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Original Research Article

DETERMINATION OF METALS IN BIOMASS FROM SOUTHERN CA SALT MARSH, USA

Mohammad Hassan Rezaie-Boroon,*[1] Sonya Diaz,[1] Vanessa Torres, Dimitri D. Deheyn[2]

1. Geosciences and Environment Department, California State University, Los Angeles, USA
2. Scripps Institution of Oceanography, UC San Diego, La Jolla, CA, USA.

Abstract

Concentrations of metals have been determined in sediments from the southern California salt marsh, Salinas de San Pedro, USA. The salt marsh receives anthropogenic inputs from surrounding sites, which are urbanized and industrialized to varying degrees (Los Angeles and Long Beach Harbors). We have analyzed selected body parts of biological samples for metals concentration. Generally, digestive organ of collected bivalves samples exhibited higher metal concentration than foot, muscle and shell . Among the analyzed bivalve species, the average concentrations (mg/g; wet weight) of heavy metals in the digestive, foot, muscle, and shell respectively were as follows: Al (0.07,0.16, 0.50, 0.07), As (0.00001, 0.0069, 0.005, 0.0000006), Cd (0.005, 0.0004, 0.0006, 0.00001), Cr (0.003, 0.005, 0.019, 0.00009), Cu (0.13, 0.17, 0.30, 0.0002), Fe (3.93, 0.39, 1.14, 0.11), Mn (3.35, 0.02, 0.04, 0.01), Ni (0.023, 0.005, 0.012, 0.0005), Pb (0.01, 0.01, 0.04, 0.0003), S (3.12, 0.72, 1.46, 3.21), Se (0.005, 0.0002,0.0002, 0,0002), Zn (3.43, 0.14, 0.32, 0.32) . The average concentrations (g/mg) of trace metals decreased in the order Fe>Mn>Zn>S>Al (for digestive), S>Fe>Al>Cu>Zn (for foot part), S>Fe>Al>Zn>Pb (for muscle), and S>Zn>Fe (for shell). Metals in oxide phase are potentially available to filter-feeding and burrowing organisms as acidic, reducing conditions are encountered in a gastro-intestinal environment. Even though the concentrations for most for snails and bivalves samples were below the limit values and also for most bioaccumulation levels were not critical, a potential danger may appear in future, depending on the local waste water and industrial activities in Los Angeles and Long Beach harbors.

Keywords: Salinas de San Pedro, Bivalves, bioconcentration factor, heavy metals, target hazard quotients (THQ)

For Correspondence:
mrezaieATexchange.calstatela.edu
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1. Introduction

Tidal salt marshes provide many important environmental functions while they act as a buffer zone between the shoreline and deeper ocean waters. They are repeatedly considered sinks for contaminants (e.g. trace metals and organic pollutants). They get important anthropogenic inputs from metropolitan areas as well as over populated urban centers and industries located on or close by. [1]

We chose bivalves and snails since they not only are widely used as bio-indicators of heavy metals pollution but also are known time integrated indication of environmental pollution. Recently, a great deal of attention has been regarded to the study of toxic trace heavy metals and persistent organic pollutant (POPs) contents in salt marshes due to a growing concern about the risks of food consumption and contamination of the marine environment e.g. in some of biomarker species such as bivalves and snails [3]. Moreover, others also noted that bivalve mollusks have often been used in metal monitoring programs since they are easy to identify and also concentrate heavy metals in their lesions such as Cd, Cr, and Pb.[4,5] Bivalve's inactive habits, filtration feeding, and their relatively easy to be identified on field, make them suitable indicators for onsite pollution conditions.[6] The filter-feeding bivalves filter large quantities of water, resulting in bioaccumulation of ambient metal.[7,8] The same research compared Cd, Cu, and Zn bioaccumulation in oysters to other species and with respect to consumption limit.[9] Thus, there is a close association between geochemical processes leading to metal mobilization and bioaccumulation. That is to say, pollutants and chemicals present at undetectable levels in water can be identified in marine invertebrate such as bivalves due to their high bioaccumulation ability.[10] According to Tessier,[11] the metal consumption by organism is also influenced by geochemical factors. These factors influence trace metal behavior, which originates from improved flux of trace metals from terrestrials and atmospheric sources to the aquatic environment due to human activities and urbanization. Nonetheless, the bioavailability of contaminant may also be influenced by its length of contact with the sediment[12]. These organisms consume either settled sediments on the mudflat or suspended fine particulate matter as a food source. The anthropogenic contaminants may be basis for severe bioaccumulation of these metals by the organism transferring them to the higher trophic levels. [13] Identification of these geochemical processes is the key for understanding the behavior, association, and distribution of metals in the geological and biological system of Salinas de San Pedro in southern California, USA. Salinas de San Pedro tidal mudflat, in particular, provides critical habitat for the migratory shorebird populations and it is the home for a wide range of aquatic invertebrates.

The results reported in this study are part of a wider research effort, which started in 2009 to make available relative baseline information on pollutants at marine ecosystems of San Pedro Bay, California. These attempts has created several reports on different types of contaminants in water, sediments, and organisms. [8, 14,15] Large populations of the worm, snails, clams, and bivalves are found in muddy sand flats. So far only few investigations have been aimed at concentration of metals in these species in a constructed salt marsh such as Salinas de San Pedro. Thus, this study is first to link the metal enrichment in biological samples in the Salinas mudflat. The specific objective of our research study is to create baseline concentrations of several metals in the tissues, foot, shell, and digestive parts of bivalves and snails as intertidal species on Salinas mudflat. The information offered here is important for the future detection or monitoring of environmental changes in the urbanized salt marshes and estuaries.

2. Materials and Methods

2.1 Study site

Salinas de San Pedro is a man made salt marsh, which was developed by the Los Angeles Port in 1985. The area is divided by habitats, representing the rocky shore, sandy beach and mudflat (soft bottom), and the open ocean.[14] The study area is limited to the 3.75 acre (15175 m^2) salt marsh mudflat and its habitat. Salt marsh grass and pickle weed grow along the banks of this wildlife refuge. The numerous holes on the mud surface are the evidence of the flourishing underground community of invertebrates. The grain size analysis of the salt marsh mud grab samples also suggests an important contribution of terrigenous material originating from some runoff of surrounding Salinas. The muddy fine sand and silt flat of Salinas marsh are inhabited by several species of mollusks and gastropods exposing during low tide (ebb) condition. Along a small tidal channel, ocean discharges a saltwater over the Salinas flat at high and low tide (Figure 1). During spring tides (Low Low Tide) the sediments remain exposed on flat for more than two hours, allowing the exposed species consumed by birds. The sediments at the Salinas flat are composed of medium to coarse, dark brown particles, compact enough to allow one to walk and stand without sinking in some locations around the rim of Salinas (Figure 1).

