved chromium concentrations are in shoal and eddy areas. The lower chromium concentrations at those two stations is likely a result of longer local hydraulic residence time, which results in more geochemical scavenging.

The chromium concentrations of the remaining stations from San Pablo Bay to the Golden Gate (Figure 5-A) demonstrate geochemical scavenging. A drop of 5 nM from the theoretical dilution line implies a scavenging loss of 780 kg throughout the entire volume (3×10^{12} L) of San Pablo Bay and the Central Bay. This corresponds to a scavenging rate of 390-780 kg d^{-1} during the period sampled, assuming a transit time of 1-2 days due to residual eulerian transport through this region (15,24). That rate is comparable to the estimated peak fluvial chromium fluxes of 380-940 kg d^{-1} at the head of the estuary, based on the estimated Delta Outflow (4000-10000 $m^3 s^{-1}$). Thus, wintertime fluvial inputs of chromium are balanced by scavenging removal of chromium, although some dissolved chromium inputs may escape the estuary.

The impact of increased flow through the Yolo Bypass is a reproducible phenomenon. After another relatively low-flow year in 1994, a series of storms in 1995 again brought massive amounts of freshwater to the estuary just prior to the February 1995 sampling cruise (Figure 6-C). In the first cruise segment, water samples were collected from the San Rafael Channel (BC60) to the Golden Gate (BC20) during the week of February 6-9. In the second segment, water samples were collected in San Pablo Bay during the week of February 13-15, when salinities were comparable to those of the central bay, but silicate concentrations were doubled (Figure 6-B). This disparity is attributed to a pulse of water through the Yolo Bypass, which peaked at 68% of Sacramento River flow on February 4 (Figure 6-C). A pulse of silicate-enriched water from the

Yolo Bypass moved into San Pablo Bay between the two cruise segments, carrying with it elevated concentrations of dissolved chromium (Figure 6-A).

Sediment sources of dissolved chromium in the northern reach of the estuary

The observation of elevated dissolved silicate and chromium associated with increased flow from the Yolo Bypass raises the question: What is the ultimate source of chromium in this water mass? Since fluvial fluxes dwarf the total direct anthropogenic chromium inputs (30 kg d^{1}) to the estuary (25), a direct anthropogenic source is unlikely.

Particulate chromium and aluminum ratios suggest that diagenesis of aluminosilicate minerals is the primary source of dissolved chromium. The atomic ratio of suspended particulate chromium to suspended particulate aluminum has been previously demonstrated to be relatively uniform throughout the estuary (5). This ≈1:1000 ratio has also been derived from the elemental data reported a decade ago (26). Consequently, the ratio of chromium to aluminum appears to have remained essentially constant in time and space within the estuary throughout the period 1992-1994, with one notable exception (Figure 7). In March, 1993, new suspended particulate matter entering the Delta was significantly ($P<.01$, simple linear correlation) depleted in chromium, relative to aluminum, compared to the rest of the estuary.

We propose that sedimentary deposits are weathered in the alluvial flood plain, releasing dissolved or colloidal chromium and silicate into the wetlands of the Yolo Bypass. These wetlands are episodically flushed, carrying accumulated chromium and silicate into the head of the estuary. The highest concentrations ever measured in the northern reach (30 nM) occurred immediately after a seven year drought (1993). That event was associated with inputs of particulate matter depleted in chromium, which suggests that continuous sediment diagenesis coupled to seasonal flushing provides the dominant source of chromium to the estuary.

Low-flow processes in the northern reach of the estuary

The data from August, 1993 provide an illuminating contrast to chromium processes observed in the high-flow winter months. During periods of low Delta outflow (<500 m^3s^{-1}), transport in Suisun Bay shifts from predominantly fluvial to predominantly wind-driven and tidal mixing (23). The hydraulic residence time of water masses in the various embayments is certainly longer in low-flow periods, it is difficult to quantify. Quantitative chromium flux calculations in the northern reach are not feasible during the low-flow summer months. However, the data do provide a qualitative picture of how the importance of internal inputs increases relative to fluvial inputs during low-flow conditions.

Dissolved silicate concentrations were conservative in the northern reach (Figure 8-B) in August, 1993, when the Sacramento River flow was relatively constant, and there was no flow in the Yolo Bypass (Figure 8-C). (The San Joaquin River does not normally affect the estuarine silicate distribution because its summer flow is negligible). During this period, the distribution of dissolved chromium was also conservative, except for a localized elevation in Grizzly Bay (Figure 8-A). This elevation of 3.3 nM chromium relative to adjacent stations corresponds to a net excess of 3.4 kg chromium in all of Grizzly Bay, which has an estimated volume of 2 x 10^7 m^3.

It is estimated that the net flux of chromium in Grizzly Bay between 3.4 and 0.34 kg d^1, based on an estimated hydraulic residence time of 1-10 days. This net flux represents the difference between internal inputs (e.g., benthic fluxes, drainage from adjacent wetlands, direct approximation can be derived for the reductive scavenging losses of dissolved chromium from the estimated volume of the shallow (<2 m) regions of Suisun Bay, 10^8 m^3, and the 3 nM change in dissolved Cr(VI) over a 24-hour period. From these data, we estimate that up to ≈20 kg of Cr(VI) can be reduced in a 24 hour period in Suisun Bay. Thus, *in-situ* reduction also becomes a relatively important source of Cr(III) during low-flow periods.

Episodic chromium inputs to the South Bay

An episodic elevation of dissolved Cr(III) in the South Bay in April, 1994 provides in interesting contrast to localized processes occurring in the northern reach of the estuary. Concentrations of dissolved chromium ranged from 30 nM in Artesian Slough (BA05) to 60 nM in Guadalupe Slough (BA06), which are the receiving waters for treated municipal sewage from the cities of San Jose and Sunnyvale, respectively. These inputs were removed by scavenging between the sloughs and the Dumbarton Bridge (BA30) (Figure 10).

Discharge records from the outfalls at San Jose, Sunnyvale, and Palo Alto show that chromium releases to that region during the period February-April, 1994 were consistent with recent historic trends (Steve Moore, personal communication). This is also true for other metals (Pb, Cu, Ag, Ni, Cd) discharged into the South Bay during that period. The absence of marked anthropogenic releases, and the coincidence of elevated chromium concentrations with other trace metal concentrations in those two sloughs, suggest that internal metal fluxes led to the observed episodic increase.

The mechanism underlying these internal fluxes can best be understood by examining the metal and nutrient concentrations summarized in Table 1. Concentrations of dissolved chromium, lead, and silver in the South Bay sloughs were all significantly higher ($P<.01$, t-test) in April, 1994 than during any other sampling period. Concentrations of dissolved nickel and copper were also somewhat elevated, whereas no significant difference ($P<.05$, t-test) was observed in the concentrations of dissolved cadmium.

This pattern follows the known geochemical behavior of these metals. For example, the metal partition coefficients ($L\ kg^{-1}$), defined as $K_{d,X} = [X]_{partic}/[X]_{diss}$, provide a measure of particle affinity for a metal (Table 1). The most particle-reactive metals (chromium, silver, lead) show the greatest inputs to the dissolved phase during this episodic event. Concentrations of silver and lead have been previously demonstrated to be substantially enriched in South Bay particulates (11,12). The least particle-reactive metal (cadmium) is essentially unchanged during this event. Metals which have moderate K_d's, but which form strong organic complexes (e.g., copper, nickel) (27), show only moderate concentration increases. Thus, sediment diagenesis appears to be the source of the dissolved metal fluxes, including chromium, during this episodic event.

Ancillary data provide an additional mechanistic link to these metal fluxes. Dissolved nitrate concentrations were significantly lower ($P<.01$, t-test) in April, 1994 (Table 1). Particulate manganese was enriched with respect to aluminum in that region (Figure 11). Fluxes of dissolved Mn(II) from anoxic zones are known to cause enriched particulate manganese as a result of Mn(II) reoxidation (28). The depletion of oxidized nitrogen, coupled to the concurrent enrichment of particulate manganese, suggests that reductive dissolution of particulate surfaces is the mechanism underlying this episodic internal flux of metals in the South Bay.

Benthic fluxes have been previously demonstrated to be an important source for nutrients (9,10, 29) and trace metals (6,11,12, 30,31,32,33) in the South Bay. Both enhanced advection of sedimentary porewater exchange due to seasonal bioturbation (9) and tidally forced exchange of shoal water with channel water (34) result in substantial sedimentary sources of dissolved metals and nutrients. Sediments, which are the sink for wintertime dissolved chromium fluxes in the North Bay, also act as transient regional chromium sources.

The magnitude of this flux in the South Bay can only be estimated, because the hydraulic residence time of the tidally mixed slough is exceedingly complex. Still, an order of magnitude estimate of this chromium flux is useful for comparison with the other chromium processes in the estuary. The high water volume of Artesian Slough (BA05) is 2.6×10^6 m^3 (35). Samples are always collected at high water in Artesian Slough, so the 22.7 nM excess chromium concentration over the mouth of Coyote Creek (BA10) represents an excess of ≈3 kg chromium. Although the flushing time due to the 5×10^5 m^3 day treated sewage discharge from San Jose is relatively long (>10 days), we consider the slough to be completely flushed twice a day by tidal exchange. This assumption is substantiated by the fact that the high-water volume of Artesian Slough is ≈20-fold greater than the low-water volume (35). Therefore, the relatively high concentration of dissolved Cr(III) observed in Artesian Slough in April, 1994 could be supported by a net benthic flux of ≈ 6 kg d^{-1}.

