

## SUBSURFACE PATHWAYS OF CONTAMINANTS TO COASTAL WATERS

D. A. Barry<sup>1</sup> and J.-Y Parlange<sup>2</sup>

### ABSTRACT

Coastal/estuarine water pollution is becoming an increasingly serious global problem largely due to input of land-derived contaminants. The resulting degradation of coastal resources affects significantly economic and social developments of coastal regions. Traditionally, terrestrial fluxes of chemicals to coastal water have been estimated on the basis of river flow alone. However, recent field observations indicate that contaminants entering coastal seas and estuaries with groundwater discharge (submarine groundwater discharge, SGWD) can significantly contribute to coastal pollution (Church, 1996; Moore, 1996), especially in areas where serious groundwater contamination has occurred. This paper examines the subsurface pathways of chemicals to coastal waters via SGWD, focusing on transport and reaction processes near the aquifer-ocean interface (exit) subject to oceanic oscillations.

### 1. INTRODUCTION

Increasing input of land-derived nutrients/contaminants has led to serious pollution in coastal waters around the world. For example, frequent outbreaks of Lyngbya in Moreton Bay (Queensland, Australia) in recent years have caused serious environmental and human health problems (Healthy Waterways Lyngbya Task Force Report, August 2001). A large Lyngbya bloom occurred in Deception Bay in summer 2001 (Fig. 1), smothering seagrass beds, mangrove roots and seedlings. Lyngbya blooms also covered seagrass meadows on the Eastern Banks, which is the primary grazing area for Moreton Bay's dugongs and turtles. Recent surveys by Queensland Parks and Wildlife Service show that dugong numbers in Moreton Bay have possibly declined from 700 in 1995 to 350 in 2000. Lyngbya, as a human health hazard, has the potential to cause skin and eye irritation after direct contact. Lyngbya contains toxins that are known tumour promoters (Osborne et al., 2001).

Recent investigations into the blooms of *Lyngbya majuscula* in Moreton Bay have identified dissolved iron, phosphorus and humic substances as important triggers of blooms. These chemicals are most likely sourced from land activities and transported by surface and ground water into the bay. Elevated iron concentrations in the bay may have resulted from iron exported from acid sulphate soils (Dennison and Abal, 1999). Acid sulphate soils (ASS) have been found in the coastal zone of Moreton Bay, especially in areas near Deception Bay where the 2000 bloom was initiated (Healthy Waterways Report S3-N2). The general form of sulphide minerals contained in ASS is

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<sup>1</sup> Professor of Environmental Engineering, Institute of Infrastructure and Environment, School of Engineering and Electronics, The University of Edinburgh, Edinburgh, EH9 3JN, UK ([d.a.barry@ed.ac.uk](mailto:d.a.barry@ed.ac.uk))

<sup>2</sup> Professor, Department of Biological and Environmental Engineering, Cornell University, Ithaca, New York 14853-5701 USA. ([jp58@cornell.edu](mailto:jp58@cornell.edu))

cubic iron pyrite ( $\text{FeS}_2$ ), which is chemically inert under reduced conditions. However, pyrite oxidises when it is exposed atmospheric oxygen (for example with a low water table during the drought), resulting in the formation of acidic oxidation products, namely  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$  and  $\text{H}^+$  (Cook et al., 2000). These products can then enter the bay directly with the groundwater discharge or via discharge to stream/creek/river (Fig. 2). The nature and relative significance of these pathways are, however, not well understood.



Figure 1. Schematic diagram of Moreton Bay, Lyngbya bloom and chemicals transport pathways (from Dennison and Abal, 1999).

