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Effect of groundwater-lake interactions on the distribution of arsenic in a freshwater beach

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Graduate Program in Civil and Environmental Engineering
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science
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EFFECT OF GROUNDWATER-LAKE INTERACTIONS ON THE
DISTRIBUTION OF ARSENIC IN A FRESHWATER BEACH

(Thesis format: Integrated Article)

by

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Graduate Program in Engineering Science
Department of Civil and Environmental Engineering

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Engineering Science

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Abstract

This thesis presents field measurements and numerical modeling that provide insight into the nearshore geochemical conditions and groundwater flows controlling the mobility of arsenic (As) in a freshwater beach aquifer and its potential discharge to Lake Erie. Field measurements were performed via shore-normal monitoring transects installed at beaches (Little Beach and Main Beach) located adjacent to a brownfield industrial harbour site that has elevated sediment and groundwater As concentrations. Detailed pore water chemistry analyses revealed elevated As (up to 0.056 mg/L) 1 - 2 m below the shoreline at all transect locations. The distributions of species in the aqueous and sedimentary phases suggest that As mobility is strongly linked with iron (Fe) redox cycling. Sediment analysis by sequential extraction revealed a layer of amorphous and crystalline Fe (hydr)oxides present at the sediment-water interface (SWI) near the shoreline. This Fe hydr(oxide) layer may be accumulating As and preventing its release to nearshore waters. Numerical modeling combined with vertical hydraulic gradient measurements indicated that wave-induced recirculation across the aquifer-lake interface was significant and this likely establishes the redox gradient that led to Fe (hydr)oxides precipitation at the SWI. Numerical and field results showed that the water infiltration/exfiltration across the groundwater-lake interface were sensitive to varying wave intensity and seasonal lake water level fluctuations. The source of As in the nearshore beach aquifers remains unknown. While Little Beach is adjacent to the East Headland of the industrial site where elevated As has been recorded, Main Beach is disconnected hydraulically from the East Headland. If the elevated dissolved As observed is from a natural geogenic source, this findings of this thesis may have widespread implications for As cycling in the nearshore areas of the Great Lakes. Finally, while this study focused on As, the nearshore geochemistry and subsurface flows investigated are be pertinent to

understanding the discharge of other chemicals (e.g., nitrate, ammonium, phosphorous) to nearshore inland coastal waters via the groundwater pathway.

Keywords: groundwater-lake interactions, wave effects, numerical modeling, Great Lakes, groundwater discharge

Co-Authorship

Jacky S. K. Lee is the principal author of this thesis including the writing, field work, sediment and water sample analysis and numerical modeling. Dr. Clare Robinson provided the initial ideas for this work, reviewed the thesis and provided recommendations and guidance for further improvements.

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CHAPTER 1

INTRODUCTION

1.1 Background

The Great Lakes are the largest system of fresh surface water in the world containing nearly 21 percent of the world's fresh water [U.S. EPA, 2012]. The lakes provide significant ecological, recreational and economic benefits for the approximately 34 million people that live in the Great Lakes Basin. They are also an important source of drinking water – for example, the Great Lakes are the drinking source for nearly 80% of Ontarians [Ontario Ministry of the Environment, 2012]. The Great Lakes are under significant stress due to population growth, industry, agriculture and contemporary issues such as climate change and emerging contaminants.

The Great Lakes are susceptible to anthropogenic pollution and pollution mitigation strategies need to be enhanced to improve water quality and also to ensure safe drinking water. Traditionally, point sources (e.g., wastewater treatment plants) have been the focus of water quality management strategies for the Great Lakes. However, it is recognized that non-point sources (e.g., storm water runoff, combined sewer overflows, groundwater discharge), although poorly quantified, are also important pathways for delivering contaminants to surface waters [International Joint Commission, 2011]. These complex non-point sources need to be addressed to improve the water quality in the Great Lakes.

Groundwater discharge is difficult to quantify as it is typically characterized by low specific flow rates and exhibits high spatial variability along shorelines [International Joint Commission, 2011]. Direct groundwater discharge to the lakes can occur where ever there is an unconfined permeable

aquifer near the shore and the groundwater watertable is elevated relative to the lake water level. Groundwater discharge fluxes are typically highest near the shore with fluxes decrease exponentially offshore [Grannemann and Weaver, 1999]. The Great Lakes has ~6150 km of highly permeable shoreline (sandy, gravel and cobble beaches) and this represents a significant area along which direct groundwater discharge may occur [Environment Canada and U.S. EPA, 2009].

This thesis focuses on understanding the delivery of pollutants, in particular arsenic (As), from groundwater to Lake Erie along permeable shoreline adjacent to a brownfield site at Port Stanley. The Clean Water Act [2006] requires Source Water Protection Planning as a first step in a multi-barrier approach to ensure safe drinking water. The Source Water Protection Plan compiled for the Elgin Area Water Treatment Plant (WTP) identified the Port Stanley Harbour site, located 2 km from the offshore WTP intake, to be a potential threat for its source water [Stantec, 2009]. The brownfield site has elevated levels of heavy metals, polyaromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylenes (BTEX) and petroleum hydrocarbons (PHCs) in the sediment and groundwater [CH2MHILL, 2009]. This thesis presents field investigations that focus on quantifying groundwater discharge and the distribution of heavy metals, specifically As, in a sandy beach (Little Beach) located adjacent to the east portion of the brownfield site. This sandy shoreline may be a zone of groundwater discharge from the site as the remainder of the brownfield site is enclosed by sheet piling, pier concrete structures and rip-rap reinforced walls [CH2MHILL, 2009].

Quantifying the flux of chemicals from groundwater to surface waters is complex as chemicals are often transformed along their subsurface pathway before being discharged. The transport of chemicals in the subsurface is often influenced by geochemical gradients (i.e., pH, redox) that

affect the transformation and mobility of chemicals. On the Great Lakes, forcing such as waves and lake level variations lead to recirculation of lake water through nearshore sandy (beach) aquifers. This recirculating lake water has a different chemical composition compared with the discharging groundwater. The mixing of the waters in the aquifer near the shore may set up important geochemical gradients and a reaction zone that strongly influences the fate of discharging contaminants and subsequent chemical fluxes to the lake. In light of its significance for controlling groundwater fluxes to surface waters, this mixing and reaction zone is commonly referred to as a riparian zone in the context of groundwater-river interactions [Carlyle et al., 2001] and a subterranean estuary in the context of groundwater-ocean interactions [Moore et al. 1999]. The physical and chemical processes occurring in this reaction zone must be understood to be able to evaluate the potential discharge of groundwater contaminants to the lake at Little Beach.

1.2 Research Objective

The objective of this thesis is to evaluate the potential discharge of groundwater contaminants, in particular As, to Lake Erie from the Port Stanley Harbour site. As a potential hotspot of groundwater discharge from the brownfield site, this thesis focuses on quantifying the groundwater-lake interactions and their impact on the discharge of As to the lake at Little Beach. For comparison, the groundwater-lake interactions and As occurrence at a nearby beach (Main Beach) are also evaluated. The specific research objectives are to:

1. Quantify the groundwater flow patterns and the magnitude of groundwater discharge and recirculating lake water at Little Beach and Main Beach.
2. Quantify the occurrence of As and other chemical species in the groundwater at Little Beach and Main Beach.

3. Assess the temporal and spatial variability in the groundwater discharge, flows and chemical species distributions and how these are influenced by changing hydraulic conditions (waves, lake level variations).
4. Evaluate the geochemical processes that influence the transport, mobility and potential accumulation of As in the beach aquifers.

1.3 Thesis outline

This thesis is written in “Integrated Article Format.” A description of each chapter is as follows:

Chapter 1: Introduces background information and provides the objectives of the study.

Chapter 2: Reviews past work focused on groundwater discharge to the Great Lakes, the transport of As in coastal aquifers and the background site conditions of the Port Stanley Harbour site.

Chapter 3: Details the field investigations, numerical model and provides discussion of the factors controlling the fate and transport of As in the nearshore aquifer.

Chapter 4: Summarizes the research results and outlines recommendations for future work.

1.4 References

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CHAPTER 2

LITERATURE REVIEW

2.1 Groundwater discharge into the Great Lakes

The nearshore water quality in the Great Lakes is degraded due to urbanization, industrialization and extensive agriculture in the Great Lakes Basin [Environment Canada and U.S. EPA, 2009]. Water quality management strategies for the Great Lakes historically focused on identifying and controlling point pollution sources. However, it is now widely acknowledged that non-point pollution sources (e.g., storm water runoff, combined sewer overflows, groundwater discharge) need to be addressed to improve nearshore water quality [International Joint Commission, 2011]. In particular the groundwater contribution is poorly quantified. Groundwater is a large uncertainty for predicting nearshore water quality because its pathway and delivery are difficult to quantify [International Joint Commission, 2011]. Pollutants of concern that may enter the lake via the groundwater pathway are varying but include toxic chemicals, nutrients, heavy metals, household products, hormones, antibiotics, pharmaceuticals and road salt [International Joint Commission, 2011].

The groundwater contribution to the Great Lakes can be separated into two components: (i) groundwater that discharges into tributaries and indirectly to the Great Lakes as a component of stream flow, and (ii) groundwater that directly flows from aquifers to the Great Lakes (Figure 2.1). While prior studies have shown the importance of indirect groundwater discharge for pollutant loading and water supply for the Great Lakes [International Joint Commission, 2011], this thesis focuses on direct groundwater discharge. The Great Lakes function as discharge areas

(sinks) for the aquifers in the Great Lakes Basin under natural flow conditions because the lakes are in a topographically low setting [Grannemann et al., 2000]. Direct groundwater discharge will occur where there is an unconsolidated permeable aquifer near the shore and the aquifer watertable is elevated relative to the lake water level. The Great Lakes has ~6150 km of highly permeable shoreline (sandy, gravel and cobble beaches) [Environment Canada and U.S. EPA, 2009]. While groundwater fluxes are typically low compared to surface water inputs (e.g., rivers and streams), direct groundwater discharge may be a significant contributor when the fluxes are integrated over the entire shoreline length. Along unconsolidated shorelines direct groundwater discharge is typically largest around the shoreline and decreases exponentially offshore [Grannemann and Weaver, 1999].

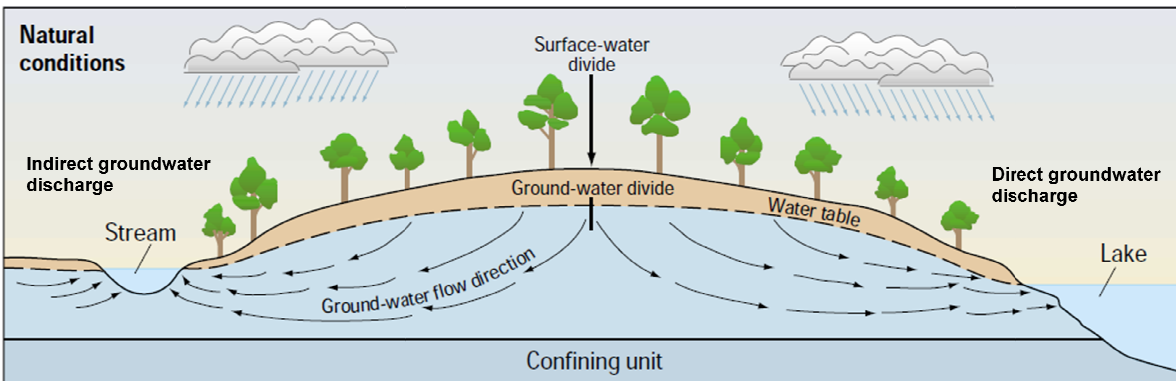


Figure 2.1: Generalized diagram showing indirect and direct groundwater discharge into the Great Lakes. This figure is reproduced from Grannemann et al. [2000].

Few studies have attempted to quantify direct groundwater discharge into the Great Lakes. Estimates of groundwater discharge into Lake Michigan vary widely from 19 - 18,300 m³/d/km of shoreline [Bergstrom et al., 1962; Cartwright et al., 1979; Sellinger, 1995]. The variability is due to different measurement methods used, the scale of the study (basin-wide c.f. localized

groundwater flow) and the locations where flows were measured [Sellinger, 1995]. Many factors influence local groundwater discharge rates including the local hydrogeology, groundwater recharge area, topography, lake bathymetry and shape of the shoreline [Cherkauer and McKereghan, 1991; Grannemann et al., 2000].

2.2 Nearshore groundwater-lake interactions

Direct groundwater discharge is defined as all pore water that discharges across the sediment-water interface (SWI). As such it is made up of not only terrestrial groundwater (derived from the aquifer) but also water that recirculates across the SWI (Figure 2.2). In marine environments, the total direct groundwater discharge (terrestrial and recirculating) is referred to as submarine groundwater discharge [Burnett et al., 2001; Taniguchi et al., 2002]. It is necessary to consider the recirculating component because it can alter flow paths and biogeochemical conditions in the nearshore aquifer [Burnett et al., 2003]. In addition, this component is included in measured estimates when direct groundwater discharge measurement techniques are adopted (e.g., seepage meters, nested piezometers). While the mechanisms contributing to total groundwater discharge rates have been well studied along marine shorelines, they are not well understood for inland coastal environments such as the Great Lakes. The coastal water level fluctuations that drive recirculation are different; for example, marine shorelines are exposed to tides and oceanic waves whereas inland coastal shorelines are exposed to long-term and seasonal lake level changes and higher frequency waves [Crowe, et al., 2009; Robinson et al., 2010].

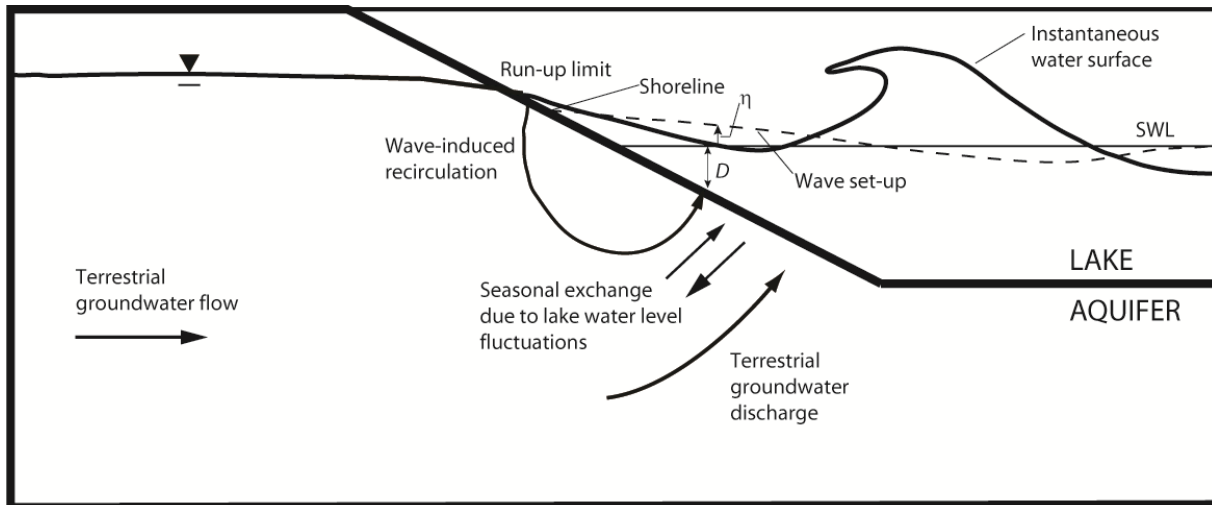


Figure 2.2: Schematic of dynamic groundwater-lake water interactions. SWL is the still water level, D is the water depth from the SWL to the shoreline and η is the height of wave set-up.

The water levels in the Great Lakes fluctuate seasonally and exhibit long-term variability. Water exchange between the aquifer and lake is driven by the hydraulic gradient between the lake and nearshore aquifer, and therefore direct groundwater discharge is influenced by these lake level variations [Crowe et al., 2009]. Terrestrial groundwater discharge to the lake increases when the lake water levels drop relative to the nearshore watertable. In contrast, water will flow from the lake into the aquifer when the lake level rises relative to the nearshore watertable. The location of the shoreline also changes in response to lake level fluctuations; i.e., the shoreline retreats as the lake water level drops [Crowe et al., 2009]. The location of the shoreline is an important factor for understanding nearshore groundwater discharge as the majority of groundwater discharge occurs at the shoreline and decrease exponentially offshore. Thus, the change in shoreline location will modify the groundwater discharge location.

The shorelines of the Great Lakes are subject to significant wave action (Figure 2.3). Studies for marine shorelines have shown that wave-driven recirculation can constitute a large proportion of

the total groundwater discharge [Xin et al., 2010; Li et al., 1999]. While waves induce rapid instantaneous pore water flows in response to individual wave fronts and wave run-up, these flows are rapidly attenuated in the beach sediment due to their high frequency [Horn, 2006]. Rather, it is the phase-averaged effects of waves that strongly control nearshore groundwater behaviour (Figure 2.4) [Longuet-Higgins, 1983; Li et al., 2000]. As waves propagate towards the shore and break, wave energy is dissipated leading to an upwards tilt in the mean coastal water level, known as wave set-up. The mean-onshore pressure gradient due to wave set-up drives a groundwater recirculation cell with infiltration near the maximum run-up limit and exfiltration near the wave breaking point (Figure 2.4). While wave-induced recirculation can account for a large proportion of total groundwater discharge [Li et al., 1999], the recirculation rate is modulated by the relative height of the watertable landward of the shoreline [Li et al., 2000]. Li et al. [2000] showed numerically that the wave-induced groundwater recirculation is greater when the landward watertable is low and the fresh groundwater discharge does not to restrict the wave-induced recirculation cell.

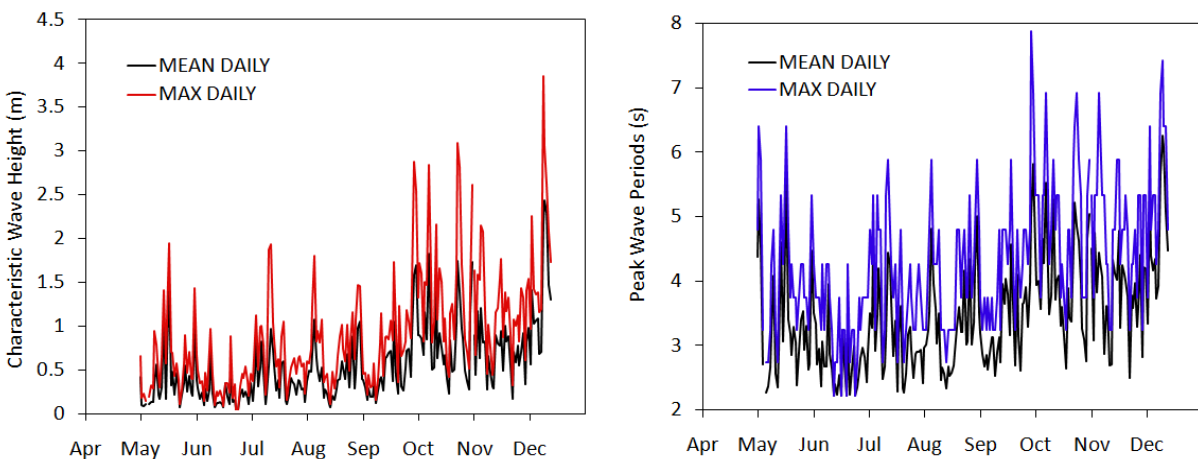


Figure 2.3: Characteristic wave height and peak wave periods for wave buoy station in South Georgian Bay from May – November 2009 [Fisheries and Oceans Canada, 2012].

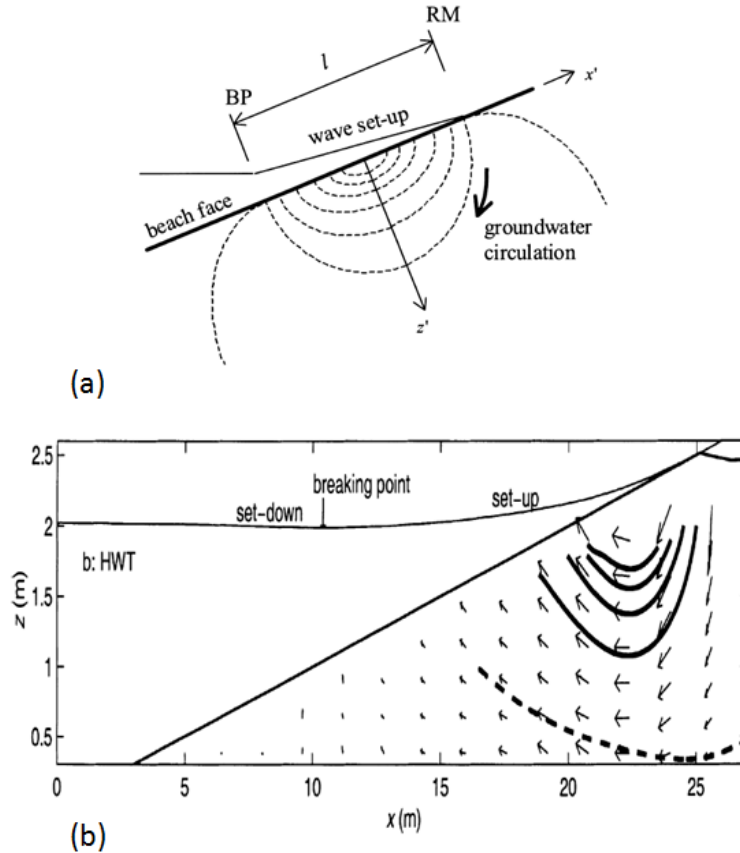


Figure 2.4: Wave set-up and phase-averaged wave groundwater circulations as described by (a) analytical solution of Longuet-Higgins [1983] and (b) BEACHWIN numerical model of Li et al., [2000]. (a) is reproduced from Longuet-Higgins [1983] and (b) is reproduced from Li et al., [2000].

It was shown numerically by Xin et al. [2010] that the effect of waves on nearshore flow and water exchange rates across the SWI can be well represented by adopting a phase-averaged wave set-up approach rather than simulating individual waves (i.e., phase-resolved approach). This approach is also significantly more computationally efficient. Solutions describing wave set-up are available, including that by Longuet-Higgins [1983], or alternatively, as done by Xin et al. [2010], instantaneous waves generated in a shallow water wave simulator such as BEACHWIN

[Li et al., 2000] may be averaged to provide a description of wave set-up. In this study, an empirical equation developed and validated by Nielson [2009] was used to estimate the wave set-up profile. This equation is given as:

$$\eta = \frac{0.4H_{rms}}{1+10\frac{D+\eta}{H_{rms}}} \quad (2.1)$$

where $\eta(x)$ is height of wave set-up along the interface (m), H_{rms} is the root mean square wave height (m) and $D(x)$ is the still water depth measured from local beach surface to the still water level (SWL) (m). These terms are defined in Figure 2.2.

2.3 Influence of groundwater-lake interactions on pollutant discharge

Quantifying the discharge of groundwater pollutants to nearshore waters is complicated because it is controlled not only by the groundwater discharge flow paths but also the specific pollutant sources and the biogeochemical conditions along the pollutant discharge pathway [Robinson, et al., 2007; Robinson, et al., 2009; Westbrook, et al., 2005]. In marine environments, it has shown that coastal water level fluctuations create dynamic flows and complex geochemistry in an unconfined nearshore aquifer [Robinson et al., 2006, 2007, 2009; Xin et al., 2000; Charette et al., 2002]. Surface water recirculating through a nearshore aquifer has a different chemical composition to terrestrial groundwater. For example, surface water can deliver oxygen and organic material to the nearshore aquifer [Horn, 2002]. When the recirculating water and terrestrial groundwater mix, this can create an active biogeochemical mixing and reaction zone in the aquifer that is often characterized by distinct pH and redox gradients [Moore et al. 1999; Robinson et al., 2007; Charette and Sholkovitz, 2006]. Chemicals undergo important transformations in this reaction zone and so this zone can control the exit conditions and

subsequent loading of land-derived groundwater chemicals to nearshore water. This zone can also affect biogeochemical cycling in coastal environments by altering the composition of recirculating water [Charette and Sholkovitz, 2006; Hays and Ullman, 2007]. Due to its importance, this mixing and reaction zone is termed a subterranean estuary in marine environments (in analogy to a surface estuary) [Moore et al. 1999]. To our knowledge there is no prior research conducted to understand the existence and role of this mixing and reaction zone for inland coastal environments such that exist on the Great Lakes. The physical processes that set-up the mixing zone are different between marine and freshwater coastal environments (e.g., tides, oceanic waves versus long-term and seasonal lake level variations and high frequency waves). However, most significantly the chemical composition and density of the recirculating waters are different (seawater versus lake water).

2.4 Occurrence of arsenic (As) in groundwater

Arsenic (As) is a carcinogenic heavy metal that occurs in groundwater worldwide. Elevated As levels threaten the health of millions of people who depend on groundwater as their drinking water source [Smedley and Kinniburgh, 2002]. In some case elevated As concentrations that exceeds regulation standard can be attributed to anthropogenic activities (e.g., mining and industry) but often As is naturally occurring in the aquifer [Smedley and Kinniburgh, 2002]. The World Health Organization (WHO) drinking water standard for As is 0.01 mg/L [WHO, 2008] and this standard is adopted by many countries including Canada. The Ontario drinking water standard for As is 0.01 mg/L (O. Reg. 169/03) [Ministry of the Environment, 2002]. In addition to drinking water standards, Ontario regulates As concentrations in groundwater. The As standard for non-potable groundwater is 1.9 mg/L (Table 3) and for background site conditions is 0.013 mg/L (Table 1) [Ministry of the Environment, 2011].

Fe (hydr)oxides and Fe sulfide minerals are the main geogenic sources of As and are strongly linked to As occurrence and cycling in the subsurface. As is strongly adsorbed to Fe (hydr)oxides that form under oxidizing condition [Smedley and Kinniburgh, 2002]. Other metal (hydr)oxides such as manganese (Mn) and aluminium (Al) can also have significant affect on As cycling if they exist in abundance. At pH < 7.5, Al (hydr)oxides are as effective as Fe (hydr)oxides in adsorbing As. In strongly reducing groundwater, As is immobilized via formation of Fe sulfides [Couture et al., 2009]. Strongly reducing conditions refer to a redox state for which sulphate (SO_4^{2-}) reduction occurs. Under undisturbed conditions, As is strongly bound to these minerals (either metal (hydr)oxides, or Fe sulphide minerals) and remains immobilized. However, a shift in the redox condition leads to mobilization of As through either reductive dissolution of metal (hydr)oxides or dissolution of sulfide minerals [Bone et al., 2006; Jung et al., 2009; Cook et al., 1995; Couture et al., 2009; Johnston et al., 2010]. Dissolution of Fe (hydr)oxides occurs under reducing conditions at neutral pH and dissolution of sulfide minerals occurs when the groundwater becomes more oxidizing. An increase in pH (> 8.5) or the presence of species that compete for adsorption site such as phosphate (PO_4^{3-}), bicarbonate (H_2CO_3), silicate (SiO_4) or organic matter may also lead to the desorption of As from metal hydr(oxides). PO_4^{3-} has a similar affinity to metal hydr(oxides) as As and so its presence is often used as an indicator for As mobilization.

2.5 Mobility of As in coastal aquifers and lake sediments

Previous studies have examined As mobility in coastal (marine) aquifers [Bone et al., 2006; Jung et al., 2009] and also in shallow lake sediments [Cook et al., 1995; Couture et al., 2009; Johnston et al., 2010]. Occurrence of elevated dissolved As at the SWI can be attributed to the shift in redox potential (Eh) and pH which triggers mineral dissolution and the release of As [Smedley

and Kinniburgh, 2002; Root et al., 2009]. The release of As from metal (hydr)oxides can be triggered in response to: (1) an increase in pH to higher than 8.5 leading to desorption of As from metal hydr(oxides) (even in oxidized conditions) [Pierce and Moore, 1981] and (2) shift to reducing conditions under neutral pH resulting in the dissolution of metal (hydr)oxides [Bone et al., 2006; Smedley and Kinniburg, 2002].

High abundance of Fe (hydr)oxides (ferrihydrite, goethite, and lepidocrocite) was observed by Charette and Sholkovitz [2002] in the shallow sediment along the shoreline of Waquoit Bay (Cape Cod, Massachusetts). They showed that these Fe (hydr)oxides precipitate as Fe-rich groundwater mixes with more oxidized seawater that recirculates through the shallow nearshore sediments. This layer of Fe (hydr)oxides was termed an 'iron curtain' as it acts as a geochemical barrier trapping chemicals that are powerfully adsorbed to the (hydr)oxide minerals and preventing their release to coastal water. A follow up study by Bone et al. [2006] showed that the 'iron curtain' adsorbs and immobilizes As diffusing upward from the reduced aquifer and this prevents As from discharging to the sea. Amorphous Fe (hydr)oxides (ferrihydrite) have higher affinity for As than crystalline Fe (hydr)oxides (goethite and lepidocrocite) and were mainly responsible for As immobilization in the nearshore sediments [Jung et al., 2009; Smedley and Kinniburgh, 2002; Bone et al., 2006; Charette and Sholkovitz, 2002]. As a result of this As immobilization, elevated pore water As (up to 0.0143 mg/L) was observed in groundwater near the shoreline while the nearshore coastal water had low As concentration [Bone et al., 2006; Jung et al., 2009]. A numerical model developed by Jung et al. [2009] estimated it would have taken ~2300 years to accumulate the 0.4 mg/kg of As to be contained in the 'iron curtain' layer at the Waquoit Bay field site.