Exports to adjacent coastal waters

Concentrations of dissolved chromium at the Golden Gate (BC20) were relatively constant (2.4 ± 0.6 nM) during both high-flow and low-flow conditions. Although relatively low (≈0.3 nM) Cr(III) concentrations were detected at times, the dominant form of dissolved chromium leaving the estuary was Cr(VI), which is consistent with the low particle affinity of CrO_4^{2-}. Fluxes of dissolved chromium to adjacent coastal waters were largely controlled by the magnitude of the Delta outflow, which ranged from 2 kg d^{-1} during periods of low Delta outflow (200 m^3s^{-1}) to 100 kg d^{-1} during peak flow periods (10000 m^3s^{-1}). The upper estimate of 100 kg d^{-1} agrees reasonably well with the difference between fluvial inputs (<980 kg d^{-1}) and scavenging removal (<800 kg d^{-1}) for high-flow periods.

Metal concentrations sediments from Green Sands Beach

Sediments collected from Green Sands Beach showed unusually high concentrations of leachable chromium and nickel (Figure 12, Figure 14). The name of this beach derives from the greenish tinge resulting from the remains of sand-blasting spoils disposed in that region which are thought to have substantially impacted metal concentrations in this region (36). The elevated concentrations of chromium and nickel in sediments from that region, compared to reference sediments from a nearby control site, the Napa River, and the San Francisco Bay estuary indicate that these sediments may be substantially contaminated.

Normalization to leachable aluminum provides a control for grain size effects, which are known to increase metal conentration in sediments (46). Examination of metal / aluminum ratios

(Figure 13, Figure 15) shows that the elevated concentrations are not an artifact of increased fine sediments. This enrichment drops to background levels within 10 meters of the most enriched sediments.

Nickel and chromium were the only two metals examined which showed substantial enrichment. Copper concentrations (Figure 16) and copper / aluminum ratios (Figure 17) were comparable to control and reference stations, as were those of lead and zinc (data not shown). This was an unexpected result, as copper is known to be present in high concentrations as a biocide in marine paints.

The unique enrichment of chromium and nickel in this region suggests that mineral assemblage may play a role in this localized phenomenon. Nickel and chromium are substantially enriched in ultramafic rocks (37). Serpentine minerals, which are relatively abundant in Northern California (38), have nickel and chromium concentrations that are as much as 20 times higher than their average crustal abundances (39).

During the hydraulic mining period of the gold rush, massive amounts ($\approx 10^9$ m^3) of sediment was deposited in San Francisco Bay, dwarfing subsequent inputs of $\approx 10^6$ m^3 per year (40). Large depths of this mining debris resides beneath an armor of fine sand and silt in San Pablo Bay. Therefore, disposal of dredging material from San Pablo Bay could also lead to the elevated Cr and Ni concentrations observed near Green Sands Beach. Additional process studies are needed to characterize the mineralogy of sediments in this region, in order to differentiate historic anthropogenic effects from more contemporary impacts.

Principal Findings, Conclusions, and Recommendations

Chromium fluxes

The upper limits of dissolved chromium flux estimates summarized in Table 2 highlight the importance of sediments as both a source and sink for dissolved in the estuarine cycling of chromium. During high-flow periods, dissolved fluxes of up to 1000 kg d^{-1} are brought to the estuary. This dissolved chromium appears to originate from weathered sediments in the Yolo Bypass. Most of it is scavenged within the estuary, although up to 100 kg d^{-1} can be exported to adjacent coastal waters during peak flows. During low-flow periods, episodic benthic fluxes cause regional elevations of dissolved chromium, which are also removed by scavenging. The magnitude of reductive scavenging also becomes relatively important during low-flow periods, potentially balancing baywide anthropogenic discharges.

Implications for future research

Reoxidation of particulate Cr(III) to Cr(VI) has not been evaluated in this study. Although oxidation of Cr(III) is limited by its kinetic inertness (41), particulate Mn(III) oxide surfaces (e.g., MnOOH, manganite) can enhance the oxidation rate of adsorbed Cr(III) (42). In this study, we have identified ephemeral enrichment of particulate manganese associated with elevated concentrations of dissolved Cr(III) which are subsequently scavenged. Research in progress now addresses on the Cr(III) adsorbed onto freshly formed particulate manganese as a potential internal Cr(VI) source.

The ephemeral flux in the South Bay also highlights the potential microbial impact on chromium cycling. The anoxic diagenesis of bottom sediments is likely microbially mediated. Furthermore, production of particulate manganese in the environment is often associated with microbially catalyzed Mn-oxidation. Therefore, further research is needed to investigate the role of sulfate-reducing and Mn-oxidizing bacteria in the estuarine cycling of chromium.

Although the predominance of dissolved Cr(III) has been established in this research, the solution speciation of Cr(III) in San Francisco Bay is as yet unknown. The dissolved (<0.45 μm) Cr(III) measured by ferric hydroxide coprecipitation may include hydrolysis products of free, ionic Cr(III), dissolved organic Cr(III) complexes, and colloidally bound Cr(III) (43). Recent research has shown that ferric hydroxide coprecipitation of coastal samples yields assays higher than chelation techniques which only bind free, ionic Cr(III) (44). Hydrophobic species of Cr(III) make up a substantial fraction of dissolved Cr(III) scavengable by ferric hydroxide in Atlantic estuarine waters (45). In San Francisco Bay, field observations suggest that much colloidal material is nucleated by addition of ferric hydroxide to a filtered (<0.45 μm) sample (6, 46). Coupled to the known colloidal speciation of other metals (e.g., Fe, Al) in the Delta (47), this suggests that much of the Cr(III) measured in this work may in fact be colloidal. Identifying the solution speciation of Cr(III) would not change the flux estimates in this study, but could have important implications for the biological availability of Cr(III) inputs to the estuary (48).

The contrasting regional and seasonal processes demonstrated in San Francisco Bay are significant to past and present studies of the biological uptake of chromium. Past studies in the

North Bay have examined bioaccumulation of chromium in bivalve outplants by comparison of tissue concentrations to sediment and water data collected at discreet intervals (49, 50, 51, 52). Our research shows that bivalve exposure to dissolved chromium in the Northern Bay can be predicted using flow data from the Yolo Bypass and Sacramento River. This may allow more accurate modeling of organismal exposure than use of discreet sampling periods.

Summary

This study has established that episodic fluvial fluxes provide the dominant source of dissolved chromium to the San Francisco Bay estuary. These inputs are almost entirely scavenged within the estuary. During low-flow periods, second-order processes (e.g., reductive scavenging, benthic fluxes) become relatively important. Direct anthropogenic inputs appear to have relatively little effect on dissolved chromium concentrations within the estuary. However, anthropogenic activities do appear to cause substantial localized Cr enrichment in sediments. Additional process studies are needed to understand the mineralogy of these enriched sediments in order to differentiate contemporary anthropogenic activities from historic impacts.

Figure 1: Map of the San Francisco Bay estuary. Sampling stations are identified by codes used in the Regional Monitoring Program. Inset: detail map of Suisun Bay.

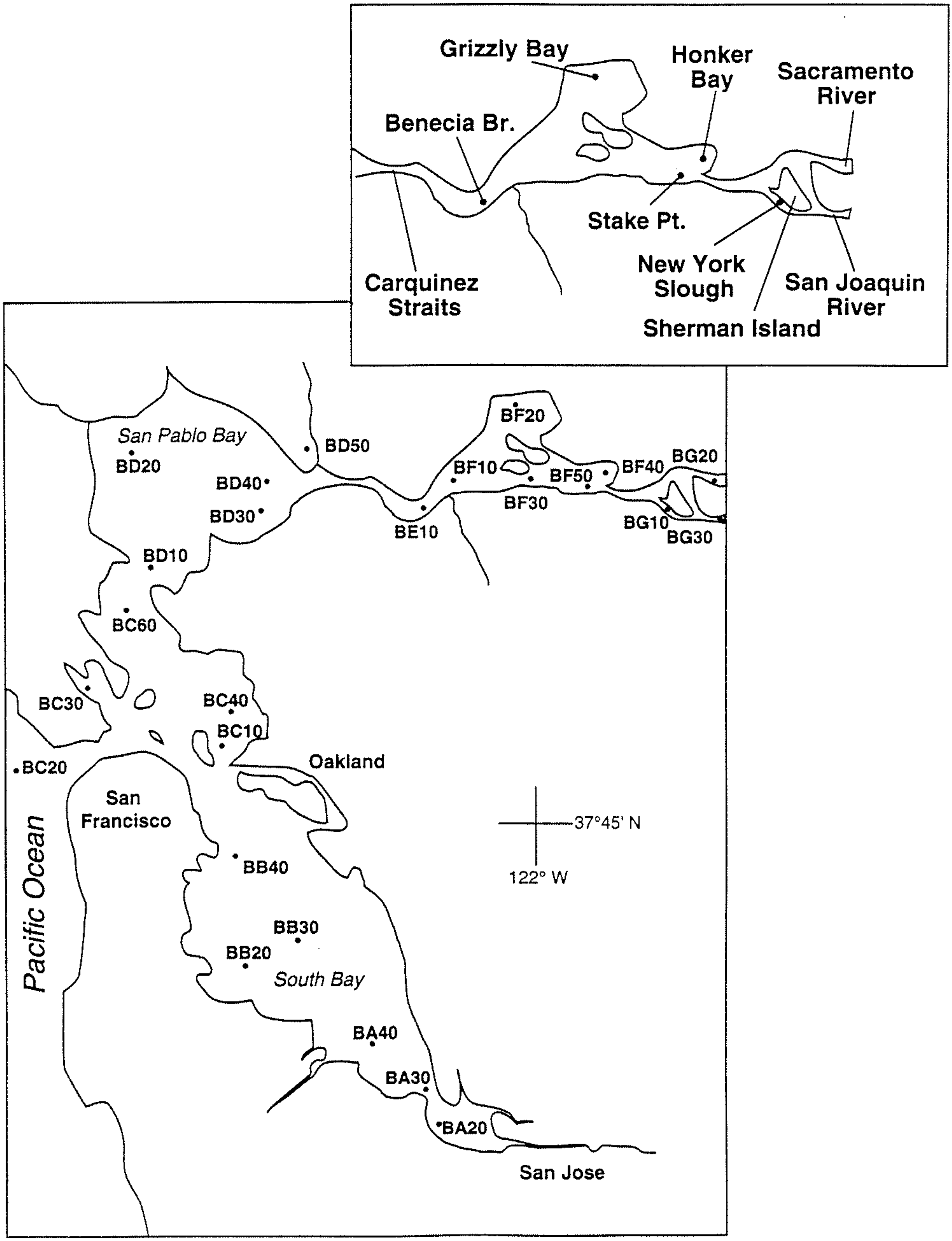
Grizzly Bay
Honker Bay
Sacramento River
Benecia Br.
Stake Pt.
Carquinez Straits
New York Slough
San Joaquin River
Sherman Island
San Pablo Bay
BD20
BD50
BD40
BD30
BD10
BC60
BC30
BC40
BC10
BC20
BF20
BF10
BF50
BF40
BG20
BF30
BE10
BG10
BG30
Oakland
San Francisco
Pacific Ocean
37°45' N
122° W
BB40
BB30
BB20
South Bay
BA40
BA30
BA20
San Jose