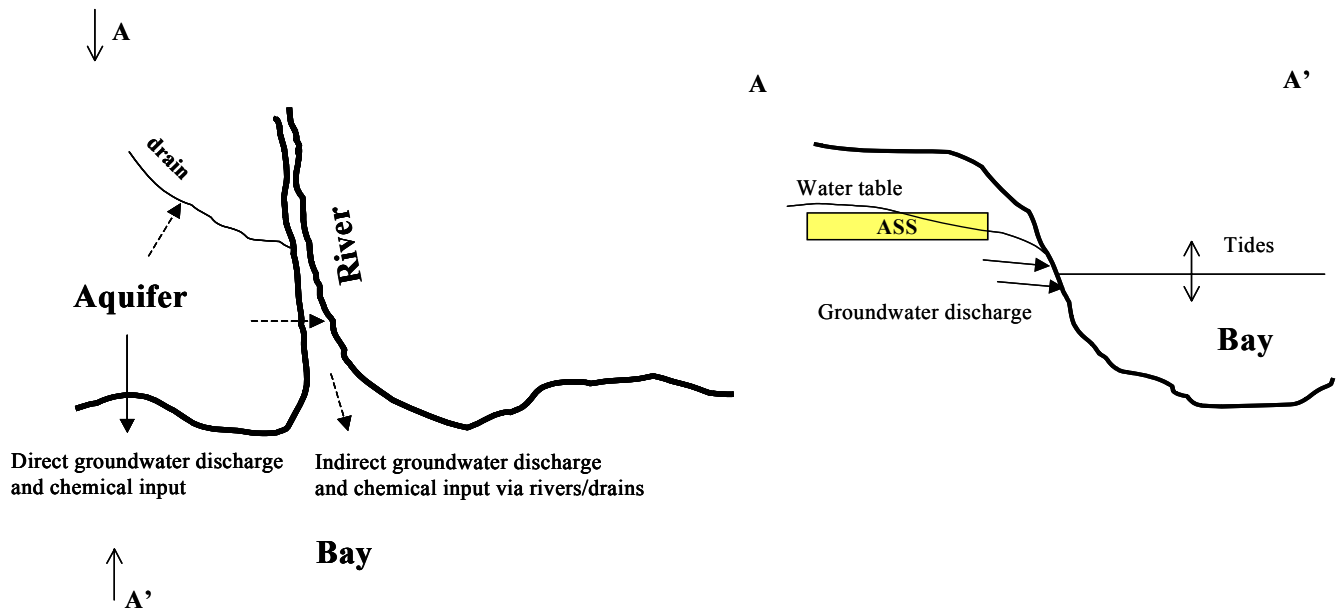


Figure 2. Pathways and fluxes of chemicals to the bay: direct groundwater discharge, and indirect discharge via drains and rivers.

The acid cations (particularly  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) may be transformed in the aquifers and rivers prior to entering the bay, depending on the local geochemical conditions. For example, the dissolved irons may precipitate as pH increases due to the mixing of acid freshwater and marine water. The acid

leachate may also react with soil particles in the aquifers, and sediments suspended in the river water and/or settled in the riverbed. These reactions modify significantly the fate and transport of iron in the aquifers and rivers, and need to be considered in determining the amount of dissolved iron discharged to the bay from acid sulphate soils. Here we mainly consider the subsurface pathways (i.e., via SGWD) of iron (more generally, reactive chemicals) to the bay, in particular, the exit conditions in the near-shore aquifer subject to tides and waves.

## 2. MIXING OF FRESHWATER AND SEAWATER NEAR THE AQUIFER OCEAN INTERAFCE

Submarine groundwater discharge consists of both groundwater flow from upland regions and water exchange at the aquifer-ocean interface (Simmons, 1992). A theoretical model of SGWD has been developed to include tidally oscillating groundwater flow ( $D_t$ ) and circulation ( $D_w$ ) due to wave set-up (i.e., on-shore tilt of the mean sea level; Fig. 3). These two local processes were found to cause a large amount of water exchange across the interface (Li et al., 1999).

