Iron As a Reference Element for Determining Trace Metal Enrichment in California Coastal Shelf Sediments

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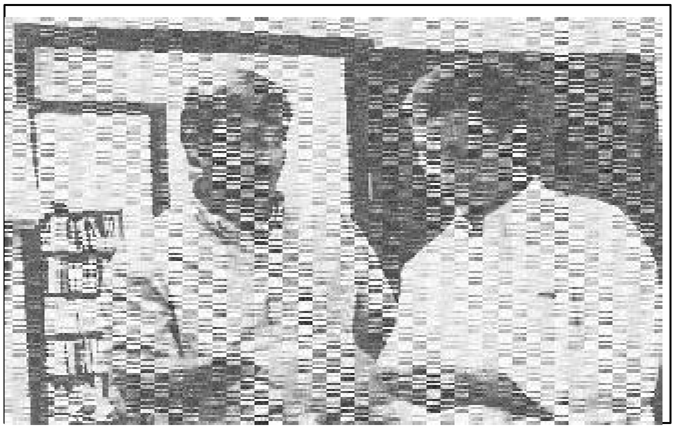


ABSTRACT

Major and trace elements occur naturally in the environment at levels which are detectable for most ocean monitoring programs. Assessments of potentially contaminated sediments are therefore confounded because measurable quantities do not automatically infer anthropogenic enrichment. In this study, we use iron as a conservative tracer to differentiate natural from anthropogenic components of bulk sediment metal concentrations in the Southern California Bight (SCB). Baseline relationships between iron and eight trace metals were established using data from non-impacted sites distant from known point and non-point sources of pollution. These baseline relationships were evaluated for geographic, depth, and analytical variance, and then were validated using an independent data set.

Using the reference element technique, we determined that over half of the 248 SCB sites measured were enriched in at least one trace metal. All trace metals investigated showed some level of enrichment: silver, cadmium, and chromium showed the greatest sediment enrichment, while arsenic and nickel showed the least enrichment. Degrees of enrichment were unevenly distributed throughout the SCB. Trace metal contamination was extensive in the Santa Monica Bay where approximately 80% of the sites were contaminated by more than three metals.

Provided that other SCB ocean monitoring programs measure iron and use comparable analytical techniques, the region-wide baseline relationships we have developed can be used to evaluate predicted natural concentrations or establish anthropogenic enrichment benchmarks. However, relationships with iron cannot be used in areas of anaerobic sediments where diagenic processes may alter its concentration.

INTRODUCTION

Unlike man-made organic compounds such as DDT, trace metals occur naturally in silt- and clay-bearing minerals of terrestrial and marine geologic deposits (Turekian and Wedepohl 1961, Word and Mearns 1979, Stull *et al.* 1986). The natural occurrence of metals in the environment complicates assessments of potentially contaminated marine sediments because measurable quantities of metals do not automatically infer anthropogenic enrichment. Several investigators have used a variety of normalizing techniques to account for natural mineralogical variations and to provide baseline relationships with which to assess metal enrichment. These normalizers include grain size (Ackerman *et al.* 1983, Horowitz and Elrick 1987), total organic carbon (Windom *et al.* 1989, Daskalakis and O'Conner 1995), iron (Trefry *et al.* 1985, Daskalakis and O'Connor 1995, Morse *et al.* 1993), aluminum (Hanson *et al.* 1993, Schropp *et al.* 1990, Bertine and Goldberg 1977), lithium (Loring 1990), rare earth elements (Olmez *et al.* 1991), and radioisotope tracers (Finney and Huh 1989, Goldberg *et al.* 1979).

Using these normalizers as conservative tracers of the natural metal-bearing phases in the fine sediment fraction requires several assumptions (Luoma 1990): first, that the normalizer covaries in proportion to the naturally occurring concentrations of the metal of interest; second, that the normalizer is insensitive to inputs from anthropogenic sources; and third, that the normalizer is stable and is not subject to environmental influences such as reduction/oxidation, adsorption/desorption, and other diagenic processes that may alter sediment concentrations.

Normalizing relationships have been developed for the eastern and Gulf coasts of the United States (Windom *et* *al*. 1989, Schropp *et al*. 1990, Daskalakis and O'Connor 1995, and Summers *et al*. 1996), as well as for countries on other continents (Din 1992), but such relationships have not been developed for the western coast of the United States. The Southern California Bight (SCB), which comprises almost 25% of the entire coastal US population (Culliton *et al*. 1990), is an area where assessing pollution impacts generates great interest. Numerous contaminant inputs, including treated municipal and industrial wastewater effluents (Raco-Rands 1996) and untreated urban runoff (Schiff and Stevenson 1996), cumulatively discharge more than 300 metric tons of metals into the area annually. In this study, we develop baseline relationships for determining naturally occurring concentrations of pollutant-associated metals using iron as a normalizing element. We validate the baseline relationships with independent data and then apply the relationships to region-wide monitoring results to illustrate which areas of the bight deviate most from the baseline relationships and thus are assumed to be contaminated from anthropogenic inputs.