Johnston et al. [2009] and Root et al. [2009] examined As mobilization in tidally-influenced aquifers and also observed high pore water As in the shallow intertidal aquifer. They showed that the As concentrations were highest in the redox transition zone between Fe oxidizing and SO_4^{2-} reducing conditions (Figure 2.5) [Johnston et al., 2009; Root et al., 2009]. The transition zone occurs where the oxygen-rich seawater mixes with the more reduced groundwater. This mixing sets up redox and pH gradients that lead to the mobilization of As and Fe. Tidal fluctuations generate an upward advective flow below the shoreline and this transports the dissolved As and Fe to the oxidized shallow sediments where an As-Fe (hydr)oxide layer (iron curtain) is formed [Johnston et al., 2009]. The As is immobilized in both the oxidized and reducing zones and thus pore water As is highest in the transition zone.

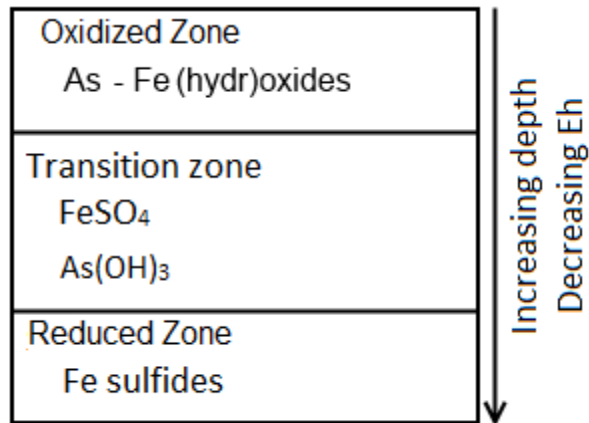


Figure 2.5: Conceptual diagram of redox zones beneath sediment-water interface in a coastal nearshore sediments. In the transition zone dissolved As and Fe complex to form $\text{FeSO}_4(\text{aq})$ and $\text{As}(\text{OH})_3(\text{aq})$ [Root et al., 2009].

2.6 Background information on Port Stanley Harbour Site

Port Stanley Harbour, located on the north shore of Lake Erie at the outfall of Kettle Creek, was identified as an area of environmental concern and potential source of contamination by the Source Water Protection Planning for Elgin Area Water Treatment Plant (WTP) [Stantec 2009a; 2009b]. The brownfield site recently transferred from Transport Canada to the Municipality of Central Elgin is divided into the West Pier, East Pier and East Headland with the Bridge Street lift-bridge as the northern boundary for the site (Figure 2.6). The lands were historically used for commercial fisheries and industrial land uses including petroleum product, grain and liquid fertilizer storage and handling and coal stockpiling. Past tenants at the East Headland were Lakes Terminals and Warehousing, Public Utilities Commission (PUC) and Works Department, Animal Shelter and Recycling Depot. Lakes Terminals and Warehousing had three 1.5 million litre above-ground storage tanks (ASTs) used to store ammonium nitrate and had open piles of coal, salt and gravel on the East Headland [CH2MHILL, 2009a]. The WTP intake is located offshore approximately 2 km to the east of the harbour, and with a portion of the East Headland located within the Elgin Area Intake Protection Zone 2 (IPZ-2), the impacted soil and groundwater at the site is a potential issue of concern for source water protection planning [Stantec, 2009b].

Over the last 15 years numerous studies have been conducted to characterize the soil and groundwater contamination at the site including the recent Environmental Site Assessments (Phase I, II, and Risk Assessment) [CH2MHILL, 2009a; 2009b; 2010]. Measurements have identified concentrations of petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and heavy metals in soil and groundwater at the harbour site exceeding the applicable Federal and Provincial criteria (summarized in Table 2.1). The soil stratigraphy at the site is complex and

reflects primarily the fill material used for the construction of the harbour lands rather than the regional geology [CH2MHILL 2009b; 2006a]. Interpolations of sediment stratigraphy at across the East Headland are presented in Figure 2.7. In addition to the industrial activities that took place on the site, reports suggest that the fill material itself, which was mainly dredged sediment from Kettle Creek, may be a significant source of contamination [CH2MHILL 2009b; 2006a; 2006b]. Water quality measurements taken at surface water stations in the harbour (three stations in recent 2009 sampling program [CH2MHILL. 2009a]) indicated elevated levels of metals including aluminum, iron and chromium in the surface water with respect to background concentrations. However, based on these measurements it was not possible to ascertain if the high levels of metals was due to contamination upstream in Kettle Creek or linked with contaminated groundwater potentially discharging from the harbour lands.

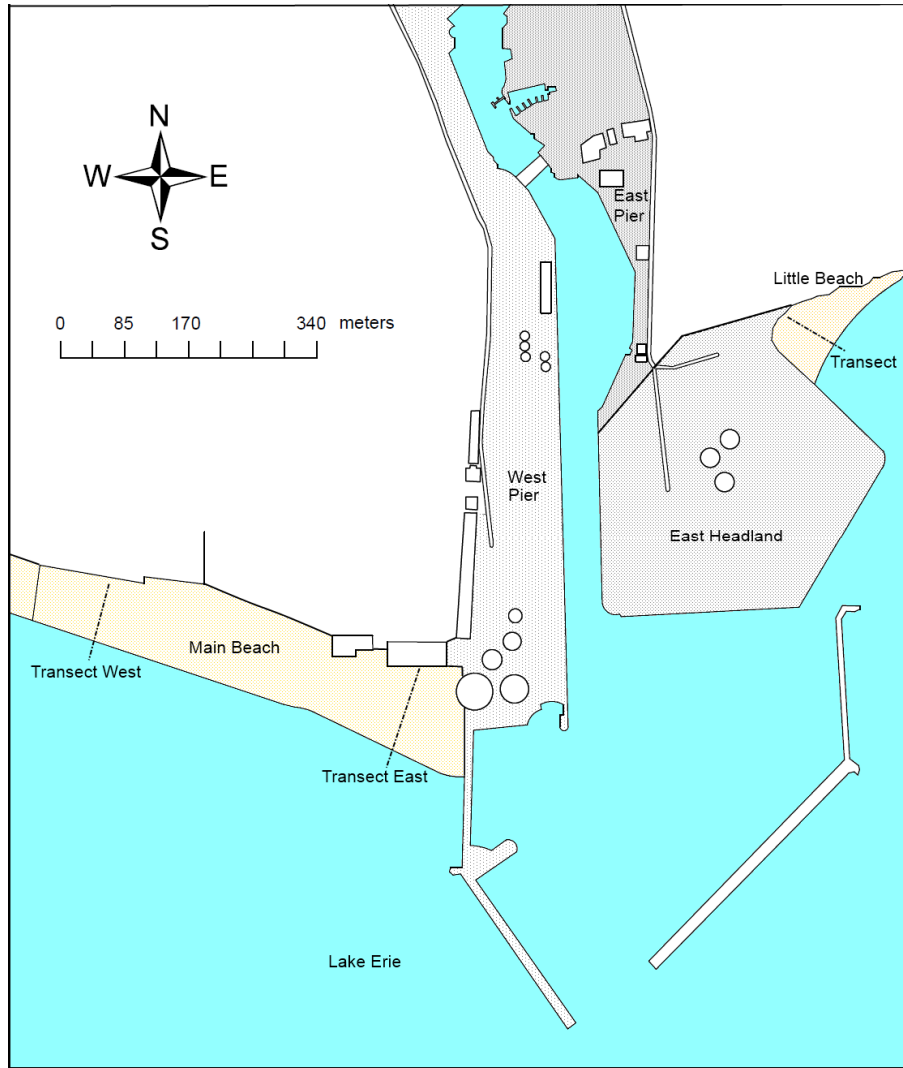


Figure 2.6: Schematic of Port Stanley Industrial Site showing the East Headland, East Pier and West Pier.

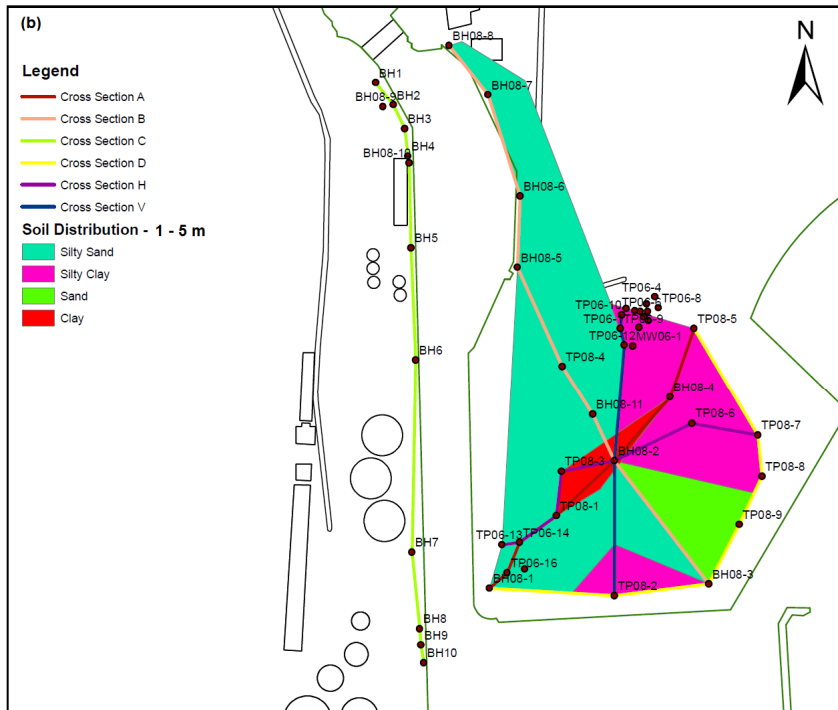
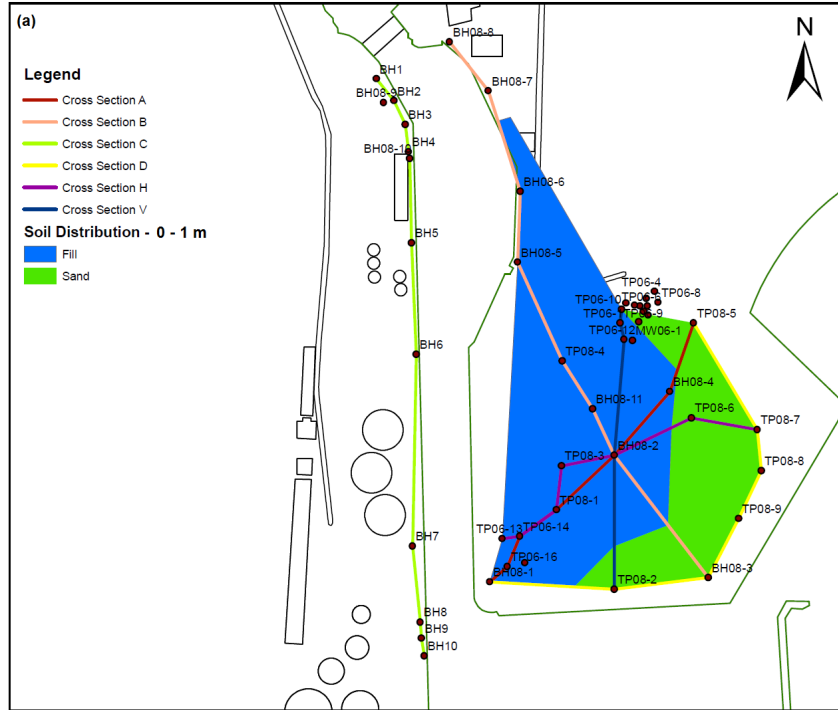


Figure 2.7: Interpolations of soil stratigraphy at East Headland: a) 0 - 1 m below ground surface and b) 1 - 5 m below ground surface [CH2MHILL, 2009b; CH2MHILL, 2006a].

Table 2.1: Contamination concentrations exceeding relevant soil and groundwater guidelines at Port Stanley Harbour site. Concentrations are provided in CH2MHILL [2009b].

	West Pier	East Pier	East Headland
Soil	Metals: Boron ^{2,3} , antimony ^{1,2} , silver ¹ , lead ^{1,2} , zinc ¹ PHCs: Toluene ¹ , F1 (C6-C10) ² , F2 (C10-C16) ² , F3 (C16-C34) ² PAHs ^{1,4}	Metals: Lead ^{1,4} PAHs ^{1,4}	Metals: Antimony ¹ , arsenic ^{1,2,4} , lead ¹ , molybdenum ¹ , cadmium ¹ , cobalt ^{1,2} , nickel ^{1,4} , selenium ¹ , zinc ¹ PHCs: Ethyl Benzene ¹ , Toluene ¹ , Xylenes (total) ¹ , F1 (C6-C10) ² , F2 (C10-C16) ^{2,3} , F3 (C16-C34) ² , F4G-SG (GHH-Silica) ² PAHs ¹
Groundwater	Metals: Chromium ⁵ , cobalt ⁵ , copper ⁵ , vanadium ⁵ , zinc ⁵ , cadmium ⁵ , lead ⁵ , flourine ⁵ PHCs: ethyl benzene ⁵ , toluene ⁵ , F1 (C6-C10) ⁶ , F2 (C10-C16) ⁶ , F3 (C16-C34) ⁶ PAHs ^{5,6,8} Nutrients: Ammonia ⁸ , nitrate ⁸	Metals: chromium ⁵ , cobalt ⁵ , copper ⁵ , lead ⁵ PHCs: toluene ⁷ PAHs: Pyrene ⁵	Metals: Arsenic ⁸ , Chromium ⁵ , cobalt ⁵ , copper ⁵ , nickel ⁵ , vanadium ^{5,7} , zinc ³ , sodium ⁷ , Iron ^{8,5} PHCs: F3 (C16-C34) ⁷ , F4 (C34-C50) ⁷ PAHs: Benzo(a)pyrene ⁵ Nutrients: Ammonia ⁸ , nitrate ⁸
Surface water around harbour	Nutrients: Ammonia, nitrite ¹ Metals: Aluminium, iron, zinc, chromium ^{1,2}		

1. MOE Table 1 (Full Depth Background Site Condition Standards) [MOE, 2011]
2. MOE Table 3 (Full Depth Generic Site Condition Standards in a Non-Potable Ground Water Condition) [MOE, 2011]
3. Canadian Soil Quality Guidelines Tier 1 levels (for petroleum hydrocarbons only) [Canadian Council of Ministers of the Environment, 2001]
4. Canadian Soil Quality Guidelines for Commercial land use and industrial land use [Canadian Council of Ministers of the Environment, 2007]
5. MOE Table 1 (Full Depth Background Site Condition Standards) [MOE, 2011]
6. MOE Table 3 (Full Depth Generic Site Condition Standards in a Non-Potable Ground Water Condition) [MOE, 2011]
7. MOE Table 2 (Full Depth Generic Site Condition Standards in a Potable Ground Water Condition) [MOE, 2011]
8. Guidelines for Canadian Drinking Water Quality [Health Canada, 2010]
9. CCME Canadian Environmental Quality Guidelines, Canadian Water Quality Guidelines for the Protection of Aquatic Life (WQGAL) [Canadian Council of Ministers of the Environment, 2007]
10. MOE Provincial Water Quality Objectives (PWQO) [MOE, 1994]

Elevated As in the groundwater and soil were recorded at the industrial site, particularly around the East Headland (Figures 2.8 and 2.9) [CH2MHILL, 2009b]. Water quality analysis performed for 19 wells across the site in September 2008 found the maximum dissolved As concentration to

be 0.02 mg/L (Figure 2.8). This maximum concentration was recorded at the well located where coal was formerly stockpiled on the East Headland. Coal typically contains pyrite (Fe sulphide minerals) to which As can be bound and so this may be the source of the elevated As observed at the East Headland [Katrinak and Benson, 1995]. Even though the coal piles are no longer present, coal fragments are still widespread in the top soil across the East Headland. The maximum As concentration observed in the groundwater at the site exceeds the O. Reg. 169/03 drinking water standard (0.01 mg/L) and MOE standard for background site conditions (0.013 mg/L, Table 1). Soil analysed from boreholes and test pits revealed that the soil at East Headland is mostly sand, silty clay and dredged fill material (gravel and coal fragment) [CH2MHILL, 2009b]. The maximum concentrations of As in sediment was recorded to be 48 mg/kg and again this maximum levels was for sediment located in East Headland (Figure 2.9). This sediment concentration also exceeded the MOE background site condition standard (Table 1, 17 mg/kg) as well as the MOE non-potable groundwater standard (Table 3, 20 mg/kg) [CH2MHILL, 2002]. Other sediment samples across the industrial site had relatively low As concentrations.

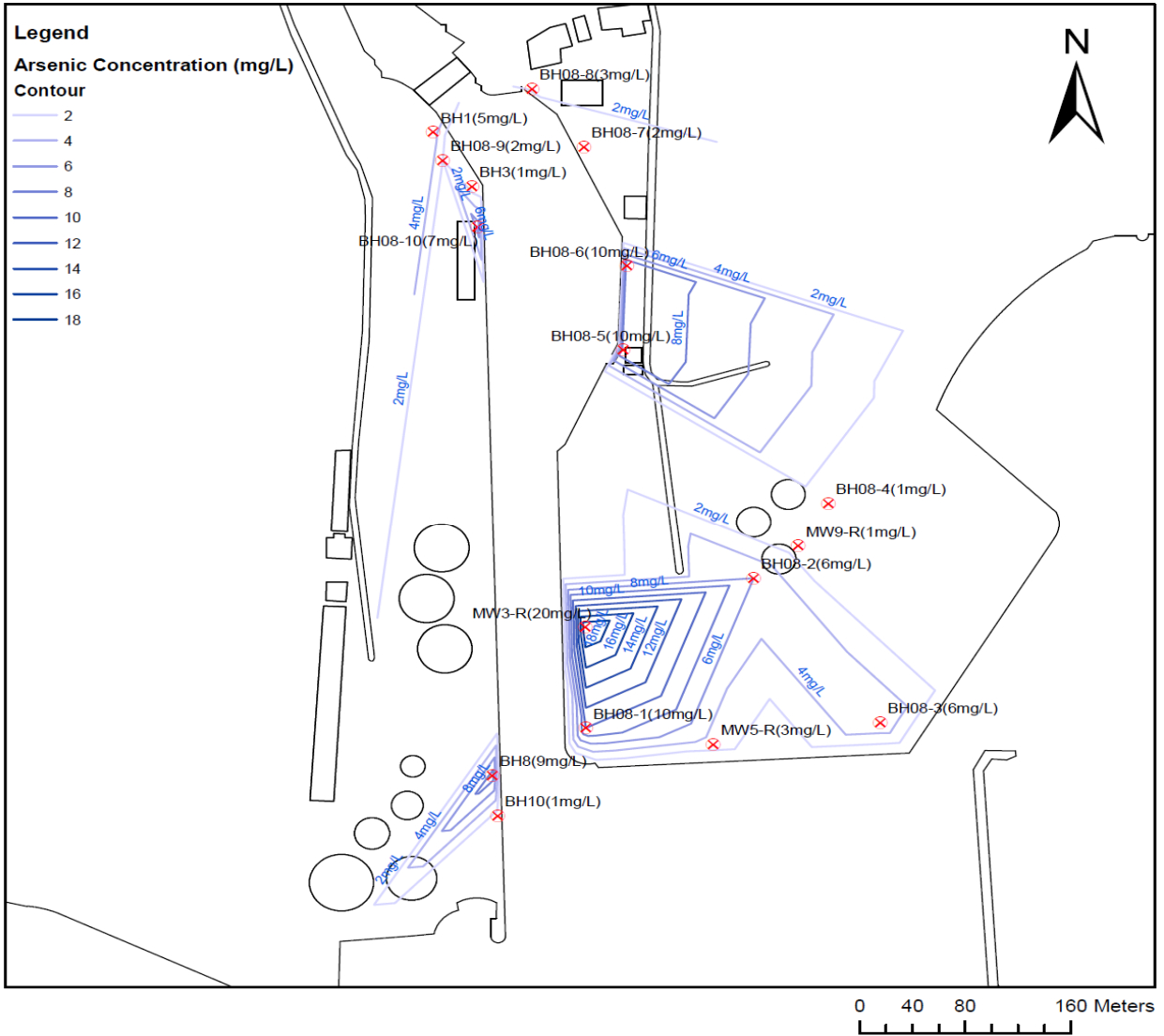


Figure 2.8: Measured dissolved As at Port Stanley industrial site [CH2MHILL, 2009b].



Figure 2.9: Measured As sediment concentrations at Port Stanley industrial site [CH2MHILL, 2009b].

2.7 Summary

This chapter has summarized the relevant background information for this thesis including prior studies on groundwater discharge to the Great Lakes, factors controlling chemical fluxes via the groundwater pathway and arsenic occurrence in groundwater including coastal aquifers. A brief description of the contamination at the Port Stanley Harbour site was also provided. While significant research has been done previously on groundwater discharge to marine environments including the physical flow and geochemical processes that control the exit conditions for chemicals, little is

known regarding the flux of chemicals via direct groundwater discharge to inland coastal seas such as the Great Lakes. The original contribution of this thesis is that the geochemical and physical flow processes controlling the As mobility in a nearshore aquifer and its subsequent discharge to the Great Lakes is examined. While this thesis focuses on As mobility, the findings are pertinent for understanding the flux of other chemicals to inland coastal waters via the groundwater pathway. The findings of this thesis are also relevant for Source Water Protection Planning for the Elgin Area WTP.

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CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Introduction

The Great Lakes contain nearly 20 percent of the world's fresh water and provide essential services for approximately 30 million people that live in the Great Lakes Basin [Ministry of Natural Science, 2012]. The nearshore water quality in the lakes continues to degrade in response to increasing urbanization, industrialization and extensive agriculture [Environment Canada and the U.S. EPA, 2009]. Water quality management strategies for the Great Lakes historically focused on identifying and controlling point pollution sources. However it is now widely acknowledged that non-point pollution sources (e.g., storm water runoff, combined sewer overflows, groundwater discharge) need to be addressed to improve the water quality [International Joint Commission, 2011]. In particular, the role of groundwater as a pathway for delivering pollutants to the lakes is poorly understood [International Joint Commission 2011].

The Great Lakes have approximately 6150 km of permeable shoreline (sandy, gravel and cobble beaches) [Environment Canada and U.S. EPA, 2009]. This shoreline represents a potentially important zone for the direct discharge of groundwater from shallow unconsolidated nearshore aquifers to the lake [Grannemann et al., 2000; Harvey et al., 2000; Crowe, et al., 2009]. Quantifying and predicting the discharge of groundwater pollutants to nearshore waters is complex as it is controlled by the specific pollutant sources, groundwater flow paths and biogeochemical processes along the pollutant subsurface discharge pathway [Robinson, et al., 2007; Robinson, et al., 2009; Westbrook, et al., 2005].

In coastal environments such as the Great Lakes, dynamic interactions between the surface water and aquifer lead to complex subsurface flow patterns and significant exchange of water and chemicals across the sediment-water interface (SWI) near the shoreline. Coastal water level fluctuations (i.e., waves) can drive significant recirculation of surface water across the SWI (Figure 3.1). The mixing of the recirculating surface water with terrestrially-derived discharging groundwater can set up an important reaction zone near the SWI due to the different chemical compositions of these waters [Robinson, et al., 2007; Ullman, et al., 2003; Robinson, et al., 2006]. This reaction zone is often characterized by strong redox and/or pH gradients and groundwater pollutants may undergo transformations or attenuation in this zone prior to their discharge to coastal water [Charette, et al., 2006]. While this reaction zone has been well studied in marine environments (commonly termed a subterranean estuary), it has not been examined for freshwater shorelines such that exist on the Great Lakes. The coastal water level fluctuations are different; for example, marine shorelines are exposed to tides and oceanic waves whereas freshwater shorelines are exposed to seasonal lake level changes and higher frequency waves (Figure 3.1) [Crowe, et al., 2009]. The chemical composition of the recirculating water is also different – the most significant difference being the absence of density-driven flow in freshwater beaches. This study is the first time that the geochemical conditions and groundwater flow patterns in a freshwater beach aquifer have been simultaneously quantified to gain insight into the dynamic processes controlling the nearshore discharge of groundwater pollutants to inland seas such as the Great Lakes.

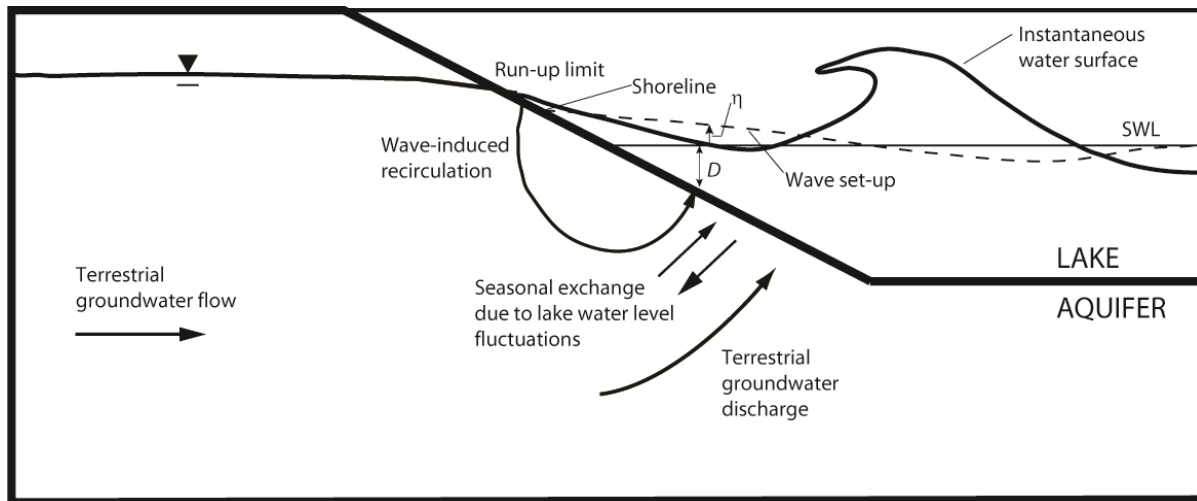


Figure 3.1: Conceptual diagram of the water levels and groundwater flows in a nearshore aquifer exposed to waves. The still water level (SWL), instantaneous water surface (thick solid line) and wave set-up profile (phase-averaged water surface) are shown. The still water depth (D), and the wave set-up height (η) are annotated on the diagram.

While the dynamic flows and reaction zone near the SWI will control the exit conditions many chemical species, this study focuses specifically on understanding their impact on transformations and transport of arsenic (As) in a sandy beach aquifer on Lake Erie and its potential discharge to nearshore waters. Arsenic is a highly toxic metal with elevated As levels in groundwater threatening the health of millions of people worldwide [Smedley, et al., 2002; Ahmed et al., 2004]. Arsenic can be naturally occurring in groundwater but in some cases its occurrence is related to anthropogenic activities such as mining and industry. The subsurface mobility and transport of As has been well studied [Ahmed et al., 2004]. In recent years, research has extended to examine the geochemical processes controlling the discharge of As from groundwater to coastal waters [Johnston et al., 2010; Bone et al., 2006; Jung et al., 2009]. Bone et al. [2006] and Jung et al. [2009] presented field and numerical investigations focused on a marine beach aquifer (Waquoit Bay, MA) that illustrated As mobility was strongly controlled by

the redox conditions near the SWI. They demonstrated that As transport was strongly coupled to iron (Fe) and manganese (Mn) redox cycling due to the adsorption of As to Fe (hydr)oxides and to a lesser extent Mn (hydr)oxides. At their field site, a layer of Fe (hydr)oxides was present where the seawater and fresh groundwater mix below the SWI. This layer, termed an ‘iron curtain’, was shown to act as a reactive barrier accumulating As and preventing its release to coastal waters. In this study we examine if this phenomenon also occurs along freshwater shorelines where the chemical composition of the coastal water and the forcing that set-up the reaction zone near the SWI are different.

This study presents field measurements that provide insight into the nearshore geochemical conditions, groundwater flows and water exchange controlling the mobility of As in a freshwater beach aquifer on Lake Erie. The field location is adjacent to a brownfield industrial harbour site that has elevated sediment and groundwater As concentrations. Numerical modeling is used to simulate the discharge rates and flows in the nearshore aquifer, including the effect of waves. While this study focuses on As, the nearshore geochemistry and subsurface flows are be pertinent to understanding the discharge of other chemicals (e.g., nitrate, ammonium, phosphorous) to nearshore inland coastal waters via the groundwater pathway.

3.2 Field Methodology

3.2.1 Field Site

Field measurements were conducted on two adjacent beaches (Little Beach and Main Beach) on Lake Erie. These beaches are separated by Kettle Creek and a brownfield industrial harbour site (Figure 3.2). The potential discharge of heavy metals from the groundwater to the lake is of particular interest along this shoreline as the brownfield site has elevated groundwater and

sediment heavy metal concentrations (As, Fe, chromium, copper, lead, nickel, cobalt, and zinc) [CH2MHILL, 2009]. The brownfield site straddles Kettle Creek and is divided into three areas: East Headland, East Pier and West Pier. The highest dissolved heavy metal concentrations have been observed at the East Headland; this area was constructed using dredged sediment from Kettle Creek over three decades until 1978. Little Beach also underwent a beach nourishment program using dredged sediment from Kettle Creek over this period.