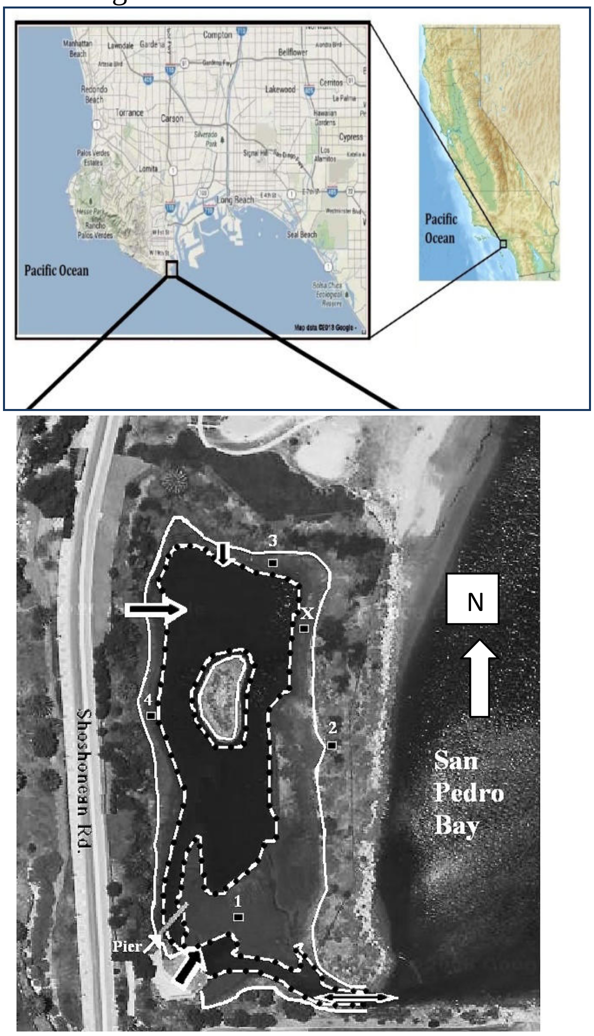

Figure 1 . San Pedro Bay and Salinas de San Pedro .

Solid line: high tide level
Dash line: low tide level
Map Scale: 1 in = 73 m

2.1 Biological sample collection and storage

The biological sample collections were took place on February 26th, 2013 at five locations of Salinas. The sediments remained exposed for more than 2 hours in low tide allowing the Salinas species to be seen on the mudflat, everywhere they were exposed to the surface. Five snail samples and two mussel along with their replicas (total of 12 samples) were randomly collected to a depth of 5 cm from sediments at Salinas edge and middle parts of Salinas. In some part of Salinas, the sediments at the sand flat are composed of fine to medium black gray sand and silt particles, compact enough to allow a person to walk and stand to pick a biological sample without sinking. Toward the middle part and the north part of the mudflat sediment were composed of grayish black clay and silt, saturated with water and very soft. After choosing specimen, sediment clumps were removed from specimens by hand while onsite, rinsed with distilled water until appearing clean (without sediment), and placed in a acid-washed polyester bags. The replicas were collected the same time and from the same location, and placed in separated acid-washed polyester bags. Samples were then sent frozen to the Deheyn lab at the Scripps Institution of Oceanography where specimens were inventoried, measured for size, rinsed with distilled water, dried on a paper towel, before being dissected with acid washed tools. During the dissection, samples of different tissues were collected and separated each into four groups of digestive parts (D group), foot (F group), muscle (M group) and shell (S group). These samples were then treated for metals analysis (see below) while the remaining was placed in a acid-washed polyester bag and stored frozen (-20ºC) for any other analyses. Total of samples prepared for chemical analysis was 1224 samples, which were analyzed by ICP-OES. For Mussel we collected 2 representative samples from different locations in Salinas. One of the location was in the vicinity of gas discharge area in the muddy flat near the center of Salinas. 72 subsamples of different parts of mussel was prepared for further chemical analysis.

2.2 Sediment Analysis

We quantified soil organic carbon, heavy metals and trace element content in sediment, and a thorough grain size analysis for entire Salinas area including total of 17 profiles, up to 6 samples in each profile (10 m apart), total of 26 bore samples (core samples, 1- 20 cm using hand core, Each sample was split in 2 samples from 1-10 cm 10-20 cm respectively), and 11 mud grab samples (scoops surface sediment up, top two to four centimeters), which all were collected from salt marsh in low tide (ebb) condition in 2009 using EPA sediment sampling guideline and method.[16] The latter sampling type is appropriate for benthic, sediment oxygen demand (in-situ), recent ambient conditions, recent contaminant investigation, and grain size analysis.[14]

2.3 Metal analyses

We determined the concentrations of metals in bivalves and snails in the intertidal mud flat sediments of the Salinas de San Pedro, CA. All metal analyses were performed at Scripps Institution of Oceanography, UCSD following full tissue Digestive using nitric acid, and the acidified solution analyzed for elemental composition using an Induced Coupled Plasma Optical Emission Spectrum (ICP-OES) spectrometer (Optima 3000 XL, Perkin Elmer). A total of 18 elements (Ag, Al, As, Ca, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, S, Se, Sr, Ti, V, and Zn) was analyzed simultaneously with detection limits from 0.05 to 4x10-6 mg/g depending on the element (Perkin Elmer, 2000). The instrument was calibrated before every run by successive dilution of a 100 μg/g multi-element instrument calibration standard solution (Fisher Scientific, CA, USA). Quality Assurance (QA) standards and internal blanks were analyzed to assess any background contamination originating from the sample manipulation (which was negligible), as routinely done in the laboratory (Deheyn et al. 2005; Deheyn and Latz, 2006). In this paper only the following elements were discussed (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S, Se, and Zn).

2.4. Physiochemical Parameters

In general, trace elements and heavy metals are sensitive to environmental condition such as dissolved oxygen (DO), pH, salinity, temperature, and the change in other chemical components for instance dissolved gasses such as H_2S and CO_2. Salinity, pH, and temperature monitored during the sampling events displayed only small differences between different locations.

