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Trace metals in an urbanized estuarine sea turtle food web in San Diego Bay, CA

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A B S T R A C T

San Diego Bay is an anthropogenically impacted waterway that is also a critical habitat for many sensitive species such as the green sea turtle *(Chelonia mydas)*. In this study, we quantified trace metal concentrations in sediment and organisms composing the green sea turtle diet, and identified bioaccumulation patterns for a suite of trace metals. We found Ag, Cd, Cu, Mn, Se, and Zn exhibited the highest bioaccumulation levels in this food web. Cu and Mn concentrations in resident biota displayed a strong spatial gradient from the mouth to the head of the Bay, which was different from the patterns found in the sediment itself. Sediment median concentrations followed a general pattern across the bay of Al > Mn > Cu ≈ Zn > Pb > As > Cd > Ag > Se > Hg. In contrast, eelgrass displayed differential patterns in the mouth versus the back of the Bay (three front Bay sites: Al > Mn > Zn > Cu > Pb > Se > Cd ≈ Ag > As; five back Bay sites: Mn > Al > Zn > Cu > Pb ≈ Se > Cd > Ag > Hg > As) with the exception of Shelter Island where levels of Zn and Cu were elevated as a result of anti-fouling paint pollution. Observed differences between sediment and biota metal patterns are likely due to complex processes related to trace metals input and bioavailability, habitat characteristics and specific metabolic functioning of the trace metals for each member of the food web. These data highlight the fact that for the San Diego Bay ecosystem, the current use of toxicity reference values scaled up from sediment and invertebrate testing ex-situ is likely to be inaccurate when transposed to the green sea turtle. Here, we illustrate how identifying spatial variability in metal exposure can improve our understanding of habitat utilization by sea turtles in highly urbanized estuaries. Monitoring contaminants directly in food webs of sensitive vertebrates may greatly improve our understanding of their direct and indirect exposure to potentially deleterious contamination, and should be considered in the future to improve traditional risk assessment approaches.

1. Introduction

San Diego Bay is a highly urbanized estuary with a long history of pollution levels that exceed national water quality standards (US EPA, 2005) as well as fauna toxicity thresholds (Long, 2000; Zeeman, 2004). However, the Bay still remains a critical habitat for many sensitive species, including a resident population of endangered East Pacific green sea turtles *(Chelonia mydas)*. Contaminants from sources both contemporary and historical (via release by dredging of otherwise sediment-trapped contaminant pools) enter into the Bay's local food webs, including seagrass, mudflat, and other soft sediment communities. Sequestration of contaminants by seagrasses and macroalgae can improve water quality (Dawes et al., 2004), but resulting bioaccumulation may have negative impacts on primary producers themselves and higher-order organisms that consume them, like green sea turtles. The widespread effects of contaminants on sensitive wildlife and overall ecosystem health has been a major issue of concern for many years in San Diego Bay (Fairey et al., 1998) which challenging management today aims towards an urbanized sustainable coastal ecosystem (Bryan and Langston, 1992; USDoN, 1999).

Contaminant risk assessment monitoring programs have been conducted in San Diego Bay since 1984 to quantify contaminants and also estimate their fate and possible toxicological effects on resident organisms using a variety of endpoints such as mean chemical concentrations in sediment and porewater, fishes and invertebrates (McCain et al., 1992; Fairey et al., 1998). This approach resulted in the development of assessment criteria like benthic biodiversity indices and toxicological thresholds (MacDonald, 1994; Meador et al., 1994; Fairey et al., 1998; Long, 2000; USDoN, 1999). Past monitoring efforts led to the conclusions that numerous essential and non-essential trace metals present

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in San Diego Bay exceed threshold concentrations known to otherwise induce toxicity, thus likely causing deleterious effects to the local biota (e.g. the case especially for copper, zinc, mercury, lead, tin, cadmium; Bryan, 1984; Fairey et al., 1998; Zeeman, 2004; Deheyn and Latz, 2006).

However, recent research has shown that bioavailable elements, i.e. those that effectively enter into the food web, have the potential to trigger toxic effects at the individual, population, and ecosystem level (Deheyn and Latz, 2006). Bioavailability and bioaccumulation are dependent on many different biological factors including organismal trophic position and physiological adaptations (Rainbow, 2002; Luoma and Rainbow, 2005), as well as physical factors like sediment grain size and dissolved organic material concentration that affect chelation capacity of the environment for specific contaminants (Bryan and Langston, 1992). Therefore, exposure and accumulation can vary greatly across geographical areas and among species, especially between taxa with different foraging behaviors and life histories (Zeeman, 2004; Luoma and Rainbow, 2005).

East Pacific green turtles in San Diego Bay forage primarily on eelgrass *(Zostera marina)* and soft-bodied invertebrates (Lemons et al., 2011). Contaminant exposure in green turtles occurs mainly via food ingestion (they are air breathers and thus have little contamination from the seawater), mainly at foraging habitats because they otherwise seldom feed during migration (Bjorndal, 1997; Lutcavage et al., 1997). To date, only a few studies have reported trace metal concentrations in organisms native to San Diego Bay considering spatial and seasonal factors (Kurtz, 2003; Zeeman, 2004; Neira et al., 2011). No scientific material is available on trace metals distribution and concentration from the main components of the green turtle diet in San Diego Bay, i.e. eelgrass and soft-bodied invertebrates. Due to the lack of such data, green sea turtle risk assessment in the Bay has been developed based on metal concentration values in sediment and the few existing eelgrass values, resulting in management models associated with high levels of uncertainty (Zeeman, 2004). Thus, despite substantial trace element data collected over the last 25 years in San Diego Bay, metal exposure and accumulation in resident green sea turtles still remain unknown.

