

# Geochemical cycling of arsenic in a coastal aquifer

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Submitted to:  
*Environmental Science and Technology*  
November 17, 2005

Revised Version:  
March 2, 2006

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**Abstract:**

Biogeochemically-modified pore waters from subterranean estuaries, defined as the mixing zone between freshwater and saltwater in a coastal aquifer, are transported to coastal waters through submarine groundwater discharge (SGD). SGD has been shown to impact coastal and perhaps global trace metal budgets. The focus of this study was to investigate the biogeochemical processes that control arsenic cycling in subterranean estuaries. Total dissolved As, as well as a suite of other trace metals and nutrients, were measured in a series of wells and sediment cores at the head of Waquoit Bay, MA. Dissolved As ranged from below detection to 9.5  $\mu\text{g/kg}$ , and was associated with plumes of dissolved Fe, Mn, and P in the groundwater. Sedimentary As, ranging from 360 to 7500  $\mu\text{g/kg}$ , was highly correlated with sedimentary Fe, Mn and P. In addition, amorphous Fe (hydr)oxides were more efficient scavengers of dissolved As than the more crystalline forms of solid-phase Fe. Given that dissolved As in the surface bay water was lower than within the subterranean estuary, our results indicate that the distribution and type of Fe and Mn (hydr)oxides in coastal aquifers exert a major influence on the biogeochemical cycling of As in subterranean estuaries and, ultimately, the fate of groundwater-derived As in marine systems influenced by SGD.

## Introduction

Coastal aquifers have been shown to be important links between terrestrial and marine biogeochemical cycles (1-3). The subterranean estuary is defined as the location where terrestrially derived fresh groundwater and seawater interact within coastal aquifers (1). Like surface estuaries, the mixing zone of the subterranean estuary can influence the biogeochemical cycling of metals and nutrients that are sensitive to changes in salinity and redox potential (1, 4).

A number of forcing functions, including hydraulic gradients and tidal pumping drive fluid from the subterranean estuary into marine surface waters, a process known as submarine groundwater discharge (SGD; 4). In recent years SGD has been garnering attention as a source of eutrophication-causing nutrients to coastal areas (1,4) and a possible source of metals as well (5, 6). Montlucon and Sanudo-Wilhelmy (6) calculated the copper mass balance for Flanders Bay, Long Island and concluded that SGD must account for a large fraction of the copper sources to the bay. Although studies such as these have addressed the importance of SGD as a source of solutes, many studies have not taken into account the chemical reactions occurring in subterranean estuaries when fluxes are calculated. Such reactions and transformations ultimately control the fate of metals and nutrients transported through aquifers and into the coastal ocean.

The study site is a subterranean estuary located at the head of Waquoit Bay, along the south shore of Cape Cod, MA. The overall groundwater geochemistry at the study site has been well documented in three previous papers (2, 7, 8). The small and confined nature of the subterranean estuary makes Waquoit Bay an ideal natural laboratory for the

study of the major biogeochemical reactions operating within the permeable sediments of a coastal aquifer with active Fe and Mn redox cycles and well-defined salinity gradients.

This paper focuses on arsenic geochemistry at the same location. There have been numerous studies on As in groundwater, with concentrations ranging from less than 1  $\mu\text{g/kg}$  to 5000  $\mu\text{g/kg}$  (9, 10). Arsenic is a highly toxic metalloid; in Bangladesh, where groundwater is the major source of potable water, an estimated 30-35 million people are currently exposed to concentrations greater than five times the current World Health Organization drinking water limit (9). It is not unusual that high levels (above the WHO limit of 10  $\mu\text{g/kg}$ ) are found in groundwater unaffected by anthropogenic inputs of As. In addition, sedimentary As has not often proven to be a good predictor of groundwater As, as high aqueous levels of As have been observed in areas with only average sedimentary As concentrations. Concentrations usually are related to the local geology and hydrology, as well as the history of the aquifer (10-13).

Despite the large amount of knowledge that has been accumulated on As geochemistry in groundwater and sediment pore waters, to the best of our knowledge there are no articles that address the importance of SGD and the subterranean estuary on As cycling in coastal marine systems. Here, we report on the analysis of dissolved As concentrations in the groundwater as well as solid-phase As associated with the sediments of a coastal aquifer on Cape Cod, MA.