Dissolved Oxygen (DO)

Daily change of DO can be explained by photosynthesis and respiration. The pore water DO was recorded from range of 1.84 – 4.70 mg/l for all locations (n = 8), which was slightly higher in some location closer to ocean water entrance in the lagoon. Oxygen is exhausted near the sediment surface by microorganism in the sediments. Microorganism use the oxidize from present in the sediment as electron acceptor, in that way decreasing the redox potential of the sediment.

pH

The pH fluctuation may relate to the amount of local waste discharge which in turn can also affect the overall pH. Algal blooms may cause the water's pH to become more basic. As aquatic plants decompose, they release carbonic acid into the water. Photosynthetic activities may adsorb CO_2 and release oxygen causing pH to rise. Nitrogen oxides and sulfur dioxides are changed to nitric acid and sulfuric acid when they interact with water in the atmosphere. These acids combine with moisture in the air and fall to the Earth as acid rain or snow. Consequently, the pH of rain influences the overall pH of the watershed. The average pH range fluctuated between 6.96 and 7.70 in our study area.

Salinity

The salinity of the central and marginal water mass is stratified. This may creates density turbulence in low tide condition. Intense vertical water exchange may occur in the upper water layer in deeper part due to wind induced currents and dynamic turbulence caused by San Pedro Harbor. The salinity rage were between 22 (min) to 34.50 $^0/_{00}$ (max).

Average salinity values were recorded in pore water 33.7‰ recorded during the lowest low tide level or ebb condition. In this condition the evaporation rate was slightly higher where sediments were exposed to the in- tense sunlight especially in summer. The results showed that there was a negative correlation between the pore water salinity and methane flux. Considering Salinas de San Pedro a polyhaline salt marsh (salinity > 18‰) the methane values were significantly lower and were consistent with prior works.

Temperature

Temperature reflects length and strength of exposing to the sunlight at daily time-scale. Temperature values were generally comparable at locations and time; some shown detectable thermal gradients because of the daily patterns with lower temperature early morning and higher temperatures during noon and after noon hours. The temperature recorded the range of 16.9 to 19 °C. Air temperature also was recorded with a range of 19°C - 22°C on sampling days and locations. Temperature reflects length and strength of exposing to the sunlight at daily time-scale. Temperature values were generally comparable at locations and time; some shown detectable thermal gradients because of the daily patterns with lower temperature early morning and higher temperatures during noon and after noon hours.

2.5 Health risk from consuming mussels

To evaluate the potential effect of heavy metals on food chain and human health we calculated target hazard quotient (THQ), after Hussein and Khaled. [3,17] For a single compound, the THQ is the ratio of CDI (chronical daily intake (mg . kg^{-1} day^{-1}) to a RfD (reference dose):

$$THQ = \frac{CDI}{RfD} \qquad \text{equation 1}$$

Where:

CDI = Chronical daily intake (mg . kg-1 day-1)

RfD (reference dose)

The intake or dose for the ingestion of fish mussel is calculated based on the equations below [17]

$$CDI = \frac{C \times Rf \times IR \times Cr \times ABS \times Ef \times ED}{BW \times AT} \qquad \text{equation 2}$$

Where:
C = Concentrations (mg/kg wet weight) of investigated pollutants in muscle tissues;
Rf = reduction factor (no unit);
IR = ingestion rate (g day-1);
Cf = conversion factor (10-3 kg/g);
ABS = ingestion absorption factor;
Ef = exposure frequency (days year-1);
Ed = Exposure duration (years);
BW = body weight (kg)
AT = average time of exposure (days)

The RF is a number between 0 and 1 that describes the fraction of the pollutants originally remains after the mussels have been cooked. Since the reduction value was not known for the two investigated mussel species, a factor of 1 was used as a conservative assumption. ABS is the fraction of pollutants absorbed during ingestion; in the present study assumed to be conservative and 100%.The IR for the mussels were obtained from the study performed by Department of Food and Drug Administration in 2005. All other parameters used in the equation were default values obtained from the USEPA documents. [18]

Statistical analysis

Correlations between metal concentrations in selected Digestive (D), Foot (F), Muscle (M), and Shell (S) parts of bivalves and between metal concentration in biological species and metal concentration in sediment were examined using the correlation coefficient in EXCEL and SPSS.

3. Results

This research study was conducted to provide information on heavy metal concentrations in biological species from Salinas sampling locations. As anticipated , major differences were found in three different categories of the selected specimen body parts in view of accumulation of the selected metals. All results showed that high level of concentration of heavy metals were in digestive parts (D) while the lowest ones were in the shell of species except Al, Ca, Fe, S, and Zn, which recorded their highest levels of heavy metals in shells. Statistical analysis was conducted for selected heavy metals concentrations (mg/g) in digestive parts (D group), foot (F group), muscle (M group) and shell (S group) in snails samples from Salinas site (N in each group = 16; for all groups and each element N=68). Fe, Mn, S, and Zn have shown the highest concentration of metals in snails digestive parts (Table 1).

Statistical analysis including average (mean), maximum (min), minimum (min) and standard deviation (sd) was conducted for selected heavy metals concentrations (mg/g) in digestive parts (D group), foot (F group), muscle (M group) and shell (S group) in snails samples from Salinas site (N in each group = 3; for all groups N=72).

The results show the mean concentration values rankings of Salinas mussel samples were in digestive part (D-Group) as Fe>S>Zn>Cu; in foot part (F-group) as S>Fe>Cu>Zn, in muscle (M-group) as S>Fe>Zn>Pb and in shell (S-group) as S>Zn>Fe>Al. Figure 2 (top) shows the concentration of metals in different category for Mussel samples (Table 2).

The results show mean concentration values rankings of Salinas gastropods samples were in digestive part (D-Group) as Fe>Mn>Zn>S>Al; in foot part (F-group) as S>Fe>Al>Cu>Zn, in muscle (M-group) as S>Fe>Al>Zn>Pb and in shell (S-group) as S>Zn>Al>Fe. Figure 2 (bottom) shows the concentration of metals in different category.

Table 1. Average (mean), maximum (min), minimum (min) and standard deviation (sd) for concentrations (mg/g) of selected heavy metals in digestive parts (D group), foot (F group), muscle (M group) and shell (S group) in snails samples from Salinas site (all groups N=92; sub group N=1225).