Figure 2: Hydrograph of the major freshwater sources to the San Francisco Bay estuary during the study period (1992-1996). Solid line indicates flow (m^3s^{-1}) in the Sacramento River at Freeport (USGS gauging station 11447650), dashed line indicates flow (m^3s^{-1}) in the Yolo Bypass near Woodlands (USGS gauging station 11453000). Solid circles on the Sacramento River hydrograph indicate sampling cruise dates. Flows at these gauging stations as provided by the USGS (53).

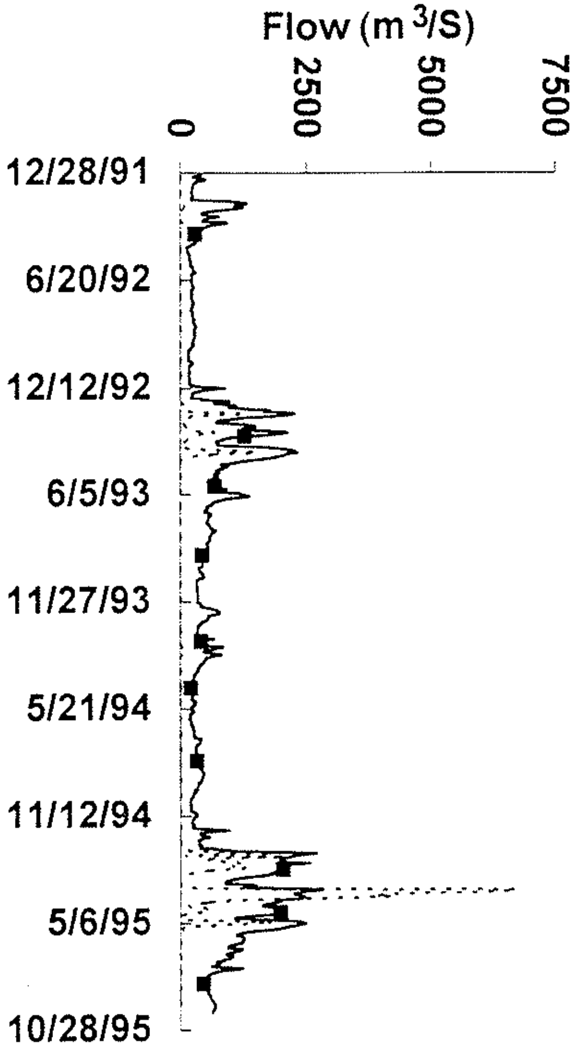

Fig 2A Abu-Saba
- [illegible]

Figure 3: Total dissolved Cr(III) + Cr(VI) concentrations (nM) vs. salinity in the San Francisco Bay estuary, 1992-1996.

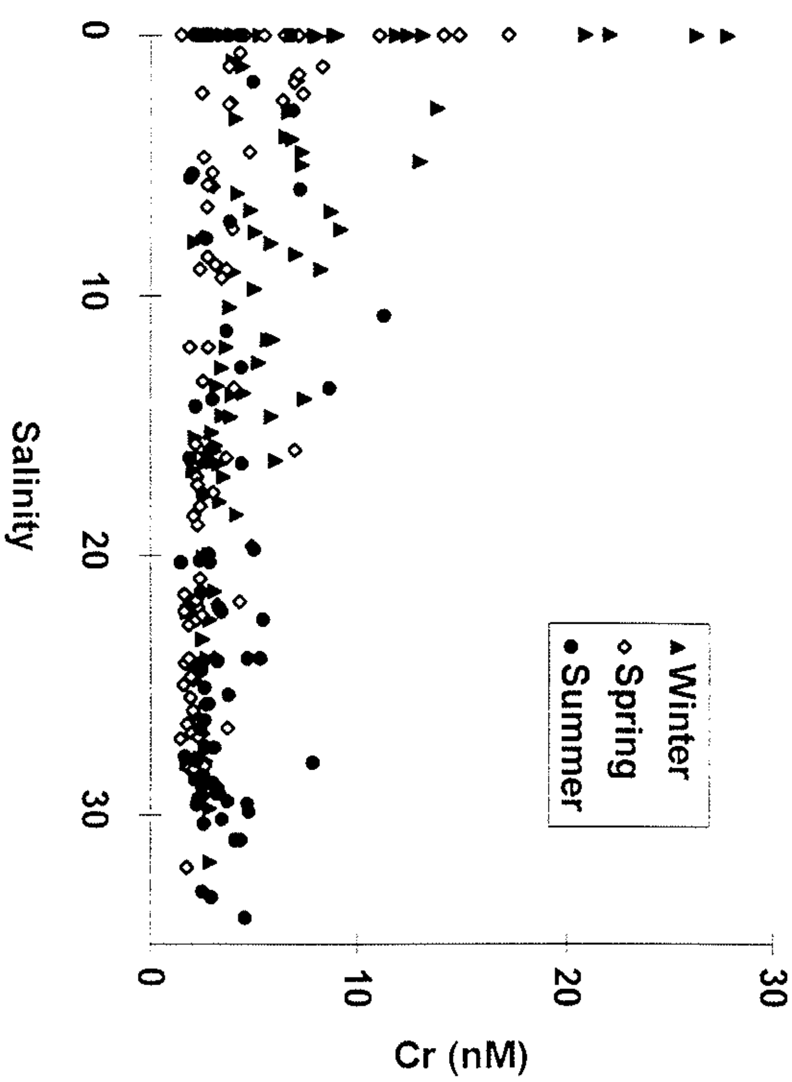

Fig 3 Abu Saba

Figure 4: Dissolved Cr(III) + Cr(VI) concentrations (nM) vs. dissolved Cr(III) concentrations (nM) in the San Francisco Bay estuary, 1992-1994.

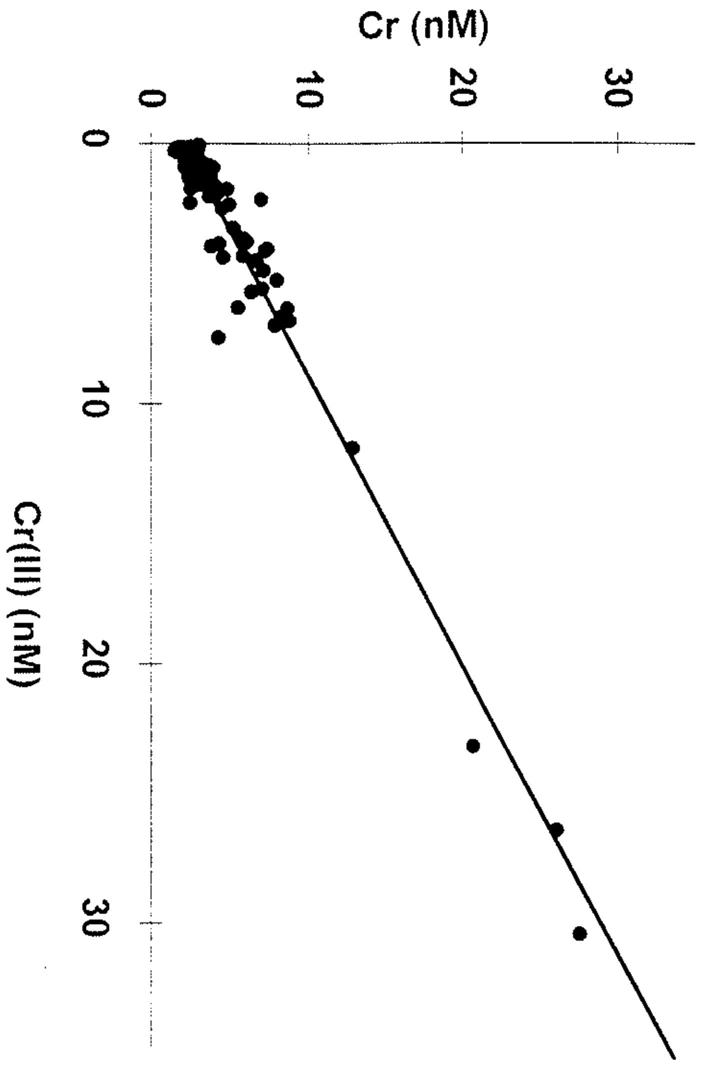

Fig 4
Abu Saba & Flegal

Figure 5: (A) Dissolved Cr(III) + Cr(VI) concentrations (nM) vs. salinity in the northern reach of San Francisco Bay (BG20-BC20) in March, 1993. The arrow indicates the concentration gradient between the Carquinez Straits and the head of the estuary. The circled points are from shoal stations in San Pablo Bay. (B) Dissolved, reactive silicate concentrations (µM) vs. salinity in the northern reach of San Francisco Bay (BG20-BC20) in March, 1993. (C) Hydrograph of the major freshwater sources to the San Francisco Bay estuary, February - March, 1993.