## Methods

### Sampling Site

The study site is located within the Waquoit Bay National Estuarine Research Reserve, Cape Cod, MA. The aquifer is made up of homogenous, permeable sand that is generally poor in organic matter (OM) (14). Because of the soil permeability on Cape Cod, much of the precipitation that falls on the region recharges the aquifer, as opposed to becoming surface runoff. Thus, most freshwater discharging into local bays and estuaries is derived from groundwater. The residence time for water in the upper 10 m of the aquifer is approximately 10 years, a relatively short time for groundwater (14). Waquoit Bay itself is largely groundwater fed, receiving SGD directly from the head of the bay, where the study site is located (Fig. 1), as well as indirectly, through the two major rivers that drain into it (the Quashnet and the Childs), which are both groundwater fed.

Iron (hydr)oxide coated sands have been observed at the study site and previous studies have revealed active Mn and Fe redox cycles in the subterranean estuary (2). Charette and Sholkovitz (2) reported on significant iron (hydr)oxide deposits at the groundwater-seawater interface in the coastal aquifer; the Fe (hydr)oxides had precipitated from a large (~11 mg/kg) dissolved Fe plume within the freshwater portion of the aquifer. This “iron curtain” acted as a geochemical barrier, preventing a large plume of groundwater-derived phosphorous from entering the surface water of the bay. The iron curtain occurs where the dissolved Fe-rich fresh groundwater upwells over the more dense saline groundwater intruding from the bay. Spiteri et al. (15) suggested that the Fe precipitation was driven by a pH increase due to mixing between the two

groundwater endmembers ( $\text{pH}_{\text{fresh gw}}=5.5$ ,  $\text{pH}_{\text{saline gw}}=7.9$ ). The high salinity groundwater, which represents the oldest water and therefore the most reducing environment, is the site of Fe remobilization.

## **Sampling Methods**

Three groundwater profiles were collected in June 2005 along a 12 m transect perpendicular to the shore (see Fig. 1). All water samples, including surface water samples, were collected within eight days of each other, with each groundwater profile collected over eight hours. Arsenic measurements were made on three of the seven profiles. The profiles were obtained using a stainless steel drive point piezometer system (“Retract-A-Tip,” AMS Inc.) and were all approximately 6-8 m deep. Groundwater samples were pumped through fluorinated polyethylene tubing using a peristaltic pump, and were collected every 0.15 m in the mixing zone (transition between fresh and saline groundwater) and every 0.3-0.6 m elsewhere. Samples were filtered in the field using an inline 0.45  $\mu\text{m}$  Pall AquaPrep 600 filter. Procedural blanks were collected by pumping MilliQ (18.2 M $\Omega$ ) water through the entire system (well point, tubing, and filter). The Oxidation Reduction Potential (ORP), pH, dissolved oxygen and temperature were measured in the field using a YSI 600XLM in a flow through cell (YSI, Inc.). ORP was converted into Eh by calibrating the probe to a standard Zobell solution.

All trace metal samples (As, Fe, Mn) were collected in 15 mL HDPE bottles that had previously been cleaned in 10% HCl (trace metal grade) and MilliQ water. The sample bottles were pre-acidified in the clean room with 50  $\mu\text{L}$  of 8M  $\text{HNO}_3$  (also trace metal grade). Two trace metal samples were taken at each depth; one was allocated for

As analysis and the other for Fe and Mn analysis. After collection, the acidified samples were stored at room temperature in plastic bags to prevent contamination. Samples for  $\text{PO}_4^{3-}$  determination were collected in 30 mL acid-cleaned scintillation vials, acidified (50  $\mu\text{L}$  of 8 N  $\text{H}_2\text{SO}_3$ ), and stored at room temperature until analysis.

## Analyses

Dissolved As was determined using hydride generation-inductively coupled plasma-mass spectrometry (HG-ICP-MS) on a Finnegan Element 2. The hydride generation was performed using a CETAC Hydride Generation system according to the procedure set forth in Klaue and Blum (16). Briefly, 100  $\mu\text{L}$  30%  $\text{H}_2\text{O}_2$  was added to each sample and standard to oxidize all As (III) to As (V), i.e. values reported here are total As; samples were allowed to sit at least 12 hours before analysis. The reagents 1M  $\text{HNO}_3$  and 1%  $\text{NaBH}_4$  in 0.1M  $\text{NaOH}$  were combined with the sample to produce arsenical hydride, which was fed along with the carrier gas mixture into the ICP torch. The gas and solution flow rates reported in Klaue and Blum (16) are the same ones used here, with the exception of the additional gas, for which the flow rate was increased to 0.9 L/min in order to maximize the instrument's sensitivity.

