

Analyses of Trace Metal Diagenetics in Estuarine Systems: Lead and Cadmium in Younger Lagoon, CA

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Abstract:

This study investigates the diagenetics of lead and cadmium in Younger Lagoon, which is one of many barrier beach systems dotting the California coast. Trace metal data is lacking or poorly understood as it relates to submarine groundwater discharge (SGD) for barrier beach systems. Near shore ocean surface water, lagoon surface water, and lagoon groundwater samples up to 120 cm depth were collected from Younger during the wet season on January 15, 2011. Lagoon and ocean surface water samples from 4 other similar sites were also collected during the 2011 wet season. All samples were filtered to 0.45 μm , acidified, and analyzed for dissolved cadmium and lead with chelating resin column partitioning-inductively coupled plasma-mass spectrometry (ICP-MS). Depth profiles for groundwater at Younger Lagoon showed that salinity increased and dissolved oxygen (DO) decreased with depth while pH fluctuated independently of depth. Cadmium levels spiked from 71 ng/L at the sediment-water interface to 170 ng/L at 50 cm and fell to 1.76 ng/L at 70 cm. Similarly, lead concentrations spiked from 27 ng/L to 41 ng/L and fell to 6 ng/L over the same depths. At 120 cm both cadmium and lead concentrations were below detection limits of 1.67 ng/L for cadmium and 2.17 ng/L for lead. Taken together, the decreasing trend in DO and the spike in dissolved metals indicates that aerobic respiration was occurring from the sediment-water interface downward to 50 cm and anaerobic respiration by dissimilatory sulfate reduction was taking place below 50 cm, resulting in deposition of the sulfur oxyanions, CdS and PbS. The fluctuations in pH from these diagenetic processes were explained by incorporating Redfield's ratio in the equation for sulfate reduction. Consequently, the dominant forces controlling metal distribution in the estuarine system appear to be diagenetic sulfate reduction and groundwater fluxes into the lagoon.

1. Introduction:

The exchange of water at the land and sea interface, known as SGD, is a major component of the hydrological cycle (Moore, 2010). The complex spatial and temporal forces of SGD (Fig 1) input dissolved chemicals to the oceans. Over the past decade SGD has been recognized as an important transport mechanism that delivers

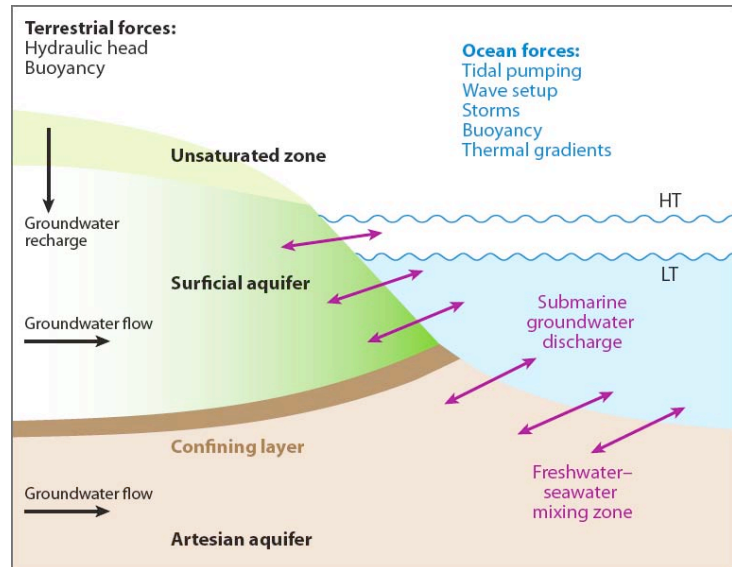


Figure 1. “SGD is a combination of terrestrial and physical ocean forces operating in a complex geologic environment”. (Moore, 2010)

dissolved nutrients to coastal ecosystems (Slomp, 2004). However, it is only recently that scientists have begun to quantify the input of other SGD constituents, such as trace metals. Recent studies by *Moore et al.* (2008) have shown that SGD in some environments may account for higher inputs of nutrients, carbon, and metals to the oceans than those provided by river systems, and *Paytan et al.* (2006) have shown that SGD is a major contributor to nutrient fluxes that sustain coastal fish and bird habitats. Moreover, the geochemical reactions occurring within the fresh and saline porewater mixing zone, known as the sub-terrain estuary (STE), alter the redox state of trace metals and may account for fluxes of trace metals insufficiently described by surface water, groundwater, atmospheric, and tidal exchanges (Montluçon and Sañudo-Wilhelmy, 2001).