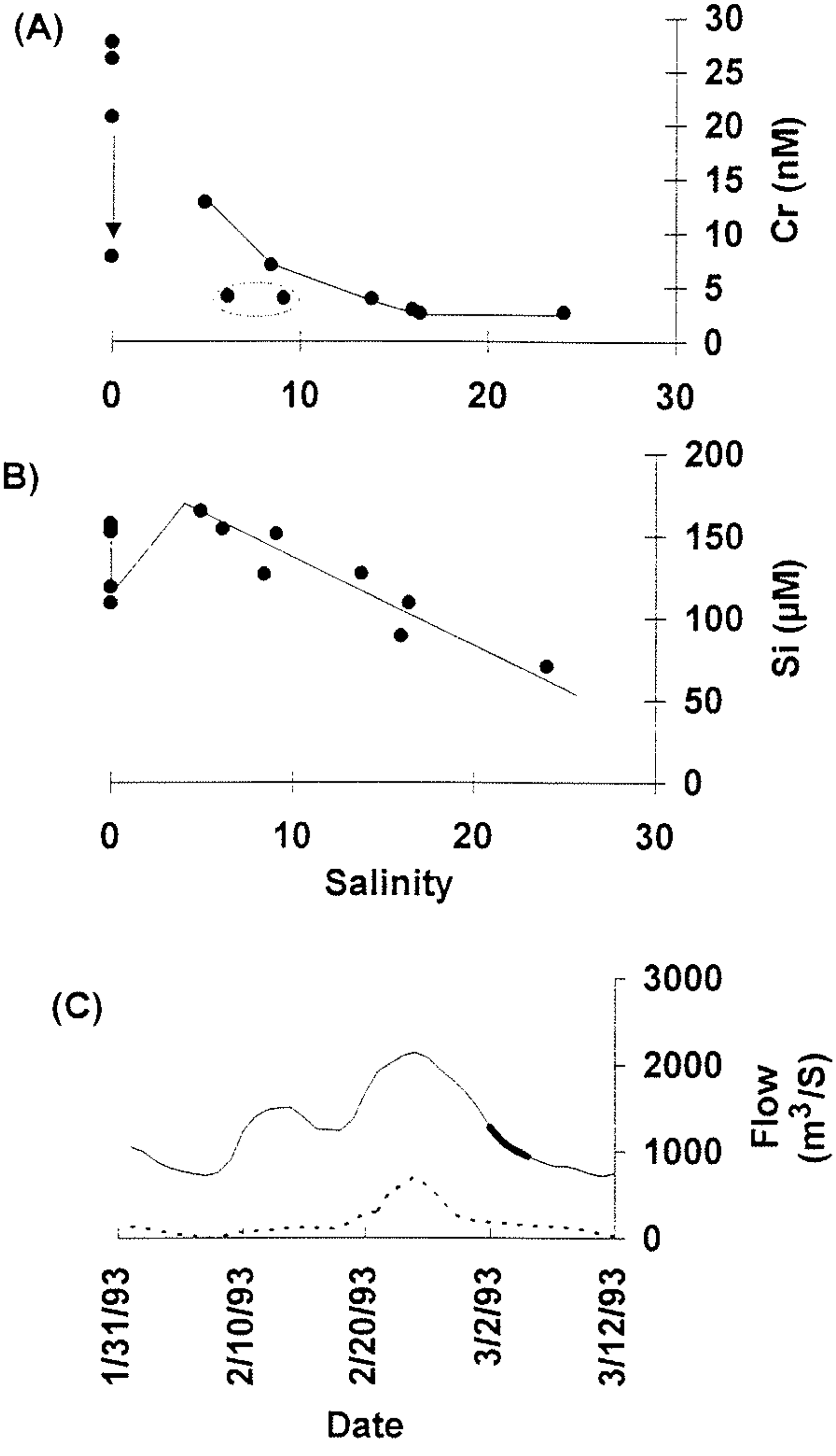
(A)
30
25
20
15
10
5
0
Cr (nM)
0
10
20
30
(B)
200
150
100
50
0
Si (µM)
0
10
20
30
Salinity
(C)
3000
2000
1000
0
Flow (m³/S)
1/31/93
2/10/93
2/20/93
3/2/93
3/12/93
Date

Fig 5
[illegible]

Figure 6: (A) Dissolved Cr(III) + Cr(VI) concentrations (nM) vs. salinity in the northern reach of San Francisco Bay (BG20-BC20) in February, 1995. (B) Dissolved, reactive silicate concentrations (μM) vs. salinity in the northern reach of San Francisco Bay (BG20-BC20) in February, 1995. (C) Hydrograph of the major freshwater sources to the San Francisco Bay estuary, January-February, 1995.

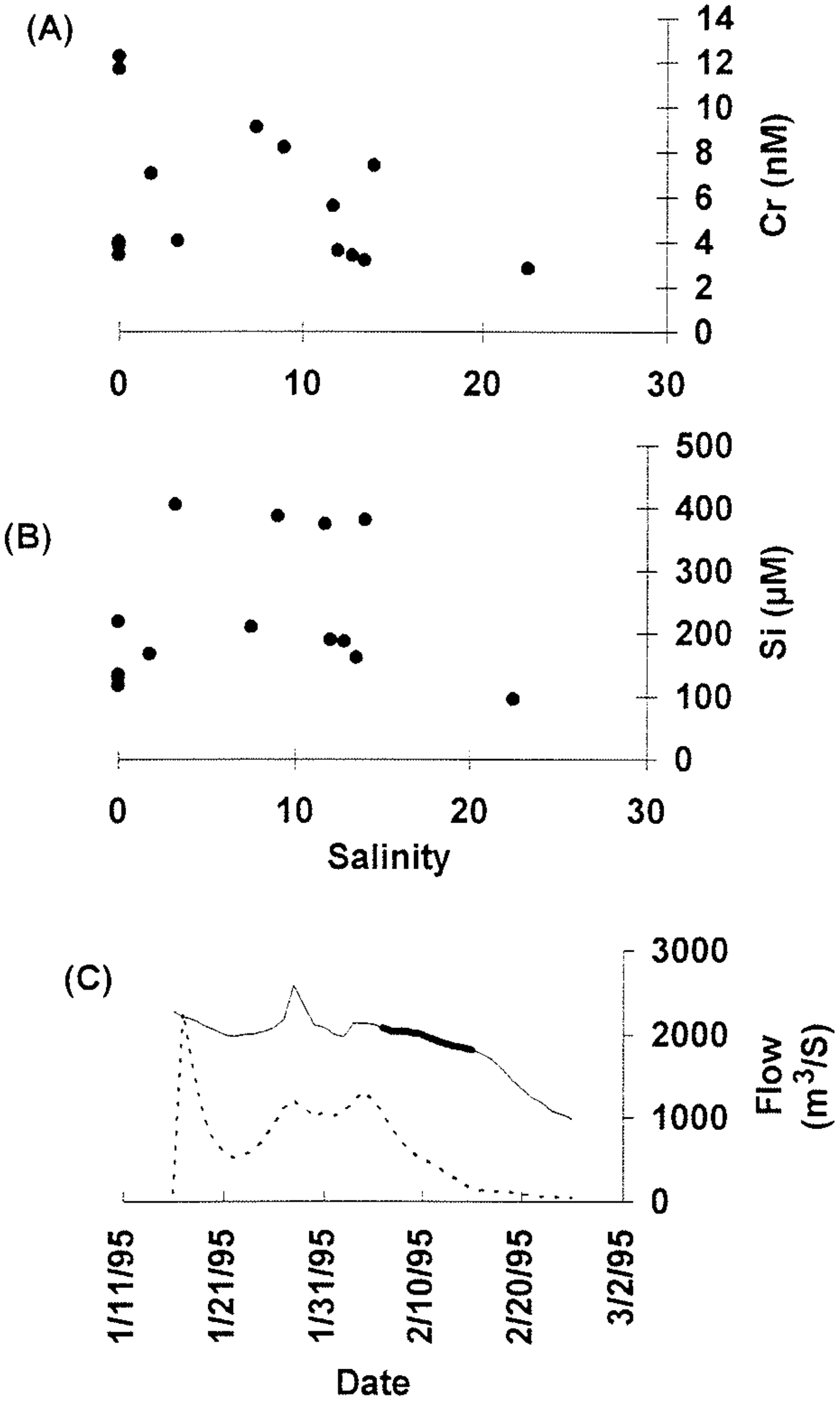

Fig 6 Ab. Saba
and Flow

Figure 7: Suspended particulate chromium concentrations (nM) vs. aluminum concentrations (μM) in the entire San Francisco Bay estuary, 1992-1994. Solid circles indicate four Delta stations (BG30, BF20, BD50, and BD40) in March, 1993.