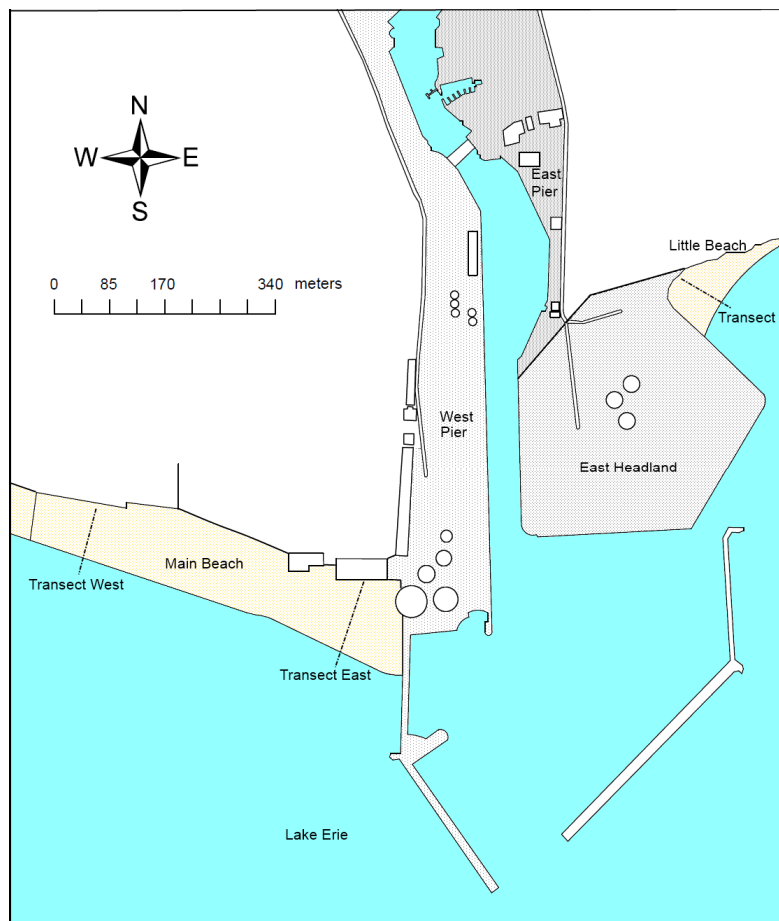


Figure 3.2: Map showing brownfield industrial site areas (East Headland, East Pier, and West Pier) and beaches (Little Beach and Main Beach). Field measurements were carried out at Little Beach and Main Beach with the dashed lines depicting where the shore-normal groundwater monitoring transects were installed.

Little Beach, located adjacent to the East Headland, was the main focus of the field investigations. As the East Headland is surrounded by a concrete pier structure along Kettle Creek and a reinforced riprap break wall along Lake Erie, groundwater contaminants may discharge to the lake via Little Beach due to the comparatively high permeability of the beach sediments. Little Beach is approximately 100 m wide and 180 m long. The beach is bounded by the East Headland to the south-west and a rock outcrop to the north-east. The width of the beach is constrained by a ~25 m high glacial till bluff. The beach slope is mild (0.005) except around the shoreline where it increases to approximately 0.1. Sediment samples collected across the beach up to a depth of 2 m below the ground surface revealed that the surficial beach aquifer is relatively homogeneous. The beach sediment is sand and silty sand with a mean sediment size of 0.207 mm and uniformity coefficient of 3. The average hydraulic conductivity of the beach sediment was estimated to be 8.06 m/d using the Krumbien and Monk [1942] equation. The parameters used for this calculation are presented in Appendix A.

To evaluate the spatial variability in groundwater discharge rates and occurrence of As in beach groundwater, field measurements were also conducted at Main Beach (Figure 3.2). Main Beach is approximately 600 m long and 85 m wide. The average beach slope is 0.025 except around the shoreline where the slope increases to 0.09. The beach sediment is similar to Little Beach with an estimated average hydraulic conductivity of 8.06 m/d. The beach sediment is relatively homogeneous except along the western portion of the beach (location of west transect) there is a gravel layer approximately 1.5 m below the ground surface.

Long term and seasonal lake level fluctuations and wave conditions will affect the nearshore groundwater flow dynamics including the groundwater discharge rates. Lake water levels and wave height data (significant wave height, H_{sig}) from a bouy located ~20 km offshore of the field

sites are shown in Figure 3.3. Wave conditions were variable but H_{sig} typically ranged from 0 to 3 m.

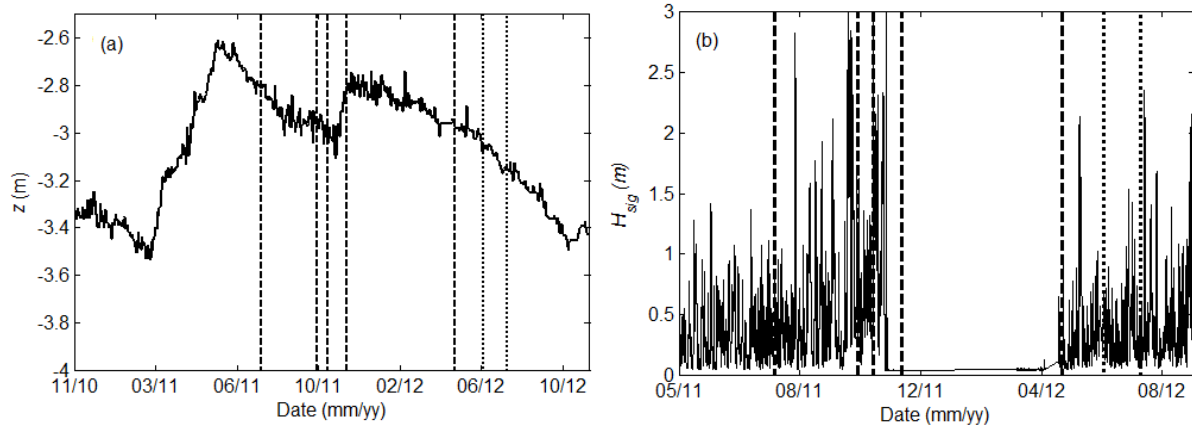


Figure 3.3: (a) Lake water levels from November 2010 to November 2012 and (b) H_{sig} from May 2011 to September 2012. Data is from a buoy located 20 km offshore of the field site [Oceans and Fisheries Canada, 2012]. The vertical height datum used in (a) has been adjusted relative to a local benchmark on Little Beach. Vertical dashed and dotted lines indicate time of monitoring events at Little Beach and Main Beach, respectively.

3.2.2 Field Methods

A shore-normal monitoring transect was installed at Little Beach with additional monitoring on either side of the transect to assess alongshore variability (Figure 3.4). The shore-normal transect extended from the bluff (landward extent of the beach) to ~20 m offshore. Multiple monitoring events were conducted at Little Beach (3 - 5 August 2011, 10 October 2011, 8 December 2011, and 14 - 18 May 2012) to assess the temporal variability in the pore water flows and chemistry. The equipment layout was similar for all monitoring events.

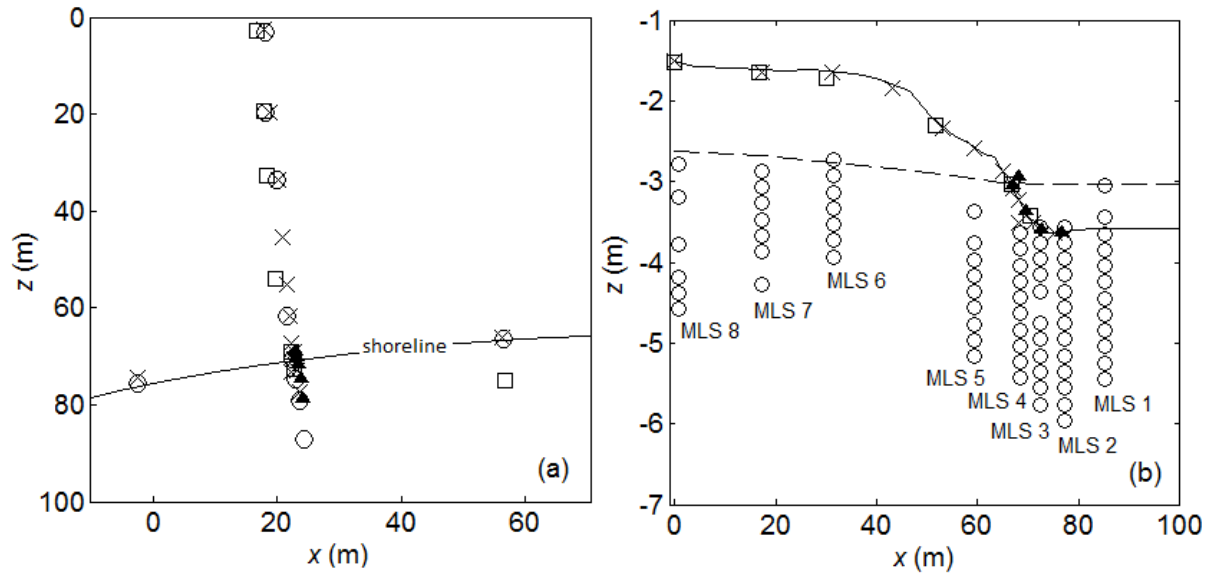


Figure 3.4: (a) Spatial and (b) cross-sectional view of monitoring equipment installed at Little Beach for 14 - 18 May 2012 monitoring event. Manometers (\blacktriangle) were installed around the shoreline and piezometers (\times) and MLS (O) were installed from the bluff ($x = 0$ m) to ~ 20 m offshore ($x = 85$ m). Six sediment cores (\square) were collected along the transect in June 2012.

Piezometers were installed along the transect and landward of the shoreline to measure the watertable and the lake level elevations. Landward of the shoreline, these were constructed from $\phi 50$ mm PVC pipe and screened at the bottom. At the shoreline and offshore, piezometers were constructed from $\phi 32$ mm clear polycarbonate tubing with external measurement tapes for water level readings. Vertical head gradients around the shoreline were measured using differential manometers connected to nested piezometers ($\phi 5$ mm) with openings at two different depths (0.4 and 1.4 m below the ground surface). Water fluxes across the SWI were inferred from these vertical gradient measurements using estimated local hydraulic conductivities. Finally, pore water samples were collected from multi-level samplers (MLS). MLS were constructed from 2.5

m long ϕ 50 mm PVC pipe with sampling ports spaced at 0.2 m depth intervals. Details of the field equipment are provided by Gibbes et al. [2007].

Two monitoring transects similar to that installed at Little Beach were installed on Main Beach. The east transect was located adjacent to the West Pier of the brownfield site and the west transect located 450 m further west (Figure 3.2). The east transect was installed and monitored from 25 - 28 June 2012 and the west transect was installed and monitored from 30 July – 3 August 2012.

3.2.3 Pore water sampling methods and analysis

Pore water sampling was performed at least 24 hours after the installation of MLS to ensure the sample was not disturbed by the installation procedure. Samples were drawn from the ϕ 1.35 mm PVC tubes connected to each MLS port using syringes. Syringes minimize air entrainment as the sample is drawn up. Two samples were collected from each MLS port: 50 mL sample for total metal analysis and 60 mL sample for nutrient and DOC analysis. Samples for metal analysis were stored in 60 mL polyethylene bottles pre-spiked with 0.5 N nitric acid and samples for nutrient, anion, dissolved organic carbon (DOC) analysis were stored in 120 mL glass bottles. All samples were filtered ($45\mu\text{m}$ nylon filters) onsite and frozen until analysis. Once samples were collected, pore water was pumped from each sampling port into a flow cell where a YSI 6600 Sonde measured the pore water temperature, pH, dissolved oxygen and redox potential (Eh).

Total metal analysis including determination of dissolved As, Fe and S was performed using an ICP-OES (Varian, Inc., Vista-Pro Axial) and anions were analyzed using an HCLP. For samples collected in 2011, ammonia was analyzed using a HACH color pocket meter set for ammonia

nitrogen (No. 5870040). For all samples collected in 2012, nutrients (ammonia, nitrate, orthophosphate, and silica) were analyzed using a Lachat 7500 Flow Injection Analysis system. DOC was analyzed using HACH's organic carbon method (No. 10129) for samples collected in May 2012 and using a Shimadzu TOC analyzer (SSM-5000A combustion unit and TOC-Vcpn analyzer) for samples collected from Main Beach in June and August 2012.

3.2.4 Sediment cores and analysis

Six ϕ 64 mm sediment cores were collected along the transect at Little Beach in June 2012 using a vibracoring method. The location of the coring is shown in Figure 3.4. To maximize the depth of the cores collected a hole was dug down to the watertable before inserting the vibracorer and extracting the sediment cores (maximum length 1.2 m). Immediately after the extraction of each sediment core, they were sectioned in the field at 0.015 cm depth intervals. Each sectioned sample was stored in a 250 mL polyethylene sampling bottle and frozen until analysis. Sediment samples were analyzed using the five-step sequential extraction method of Wenzel et al. [2001]. This method targets non-specific bound arsenic, specific bound arsenic, amorphous hydr(oxides), crystalline hydr(oxides) and residual metals. Details of the extractant, extraction conditions, soil to solution ratio (SSR) and wash method for each step are provided in Table 3.1. Sediment samples were air dried and then 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 3.1. After each extraction, the sample was centrifuged for 15 min at 4000 rpm and 20 mL of the solution was filtered (45 μ m nylon filter) and analyzed using ICP-OES. Before proceeding to the next extraction step, the samples were washed with solutions specified in Table 3.1. Select sediments samples were also analyzed for total elemental S at the

Agricultural and Food Laboratory at University of Guelph using LECO combustion method SC444.

Table 3.2: Details of five-step sequential extraction method of Wenzel et al. [2001].

Step	Extractant	Extraction conditions	SSR	Wash step
1	0.05 M (NH ₄) ₂ SO ₄	Shake for 4 hours	1:25	D.I. water
2	0.05 M (NH ₄)H ₂ PO ₄	Shake for 16 hours	1:25	D.I. water
3	540 mL 0.2 M (NH ₄) ₂ C ₂ O ₄ + 460mL of 0.2 M H ₂ C ₂ O ₄ .H ₂ O (adjust pH to 3.25). This solution is referred to as “pH solution”.	Cover bottle with aluminum foil and shake for 4 hours	1:25	Add 94 mL of pH solution, cover bottle with aluminum foil and shake for 10 min
4	41 mL of 0.2 M (NH ₄) ₂ C ₂ O ₄ + 959mL of 0.2 M H ₂ C ₂ O ₄ .H ₂ O + 17.61g of C ₆ H ₈ O ₆	Water bath (96°C) under bright light for 20 min	1:25	Add 94 mL of pH solution, cover bottle with aluminum foil, shake for 10 min, 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 digester	1:28	D.I. water

3.3 Numerical groundwater model

Numerical steady-state groundwater flow simulations were conducted in MODFLOW-2005 [Harbaug, 2005] to provide insight into the nearshore groundwater flows and water exchange rates. The governing equation used by MODFLOW-2005 is described in Appendix B. Groundwater models were developed to represent the shore-normal transects at Little Beach and Main Beach for each monitoring event. Alongshore variability is considered negligible at the sites and therefore three-dimensional flow was not considered. A schematic of the model domain adopted to simulate groundwater flow at Little Beach (May 2012) is shown in Figure 3.5. This

domain for the models of Little Beach was 100 m long and extended from the most landward monitoring well ($x = 0\text{m}$) to 17 m lakeward of the shoreline. The simulated depth of the unconfined aquifer was 10 m. Additional simulations performed to evaluate the sensitivity of the results to the aquifer depth are provided in Appendix C. The slope of the aquifer-lake boundary (AC) was modified for each model to match the measured beach profile for the monitoring event being simulated. The length of the model domain for the Main Beach east and west sites were adjusted to 140 m to correspond to the monitoring transects installed at these locations. Calculated spatially-varying hydraulic conductivities were used to parameterize the model domain. The estimated hydraulic conductivity values ranged from 1 - 21 m/d with a mean value of 8.06 m/d and standard deviation of 5 m/d. The Krumbien and Monk [1942] equation and particle size distributions used to calculate are provided in Appendix A. For all models the aquifer was assumed to be isotropic and the effective porosity (n_e) was set to 0.25.

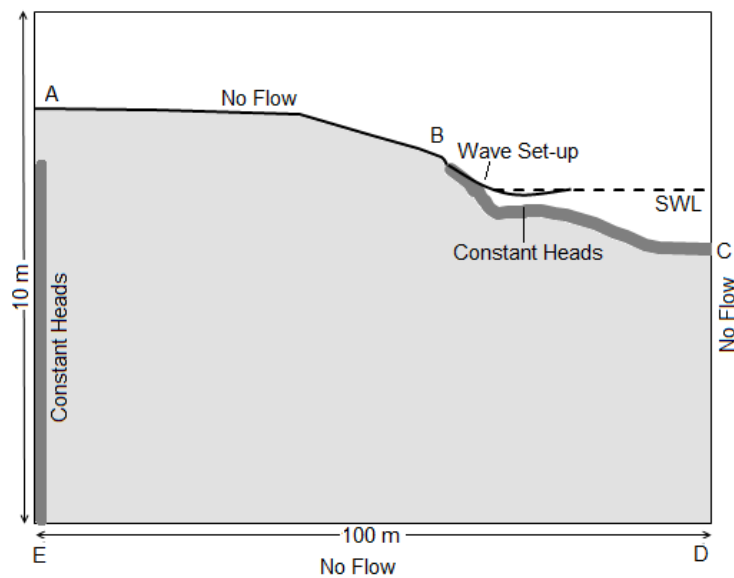


Figure 3.5: Numerical model domain of Little Beach including boundary conditions. The shaded region represents the active model (aquifer) region. The dark shaded regions depict the constant head cells along the landward boundary and SWI.

The boundary conditions for the groundwater flow equation were adjusted for each simulation based on the landward groundwater head, lake water level and wave conditions. A constant head condition was applied at the landward boundary (AE) with the head value corresponding to watertable measurements at the most landward well ($x = 0$ m). A no flow boundary was specified along the bottom of the domain (DE) to represent an impermeable aquifer base. The vertical offshore boundary (CD) was also set as no flow. This no flow conditions does not affect the flow simulations as the pore water flows and discharge are greatest around the shoreline and become negligible offshore. The upper boundary (AB) is a phreatic surface with negligible recharge.

Constant heads corresponding with the lake level and wave conditions were applied along the submerged aquifer-lake boundary (BC). Wave effects were included in the model by simulating the wave-induced onshore pressure gradient (termed wave set-up). Xin et al. [2010] showed that this phased-averaged approach of representing waves produces similar groundwater flows and water exchange rates as simulation of individual waves. An empirical equation developed and validated by Neilson [2009] was used to estimate the wave set-up profile that was applied as constant heads along the boundary BC. This equation is given as:

$$\eta = \frac{0.4H_{rms}}{1 + 10 \frac{D + \eta}{H_{rms}}} \quad (3.1)$$

where $\eta(x)$ is the elevation in head above the SWL due to wave set-up (m), H_{rms} is the root mean square wave height (m) and $D(x)$ is the still water depth measured from local SWI surface to still

water level (SWL) (m). H_{rms} was calculated from H_{sig} values (Figure 3.5) using equation [Nielson, 2009]:

$$H_{sig} = \frac{H_{rms}}{\sqrt{2}} \quad (3.2)$$

The SWL, H_{rms} and landward head values used to simulate each monitoring event are provided in Appendix C.

The size of grid cells were uniform with $\Delta x = 0.125$ m and $\Delta z = 0.1$ m. Grid discretization tests were performed to ensure that the model was converged and independent of the grid size. The observed field groundwater level measurements were used as initial heads for each model. Conservative particle tracking was performed in MATLAB using the steady state flows simulated by MODFLOW to determine the advective flow paths and corresponding transit times for groundwater discharging and lake water recirculating through the aquifer. Conservative particles were released along a vertical line at $x = 0$ m with 1 m vertical interval and along the SWI at 0.2 m interval. The time step used for the particle tracking was 0.1 d.

3.4 Results and discussion

3.4.1 Aqueous and sediment phase geochemistry at Little Beach

Dissolved As was elevated in the groundwater below the shoreline ($x = 68 - 77$ m) at Little Beach for all monitoring events with maximum As ranging from 0.022 mg/L (May 2012) to 0.033 mg/L (August 2011). The subsurface As distribution was similar for all sampling events. The distributions of select dissolved species, including As, are shown in Figure 3.6 for the May 2012 sampling event and in Appendix D for other sampling events. The pore water As concentrations observed were greater than the maximum As concentrations historically recorded

at the adjacent industrial site (0.020 mg/L) [CH2MHILL, 2009]. These concentrations also exceeded the Ontario standards for non-potable groundwater (Table 3, 0.019 mg/L) and industrial/commercial background site conditions (Table 1, 0.013 mg/L) [Ministry of the Environment, 2011].

From Figure 3.6 and 3.7, it can be seen that during the May 2012 monitoring event As was elevated at sampling ports ~1.4 – 2.4 m below the SWI ($z = -4.4 - -5.4$ m) around the shoreline (MLS 3 –5; $x = 68 -77$ m). Dissolved As sharply decreased at shallower depth with concentrations decreasing to below detection (0.0015 mg/L) ~ 1 m below the SWI ($z = -4$ m). Dissolved As concentrations were mostly below detection landward of the shoreline (MLS 6, 7 and 8) and further offshore (MLS 1). It is possible that a groundwater-derived As plume existed below the sampling zone but this could not be captured due to our limited water sampling depth (up to 2.5 m below ground surface).

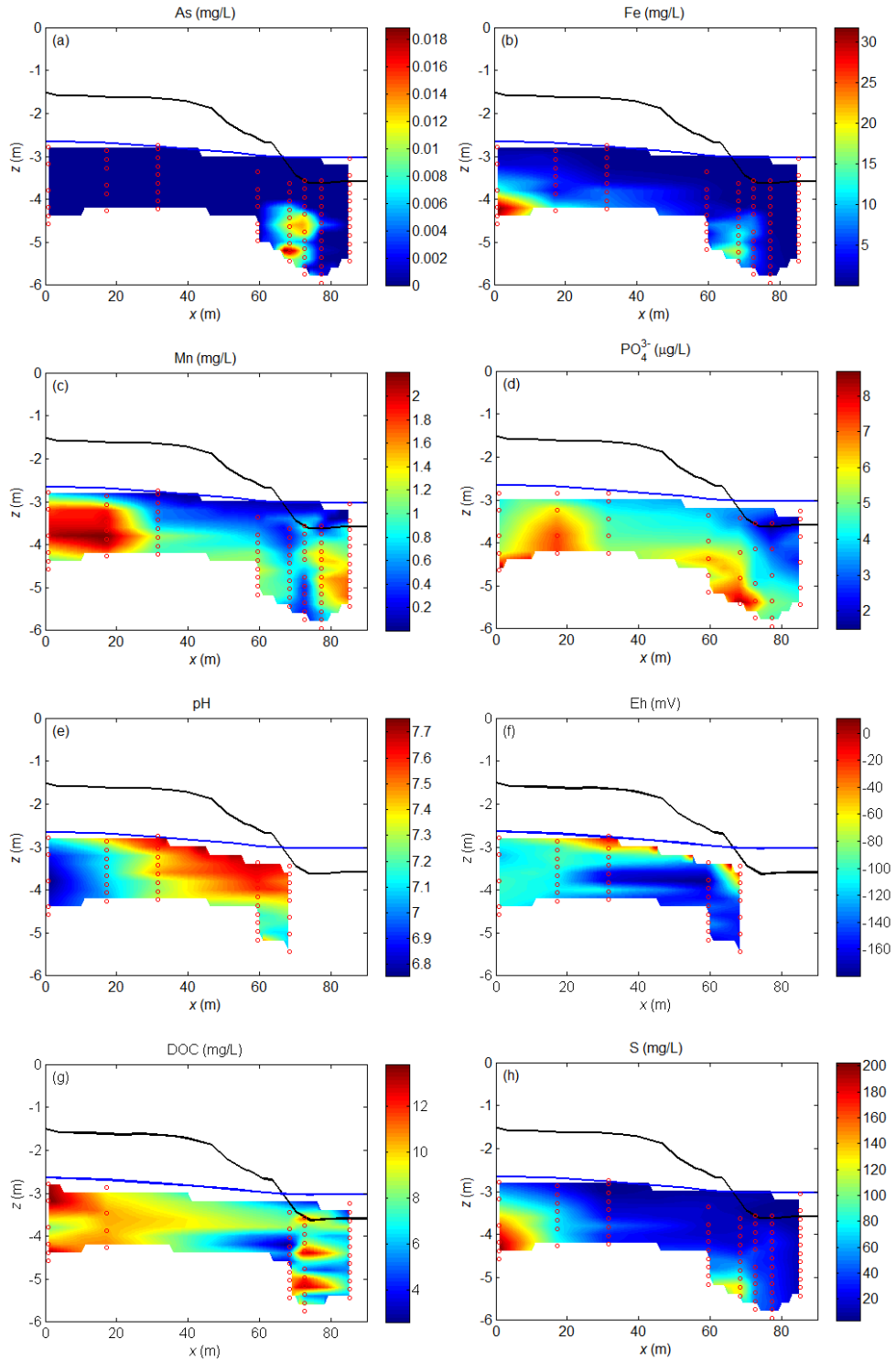


Figure 3.6: Distributions of dissolved (a) As (mg/L), (b) Fe (mg/L), (c) Mn (mg/L), (d) PO_4^{3-} ($\mu\text{g/L}$), (e) pH, (f) Eh (mV), (g) DOC (mg/L) and (i) S (mg/L) at Little Beach for May 2012 field sampling event. MLS ports where samples were collected are depicted by the red circles.

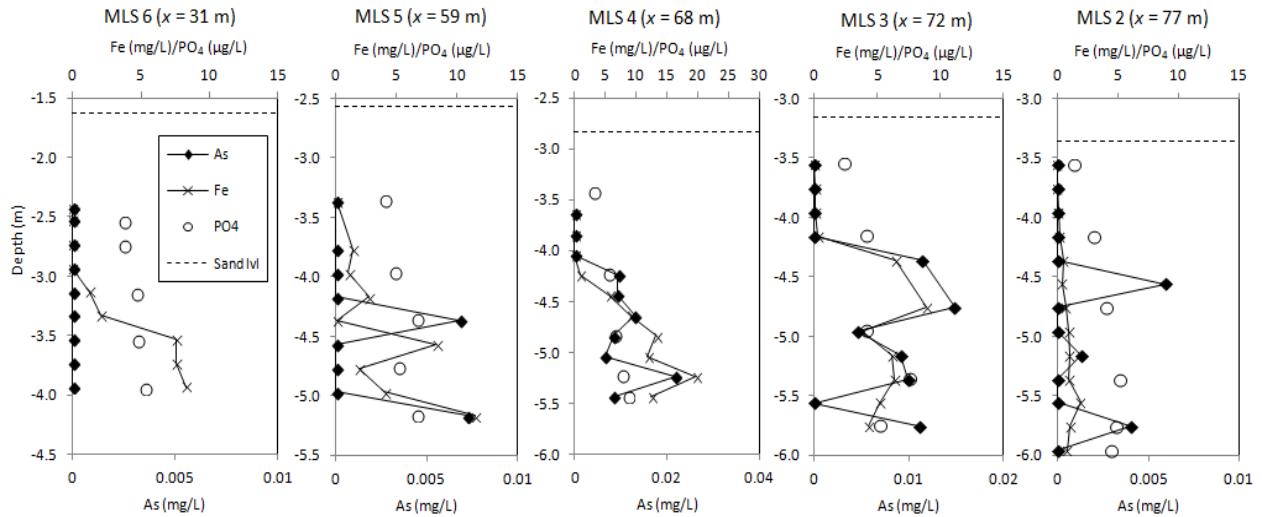


Figure 3.7: Dissolved As, Fe and PO₄³⁻ vertical profiles for MLS installed in close to the shoreline (MLS 6 - 2). Note the change in the concentration scale between subplots. The dashed horizontal lines depict the sand surface elevation.

The vertical dissolved As profiles near the shoreline (MLS 3, 4 and 5) match well with the Fe profiles with maxima for these species coinciding at $z = -5.24$ m at MLS 4 (Figure 3.6 and 2.7). Dissolved Fe decreased at shallow depth ($z \approx -4.25$ m) at MLS 3 and 4 and low concentrations were observed offshore (Fe < 2 mg/L at MLS 1 and 2). Elevated As was observed further offshore than Fe (Figure 3.7, MLS 2) and slightly shallower in the MLS 4 and 5 depth profiles. There is a discontinuity between As and Fe landward of the shoreline - maximum dissolved Fe (32 mg/L) was observed at the most landward MLS (MLS 8) with an Fe-rich plume extending along the bottom of the sampling zone ($z < 3.5$ m). Despite this discontinuity the correlation between Fe and As vertical profiles at MLS 3 - 5 indicates that As mobility is coupled to Fe redox cycling near the shoreline. This has behaviour has been observed previously in beach and lake sediments [Bone et al. 2006; Johnston et al., 2010, Couture et al., 2010]. The rapid attenuation of dissolved Fe and As at shallow depth may be due to the precipitation of Fe

(hydr)oxides and subsequent As adsorption as the groundwater becomes less reducing near the SWI [Smedley, et al., 2002]. By accumulating chemical species such as As that are strongly adsorbed to them, Fe hydr(oxides) can control the flux of chemical species to surface waters [Charette and Sholkovitz et al., 2002].

The concentrations of As and Fe in the sediment cores further support the existence of an ‘iron curtain’ barrier near the SWI at the shoreline. Step 1 and 2 of the selective extraction showed that sedimentary non-specific and specific bound As was low (Appendix E). Higher As concentrations were released by steps 3, 4 and particularly 5, indicating that sedimentary As was associated with amorphous (hydr)oxides, crystalline (hydr)oxides and residual mineral phases. Step 3 extracted concentrations show that the highest abundance of As associated with amorphous Fe hydr(oxides) occurred near the SWI at the shoreline with high As (up to 2.1 mg/kg) and Fe (up to 1500 mg/kg) was released from sediment at this location (Figure 3.8a). In addition to the high As and Fe content associated with amorphous solid phases below the shoreline, the step 3 and 4 extractions showed that amorphous and crystalline Fe hydr(oxides) and associated As were present through the beach aquifer (As = 0.9 – 3.2 mg/kg and Fe = 620 – 3430 mg/kg). As can be seen in Figure 3.8a and b, for step 3 and 4 there was a reasonable correlation between the sedimentary Fe and As concentrations for all sediments except the deepest samples from the landward cores ($x = 0$ m and $x = 17$ m). Arsenic associated with residual solid phases was significantly elevated for a number of sediment samples (Figure 3.8 and 3.9). The deepest sample analyzed from the core at the shoreline ($x = 67.5$ m, $z = -3.94$ m) had the highest As (26 mg/kg) associated with the residual phase. The residual Fe was also elevated at this location (3985 mg/L). Cores were only collected to a depth of 1.5 m below the watertable and so this location where maximum sedimentary Fe and As was detected in the

residual phases was ~ 0.3 m above where dissolved Fe and As decreased at shallower depth (Figure 3.8 and 3.6a). Compared to the As and Fe released from steps 3 and 4, there was poor correlation for the As and Fe content associated with residual mineral phases (Figure 3.9c).