For example, the depletion of porewater uranium in the STE occurs by SGD circulation through reducing permeable sediments, as evidenced by higher concentrations in the adjacent ocean water relative to bay surface water (Charette and Scholkovitz, 2006). On the other hand, depositions of trace metals in sediments are largely controlled by iron and manganese

(hydr)oxides, as demonstrated by enrichment of thorium with iron (hydr)oxides and enrichment of barium with manganese (hydr)oxides in an STE sediment core (Charette *et al.*, 2005).

According to the United State's Agency for Toxic Substances and Disease Registry (2007), elevated levels of lead and cadmium, are toxic to humans and destructive to ecosystems. In fact, under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the EPA has ranked lead second and cadmium seventh on the Priority List of Hazardous Substances (CERCLA, 2007). Therefore, monitoring lead and cadmium distributions in coastal environments is essential in determining human and environmental health.

1.1 Study Sites

Our primary study site was Younger Lagoon, a barrier beach located on the property of Long Marine Laboratory (Fig 2). Barrier beach lagoons are abundant throughout the California coastline. They are geochemically active ecosystems that provide habitat for a diverse group of freshwater, estuarine, and marine wildlife. By sampling surface and groundwater, our investigation was two-fold, enabling us to evaluate metal fluxes in groundwater as well as changes in surface water geochemistry in barrier beach ecosystems. Although this study focuses on quantifying trace metal concentrations and diagenetic processes, other researchers are simultaneously compiling complimentary data (e.g., mercury species, nutrients, dissolved organic carbon, cations, anions, and water flux). We are collaborating with the US Geological Survey's (USGS) Pacific Coastal and Marine Science Center to characterize the geochemistry of coastal lagoon surface water, down gradient groundwater (i.e., SGD), and coastal ocean water. In addition to Younger Lagoon, we collected surface water samples from four other lagoon systems in and around the Monterey Bay area (Pescadero, Waddell, Scott Creek, and San Lorenzo), which are located in Fig 3. Seasonal data from these sites will provide information about geochemical

changes over time in lagoon systems and comparison to groundwater collected from Younger will help us determine which sites warrant further investigation. Additionally, our combined data will form the foundation for a mass balance model of SGD trace metal fluxes to California's coastal waters.



Figure 2. Younger Lagoon SGD sampling site at Long Marine Laboratory.



Figure 3. Sampling site locations in the Northern Monterey Bay.

2. Methods:

2.1 Sample Collection

During the 2011 wet season (January 15, 2011), we collected hourly groundwater, surface water, and coastal ocean water at our Younger Lagoon site for an approximately ten-hour period. During this period the lagoon was not breached, therefore trace metal fluxes between the lagoon and the ocean were subterranean (Fig 4). We scheduled our sampling event to characterize conditions during and immediately following a receding tide (+1.15 m – 0 m – 0.55 m), which is typically the period of maximum groundwater flux. Concurrently, we collected surface water and coastal ocean water samples from the four other barrier beach lagoon sites (Fig 3). We are collaborating with the USGS to conduct a similar sampling during the dry season (October, 2011) that will enable us to document seasonal changes in these systems.

Surface seawater samples were collected in large trace metal clean vessels from a standing depth of ~1 m. Surface water samples were pumped through acid cleaned Teflon lines using a peristaltic pump coupled with C-flex tubing. The line was flushed for approximately 1 minute between samples collections. Groundwater samples were collected through a piezometer containing dedicated Teflon lines for each port. To limit subterranean cross contamination of groundwater samples, no two ports were spaced less than 20 cm apart and pumping time on each port was minimal (Fig 4). All samples were filtered in-line with a high-capacity Geotech 0.45 μm disposable filter capsule and collected in 60mL trace metal clean low-density polyethylene (LDPE) bottles (see Flegal et al., 1991 for detailed procedure). Water samples were triple-bagged in polyethylene bags, stored over ice, and transported to a class 100 clean lab where they were acidified with high purity (Optima-grade) HNO_3 to $\text{pH} < 2$, refrigerated, and stored for at least 90 days prior to analysis with ICP-MS.