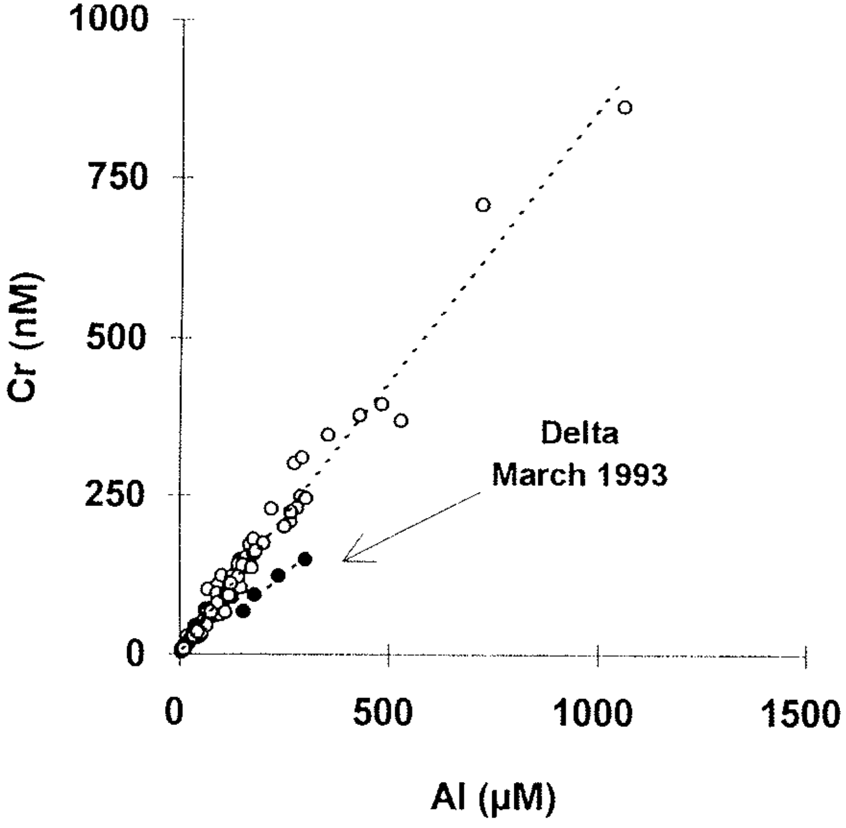

Fig 2 Abu Siba
and [illegible]

Figure 8: (A) Dissolved Cr(III) + Cr(VI) concentrations (nM) vs. salinity in the northern reach of San Francisco Bay (BG20-BC20) in August, 1993. (B) Dissolved, reactive silicate concentrations (μM) vs. salinity in the northern reach of San Francisco Bay (BG20-BC20) in August, 1993. (C) Hydrograph of the major freshwater sources to the San Francisco Bay estuary, July - August, 1993.

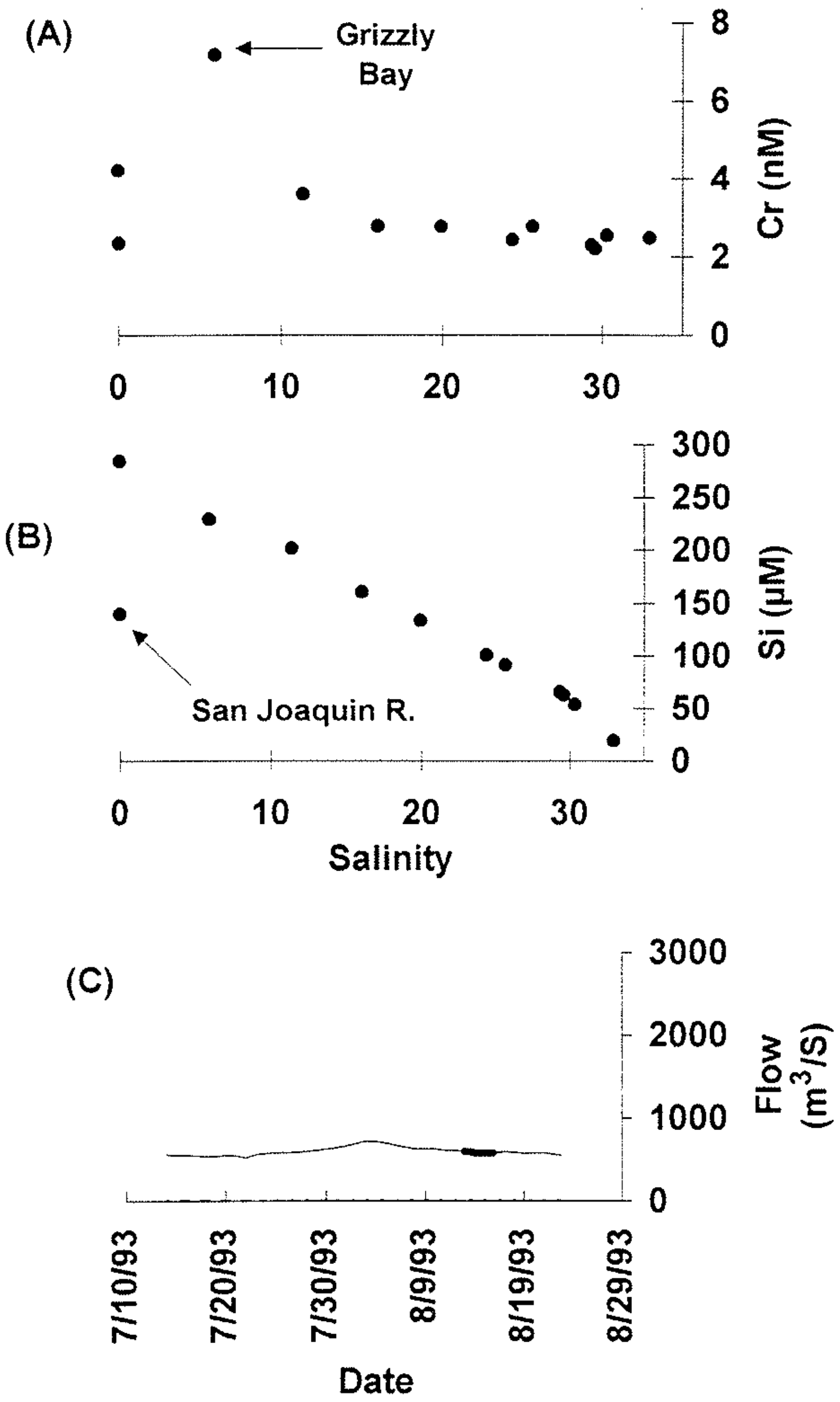

Fig 8 Abu-Saba and Flegal

Figure 9: Concentrations (nM) of dissolved Cr(VI) (dashed line) and total suspended solids (mg/L) (solid line) over a 36 hour sampling period in Honker Bay, July 27-28, 1995.

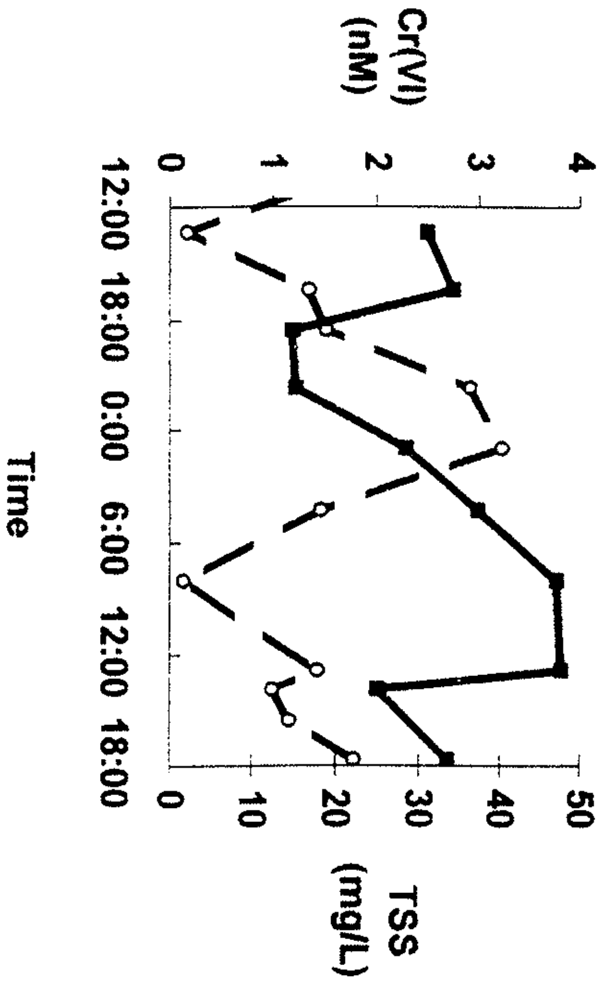

Fig 7 Abu-Saba and Flegal

Figure 10: Concentrations (nM) of dissolved Cr(III) vs. salinity in the South Bay in April, 1994. The single square is Guadalupe Slough (BA06), the circles are contiguous stations from Artesian Slough (BA05) to the Dumbarton Bridge (BA30)

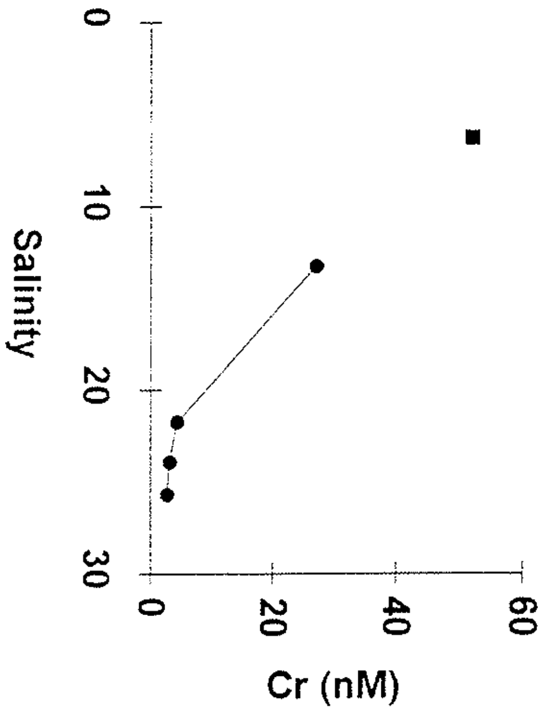

Fig 10 Abu-Saba
+ Flegal

Figure 11: Suspended particulate manganese concentrations (nM) vs. aluminum concentrations (µM) in the entire San Francisco Bay estuary, 1992-1994. Solid circles indicate three stations (BA05, BA06, BA10) in the South Bay in April, 1994.