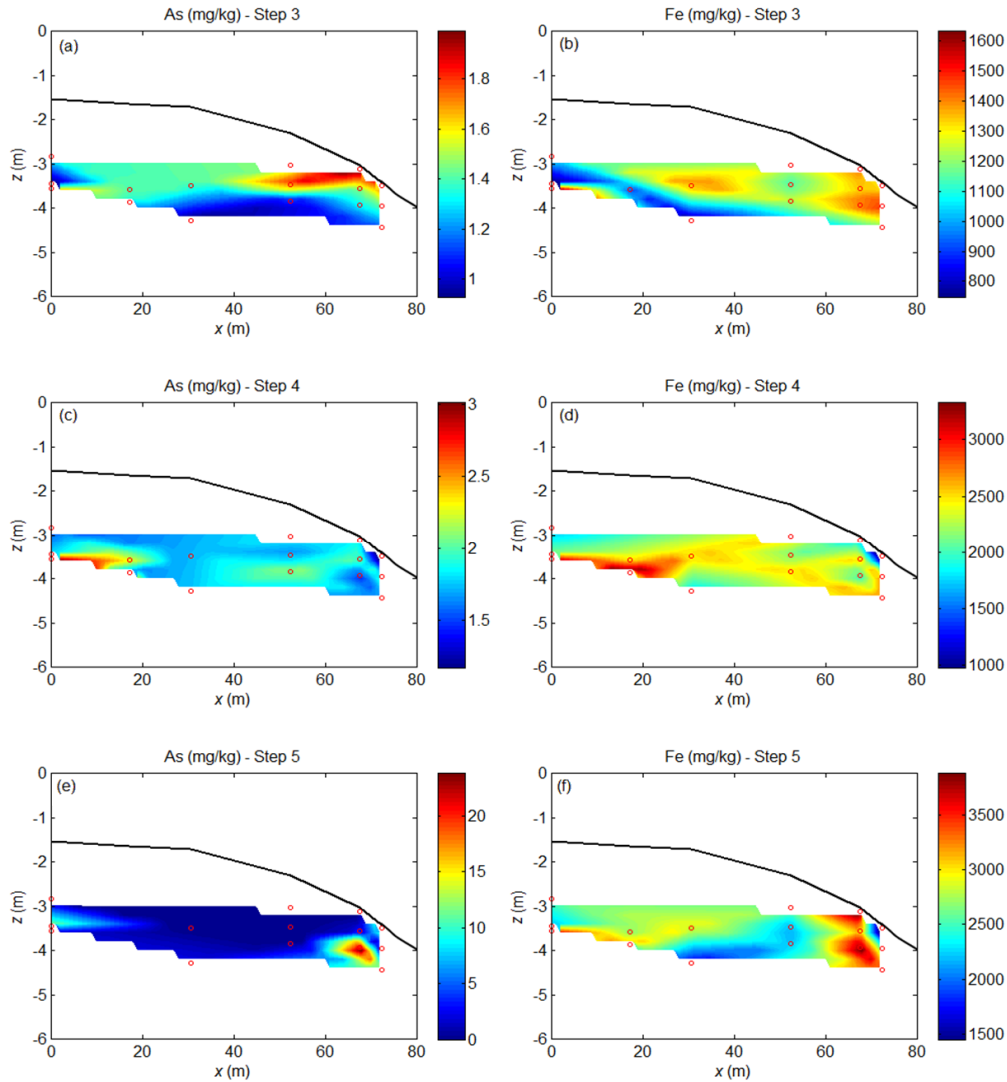


Figure 3.8: As and Fe extracted from sediment cores collected at Little Beach in June 2012: (a) As (mg/kg) extracted from step 3 (amorphous (hydr)oxides), (b) Fe (mg/kg) extracted from step 3 (amorphous (hydr)oxides), (c) As (mg/kg) extracted from step 4 (crystalline (hydr)oxides), (d) Fe (mg/kg) extracted from step 4 (crystalline (hydr)oxides), (e) As (mg/kg) from step 5 (residual mineral phases), and (f) Fe (mg/kg) extracted from step 5 (residual mineral phases).

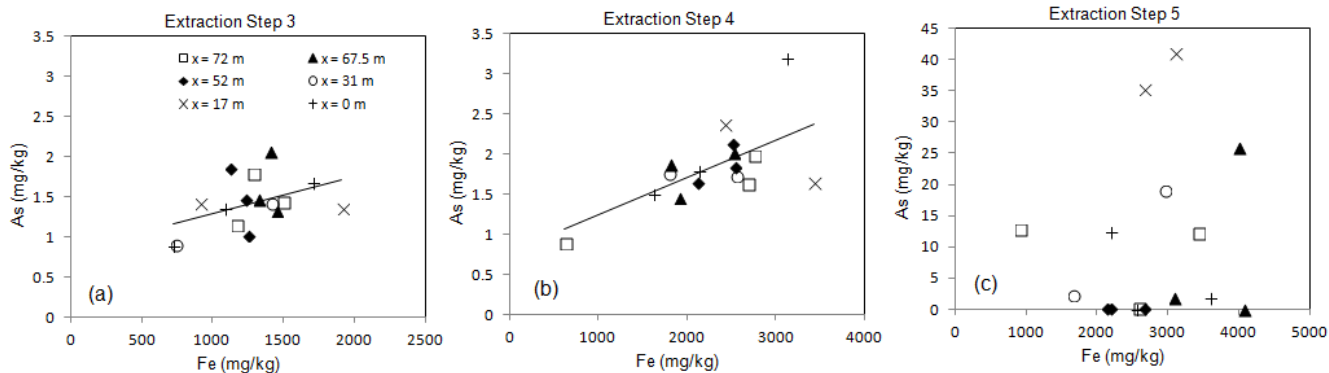


Figure 3.9: Sedimentary As versus Fe for extraction step 3 (amorphous (hydr)oxides), step 4 (crystalline (hydr)oxides) and step 5 (residual minerals). The different symbols denote the location of the sediment core from which the sample was collected. Note the change in concentration scales for (c).

The Eh measurements are consistent with precipitation of Fe hydr(oxides) and subsequent As sequestration at shallow depth below the shoreline (Figure 3.6f). The groundwater was less reducing at shallower depth ($z > -4.24$ m) near the shoreline these conditions would have promoted the precipitation of Fe hydr(oxides). Higher pH (7.5 - 7.8) was observed in the shallow pore water, particularly around the shoreline, compared to deeper in the aquifer ($z < -4.35$ m) and further landward (pH = 6.75 - 7). The elevated pH was likely associated with the recirculation of lake water through the beach sediments (average pH = 7.76 for lake water, see Section 3.4.3). At MLS 4, the increasing pH and Eh above $z = -4.24$ m coincided with a sharp decrease in dissolved As. We did not measure the oxidation state of As so we cannot conclusively determine the relative concentrations of As(III) and As(V), however thermodynamically the increase in pH and Eh may have oxidized As(III) to As(V). As(V) is more strongly adsorbed to Fe hydr(oxides) than As(III) at near-neutral pH [Smedley, et al., 2002]. A change in redox state from As(III) to As(V) may explain why As was rapidly sequestered at this depth ($z = -4.24$ m) compared with Fe

which decreased gradually between -4.84 to -4.24m. The pH gradient may also have changed the speciation of ions that compete with As for adsorption sites (e.g., HCO_3^- , P, Si) such that As preferentially adsorbed at this depth.

Some studies have shown that surface water can deliver high DOC to shallow pore waters leading to more reducing rather than oxic conditions near the SWI [e.g., Canavan et al., 2006]. Reducing conditions would drive reductive dissolution rather than precipitation of Fe (hydr)oxides near the SWI. However, measurements indicate that DOC is spatially heterogeneous through the beach aquifer with higher DOC levels at the most landward MLS (MLS 8, 14.2 mg/L) compared with the lake water (2.8 mg/L; Figure 3.6g). This suggests that the recirculation of lake water with high dissolved oxygen (up to ~10 mg/L) and low DOC relative to the landward groundwater end member leads to the more oxidized conditions in pore water below the shoreline - this would promote the precipitation of Fe hydr(oxides) and subsequent As accumulation.

At near-neutral pH, PO_4^{3-} behaves similarly to As(V) and is also strongly adsorbed to Fe (hydr)oxides [Smedley, et al., 2002]. While dissolved PO_4^{3-} is more uniformly distributed with depth across the entire sampling zone, suggesting a shallower and more extensive groundwater source, similar to As and Fe, dissolved PO_4^{3-} decreases with depth at MLS 3 and 4 near the shoreline and decreases offshore (Figure 3.6 and Figure 3.7). Fewer pore water samples were analyzed for PO_4^{3-} compared with As and Fe and this is the cause of some discrepancy between the species distribution contours and vertical profiles shown in Figure 3.6 and 3.7. Nevertheless the decrease in PO_4^{3-} with depth at MLS 3 and 4 near the shoreline indicates that adsorption to Fe hydr(oxides) may also be controlling the mobility of PO_4^{3-} at the site and preventing PO_4^{3-} release to the nearshore water.

Mn cycling also often affects the mobility of As and PO_4^{3-} as these species are powerfully adsorbed to Mn (hydr)oxides [Smedley, et al., 2002]. At Little Beach, the dissolved Mn distribution does not compare well with the As and PO_4^{3-} distributions suggesting that Mn cycling does not significantly affect the As and PO_4^{3-} geochemistry (Figure 3.6). This is likely because the Mn in the beach groundwater (maximum = 2.3 mg/L) is over an order of magnitude lower than the Fe (maximum = 32 mg/L). Similarly there was little correlation between the sedimentary As and Mn content and Mn sediment concentrations (ranged from 99 - 325 mg/kg, Appendix E) were significantly lower than Fe concentrations (ranged from 2832 - 8456 mg/kg). This implies Fe rather than Mn cycling controls the mobility of As (and other species such as PO_4^{3-}) at the site.

Fe and As geochemistry are also often influenced by S cycling [Couture et al., 2010]. In reducing conditions As can be immobilized by the precipitation of As-sulphide minerals or by attaching to Fe-sulphide minerals. Similar to Fe, dissolved S was elevated at the landward MLS (MLS 8) below $z = -5$ m (67 - 137 mg/L) and a S-rich plume was present along the base of the sampling zone. The speciation of S was not determined and therefore the S redox cycling between SO_4^{2-} and S^{2-} is unknown. Total sedimentary S at six locations in the beach aquifer are provided in Table 3.2. Sediment analyzed from the most landward sediment core had the highest abundance of total S (2900 mg/kg) this sample also had the highest total Fe (8456 mg/kg; sum of extraction steps). The similar dissolved and sedimentary Fe and S distributions suggest that the high Fe and S in the beach groundwater may be attributed to a mineralogical source such as dissolution of Fe-sulphide minerals. The low pH observed at the landward MLS (MLS 8) is consistent with Fe-sulphide dissolution as this process generates acidity. Similar to Fe, dissolved S concentrations decreased towards the shoreline however S was attenuated at greater depth and more landward

than for. Sedimentary total S concentrations were also high near the shoreline (400 mg/kg - 1100 mg/kg) with higher S content in the sediment at shallower depth (Table 3.2). The form of the solid phase S is unclear but as the vertical profiles of dissolved S do not correlate as well with the dissolved Fe and As below the shoreline (MLS 4 and 5) it is unlikely that the formation of sulphide minerals is responsible for the accumulation of As in the shallow sediments near the shoreline.

Table 3.3: Total S sedimentary concentrations for select samples at Little Beach.

x (m)	z (m)	Total S (mg/kg)
72	-3.5	1100
72	-4.4	600
68	-3.1	700
68	-3.94	400
17	-3.88	<200
0	7	2900

3.4.2 Aqueous phase geochemistry at Main Beach

Sampling was conducted at two shore-normal transects on Main Beach to determine if the elevated dissolved As observed at Little Beach was an isolated occurrence. Consistent with Little Beach, high dissolved As was observed in the groundwater below the shoreline and offshore at Main Beach with maximum As of 0.056 mg/L and 0.036 mg/L detected at the east and west transects, respectively. Dissolved As, Fe, S, PO_4^{3-} , pH and Eh distributions for the east transect are shown in Figure 3.10. The distributions for other chemical species and distributions for the west transect are provided in Appendix F. At both sites elevated dissolved As was observed at depth ~5 - 10 m lakeward of the shoreline with As concentrations sharply decreasing at shallower depth approximately 0.7 m below the SWI ($z = -3.8$ m at MLS 1 and 2). The As and Fe

vertical profiles displayed similar trends near the shoreline and offshore (MLS 1 and 2, Figure 3.10). This suggests that the Fe redox cycling also governs subsurface mobility of As and its potential discharge from the groundwater to the lake at the Main Beach sites. In contrast to Little Beach, Fe was only elevated lakeward of the shoreline and not at depth across the beach transect at the Main Beach sites. Deeper sampling is required to determine if Fe and As plumes are present below the sampling zone. Deeper Fe and As plumes may account for high dissolved As and Fe being detected at depth further offshore than at Little Beach. While the dissolved PO_4^{3-} distribution was relatively consistent with the As and Fe distributions at the west transect, elevated PO_4^{3-} (8.8 mg/L) was only detected in the shallow groundwater at the landward MLS at the east transect (MLS 6, $x = 0$ m; Figure 3.10). Eh was much higher in the shallow groundwater at the east transect and less reducing conditions may have led to PO_4^{3-} attenuation further landward. Dissolved S was significantly lower at both Main Beach sites compared with Little Beach (maximum S was 18 mg/L and 42 mg/L at the west and east transects, respectively, compared with 209 mg/L at Little Beach). In addition, the pH at the landward MLS and along the base of the sampling zone was higher at the Main Beach transects (8.3 - 9 at the east and west transects). As the groundwater end member pH was higher than the lake water pH it set up a reversed pH gradient compared to that observed at Little Beach. Despite these distinctively different geochemical conditions the occurrence of As and the importance of Fe redox cycling in controlling As mobility near the shoreline was consistent at all beach sites.

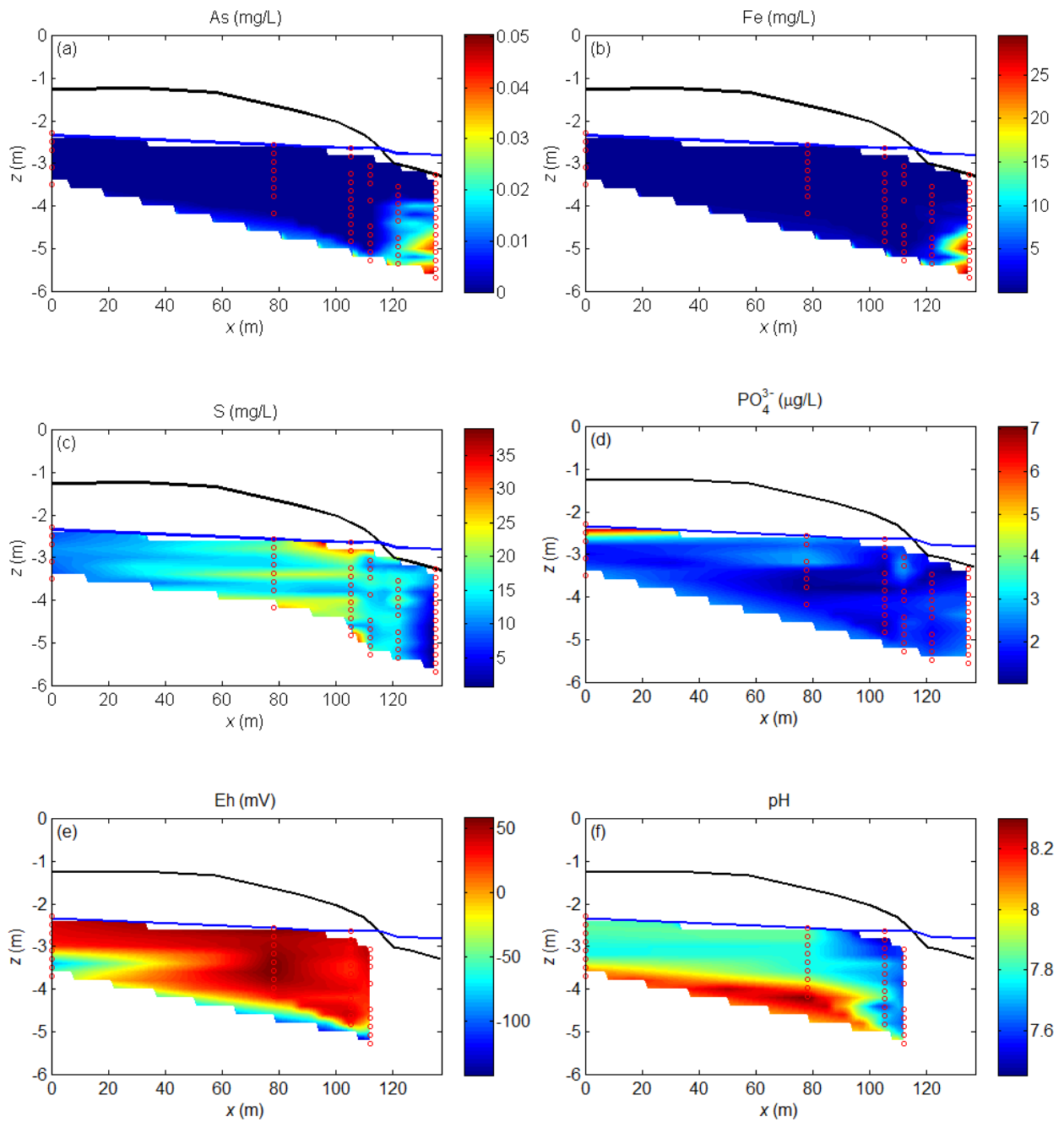


Figure 3.10: Contoured distributions of dissolved (a) As (mg/L), (b) Fe (mg/L), (c) S (mg/L), (d) PO_4^{3-} ($\mu\text{g/L}$), (e) pH and (f) Eh (mV) at Main Beach east transect for June 2012 monitoring event. MLS ports where samples were collected and analyzed are depicted by the red circles.

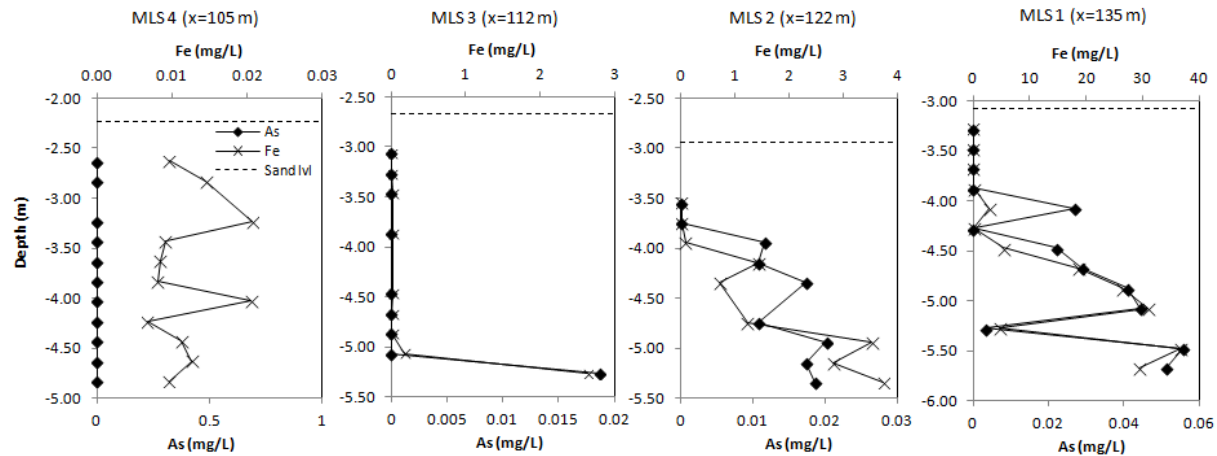


Figure 3.11: Dissolved As and Fe vertical profiles at Main Beach east transect for MLS installed in proximity to the shoreline and offshore (MLS 1-4). Note the change in the concentration scale between subplots. The dashed horizontal lines depict the sand surface elevation.

3.4.3 Groundwater flows and exchange rates

The beach groundwater flows are dynamic as they respond to a range of forcing including low (e.g., seasonal) and high (e.g., waves) frequency lake level fluctuations and variations in the landward hydraulic gradient. Water level measurements at Little Beach indicated that the groundwater flows, including the flow direction across the beach (landward versus lakeward) changed depending on the relative magnitude of the landward hydraulic gradient and wave conditions. For example, on 5 August 2011, a positive groundwater hydraulic gradient (0.0025) was observed from the landward well ($x = 0$ m) to the well just landward of the shoreline ($x = 64$ m), compared to 15 May 2012 when a negative gradient was observed (-0.0058; Figure 3.11). The SWL were lower on 15 May 2012 while landward water level is higher (-2.63 m and -3.04 m, respectively) compared with 5 August 2011 (-2.69 m and -2.83 m, respectively) and the offshore H_{sig} was greater (0.27 – 0.45 m on 15 May 2012 c.f. 0.11 - 0.22 m on August 5 2011). On both these sampling dates, wave set-up was evident from the stilling well measurements, but

only on 5 August 2011 did the wave set-up cause the water level at the shoreline ($z = -2.20$ m) to be higher than the landward groundwater level ($z = -2.25$ m).

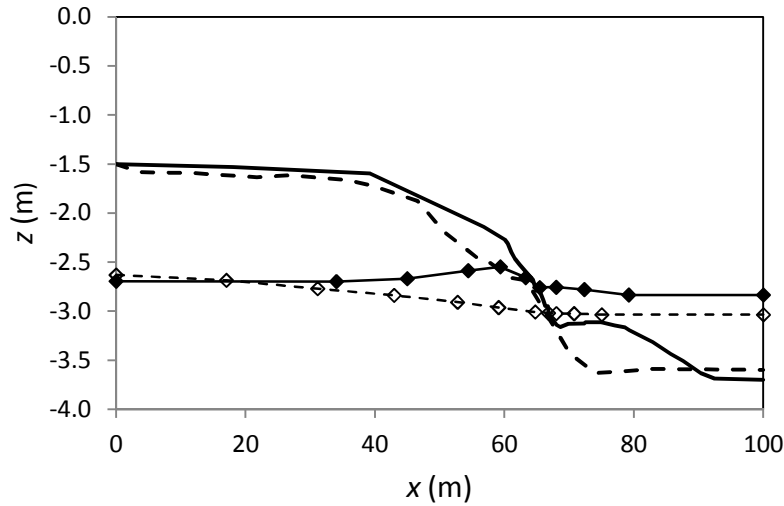


Figure 3.12: Water level and sand level measurements at Little Beach on 5 August 2011 and 15 May 2012. The water levels and sand levels for 5 August 2011 are depicted by \blacklozenge and the solid line (-). The water levels and sand levels for 15 May 2012 are depicted by \diamond and the dashed line (--).

The simulated steady-state groundwater flows for 5 August 2011 and 15 May 2012 are shown in Figure 3.12. Water levels and simulation results for other monitoring dates and for the Main Beach sites are provided in Appendix G. As expected the simulated groundwater flow direction was landward on 5 August 2011 and lakeward on 15 May 2012. At both times the model indicates that wave set-up would have led to the recirculation of lake water across the SWI from the wave set-up point to offshore ($x = 62.5 - 72.2$ m on 5 August 2011 and $x = 65 - 68$ m for 15 May 2012). The simulated flow recirculation cell was larger on 5 August 2011 with lake water recirculating to a depth of 4.35 m ($z = -6.85$ m) below the SWI compared to a depth of 0.9 m ($z = -3.9$ m) for 15 May 2012. Consistent with Xin et al. [2010], weaker wave-induced flow

circulations occur when the magnitude of the landward hydraulic gradient is strong relative to the wave set-up gradient (i.e., high groundwater discharge restricts the wave-induced flow circulations). Particle tracking revealed that while the steady-state recirculation flow paths are deep, particularly for 5 August (~4.35 m below SWI) the time for lake water to recirculate through the aquifer is slow. The average recirculation time was calculated to be 25 d for 5 August and 24 d for 15 May 2012. The wave conditions are constantly varying and therefore in reality infiltrating water would not penetrate to this depth before the wave intensity (and set-up) diminished. For both monitoring times, the simulated infiltration/exfiltration rates across the SWI around the shoreline and offshore compare well with the rates estimated from the manometer measurements (Figure 3.14) - infiltration occurred close to the wave set-up point and exfiltration decreased offshore. The good match for the simulated and measured exchange rates indicates that the steady state modeling approach simulates well the water exchange around the shoreline in response to the wave conditions and landward hydraulic gradient. For 5 August 2011, the total rate of lake water infiltrating into the aquifer was simulated to be 0.73 m²/d compared to only 0.08 m²/d for 15 May 2012. The total groundwater discharge rate was also greater for the 5 August 2012 simulation (0.73 m²/d c.f. 0.46 m²/d) due to significant increase of infiltration.

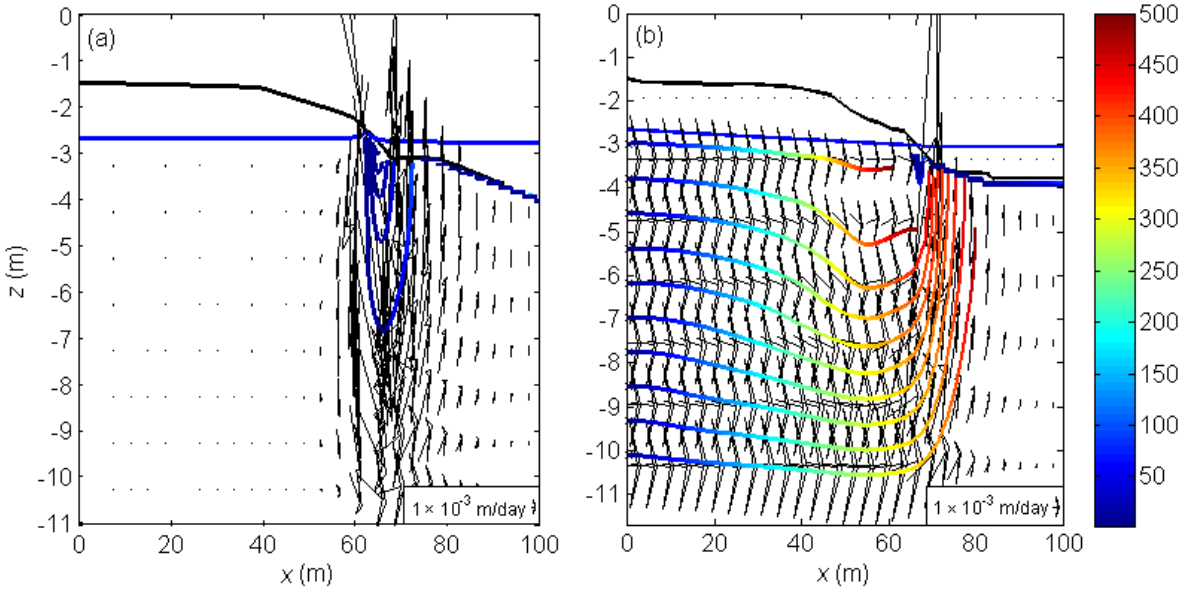


Figure 3.13: Simulated flow velocities and particle flow paths for (a) 5 August 2011 and (b) 15 May 2012 (Little Beach). The line colouring indicates the travel times (up to 500 d) as particles move along their flow path.

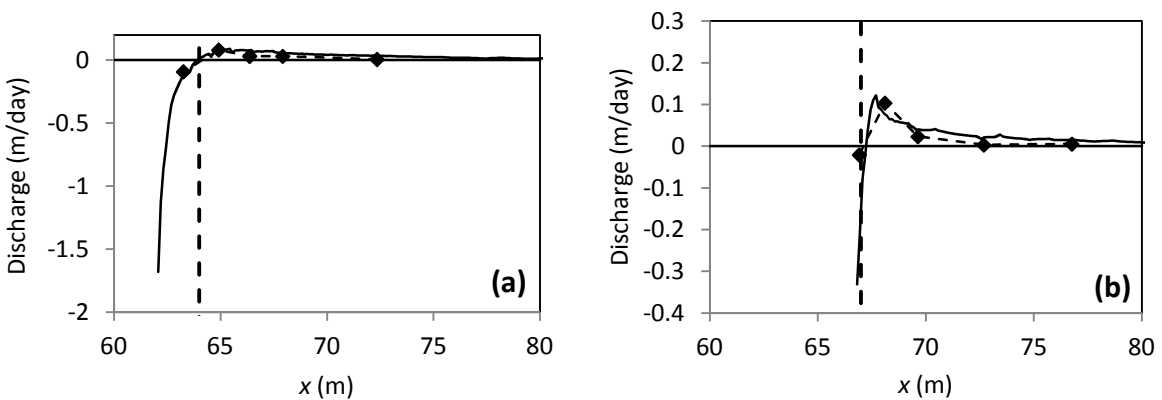


Figure 3.14: Observed (◆) and simulated (-) groundwater discharge along shore-normal transect at Little Beach for (a) 5 August 2011 and (b) 18 May 2012. The dashed vertical line indicates the location of the shoreline.