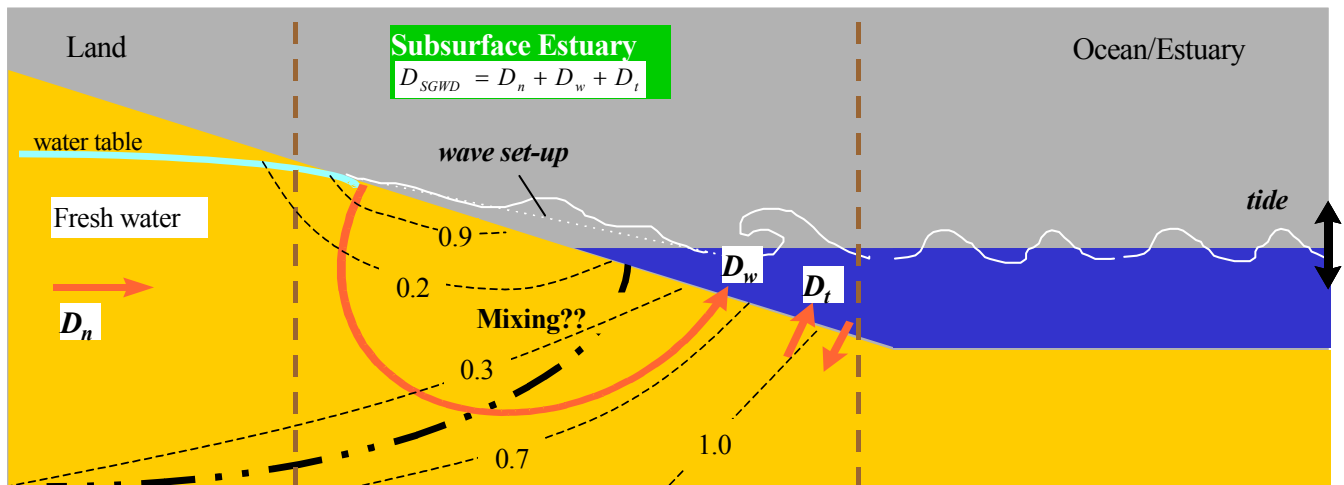


Figure 3. A simple model of SGWD consisting of inland fresh groundwater flow ( $D_n$ ) and seawater recycling (water exchange due to wave set-up  $D_w$ , and due to tides  $D_t$ ). The mixing of the recycling water with fresh groundwater results in the near-shore salinity profiles as schematically shown by the thin dash-lines (in contrast with the traditional saltwater wedge view shown by the thick dot-dashed line).

Although the exchanging/recycling water is largely of marine origin, it mixes and reacts with groundwater and aquifer sediments, modifying the composition of the discharging water. The exchange processes can reduce the residence time of chemicals in the mixing zone of the aquifer, similar to tidal flushing of a surface estuary (Li, et al., 1999). As a result, the rates of chemical fluxes from the aquifer to the ocean increase but the exit chemical concentrations are reduced (dilution effects). More importantly, the exchange processes affect how the fresh groundwater discharges to the ocean. Previous studies, neglecting the tidal and wave effects, predict that the freshwater overlies the intruded seawater and discharges to the ocean, undergoing little mixing with the saltwater. The limited mixing, driven by the density effects, occurs only along the saltwater wedge. Numerical simulations of density-dependent groundwater flow in a coastal aquifer subject to tidal oscillations have revealed a very different salinity profile with two saline plumes near the shore (Fig. 4). First, a saline plume was formed in the upper part of the beach. The freshwater discharged to the sea

through a “tube” between this upper saline plume and the intruding saltwater wedge. Secondly, the freshwater discharge tube contracted and expanded as the tide rose and fell (shown in the attached animation), suggesting considerable mixing activities. Such mixing is also indicated by the salinity gradient shown in the figure. The mixing zone is in contrast with the traditional saltwater wedge. The simulations also revealed considerable tide-induced variations of flow velocities and salinity in the intertidal zone of the aquifer (Li et al., 2004). This suggests that the mass transport of salinity be affected by tides significantly.

