PS The Geochemistry of Heavy Metals in Mudflat of Salinas De San Pedro Lagoon, California*

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Abstract

The Salinas de San Pedro, CA lagoon develops mainly into a mudflat habitat, which spreads in an enclosed coastal area containing freshwater as well as saltwater saturated sediments, resulting in a rich biodiversity. Many species depend on this fragile but threatened gradient-based habitat.

In this study, short sediment cores (up to 20 cm deep) from the Salinas de San Pedro seafloor were used to assess the recent pollutant deposition processes in response to extensive human activity. The cores consisted of alternating layers of clays and silts, with isolated sandy horizons. Analysis of the sediment cores for heavy metals (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, Ti, V, and Zn) was conducted with Inductively Coupled Plasma Optical Emission spectrometry (ICP-OES) for 20 sites showing enrichment for some of these metals.

In general, heavy metals appeared to be spread homogeneously throughout the lagoon, sometimes reaching higher levels in various sites, and most often mainly concentrated in fine-grained sediments.

Heavy metal concentrations in surface sediments varied greatly for each metal, with concentration values (mg/g) ranging from 1.05-4.8 (Al); 0.003-0.011 (As); 0.001-0.005 (Cd); 0.02 to 0.82 (Cr); 0.085-0.47 (Cu); 5.98 - 14.22 (Fe); 0.06-0.19 (Mn); 0.03-0.67 (Ni); 0.05-0.38 (Pb); <0.008-0.069 (Se); 0.18-0.63 (Ti); 0.040-0.091 (V) and 0.149-0.336 (Zn). Arsenic, cadmium, chromium, copper, nickel, and zinc showed overall concentrations above the probable toxic effect level (PEL). The arsenic, cadmium and selenium retention in the sediments is highly variable and controlled by local processes resulting in a complex diversity of metal speciation. Assessment of the results using geo-accumulation index was correlated with the data on metal speciation. The geochemistry of these sediments is particular because of the association with the iron-rich clays. Iron was found in the highest concentration, acting as possible nutrient source for the lagoon. Enrichment factors (EFs>1) for these

elements and their statistical association suggest anthropogenic inputs for most metals. The most likely sources for these element enrichment (especially As, Cr, Pb, Se, Ti, and Zn) are intensive industrial activities in the local harbor as well as the Tin, Copper and Lead based paint used intensively for boating activities during the last two decades.

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Introduction

Identification of geochemical processes is the key for understanding metals behavior, association, and distribution in the geological and biological system of Salinas de San Pedro in California.

It is widely recognized that behavior, transport, and fate of metals in aquatic systems are determined by nature of their association with solid substrate and/or organic material. The geochemical nature of such aquatic particles (e.g., sediments) will determine the presence and form of trace metals in a lagoon environment. The geochemical association interferes with the uptake capabilities of an organism to dictate the subset of metals that are available in free ionic form versus bond to particulate/sediment material from which they can be released.

This research study is focused on characterizing the suspended particulate matters and deposited sediments and their geochemical features in a local salt marsh- Salinas De San Pedro, CA, where such material provides food to a wide range of aquatic invertebrates.

Metals are associated with particulate transport and their disposal through lagoon is a function of hydraulic condition. Hydraulic condition by flood and ebb in San Pedro Salinas lagoon controls sorting and mixing processes, where contaminated and uncontaminated sediments are added to the lagoon's storage and deposition.

The Salinas de San Pedro mudflat habitat provides an interesting case study in metal geochemistry in a system with a high suspended particulate concentration through ebb and flood. Salinas de San Pedro is an anthropogenically impacted manmade lagoon, which is also a critical habitat for many sensitive species such as the benthic bivalves. In this study, we quantified trace metal concentrations in sediment and identified potential bioaccumulation patterns for a suite of trace metals and their origins.

Cabrillo Marine Salt Marsh (Salinas de San Pedro) is entirely manmade, which was created by the Port of Los Angeles in 1985 to replace lost shallow-bottom fish habitat. The area is divided by habitats, representing the rocky shore (hard substratum), sandy beach and mudflat (soft shifting bottoms), and the open ocean. The study area is limited to the 3.75 acre (15175 m^2) salt marsh mudflat and its habitat (fig 1).

Methods

Figure 1. Map of sampling and study location (adapted and modified from Google earth, 2012)
(A) Map of cores composite samples (0-20 cm depth) using hand core sampler. The total of 17 profiles was taken in 3.75 acre of salt marsh in six evenly spaced (10 m) locations. Core samples taken from each profile varies
(B) Scoops and grab samples from mudflat surface deposits (from top 2-4 cm).