Dissolved Fe and Mn were determined as per Charette et al. (7). Briefly, a 1:20 dilution of each sample, to which an indium standard had been added to correct for signal suppression and instrument drift, was measured using ICP-MS on a Finnegan Element 2. The phosphate samples were analyzed using standard continuous colorimetric methods (17) on a Lachat QuickChem 800 Flow Injection Analyzer.

In the summer of 2002 three cores were taken at the study site (see Fig. 1). The cores were sectioned and analyzed for Fe, Mn, OC, and P content. We assumed that there was no change in the redox state of the sediments and thus the Fe (hydr)oxide composition of the sediments because the color stratigraphy observed initially was maintained over time. The cores were air dried and then hand-sieved with a nominal retention diameter of 1 mm (7, 2). In addition, three samples, one from each core, were analyzed via EXAFS (extended x-ray absorbance fine structure) analysis to determine the various forms of Fe (hydr)oxides present. The methods and data have been published in Charette et al.(7). The sedimentary concentrations reported in this paper corresponds to their reported values for the “L3+L4” leach, which was designed to target both amorphous and crystalline Fe and Mn (hydr)oxides.

A select set of samples from the archived sediment cores were analyzed for sedimentary As content. Samples were strategically chosen based on Fe and Mn content as well as Fe (hydr)oxide type. Several samples from cores 2 and 3 were analyzed, as well as the one sample from core 5 that had been analyzed via EXAFS. The digestion method used corresponds to the “L3+L4” leach used in Charette et al. (7), which was adapted from Hall et al. (18). Briefly, 15 mL of 1M hydroxylamine hydrochloride in 25% acetic acid was added to approximately 0.4 g sediment and then heated in an oven at 90°C for three hours. After this time, the aqueous phase was removed and saved. This process was repeated and combined with the existing solution. This solution was diluted 20-fold with 1M HNO<sub>3</sub> before analysis with HG-ICP-MS using the CETAC Hydride Generation system described earlier.



The detection limit for As using our HG-ICP-MS was determined to be 0.01 µg/kg. Methods blanks, both collected and treated in the same fashion as the samples, were determined for all procedures. Samples were corrected for instrument drift by monitoring the response in a check standard, which was run every 5-15 samples. The relative standard deviation for each measurement was on average 4%.

## **Results and Discussion**

### **Sedimentary phase As**

Selected samples from cores 2, 3, and 5 were analyzed for sedimentary As, Fe, Mn, and P content. Samples were chosen that represented a wide range of expected Fe content. The Fe and Mn concentrations correspond to the reactive phases of these metal (hydr)oxides and do not necessarily represent the total Fe or Mn in the sediment. Total sedimentary Fe and Mn concentrations were not determined for these samples. The arsenic in the sediments ranged from 500 to 7500 µg/kg. As was generally well correlated with Fe and P (Fig. 2, Table 1). There is one depth in core 2, however, at which As exhibited a mid-profile maximum that was not observed for either P or Fe. This As maximum was seen at the same depth as a very minor sedimentary Mn maximum. However, this As maximum is only supported by one data point. For core 3 (Table 1), Mn also generally increased with increasing As, although Mn peaked mid-profile, while As, Fe, and P continued to increase. Elsewhere in the profiles there was no correlation between sedimentary As and Mn.

A plot of As versus Fe for all sediment samples is shown in Figure 2. All the data from cores 2 and 3, except for the anomalous mid-core maximum in core 2 and the single sample from core 5, fell along a similar regression line ( $\text{As:Fe} = 0.54 \mu\text{g/mg}$ ;  $r^2 = 0.95$ ). The strong correlation between these elements provides solid evidence that As is linked to the Fe redox cycle at this location. Correlations between As and Fe have been documented by many authors in a variety of environments, often with the explanation that As adsorbs onto Fe (hydr)oxides under oxidizing conditions and is then released when the (hydr)oxide undergoes reductive dissolution (19-23).