MATERIALS AND METHODS

Sediment samples were collected at 248 sites from Point Conception to the United States/Mexico International Border between July 2 and August 22, 1994. Sample sites were selected using a stratified random design, with strata consisting of three depth zones (10-25 m, 25-100 m, and 100-200 m), and secondary strata within these depth zones located near known input sources. Additional details about the sampling design are provided by Stevens (in press) and Bergen (1996).

Samples were collected using a 0.1 m^2 modified Van Veen grab. The top 2 cm were removed using a Teflon or polyethylene spoon, taking care to avoid sediments in contact with the wall of the grab. Samples were stored frozen (≤ -4° C) in 500 ml borosilicate glass containers.

Approximately 0.5 gm of freeze-dried, fine-ground sediment was digested using 5 mL of 1:1 trace metal grade nitric acid and 10 mL of 1:4 hydrochloric acid. The acidified samples were heated to a gentle boil and swirled periodically for two hours. Samples were transferred to polypropylene centrifuge tubes and brought to volume of 30 mL with reagent grade water, and the solids removed by centrifugation. Metal concentrations in the supernatant were measured by inductively coupled plasma-mass spectroscopy (aluminum, cadmium, [total] chromium, copper, iron, lead, nickel, silver, and zinc), graphite furnace atomic absorption spectrometry (arsenic), or cold vapor atomic absorption spectrometry (mercury). Instrument blanks were run to identify sample carry-over. Matrix spikes, matrix spike duplicates, sample duplicates, blank spikes, and Certified Reference Material MESS-2 (National Research Council) were analyzed with approximately every 10 samples to assess accuracy and precision.

Data Analysis

Two criteria were used to identify "unenriched" sites for which to define baseline metal:iron reference element relationships. The first criterion, location in a non-contaminated environment, resulted in *a priori* deletion of the sites that are located in the vicinity of known sources of trace metal inputs. This represented 134 sites, including those located in proximity to wastewater outfalls, within 3 km of large creeks and rivers that drain into the SCB, and all sites within Santa Monica Bay. The second criterion was based upon identification of outliers from the remaining sites using regression analysis. To meet the requirements of this criterion, we developed regressions between each metal and iron, and then examined the residuals from the regression for normality. Normality was assessed using the Kolmogorov-Smirnov test. If a normal distribution was not achieved, sites with residuals greater than two standard deviations were eliminated and the regression was recalculated. The process of testing for normality and selection of outliers based upon standardized residuals was iterated until a normal distribution was achieved.

The baseline relationship between the trace metal of interest and the reference element represents the expectation, or "prediction," of naturally occurring concentrations. In order to define when a sample is enriched or contaminated, a threshold must be developed that exceeds our expectation. For the purposes of comparing individual samples to our baseline relationship, the 99% prediction interval was chosen as our threshold for contamination. The 99% prediction interval represents a reasonably conservative estimator of those individual samples that are enriched, and falls above (or below) the threshold 1% of the time based upon random chance alone.

Validation of the Baseline Relationships

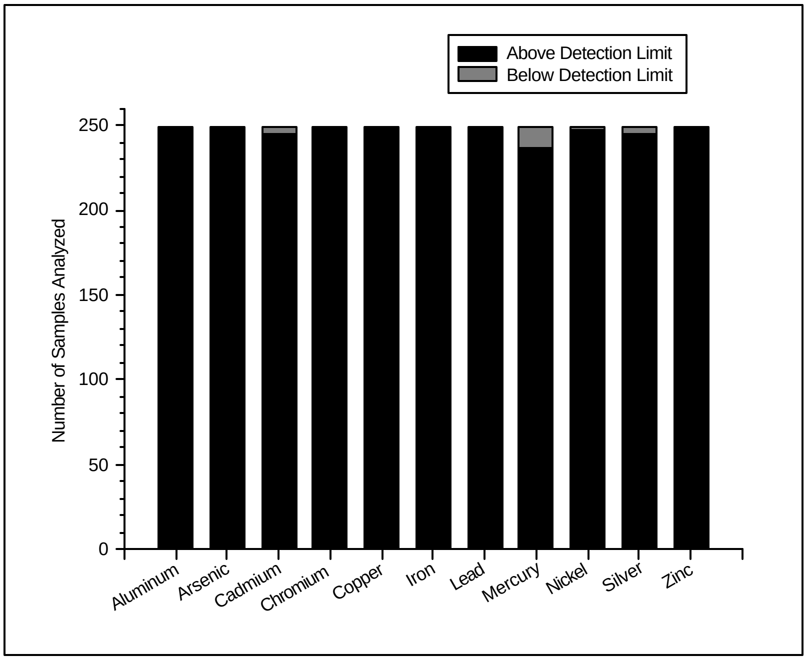
We validated our baseline relationships by: (1) assessing whether our relationships were consistent along geographic and depth gradients, (2) assessing whether the variances around the regression lines were consistent with laboratory measurement error, and (3) applying our results to independent data from unimpacted sites.