The flow paths (500 d only) for particles originating at the landward boundary can be seen in Figure 3.13. Due to the lakeward-directed hydraulic gradient transport of particles flows landward for 5 August 2011. On the other hand, the particles were transported lakeward for the 15 May 2012 conditions and the average transit time was 464 d. For this case, the particles were transported horizontally before migrating downwards around the wave-induced flow recirculations and discharging offshore of these circulations. The simulated flow paths for the land-derived particles compare well with the observed S and Fe plumes (Figure 3.6), except in the field Fe and S are sequestered to solid phases along their subsurface discharge pathway. The simulations illustrate the importance of waves on the subsurface discharge flow paths in addition to driving significant recirculation of lake water across the SWI. The temporal variability in the wave conditions and landward hydraulic gradient causes complex flows and geochemical conditions in the beach aquifer. The subsurface flows were slow as indicated by the long transit times – this provides significant time for solid-aqueous phase interactions. The mixing of recirculating lake water with the discharging groundwater below the shoreline would have set up the distinct redox and pH gradients observed below the shoreline, and this in turn controls the distribution of chemical species and their movement from the groundwater to the lake. The implications for chemical fluxes to the lake are discussed in Section 3.6.

3.5 Source of As in beach groundwater

The elevated dissolved As consistently observed in the groundwater below the shoreline at Little Beach and Main Beach was, as previously stated, higher than concentrations previously detected at the adjacent brownfield site (0.05 mg/L) and Ontario standards for non-potable groundwater [Ministry of the Environment, 2011]. The occurrence of As below the shoreline at the Main Beach sites - not directly hydraulically connected with the East Headland – suggests that the

brownfield site may not be source of As in the beach groundwater. Further, while Little Beach underwent a beach nourishment program using sediment from Kettle Creek (possibly contaminated), this nourishment program not occur on Main Beach – again implying that this also is not the As source.

While the concentrations of As observed are often associated with mining and industrial activities, elevated As can also be attributed to naturally occurring geogenic processes. In fact, high concentrations of As in groundwater have previously been recorded in aquifers in southwestern Ontario [MNDM, 2012]. The acidity and high dissolved Fe and S observed at the landward MLS at Little Beach suggest that As may have been released by the dissolution of sulphide minerals (e.g., pyrite and arsenopyrite) [Smedley and Kinniburgh, 2002]. While not tested it is possible that minerals may be naturally occurring in the unconsolidated aquifer at the sites. While As was not observed at the landward MLS at any sites it may have been present below our sampling zone. Further field investigation is required to determine if the source of As is geogenic. Other potential As sources include (i) air borne deposition from the industrial site, (ii) historical application of As-containing fertilizers/pesticides in the surrounding agricultural region and (iii) recirculation of lake water with low As concentrations through the sediments and subsequent accumulation to Fe hydr(oxides). Further study is required to determine the regional extent of the elevated As and its accumulation along the shores of the Great Lakes. If the As is naturally occurring and widespread it may have important implications for As biogeochemical cycling in the Great Lakes.

3.6 Implications for As and chemical fluxes to the Great Lakes

This study has revealed that As mobility in the nearshore aquifer and subsequent discharge to the lake is strongly linked with Fe redox cycling at the studied field sites. The redox conditions near

the SWI are controlled by the recirculation of lake water through the nearshore sediments. While this recirculation was driven primarily by waves, the groundwater flows and infiltration/exfiltration across the SWI was complex due to varying wave intensity, lake levels and the landward groundwater hydraulic gradient. To our knowledge, this study is the first to demonstrate that, as can occur in marine environments, an ‘iron curtain’ may form below the SWI at freshwater shorelines. This layer of Fe hydr(oxides) may control the discharge of chemical species that are strongly adsorbed to these minerals. While this study focused on As, other species such as PO_4^{3-} are also powerfully adsorbed to Fe hydr(oxides). Phosphorous inputs into the Great Lakes are of considerable concern with elevated P implicated in outbreaks of harmful algae blooms. Where present this ‘iron curtain’ barrier may accumulate P in the nearshore sediments and prevent its release from the groundwater to nearshore water.

While the field results indicate that the presence of Fe hydr(oxides) accumulates chemical species such as As, it remains unclear under what conditions these accumulated species may desorb and subsequently discharge to nearshore waters. The nearshore groundwater flow dynamics are complex and certain hydraulic changes such as seasonal changes in the lake water level or an episodic wave event may stimulate the release of adsorbed species. Also, for example, an increase in organic matter availability along the shoreline (e.g., due to algae build-up at the shoreline) could promote reductive dissolution of Fe hydr(oxides) in shallow sediments and the remobilization of As and other adsorbed species. Additional research is needed to determine to conditions that control the remobilization of species and their potential release to nearshore waters.

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CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

This thesis has investigated the transport and mobility of As in a nearshore aquifer and its potential discharge to Lake Erie. Field studies were conducted along transects at Little Beach and Main Beach at Port Stanley, Ontario. Little Beach is located nearby to the East Headland of the Port Stanley industrial harbour where elevated As concentrations (0.02 mg/L) have been recorded [CH2MHILL, 2009]. The Main Beach field sites were located on the opposite site of Kettle Creek and not directly hydraulically connected to the areas where there was As contamination at the industrial site. Field investigations revealed elevated dissolved As concentrations (up to 0.056 mg/L) below the shoreline at all field sites. Distributions of species in aqueous and sedimentary phases showed that the As mobility in the nearshore aquifer and subsequent discharge to the lake was strongly linked with Fe redox cycling. While dissolved As and Fe concentrations were elevated approximately 1-2 m below the shoreline at all sites concentrations sharply decreased at shallower depth towards the sediment-water interface (SWI). Analysis of sediment cores via a five-step selective extraction procedure indicated that the attenuation of As and Fe at shallow depth (i.e., prior to discharge to the lake) is because the groundwater becomes less reducing and this leads to Fe hydr(oxides) precipitation and the subsequent adsorption of As to this solid phase. To our knowledge, this study is the first to demonstrate that, as can occur in marine environments, a Fe hydr(oxide) layer (also termed an ‘iron curtain’) may form below the SWI at freshwater shorelines. This ‘iron curtain’ may strongly impact the fate of As and other groundwater-derived species discharging to the

nearshore waters of the Great Lakes. Phosphate shows a similar distribution to As and Fe near the shoreline at Little Beach; this suggests that this iron curtain barrier may also control phosphorous loading to the lakes.

The redox gradient near the SWI that led to the formation of the Fe hydr(oxides) was set up by the recirculation of lake water through the nearshore sediments. Measurements of the vertical hydraulic gradients around the shoreline combined with steady state groundwater flow modeling showed that this recirculation was driven primarily by waves. However, the groundwater flows and infiltration/exfiltration across the SWI are very complex and are influenced by the varying wave intensity, lake levels and the landward groundwater hydraulic gradient. Numerical simulations for the different monitoring events show that the landward groundwater level, lake water level and wave conditions control the water exchange across the SWI. The direction of flow (lakeward vs. landward) in the nearshore aquifer was seen to reverse depending on the relative water levels and wave conditions.

The source of the elevated dissolved As in the nearshore groundwater at the field sites remains unknown. The Main Beach sites are not hydraulically connected with the industrial site and also never underwent a beach nourishment program as occurred at Little Beach. Therefore the occurrence of elevated As at Main Beach suggest that the As may be from a naturally-occurring geogenic source. The acidity and high dissolved Fe and S observed at the landward MLS at Little Beach suggest that As may be released by the dissolution of sulphide minerals (e.g., pyrite and arsenopyrite) [Smedley and Kinniburgh, 2002]. Other potential As sources include (i) air borne deposition from the industrial site, (ii) historical application of As-containing fertilizers/pesticides in the surrounding agricultural region and (iii) recirculation of lake water

with low As concentrations through the sediments and subsequent accumulation to Fe hydr(oxides).

4.2 Recommendations

This thesis has provided important insight into the factors affecting the transport and fate of groundwater-derived chemical species, in particular As, in a near-shore freshwater aquifer and the potential discharge of these species to the Great Lakes. The persistent occurrence of elevated dissolved As below the shoreline at the three beach sites investigated raises questions regarding the widespread occurrence of As in nearshore sediment and groundwater along the shores of the Great Lakes. If this phenomenon is naturally-occurring and widespread it may represent a significant As sink and have important implications for As cycling in the Great Lakes. The aqueous and sedimentary phase chemistry at the field sites indicated that As was trapped below the shoreline by an ‘iron curtain’ (Fe (hydr)oxide) layer. This ‘iron curtain’ may impact the mobility of other chemicals at these field sites and also, if widely occurring, could affect the mobility and discharge of other chemical species such as PO_4^{3-} all along the shores of the Great Lakes. It is recommended that additional field work be performed at other beach sites on the Great Lakes to determine the occurrence and role of the ‘iron curtain’ layer along the freshwater shorelines and also the prevalence of elevated As in nearshore groundwater.

Recommendations for enhancing understanding of the source of As and geochemical conditions controlling the mobility of As (and other chemical species) in the nearshore groundwater are outlined below.

- Analysis of redox species, particularly As(III)/As(V) and S(II)/S(IV) would provide improved understanding of the redox cycling processes, in particular the linkages between the S and Fe cycling and subsequent affect on As mobility in the nearshore groundwater.
- Extension of the water sampling zone deeper and further landward and offshore is needed to determine if there is a deeper landward source of As at the field sites.
- Deeper sediment cores are required to provide As, Fe and S sedimentary concentrations in areas where the groundwater concentrations were greatest below the shoreline and at the landward boundary.

Finally the interacting flow and geochemical process controlling As mobility at the field sites are extremely complex. Individual steady state groundwater flow models were developed in this thesis to provide insight into the instantaneous flow patterns. However, these steady state flow simulations are not entirely realistic because the hydraulic gradient and wave conditions are continuously varying. Transit groundwater flow simulations incorporating this variability would provide more accurate representation of the dynamic beach groundwater flows. In addition, it is recommended that the field data be used to develop a numerical reactive transport model capable of simulating the transport and mobility of As in a nearshore aquifer. A validated model would be an extremely valuable tool to identify the conditions that may lead to release of As from sediments and the subsequent discharge of As to the nearshore waters. For example, this tool could be used to evaluate if lake water level variations, wave conditions and episodic input of organic-rich lake water would affect the release of As to the nearshore waters.

4.3 References

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Appendix A – Grain Size Distribution and Hydraulic Conductivity Estimation

Sediment samples were collected along the shore-normal transect at Little Beach in August 2011. Particle size analysis was performed on all samples and the hydraulic conductivities were estimated with Krumbein and Monks [1942] formula. This formula is given as:

$$K = \frac{k\rho g}{\mu} \quad (\text{A-1})$$

where K is hydraulic conductivity [L/T], ρ is density [M/L³], g is gravity [L/T²], μ is viscosity [M/LT] and k is the property of the medium calculated by:

$$k = 760d_{50}^2 e^{-1.31\sigma} \quad (\text{A-2})$$

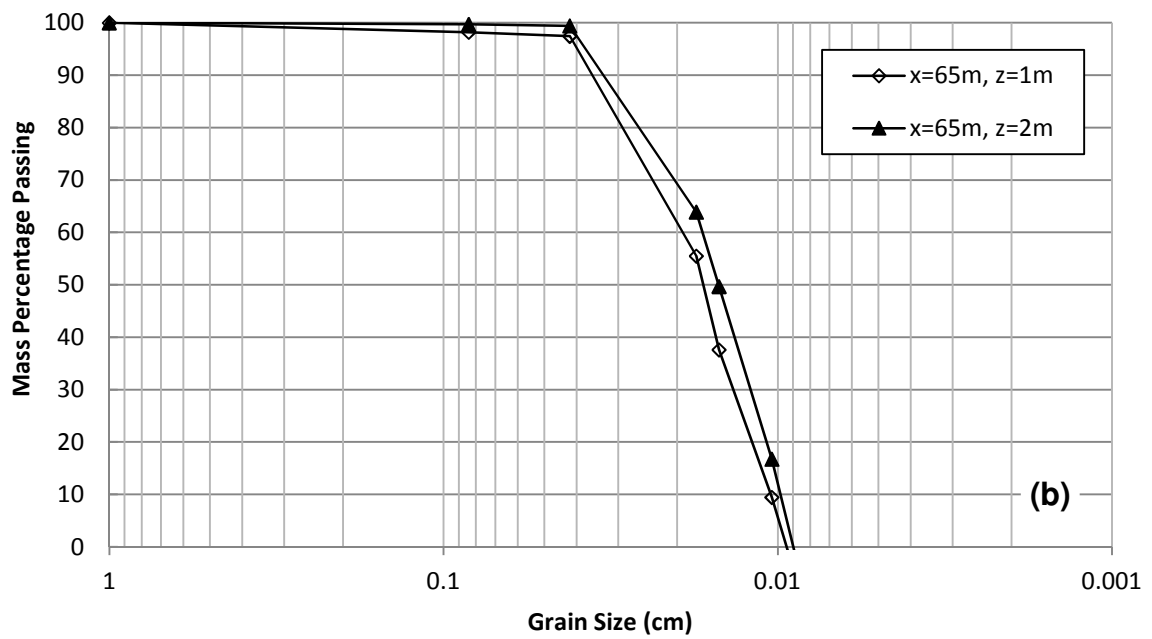
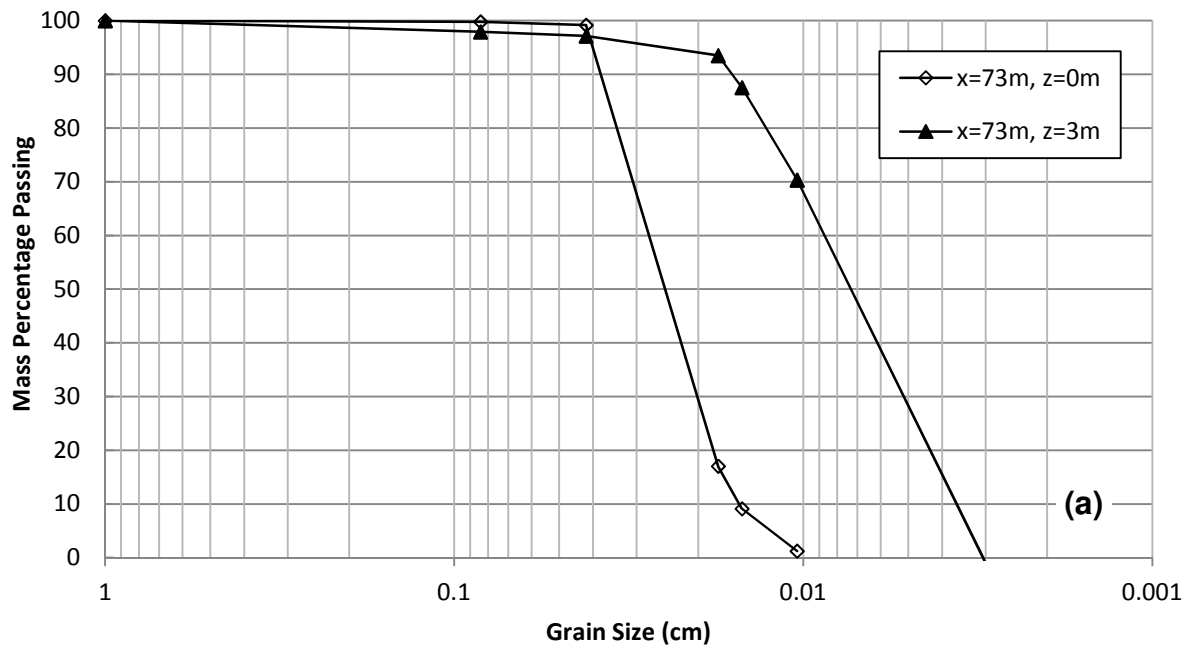
where d_{50} is the particle size having 50% passing [L] and σ is the standard deviation of particle size distribution.

Table A1: Parameters for Krumbien and Monks [1942] formula.

Parameters	Values
ρ , density (g/cm ³)	0.9982 at 20°C
g , gravity (cm/sec ²)	980
μ , viscosity (g/(cm.sec))	0.01 at 20°C

Table A2: Particle size distribution and estimated hydraulic conductivities.

Well	x (m)	z (m)	Particle Size Passing					K (m/d)
			d95	d5	d84	d16	d50	
MLS1	73	0m	0.40	0.14	0.36	0.17	0.25	20.58
MLS1	73	3m	0.25	0.04	0.14	0.04	0.07	1.09
MLS2	65	1m	0.40	0.10	0.33	0.11	0.16	6.49
MLS2	65	2m	0.37	0.09	0.30	0.10	0.15	5.75
MLS3	54	0.3m	0.40	0.10	0.35	0.14	0.21	12.33
MLS3	54	1.2m	0.36	0.10	0.29	0.11	0.16	6.58
MLS3	54	2.5m	0.31	0.07	0.18	0.08	0.12	3.67
MLS4	34	0.3m	0.37	0.10	0.32	0.12	0.17	7.93
MLS4	34	3m	0.36	0.10	0.32	0.12	0.17	8.08
average (m/d)								8.06
standard deviation (m/d)								5.30
min (m/d)								1.09
max (m/d)								20.58



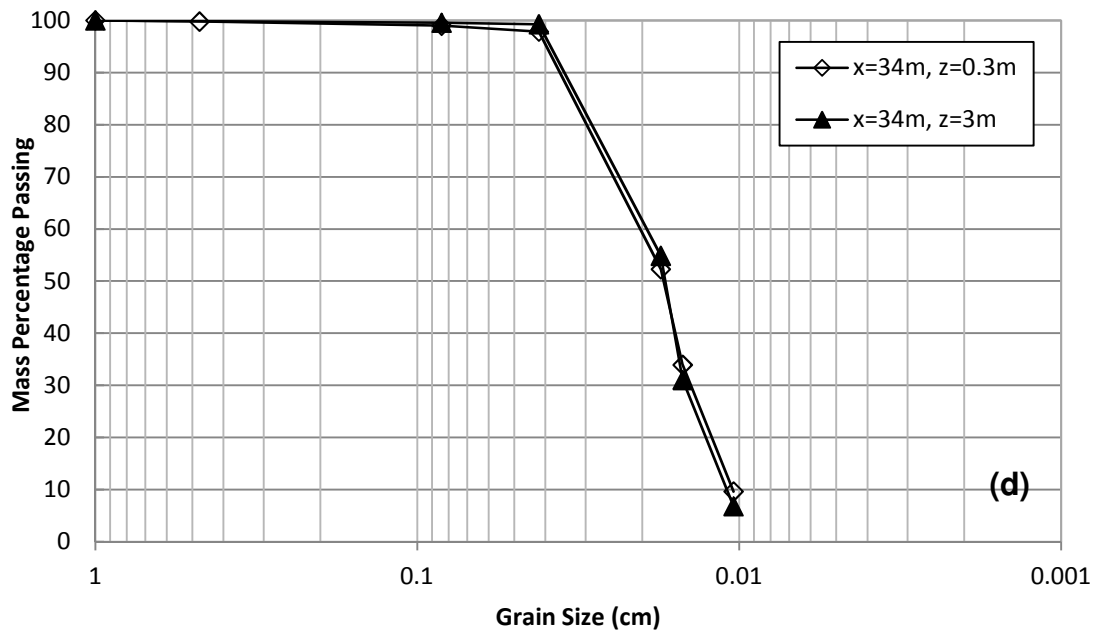
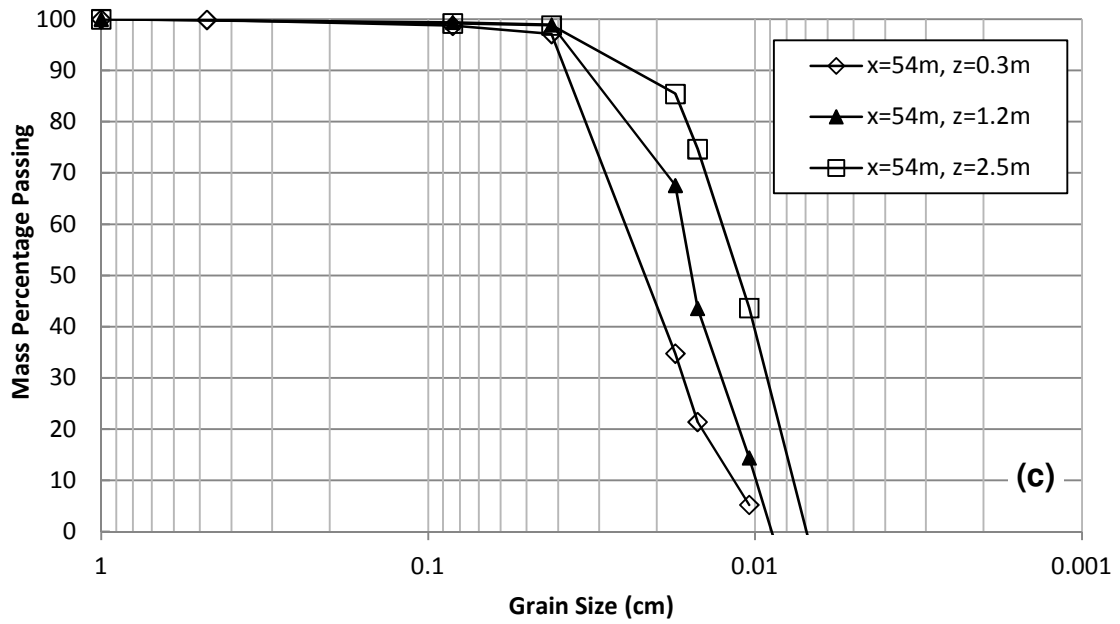


Figure A1.1: Grain size distribution for sediment samples collected from Little Beach in August 2011: (a) MLS 1, (b) MLS 2. (c) MLS 3 and (d) MLS 4.

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Appendix B – Governing Equation for MODFLOW-2005

MODFLOW-2005 was used to simulate groundwater flow in an unconfined beach aquifer and water exchange between the aquifer and Lake Erie. MODFLOW is a finite-difference saturated groundwater flow model developed by the U.S. Geological Survey [Harbaug, 2005]. Groundwater flow is described by:

$$\frac{\partial}{\partial x} \left(K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial h}{\partial z} \right) + W = S_s \frac{\partial h}{\partial t} \quad (\text{B1})$$

where K_{xx} , K_{yy} , and K_{zz} are the hydraulic conductivities [L/T] along the x , y , and z coordinate, h is the head [L], W is the volumetric flux per unit volume representing sources or sink of water [T^{-1}], S_s is the specific storage of the porous media [L^{-1}], and t is time [T] [Harbaug, 2005].

References

Harbaug, A. W. (2005). MODFLOW-2005, The U.S. Geological Survey modular groundwater model – the groundwater-water flow process, *U.S. Geological Survey Techniques and Method*, 6-A16.

Appendix C – Model input parameters and sensitivity analyses

C.1 Numerical model input parameters

Input parameters used in the two-dimensional steady-state groundwater models simulating flow conditions at Little Beach (August 2011, December, 2011, and May 2012), Main Beach East (June 2012) and Main Beach West (August 2012) are provided in Table C1.

Table C1: Inputs for defining lake and landward boundary conditions for each monitoring event.

	5 Aug 11	8 Dec 11	15 May 12	21 Jun 12	02 Aug 12
H_{rms} (m)	0.582	0.400 ¹	0.110	0.321	0.120
SWL (m)	-2.785	-3.387	-3.060	-2.819	-3.407
Inland head (m)	-2.697	-1.908	-2.659	-2.347	-3.135

1 – Estimated H_{rms} applied because H_{sig} was not available from wave buoy.

C.2 Influence of aquifer depth and grid discretization

The model for Little Beach May 2012 was run with various aquifer depths including: 6 m, 10 m and 15 m. The models with aquifer depth of 10 m and 15 m were also run with $\Delta x = 0.25$ m and 0.125 m to ensure the solution was independent of the grid discretization. Similar flow patterns were observed for the models with different grid discretization (Figure C1). The average transit times for particles originating at the landward boundary to discharge and recirculating particles changes as the aquifer depth changes. The transit times are also slightly greater for the models with finer grid discretization. The simulated discharge pattern changed between different Δx discretization but remained relatively similar between the

simulations with different aquifer depth (Figure C2). In both models with aquifer depth 10 and 15 the infiltration/exfiltration is higher in the model with $\Delta x = 0.125$ m compare to $\Delta x = 0.25$ m.

Table C2: Calculated average transit times and total infiltration and exfiltration rates.

	Avg. Recirculation Time (d)	Avg. Transit Time (d)	Total Infiltration (m ² /d)	Total Exfiltration (m ² /d)
Depth = 6 m, $\Delta x = 0.25$ m	34.5	509	0.08	0.28
Depth = 10 m, $\Delta x = 0.25$ m	27	470	0.07	0.45
Depth = 10 m, $\Delta x = 0.125$ m	24	464	0.08	0.46
Depth = 15 m, $\Delta x = 0.25$ m	20.75	517	0.06	0.67
Depth = 15 m, $\Delta x = 0.125$ m	17.7	500	0.07	0.60

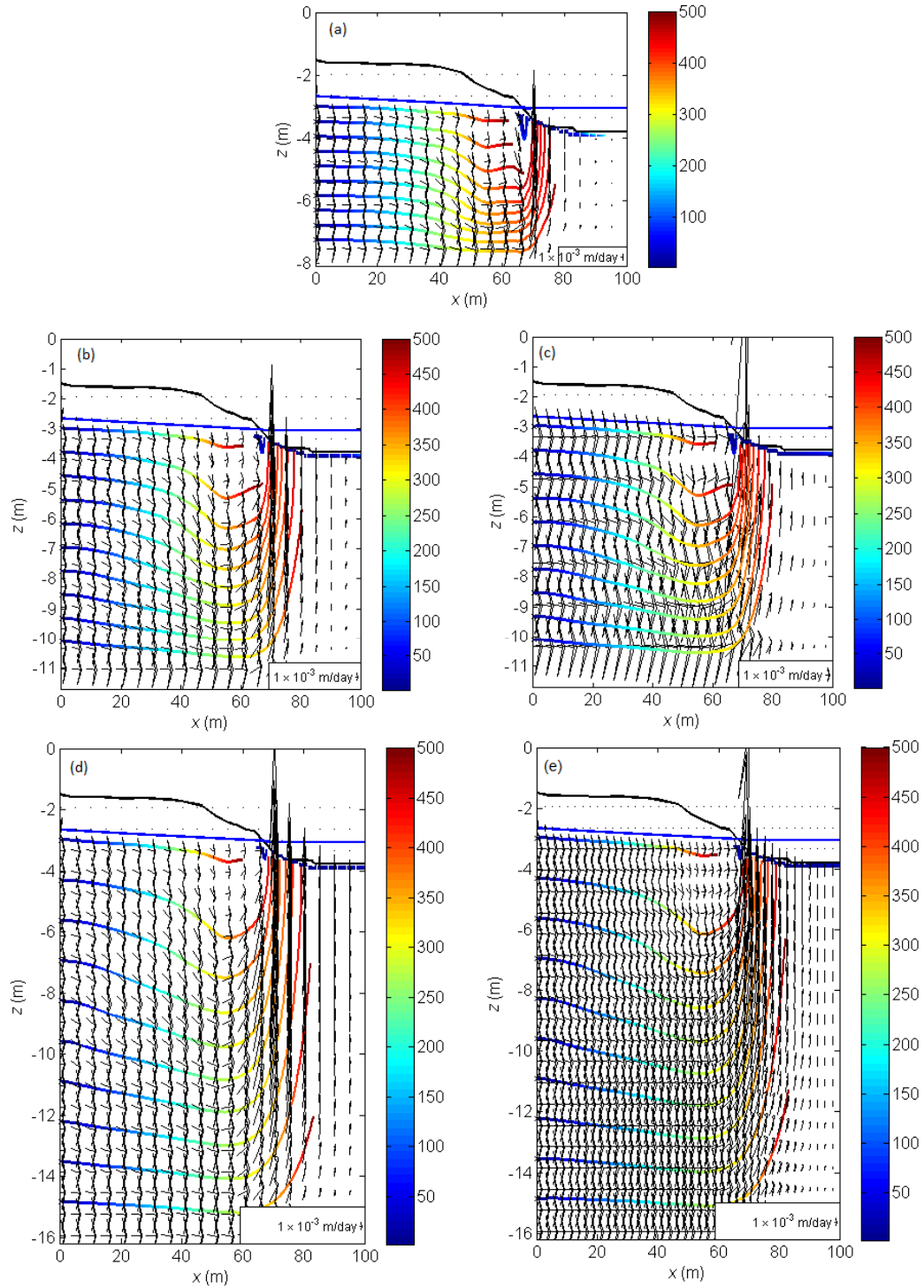


Figure C1: Simulation results for models with different aquifer depth and grid discretization:

a) 6 m depth model domain and $\Delta x = 0.25$ m, b) 10 m depth and $\Delta x = 0.25$ m, c) 10 m depth and $\Delta x = 0.125$ m, d) 15 m depth and $\Delta x = 0.25$ m, and e) 15 m depth and $\Delta x = 0.125$ m.