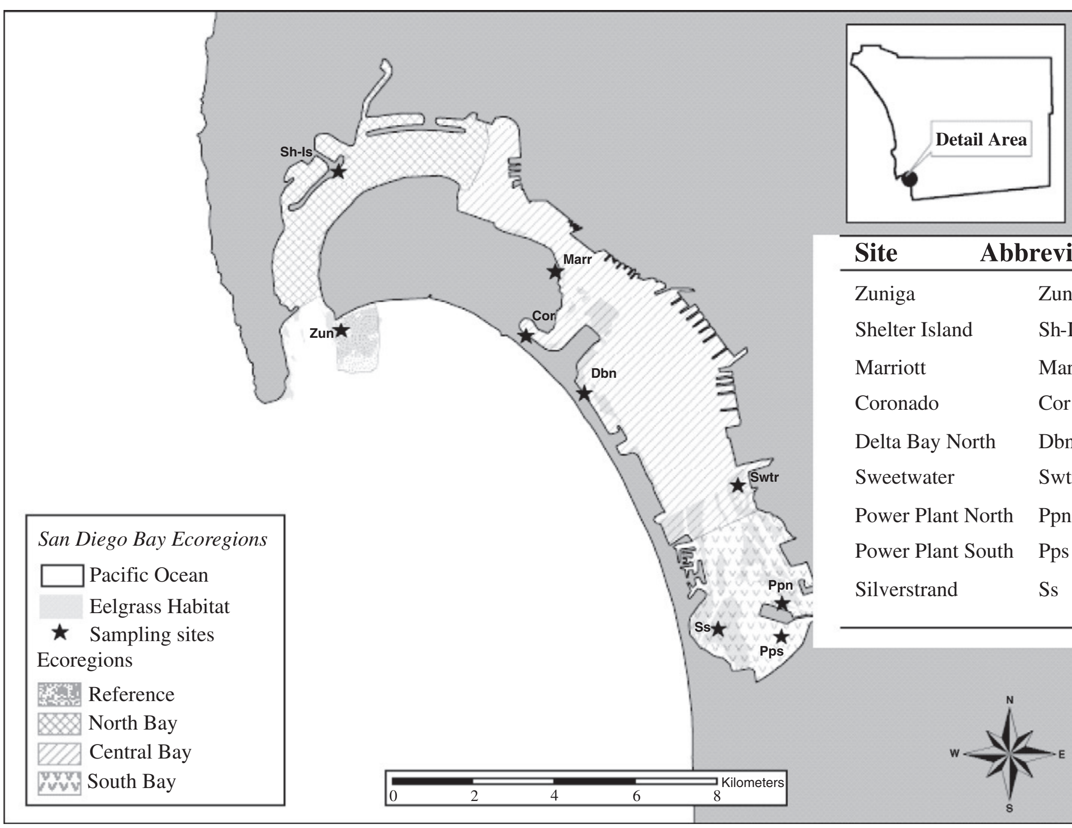
The present study fills this gap by analyzing trace metal concentrations in organisms on which the green sea turtles forage throughout San Diego Bay. We present the first dataset combining bioaccumulation patterns and spatial variability of key trace metals in the green sea turtle food web. This comprehensive study provides the necessary components for robust contamination risk assessments in sea turtles and other higher-order species living in an urban, yet biodiverse coastal environment.

2. Materials and methods

2.1. Study site and sample collection

San Diego Bay, CA (N32°40.0′ W117°13.7′) is a semi-enclosed estuarine system encompassing over 57 km^2 (Fig. 1). It is bordered by the densely populated metropolis of San Diego and is the terminus of three main watersheds encompassing over 660 km^2. Connected to the Pacific Ocean by a narrow Northwest channel, water residence time is largely driven by tidal pumping (Chadwick and Largier, 1999a). Depth across the Bay ranges 5–15 m (Chadwick and Largier, 1999b), and temperatures vary seasonally between 13 and 25 °C (Delgadillo-Hinojosa et al., 2008). The Bay is also dissimilar from typical estuaries in that relatively low freshwater input coupled with evaporative processes during summer months frequently create hypersaline conditions that intensify from the head to the back of the Bay (Largier et al., 1997; Delgadillo-Hinojosa et al., 2008).

We sampled eight eelgrass bed sites within three regions of San Diego Bay (Fig. 1), and a ninth (reference) site directly outside the Bay for comparison with inside Bay eelgrass beds. To include seasonal



Site	Abbreviation	Region
Zuniga	Zun	Reference
Shelter Island	Sh-Is	North Bay
Marriott	Marr	Central Bay
Coronado	Cor	Central Bay
Delta Bay North	Dbn	Central Bay
Sweetwater	Swtr	Central Bay
Power Plant North	Ppn	South Bay
Power Plant South	Pps	South Bay
Silverstrand	Ss	South Bay

Fig. 1. Map of San Diego Bay with designated ecoregions and sampling site abbreviations indicated on map and used throughout text.

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variability, we sampled each site in summer (June–July), fall (November) and spring (April–May) during 2007–2008, collecting a minimum of five sediment and eelgrass samples via SCUBA at each location. Red algae (*Gracilaria* spp.; n = 0–8 per site/sampling season), green algae (*Ulva* spp.; n = 0–5 per site/sampling season) and soft-bodied invertebrates (i.e. *Zoobotryon* spp.; n = 0–3 per site/sampling season and sponges; n = 0–4 per site/sampling season) were collected opportunistically at various sites, as these species have variable spatial and temporal distributions throughout the Bay (see Appendix 1 for details).

Forty-one live green sea turtles were captured between November 2007 and March 2009 using large mesh gillnets deployed from a U.S. National Marine Fisheries Service vessel in the south San Diego Bay. As part of a broader ecological study examining the demography and foraging ecology of green sea turtles (Eguchi et al., 2010) individuals were brought ashore for morphological measurements and tagging. Carapace tissues were then sampled according to modified protocols of Day et al. (2005) and processed for metal analyses. Full details of methodology and results from these analyses made only on sea turtles are reported in Komoroske et al. (2011); of this dataset only the concentration values relevant to calculate bioaccumulation factors are used in the present study and otherwise only reports metals analysis of the green sea turtle food web.

2.2. Trace metal analysis

Trace metal analyses were conducted at Scripps Institution of Oceanography (University of California, San Diego) following a routine protocol (Deheyn and Latz, 2005). In summary, sampled were dried, weighted and then digested in nitric acid and hydrogen peroxide using a Microwave digestor (Ethos Milestone). The resulting solution was then processed for simultaneous quantification of 15 trace metals (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, Ti, V, Zn) with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 3000 XL; Perkin Elmer), with detection limits from 0.05 to 4×10^{-6} mg g^{-1} depending on the element (Perkin Elmer, 2000). Methodological blanks were prepared according to exactly the same protocol as samples, but contained only nitric acid and nanopure water. Mean blank values were subtracted from sample concentrations after each run to adjust for background contamination throughout the sample processing (for details see Appendix 1, and Deheyn and Latz, 2005. Cold vapor atomic fluorescence spectrometry (CV-AFS) determined total mercury concentration in turtle carapace tissues as reported in Komoroske et al. (2011). A subset of sediment and eelgrass samples were analyzed using EPA method 7471A Total Mercury via cold vapor atomic absorption spectrophotometry (CV-AAS) at CalScience Environmental Laboratories, Inc. (Garden Grove, CA).