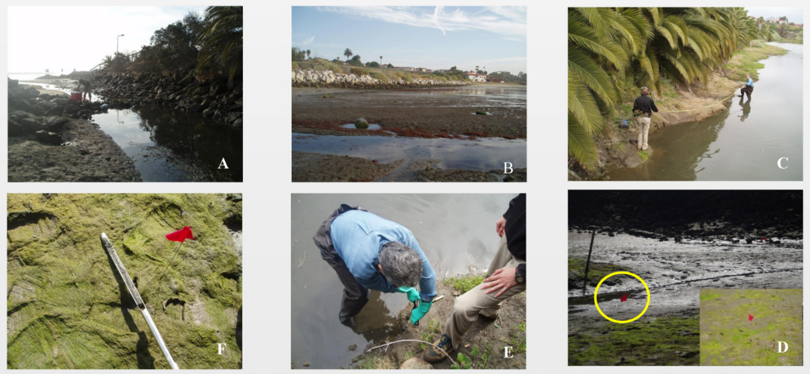
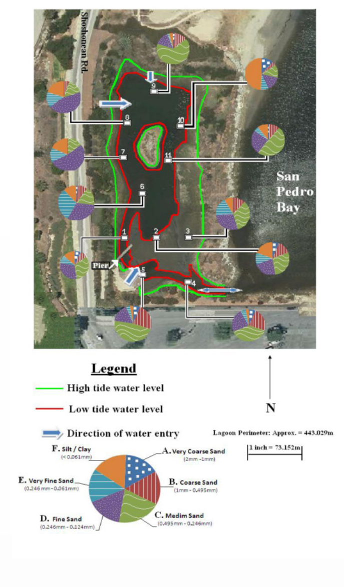


Figure 2. Clockwise from left to right A) The entrance and exit of Salinas de San Pedro Lagoon at lowest tide level, Spring 2009. B) Salinas de San Pedro at lowest low tide water; looking west. C) Measuring the distance between profiles to position the red flags. D) Red flag shows the sampling location. E) A hand sediment core sampler was used as a sampling device to collect samples from depth of 0-20 cm below surface. F) The core sample was split in 2 subsample from 0-10 cm and 10-20 cm respectively.

Results

Sediment Deposit for Salinas Lagoon, California



Sediments Characteristics:
Overall, sediment samples were greenish grey to brownish color with rust stains. The change in color from lighter to darker (from 0-20 cm depth) in the core samples was evident.
Sediment samples had "rotten egg" and very oily smell.
Bioclast were present in most samples.
Salt grass and pickle weed grow along the banks of this wildlife refuge. The numerous holes on the mud surface are the evidence of the thriving underground community of invertebrates that dominate the marsh mud.
The grain size analysis of the lagoons grab samples (fig 3) also suggests an important contribution of terrigenous material originating from runoff of surrounding lagoon. Indeed, the lagoons contain mainly fine silt/clay material with high LOI level (Los Of Ignition [%]).

Figure 3. Sediment grain size analysis in lagoon environment. The map shows the Salinas de San Pedro lagoon with grab sampling locations. The pie diagrams show the grain size distribution in each location.

Sampling location	DO [mg/l]	Salinity [‰]	pH	Temp [°C]
L1	3.00	34.25	6.96	18
L2	2.10	32.50	7.20	17.5
L3	1.84	32.50	7.30	16.9
L4	2.40	34.00	7.58	17.7
L5	4.13	34.25	7.58	17.5
L6	3.76	34.25	7.61	17.8
L7	4.70	22.00	7.30	19
L8	2.80	24.00	7.70	19
L9	3.90	28.50	7.60	18.9
L10	3.50	34.50	7.48	18.6

Table 1: The physio-chemical parameters for 10 sampling locations in Salinas de San Pedro measured in Summer 2009. The extremely low oxygen level and high biological oxygen demand (BOD) for L2, L4, L6 and L8 sampling locations correlate with the locations of hydrogen sulfide gas discharge.

The geochemistry of lagoon sediments were contrasted over a 2-year s period within San Pedro Lagoon in CA in different seasons.
We detected several trace metals that are anthropogenically and naturally enriched in San Pedro Lagoon's sediment. This evidence support our studies that attribute contamination to both historical and current inputs.

