Supporting Information:

Effect of groundwater-lake interactions on arsenic enrichment in freshwater beach aquifers

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Contents

1. Processes influencing nearshore groundwater dynamics in the Great Lakes

For large inland waters such as the Great Lakes the main processes influencing nearshore groundwater flows and water exchange across the sediment-water interface (SWI) are terrestrial groundwater discharge, and lake water level fluctuations including seasonal lake level changes and high frequency waves[1] (Figure S1). The water level fluctuations in the Great Lakes are different to marine environments where shorelines are exposed to tides and oceanic waves. The chemical composition of the recirculating water is also different, most notably for its influence on flow dynamics, there is an absence of density effects in the Great Lakes environment.

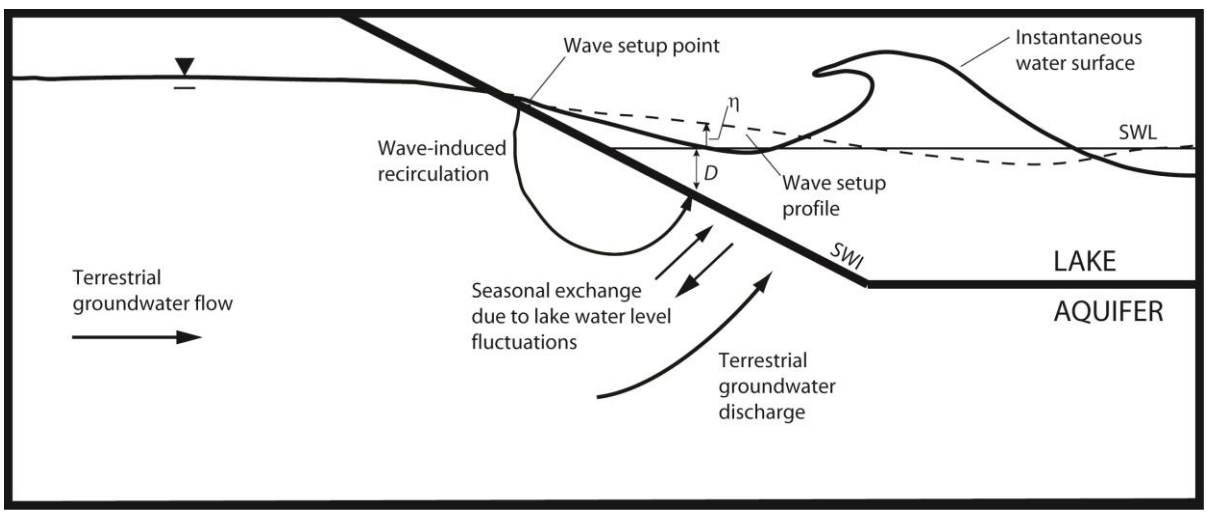

Figure S1. Conceptual diagram of the groundwater flows in a beach aquifer exposed to waves and lake water level changes. The sediment-water interface (SWI), still water level (SWL), instantaneous water surface (thick solid line) and wave setup profile (phase averaged surface water level, dashed line) are shown. The still water depth (D), and the wave setup height (η) are also annotated in the figure.

The instantaneous water surface induced by waves, in addition to the wave setup profile, is shown in Figure S1. Wave setup is the onshore upward tilt in the phase averaged surface water level (instantaneous surface water level averaged over a wave cycle)[2]. Wave setup extends from the offshore wave breaking point to the maximum wave runup limit. In this study, the effect of waves on nearshore groundwater flows is quantified by consideration of wave setup rather than the instantaneous surface water levels (SI Section 5.2).