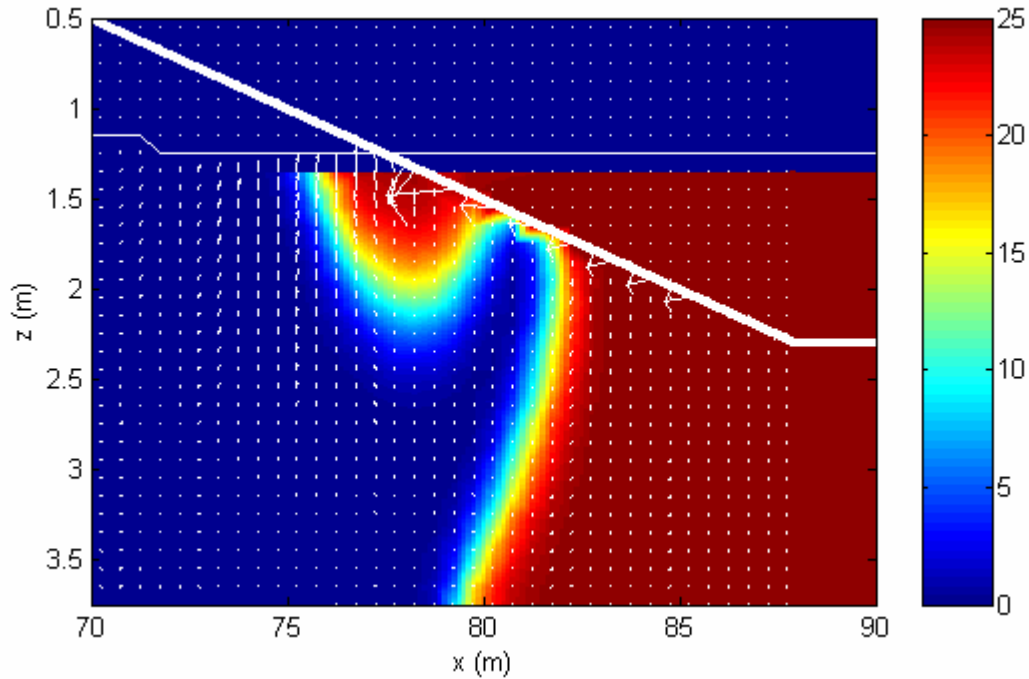


Figure 4. Salinity distribution in the near-shore area of the aquifer: tidal effects leading to the formation of the upper saline plume and the freshwater discharging tube, and considerable mixing between the freshwater and seawater.

The simulated salinity profile is consistent with recent results from laboratory experiments (Robinson and Li, 2004). A phase-averaged salinity distribution from Robinson and Li's experiments is shown in Fig. 5. The experimental data show that the tidal oscillations led to a possibly unstable salinity distribution in the intertidal region with saltwater overtopping the freshwater. The conventional saltwater wedge is also evident. The upper saline plume and the lower saltwater wedge confine a freshwater discharge tube, which exits near the low tide mark. The surficial mixing zone is the most extensive vertically in the middle of the intertidal region, and becomes thinner towards the boundaries of the intertidal zone. These results are similar to the numerical predictions.

The water exchange and subsequent mixing of the recycling seawater with fresh groundwater, driven by the oceanic oscillations, lead to the creation of an active/reactive buffer zone between the terrestrial groundwater and seawater. This zone, in many aspects, is an analogue to surface estuary and hence is called subsurface estuary here. The role of a subsurface estuary in determining the terrestrial chemical input to the sea may be compared with that of a surface estuary. Most previous studies of coastal groundwater, focussing on large-scale saltwater intrusion in aquifers, have ignored the dynamic effects of tides and waves on the flow and mixing processes in the near-shore area of the aquifer (e.g., Huyakorn et al., 1987). However, these mixing processes can alter the geochemical conditions (redox state) in the aquifer and affect the chemical reactions. For example, it has been shown numerically that the exchange enhances the mixing of oxygen-rich seawater and

groundwater, and create an active zone for aerobic bacterial populations in the near-shore aquifer. This zone leads to a considerable reduction in breakthrough concentrations of aerobic biodegradable contaminants at the aquifer-ocean interface (Enot et al., 2001; Li et al., 2001; Li et al., 2004).