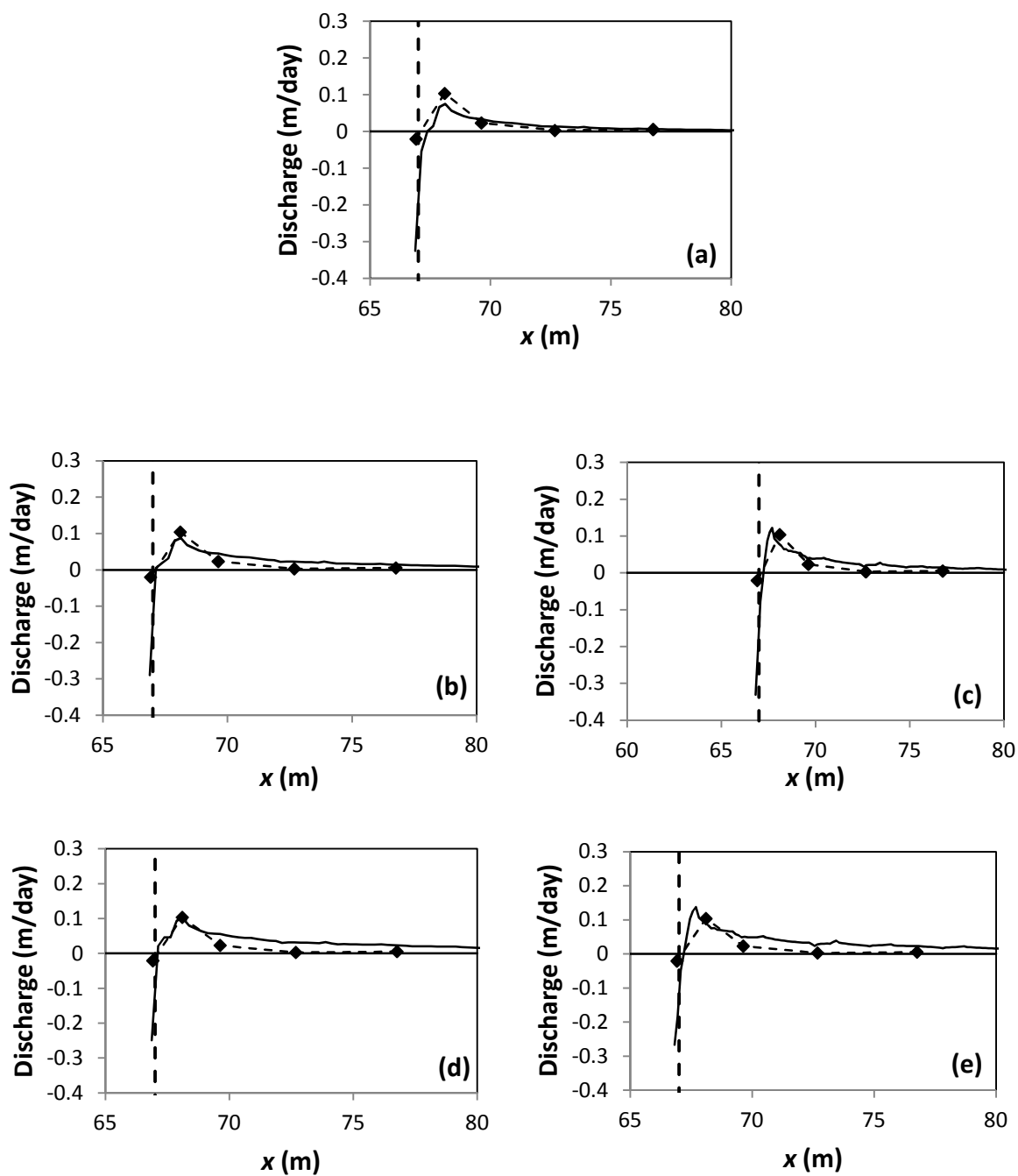


Figure C2: Simulated discharge from models with different grid discretization and aquifer depth including: a) 6 m depth model domain and $\Delta x = 0.25$ m, b) 10 m depth and $\Delta x = 0.25$ m, c) 10 m depth and $\Delta x = 0.125$ m, d) 15 m depth and $\Delta x = 0.25$ m, and e) 15 m depth and $\Delta x = 0.125$ m.

Appendix D – Pore water chemistry distributions at Little Beach

D.1 Pore water chemistries at Little Beach from 3 – 5 August 2011

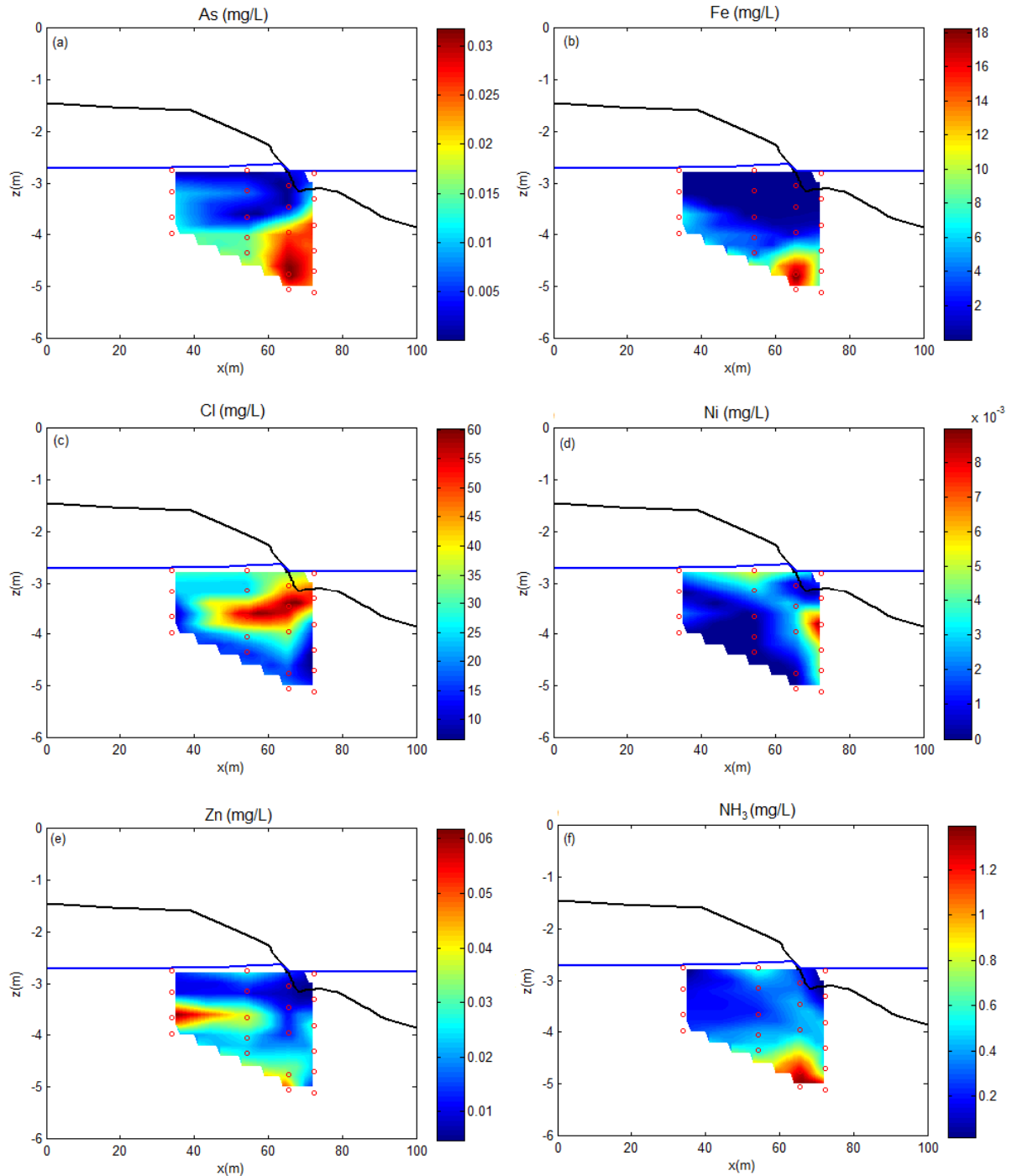
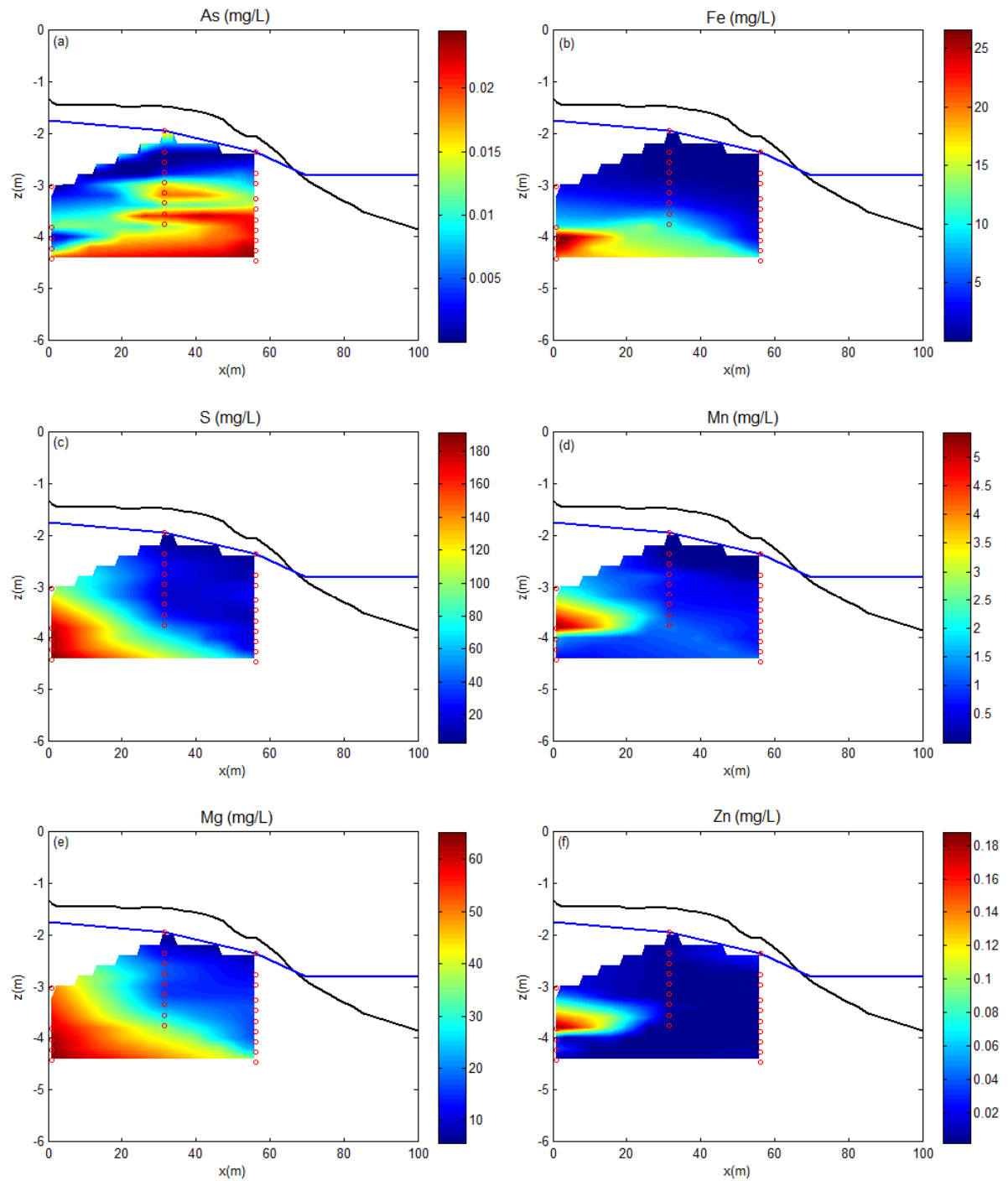


Figure D1: Groundwater distribution of dissolved: (a) As (mg/L), (b) Fe, (c) Cl, (d) Ni, (e) Zn, (f) NH_3 at Little Beach for 3-5 August 2011.

D.2 Pore water chemistries at Little Beach for 8 December 2011



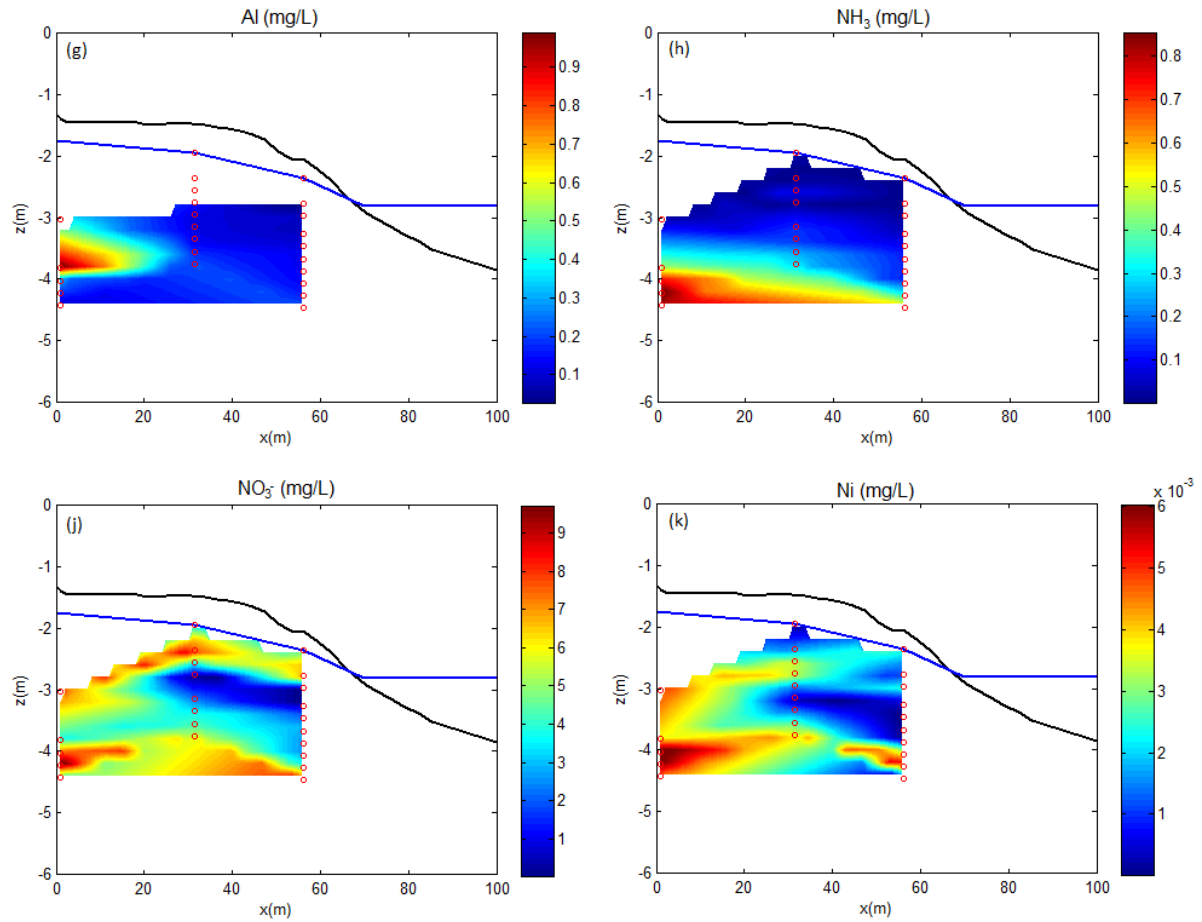
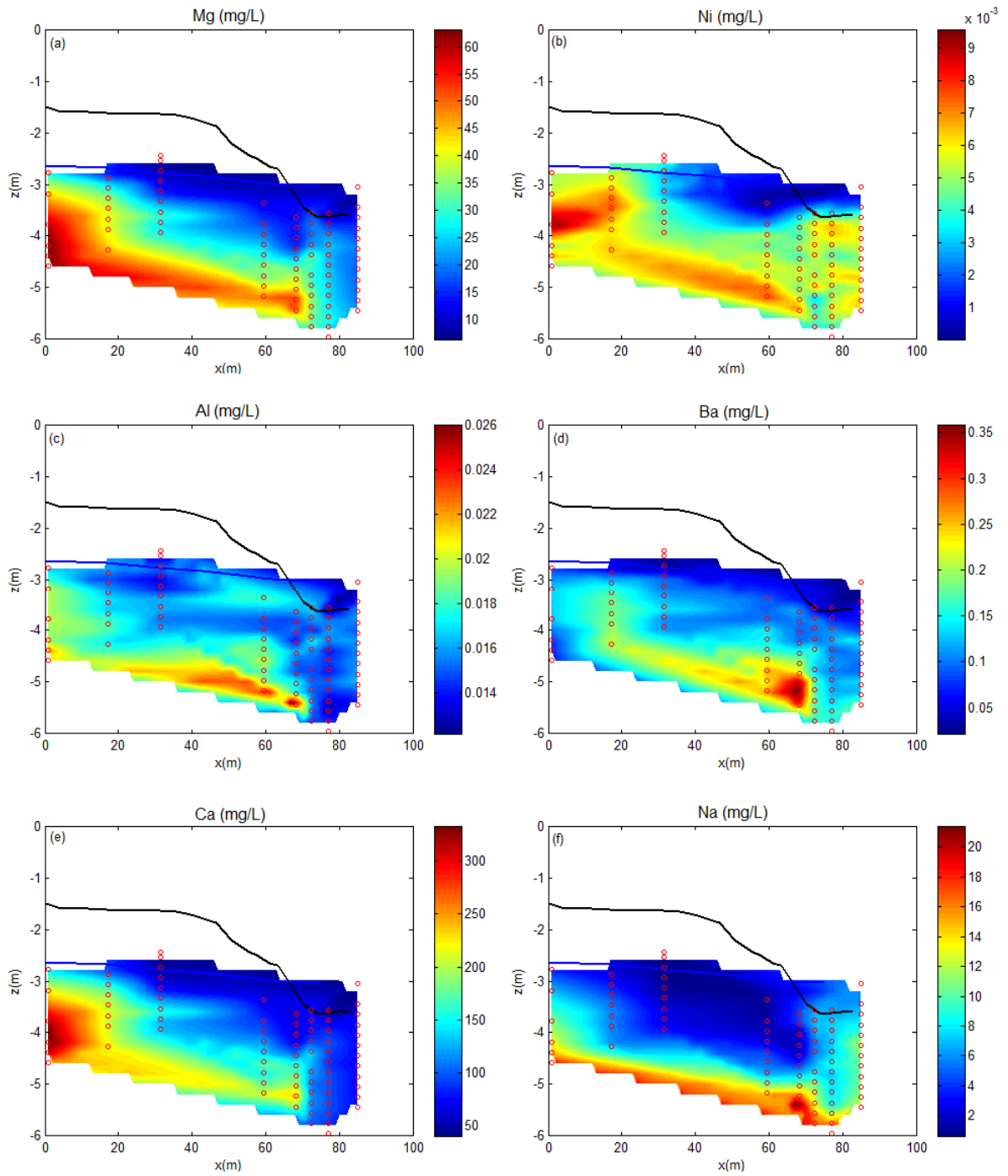
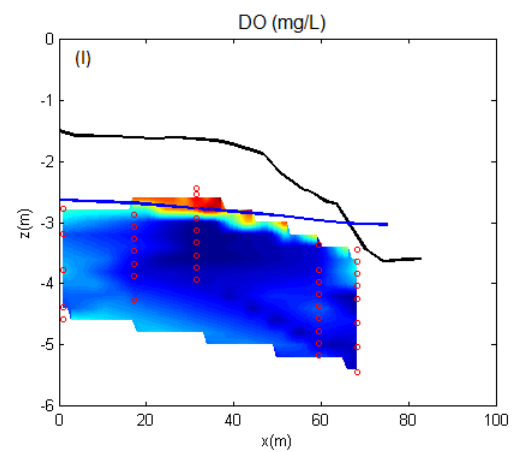
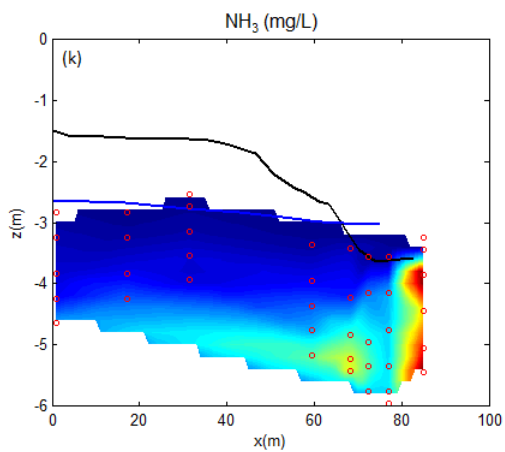
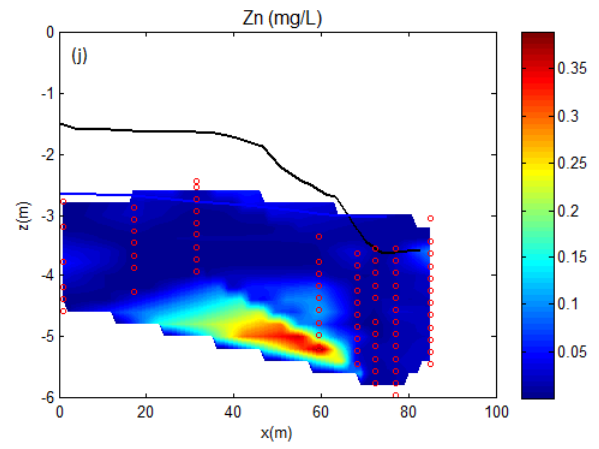
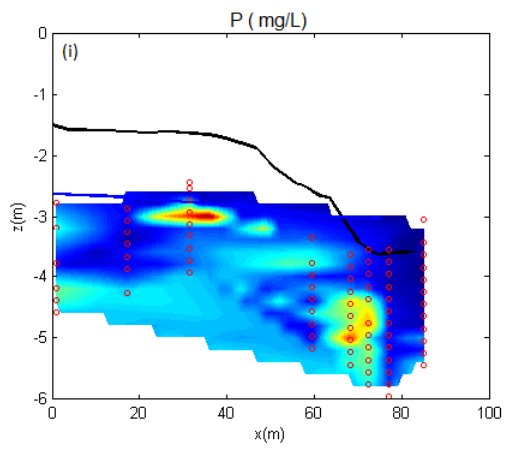
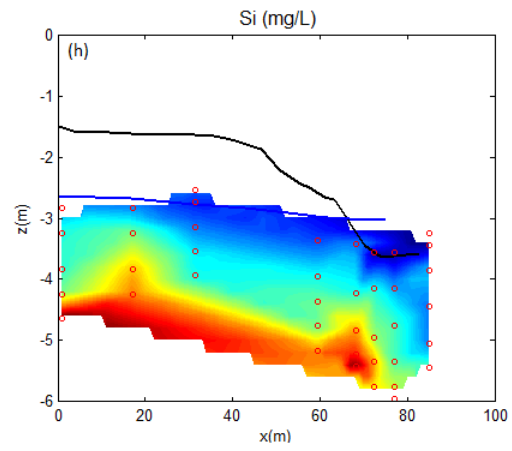
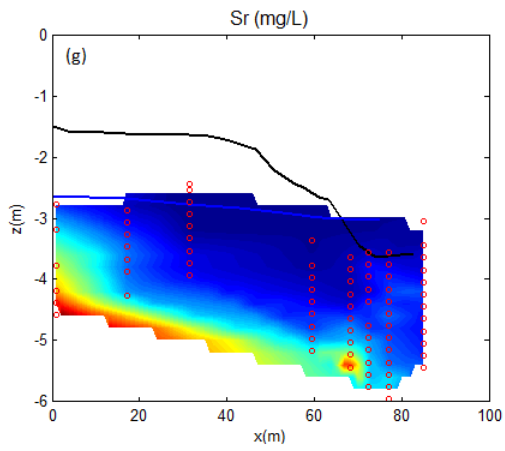


Figure D2: Little Beach groundwater distribution of dissolved species on 8 December 2011: (a) As (mg/L), (b) Fe (mg/L), (c) S (mg/L), (d) Mn (mg/L), (e) Mg (mg/L), (f) Zn (mg/L), (g) Al (mg/L), (h) NH₃ (mg/L), (i) NO₃⁻ (mg/L), and (j) Ni (mg/L).

D.3 Pore water chemistries at Little Beach for 14-18 May 2012





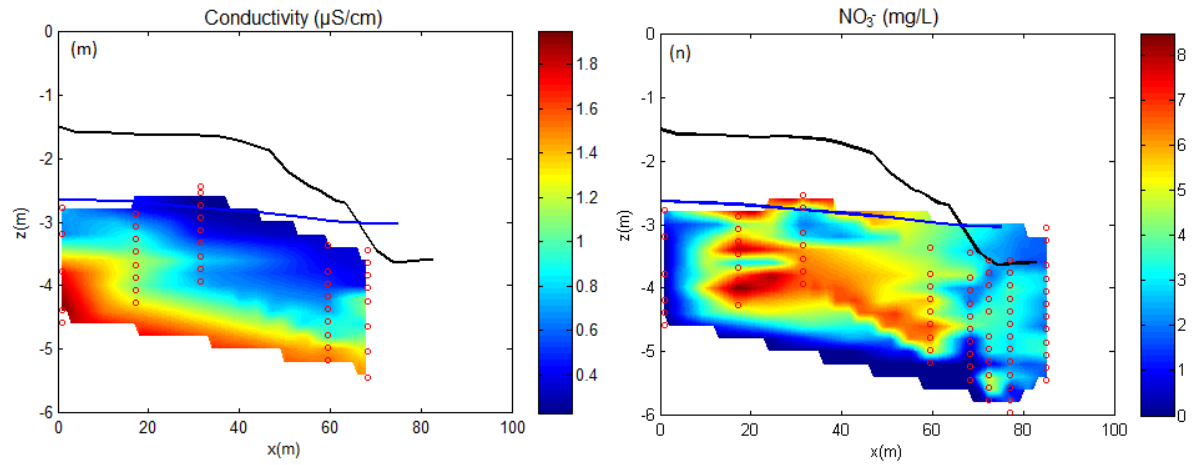


Figure D3: Little Beach groundwater distribution of dissolved species on 14-18 May 2012:
 (a) Mg (mg/L), (b) Ni (mg/L), (c) Al (mg/L), (d) Ba (mg/L), (e) Ca (mg/L), and (f) Na
 (mg/L), (g) Sr (mg/L), (h) Si (mg/L), (i) P (mg/L), (j) Zn (mg/L), (k) NH₃ (mg/L) and (l) DO
 (mg/L), (m) conductivity (µS/cm) and (n) NO₃⁻ (mg/L).

**Appendix E – Supplementary results from selective extractions performed on sediments
from Little Beach**

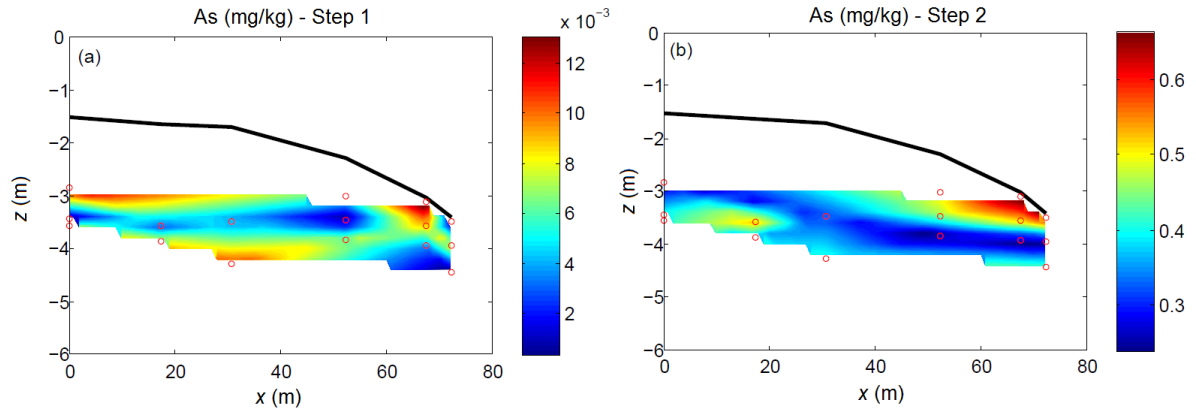


Figure E1: Arsenic extracted from sediment cores collected at Little Beach (June 2012): (a) As (mg/kg) extracted from step 1 (non-specific bound) and (b) As (mg/kg) extracted from step 2 (specific bound).