2. Location of field sites

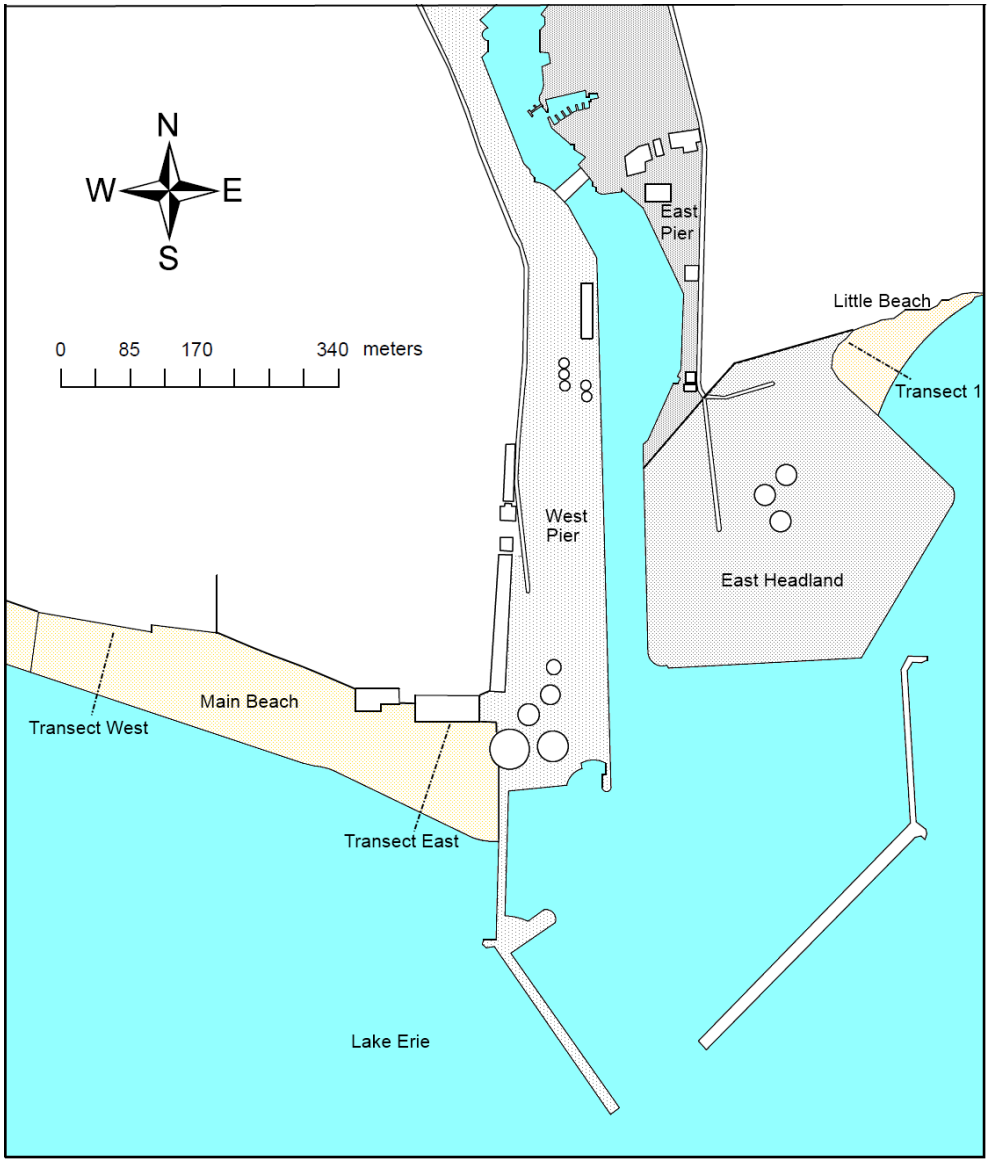

Figure S2. Location of field sites (Little Beach and Main Beach) and brownfield harbour areas (East Headland, East Pier, and West Pier). Field measurements were conducted at Little Beach and Main Beach with the locations of the shore-normal groundwater monitoring transects shown.