The first test of our baseline relationships assessed the underlying assumption that the metal:iron correlations were consistent throughout the study area. To test this assumption, the observed concentrations at non-enriched stations were divided by their predicted concentrations calculated from the baseline regression, and plotted against depth and latitude. Slopes from these relationships were evaluated to determine if they differed significantly from zero.

The second test of our baseline relationships compared the mean square error from our regression relationships with the analytical precision estimated from laboratory duplicates and certified reference material samples. If contaminated sites are effectively removed from the baseline data set, these error terms should be equivalent. Comparisons of error terms for each metal were conducted using the variance ratio test (F-test).

The final test of our baseline relationships divided metal concentrations from an independent data set by our predicted values to assess whether they fell within the bounds of our relationships. The independent data were collected from 18 sites distant from presumed point sources between Point Conception and the United States/ Mexico International Border in depths of 30 to 150 m, using field and laboratory procedures similar to those employed in our study (Thompson *et al.* 1993). These data were plotted and visually compared to our baseline relationships and then analyzed for possible inclusion within our 99% prediction intervals.

FIGURE 1. Rate of non-detectable measurements (N=248).



RESULTS

Two hundred and thirty-three of our 248 samples contained measurable quantities of all metals analyzed (Figure 1). Mercury was below detection limits at 12 sites, the most of any metal. Other metals were below detection limits including cadmium (4 sites), silver (4 sites), and nickel (1 site). Bight-wide mean concentrations (area-weighted) and 95% confidence intervals, plus the range and quartile distributions for each element, are provided in Table 1.

Of the 115 sites presumed *a priori* to be anthropogenically unenriched (i.e., distant from pollutant sources), approximately 43% fit the baseline metal:iron regression relationships for all eight metals of interest (Figure 2). Using the standardized residual technique for determining outliers, we found that 65 of the sites were enriched in at least one metal. Nearly half of these outlier sites were enriched by more than a single metal, with the maximum number of co-occurring metals at a single site being eight. On a metal-by-metal basis, between five sites (for nickel or arsenic) and 32 sites were removed (for cadmium), with an average of 18 enriched sites among all eight metals of interest (Table 2). Although cadmium had more outlier sites than any other metal, at least one other metal (most commonly chromium, copper or zinc) was also enriched at two-thirds of the sites. Sites for lead or nickel were not determined to be outliers unless at least one other metal was enriched.

Baseline relationships using iron as a reference element were highly significant ($P < 0.0001$) for all eight metals of interest (Table 3). Covariance with iron accounted for the majority of the variances observed in the distribution of metal concentrations. In fact, regression coefficients exceeded 0.7 for all metals except nickel and silver. Only a nominal relationship was shown between iron and mercury ($p=0.058$). Regression coefficients with mercury were also low ($r^2 = 0.068$).

Validation of the Baseline Relationships

There was no apparent bias in the baseline relationships at non-enriched stations over the depth of our study area, with the ratio of observed-to-predicted concentrations remaining near unity throughout the range (Figure 3). With the exception of nickel, latitude had no apparent effect on the baseline relationships (Figure 4). For nickel, a distinct increase in the reference element baseline relationships was found at the northernmost latitudes; these stations occurred primarily in the Santa Barbara Basin. The reason for this latitudinal difference is not yet known, but it did contribute to the overall increase in variance for this specific metal:iron baseline relationship.

Our second test of the metal:iron baseline relationships was to compare the mean square error of each baseline

TABLE 1. Sediment chemistry summary statistics (N=248).

	Mean	95% Confidence Interval	Minimum	25th Quartile	Median	75th Quartile	Maximum
percent (%), dry weight							
Fines (Silt+Clay)	42.53	3.97	0.00	24.30	38.49	57.61	99.97
Aluminum	1.05	0.09	0.16	0.69	0.94	1.27	3.73
Iron	1.86	0.15	0.31	1.20	1.68	2.21	10.46
µg/g (ppm), dry weight							
Arsenic	5.1	0.3	1.0	3.7	4.8	6.0	20.4
Cadmium	0.33	0.04	< 0.02	0.14	0.29	0.51	7.18
Chromium	39	4	7	21	34	57	361
Copper	15	2	1	7	12	23	166
Lead	10.9	1.0	0.9	6.6	10.2	17.9	77.7
Mercury	0.050	0.007	< 0.005	0.020	0.040	0.090	0.580
Nickel	18.1	1.9	0.9	9.8	16.3	24.8	84.7
Silver	0.34	0.08	< 0.01	0.08	0.17	0.60	15.37
Zinc	59	5	6	38	56	84	294