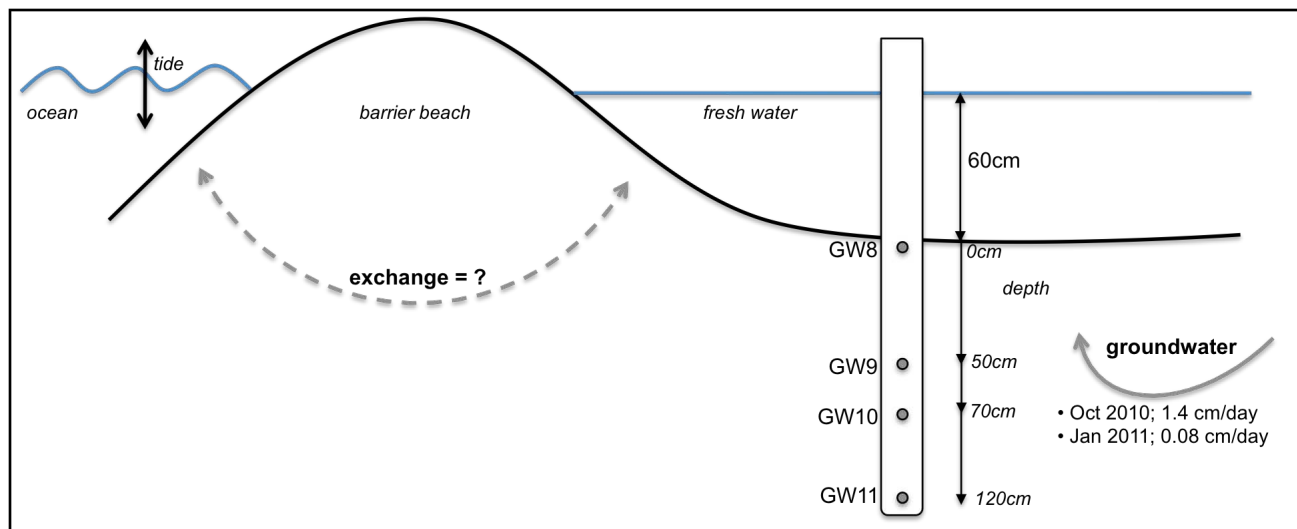


Figure 4. Younger Lagoon groundwater port positions and seepage rates.

2.2 Ancillary Parameters

We measured pH, temperature, conductivity, and DO *in situ* for each sample using a calibrated YSI 556 water quality multi-probe. Ancillary parameters were measured on samples in

60 mL trace metal clean LDPE bottles within one minute of collection, and the probe tip was thoroughly rinsed with high purity (18.3 MΩ cm) Milli-Q® water between measurements. The YSI probe was calibrated in-house on the evening prior to all sampling events.

2.3 Trace metals (lead and cadmium)

All of our field and laboratory methodologies were conducted using trace metal clean techniques (Flegal, 1991; Ndung'u, 2003). Filtered samples were acidified to 24 mM (pH <2) in a class 100 clean lab with Optima grade HNO₃ and analyzed for dissolved lead and cadmium concentrations with chelating resin column partitioning-inductively coupled plasma-mass spectrometry (ICP-MS) with a Thermo Element XR ICP-MS (see Ndung'u 2003 for a schematic of the flow injection). The sample-buffer was prepared from acetic acid and ammonium hydroxide and brought to pH 9. The buffer wash was a 1:10 sample-buffer:Milli-Q® dilution. The elution acid was 1.5 N high purity (Optima grade) HNO₃. This method separates and pre-concentrates trace metals from major ions present in natural waters using a 1 cm micro-column (part #MC-1CNM, Global FIA, Fox Island, WA) packed with Toyopearl AF chelate-650M (Tosoh Bioscience, Montgomeryville, PA) cation exchange chelating resin.