3. Lake water level and offshore wave data

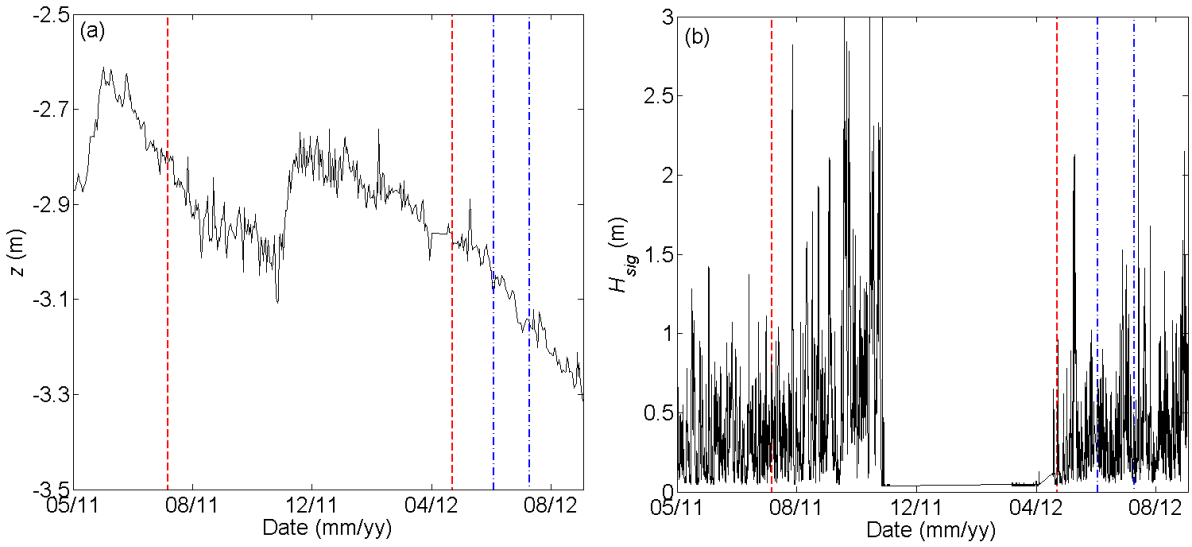

Figure S3. (a) Lake water levels and (b) significant wave height (H_{sig}) from May 2011 to September 2012. Data was recorded at a buoy located 15 km offshore of the field sites[3]. The vertical height datum used in (a) has been adjusted relative to a local benchmark on Little Beach. Vertical lines indicate the timing of field events at Little Beach (red) and Main Beach (blue). Note for (b) that wave data was not available from mid-November 2011 to mid-April 2012.

4. Sediment sample collection and analysis

4.1 Sediment sample collection

Sediment core samples were collected using a vibracorer. In this method a clear PVC tube is driven into the sediment by the force of gravity combined with vibrations. The extracted core is relatively undisturbed with only sediment close to the wall of the tube disturbed by the insertion of the tube. The sediment is slightly compacted in the tube, but a compaction factor was calculated for each core and used in determining the depth at which the sediment was extracted. Using this method sediment cores up to 1.2 m in length were collected. The vibrations are rapidly dampened with depth in sandy sediment and therefore it was not possible to collect deeper cores. The locations at which cores were collected are shown in Figure 1a. Sediment cores were sectioned at 15 cm depth intervals immediately upon extraction, and samples were stored in 250 mL polyethylene bottles and frozen until analysis.

4.2 Sequential extraction procedure

A five-step sequential extraction procedure adapted from Wenzel et al.[4] was used for solid phase analysis. This method was used as it is specifically targets fractions of As oxyanions in the solid phase, in contrast to other procedures that are designed to target P or other cationic metals. Samples from sectioned sediment cores were air dried and 7.5 g of dried sample was weighed and placed in a 250 mL polyethylene centrifuge bottle. Extractant was added to the centrifuge bottle and placed under the conditions described in Table S1. After each extraction, the sample was centrifuged for 15 min at 4000 rpm and 20 mL of the solution was filtered (0.45 μm nylon filter) and analyzed using ICP-OES. Before proceeding to the next extraction step, the samples were washed with solutions specified in Table S1.

