PROJECT: "Factors responsible for limiting the degradation rate of Exxon Valdez oil in Prince William Sound beaches".

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In 2009 a team from Temple University conducted on Beach EL056C and Beach SM006C measurements of the background concentrations of dissolved oxygen, nutrients (nitrate, ammonia, phosphate) and salinity. These measurements indicated that the concentrations of oxygen and nutrients in pore water are lower than considered necessary for natural biodegradation of lingering oil to occur. Due to the contrasting properties of these two beaches, similar values of nutrients and oxygen are expected to occur throughout the beaches of Prince William Sound. The team had hypothesized that if oil is bioavailable to pore water concentrations, that is if the oil is not sequestered and sheltered from water flow in the beach, then adding oxygen and nutrients would enhance the biodegradation of the oil. The report on this topic as related to Beach EL056C is in the document titled: eco_eleanor.pdf. The document is also located at www.temple.edu/environment/eco_eleanor.pdf. We are finalizing the document containing nutrients and oxygen measurements for Beach SM006C, and it will be at www.temple.edu/environment/eco_smith.pdf

In 2009, means for delivering dissolved chemicals to bioremediate oil from the *Exxon Valdez* Oil Spill were investigated at two beaches: Beach EL056C and Beach SM006C. These investigations revealed that high pressure injection and ambient pressure release, could be used to deliver nutrients and oxygen to the layer of the beaches where lingering Exxon Valdez oil resides. The reports are provided in two files:delivery_eleanor.pdf and delivery_smith.pdf.
The files are located at:
www.temple.edu/environment/delivery_eleanor.pdf
www.temple.edu/environment/delivery_smith.pdf

Nutrients and oxygen measurements on EL056C

Measurements of the background concentrations of nutrients, dissolved oxygen (DO), and salinity were obtained from Beach EL056C, which harbors Heavy Oil Residue from the Exxon Valdez oil spill in 1989. Two transects were set across the beach face; one passed through an oil patch while the other transect was clean. Three pits were dug in each transect and they ranged in depth from 0.9 m to 1.5 m. The DO was less than 1.25 mg/L at oiled pits and greater than 5 mg/L at clean pits. The average nutrient concentrations in the beach were 0.39 mg-NL^{-1} and 0.020 mg-PL^{-1}. Both concentrations are lower than values needed for natural biodegradation (2 to 10 mg-NL^{-1} and 0.40 mg-PL^{-1} to 2.0 mg-PL^{-1}), which suggests that they are both limiting the biodegradation process. The lowest nitrate values were found in the oiled pits, and given the low DO at these pits, we have concluded that either nitrification (i.e., generation of nitrate) is prevented from occurring or removal of nitrate through denitrification is taking place. All factors being equal within the pore water of the beach, either situation would reflect the lack of oxygen. Therefore if oil consumption by microorganisms is occurring, it is probably doing so under anoxic conditions, a process that is extremely slow in comparison with aerobic biodegradation.

Delivery of nutrients and oxygen on EL056C, Eleanor Island and SM006C, Smith Island

Two alternative mechanisms were investigated for delivering nutrients and dissolved oxygen to the oiled zones of Beach EL056C on Eleanor Island and SM006C on Smith Island in Prince William Sound. The delivery technique chosen for EL056C, where the beach is comnposed of sedimentary materials, was High Pressure Injection (HPI) of an inert tracer, lithium, at the approximate depth of 1.0 m into the beach near the mid-tide line. The results revealed that the maximum injection flow rate was 3.0 L/min (around 0.8 gpm) and the associated pressure was around 20 m (30 psi). Therefore, exceeding any of these values would probably cause failure of the injection system. The injected tracer was monitored at multiple depths of four surrounding observation wells, and the results showed that the tracer plume occupied an area of 12 m^2 (around 130 ft^2) within 24 hours. The tracer plume travelled at the average speeds of 10 m/day in the seaward direction and 1.7 m/day in other directions. The rapid movement under HPI and the large diameter of influence (3.0 m) indicated that this method is promising for enhancing biodegradation of the *Exxon Valdez* oil if the biodegradation is limited by nutrient and/or oxygen availability.