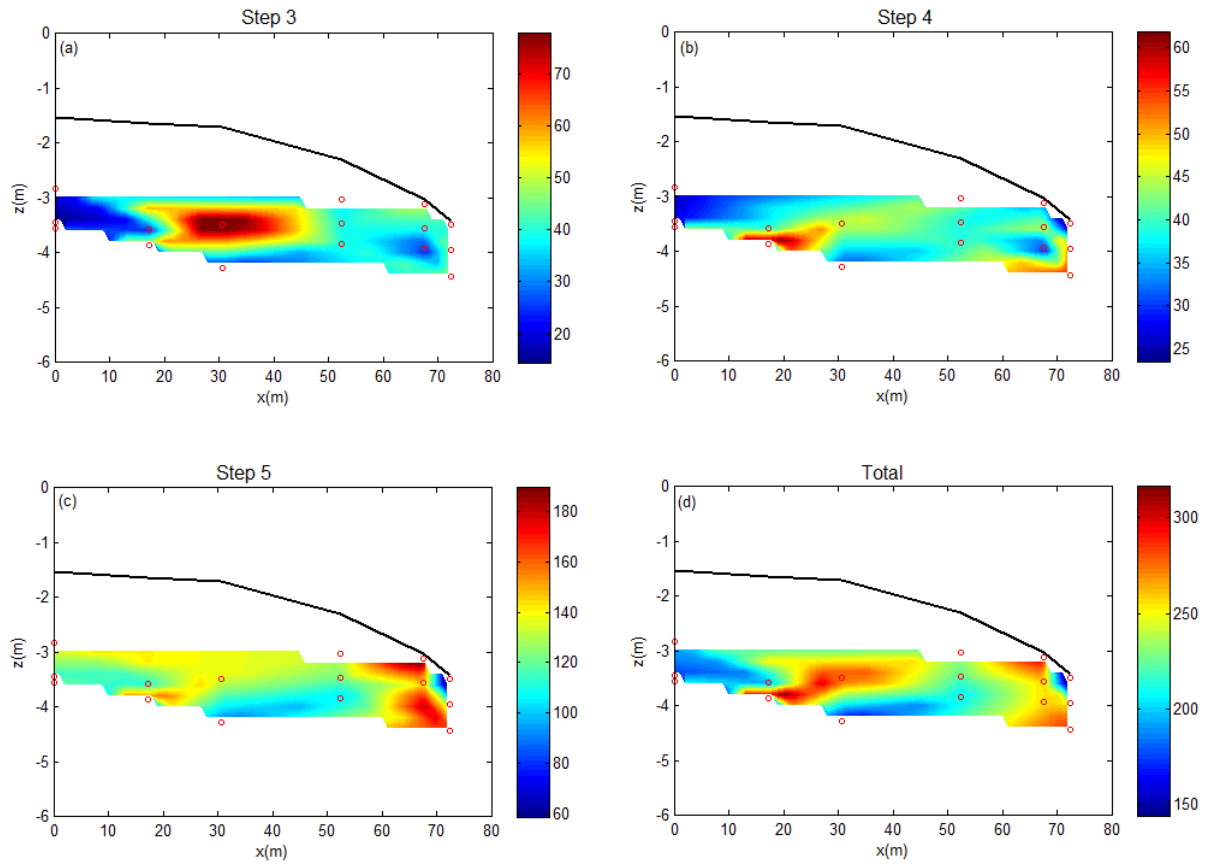


Figure E2: Mn extracted from sediment cores collected at Little Beach (June 2012): (a) step 3 (extracted from amorphous hydr(oxides) (mg/kg)), (b) step 4 (extracted from crystalline hydr(oxides) (mg/kg)), (c) Step 5 (residual mineral phase extraction (mg/kg), and (d) total concentration (mg/kg).

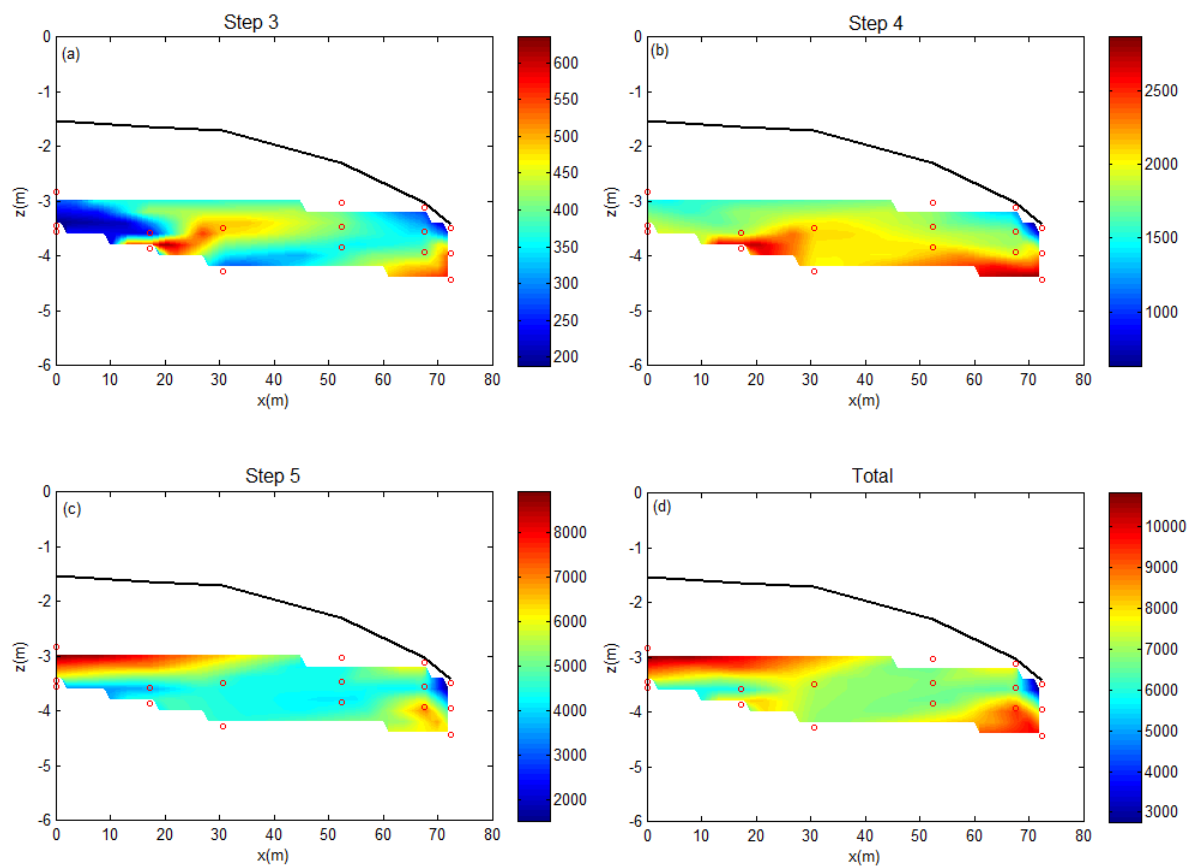


Figure E3: Mg extracted from sediment cores collected at Little Beach (June 2012): (a) step 3 (extracted from amorphous hydr(oxides) (mg/kg)), (b) step 4 (extracted from crystalline hydr(oxides) (mg/kg)), (c) Step 5 (residual mineral phase extraction (mg/kg)), and (d) total concentration (mg/kg).

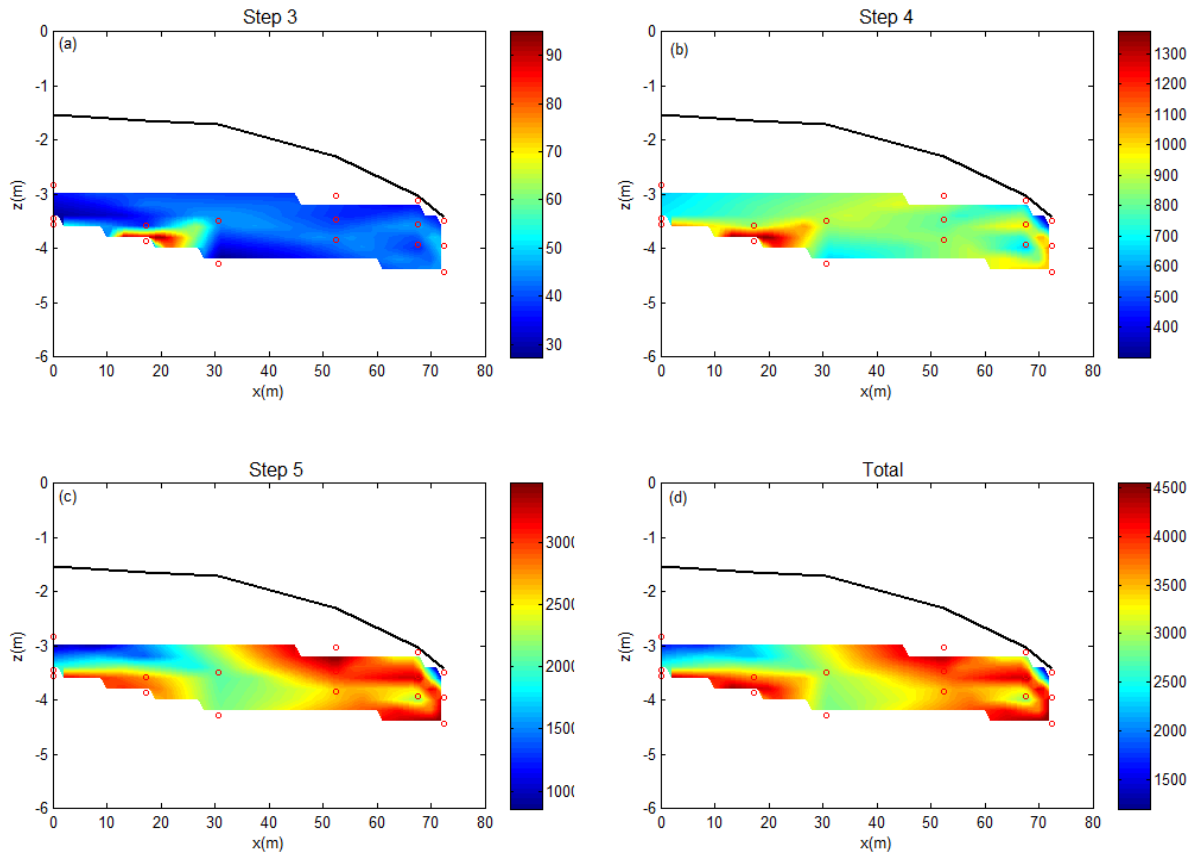


Figure E4: Al extracted from sediment cores collected at Little Beach (June 2012): (a) step 3 (extracted from amorphous hydr(oxides) (mg/kg)), (b) step 4 (extracted from crystalline hydr(oxides) (mg/kg)), (c) Step 5 (residual mineral phase extraction (mg/kg)), and (d) total concentration (mg/kg).

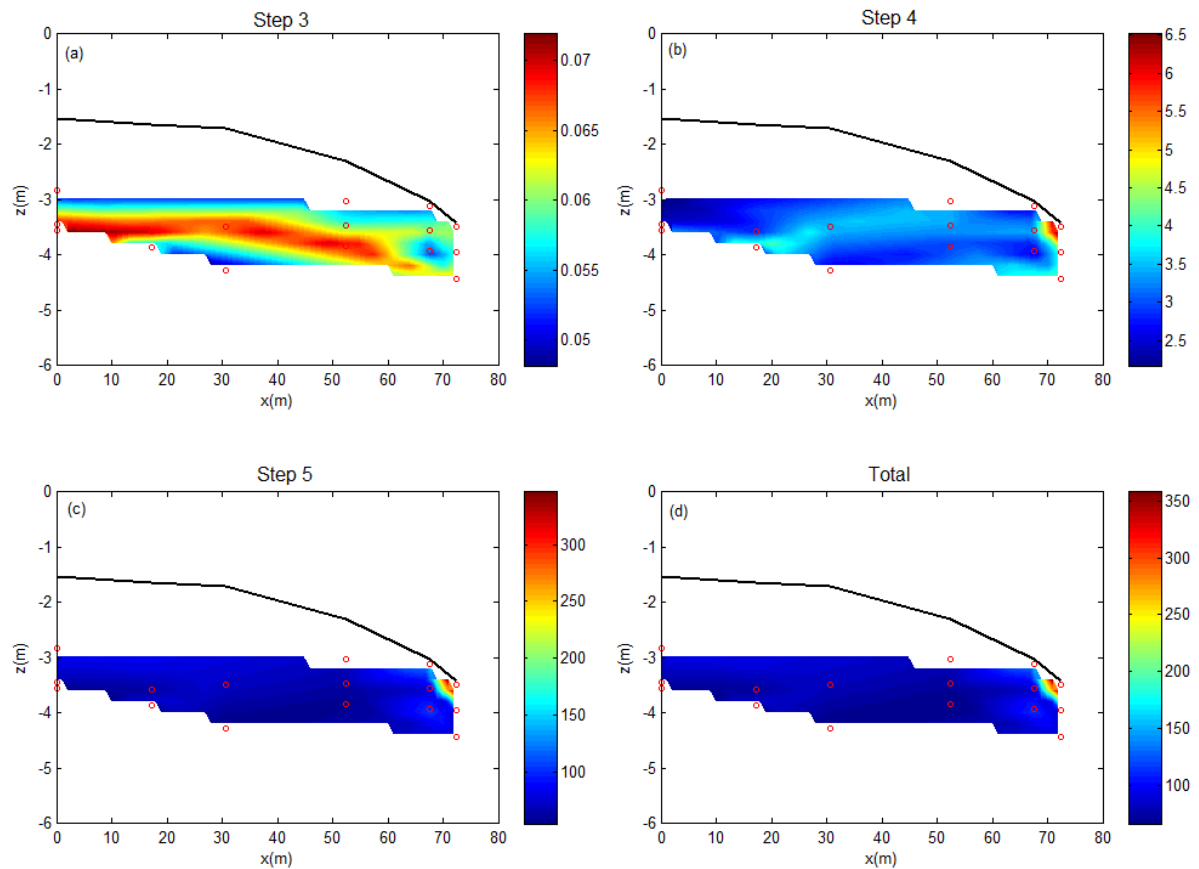


Figure E5: Sr extracted from sediment cores collected at Little Beach (June 2012): (a) step 3 (extracted from amorphous hydr(oxides) (mg/kg)), (b) step 4 (extracted from crystalline hydr(oxides) (mg/kg)), (c) Step 5 (residual mineral phase extraction (mg/kg)), and (d) total concentration (mg/kg).

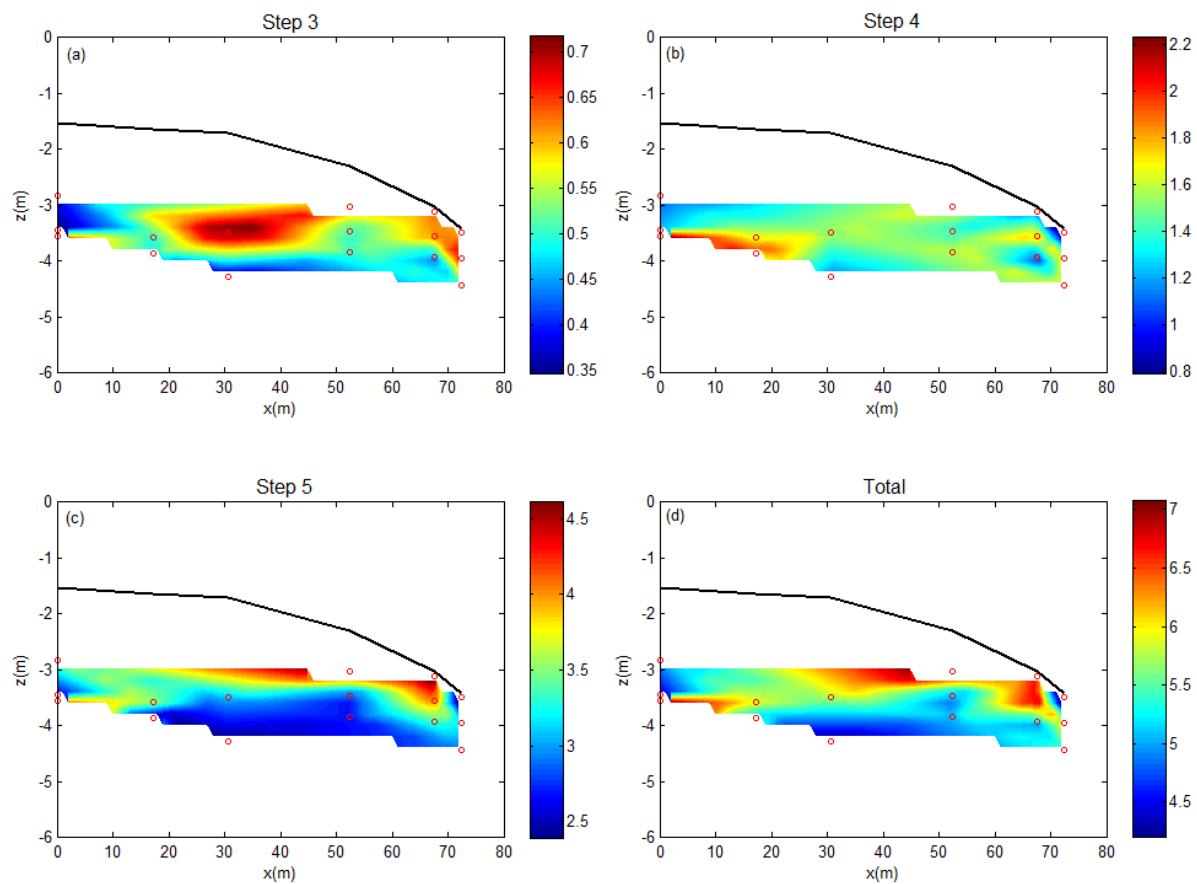


Figure E6: Ni extracted from sediment cores collected at Little Beach (June 2012): (a) step 3 (extracted from amorphous hydr(oxides) (mg/kg)), (b) step 4 (extracted from crystalline hydr(oxides) (mg/kg)), (c) Step 5 (residual mineral phase extraction (mg/kg)), and (d) total concentration (mg/kg).

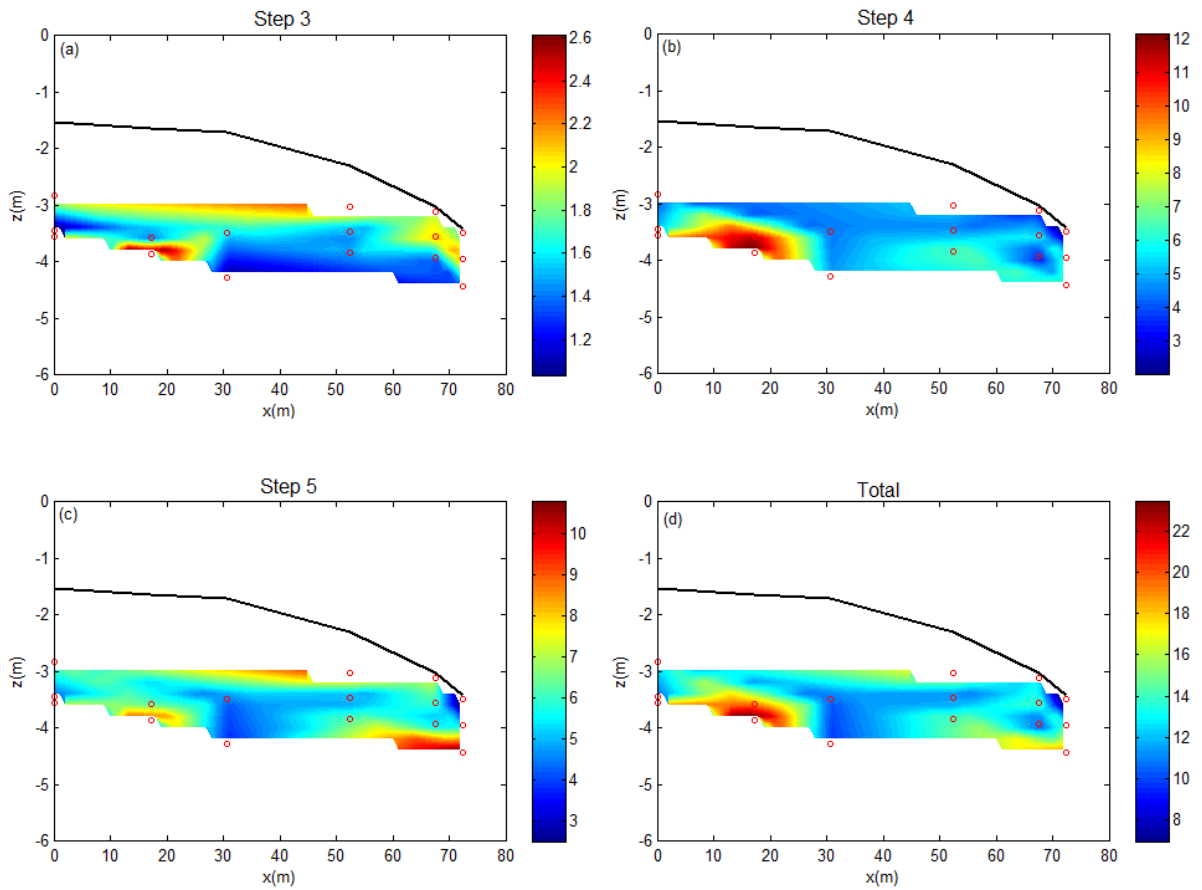


Figure E7: Zn extracted from sediment cores collected at Little Beach (June 2012):: (a) step 3 (extracted from amorphous hydr(oxides) (mg/kg)), (b) step 4 (extracted from crystalline hydr(oxides) (mg/kg)), (c) Step 5 (residual mineral phase extraction (mg/kg)), and (d) total concentration (mg/kg).

Appendix F – Supplementary results from Main Beach groundwater investigations

F.1 Supplementary data for Main Beach east transect: 25 – 28 June 2012

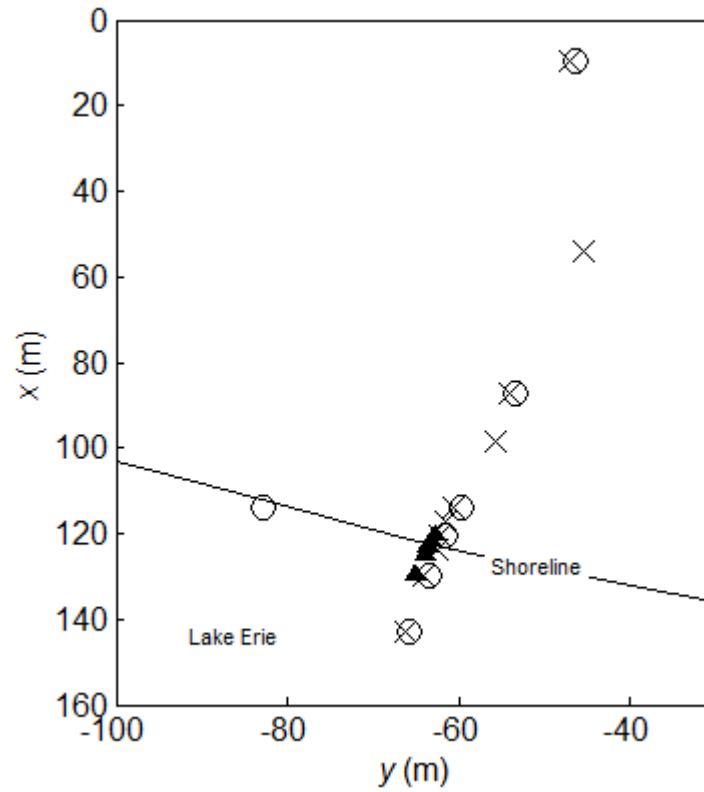
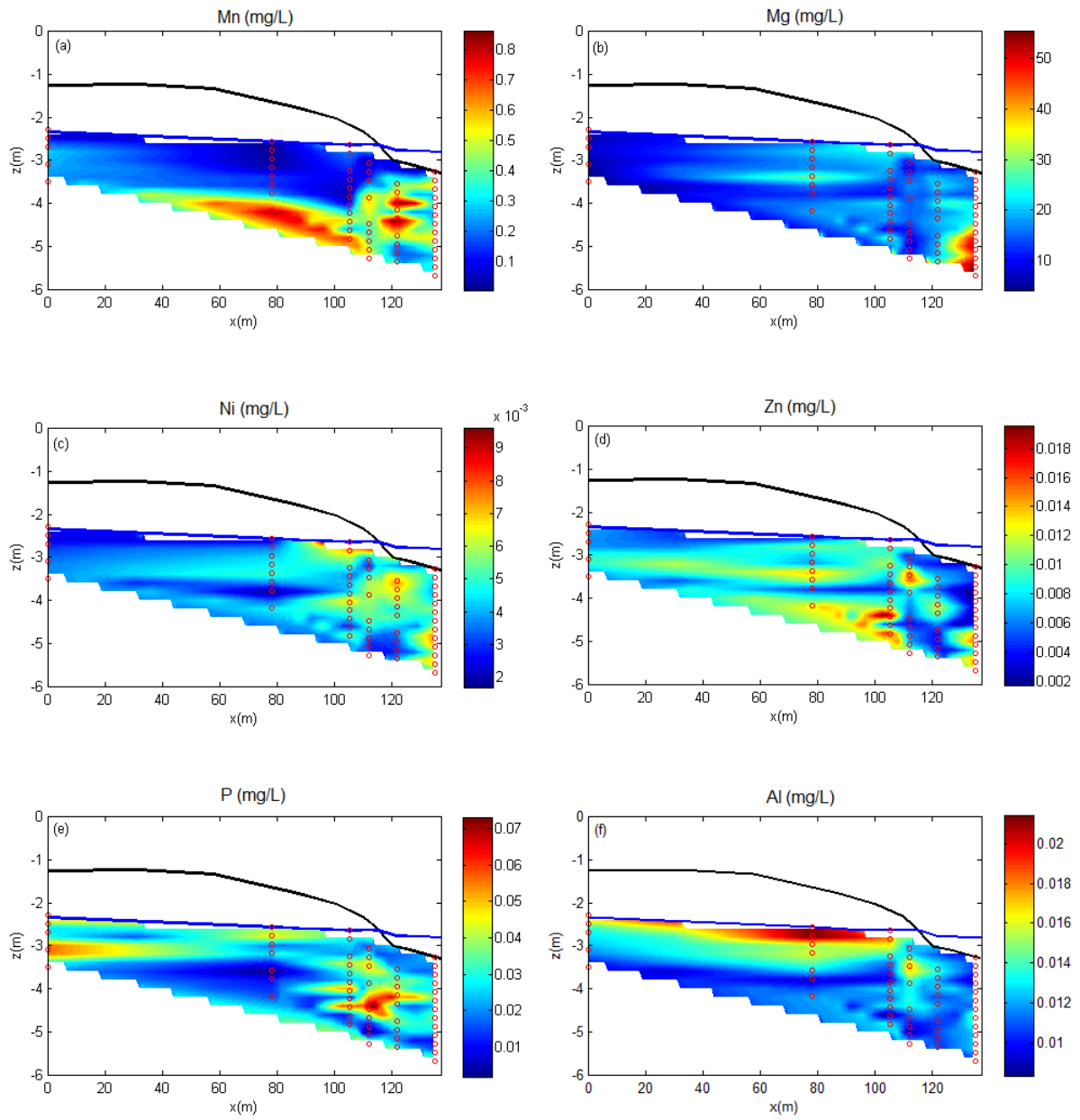


Figure F1.1: Layout of monitoring equipment at Main Beach east transect.



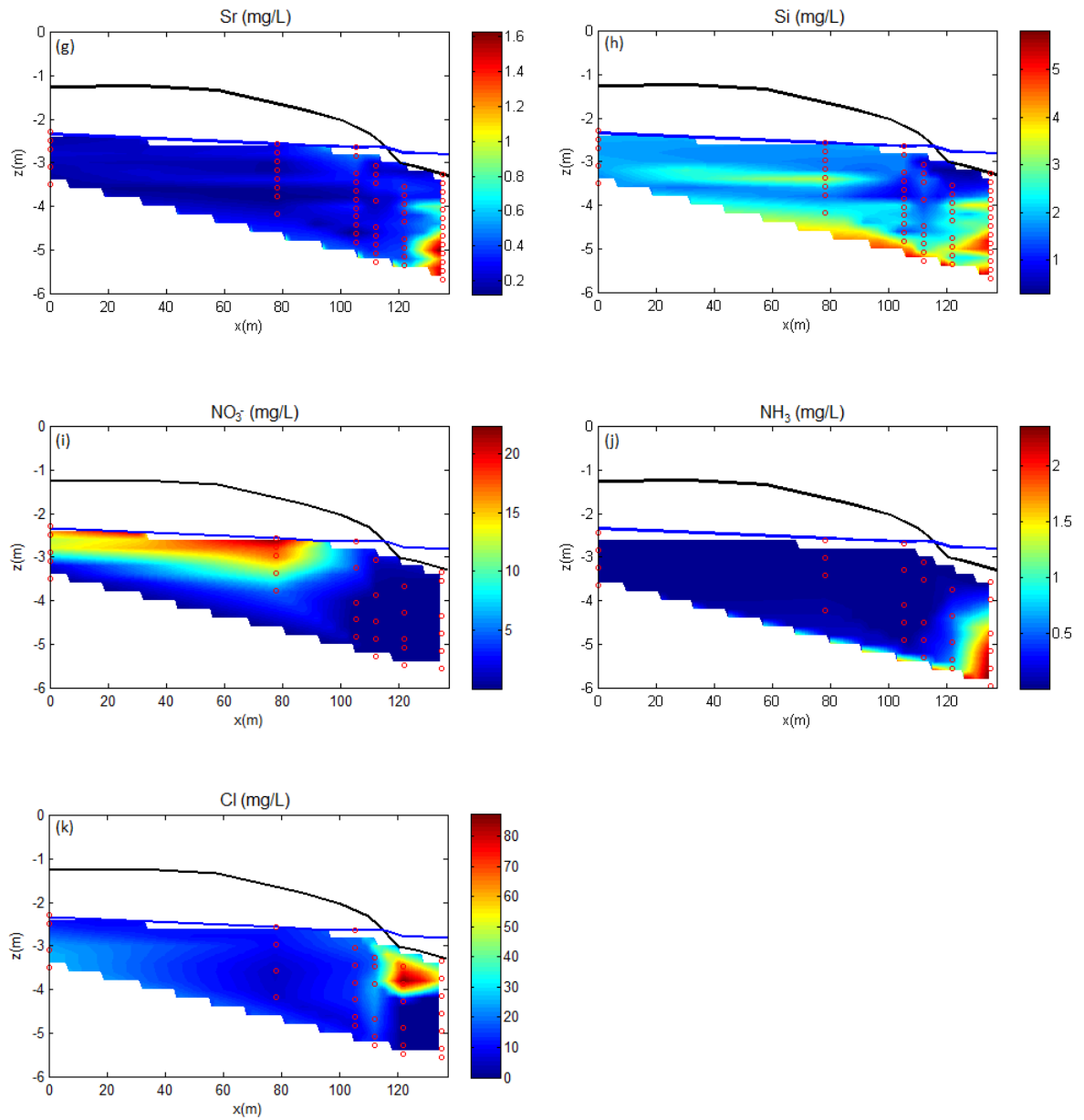


Figure F1.2: Distribution of dissolved species at Main Beach east transect (25- 28 June 2012): (a) Mn (mg/L), (b) Mg (mg/L), (c) Ni (mg/L), (d) Zn (mg/L), (e) P (mg/L), (f) Al (mg/L), (g) Sr (mg/L), (h) Si (mg/L), (i) NO₃⁻ (mg/L), (j) NH₃ (mg/L), and (k) Cl (mg/L).