Figure 11: Suspended particulate manganese concentrations (nM) vs. aluminum concentrations (μM) in the entire San Francisco Bay estuary, 1992-1994. Solid circles indicate three stations (BA05, BA06, BA10) in the South Bay in April, 1994.

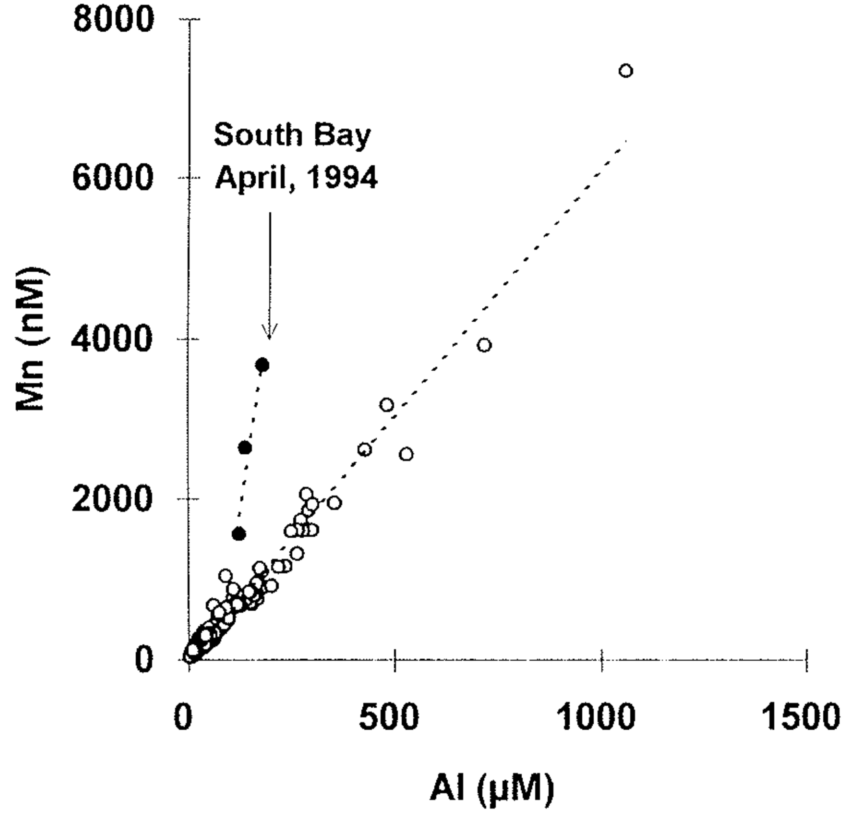

Fig 11 Abu-Saba
and Flegal

Figure 12: Concentrations of leachable (0.5N HCl) Cr in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

Figure 12: Concentrations of leachable (0.5N HCl) Cr in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

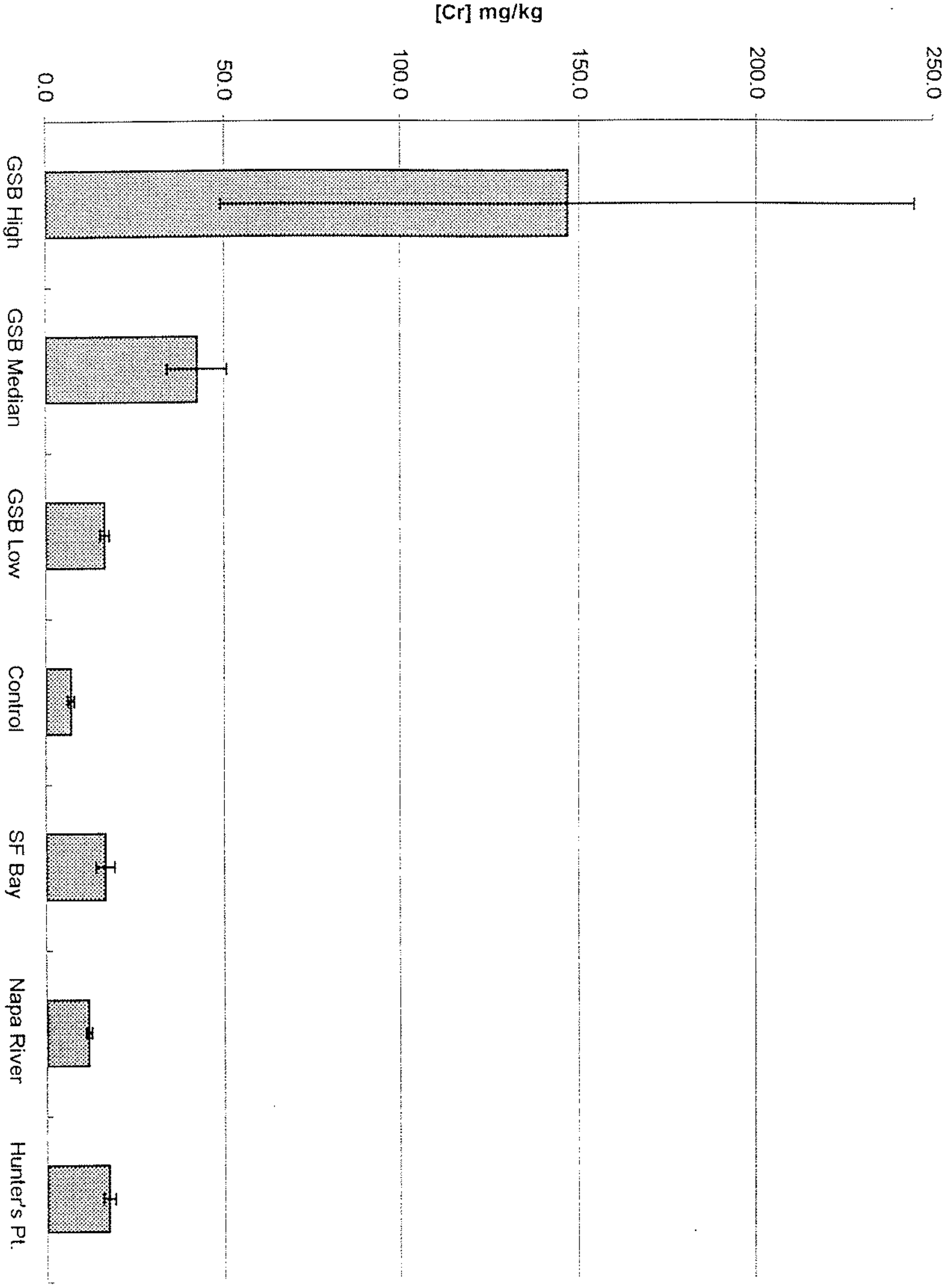
[Cr] mg/kg
0.0
50.0
100.0
150.0
200.0
250.0
GSB High
GSB Median
GSB Low
Control
SF Bay
Napa River
Hunter's Pt.

Figure 13: Leachable (0.5N HCl) Cr /Al ratios in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

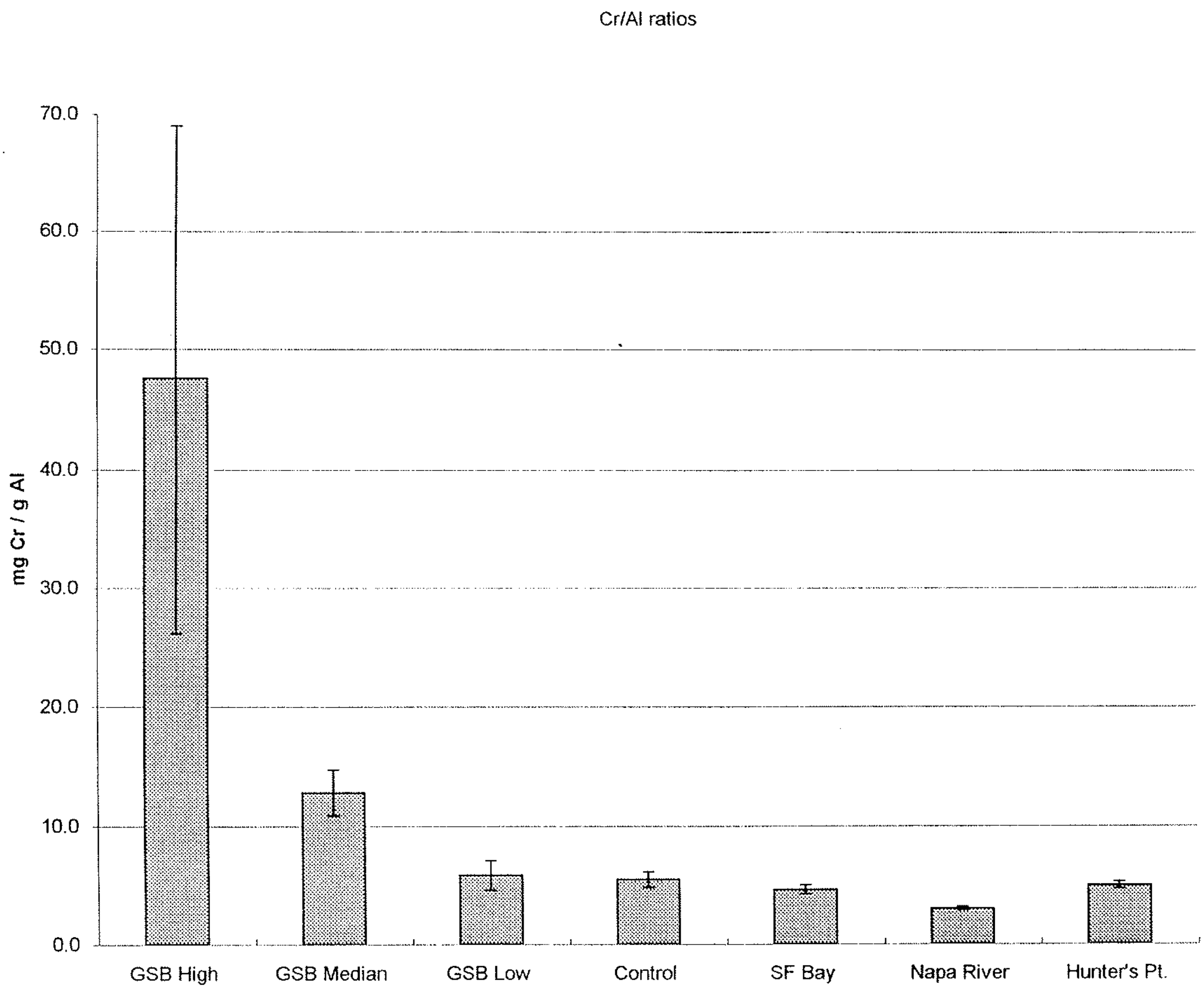
Cr/Al ratios
mg Cr / g Al
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
GSB High
GSB Median
GSB Low
Control
SF Bay
Napa River
Hunter's Pt.