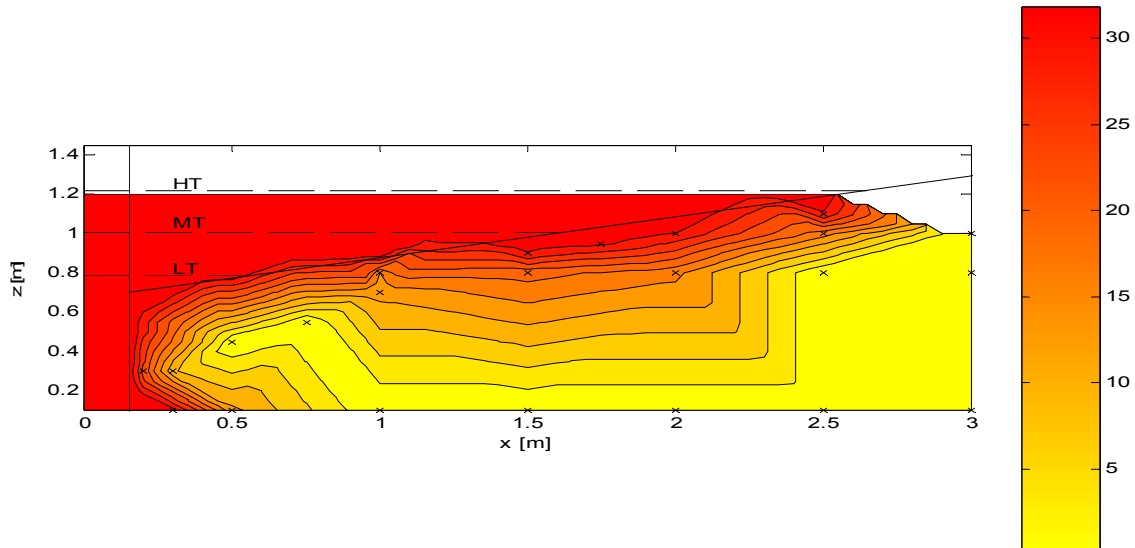


Figure 5. Time-averaged relative salinity profile.

MODFLOW and PHT3D were used to model contaminant transport and biodegradation in coastal aquifers affected by tidal oscillations. Two mobile chemicals were included in the simulation: oxygen as the electron acceptor and toluene as a representative biodegradable contaminant. An aerobic bacterium was included as an immobile phase. The biodegradation process was oxygen-limited (i.e., sufficient substrate). The inland contaminant source was specified near the water table. The simulation was run first without tides until a steady state of chemical concentrations was reached. Tides started after that. The image plots of steady state concentrations for toluene, oxygen and bacteria are shown in Fig. 6. Due to the lack of oxygen, little degradation of toluene occurred except in the smearing diffusive layers. Correspondingly, little growth of bacteria was observed. The chemical concentrations at a high tide after 5 tidal cycles were shown in Fig. 7. The tidal effect is clearly evident: first it created an oxygen-rich zone near the shoreline, which led to biodegradation of toluene. Secondly, it enhanced the mixing process. The smearing layer was thickened. The results at the low tide show similar patterns and changes in the chemical concentrations. In short, the simulation demonstrates that tidal oscillations lead to the formation of an oxygen-rich zone in the near-shore aquifer area. Aerobic bacterial activity sustained by the high  $O_2$  concentration in this active zone degrades the contaminants. These effects, which determine the exit condition for chemical input to the sea, have significant implications for studies of coastal pollution.