2.3. Quality assurance and quality control

Vials and all other tools used to handle samples were soaked for at least 72 h in 2% HNO_3 prior to use, and all sample processing was conducted in a class 1000 clean room. There are no certified values for weak acid treatment used to extract bioavailable trace metals from the sediment (Cantillo and Calder, 1990), nor for full digestion of plant material; therefore, accuracy of analyses was only based on measurements done from the biota (DOLT-2, National Research Council Canada-NRCC, Ottawa, ON). Percent recoveries depended on the metal, with a median value of 89% IQR ranging from 73.6% to 93.22%, with the exception of two outliers (Pb and Ni) that had particularly high percent recovery values and should therefore be interpreted with caution (Appendix Table S1). Variability was likely due to the simultaneous measurement of all 15 metals, as blanks were always low in metal concentrations relative to samples and internal calibration curves passed all standards tests (within 90% true value). Median values are reported for all metals in Appendix 1, but trace metals with poor recovery values were not considered in individual analyses. However, all biologically relevant metals were retained for comparative and multivariate analyses investigating relative differences and metal signatures, as deviations in true values should be consistent across samples for each metal and therefore not influence these analyses. NRCC CRM DOLT-2 *Dogfish liver* was used for methodological validation of CV-AFS for turtle carapace tissues, (mean recovery = 79.7%), and spiked samples were used for quality control of CV-AAS for sediment and eelgrass (mean recovery = 92.0%).

2.4. Statistical analysis

All statistical analyses were completed with SYSTAT 12 (Chicago, IL). Laboratory replicates were averaged by sample. Each sample type had at least 5 replicates for each location and each season, with the exception of some algae, bryozoans, and sponges, which exhibited high spatial and temporal variability. We report values and conducted analyses for a subset of the 15 quantified metals toxicologically relevant to our study. In order to compare our values to established toxicity reference concentration values, we also calculated means and medians for each sample type per sampling event including only detected values and corresponding N > LOD (limit of detection). We replaced non-detected values with the method detection value (10^{-6} ug·g^{-1}) as determined by the averaged minimum levels for which spectral peaks for each metal could be detected (Deheyn and Latz, 2006). We applied natural log transformations when data did not meet the assumptions of normality and verified results of all statistical tests with analogous non-parametric tests. Significance level was set at $\alpha = 0.05$ for all statistical tests and qualitative assessment thresholds are indicated in the corresponding text. We calculated enrichment and bioaccumulation factors to evaluate patterns among sites and used paired t-tests to detect overall bioaccumulation patterns for each forage type (see section 3).

To distinguish spatial relationships, we employed main effects Analysis of Variance (ANOVA) models by forage type for each metal and deconstructed the variance to determine the percentage of variability explained by each predictor. We compared the Bayesian Information Criterion (BIC) between fine (i.e. site and season) and coarse (i.e. bay region and season) models to identify if spatial differences were dependent on local "hotspot" site metal levels, or exhibited larger scale bay-wide patterns. To identify persistent spatial trends for each metal we compared main effects ANOVA models at different spatial scales for both $\ln(x + 1)$ and ranked data across all sampled biota. Pearson and Spearman rank correlations identified co-occuring metals spatially and between forage types, and were used to inform the multivariate analyses. Principal Components Analysis (PCA) was used to described overall correlation patterns for sediment and biota and to create multivariate metal factors. Using these metal factors and other uncorrelated trace metals, general linear models evaluated spatial patterns in both composite metal factors and individual trace metals. Finally, results from these analyses were compared to green turtle carapace trace metal concentrations (Komoroske et al., 2011). To account for environmental variability and analytical differences, we compared medians of forage items to carapace concentrations for each metal to identify any obvious bioaccumulation, defined as a difference of one order of magnitude or more between the sea turtle metal concentrations and forage item groups.

3. Health indices calculation

3.1. Enrichment Factor (EF)

Since trace metals occur naturally in the earth's crust, it cannot be presumed that an environment is automatically anthropogenically contaminated when trace metals are found in its sediments. We utilized the *Enrichment Factor (EF)* method, a widely used normalizing metric, to distinguish between natural and anthropogenic metal sources (Selvaraj et al., 2004; Valdes et al., 2005; Chen et al., 2007). Using earth crust values (Turekian and Wedepohl, 1961) with aluminum as a normalizing factor, the EF is defined as:

$$\mathrm{EF} = \frac{(\mathrm{Me}/\mathrm{Al})\ \text{sediment sample}}{(\mathrm{Me}/\mathrm{Al})\ \text{average shale value}}$$

where Me = the concentration measured for a given metal in a given sample or the reference value for that metal., We then used criteria set by Birth (2003) to score the severity of the EFs, in which EF<1 is equal to no enrichment, 1–3 is minor enrichment, 3–5 is moderate enrichment, 5–10 is moderately severe enrichment, 10–25 is severe enrichment, 25–50 is very severe enrichment, and >50 is extremely severe enrichment.

3.2. Bioaccumulation factor (BAF)

To examine bay-wide patterns of food web accumulation within and between each forage type, we calculated bioaccumulation factors (BAF) defined as:

$$\frac{\mathit{metal\ concentration}_{biota}}{\mathit{metal\ concentration}_{sediment}}$$

BAFs were averaged across seasons for each metal in which greater than 50% of the sites exhibited accumulation. BAF's greater than 10 likely indicate strong bioaccumulation or another source of contamination (i.e. water), so calculated values > 10 were replaced with 10 to normalize the distribution without losing qualitative value.