Figure 14: Concentrations of leachable (0.5N HCl) Ni in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

Figure 14: Concentrations of leachable (0.5N HCl) Ni in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

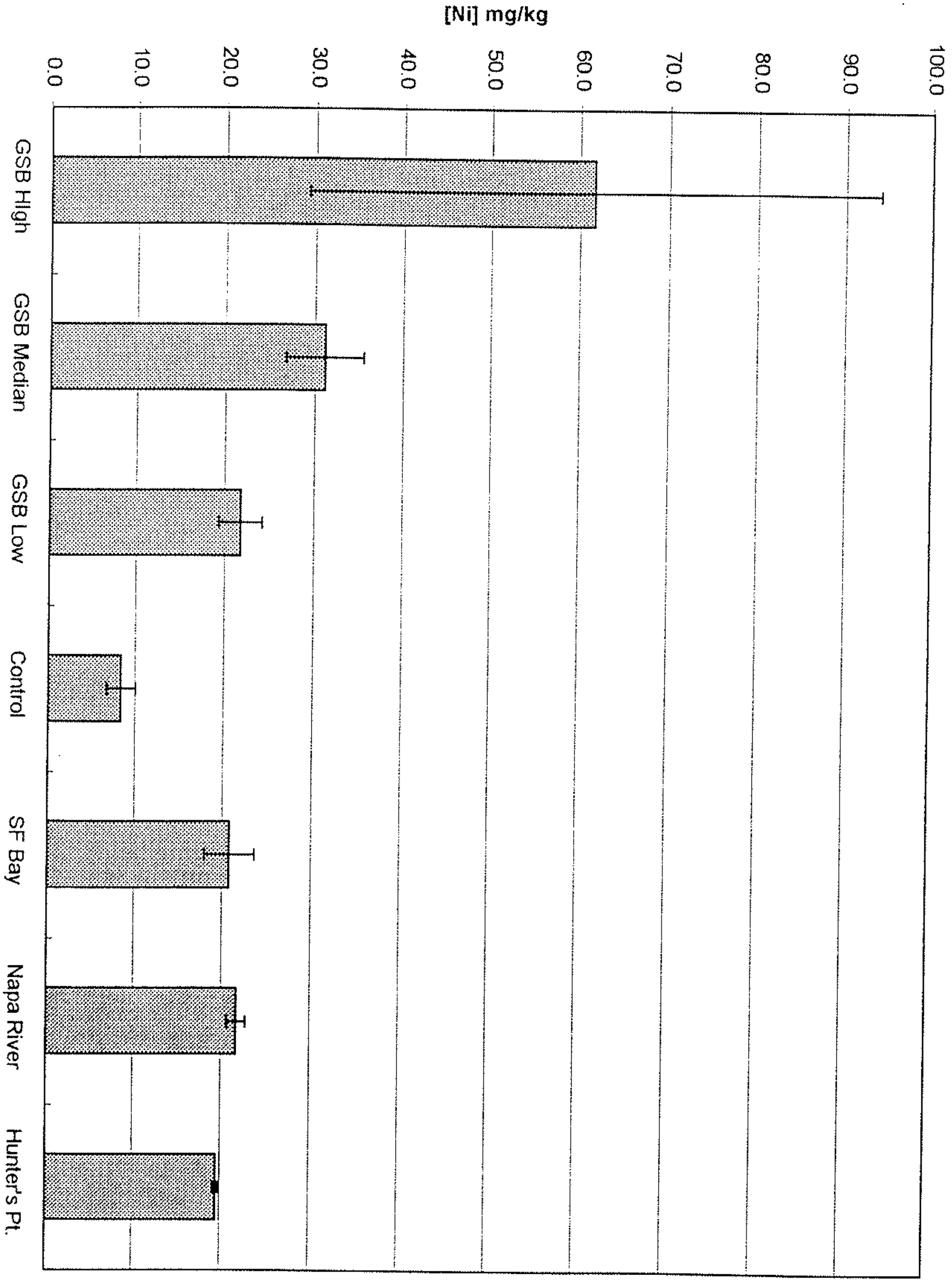
[Ni] mg/kg
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
GSB High
GSB Median
GSB Low
Control
SF Bay
Napa River
Hunter's Pt.

Figure 15: Leachable (0.5N HCl) Ni /Al ratios in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

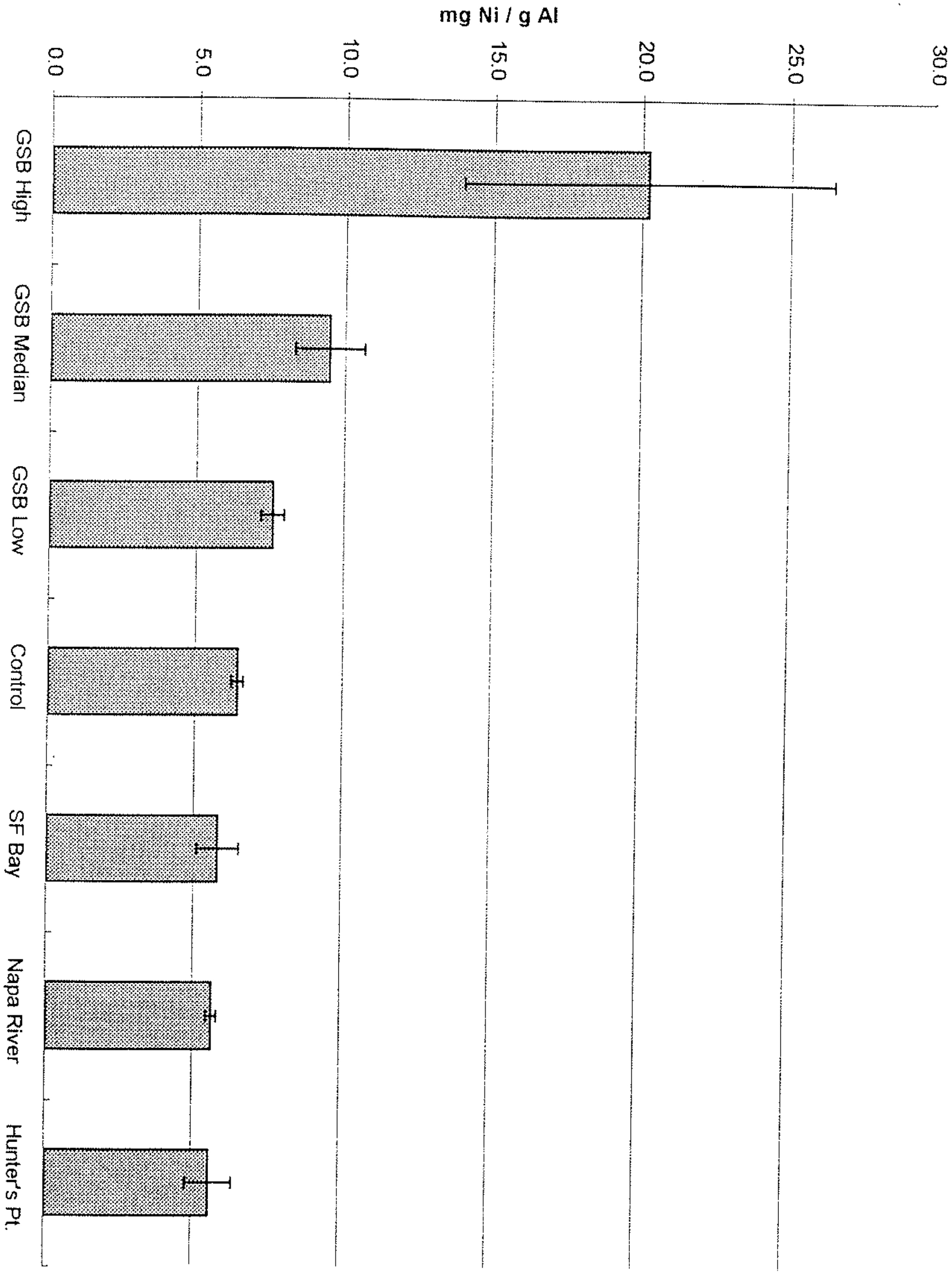
mg Ni / g Al
0.0
5.0
10.0
15.0
20.0
25.0
30.0
GSB High
GSB Median
GSB Low
Control
SF Bay
Napa River
Hunter's Pt.