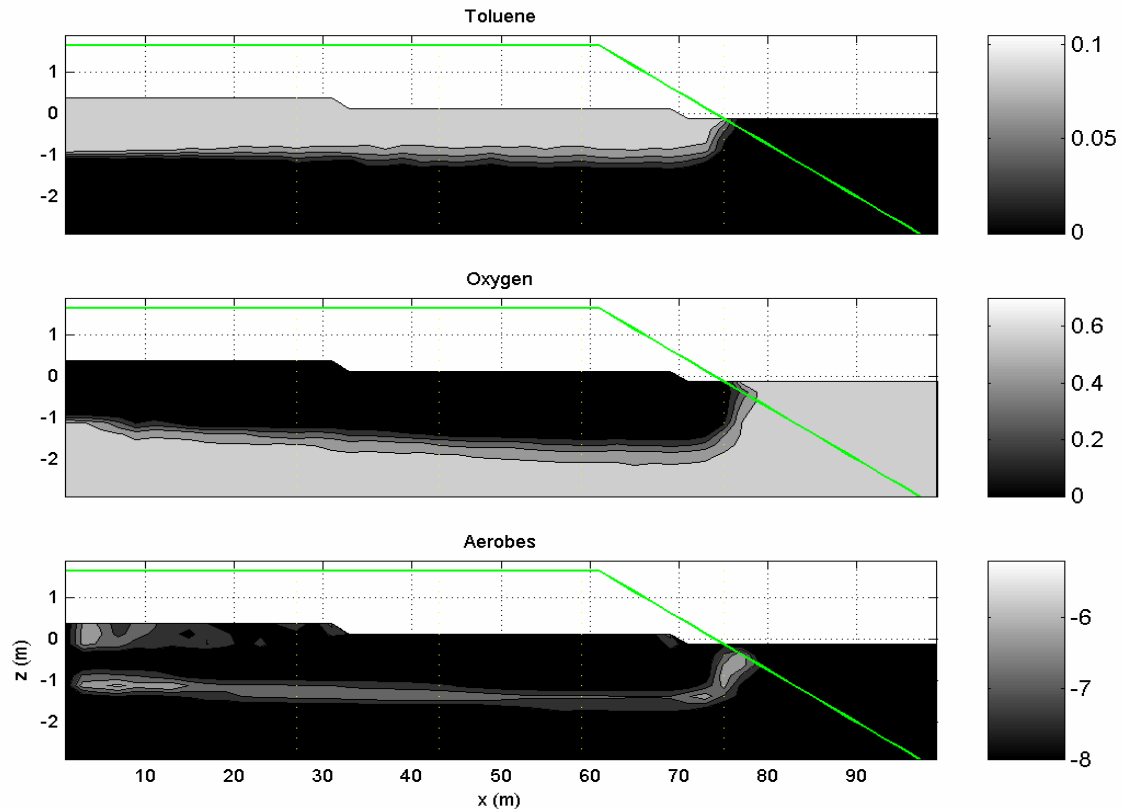


Figure 6. Image plots of the steady state concentrations for toluene (top panel), oxygen (middle panel) and bacteria (bottom panel).

### 3. CONCLUDING REMARKS

Coastal water pollution has become a serious environmental problem around the world. Most contaminants are believed to be sourced from the land. To develop sound strategies for coastal water pollution control, we need to quantify the sources, pathways and fluxes of contaminants to the coastal zone. Traditionally, terrestrial fluxes of chemicals to coastal water have been estimated on the basis of river flow alone. Recent studies suggest that contaminants entering the coastal zone with groundwater discharge can significantly contribute to coastal marine/estuarine pollution.

To determine the fluxes of chemicals to coastal water, it is important to quantify both the chemical transport processes and reactions on the pathway. There has been a large amount of research work conducted on how the chemicals may be transformed during the transport along the surface pathway, i.e., the role of a surface estuary. In contrast, little is known about the chemical transformation in the near-shore area of a coastal aquifer prior to chemicals' discharge to coastal water.