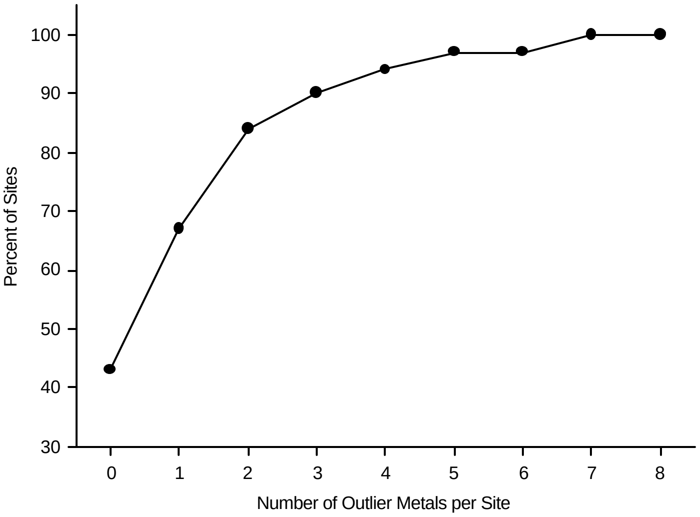


FIGURE 2. Percent of *a priori* sites presumed to be unenriched and determined to be outliers by regression analysis using iron as a reference element.

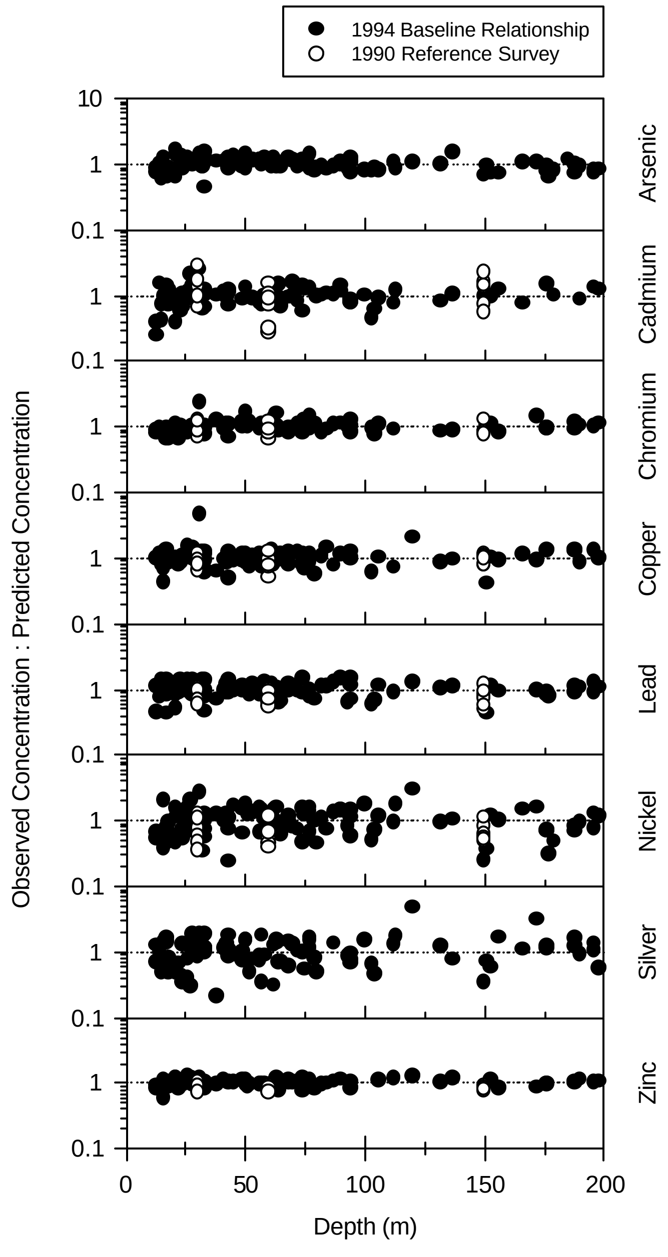
TABLE 2. Frequency of anthropogenic enrichment at sites *a priori* presumed to be reference locations. Enrichment determined by selecting outliers from the baseline metal:iron regression using standardized residuals (see text for details).

	Total Number of Outlier Sites	Percent of Outlier Sites With Any Two Metals Co-Occurring	Percent of Outlier Sites By Co-Occurrying Metal							
			Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Silver	Zinc
Arsenic	5	60	-	40	20	20	20	0	20	40
Cadmium	32	66	6	-	34	25	9	9	22	28
Chromium	27	89	4	41	-	41	41	19	26	59
Copper	19	89	5	42	58	-	58	21	32	74
Lead	12	100	8	25	92	92	-	33	42	100
Nickel	5	100	0	60	100	80	80	-	40	80
Silver	16	69	6	44	44	38	31	13	-	44
Zinc	28	86	7	32	57	50	43	14	25	-

TABLE 3. Regression results of metal:iron baseline relationships in Southern California Bight sediments. All relationships are significant at P < 0.0001.