	Snail	D	F	M	S		Snail	D	F	M	S
Al	max	3.46E-01	1.30E+00	2.33E+00	2.56E-01	Mn	max	15.50467	1.51E+00	3.66E+00	3.69E-01
	min	1.05E-02	1.44E-02	6.83E-02	9.75E-05		min	0.001878	2.22E-06	9.35E-06	0.00E+00
	mean	7.60E-02	1.86E-01	5.64E-01	6.33E-02		mean	2.002379	2.04E-01	5.32E-01	4.87E-02
	sd	0.097101	0.311577	0.643847	0.065002		sd	4.471535	0.434484	1.06639	0.108017
As	max	5.21E-06	0.082375	0.055196	8.62E-07	Ni	max	0.121674	0.015608	0.074146	0.00146
	min	3.22E-07	1.91E-06	4.27E-06	5.2E-07		min	0.00683	2.22E-06	9.35E-06	6.86E-07
	mean	1.62E-06	0.007844	0.005705	6.44E-07		mean	0.024698	0.005419	0.012893	0.000584
	sd	1.46E-06	0.02163	0.014141	8.69E-08		sd	0.027521	0.004629	0.017783	0.000416
Cd	max	0.012591	0.001122	0.001305	7.56E-05	Pb	max	0.088957	0.089697	0.177344	0.002221
	min	0.001978	1.17E-05	7.89E-06	5.25E-07		min	0.00316	3.25E-06	3.23E-06	5.36E-07
	mean	0.004836	0.000494	0.000667	1.09E-05		mean	0.019776	0.018982	0.045416	0.000381
	sd	0.002864	0.000343	0.000367	2.02E-05		sd	0.021538	0.02345	0.046784	0.000747
Cr	max	0.009703	0.018078	0.156466	0.000427	S	max	5.819628	1.083114	4.186276	3.685833
	min	0.001878	0.001472	0.003225	0		min	1.35817	0.014981	0.416763	2.928481
	mean	0.003883	0.006347	0.020596	0.000114		mean	3.10079	0.697458	1.43756	3.201562
	sd	0.00227	0.005368	0.037347	0.000146		sd	1.110044	0.30949	0.909123	0.197572
Cu	max	0.121674	0.015608	0.074146	0.00146	Se	max	0.025198	0.003669	0.003767	0.003767
	min	0.00683	2.22E-06	9.35E-06	6.86E-07		min	1.28E-06	1.59E-06	3.23E-06	3.23E-06
	mean	0.024698	0.005419	0.012893	0.000584		mean	0.004735	0.00025	0.000244	0.000244
	sd	0.027521	0.004629	0.017783	0.000416		sd	0.006512	0.000946	0.000939	0.000939
Fe	max	15.50467	1.507959	3.656528	0.368821	Zn	max	7.742193	0.274358	0.184514	1.369222
	min	1.036309	0.131793	0.191441	0.010383		min	1.589351	0.077161	0.102134	0.102134
	mean	3.596944	0.402804	1.19274	0.11164		mean	3.185333	0.141387	0.273234	0.273234
	sd	3.692173	0.349256	1.022363	0.090756		sd	7.742193	0.274358	1.369222	1.369222

The statistical analysis of samples shows that F and M groups correlates very well together (r= 0.98) whereas D and F group do not show any strong correlation together in regards to concentration values (r= 0.61). F and S groups also showed a moderate correlation (r= 0.86). We have also correlated the mean of trace elements/metals values together to see which shows the strong and weak correlation.

Table 2. Average (mean), maximum (min), minimum (min) and standard deviation (sd) for concentrations (mg/g) of studied selected heavy metals in digestive parts (D group), foot (F group), muscle (M group) and shell (S group) in snails samples from Mussels from Salinas site (N in each group = 3; sub group N=72).

	Mussel	D	F	M	S		Mussel	D	F	M	S
Al	Max	0.069857	0.016204	0.072900	0.063481	Mn	max	0.02394732	0.04150857	0.01087392	0.01087392
	Min	0.018135	0.007166	0.068013	0.048704		min	0.02253842	0.02678477	0.00663184	0.00000059
	Mean	0.043996	0.011685	0.070457	0.056092		mean	0.02324287	0.03414667	0.00875288	0.00583545
	Sd	0.036573	0.006391	0.003455	0.010449		sd	0.00099625	0.01041130	0.00299960	0.00548024
As	Max	0.000001	0.000005	0.000929	0.000001	Ni	max	0.01890739	0.00432376	0.01120185	0.00009143
	Min	0.000001	0.000003	0.000007	0.000001		min	0.01765954	0.00000454	0.00744768	0.00000051
	Mean	0.000001	0.000004	0.000468	0.000001		mean	0.01828346	0.00216415	0.00932476	0.000030
	Sd	0.000000	0.000001	0.000652	0.000000		sd	0.000882	0.003054	0.002654	0.000052
Cd	Max	0.011430	0.000888	0.001622	0.000011	Pb	max	0.019879	0.045599	0.060229	0.000059
	Min	0.001587	0.000217	0.000008	0.000001		min	0.019303	0.003171	0.057943	0.00000001
	Mean	0.006508	0.000552	0.000815	0.000004		mean	0.019591	0.024385	0.059086	0.000020
	Sd	0.006960	0.000475	0.001141	0.000006		sd	0.000407	0.030001	0.001616	0.000034
Cr	Max	0.004081	0.004397	0.010023	0.000154	S	max	4.13980984	1.16843276	2.27893287	3.54114177
	Min	0.003590	0.000724	0.009132	0.000001		min	2.43013222	0.73233065	1.02738264	3.34798046
	Mean	0.003836	0.002561	0.009577	0.000052		mean	3.28497103	0.95038171	1.65315775	3.44456111
	Sd	0.000347	0.002597	0.000630	0.000088		sd	1.20892464	0.30837076	0.88497966	0.13658568
Cu	Max	0.175743	0.255552	0.347717	0.000001	Se	max	0.01293433	0.00000454	0.00000773	0.00000773
	Min	0.072472	0.052624	0.270748	0.000001		min	0.01124689	0.00000270	0.00000745	0.00000745
	Mean	0.124107	0.154088	0.309233	0.000001		mean	0.01209061	0.00000362	0.00000759	0.00000759
	Sd	0.073024	0.143491	0.054425	0.000000		sd	0.00119320	0.00000130	0.00000020	0.00000020
Fe	Max	7.055498	0.449867	0.744070	0.212001	Zn	max	4.34707407	0.13059429	0.16088947	0.16088947
	Min	6.302761	0.294609	0.740212	0.180382		min	1.68303279	0.09852869	0.14873417	0.14873417
	Mean	6.679130	0.372238	0.742141	0.194384		mean	3.01505343	0.11456149	0.15481182	0.15481182
	Sd	0.532266	0.109784	0.002728	0.016117		sd	1.88376165	0.02267380	0.00859509	0.00859509

Al correlates strongly with Cr , Cu, and Pb (r = 0.98, 0.87,0. 91). As does not show any correlation with other metals except weakly correlated with Cu. Cd also correlates strongly with Fe, Mn, Ni, Se and Zn respectively (r= 0.98, 0.99, 0.92, 0.99, 0.99). Cr correlates with S very strongly (r=0.98) . Cu correlates with Fe, Mn, Se and Zn (r= 0.97, 0.96, 0.97). Fe also shows strong correlation with Mn, Ni, Se, and Zn (r=0.97,0.88, 1.00, 0.99). The highest correlation was shown between Mn and other metals such as Pb, S, Se, and Zn showed strong correlation (r = 0.88, 1.00, 0.99, 0.99). Ni correlated very well with Se and Zn (0.87). Se has shown a strong correlation with Zn (r = 0.99) (Table 3).