Table S1. Details of sequential extraction procedure adapted from Wenzel et al.[4]

Step	Extractant	Extraction conditions	SSR*	Wash step
1	0.05 M $(NH_4)_2SO_4$	4 hours shaking	1:25	D.I. water
2	0.05 M $(NH_4)H_2PO_4$	16 hours shaking	1:25	D.I. water
3	540 mL of 0.2 M $(NH_4)_2C_2O_4$ + 460 mL of 0.2 M $H_2C_2O_4.H_2O$ (adjust pH to 3.25) - this is referred to as pH solution	4 hours shaking, in the dark	1:25	Add 94 mL of pH solution, 10 min shaking in the dark
4	41 mL of 0.2 M $(NH_4)_2C_2O_4$ + 959 mL of 0.2 M $H_2C_2O_4.H_2O$ + 17.61g of $C_6H_8O_6$	20 min water bath (96°C) under bright light	1:25	Add 94 mL of pH solution, 10 min shaking in dark, dry residual soil at 60°C
5	250 mg of sediment with 7 mL of aqua regia reagent (v/v: 2/3 HCl + 1/3 HNO_3)	Microwave digestion	1:28	D.I. water

*SSR: Soil solution ratio.

The SEP results are operationally-defined but according to Wenzel et al[4] the fractions are nominally associated with: (Step 1) non-specifically sorbed; (Step 2) specifically sorbed; (Step 3) amorphous (hydr)oxides; (Step 4) well-crystallized (hydr)oxides, and (Step 5) residual phases. Arsenic released in Step 1 represents the fraction that is weakly retained on solid surfaces by weak electrostatic interactions and is readily available to leach to groundwater[4]. The amount of readily labile As extracted in Step 1 is typically minor compared to As released in subsequent extraction steps[4]. Arsenic extracted in Step 2 (specifically sorbed) is generally that which is strongly adsorbed, via surface complexation, to the (hydr)oxides. This fraction can be readily mobilized, however, due to changes in groundwater pH, redox conditions or as other anionic species, such as CO_3^{2-} or PO_4^{3-}, outcompete As for sorption sites at the (hydr)oxide surfaces. Steps 3 and 4 target As that is

incorporated with amorphous and crystalline (hydr)oxides, respectively, by a combination of co-precipitation, irreversible sorption onto heterogeneous sites, or penetration of the lattice[5,6]. Reduction and subsequent dissolution of the (hydr)oxides are responsible for the As released in Steps 3 and 4. While not as readily mobile, similar to the Step 2 fraction, these fractions can also be released by changes in solution chemistry. Step 5 releases As associated with residual phases such as recalcitrant silicate and other As-bearing minerals. This fraction is poorly labile and not readily mobile in groundwater[4].

5. Supplementary information on numerical groundwater model

5.1 Hydraulic conductivity

Sediment samples were collected along the shore-normal transect at Little Beach in August 2011. Particle size analysis was performed on these samples and the hydraulic conductivities were estimated using the formula of Krumbein and Monk[7]. The estimated hydraulic conductivities (Table S2) were spatially interpolated to parameterize the groundwater model domain. These hydraulic conductivity values were also used to infer water exchange rates across the SWI based on vertical head gradient measurements (Figure 2d,e).