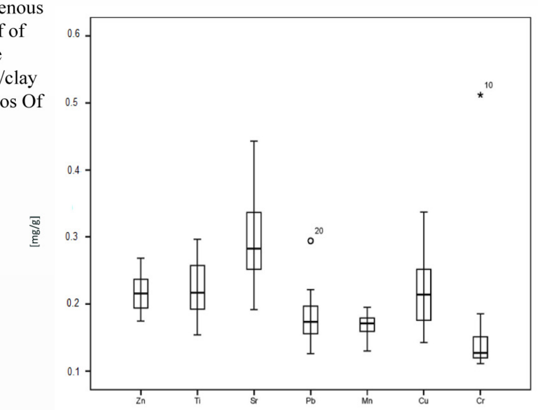


Figure 3. Box-Plot of trace metal distribution in Salinas de San Pedro Lagoon. A noticeable decrease in Cr, Cu, Mn and Pb was observed when comparing concentrations in the surface layers of the sediment with those found in the bottom (10-20 cm). On the contrary, metals with higher attraction to organic matter (i.e. Cu and Zn) followed a scattered variation with overall higher concentration.

N= 20	Ag	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Se	Sr	Ti	V	Zn
MAX [mg/g]	0.020	4.844	0.011	0.005	0.824	0.474	14.226	0.190	0.670	0.388	0.069	0.685	0.393	0.091	0.336
MEAN [mg/g]	0.002	3.392	0.007	0.003	0.140	0.244	10.060	0.139	0.116	0.172	0.014	0.402	0.256	0.060	0.235
MIN [mg/g]	0.000	1.054	0.003	0.001	0.022	0.085	5.986	0.060	0.033	0.051	0.00	0.184	0.107	0.040	0.149
STDV	0.006	1.707	0.002	0.001	0.222	0.117	2.374	0.036	0.179	0.086	0.021	0.154	0.082	0.013	0.059

Table 2: Concentration of several trace metals for 20 samples were taken from San Pedro Lagoon. Trace metal concentrations in the upper and bottom sediments sediment core material are compared. Even though with the same tendency over the surveyed years: Al, Cu, Fe, Ni, Pb, Ti, and Zn concentrations were higher in the upper core samples (0-10 cm) than in the lower core samples (1-20 cm).

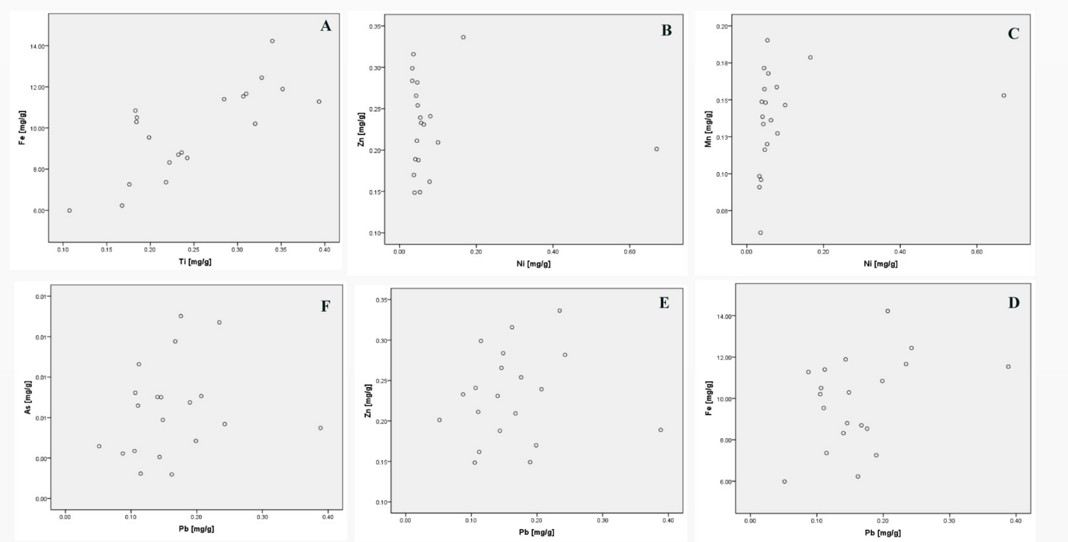


Figure 4: Several trace metals showed medium to high correlations within and between sample types. Biogenic metals (i.e. Cd, Co, Cu, Ni, Pb and Zn) are normally associated to organic matter as it's their main carrier phase. There is a good correlation between Ti-Fe, Pb-Zn , Pb-Fe, Pb-Zn, and Pb-As for the sediments of the Salinas de San Pedro.