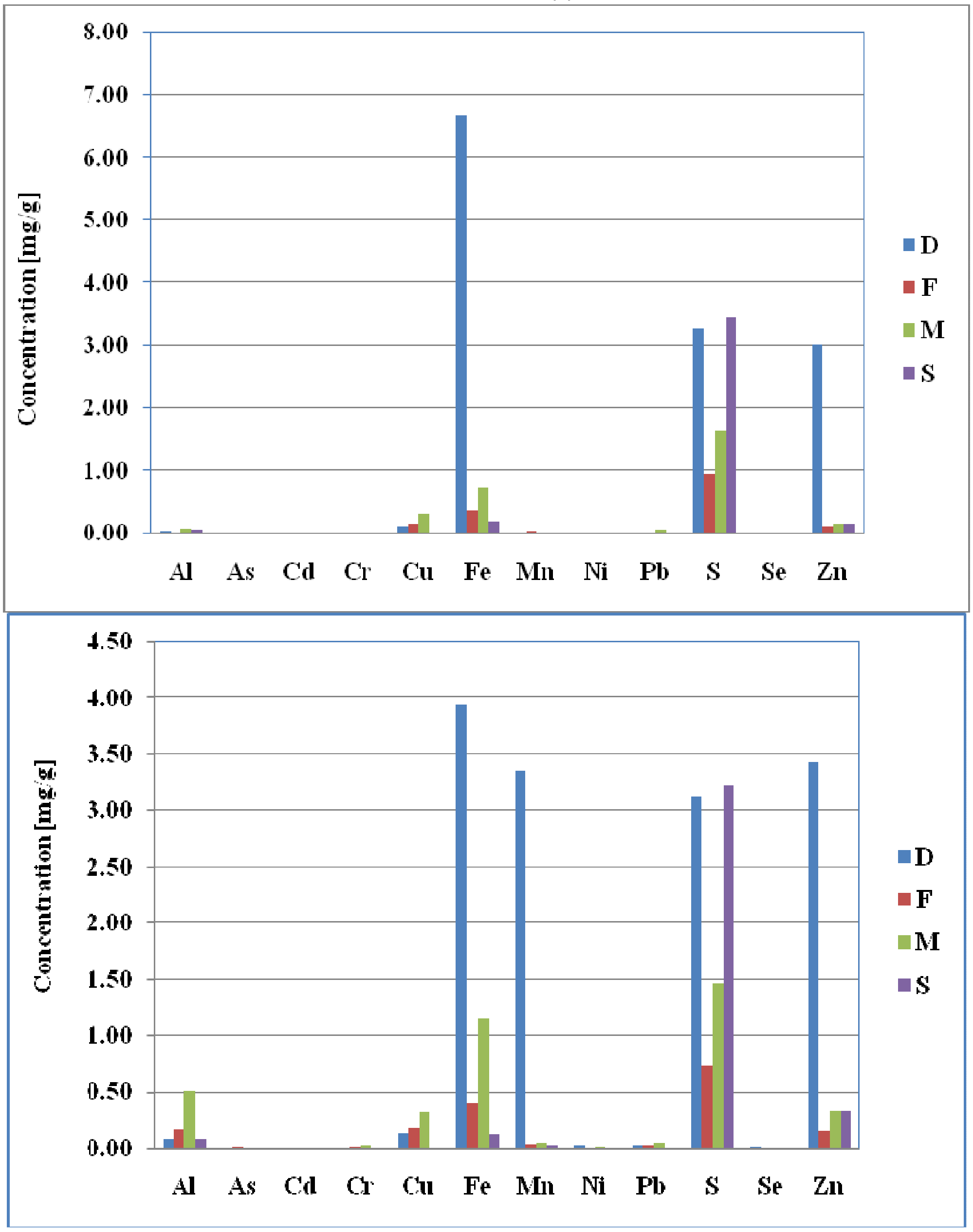

Figure 2. The average concentration of heavy metals in various parts of collected biological invertebrates: Top diagram shows mussel samples (N=72); bottom diagram shows snail samples (N=92) from Salinas including digestive (D), foot (F), muscle (M), and shell (S) sections.

The correlation within the species groups had different results. Figure 3 and table 3 represent very strong / moderate to weak correlation between different species parts including *Digestive (D), Foot (F), Muscle (M), and Shell (S).*

For example Al- D and As-M shows a moderate correlation between Al in digestive and As in muscle parts of species. The data showed a very strong correlation between Zn concentration in muscle and shell parts as well as Se concentration in muscle and shell respectively (r = 1). As - S, Cr - Se, Cu - Se, Cu - Cr, Fe - Pb, and Se - Zn correlate strong to very strongly within group of body parts and with different parts. The mean concentration of all parts also corresponds the singles body parts.

Moreover, species in sandy sediments showed lower trace metal values than those found on finer (silt and clay) sediments. Factors may affect on bioavailability of metals in the salt marsh species include pH, redox potential, salinity, particle size, and organic matter content. From food chain and human health point of view, the heavy metal THQ values (<1) showed no risk for consumer of investigated mussel from Salinas. Although the overall THQ values are low and insignificant, the THQ for specific heavy metals (S, Fe, and Cu) was ranked much higher in compare to other metals including S>Fe>Cu>Zn>Al>Pb. This ranking order corresponds approximately the same as heavy metal concentration in mussels.

Bio-concentration Factor

Metal bioconcentration factor was calculated using the ratio of mean concentration values of biological species Digestive, foot, muscle and shell parts to mean concentration values associated with sediment at that site. The result showed that the bioconcetration factor (>1)was highest for both snails and bivalves for Zn and Cd, followed by Cu and Mn for various parts (Table 4).

4. Discussion

The trace metal's biological and geochemical interactions in the salt marsh environment is very complex and accumulated trace metal concentrations in aquatic invertebrates therefore vary greatly.[19] As a result, we interpret the results based on composite geochemical condition and biogeochemical significance in the Salinas de San Pedro.