Iron (% dry) *versus*	Sample Size	r^2	Slope (m)	Intercept (b)	± 99% Prediction Interval
Arsenic (μg/dry g)	110	0.752	1.90	1.49	2.80
Cadmium (μg/dry g)	83	0.734	0.0978	0.0055	0.1274
Chromium (μg/dry g)	88	0.882	16.50	-0.021	11.56
Copper (μg/dry g)	96	0.833	7.40	-2.01	6.50
Lead (μg/dry g)	103	0.738	4.350	0.836	5.199
Nickel (μg/dry g)	110	0.533	9.850	-0.407	19.596
Silver (μg/dry g)	99	0.581	0.0795	-0.0183	0.1426
Zinc (μg/dry g)	88	0.967	31.50	-1.95	15.45

FIGURE 3. Relationship of observed-to-predicted concentrations by depth (10-200 m). Closed circles (●) are unenriched sites from this study; open circles (○) are from the 1990 Reference Survey (Thompson *et al.* 1993).



regression to the mean error of laboratory duplicates and replicate analysis of certified reference materials. The error terms were not significantly different for seven of eight metals (Table 4), indicating that the error term in the regression was, for the most part, due to the imprecision of our analytical techniques. This imprecision does not imply any QA/QC deviation by the laboratory; the laboratory met or exceeded all QA/QC criteria. Rather, the laboratory imprecision can be attributed to the protocols selected and the state of the art of current analytical technology. Nickel was the only trace metal that had significantly more variance in the baseline relationship than could be accounted for by analytical error. One probable explanation for this variance is the regional differences shown in Figure 4.

Our metal:iron baseline relationships for cadmium, chromium, copper, lead, nickel, and zinc corresponded well with the independent data set (Figures 3 and 4). Not only did our predicted concentrations closely match the 1990 Reference Survey measurements, but the range of values fell within our 99% prediction intervals (not shown). Comparisons between data sets for arsenic were not available because this constituent was not measured in 1990. Similarly, comparisons with silver could not be completed due to the large number of non-detectable results in 1990.

Application

Figure 5 plots the reference element baseline regressions, 99% prediction interval thresholds, and individual site results for each of the eight metals in our study. Arsenic (n=8) and nickel (n=10) had the smallest number of anthropogenically enriched sites and, where enrichment was observed, the magnitude of contamination was relatively low. In contrast, cadmium (n=100), chromium (n=88), and silver (n=86) had the largest number of

FIGURE 4. Relationship of observed-to-predicted concentrations by latitude (San Diego to Point Conception, California). Closed circles (l) are unenriched sites from this study; open circles (!) are from the 1990 Reference Survey (Thompson *et al.* 1993).