Sedimentary As:Fe ratios were determined for three core samples, one sample from each core, for which the iron (hydr)oxide form had been determined. For a detailed discussion of iron type in the cores see Charette et al. (7). The sample from core 5, with the highest percent of goethite, an older, more crystallized form of Fe (hydr)oxide, contained the lowest As:Fe ratio ( $\text{As:Fe} = 0.1 \mu\text{g/mg}$ ), while the samples from cores 2 and 3, which contained higher percentages of ferrihydrite and lepidocrocite, had As:Fe ratios of 0.6 and 0.7, respectively. This indicates that As adsorbs more readily to amorphous Fe (hydr)oxides, an interpretation that is explained by the decrease in surface area in going from ferrihydrite to the more crystalline Fe (hydr)oxide goethite (24). The consistency of the As:Fe ratio in cores 2 and 3, as indicated by the correlation coefficient, suggests that the mixtures of Fe (hydr)oxides present at these two sites have a fairly uniform affinity for As. The data points that deviate from the regression line likely represent samples that contain a mixture of Fe (hydr)oxides that have either a higher or lower affinity for As, depending on their crystallinity. Charette and Sholkovitz (2) documented a variety of Fe (hydr)oxide types present within a relatively small horizontal

transect of the aquifer (cores separated by 50-200 m), which they attributed to differences in Fe (hydr)oxide age.

### **Aqueous phase As**

The study site is characterized by sandy sediment that is low in organic matter. Additionally, previous research at the site has demonstrated that, although there may be some sulfate reduction occurring, there is no build up of sulfide, and iron sulfide minerals have not been observed in the subterranean estuary at the study site (7). We hypothesize that As geochemistry at this site will be largely governed by Fe and Mn redox cycles, both because Fe (hydr)oxides and, to a lesser extent Mn (hydr)oxides, are known to be powerful absorbers of As (10), and because Fe and Mn dominate the redox chemistry of the subterranean estuary. More specifically, we hypothesize that redox conditions in subterranean estuaries are such that increases in dissolved As concentrations will be the result of the reductive dissolution of Fe, and possibly Mn, (hydr)oxides.

Figure 3 shows depth profiles of dissolved As,  $\text{PO}_4^{3-}$ , Fe, and Mn for the piezometer profiles 10 (PZ10), 6 (PZ6), and 3 (PZ3). Also shown in this figure are Eh and pH depth profiles. The dissolved As varied from below detection limit ( $<0.01 \mu\text{g/kg}$ ) to  $9.5 \mu\text{g/kg}$ . Three regions of relatively high As in the subterranean estuary were captured by these groundwater profiles: (1) a 2 m deep,  $\sim 8 \mu\text{g/kg}$  maximum As plume within the freshwater portion of the aquifer at PZ10, (2) intermediate salinity plumes ( $\sim 1$ - $2 \mu\text{g/kg}$ ) at PZ6 and PZ3 associated with Mn plumes, and (3) As ( $\sim 2$ - $10 \mu\text{g/kg}$ ) at high salinity toward the bottom of PZ6 and PZ3 associated with elevated Fe concentrations.

PZ10 is a profile of fresh groundwater before it transits the mixing zone. Between 3 and 4 m the redox potential (Eh) exhibited a minimum that coincided with peaks in dissolved As, Fe, and Mn. Dissolved phosphate also exhibited a maximum in this profile, however, the peak occurred at a shallower depth, and was associated with a small peak in salinity. Furthermore, the Eh and pH conditions at the location of the As, Mn, and Fe maxima are such that the  $\text{H}_3\text{AsO}_3$  form of As is thermodynamically stable (10). Because we did not measure the oxidation state of As, we cannot conclusively say that As exists as this species. The conclusion that As(III) is the dominant As form at this location is supported, however, by the fact that the As and phosphate peaks do not coincide. We might expect them to act geochemically similar if As was in the +5 oxidation state because this form has similar a coordination as phosphate.

In the high salinity zone (below 6.7 m in PZ6 and below 4.8 m in PZ3) Fe was remobilized under reducing conditions. As and phosphate followed Fe closely in this zone, with all three solutes reaching maximum concentrations at depth. The dissolved As:Fe ratio ( $\mu\text{g}/\text{mg}$ ) ranged between 1.4 and 4.9 in this zone (see Supporting Material). The ratios were generally higher than the average As:Fe ratio observed in the sediment ( $0.54 \mu\text{g}/\text{mg}$ ), but still fell within the range of observed sedimentary As:Fe ratios ( $0.1$  to  $5 \mu\text{g}/\text{mg}$ ). In support of this observation, Smedley and Kinniburgh (10) have noted that during reductive dissolution of Fe (hydr)oxides, dissolved As:Fe ratios are often higher than the As:Fe ratios observed in the solid. The primary mechanism cited for this observation was the association of As with very fine ferrihydrite particles (abundant in our sediment cores), which were more labile and therefore more likely to be preferentially reduced.