In this paper, we discussed the effects of tides and other oceanic oscillations on the chemical transport and transformation in the aquifer near the shore, drawing an analogy to the surface estuary – subsurface estuary. The discussion, based on several on-going studies, illustrated the important role that a subsurface estuary may play in determining the subsurface chemical fluxes to coastal waters. Although the tidal influence on the water table dynamics has been subjected to numerous

studies, the effects of tides on the fate of chemicals in the aquifer have not been investigated adequately. Quantification of these effects is clearly needed in order to

- provide better understanding of the pathway of land-derived nutrients and contaminants entering coastal waters; and
- provide useful information for integrating the management of upland and lowland catchments, and for improving strategies for sustainable coastal resources management and development.

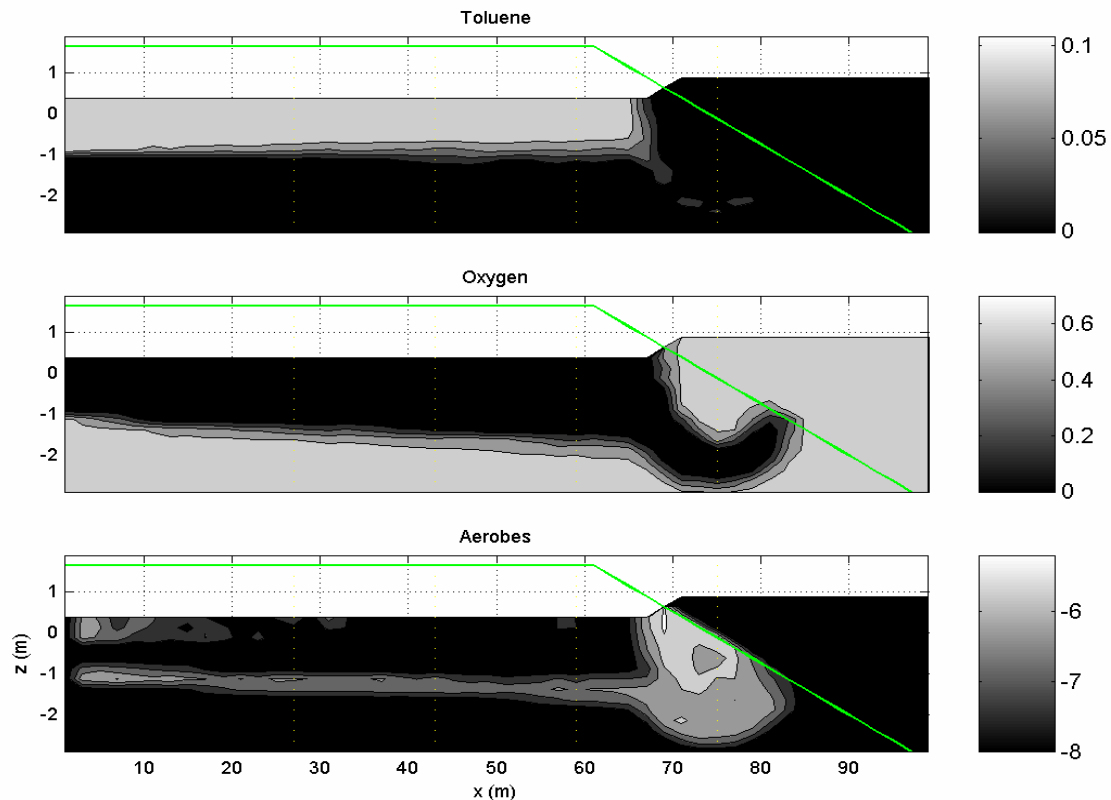


Figure 7. Image plots of the concentrations for toluene (top panel), oxygen (middle panel) and bacteria (bottom panel) at the high tide after five tidal cycles.

## ACKNOWLEDGEMENTS

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