4. Results

4.1. Trace metal concentrations

Metal median concentrations varied over a wide range (0.008ug/g-5.64 mg/g dry weight) for all samples analyzed (total n: sediment = 130, eelgrass = 142, red algae = 73, green algae = 35, bryozoan = 8, sponge = 10, turtle carapace = 38). Basic statistics of metal concentrations for each site, season and sample type are included in Appendix 2. Median concentration rankings of turtle carapace were Zn > Al > Mn > Pb > Cu > Se > As > Ag > Hg > Cd. Sediment median concentrations rankings varied moderately between sites, but followed a general pattern across the bay of: Al > Mn > Cu ≈ Zn > Pb > As > Cd > Ag > Se > Hg. In contrast, eelgrass metal concentration rankings displayed differential patterns in the mouth versus the back of the Bay (three front Bay sites: Al > Mn > Zn > Cu > Pb > Se > Cd ≈ Ag > As; five back Bay sites: Mn > Al > Zn > Cu > Pb ≈ Se > Cd > Ag > Hg > As), with the exception of Shelter Island boat harbor where concentrations of zinc and copper were more elevated (Al > Zn > Cu > Mn > Pb > Ag ≈ Cd ≈ Se > Hg > As) likely as a result of anti-fouling paint pollution (Neira et al., 2009). Small sample sizes of green algae, red algae, bryozoans and sponges prevented robust analyses, but overall metal median concentrations of Al, Mn, Cu, Zn, and Pb were consistently higher than Se, Cd, As, and Ag in all four groups.

4.2. Enrichment factors

The majority of trace metals scored as moderately enriched or higher in San Diego Bay (Table 1; Birth, 2003), with no trend of increasing or decreasing enrichment along the estuarine gradient. In general, Ag, As, Cd, Cu, Pb, and Zn ranked as moderately severe enrichment, severe enrichment, or very severe enrichment inside the Bay (EF > 5). Trace metals were generally consistent across seasons within a site, except in the two most Southern sites (Pps and Ss) where almost all trace metals were ranked as very (EF = 25–50) or extremely severe (EF > 50) in the Fall, but mostly moderate (EF = 3–5) or moderately severe (EF = 5–10) during the Summer. The reference site (Zun) showed no to moderate enrichment of most trace metals (EF > 5) with the exceptions of silver (EF = 173) and lead (EF = 6.35).

4.3. Overall biota bioaccumulation trends

Variance deconstruction of main effects ANOVA for site and season predictors of each metal determined that site accounted for more than 20% of the variability observed in the majority of cases, as measured by the coefficient of determination. This made it inappropriate to treat each sampling event as independent. Therefore, we used the geometric mean of each site pooled across seasons for statistical tests of bioaccumulation to reduce the effects from seasonal variability. Choosing this conservative approach assured that any significant effect detected in paired t-tests and Wilcoxon sign rank tests resulted from clear differences among sites, not Type I error.

Most trace metals were significantly higher in sediment compared to eelgrass and both red and green algae across sites (Fig. 2), specifically Ti, Fe, Ni, Pb, Cr, and Al ($p \leq 0.02$). This suggested that these trace metals likely do not strongly bioaccumulate directly from sediment in these biota in San Diego Bay. However, eelgrass concentrations of Ag, Cu, Mn, Se, Sr, V, and Zn were significantly higher than corresponding sediment, but these patterns were not observed for algae or invertebrate groups. Red and green algae also had significant differences in significant bioaccumulation trends (As, Mn, Pb, V; Fig. 2), suggesting that different types of algae may be dissimilar in their uptake and metal accumulation from the environment.

4.4. Bay-wide trends of bioaccumulation factors (BAF)

Comparisons of bioaccumulation patterns among Bay regions and forage type revealed variation in BAF patterns by trace metal (Fig. 3). Cu and V showed little BAF variation between forage type and regions, while Ag, As, and Se differed between forage types but were consistent across all Bay regions. Cd, Mn, Sr, Zn were influenced by a combination of both factors. Complete ranges of BAFs for each biota, region and metal are listed in Appendix 1 (Table S2).

For many trace metals (Ag, Cd, Cu, Mn, Sr, Zn), eelgrass BAFs were consistently higher than other forage groups in most regions. Copper exhibited a very strong trend of decreasing bioaccumulation along the entire estuarine gradient for all biota groups, while Mn had a reverse trend of increasing bioaccumulation from front to back of the Bay. It is important to note that Se BAF's were elevated at most sites for all biota groups mainly because sediment concentrations were below detection limits for the majority of sites and seasons while Se was detected in most biota samples at relatively high concentrations.

Table 1
Qualitative enrichment classification for trace metals at each site averaged across seasons. Refer to Fig. 1 for definitions of site codes and corresponding regions. Trace metals found in the lowest two categories (i.e. no enrichment and minor enrichment) were omitted (see text). Numbers correspond to the following categories: (1) Moderate enrichment (2) Moderately severe (3) Severe (4) Very severe (5) Extremely severe, according to criteria of Birth (2003).

Site	Enrichment Category				
	1	2	3	4	5
Zun	As	Pb			Ag
Sh-Is		As	Cd, Cu, Pb	Zn	Ag
Marr		As, Cd,	Cu, Zn	Pb	Ag
Cor	As	Cd, Zn	Cu, Pb		Ag
Dbn		As	Cu, Pb, Zn	Cd	
Swtr	Mn	As, Cd, Zn	Cu, Pb		Ag
Ppn		Cu	Pb, Zn	As, Cd	Ag
Pps			Cu, Mn, Pb, Se, Zn	As, Cd	Ag
Ss	Zn	Mn, Pb	Cd, Cu, Se	As	Ag