The method of delivering nutrients and dissolved oxygen chosen for Beach SM006C, which is underlain by bedrock at a shallow depth, was Ambient Pressure Release (APR). Two transects of wells for tracer application were installed in the beach, one at the right (clean) side of the beach, and one at the left side known to be polluted with heavy oil residue. The tracer delivery occurred under ambient pressure from manifolds 0.60 and 0.45 m deep at the right and left transects respectively. Lithium in a lithium bromide solution made with seawater was used as the inert tracer. The solution was released for 58.5 hours at an average concentration of 82.6 mg/L of lithium at a constant flow rate of 0.23 LPM. The application was then switched to seawater-only for 16 hours at the same flow rate. The tracer was monitored at multiple depths at locations seaward and landward of the manifolds. The results show that the tracer fluctuated with the tidal cycle, moving landward with rising tides, and seaward with falling tides. The plume got deeper as it moved landward and shallower as it moved seaward of the maniford. As the oil is entrapped in the top 10 cm on this beach, applied nutrients and dissolved oxygen by this technique would reach the entrapped oil from beneath as they travel seaward of the manifold. Therefore, if nutrients and/or dissolved oxygen are limiting the biodegradation on this beach, this techniqure of delivery would enhance it. The large travelling speed of the plume in the seaward direction (around 1.5 to 2.0 m/day) suggests that this technique is logistically feasible from a hydraulic point of view.

In summary, our measurements in 2009 have demonstrated that the concentrations of nutrients and dissolved oxygen at oiled locations within Prince William Sound are too low for any significant biodegradation of the Exxon Valdez oil. Our investigation of two techniques to deliver additional nutrients and dissolved oxygen resulted in the following findings: High Pressure Injection (HPI) is advisable for sedimentary beaches, such as EL056C on Eleanor Island, while Ambient Pressure Release (APR) is advisable for beaches with a shallow bedrock, such as SM006C on Smith Island. If the biodegradation of the lingering *Exxon Valdez* oil is limited by the availability of nutrients and oxygen in pore water, then these delivery techniques could enhance the biodegradation process.

Request for Supplementation of Portions of 2009 Field Work and Extension of the Placement of Equipment on Eleanor Island and Smith Island Beaches

We are requesting monies to repeat the tracer delivery investigation at the Eleanor and Smith Island beaches previously studied (EL056C and SM006C). Specifically, we propose to repeat the lithium tracer releases and measurements conducted during the 2009 field season. This would be done using the same lithium release piping and monitoring well piping that was put in place in 2009 and has remained in place since that time. In addition, as in 2009, we propose to take samples of pore water from the previously-installed monitoring wells using the 2009 protocols and to measure those samples for dissolved oxygen, salinity, and temperature. Our 2009 proposal detailed these protocols and is attached for reference.

This proposed additional work will help address two important questions raised by the field work done in 2009. First, there is some question about whether the beaches had been restored to their normal, undisturbed state at the time the 2009 field work was conducted. The lithium tracer investigations conducted in 2009 occurred approximately two months after the excavation and refilling of pits on the beaches in which the delivery equipment was and monitoring wells were installed. Information at that time had led us to conclude that the beaches had resettled to their normal state within two months, and we began delivery and measurement of the tracer thereafter. Using the same protocols employed in 2009 with the equipment installed in 2009, which will have been in place for over a year, would definitively address this question. If the results obtained in 2010 are substantially the same as those obtained in 2009, this would confirm the 2009 data on beach characteristics (including the rate and distance of travel of chemicals through the beach strata) and would add credence to the possibility of delivering bioremediation chemicals to the sequestered lingering oil using this type of equipment. Conversely, if results in 2010 show substantially reduced travel of the lithium tracer through the beach strata, that might suggest that this technology would not be effective for delivery of remediation chemicals to sequestered lingering oil. Any differences between the 2010 data and the 2009 data would be important because we expect that bioremediation using this kind of technology would take place over a matter of months (rather than weeks), possibly in several successive field seasons, post-installation of the delivery systems.

The second important question that the proposed 2010 work would help address is the presence of oxygen in the areas of the beaches where lingering oil is found. Our 2009 work found very low levels of oxygen in these areas, which strongly suggests lack of oxygen as a factor limiting biodegradation of lingering oil. In contrast, work done through studies funded by Exxon Mobil (Atlas and Bragg, 2009a,b) found levels of oxygen much higher than those found in our work. Because the question of oxygen levels in beach areas containing lingering oil is critical to understanding the factors limiting lingering oil biodegradation, additional data from beach areas that undoubtedly have returned to their natural, undisturbed state would be significant.

Finally, we note that our proposal included monies for removing the delivery systems, multiport sampling wells, and sensors that were previously installed in the beaches on Eleanor and Smith Islands. Our intent was to remove them in Summer 2010. However, if pilot testing of bioremediation is adopted on these beaches, these systems could be needed to deliver nutrients and dissolved oxygen. It would be less costly and would cause less disturbance to the beach environments to use these systems rather than remove them and re-placing them at some future date. In addition, even if another method of delivery is explored, the observation wells could be used to monitor the progress of bioremediation. Thus, even if the Trustee Council decides not to fund this proposal for additional field work in 2010, we propose to extend the period within which this equipment would remain on the beaches until their presence is no longer useful to the Trustee Council.