In the intermediate salinity zone (from approximately 5.6-6.7 m in PZ6 and 4-4.8 m in PZ3), the precipitated Mn was remobilized under reducing conditions, resulting in a plume of high Mn. Additionally, minor peaks in Fe were also observed at these depths in PZ6 and PZ3. In this zone, As and phosphate exhibited maxima that coincided with the Mn maxima. Both As and P have a much higher affinity for Fe (hydr)oxides and Mn (hydr)oxides (25), which is evidenced in our data by a major increase in dissolved As concentrations that occurred concomitant with a major increase in dissolved Fe concentrations in the high salinity zone where Mn concentrations were declining. However, several authors have documented adsorption of the oxyanions of P and As onto Mn (hydr)oxides under natural conditions (26-29). Although As is generally thought to have a higher affinity for Fe (hydr)oxides than for Mn (hydr)oxides, the most likely scenario is that the As peaks in the intermediate salinity zone were derived from reductive dissolution of As-bearing Mn (hydr)oxides. In support of this suggestion, the dissolved As:Fe ratios observed in this zone were ~10-20 times higher than those observed in the high salinity zone, where As and Fe are strongly associated (see supporting material).

If aqueous As is indeed partially controlled by Mn, then we might expect to see some covariation of sedimentary As and Mn, however, there were few observable similarities between As and Mn in the sediment core profiles and a regression revealed that there was no strong correlation between the two. The reason for this discrepancy between the dissolved As data and the sedimentary As data could simply have to do with both the composition and the location of the cores. In all of the sediment cores, Fe (hydr)oxides dominated over Mn (hydr)oxides by over 2 orders of magnitude (by

weight); the Fe concentrations ranged from ~800 to ~8000 mg/kg, whereas the Mn concentrations ranged from ~4 to ~25 mg/kg, thus any relationship between sedimentary As and Mn in the cores may have been masked by the magnitude of the sedimentary As and Fe relationship. It is also possible that we have not captured the full extent of Fe and Mn (hydr)oxide deposits in the subterranean estuary of this system: whereas our piezometer profiles extend to over 8 m, all sediment cores were only 1-2 m long.

The timescale of water flow between adjacent piezometer profiles in the subterranean estuary is on the order of days to weeks (A. Mulligan, pers. comm.), thus it is substantially longer than either As(III) oxidation by Mn (hydr)oxides or As sorption by Mn/Fe (hydr)oxides (30, 31). It is therefore possible that, during this transit time, a large fraction of As(III) has been exposed to Mn (hydr)oxides and become oxidized to As(V). Amirbahman (31) studied the adsorption and oxidation of As by Mn and Fe (hydr)oxide coated sands taken from an aquifer in Cape Cod with similar geochemistry to the Waquoit Bay study site. They concluded that even at low Mn:Fe ratios, As(III) oxidation could be a significant source of As(III) removal in sandy aquifers, given a long enough reaction time. Additionally, as the arsenic and phosphate profiles in PZ6 and PZ3 exhibited highly similar features, it is possible that As existed mainly in the As(V) oxidation state in the mixing zone of PZ6 and PZ3.

### **The subterranean estuary as natural reactive barrier for As removal from coastal groundwater systems**

A sample was taken both at the head of the bay (adjacent to the sampling site), as well as in Vineyard Sound, which is connected to Waquoit Bay by a narrow channel.

The concentration of dissolved As in the surface water at the head of the bay was relatively low (0.63  $\mu\text{g/kg}$ ), and was lower than the dissolved As concentration in Vineyard Sound (0.93  $\mu\text{g/kg}$ ). These concentrations are lower than the average dissolved As concentrations found in seawater and estuarine waters (10). Different authors (20, 21, 28) studying pore-water concentrations of As in coastal areas have noted that the As concentrations in the above water column were low and attributed this to a layer of metal (hydr)oxides in the sediment near the oxic sediment-water interface. As diffusing upwards was adsorbed by the metal (hydr)oxides, preventing its release into the water column. It therefore appears that the subterranean estuary and its “iron curtain” could be acting as a natural reactive barrier for As removal from groundwater (and possibly seawater during entrainment of bay water into the aquifer), effectively preventing its release into coastal waters.