Table S2. Estimated hydraulic conductivities of sediment samples.

x (m)	*z* (m)	*K* (m/d)
95	-3.5	1.9
73	-2.4	14.4
73	-5.4	0.96
65	-3.3	6.1
65	-4.3	5.4
54	-2.1	9.3
54	-3.0	5.88
54	-4.3	3.67
34	-1.5	7.93
34	-4.2	8.08
0	-4.1	7.17

5.2 Model boundary conditions

The model boundary conditions along **AE** and **BC** were adjusted for each field event based on the landward water table elevation, lake water level and offshore wave height during each field event. A specified head condition was applied at the landward boundary (**AE**) with the head value corresponding to that measured at the most landward piezometer (x = 0 m, Table S3). Specified heads corresponding with the lake level and wave height were applied along the submerged SWI (**BC**). Wave effects were included in the groundwater flow model by

consideration of wave setup along this boundary (see SI Section 1). Xin et al.[8] showed that using this phase averaged approach produces similar water exchange rates and groundwater flows in the nearshore aquifer as simulation of individual waves. Using the same approach as Robinson et al.[9], an empirical equation developed and validated by Nielson[10] was used to estimate the wave setup profile along the boundary **BC**. This equation is:

$$\eta = \frac{0.4H_{rms}}{1+10\frac{D+\eta}{H_{rms}}} \quad \text{(S1)}$$

where η is the elevation in head above the still water level (SWL) due to wave setup (m), H_{rms} is the root mean square wave height (m) and $D(x)$ is the still water depth measured from the local SWI elevation to the SWL (m). See Figure S1 for explanation of terms. H_{rms} was calculated from H_{sig} values using[10]:

$$H_{rms} = \frac{H_{sig}}{\sqrt{2}}. \quad \text{(S2)}$$

The parameter values used to set the boundary conditions along **BC** for each field event are provided in Table S3.

The upper model boundary (**AB**) was a phreatic surface with negligible recharge. No flow boundaries were specified along the bottom of the model domain (**DE**) and the vertical offshore boundary (**CD**). Sensitivity simulations were conducted to ensure that these no-flow conditions did not affect the simulated groundwater flows in the shallow beach aquifer.

Table S3. Values used to specify the submerged lake (**BC**) and landward (**AE**) boundaries.

	5 Aug 11	15 May 12
H_{rms} (m)	0.582	0.110
SWL (m)	-2.785	-3.060
Landward head (m)	-2.697	-2.659

6. Pore water chemistry distributions for Little Beach (3-5 August 2011)

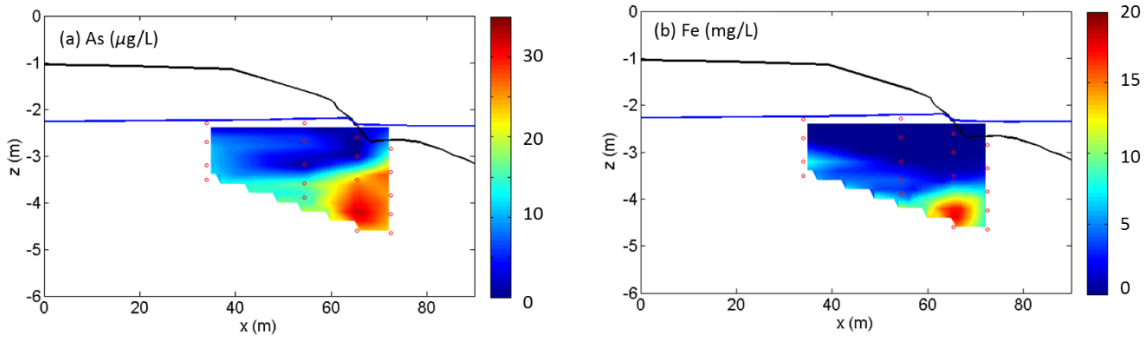

Figure S3. Distributions of dissolved (a) As (μg/L) and (b) Fe (mg/L) at Little Beach for 3-5 August 2011 field event. MLS ports where samples were collected are depicted by the red circles. The solid black line depicts the sand profile (SWI) and the solid blue line depicts the lake and water table elevations.

Note that all contoured concentration distributions presented were generated in MATLAB by applying a linear gridding interpolation algorithm to the concentration data.