REFERENCES

Atlas, R., Bragg, J.R., 2009a. Evaluation of PAH Depletion of Subsurface *Exxon Valdez* Oil Residues Remaining in Prince William Sound in 2007-2008 and their Likely Bioremediation Potential. AMOP Proceedings, 2009, 2,723-747.

Atlas, R., Bragg, J.R., 2009a. Bioremediation of marine oil spills: when and when not – the *Exxon Valdez* experience. Microbial Biotechnology 2, 213-221.

BUDGET AND BUDGET JUSTIFICATION

	Amount ($)
Travel	7,500
Boat rental (12 days X $2,000/day)	24,000
Summer wage for two graduate students	12,000
Supplies for lithium studies	5,000
Lithium analysis	4,500
Shipping	6,000
Direct cost	59,000
Overhead from Temple University(26%)	15340
Total	74,340
total cost with G&A at 9%	**$81,030.60**

Five people will travel from Philadelphia to Whittier to take the boat. The airline ticket per person is estimated at $1,000. In each direction, a one night stay in an Anchorage hotel at $200. Per diem for two days is $100. Thus, for five people 5X$1500=$7,500.

The boat Auklet will be rented to house six people during 12 days to conduct the installation. Costs are $2,000/day for 12 days = $24,000.

Two graduate students will be paid for three months (the summer semester) to work on this project. 2 X $2000/monthX 3 months=$12,000.

Cost of conducting the tracer studies on two beaches, $5,000.

Lithium analysis will be conducted. The budget includes 300 samples at the cost of $15 per sample = $4,500.

Shipping of equipment through carrier (e.g., ABF) to Anchorage and transport via rented trucks to Whittier for loading on the boats. Returning the equipment to Philadelphia. Shipping water and sediment samples to Philadelphia. Total costs estimated at $6,000.

The total direct cost is: $59,000. Temple University's overhead rate is 26%, which would result in $15,340. The total cost is $74,340. NOAA receives an additional 9% for G&A which would total to $81,030.

High pressure delivery of nutrients and oxygen into a beach for the bioremediation of the Exxon Valdez oil spill

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Abstract

Delivery of nutrients and dissolved oxygen for the potential bioremediation of oil from the Exxon Valdez Oil Spill was investigated at Beach EL056C of Eleanor Island, Prince William Sound, Alaska. The delivery technique was High Pressure Injection (HPI) of an inert tracer, lithium, at the approximate depth of 1.0 m into the beach near the mid-tide line. The results revealed that the maximum injection flow rate was 3.0 L/min and the associated pressure was around 20 m. Therefore, exceeding any of these values would probably cause failure of the injection system. The injected tracer was monitored at multiple depths of four surrounding observation wells, and the results showed that the tracer plume occupied an area of 12 m^2 within 24 hours. The tracer plume travelled at the average speeds of 10 m/day in the seaward direction and 1.7 m/day in other directions. The rapid movement under HPI and the large diameter of influence (3.0 m) indicated that this method should be adopted if biodegradation of the Exxon Valdez oil is limited by nutrient and/or oxygen availability.

Keywords: Exxon Valdez Oil Spill, Injection, Tracer, Lithium, Nutrients, Tide, Beach, Prince William Sound, Alaska.

1. Introduction

The 1989 Exxon Valdez oil spill polluted around 800 km of intertidal shorelines within Prince William Sound, Alaska [*Bragg et al.,* 1994; *Neff and Stubblefield,* 1995; Neff et al., 1995]. Recent studies by scientists from the National Oceanic and Atmospheric Administration (NOAA) [*Short et al.,* 2004; *Short et al.,* 2006] estimated that between 60 and 100 tons of subsurface oil persists in many initially-polluted beaches in Prince William Sound (PWS). The persistence of oil was noted by other studies [*Michel and Hayes*, 1999; *Taylor and Reimer*, 2008; Page et al., 2008, *Li and Boufadel,* 2010]. *Short et al.* [2004] found that the oil contains a relatively high percentage of Polycyclic Aromatic Hydrocarbons (PAH) known to be toxic to the fauna and flora [*Carls et al.,* 2001]. *Short et al*. [2006] reported that sea otters and harlequin ducks foraging the beaches in northern Knight Island would encounter subsurface lingering Exxon Valdez oil.