The subterranean estuary at Waquoit Bay is a zone of active arsenic cycling, which appears to be coupled to both the Fe and Mn redox cycles. Active redox cycling of trace metals is not unique to our system: subterranean estuaries in other parts of the world have reducing conditions as one of their primary characteristics despite low (sedimentary) organic carbon (32, 33). Their importance with respect to As cycling remains to be seen. Another unanswered question is the role of sea level rise, which will lead to encroachment of saline groundwater (and likely reducing conditions) into coastal aquifers that may have an abundant reservoir of sedimentary As. In either case, the distribution and type of Fe (hydr)oxides (and to a lesser extent Mn (hydr)oxides) in coastal aquifers will exert a major influence on the biogeochemical cycling of As in

subterranean estuaries and, ultimately, the fate of groundwater-derived As in marine systems influenced by SGD.

**Acknowledgements:**

The authors would like to thank Paul Henderson, Carl Lamborg, Adam Rago, and Prae Supcharoen for assistance with sample collection and analysis. We thank Ann Mulligan for discussions on the hydrogeology of our study site. We extend our continued appreciation to the director and staff of the Waquoit Bay National Estuarine Research Reserve for their assistance with logistics during field sampling. We would also like to thank Dave Schneider and the WHOI ICP-MS facility for assistance with the trace metals analyses. S.E.B. was supported through a National Science Foundation (NSF) REU grant to WHOI. This research was supported by a National Science Foundation grant (OCE-0425061) to M.A.C.



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Table 1. Sedimentary concentrations of As, Mn, P, and Fe, as well as As:Fe and As:Mn ratios for three cores.

Core	Sediment		As ( $\mu\text{g/kg}$ )	P ( $\text{mg/kg}$ )	Fe ( $\text{mg/kg}$ )	Mn ( $\text{mg/kg}$ )	As:Fe ( $\mu\text{g/mg}$ )	As:Mn ( $\mu\text{g/mg}$ )
	sample ID	depth (cm)						
3	3_17	3.2	520	33.1	906	9.38	0.57	55
	3_11	46.1	1180	73.6	2580	11.3	0.46	110
	3_9	61.8	1840	113.0	4020	18.3	0.46	100
	3_7	75.6	2600	131.0	4880	26.0	0.53	100
	3_3	101.7	4060	184.0	7590	21.9	0.53	190
	3_1	110.5	3650	145.0	6020	13.0	0.61	280
2	2_1	2.5	651	45.6	785	22.9	0.83	28
	2_15	72.5	410	44.4	791	3.47	0.52	120
	2_20	97.5	7470	55.9	1370	9.22	5.45	810
	2_28	132.5	2340	145.0	3260	7.23	0.72	320
	2_41	173.0	1310	84.0	2800	-	0.47	-
5	5_33	160.0	361	-	3470	-	0.10	-

Figure 1. Map of study site with locations of piezometer wells and sediment cores.

Figure 2. Sedimentary Fe versus As for cores 2, 3, and 5 ( $r^2=0.95$ ,  $n=11$ , slope [As:Fe in  $\mu\text{g}/\text{mg}$ ] = 0.54). The circled data point corresponds to the outlier in core 2, which was associated with a mid-core Mn (hydr)oxide maxima. The core 5 sample contained a large fraction of goethite, a highly crystalline form of Fe (hydr)oxide, which has been documented to have a lower affinity for As. These two outliers were not included in the regression analysis.

Figure 3. Piezometer profiles showing dissolved As,  $\text{PO}_4^{3-}$ , Fe, Mn, Eh, and pH. Salinity is plotted as a gray solid on each panel and its scale bar is at the bottom of each column. Note the break in scale in PZ3 As and the changes in scale between PZ10, PZ6, and PZ3 for phosphate, As, Mn and salinity.

Brief: Iron and manganese hydr(oxides) in a coastal aquifer act as a natural geochemical barrier to arsenic transport to the coastal ocean via submarine groundwater discharge.