This study compares the metal concentration in selected body parts of a group of biological species such as marine invertebrate (snails and mussels) with the concentration of those metals in sediment at the site on the Salinas mudflat. The concentrations of metal determined in Digestive (D), Foot (F), Muscle (M), and Shell (S) from marine invertebrates did not follow a frequent pattern within specimens parts from a single species, even for a single metal except for few elements such as Fe, Mn, S, and Zn. Moreover, the standard deviation (sd) of metal analysis ranges in this study from min ±0.000006 to max of ±0.64 analysis. The reasons for this inconsistency include species biology, their unique environment, age, health, and factors such as the oxidation number of the chemical species associated to these factors may be large standard deviations in the precision of the analysis.[19] Yet, one of the most important factors influencing the distribution and speciation of trace metals in salt marsh water is the binding to organic substances.[14] Similarly, trace metals are present in Salinas waters in a number of physio-chemical forms including free ions, inorganic complexes (such as CO_3^{2-} and Cl^-), organic complexes with fluvic and humic acids.[20] In addition, they are associated with colloidal and particulate materials such as clay minerals, hydrous oxides of Fe and Mn and biogenic material as living algae and detritus[14]. As has been noted, trace metal in Salinas seawater can exist in different oxidation state and chemical forms or species including free ions, inorganic complexes (e.g., with Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}), organometallic compounds and organic complexes such as phytoplankton metabolite and proteins.[21]

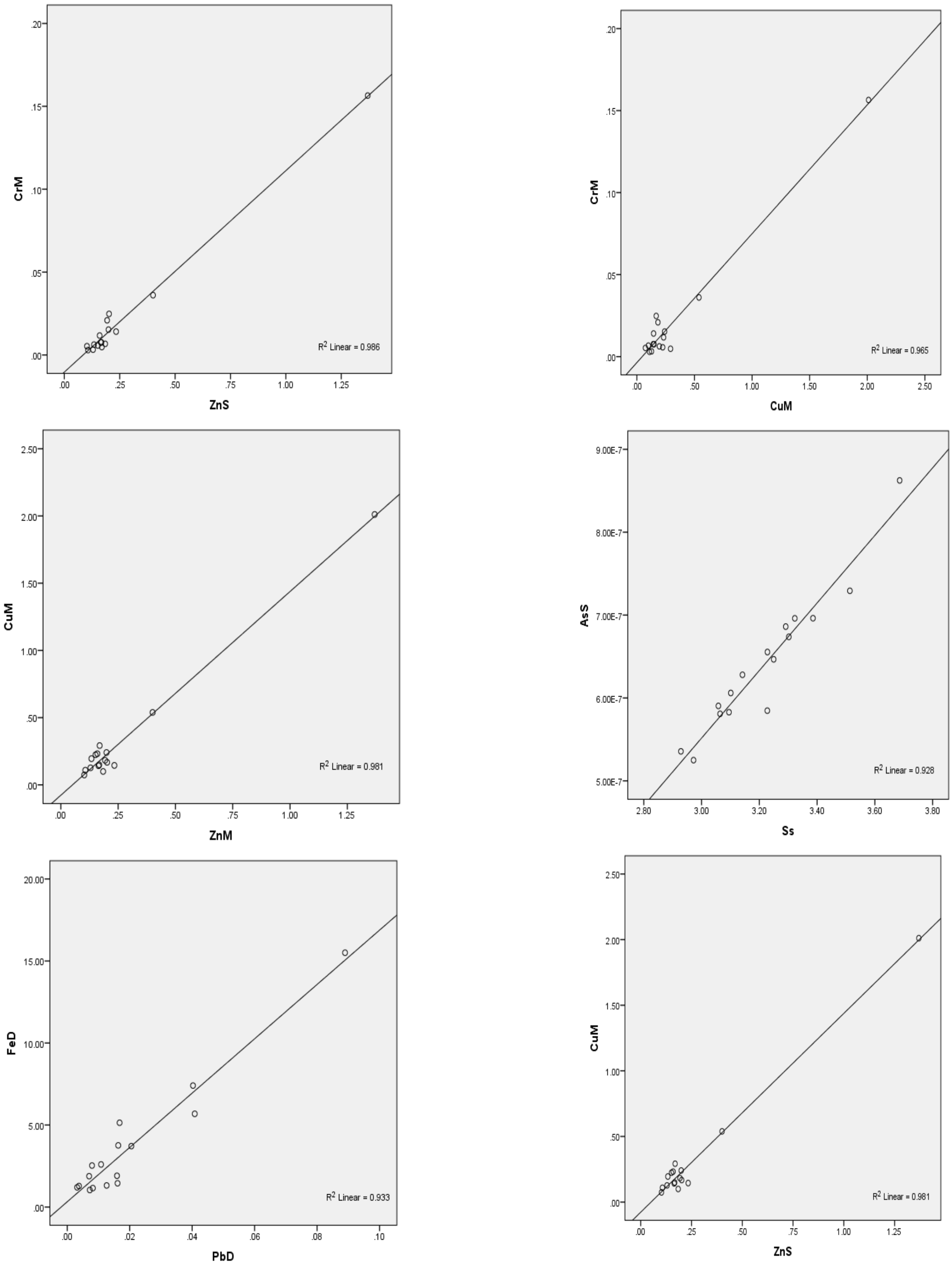

Figure 3. Correlation of different metals with each other within group and from different categories including digestive (D), foot (F), muscle (M), and shell (S) sections.

Fe^{3+} has a great tendency to form complexes with natural organic ligand.[22] Thus, we believe that the organic complexation is more likely responsible for elevated concentration of dissolved Fe in Salinas water as well as sediment and consequently higher concentration in biological species such as snails and mussels. Zn shows strong correlation with other elements such as Cr, Cu, Mn, Ni, S, and Se. It is important to realize also that the salt marsh sediment (here essentially silt/very fine sand) is rather convenient for clams and bivalves than for those species that are more naturally situated on coarser sandy bottom. Metal bioconcentration factor, also was an indication that Cd, Cu, Mn, and Zn has shown an increase in adsorption of the heavy metal from bottom sediments.

Table 3. The correlation between different species and their body parts including Digestive (D), Foot (F), Muscle (M), and Shell (S).