7. Supplementary pore water chemistry distributions for Little Beach (14-18 May 2012)

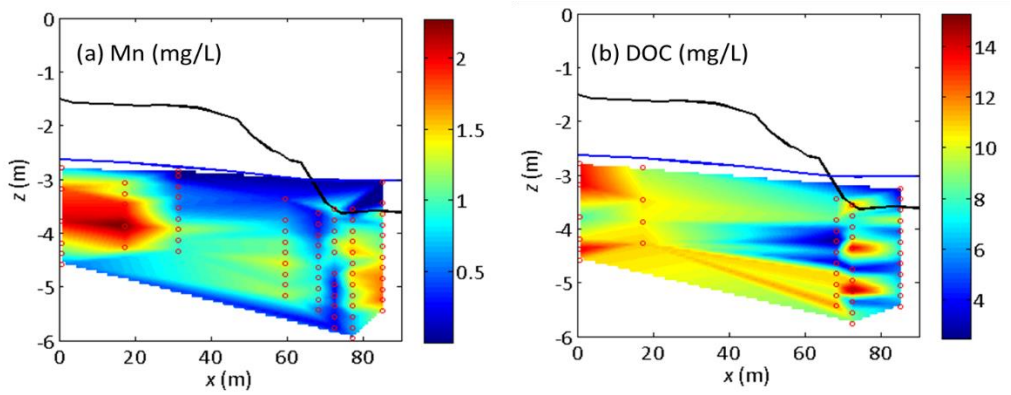

Figure S4. Distributions of (a) dissolved Mn (mg/L) and (b) DOC (mg/L) at Little Beach for 14-18 May 2012 field event. MLS ports where samples were collected are depicted by the red circles. The solid black line depicts the sand profile (SWI) and the solid blue line depicts the lake and water table elevations.

8. Supplementary solid phase results for Little Beach

Table S4. Solid phase SEP results for As (Steps 1-5), Fe (Steps 3-5), and Mn and Al (Steps 3 and 4), as well as As:Fe ratios (Steps 3 and 4), and total S, total C and organic C.

			Step 1	**Step 2**	**Step 3**					**Step 4**					**Step 5**				
			As	As	As	Fe	As:Fe	Mn	Al	As	Fe	As:Fe	Mn	Al	As	Fe	Total S[1]	Total C[1]	Organic C[1]
Core	*x* (m)	*z* (m)	(µg/kg)	(µg/kg)	(µg/kg)	(mg/kg)	(µg/mg)	(mg/kg)	(mg/kg)	(µg/kg)	(mg/kg)	(µg/mg)	(mg/kg)	(mg/kg)	(µg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
1	72	-3.5	BD[2]	658	1777	1289	1.8	40	97	894	622	1.4	19	160	12650	920	1100	63,300	18,800
	72	-4.0	8.5	223	1429	1503	1.4	45	146	1981	2757	0.7	52	1175	2100	2595			
	72	-4.5	BD	431	1143	1178	1.1	46	126	1641	2680	0.6	57	1058	12082	3421	600	29,700	2,000
2	68	-3.1	14.7	684	2051	1409	2.1	51	93	1866	1809	1.0	34	621	200	4063	700	46,000	5,000
	68	-3.6	8.7	527	1459	1329	1.5	39	129	2004	2523	0.8	44	999	1833	3086	400	25,900	<5,000
	68	-3.9	3.7	212	1321	1449	1.3	22	103	1449	1913	0.8	26	571	25874	3985			
3	52	-3.0	5.5	514	1468	1234	1.5	36	109	1851	2538	0.7	43	955	800	2658			
	52	-3.5	BD	464	1847	1131	1.8	39	107	1649	2110	0.8	38	770	400	2143	<200	33,350	17,900
	52	-3.9	7.2	226	1016	1255	1.0	39	124	2125	2507	0.8	39	845	600	2195			
4	31	-3.5	3.3	314	1416	1418	1.4	87	130	1730	2566	0.7	46	904	19041	2949			
	31	-4.3	10.7	412	907	747	0.9	20	70	1753	1795	1.0	30	625	2337	1665			
5	0	-2.8	2.7	535	1412	1084	1.4	22	108	2360	1630	1.4	25	629	35268	2570			
	0	-3.4	8.0	367	1355	722	1.4	14	77	1634	2135	0.8	28	690	41023	2201			
	0	-3.6	13.2	250	1365	09	1.4	25	141	1501	3136	0.5	41	1068	1400	3609	2900	23,000	1,900