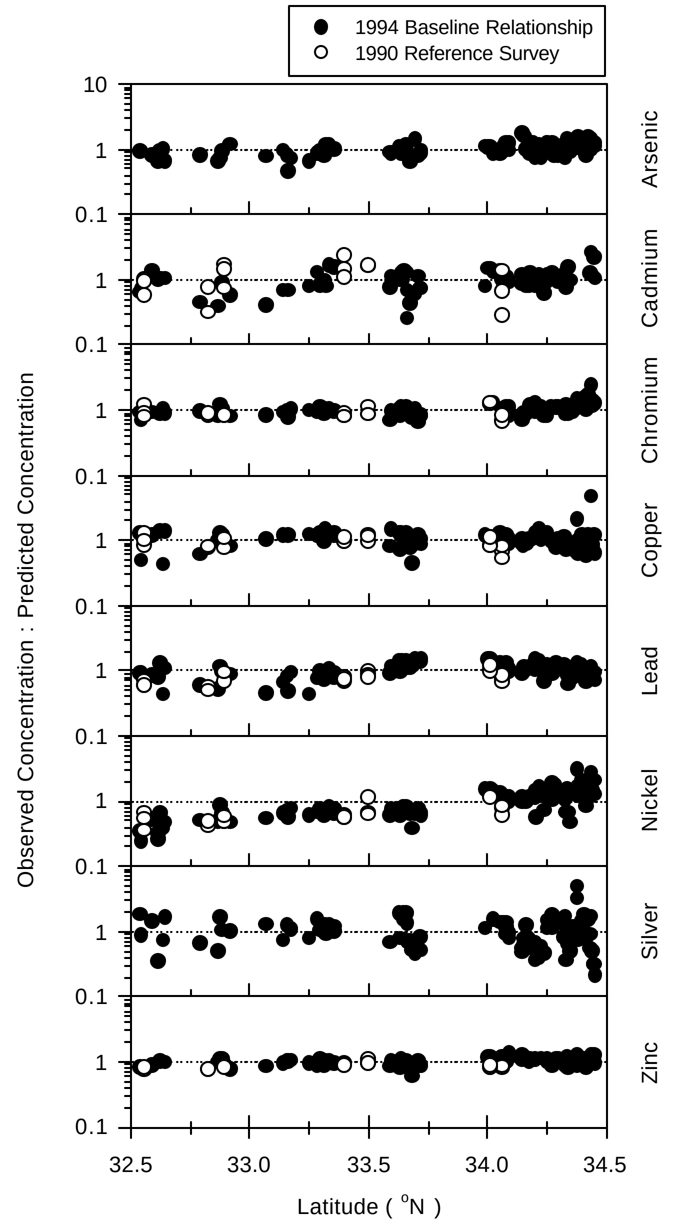


TABLE 4. Comparison of baseline regression variance and the analytical variance.

Iron vs. MSE	Combined Regression Variance*	Variance Mean (F Statistic)	Ratio
Arsenic	1.12	0.61	1.8
Cadmium	0.0023	0.0018	1.3
Chromium	18.8	28.1	1.5
Copper	5.89	4.34	1.4
Lead	3.85	1.7	2.3
Nickel	54.9	3.51	15.6**
Silver	0.0016	0.0021	1.3
Zinc	33.6	36.6	1.1

* Includes combination of laboratory duplicate and replicate certified reference material results.

** Indicates variance terms are significantly different, $P < 0.05$.

enriched sites, at times exceeding the enrichment thresholds by an order of magnitude.

Figure 6 maps the locations and degrees of enrichment in the SCB using the metal:iron reference element relationships. Over half (61%) of the SCB sites were enriched in at least one metal. Nearly 30% of all sites studied were enriched in more than three metals. Although vast stretches of the coastline were not contaminated, trace metal enrichment was observed throughout the SCB, from Point Conception to the United Sates/Mexico International Border.

Enrichment was consistently measured in Santa Monica Bay (97% of the sites) (Figure 6, inset). Furthermore, the greatest magnitude of enrichment was found in Santa Monica Bay. Approximately 79% of the sites were enriched in more than three metals. Only one sample in the entire SCB was shown to be enriched in all eight metals. This site is located near the terminus of the Hyperion Treatment Plant sludge disposal line in Santa Monica Bay, which was decommissioned in 1987.

DISCUSSION

As a reference element, iron proved to be a good predictor of naturally occurring concentrations for arsenic, cadmium, chromium, copper, lead, and zinc. Covariance with iron accounted for 73 to 97% of the variability in these trace metal concentrations from non-impacted areas of the SCB. With the exception of nickel, the variances observed in our metal-to-iron relationships were attributable to the imprecision of our analytical methods and the limitations of current technology. The variance observed in our nickel:iron relationship was augmented by a latitudinal gradient of regional variability within the SCB. We

FIGURE 5. Metal:iron plots overlaid with reference element baseline relationships. Sites which fall within the prediction interval (!) are considered uncontaminated; sites which lie above the prediction (s) interval are considered anthropogenically enriched.