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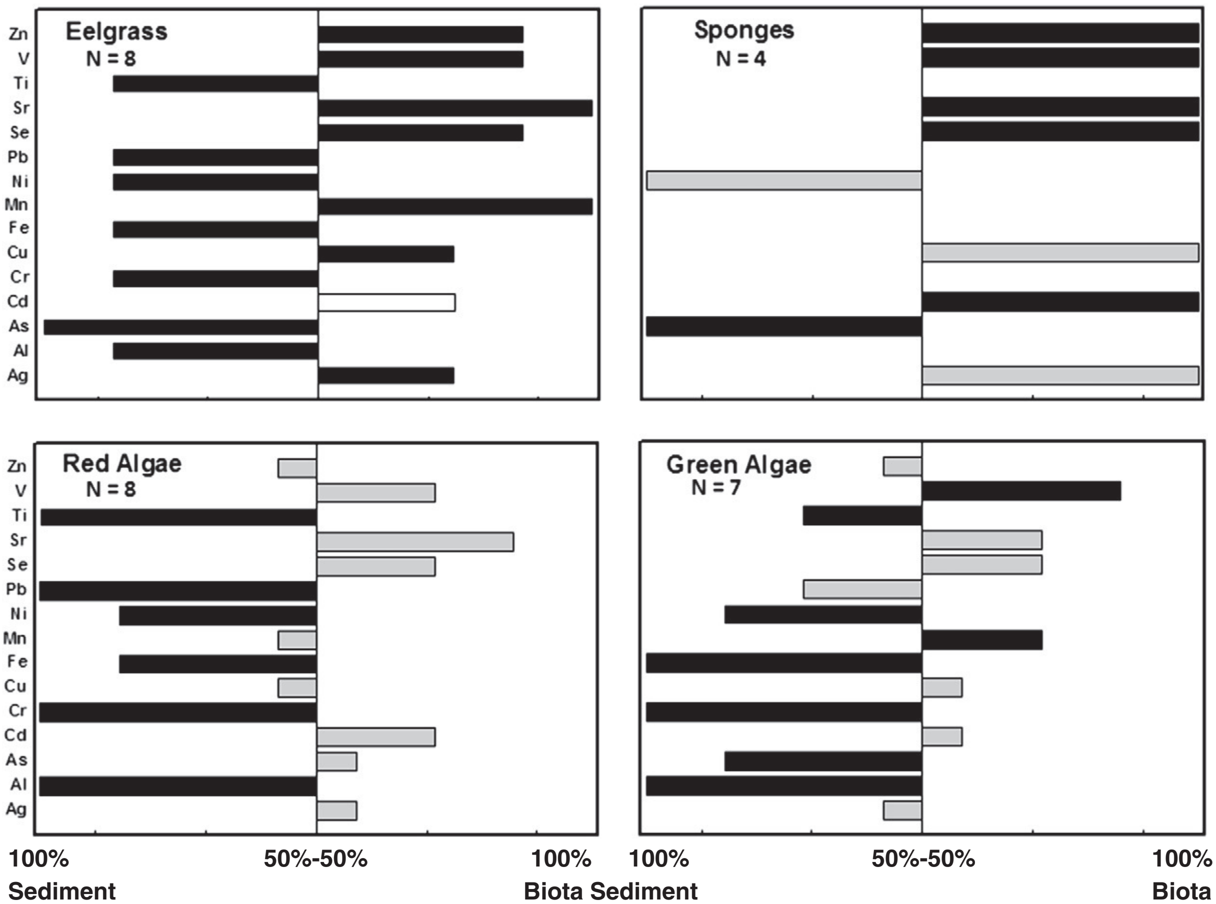

Fig. 2. Percentage of sites exhibiting bioaccumulation in eelgrass, red algae, green algae, and sponges averaged across seasons. Bryozoans are not depicted because they were not located at enough sites to statistically evaluate. X-axes indicate to the right: 100% biota: samples at all sites had higher concentrations than that of corresponding sediment; X-axes indicate to the left 100% sediment: no bioaccumulation — metal levels in sediment had higher concentrations than samples. Trace metals with significant relationships ($\alpha = 0.05$) from paired t-tests are indicated by black bar coloration.

4.5. Spatial and temporal variability

Overall, coarse models with *season* and *Bay region* predictors exhibited better model fit compared to fine scale *season* and *site* models according to the BIC index. Models using ranked data produced very similar results to those using data for all sample groups, so coarse models were used for all further analyses (Table 2). Bay region was a significant predictor in sediment for Cu and Mn. However, season was also often significant, and for Mn, season explained larger amounts of variance than region. In biota, eelgrass exhibited the most significant Bay-wide variation ($p<0.05$ for Ag, Cd, Cu, Mn) while algal and invertebrate groups exhibited less clear trends. Season accounted for more variance than region for Ag in eelgrass and As in red algae.

4.6. Metal signature trends

Several trace metals exhibited high correlations within and between sample types. However, many trace metals in sediments correlated dissimilarly from trace metals in biota across regions and seasons, so sediment and biota were separated for further analyses of metal signature trends using PCA. In sediment, we identified two metal PCA factors that effectively represented multiple trace metals *(PCA factor score ≥ 0.8)* and explained 75.8% of the variance (Factor 1 $\lambda = 5.8$, Factor 2: $\lambda = 5.6$). In biota, a single strong metal PCA factor emerged, and in conjunction with a weaker second PCA factor explained much less (53.5%) of the variance (Factor 1: $\lambda = 6.2$, Factor 2: $\lambda = 1.8$).

The resulting PCA factor scores for each site from these analyses essentially compose new variables that encompass the patterns of multiple individual metals as described above. Using these PCA factors as new response variables in main effects ANOVAs gives the additional advantages of reducing the number of variables, removing confounding issues of covariation between metals, and providing a broader view of spatial differences of overall metal patterns. Both PCA sediment factors displayed significant regional variation, (Main effects ANOVAs — Sediment Factor 1: bay region $p = 0.018$, $\rho R^2 = 11.7\%$; season $p < 0.001$, $\rho R^2 = 40.2\%$; Sediment Factor 2 bay region $p < 0.001$, $\rho R^2 = 41.1\%$; season $p = 0.226$, $\rho R^2 = 3.7\%$), indicating that trace metals composing both PCA Sediment Factor 1 and 2 have distinct spatial distribution patterns across the Bay. These differences are visualized in Fig. 4a, where plotting the scores for PCA sediment factor 1 versus PCA sediment factor 2 results in the clustering of sampling points by bay region, with little overlap of 95% confidence ellipses. In contrast, the only strong PCA biota factor showed no significant spatial differences across the Bay (region $p = 0.552$, $\rho R^2 = 3.2\%$; season $p = 0.774$, $\rho R^2 = 0.77\%$). Plotting of PCA biota factor scores do not exhibit any clustering by bay region, and have broad, largely overlapping 95% confidence intervals (Fig. 4b). However, we did detect significant spatial trends in biota that were driven by Cu and Mn only (Fig. 5; Wilk's $\lambda = <0.001$, 74% classification success). Thus, both sediment and biota exhibited significant trace metal spatial trends, but they were highly dissimilar from one another.