Figure 16: Concentrations of leachable (0.5N HCl) Cu in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

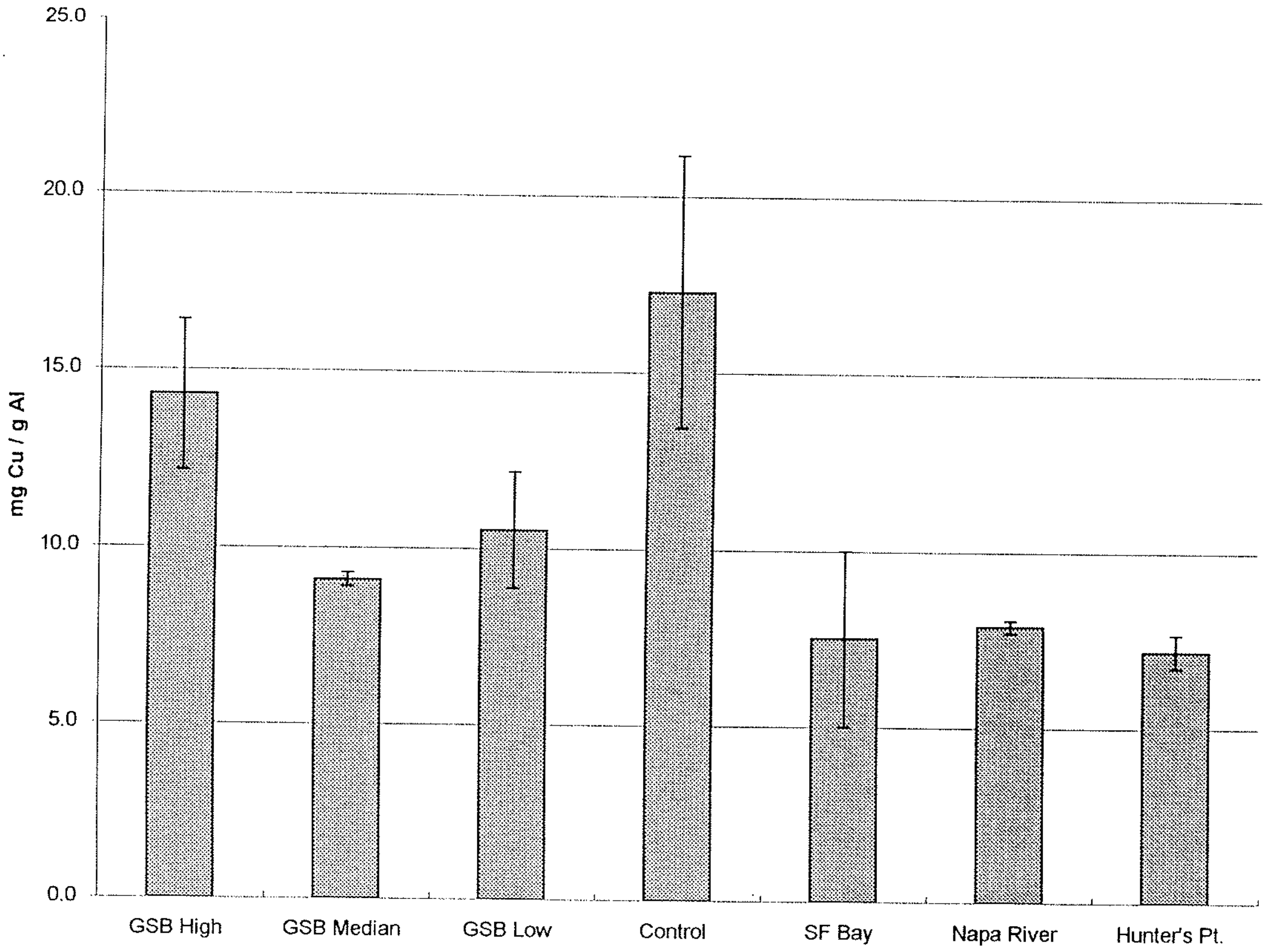
mg Cu / g Al
25.0
20.0
15.0
10.0
5.0
0.0
GSB High
GSB Median
GSB Low
Control
SF Bay
Napa River
Hunter's Pt.

Figure 17: Leachable (0.5N HCl) Cu /Al ratios in sediments collected from Green Sands Beach. Error bars represent spatial heterogeneity (one standard deviation).

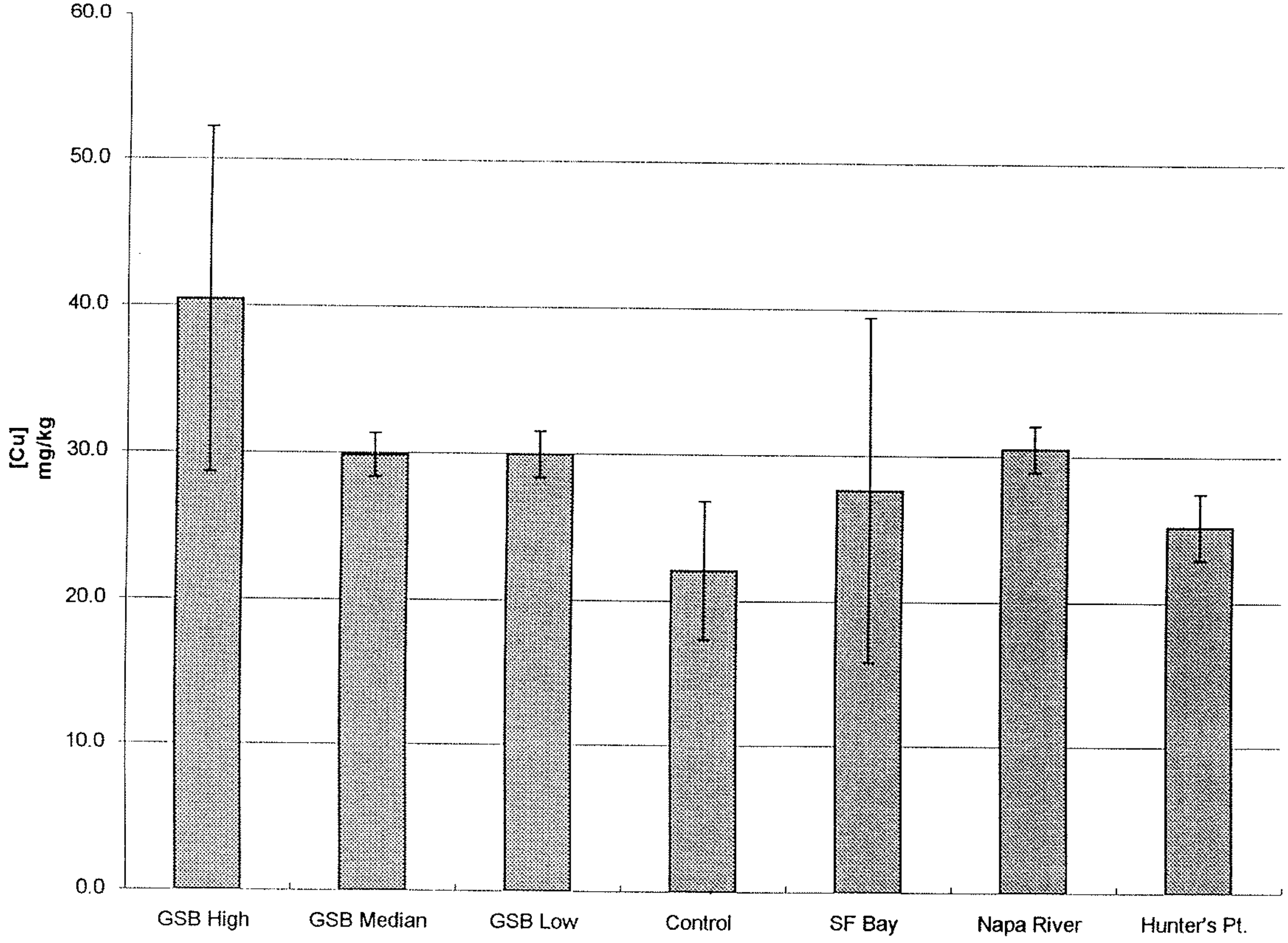
[Cu]
mg/kg
60.0
50.0
40.0
30.0
20.0
10.0
0.0
GSB High
GSB Median
GSB Low
Control
SF Bay
Napa River
Hunter's Pt.

Table 1: Concentrations of dissolved constituents in the South Bay Sloughs associated with an episodic Cr(III) flux in April, 1994. The background concentrations at each slough are the mean and standard deviations for each constituent measured in February, 1994, August, 1994, February, 1995, April, 1995, August, 1995, and February, 1996. The partition coefficients (L/kg) reflect baywide median values calculated from the current Regional Monitoring Program data set, 1989-1995, and are consistent with published distribution coefficients for estuarine and coastal waters (12, 47, 54)

Parameter	Partition Coefficient (log K_d)	Concentration in Artesian Slough (BA05)		Concentration in Guadalupe Slough (BA06)	
		April, 1994	Background	April, 1994	Background
Cr (nM)	5.9	27	4 ± 2	52	5 ± 2
Pb (nM)	6.3	3.9	1 ± 1	6.0	1 ± 0
Ag (pM)	5.2	112	19 ± 9	316	42 ± 62
Cu (nM)	4.8	93	54 ± 11	76	42 ± 19
Ni (nM)	4.5	150	125 ± 34	116	71 ± 23
Cd (pM)	3.3	910	753 ± 408	341	484 ± 343
NO_3^- (μM)	NA	71	337 ± 164	61	279 ± 176

Table 2: Summary of estimated dissolved chromium fluxes in the San Francisco Bay estuary.

Process	dissolved Cr flux (kg d^{-1})	Reference
high-flow fluvial inputs	< 1000	this study
scavenging losses to sediments	< 800	this study
export to coastal waters	< 100	this study
direct anthropogenic inputs	< 30	(5, 25)
in-situ reduction	< 20	this study
low-flow fluvial inputs	< 15	this study
other internal inputs	< 6	(5), this study
oxidative inputs	unknown	

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