Possible responses for dealing with the persistent Exxon Valdez Oil in the subsurface of beaches of PWS range from vigorous mechanical removal of contaminated sediments [*Etkin and Tebeau,* 2005; *Owens et al.,* 2005; *Taylor and Owens,* 2005; Michel et al., 2006] to "natural attenuation" (or no-action), passing by intermediate approaches such as hot water injection [*Michel and Benggio,* 2005; *Mauseth et al.,* 2005a; *Mauseth et al.,* 2005b; *Card and Meehan,* 2005; *Thumm et al.,* 2005] and in-situ bioremediation. The latter is particularly appealing because it does not require displacement of beach sediments or oil; it simply relies on delivering needed chemicals, namely nutrients and dissolved oxygen, to the oiled zone.

The low concentration of nutrients, such as nitrate and phosphate was noted early on during clean-up of the spill (from 1989 through 1992), and led to a major effort where around 55 tons of nutrients were applied on some of the beaches of PWS [*Bragg et al.,* 1994]. More recently, *Eslinger et al*. [2001] found that the maximum concentration of nutrients is less than 0.20 mg-N/L. A recent study by Atlas and Bragg (2009) on the beach under study in this paper found an average nutrient concentration of 0.24 mg-N/L. Therefore, the nutrient nitrogen concentration is an order of magnitude smaller than the minimum needed for optimal biodegradation of hydrocarbons, which ranges from 2.0 to 10 mg/L [*Boufadel et al.,* 1999; *Du et al.,* 1999; *Zhu et al.,* 2001]. Atlas and Bragg (2009) noted that the ratio of nitrogen to non-polar hydrocarbons (Bragg et al., 1994) is high, and they concluded that adding nutrients to the beach would not enhance the biodegradation of oil. Atlas and Bragg (2009) and Owens et al. (2008) argued that the oil is sequestered within the sediments, and is thus inaccessible to pore water nutrients. We believe that the ratio is important from a stoichiometric point of view but may not be as important from a kinetics point of view, where the micro-organisms need to witness high concentrations (i.e., 2 to 10 mg/L). Oil sequestration is an important issue. However, it can be only addressed through a pilot study of bioremediation where nutrients and dissolved oxygen are added to the beach and the biotransformation of oil is monitored.

This work relies on a tracer study to address delivery of the nutrients and dissolved oxygen in Beach EL056C located on Eleanor Island at the coordinates 147° 34’ 17.42” W, 60° 33’ 45.57” N. The beach is a single pocket beach with an along-shore width of ~40 meters and an across-shore length of ~50 meters. The sediments are coarse ranging from gravel (a few millimetres) to pebbles and cobbles (10-20 cm) interdispersed between boulders (up to 100 cm). The grain size distribution is described in detail in the Supplementary Information of Li and Boufadel (2010). The beach was heavily polluted with the Exxon Valdez oil spill and was subject to extensive treatment (Page et al, 2008; Taylor and Reimer 2008). However, oil persists on this beach at the amount considered to be Heavy Oil Residue (HOR) according to the ASTM F1687-97, 2003 classification (see also (Short et al. 2004)), and it is located on the right side of the beach between the mid-tide level and the low-tide level (Supplementary Figure 1). The left side of the beach is clean. Our recent measurements at a depth of 0.80 m at this beach confirmed the lack of nutrients on this beach. In addition, a recent study by Li and Boufadel (2010) found that near-anoxic conditions existed in this beach. That study was followed by additional studies where we confirmed the findings of Li and Boufadel (2010). Therefore, not only the concentration of nutrients is small but also the concentration of dissolved oxygen.

Li and Boufadel (2010) also found that this beach consists of two layers, an upper layer that has a high permeability and is underlain by a layer that a very low permeability, 100 to 1000 times smaller than that of the upper layer. They also found that the oil is entrapped in the lower layer, a few centimeters below the interface of the two layers. The two-layer configuration implies that chemicals applied on the beach surface would not propagate deep enough to reach the oiled zone. Therefore, deep injection into the beaches emerged as an alternative technology.

Injection in aquifers is a common technique; Fox et al. (2010) performed injection test in distinct biogeochemical zones of sand and gravel aquifer in Cape Cod, MA, to study the chemical reaction and transport of selected chemicals in a field setting. Kloppmann et al. (2009) conducted 38 days injection test with Bromide and Boron and Lithium isotopes in sandy aquifer to assess the behaviour of emerging chemical pollutants. Riva et al. (2008) conducted a forced gradient tracer test using sodium bromide to analyze the relative importance of the selection of geostatistical model for heterogeneous aquifer and to describe the main aspects of solute transport at experiment site in bingen, Germany. Hartmann et al. (2007) also studied a multi-borehole radial tracer test in confined aquifer of E.Yorkshire, UK. However, we are not aware of any study evaluating the spreading of solutes following injection in a beach subjected to tide.