Species Parts		Correlation Rate	Correlation Coefficient	Species Parts		Correlation Rate	Correlation Coefficient
Al-D	As-M	Moderate	0.77	Fe-D	Ni-D	very strong	0.92
Al-F	Al-S	Moderate	0.85	Fe-M	Mn-M	moderate	0.79
Al-M	Al-S	Moderate	0.85	Fe-S	Cr-D	moderate	0.74
Al-S	Ni-M	Moderate	0.71	Mn-F	Zn-F	very strong	0.92
As-D	Pb-D	Strong	0.92	Mn-M	Cu-S	moderate	0.73
As-M	Cd-D	Moderate	0.72	Ni-D	Pb-D	strong	0.92
As-S	S-S	very strong	0.96	Ni-D	Zn-D	moderate	0.74
Cr-D	As-D	strong	0.92	Ni-F	S-D	moderate	0.70
Cr-M	Cu-M	very strong	0.98	Ni-F	Ni-M	moderate	0.71
Cr-M	Ni-M	strong	0.93	Ni-F	Ni-M	moderate	0.71
Cr-M	Se-S	very strong	0.97	Ni-M	Cu-S	very strong	0.92
Cr-M	Se-S	very strong	0.97	Ni-M	Se-M	strong	0.92
Cr-M	Zn-M	very strong	0.99	Ni-M	Se-S	strong	0.92
Cr-M-	Zn-S	very strong	0.99	Ni-M	Zn-M	strong	0.93
Cu-D	Cr-D	moderate	0.69	Ni-M	Zn-S	strong	0.93
Cu-M	Se-M	very strong	0.97	Pb-D	Cr-D	strong	0.88
Cu-M	Se-S	very strong	0.97	Se-F	As-S	moderate	0.70
Cu-M	Zn-S	very strong	0.99	Se-M	Se-S	very strong	1.00
Cu-M	Zn-M	very strong	0.99	Se-M	Zn-M	very strong	0.98
Cu-S	Ni-D	moderate	0.71	Se-M	Zn-S	very strong	0.98
Cu-S	Mn-M	moderate	0.73	Se-S	Zn-M	very strong	0.98
Fe-D	As-D	strong	0.92	Se-S	Zn-S	very strong	0.98
Fe-D	Cr-D	strong	0.86	Zn-F	Cr-F	moderate	0.77
Fe-D	S-D	moderate	0.74	Zn-M	Zn-S	very strong	1.00
Fe-D	Pb-D	very strong	0.97				

The concentration of Cu and Fe in Salinas sediment have been found to be controlled by sulfide formation.[14,23] Another model for copper describes that it most likely reaches the Bay water in dissolved from before being transformed into the particulate form, which will sink into the seafloor sediment eventually.[24,25] Rainbow et. al. have found similar results as we found in our study, namely showed the higher level of concentration in Zn, Cu, and Cd in their analysis of a selection of body of crustaceans from clean and metal-contaminated sites concentrations (mg/g dry weight).[19,26,27]

We observed also a significant correlations between total concentrations of trace elements in muscle (M) with those in sediment (r=0.98). There was a good correlation between Digestive (D) part of biota and total concentration of trace element in sediments. The metal concentration in foot (F) and shell (S) parts of selected biological samples did not correlate well (r = 0.58 and r = 0.66 respectively). These results confirm that frequent exchange and /or transfer of trace elements occur at the Salinas sediment water interface in the organic rich environment[15] and the fact that San Pedro Bay Salinas sediments appears more reducing.

Table 4. Bioconcentration of metals in various parts of snails and bivalves.

	Snails					Bivalves			
	Digestive	**Foot**	**Muscle**	**Shell**		**Digestive**	**Foot**	**Muscle**	**Shell**
Al	0.022418	0.05481	0.166168	0.018649	Al	0.012971	0.003445	0.020772	0.016537
As	0.000245	**1.191021**	0.866216	9.78E-05	As	0.000182	0.000549	0.071095	9.20E-05
Cd	**1.799100**	0.183814	0.24825	0.004065	Cd	**2.421236**	0.205464	0.303092	0.001489
Cr	0.027763	0.045376	0.147243	0.000812	Cr	0.027422	0.018306	0.068471	0.000369
Cu	0.101078	0.022178	0.052767	0.002388	Cu	0.507913	0.630611	**1.265545**	2.52E-06
Fe	0.357564	0.040042	0.118568	0.011098	Fe	0.663957	0.037003	0.073775	0.019323
Mn	0.022418	0.991258	**2.931976**	0.268605	Mn	0.166725	0.244939	0.062786	0.041859
Ni	0.212653	0.046660	0.111014	0.005024	Ni	0.157422	0.018633	0.080287	0.000266
Pb	0.114756	0.110152	0.263546	0.002211	Pb	0.113685	0.141507	0.342874	0.000118
Se	0.345652	0.018258	0.017807	0.017807	Se	0.882598	0.000264	0.000554	0.000554
Zn	**13.53064**	0.600584	**1.160643**	**1.160643**	Zn	**12.80732**	0.486634	0.657609	0.657609

Recent study on San Diego Bay, CA reveals similar condition as in San Pedro Bay, CA. The trace element contamination in the San Diego Bay is repeatedly considered originating from non-point sources because of the numerous and continual nature of individual sources spread around and in the Bay (i.e, boats, marinas, and shipyards), but also because of the water circulation of the San Diego Bay waters sustained mainly by tidal forces, as well as by vertical mixing due to wind and/or day/night temperature difference of water masses, especially in the shallower parts of the back of the Bay [25,28,29]. These two conditions causes the retention of contaminants in benthic environment species as well as mud flat sediment of the Salinas de San Pedro.

The target hazard quotient (THQ) calculation showed that overall consumption of mussels does not implicate human risk for human, yet bioaccumulation levels (factors) are critical for some elements and further monitoring program should be conducted. Overall, bioavailable metals have the potential to be toxic, given that they can set off harmful effects at the individual, population, and/or ecosystem level. So, in conclusion, salt marsh invertebrates show a vast range of accumulated trace metal concentrations. The particular accumulation patterns used by particular invertebrates for specific trace metals could be a potential reason. This can provide a great deal of information of useful application in terms of the ecological and environmental variation in the bioavailabilities of toxic metals in aquatic systems.