4.7. Comparison to green sea turtle trace metal concentrations

We then compared carapace metal concentrations to sediment, eelgrass, red algae, green algae, bryozoans, and sponges and found no

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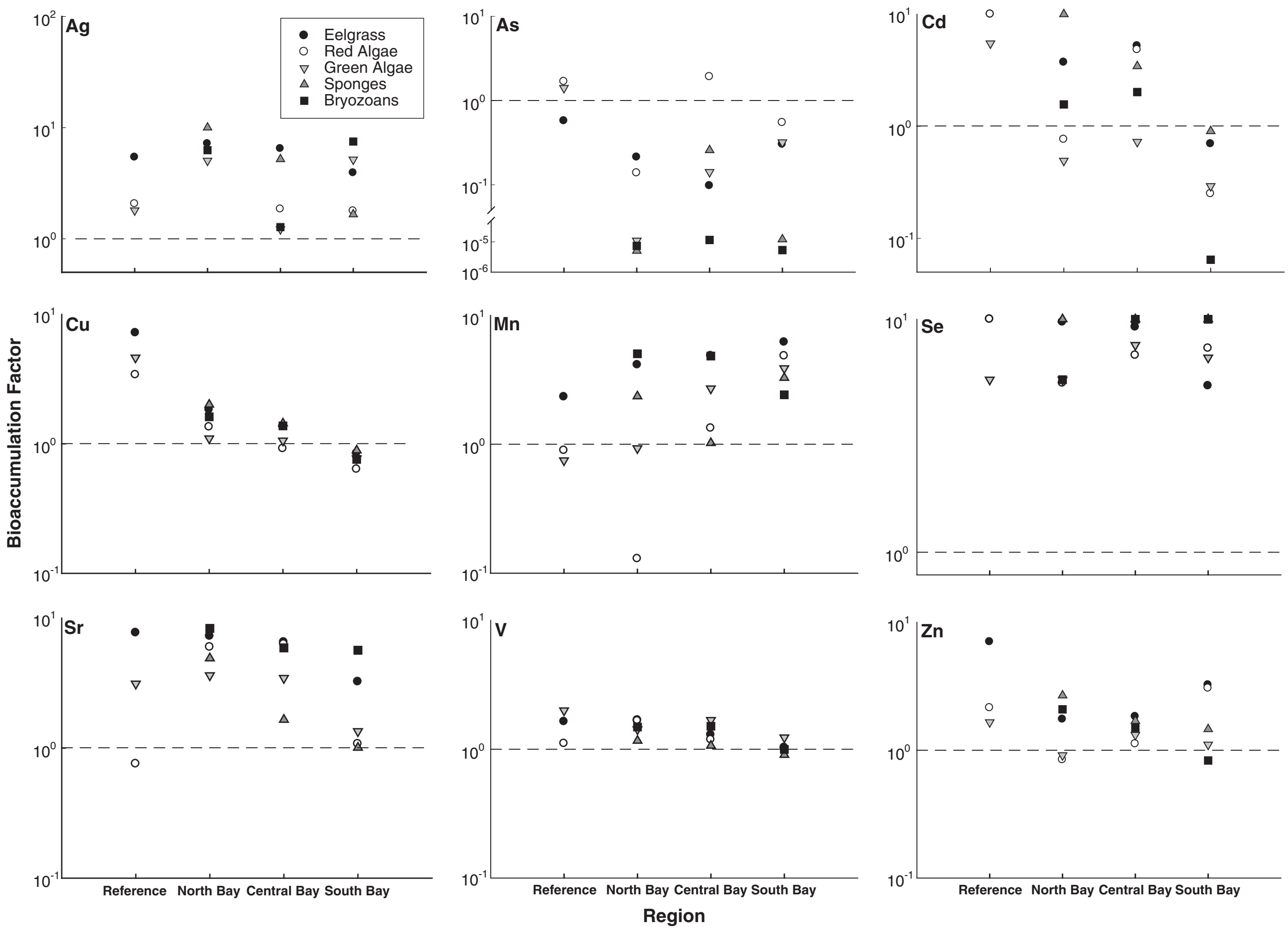

Fig. 3. Bay-wide bioaccumulation trends across species types. Only trace metals with bioaccumulation >50% of the sites for at least one species type are shown. Bioaccumulation factor is defined by the biota concentration/sediment concentration averaged across sites within a bay region. Dashed line indicates 1:1 line above which the corresponding metal exhibits bioaccumulation.

significant evidence of bioaccumulation in green sea turtles (Appendix Table S2). Many trace metals were within similar ranges of concentration in forage items and turtle carapace tissue. In trace metals that differed in concentration by a magnitude or more, all were higher in forage items with the exception of Zn. Green sea turtle blood concentrations (whole blood and red blood cells) were similar or significantly

Table 2
Main effects ANOVA results with individual metal response variables. Sponges and byrozoans are not included because no metals were consistently statistically significant due to small sample sizes. Percent variance explained by the predictor indicated by "%" columns. Statistical significance ($p<0.05$) indicated by bolded p-values.

		Sediment	Eelgrass	Red algae	Green algae
	Factor	ρR^2(p-value)	ρR^2(p-value)	ρR^2(p-value)	ρR^2(p-value)
Ag	Region	8.3 (0.529)	27.5 (**0.043**)	16.6 (0.169)	24.4 (0.46)
	Season	19.0 (0.098)	22.7 (**0.034**)	43.4 (**0.006**)	7.3 (0.667)
Al	Region	8.6 (0.409)	28.5 (0.060)	12.4 (0.588)	18.8 (0.615)
	Season	34.6 (**0.009**)	13.7 (0.147)	0.4 (0.967)	1.7 (0.917)
As	Region	4.6 (0.775)	14.3 (0.260)	39.2 (**0.014**)	24.5 (0.064)
	Season	13.2 (0.227)	26.9 (**0.034**)	24.3 (**0.028**)	57.6 (**0.003**)
Cd	Region	20.8 (0.160)	38.0 (**0.019**)	28.9 (0.148)	8.1 (0.832)
	Season	6.7 (0.410)	8.9 (0.248)	6.6 (0.507)	17.0 (0.441)
Cu	Region	34.1 (**0.021**)	57.5 (<**0.001**)	32.0 (0.129)	52.9 (0.088)
	Season	9.6 (0.206)	9.1 (0.114)	1.4 (0.865)	2.0 (0.84)
Mn	Region	21.1 (**0.040**)	59.4 (<**0.001**)	53.5 (**0.009**)	93.0 (<**0.001**)
	Season	36.8 (**0.002**)	6.7 (0.197)	3.0 (0.621)	5.1 (**0.007**)
Pb	Region	12.9 (0.156)	5.1 (0.801)	29.1 (0.150)	9.1 (0.834)
	Season	42.7 (**0.001**)	3.2 (0.733)	5.6 (0.562)	5.7 (0.771)
Se	Region	8.8 (0.508)	5.4 (0.735)	13.4 (0.423)	15.6 (0.623)
	Season	17.7 (0.115)	19.5 (0.125)	23.7 (0.107)	16.8 (0.412)
Zn	Region	21.9 (0.063)	15.0 (0.356)	3.5 (0.748)	18.1 (0.38)
	Season	27.0 (**0.014**)	7.0 (0.461)	56.3 (**0.002**)	40.8 (0.064)