[1] Solid phase Total S, Total C and Organic C were determined for select sediment samples by LECO SC444 combustion method[11].
[2] BD denotes Below Detection

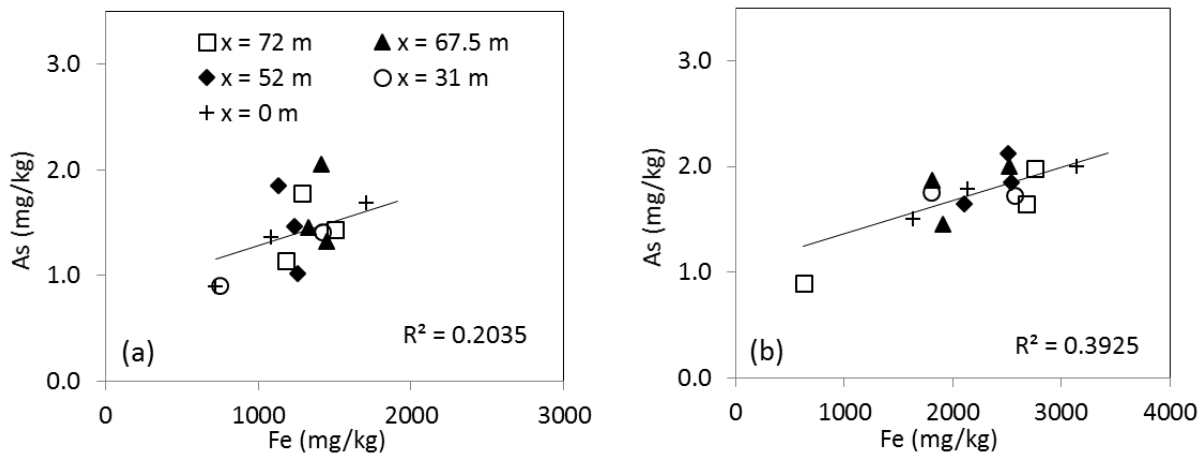

Figure S5. Solid phase As versus Fe for SEP (a) Step 3 (nominally amorphous (hydr)oxides) and (b) Step 4 (nominally crystalline (hydr)oxides). The different symbols denote the location of the sediment core from which the sample was obtained.