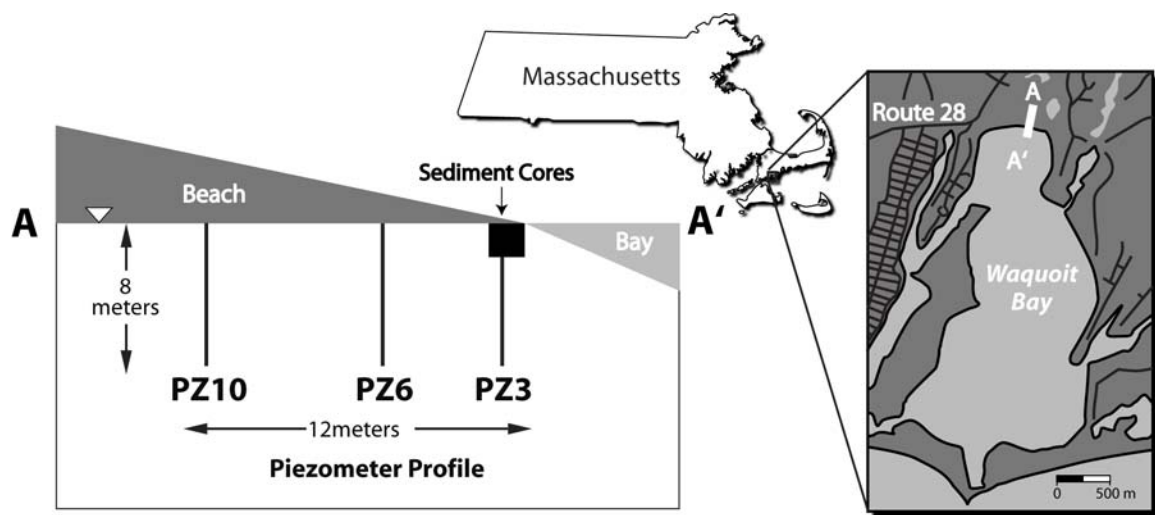


Figure 1

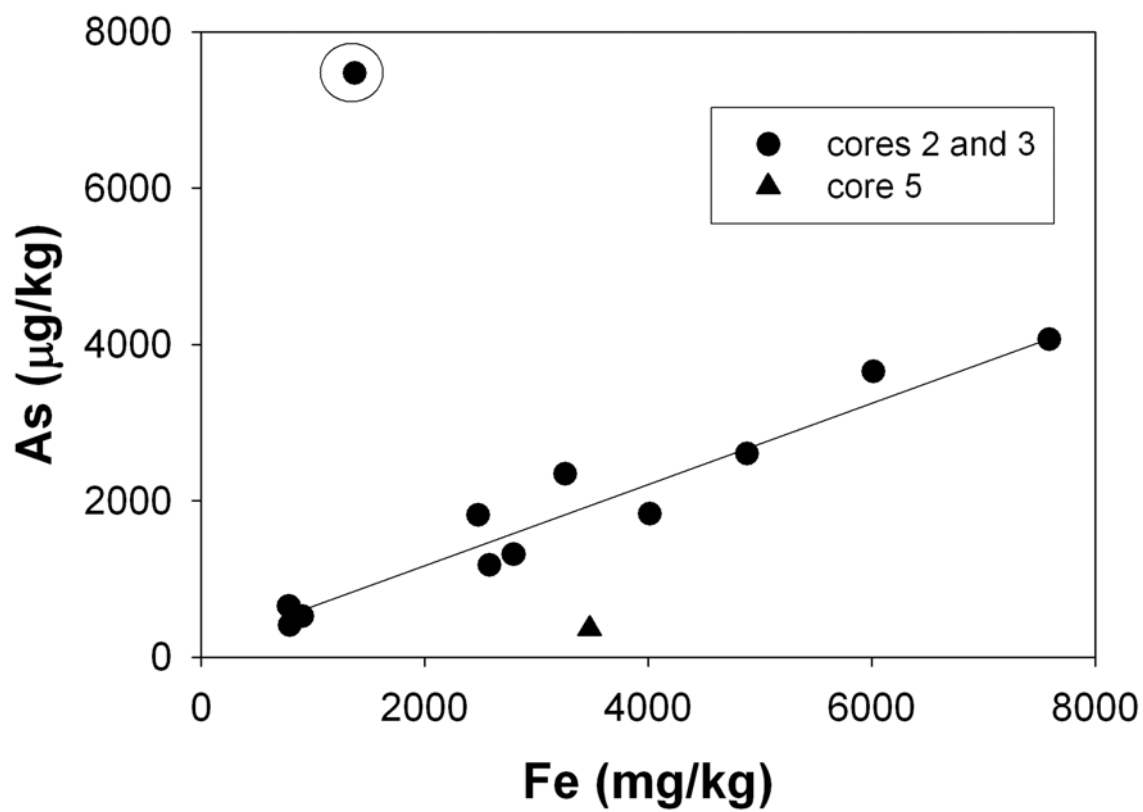