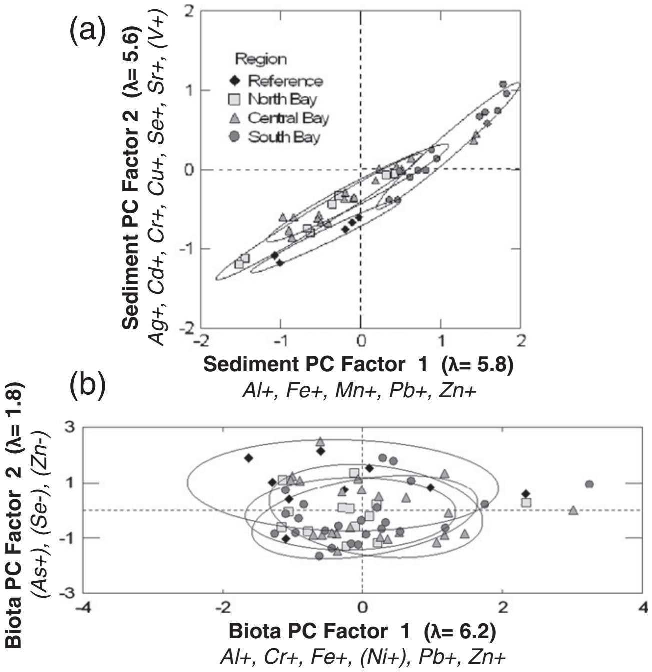

Fig. 4. Bay-wide patterns of (a) sediment and (b) biota metal signatures from principal components analysis. Axes are scaled to reflect λ weight. Individual trace metals strongly correlated with each axis with +/− indicating direction and () indicating moderately correlating trace metals as defined in the text.

below those of carapace tissues (as reported in Komoroske et al., 2011), and therefore also did not indicate any clear bioaccumulative relationships with forage items.

5. Discussion

Seagrass communities have many well documented ecological roles (Dawes et al., 2004), including supporting food webs, sediment stabilization, carbon and nutrient cycling (Lewis et al., 2007), and fish nursery habitat (Jackson et al., 2001). San Diego Bay's eelgrass ecosystem serves as critical habitat for a large range of sensitive and commercially important species, including the green sea turtle, the California spiny lobster (*Panulirus interruptus*) and the California halibut (*Paralichthys californicus*), and maintaining and restoring the health of this habitat influences this diverse group of species. San Diego Bay is typical of many coastal areas that provide protection from harvest and bycatch, making it a critical habitat for species like sea turtles that are vulnerable to these threats. Coastal estuarine ecosystems provide good habitat quality for sea turtles. However chronic exposure to contaminants in these coastal habitats, may pose a chronic threat to sea turtle population and species' viability.

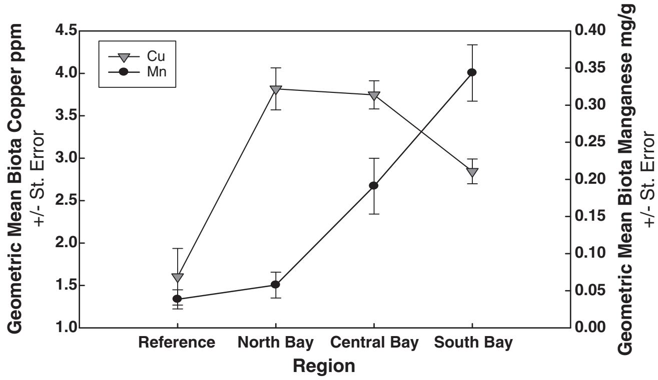

Fig. 5. Geometric means of biota each bay region for Cu and Mn +/− st. error of the mean.

Effective protection and management of ecological resources rely on risk assessment models that accurately integrate impacts of stressors (Crain et al., 2008; Halpern et al., 2008). Risk assessments for higher order species typically rely on sediment or lower-order species as a proxy of exposure and contamination. However, the accuracy of these proxies for long-lived species has been difficult to evaluate. This data gap is particularly problematic for populations already in decline or highly impacted by other known stressors, such as the case for marine turtles. As a result, evaluating effects of pollution on critical habitats and organisms has been identified as a top global research priority for marine turtle conservation (Hamann et al., 2010).

We detected several trace metals that are anthropogenically enriched in sediments of San Diego Bay eelgrass ecosystems, supporting previous studies that attribute contamination to both historical and contemporary sources (Katz and Kaplan, 1981; MacDonald, 1994; Fairey et al., 1998; USDoN, 1999). However, presence of trace metals-enriched sediments did not uniformly correspond to bioaccumulation of trace metals in local biota, perhaps due to complex processes of bioavailability and physiological functions. Eelgrass was the strongest accumulator of trace metals across sites, perhaps because eelgrass accumulates trace metals both via roots and blades, reflecting trace metals in the water column as well as in sediment (Coelho et al., 2009). Red and green algae exhibited weaker accumulation trends, which may be related to the lack of root systems in these species such that they principally accumulate metals from seawater. Macroalgae is often used as biomonitors for dissolved trace metals (Rainbow and Phillips, 1993), and traditional comparisons to sediment concentrations may not be overly meaningful. Finally, bryozoans and sponges displayed the fewest accumulation trends. This may be the result of small sample sizes due to their inherent patchy distributions in the Bay. However, given the differences in metal sources among sampled species, diet appears to be a major route of metal exposure and bioaccumulation for green sea turtles inhabiting San Diego Bay.