Standard curves were made from multi-element SRM # 3179 obtained from the National Institute of Standards and Technology (NIST) to final lead and cadmium concentrations between 2 ng/L and 240 ng/L (Appendix, Table A1). To account for differences between fresh, estuarine and saline ground and ocean water sample matrixes, standard curves and reagent blanks were prepared in Milli-Q and California Current cleaned seawater (low metal concentration, open ocean seawater). Internal indium and bismuth standards were used to correct for instrumental drift (equation 1) of the counts per second (cps) for the two most common isotopes of cadmium (¹¹⁰Cd and ¹¹¹Cd) and for ²⁰⁸Pb. Then, concentrations were extrapolated from a standard curve in MQ matrix.

$$\frac{Cd_{cps} * In_{cps}}{In_{cps_{average}}} \sim OR \sim \frac{Pb_{cps} * Bi_{cps}}{Bi_{cps_{average}}} \quad \text{Eqn 1}$$

For each matrix two sets of standard curves were taken, one at the onset of the experiment, and one after all samples had been analyzed (Appendix Figure B1). A weighted average of concentrations from these standard curves was used to correct for instrumental drift (equation 2).

$$\left\{ \left(\frac{\# samples_{tot} - sample\#}{\# samples_{tot}} \right) * conc_{1^{st} curve} \right\} + \left\{ \left(\frac{sample\#}{\# samples_{tot}} \right) * conc_{2^{nd} curve} \right\} \quad \text{Eqn 2}$$

Further, to make blank correction while simultaneously correcting for drift in blank measurements, acidified MQ blanks were run every 3-8 samples until the signal stabilized. Then weighted averages of the blanks immediately proceeding and following sample sub-sets were subtracted from the standard curve drift corrected concentrations to calculate the final metal concentration values. Detection limits were calculated as 3 times the standard deviation of the blanks (Table 1). For all of the unknown samples with concentrations above detection limits, the average % difference between ^{110}Cd and ^{111}Cd using the MQ and seawater curves was 1.43% and 1.58%, respectively, and it was 1.37% for lead, thus there was no distinction between either isotope of cadmium (see table 1) and we proceeded with the average cadmium concentrations from here on. Similarly, matrix effects on cadmium detection limits were inconsequential (between 0.01 ng/L and 0.03 ng/L, see Table 1), therefore neither matrix was preferable and we arbitrarily chose to proceed with concentrations derived from the MQ standard curves from here on (see complete data set in appendix Table A2). With these methods the lower limits for cadmium and lead were 1.67 ng/L and 2.17 ng/L, respectively.

TABLE 1. Detection limits

Blank Parameter	[Blank] _{AVG} (ng/L)	Std. Dev.	Detection Limit (ng/L)
¹¹⁰ Cd in MQ	1.00	0.54	1.61
¹¹⁰ Cd in SW	1.08	0.55	1.64
¹¹¹ Cd in MQ	0.98	0.57	1.72
¹¹¹ Cd in SW	1.05	0.56	1.69
²⁰⁸ Pb in MQ	2.26	0.72	2.17
²⁰⁸ Pb in SW	2.26	0.72	2.16

2.4 Quality Assurance

To determine accuracy and precision of unknowns, two standard reference materials (SRM) representing different water types were cross checked every 8-10 samples. SRM SLEW-2 was used to evaluate estuarine water, and SRM CASS-3 for near shore ocean water. Both SRM's are certified by the National Research Council of Canada. The percent recoveries for SLEW-2 and CASS-3 are presented in table 2.

TABLE 2. Recovery of trace metals from SRMs.

Metal	Certified Value (ng/L)	Measure Value (ng/L, n=6) Mean ± SD	% recovery
SRM CASS-3			
Cd	30 ± 5	25.38 ± 6.43	85%
Pb	12 ± 4	12.13 ± 3.98	101%
SRM SLEW-2			
Cd	19 ± 2	20.41 ± 1.25	107%
Pb	27 ± 5	21.58 ± 1.75	80%

For filter blanks, a peristaltic pump was used to pass MQ through the filter post *in situ* sample collections and cadmium and lead concentrations were -0.07 ng/L and 2.87 ng/L, respectively. The cadmium concentration from the filter was below the detection limit and no correction was needed. The lead concentration was 0.7 ng/L above the detection limit. Given that the filter may have built up this small amount of lead over time, and that 0.7 ng/L lead is inconsequential in determining the trends established with this study, the effect of the filter was considered null and no correction for lead was made regarding the filter blank.