F.3 Supplementary data for Main Beach west transect: 30 July – 3 August 2012

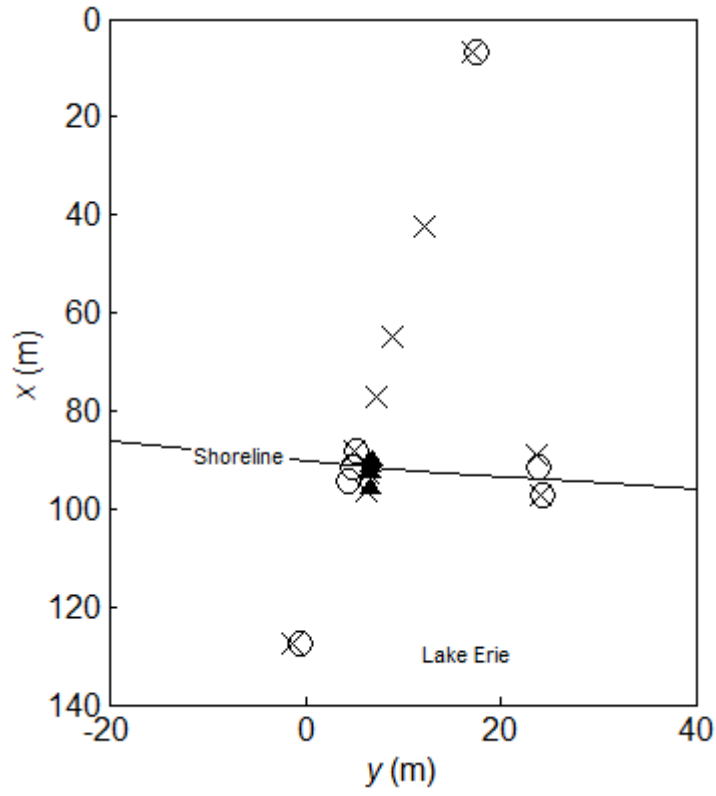
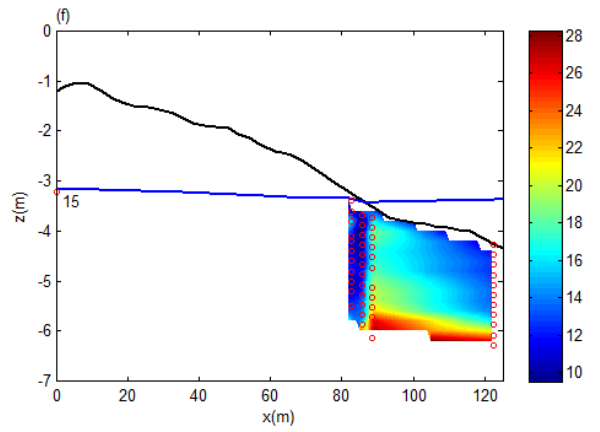
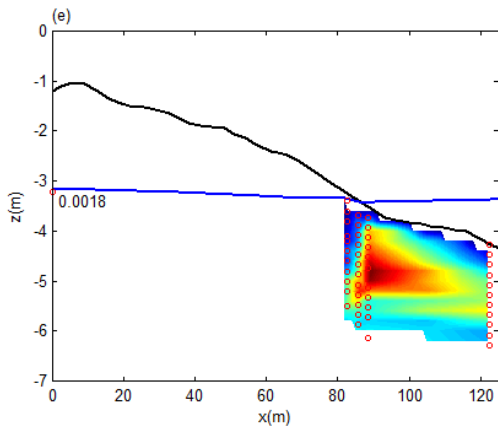
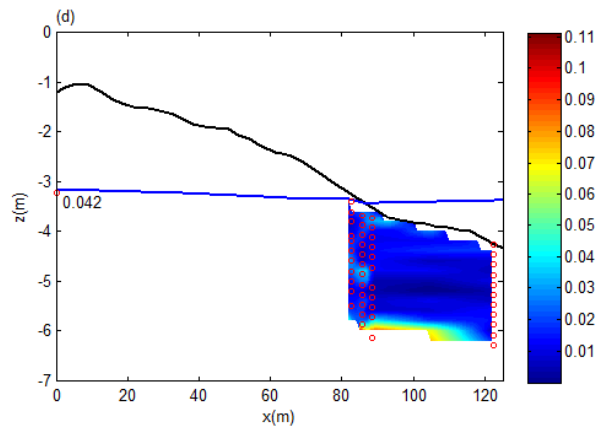
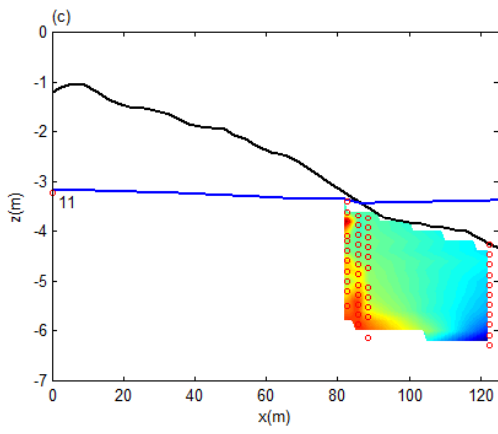
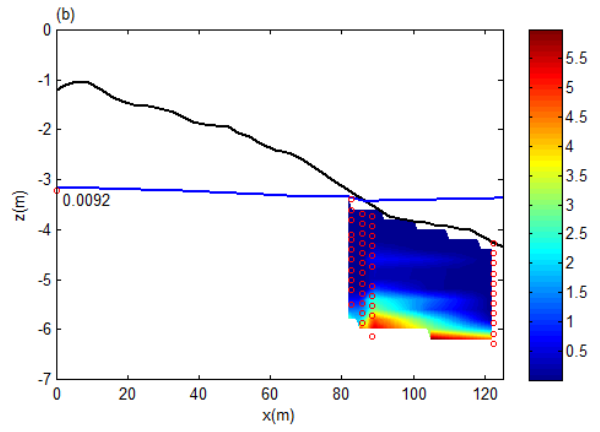
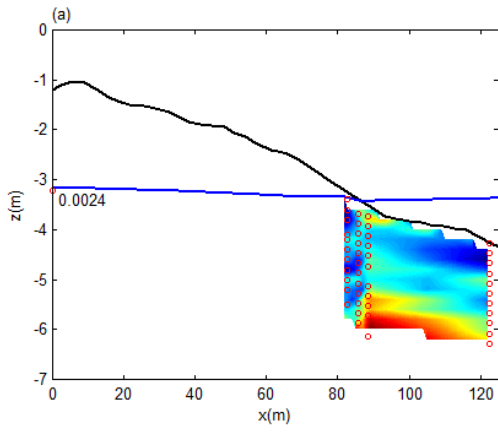
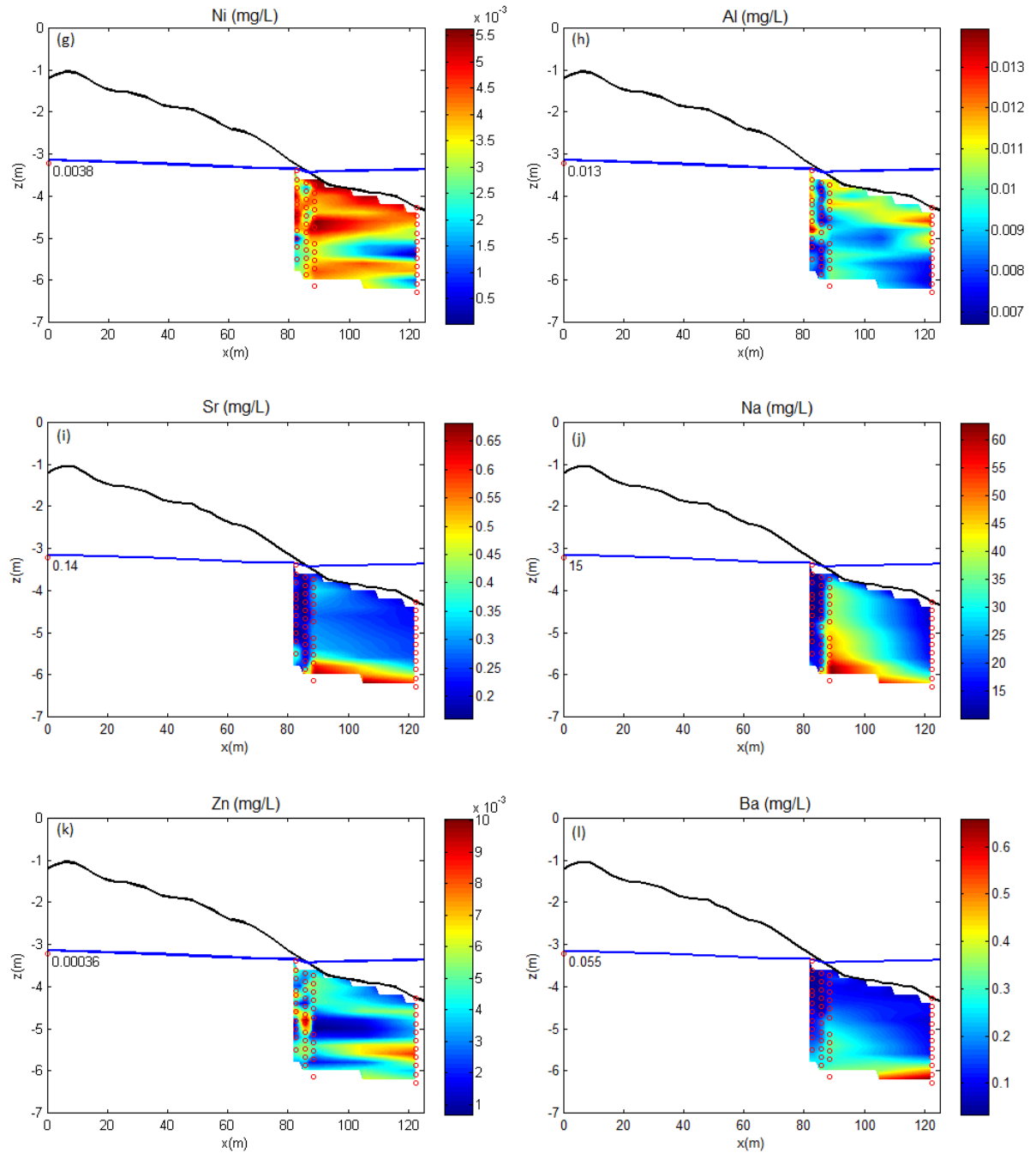


Figure F2.1: Layout of monitoring equipment at Main Beach west transect.





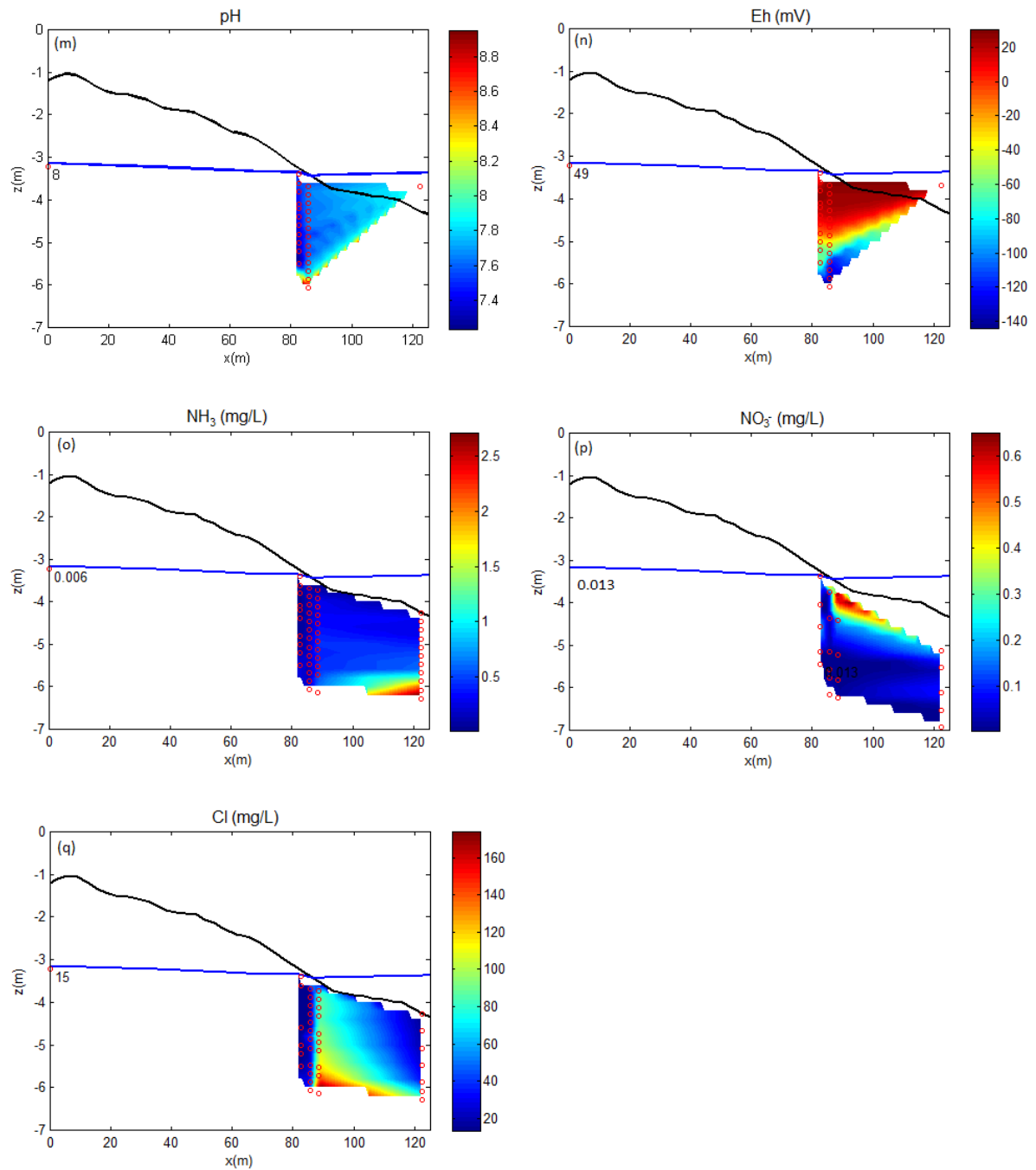


Figure F2.2: Distribution of dissolved species at Main Beach west transect (30 July - 3 August 2012): (a) As, (b) Fe, (c) S, (d) P, (e) Mn, (f) Mg, (g) Ni, (h) Al, (i) Sr, (j) Na, (k) Zn, (l) Ba, (m) pH, (n) Eh, (o) NH_3 , (p) NO_3^- , and (q) Cl.

Appendix G - Groundwater hydrology at Little Beach and Main Beach

G.1 Simulated and observed water level and water exchange rates at Main Beach

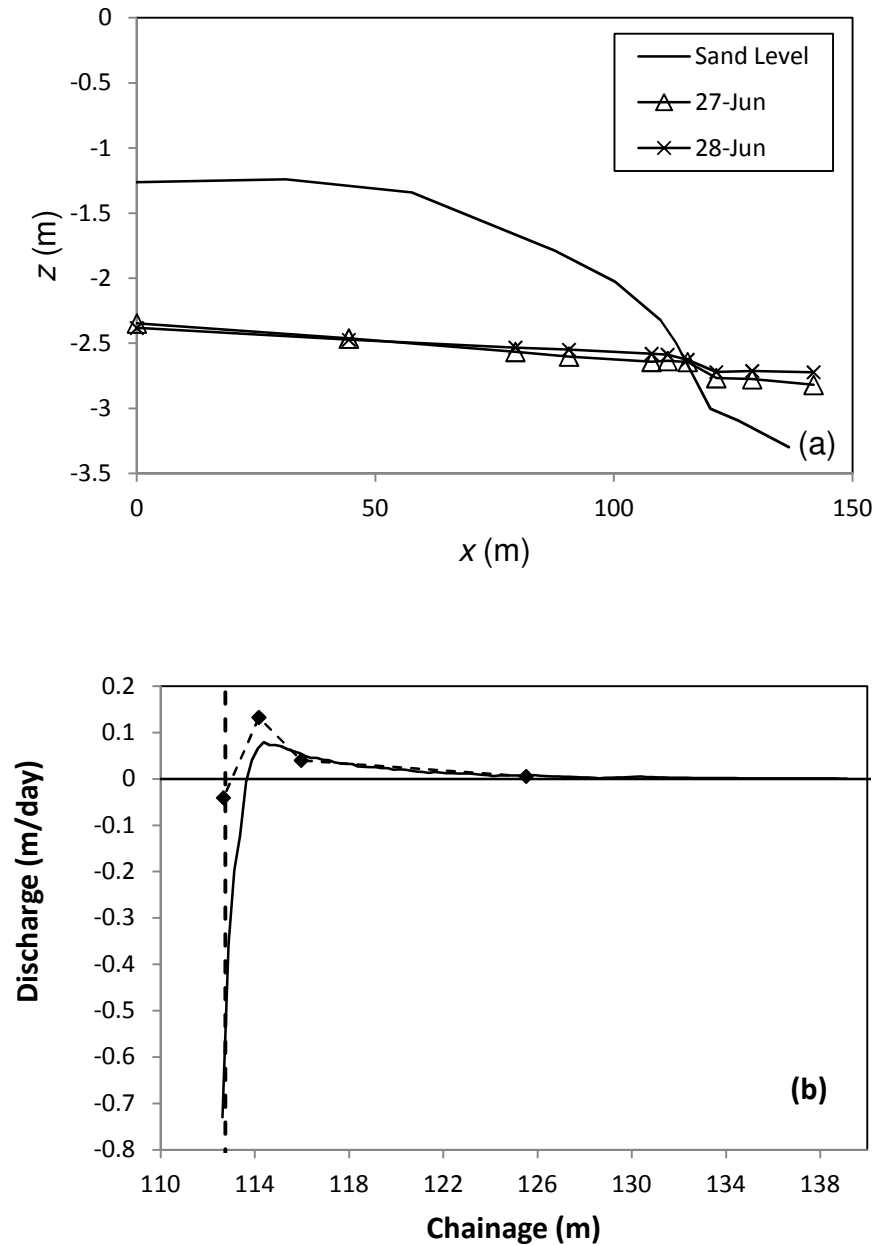


Figure G1: Main Beach East (a) groundwater level and (b) observed (◆) and simulated (-) groundwater discharge along shore-normal transect.

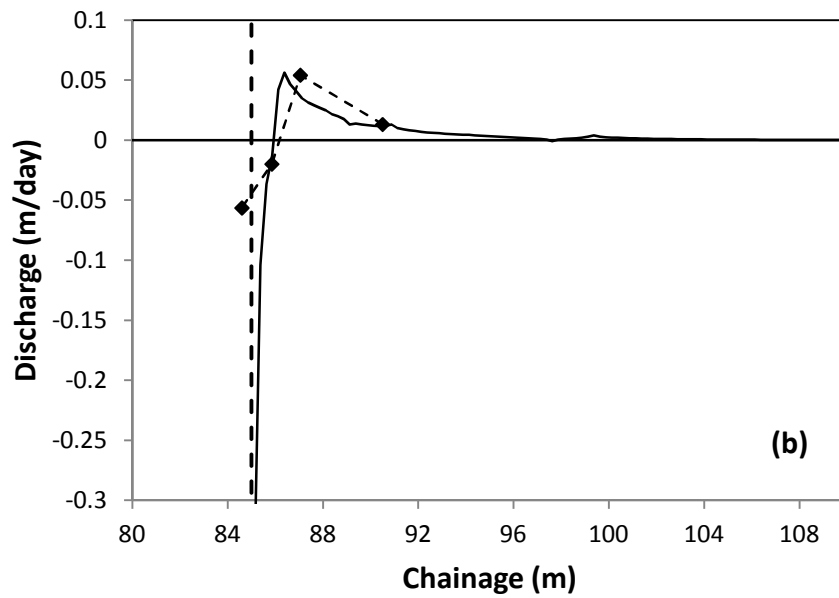
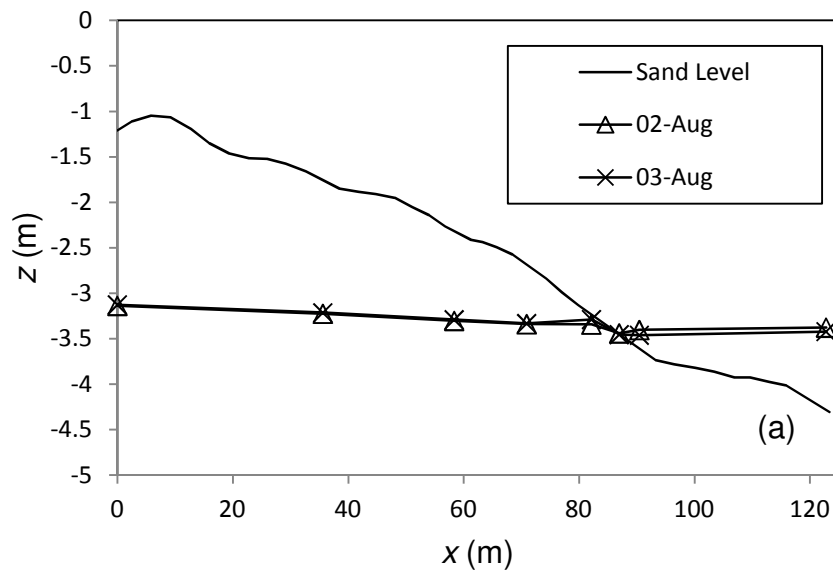


Figure G2: Main Beach West (a) groundwater level and (b) observed (◆) and simulated (-) groundwater discharge along shore-normal transect.

G.2 Simulated groundwater flow and particle tracking for Little Beach and Main Beach monitoring events.

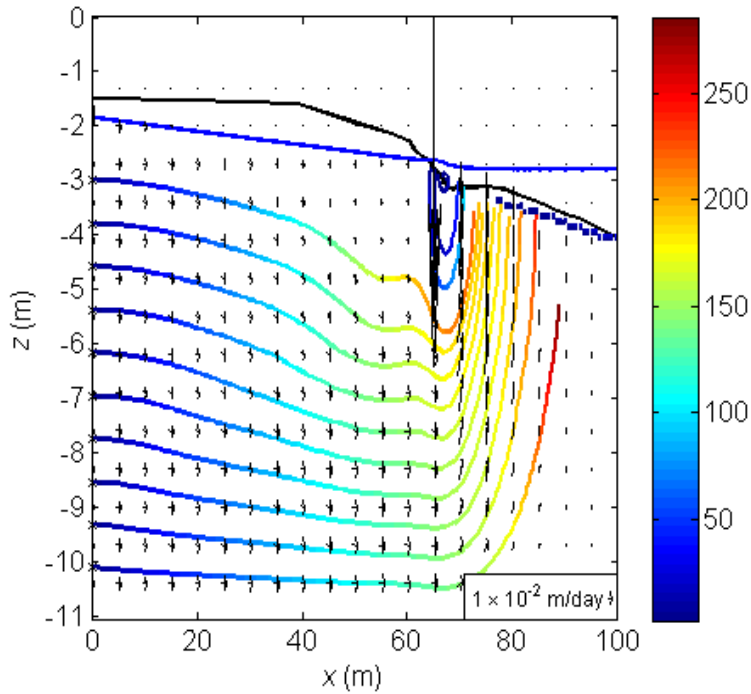


Figure G3: Simulated flow velocities and particle flow paths for December 2011 simulation of transect at Little Beach. The line colouring indicates the travel times (up to 500 d) as particles move along their flow path.

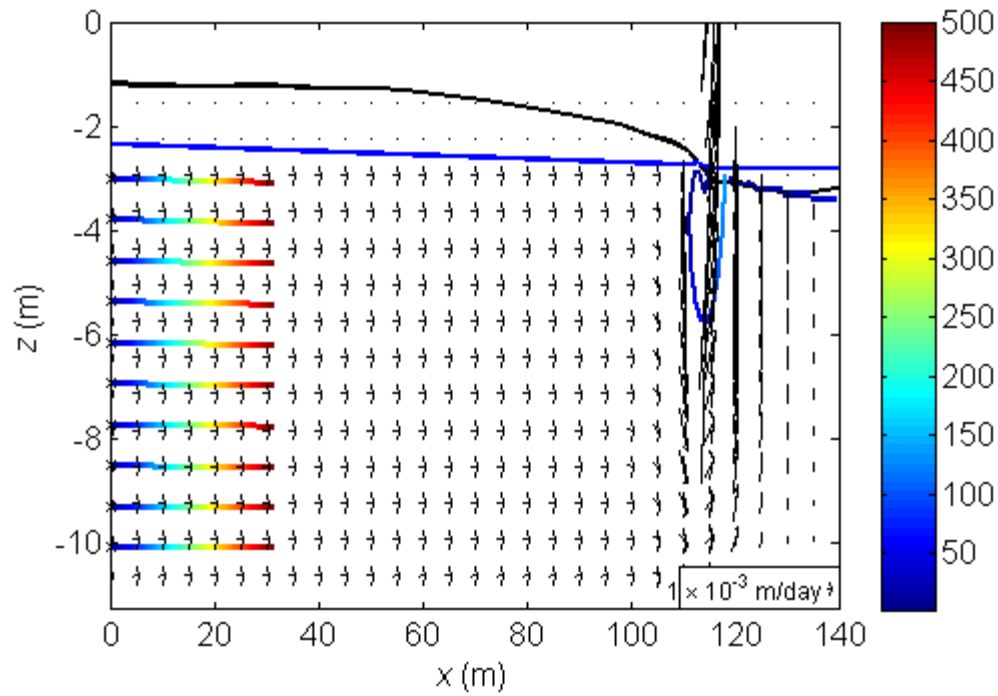


Figure G4: Simulated flow velocities and particle flow paths for June 2012 simulation of east transect at Main Beach. The line colouring indicates the travel times (up to 500 d) as particles move along their flow path.

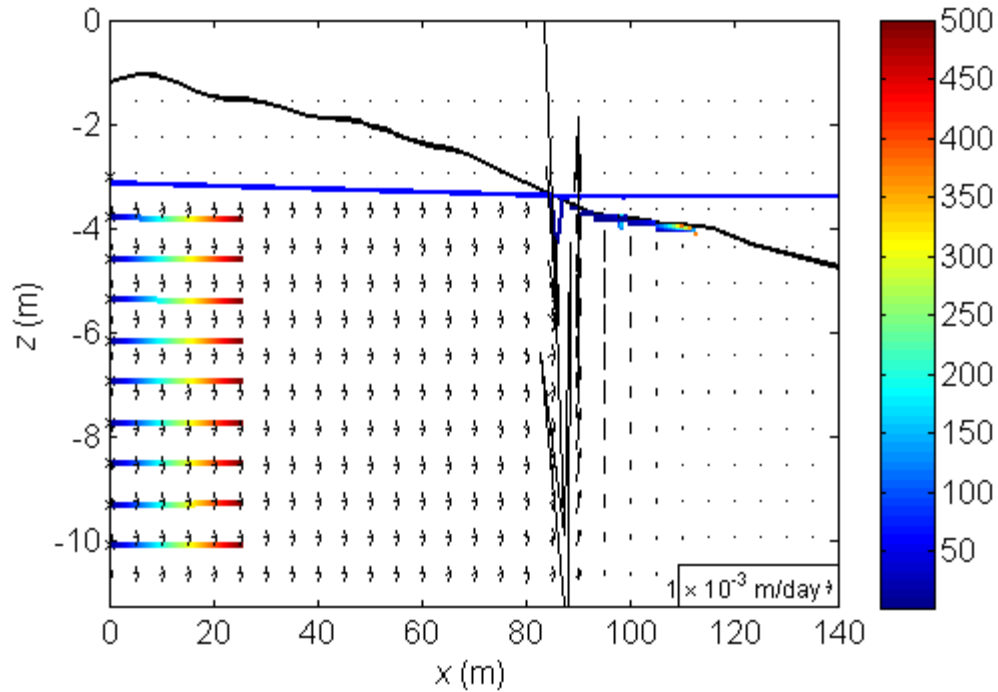


Figure G5: Simulated flow velocities and particle flow paths for June 2012 simulation of west transect at Main Beach. The line colouring indicates the travel times (up to 500 d) as particles move along their flow path.

Table G1: Calculated average transit times and total infiltration and exfiltration rates.

	Avg. Recirculation Time (d)	Avg. Transit Time (d)	Total Infiltration (m²/d)	Total Exfiltration (m²/d)
Little Beach - December 2011	22	210	0.28	1.14
Main Beach East - June 2012	44.5	2028	0.27	0.41
Main Beach West - August 2012	11	1900	0.10	0.21

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 - 2) Lee, J S K. (2012). "Occurrence of Heavy Metals in a Freshwater Beach, Great Lakes", 9th ANNUAL Earth Day Colloquium, London, ON, April 13, 2012.
 - 3) Lee, J S K and Robinson, C. "Influence of Lake Hydraulics on the Distribution of Heavy Metals in a Freshwater Beach, Lake Erie ", 39th IAHR Congress, Niagara Falls, ON, September 16 - 21, 2012.