9. Supplementary pore water chemistry results for Main Beach sites

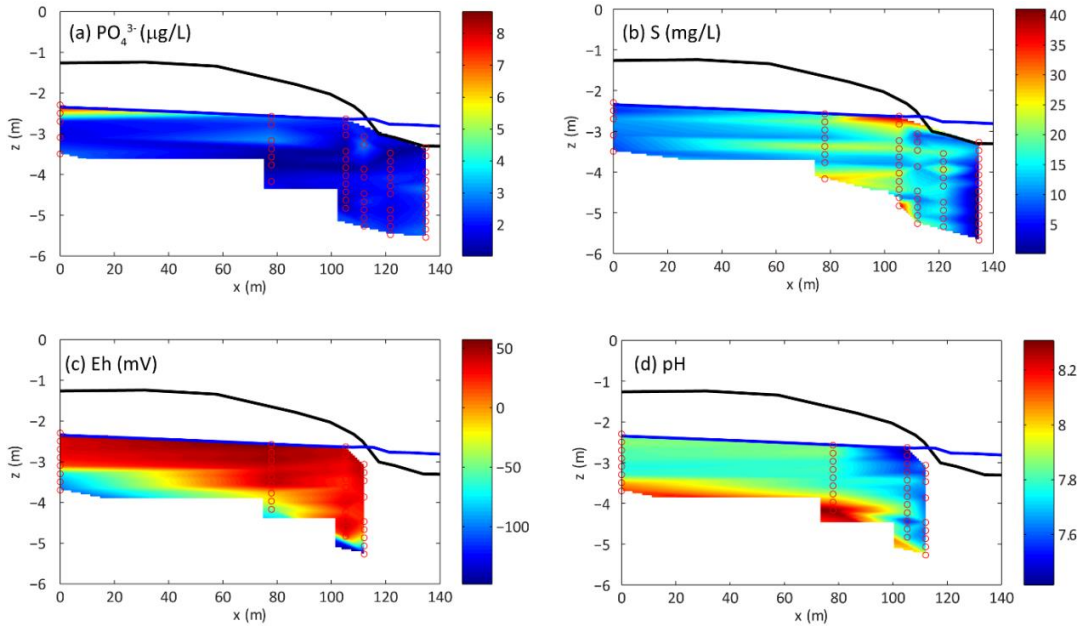

Figure S6. Distribution of additional dissolved species at Main Beach east transect (25-28 June 2012): (a) PO_4^{3-} (µg/L), (b) S (mg/L), (c) Eh, and (d) pH.

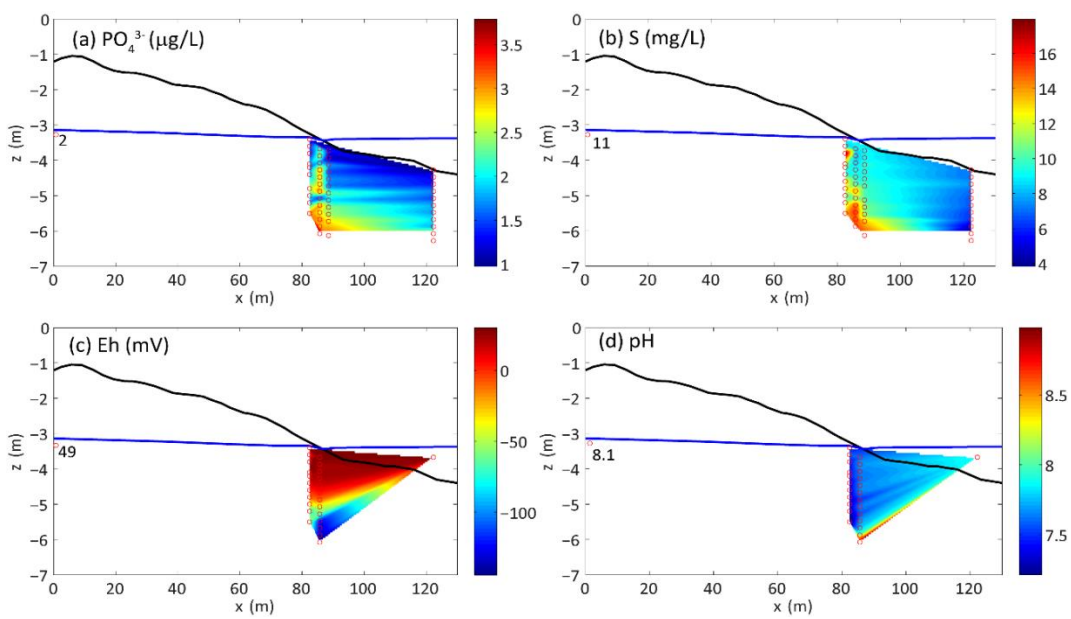

Figure S7. Distribution of additional dissolved species at Main Beach west transect (30 July-3 August 2012): (a) PO_4^{3-} (µg/L), (b) S (mg/L), (c) Eh, and (d) pH.

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