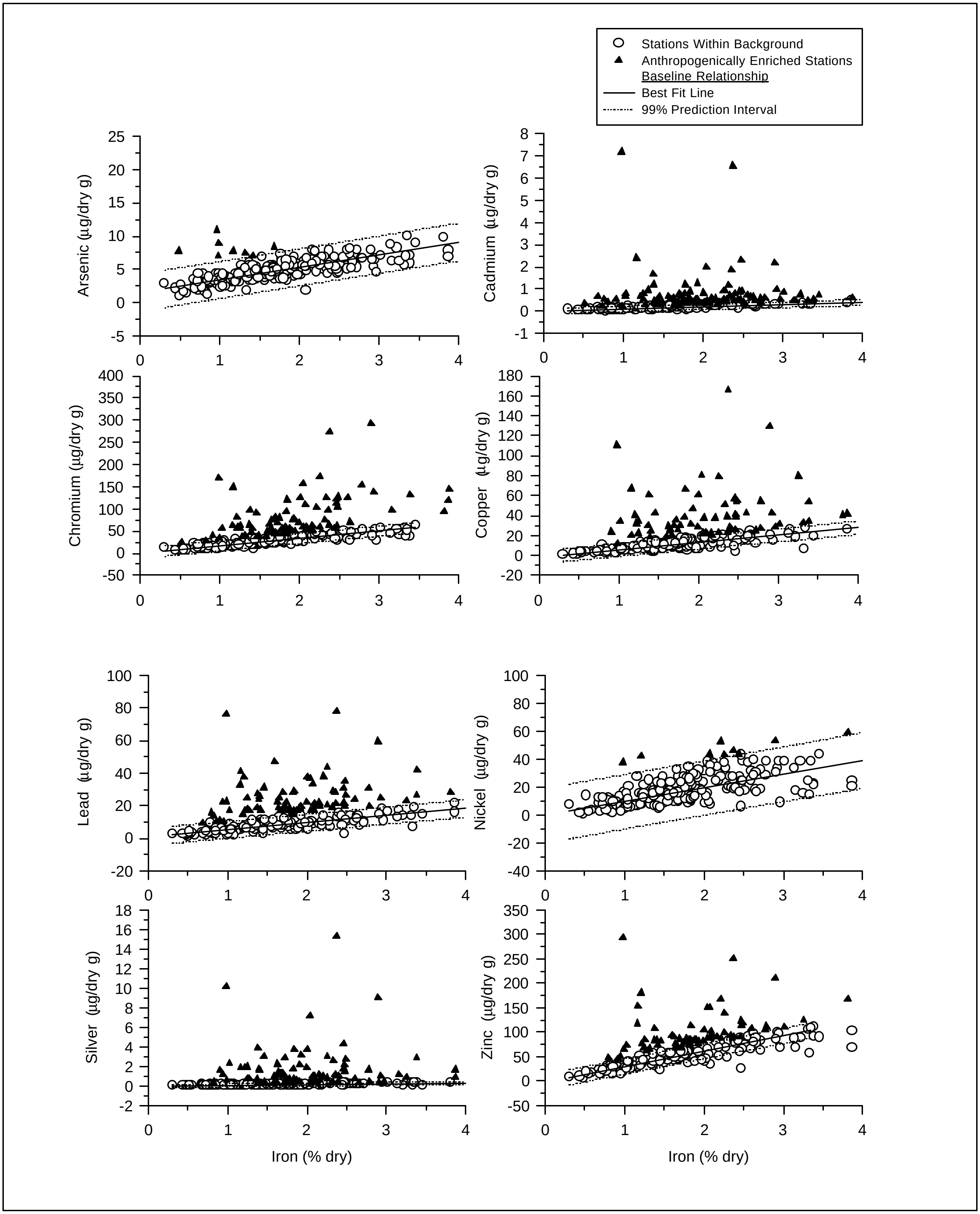
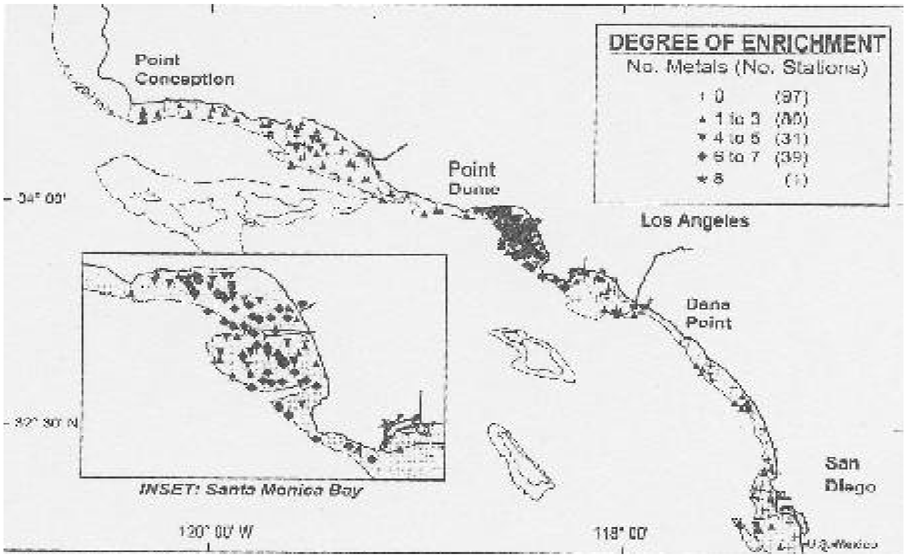


FIGURE 6. Map of sites in the Southern California Bight determined to have anthropogenically enriched sediment metal concentrations. Enrichment was assessed using iron as a reference element to determine background concentrations.



were unable to develop satisfactory mercury:iron relationships, a problem that has occurred in other studies and has been attributed primarily to organic phase contributions (Windom *et al.* 1989). We also noted that the very low natural abundance in the environement inhibited regression modeling by yielding low slope values and amplifying the relative error. Even small laboratory variance resulted in large changes to the bulk sediment concentration.