We observed significant seasonal variability for some trace metals, which may be attributed to true temporal changes and/or local variability within each site. However, since green sea turtles typically exhibit high site fidelity to foraging areas, it is unlikely that the animals would respond to seasonal variations in metal concentrations by moving to a different areas of San Diego Bay to forage. If green sea turtles and other long-lived organisms exhibit consistent foraging ranges, identifying and mapping Bay-wide trace metal exposure risk would provide a more accurate assessment of persistent spatial trends of contamination.

While composite metal signatures were detected in sediment among regions of San Diego Bay, biota accumulation trends were completely dissimilar from sediment trends. These differences highlight the need to recognize that sediment metal concentrations and variation are not representative (or reflective) of those found in biota unless they are deposit feeders (i.e. organisms that directly ingest sediment). Additionally, it is important to consider that most laboratory trace metal toxicity evaluations do not consider interactions amongst multiple metals, which are likely to occur in organisms *in situ*, and therefore probably underestimate natural conditions of exposure. If metal-specific biological processes of accumulation and regulation are involved, ecosystem health assessments and risk for higher vertebrate organisms may be better served by monitoring species that are integral to the food webs of interest across a representative area. Metal exposure risk for higher organisms like the green sea turtle are likely driven by forage area choice, specific food preferences, or a combination of these factors. We observed clearly different patterns of bioaccumulation among foraging areas and between biota types, and discerned that the driving forces for green sea turtle risk are likely to be species and location dependent. We quantified trace metals in biota found to be preferred forage for green turtles at other locations in the eastern Pacific

(Seminoff et al., 2002; Lopez-Mendilaharsu et al., 2005). However, more recent work on diet on green turtles in SD Bay suggests that this population also relies heavily on mobile invertebrates (e.g. sea hares) that reside in eelgrass (Lemons et al., 2011). Their results confirmed that green turtles in San Diego Bay feed on at least two trophic levels. These new data aid the interpretation of the results presented here, suggesting that trace metals concentrations and bioaccumulation in seagrasses are more relevant to San Diego Bay green turtle risk exposure than those of algae, bryozoans, or sponges. Given the importance of mobile invertebrates in the green turtle diet, futher work will be needed to test metal levels in these species as a potential source of contaminant exposure.

Our study provides the first bioaccumulation estimates for green turtles and their food sources in San Diego. We did not observe strong bioaccumulation of trace metals in green sea turtle carapace relative to trace metals in forage items. Using only carapace-forage BAF metrics to measure toxicological risk, it might be interpreted that the trace metals we investigated may not pose a high risk to the turtles despite the highly enriched presence of some trace metals in Bay sediments. However, many trace metals are known to exert acute toxic effects although they ultimately can be metabolized and excreted in vertebrates (Bryan, 1984), and continuous exposure to contaminated forage items can result in chronic stress. Additionally, bioaccumulation for individual trace metals may also be organ or tissue specific (e.g. liver or kidney), and may not be detected via non-invasive carapace sampling alone. Therefore, the absence of strong bioaccumulation using carapace-forage BAFs does not preclude trace metal exposure or negative impacts on green turtles, particularly when it is known that concentrations for many metals exceed *no-effects* thresholds for other organisms in San Diego Bay (Fairey et al., 1998; Zeeman, 2004; Deheyn and Latz, 2006). Rather, our findings are the first step in understanding the risks trace metal pollution poses to green turtles in San Diego Bay. Though sediment toxicity reference values or bioaccumulation quotients alone may be sufficient for species in which bioaccumulation and toxicity relationships are well characterized (Fairey et al., 1998; Long et al., 2001; Zeeman, 2004), risks associated with trace metal exposure for organisms feeding on multiple trophic levels is complex and not yet understood. Trace metal toxicity thresholds are not well studied in reptiles (Linder and Grillitsch, 2000), with very little known for marine turtles (except for Day et al., 2007). Additional studies need to address these relationships using a combination of approaches since bioaccumulation markers alone could underestimate trace metal risk to green turtles.

A central limitation of this study is that our data do not link specific metal contamination sources with toxic effects in San Diego Bay resident green turtles. However, successfully conducting these studies requires robust background information (i.e. to identify ecologically relevant candidate pollutants of toxicological concern and knowledge of spatial pollutant trends to ascertain possible contamination sources and activities). Prior to our study, this information was not available for green turtle food webs in San Diego Bay. As a result, risk models for San Diego Bay green turtles have been based on sediment values and two samples of eelgrass taken from a shipyard area unlikely to be highly frequented by turtles (MacDonald et al., in review), leading to very high model uncertainty (Zeeman, 2004). Thus, while our study cannot completely quantify the sources and toxicological threats of metal contamination to San Diego Bay green turtles, quantification of metal concentrations in green turtles and their food web provides critical foundational data to inform future studies targeting these questions. By incorporating the knowledge gained from our study with additional studies investigating persistent organic pollutants (Komoroske et al., 2011), diet composition via stable isotopes (Lemons et al., 2011), and spatial habitat use via tracking technologies (MacDonald et al., in review), we will greatly enhance our understanding of the contaminant risks facing green turtles in San Diego Bay and other long-lived vertebrates inhabiting urbanized estuaries.

6. Conclusions

Based on the patterns we observed in this study, San Diego Bay green sea turtle metal exposure risk appears to be most strongly influenced by the metal-specific bioavailability and bioregulation abilities of the biota composing the green sea turtle diet. These findings provide evidence that for the San Diego Bay ecosystem, the current use of toxicity reference values scaled up from sediment and invertebrate testing *ex-situ* is likely to be inaccurate when transposed to the higher trophic level of the green sea turtle. Thus, assessing trace metals patterns in the food webs of these prey organisms may be a more accurate benchmark by which to gauge thresholds of individual species and ecosystem health. Here, we show that direct monitoring of contaminants in food webs of sensitive vertebrates informs our understanding contaminant exposure risk. Identifying spatial variability in metal exposure and habitat use may further improve risk assessments in urbanized estuaries. These approaches can strengthen traditional risk assessment approaches (Luoma and Rainbow, 2008), particularly for higher trophic level species such as sea turtles inhabiting highly urbanized environments.

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