Figure 2

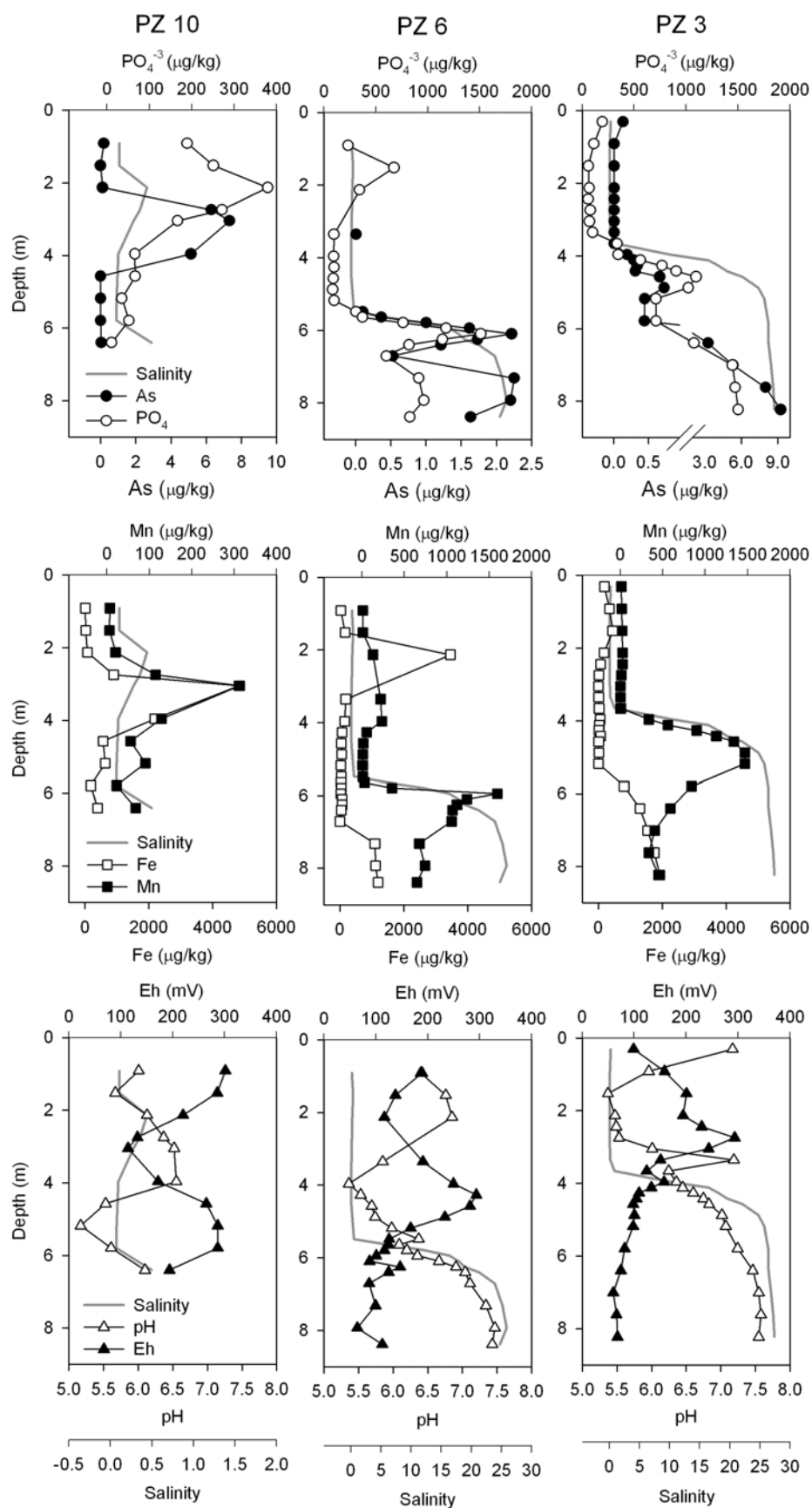


Figure 3