A number of studies during the last decade have developed reference element relationships to segregate anthropogenic from natural components of bulk sediment metal concentrations. Most studies have used aluminum as the conservative trace element (Hanson *et al.* 1993; Schropp *et al.* 1990). We chose iron instead of aluminum because we had an existing independent iron data set available to use for validation, which we did not have for aluminum. To assess whether aluminum or grain size would make a more effective conservative tracer, we calibrated baseline relationships for these normalizers using the same methodology we used for iron. We then compared the strength of the regression relationships among the three normalizers (Table 5). Although all of the correlations were statistically significant with each of the three candidate tracers, iron performed as well as, or better than, grain size or aluminum. We found that iron produced the highest regression coefficients for over half of the eight metals of interest. Iron explained substantially more variance than aluminum for six of the eight metals. Our data also showed that iron explained more of the variance in metal concentrations than grain size for six of eight metals. Furthermore, the usefulness of grain size as a conservative tracer is compromised at some locations of anthropogenic inputs in the SCB. Inputs such as treated municipal wastewater discharges from deep ocean outfalls or urban runoff from large river and creek mouths contribute not only varying levels of pollutants, but large quantities of silt and clay-sized particulates (< 63 µm diameter). These inputs can significantly alter the proportions of fine-grained materials (Bergen *et al.* 1995, Drake and Kolpack 1990).

One possible limitation of using iron as a reference element is that iron has a greater reduction potential in anaerobic sediments than does aluminum (Luoma 1990). When sediments become anoxic, iron will be reduced to a more water soluble form, which can then migrate up through the pore waters between sediment particles. Once in contact with aerobic layers at or near the sediment-water interface, iron will be oxidized and precipitate out of solution. This reduction/oxidation process effectively concentrates iron in surficial sediments and could invalidate an assumption of the reference element normalization technique, resulting in samples that fall below the reference element prediction interval (Finney and Huh 1989). Of the 248 sites sampled in our study, only one site in Santa Monica Bay was observed to be anaerobic; this site also had noticeably higher iron concentrations (>10% dry wt). All other sites, however, appeared to be normal with respect to aerobic surficial sediments. Nowhere in the survey were near-bottom waters within 1 m of the sea floor observed to be oxygen depleted (SCCWRP, unpublished data).

TABLE 5. Comparison of reference element normalizers. All correlations are significant at P< 0.001.

	Sample Size	Correlation Coefficient (r^2)		
		Iron	Aluminum	Fines
Iron	115	-	0.36	0.47
Aluminum	115	0.36	-	0.49
Fines	115	0.47	0.49	-
Arsenic	102	0.60	0.21	0.49
Cadmium	82	0.74	0.58	0.65
Chromium	87	0.88	0.44	0.70
Copper	89	0.77	0.78	0.74
Lead	96	0.67	0.39	0.52
Nickel	110	0.53	0.14	0.58
Silver	88	0.50	0.56	0.54
Zinc	88	0.94	0.50	0.74

Iron was selected as the more appropriate conservative tracer than aluminum for our study due, in part, to our digestion technique. In this study, we utilized a strong acid digestion with nitric acid, which is not as rigorous as the total dissolution digestion with hydrofluoric acid used in many of the studies that rely upon aluminum as the conservative tracer. Hydrofluoric acid digests entire sediment particles, including the alumina-silicate lattice structures of fine-grained clays and silts. Nitric acid is less extreme, digesting organic-rich particle surface layers and only partially extracting metals in the lattice structure of fine-grained sediments.

Other authors have noted differential recovery of metals when comparing nitric acid to hydrofluoric acid digestions (Bothner *et al*. 1980). Of particular interest, we noted that the recovery was much higher for iron (80%) than for aluminum (20%) when comparing the two digestion techniques on a limited number of samples. In addition, the nitric acid digestion is the prevailing sediment extraction technique employed by ocean monitoring programs of the SCB for the last 25 years, allowing us to provide some historical continuity to our study, utilize regional independent data sets, and derive tools applicable to local monitoring agencies.

Our study was the first to objectively evaluate a reference element for normalizing sediment trace metal concentrations in the SCB. Its success was due to many factors including: (1) a large spatial extent was examined, enabling regional and depth variability evaluations; (2) a large sample set was used, especially from non-contaminated areas, which dramatically improved modeling baseline relationships; and (3) an independent data set was available to validate our calibrated baseline relationships. Application of the reference element technique identified many contaminated areas (i.e., Santa Monica Bay) consistent with expectations from other studies which examined bulk sediment concentrations alone (Word and Mearns 1979). The normalization technique, however, enabled us to assess the magnitude of enrichment relative to naturally occurring concentrations rather than relying on a limited number of measurements from presumed reference areas. The second accomplishment of this study was that trace metal enrichment was found not only near point sources of pollutant inputs (i.e., treated wastewater outfalls), but was widespread throughout the SCB including some of the presumed reference areas measured previously. By providing the slopes, intercepts, and thresholds for each of the baseline reference element relationships, other investigators now have a tool for assessing natural background levels of potentially important sediment contaminants. This is a tool scientists and managers have been lacking when evaluating results from local monitoring programs or other independent projects.

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