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References

1. Mucha Ana P., Almeida, C. Marisa R., Bordalo, Adriano A., Vasconcelos, M. Teresa S.D..(2008). Salt marsh plants (*Juncus Maritimus and Scirpus Maritimus*) as sources of strong complexing ligands. *Estuarine, Coastal and Shelf Science, 77,* 104-112.
2. Mucha, Ana P. Almeida, C. Marisa R. Magalhães, Catarina M., Vasconcelos, M. Teresa S.D., Bordalo, Adriano A.. (2011). Salt marsh plantemicroorganism interaction in the presence of mixed contamination. *International Biodeterioration & Biodegradation, 65,* 326e333.
3. Hussein, A., and Khaled, A. (2014). Determination of metals in tuna species and bivalves from Alexandria, Egypt. *The Egyptian Journal of Aquatic Research, 40*(1), 9-17. doi:http://dx.doi.org/10.1016/j.ejar.2014.02.003
4. Menzel, W. (1979.). Clams and snails (mollusca: Pelecypoda, except oysters), and gastropoda. *in*: Hart, C.W. and S.L. H. fuller (eds). *Pollution Ecology of Estuarine Invertebrates. Academic Press, New York. U.S.A.,* , 371-396.
5. Alfonso, J. A., Azocar, J., LaBrecque, J., García, B., Palacios D. Benzo, Z. (2008) Trace metals in bivalves and sea grass collected from Venezuelan coastal sites. Rev. Biol. Trop., 56 (Suppl. 1), 215-222.
6. Guzmán-García, X., Botello, A.V., Martínez-Tabche, L., González-Márquez, H. (2010) Effects of heavy metal on the oyster (*Crassostrea virginica*) at Mandinga Lagoon, Veracruz, Mexico. Rev. Biol. Trop., 2010., 57:, 955-962.
7. Baudrimont M, Andre `s S, Durrieu G, Boudou A. (2003). Key role of metallothioneins in the bivalve *corbicula fluminea* during the depuration phase, after an in situ exposure to Cd and Zn. *Aquat Toxicol., 63*, 89-102.
8. Ander's, S. Baudrimont,. M., Lapaquellerie, Y., Ribeyre, F., Maillet, N., Latouche C. (1999). Field transplantation of the freshwater bivalve C*orbicula Fluminea* along a polymetallic contamination gradient(lot river, France): Part I: Geochemical characteristics of the sampling sites and cadmium and zinc bioaccumulation kinetics. *Environ Toxicol Chem, 18*, 2462-2471.
9. Baudrimonta, M. (2005). Geochemical survey and metal bioaccumulation of three bivalve species (C*rassostrea Gigas, Cerastoderma Edule* and *Ruditapes Philippinarum*) in the Nord Me´doc salt marshes (Gironde Estuary, France), J. Schaferb, V. mariea, R. maury-bracheta, C. bossyb, A. boudoua, G. blancb. *Science of the Total Environment, 337*, 265– 280.
10. Zuykov, M., Pelletier, E., Harper, D. A. T. (2013). Bivalve mollusks in metal pollution studies: From bioaccumulation to biomonitoring. *Chemosphere, 93*(2), 201-208. doi:http://dx.doi.org/10.1016/j.chemosphere.2013.05.001
11. Tessier, A., Campbell, P. G. C., Auclair, J. C., Bisson, M. (1984). Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc *Elliptio Complanata* in a mining area. . *Can. J. Fish. Aquat. Sci., 41*, 1463±1472.
12. Andrews. E. J., Brimblecombs, P. , Jickells, T., Liss, P. S., Reid, B. (2005). An introduction to environmental chemistry. *Book 2nd Edition, 1,* 296 p.
13. Stecko, J.R. Pierre, Bendell-Young, Leah I. (2000). Contrasting the geochemistry of suspended particulate matter and deposited sediments within an estuary. *Applied Geochemistry, 15*, 753-775.
14. Rezaie-Boroon, M. H. , Toress,V, Diaz, S. Lazzaretto, T. Tsang, M. Deheyn, D.D. (2013) The Geochemistry of Heavy Metals in the Mudflat of Salinas de San Pedro

Lagoon, California, USA. Journal of Environmental Protection, 4, 12-25.

15. Rezaie-Boroon, M.H., Diaz, S., Torres, V., Lazzaretto, Deheyn, D. D. (2013) Coupling Between the Changes in CO_2 Concentration and Sediment Biogeochemistry in Mudflat of Salinas De San Pedro, California, USA. Journal of Environmental Protection (JEP), 4, 10. 1173-180. http://dx.doi.org/10.4236/jep.2013.410134 P.
16. EPA Region 9 Water Division-Tetra Tech, Inc. (2004). Los Angeles and long beach harbor complex framework for calculating TMDLs. *EPA Draft Report,*
17. EPA Report: Risk Based Concentration Table (2000). www.epa.gov
18. US EPA (1991). Human Health Evaluation Manual, Standard Default Exposure Factor. OSWER Directive 9285- 6-03, Washington DC.
19. Rainbow, P. S. (1997). Ecophysiology of trace metal uptake in crustaceans. *Estuarine, Coastal and Shelf Science, 44,* 169–175.
20. Borg, H. (1987). Trace metals and water chemistry of forest lakes in northern Sweden. *Water Research, 21*(1), 65-72. Doi:http://dx.doi.org/10.1016/0043-1354(87)90100-X
21. Donat, J. R., and Bruland, K. (1995). Trace elements in seawater. *Trace Elements in Natural Waters. Boca Raton: CRC Press., 1*, 247-281.
22. Wu, J. and Luther, G. W. (1995). Complexation of Fe(III) by natural organic ligands in the northwest Atlantic ocean by a competitive ligand equilibration method and a kinetic approach. *Marine Chemistry, Volume 50,*(1–4,), 59–177.
23. Hong, J., Calmano, W. Forstner. U. (1995). Intertrestial waters. *Trace Elements in Natural Waters. Boca Raton: CRC Press., Ch 6*, 117-150.
24. Zirino, A., Lieberman, S.H., Clavell, C. (1978). Measurement of Cu and Cn in San Diego bay by automated anodic stripping voltametry. *Environ. Sci. Technol., 12*, 73-79.
25. Chadwick, D. B., Ziniro, A., Richardson, H.S., Katz, C.N., Blake. A.C. (2004). Modeling the mass balance and fate of copper in San Diego bay. *Limnol. Oceanogr., 49*, 355-366.
26. Rainbow, P. S. (2002). Trace metal concentrations in aquatic invertebrates: Why and so what? *Environmental Pollution, 120*, 497–507.
27. Rainbow, P. S. (1988). The significance of trace metal concentrations in decapods. in: Fincham, A.A., Rainbow, P.S. (eds.), aspects of decapod crustacean biology. . *Symposia of the Zoological Society of London, 59*, 291–313.
28. Deheyn, D. D., Latz, M.I. (2006). Bioavailability of metals along a contamination gradient in San Diego Bay (California, USA). Chemosphere, 2006, 63, 818-834.
29. Chadwick, D.B., Largier, J.L., Cheng, R.T. (1994). The role of thermal stratification in tidal exchange at the mouth of San Diego bay. D.G. Aubrey, C.T. Friedrichs (Eds.), Buoyancy Effects on Coastal and Estuarine Dynamics, Coastal Estuarine Studies, 155–174.