Discussion

The uptake of metals by organisms is influenced by geochemical factors that can cause metals to be more or less bioavailable (fig 5).
According to geophysical investigation by USGS in 2007, earthquake faults are buried beneath the Salinas de San Pedro Bay and lagoon in southern California. These faults release hydrogen sulfide gas to the mudflat (fig 6). This was evident by observing bubbles that were coming up through the water and sediments in parts of the salt marsh.
Additional hydrogen sulfide gas is generated by the decomposition of organic material in the marsh. Both conditions could naturally increase the easily reducible metals (e.g. Fe^{3+}) and metal oxide (e.g. Fe_2O_3), organic matter (LOI-loss of ignition), and total metal (e.g. Cu, Pb, and Zn) .

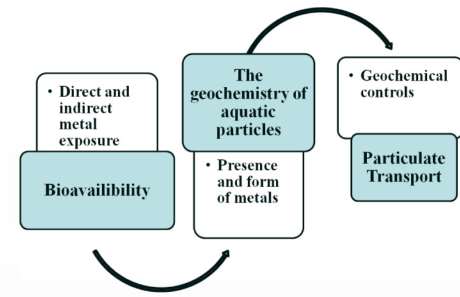


Figure 5. Flow chart of geochemistry of aquatic particles .

The Fe^{3+} and sulfate reductions are dominant electron-accepting processes in the surface sediments of Salinas de San Pedro Lagoon. The role of H_2S in controlling the dissolved metal availability has not been widely investigated, however, it is important to consider for the bioavailability of metals e.g., Zn^{2+}, Cd^{2+}, and Pb^{2+} in anoxic sediments environment.

$$H_2S_{(aq)} \leftrightarrow HS^-_{(aq)} + H^+_{(aq)}$$

$$HS^-_{(aq)} \leftrightarrow S^{-2}_{(aq)} + H^+_{(aq)}$$

$$H_2O \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$$

The boating area, Cabrillo Aquarium waste water and sewage runoff are considered as anthropogenic sources of contamination and direct exposure in Salinas de San Pedro. This could also increase the dissolved levels of metals that may lead to the formation of organic complexes and be adsorbed by particulate organic matter. The dissolved particulate organic matter can flocculate or coagulate acting as a carrier for the trace metals to be digested by mudflat organism. Since metal sulfides are substantially less soluble in water, this promotes adsorption of HS^- ions to the particle surface, contributing to a strong negative charge, which stabilizes the colloidal suspension. Therefore, such geochemical process provides contaminated food to a wide range of aquatic invertebrates.

Gas discharge location through earthquake fault line

Figure 6. The above picture shows one of the gas discharge location through fault line. Onshore, the earthquake faults such as Palos Verdes fault bounds the eastern margin of the uplifted Palos Verdes Hills, and extends offshore at the Port of Los Angeles southwestward into San Pedro Bay. Salinas de San Pedro lagoon is located on the SE segment of the fault.

Abstract

Assessing environmental quality of coastal lagoons is rather difficult due to their intrinsic high variability that limits the power of standardized analytical geochemistry and ecotoxicological approaches. The purpose of this study was to assess the contamination in lagoon sediments where it is mainly attributed to street runoff flowing through heavily populated urbanized area like San Pedro, CA and to wastewater discharge like around the Cabrillo Marine Aquarium area. In both cases, the contamination is dispersed through various water channels that carry untreated effluent of various sources ending up into the small manmade Salinas de San Pedro lagoon, before being ultimately dispersed into the Pacific Ocean by tidal mixing. The Salinas de San Pedro lagoon develops mainly into a mudflat habitat, which spreads in an enclosed coastal area containing freshwater as well as saltwater saturated sediments, resulting in a rich biodiversity. Many species depend on this fragile but yet threatened gradient-based habitat. Indeed, Salinas de San Pedro is home to an incredible number of small invertebrates (from worms, clams, ghost shrimp, to fiddler crabs), which most often are found burrowed in the mud. However, commercially important fish, such as the California halibut, use this type of habitat as a nursery ground which provides protection and a rich source of food.
In this study, short sediment cores (up to 20 cm deep) from the Salinas de San Pedro seafloor were used to assess the recent pollutant deposition processes in response to extensive human activity. The cores consisted of alternating layers of clays and silts, with isolated sandy horizons. Analysis of the sediment cores for heavy metals (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, Ti, V, and Zn) was conducted with Inductively Coupled Plasma Optical Emission spectrometry (ICP-OES) for 20 sites showing enrichment for some of these metals.
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