The Objective of this manuscript is to explore the delivery of nutrients and dissolved oxygen into lower layer of Beach EL056C using lithium as an inert tracer. A lithium bromide solution is used as surrogate for the nutrients and dissolved chemicals and is injected into the lower layer of the beach under pressure- we label this approach High Pressure Injection (HPI)- and the extent of spreading of the plume is monitored by measuring the concentration of lithium.

METHODS

As it is practically impossible to drive sensors into the beach, one needs to excavate pits to place the sensors in them and then refill the pit. However, if the concentration in the lower layer is sought, then one needs to provide a sufficient time for the soil to "heal" after excavation (i.e. to return to the original two-layer configuration). Otherwise, the measurements from sensors from the lower layer would be "contaminated" by water from the upper layer. We found, based on the measurements conducted in 2008, that a minimum period of 6 weeks is needed for this to occur. For this reason, we designed the field study in 2009 to have 8 weeks between the task of excavation and placement of sensors and the task of conducting measurements. This required two field trips in the summer of 2009. The first was June 16-28 and the second was August 18-29 when the measurements were conducted.

In total, six pits were dug for the purpose of evaluating chemicals delivery. One pit was dug for the purpose of placing an injection well where only seawater was injected under pressure to test the limiting capacity of the beach until failure. We label this well as the "blowout well". The results of the blowout well allowed us to determine the operational pressure and injected flow rate into the beach for the tracer injection well. Four pits were dug around an injection well (Figures 1 and Supplementary Figure 1). They were labeled as: InjSea, InjLand, InjLeft, and InjRight to represent the locations seaward, landward, left (looking landward), and right of the tracer injection well (Figures 1 and Supplementary Figure 1). The High Pressure Injection (HPI) was considered promising on this beach because the beach has a bedrock around 2.0 to 3.0m, which is deep enough to allow for this approach.

The overall approach was to place in each pit a PVC pipe, a multiport sampling well, and two Sampling Boxes (SB). The PVC pipe had an inner diameter of one inch, and was slotted across over the whole length to allow water passage. A pressure transducer (Mini-Diver, dataLogger) was placed at the bottom of the PVC pipe to record the water pressure at an interval of 10 minutes. The barometric pressure, monitored by an air-pressure sensor (BaroLogger, DL-500, Schlumberger), was subtracted from the readings of the pressure transducers to obtain the water level. No rainfall occurred during the field measurement period in August.

The multiport sampling wells were made of stainless steel and contained sampling ports (SP) at various levels. The ports were spaced at the interval of 0.23 m and were labeled A, B, C, and D from the bottom up. Each port was connected via a tubing that extended to the top of the pipe. A tygon tube was placed on each of the tubings, and it was connected to a luer lock three-way valve. To prevent blockage by fine sediments to guarantee good hydraulic connection between the beach pore water and the water inside the well, the ports were wrapped with fine stainless-steel screen.

The sampling box (SB) consisted of two perforated concentric cylinders made of PVC schedule 40. The chamber between them was filled with Sand #16 from Alaska Sand and Gravel Co. (http://www.anchsand.com/). The diameter of the sand grains ranged from 0.21 to 1.41 mm with an average size of 0.88 mm. The uniformity coefficient was 1.68, and both cylinders were covered with a 100X100 steel screen. The diameter of the inner cylinder was 5 cm (2 inches) the length was 15 cm (6 inches), which results in a volume of 200 mL. The inner diameter of the outer cylinder was 10 cm (four inches), and considering the thickness of the inner cylinder wall, the spacing between the cylinders was around 1.5 cm. Forty SBs were designed and build for the dual purpose of measuring the Dissolved Oxygen (DO) of pore water and as a backup for taking water samples in case the Sampling Ports (SPs) were clogged.

Lithium in a technical grade anhydrous (ReagentPlus (Registered) grade, assay >%99) LiBr (Sigma-Aldrich Co., St. Louis, MO) was used as the conservative tracer in these experiments. It was used successfully in previous beach tracer studies (Wrenn et al. 1997; Wrenn et al. 1997b) Water samples (approximately 100 mL) were collected with 50-mL luer lock syringes from the multiport sampling wells and placed in 125-mL polyethylene bottles (Fischer Scientific, Fairlawn, NJ) shipped to the laboratory at Temple University in Philadelphia, PA for analysis (of

Lithium) by atomic absorption spectroscopy with an air-acetylene flame at 670.8 nm. To provide an idea of the movement of the tracer in the field, the bromide was sampled using a Thermo Scientific (Beverly, MA) Bromide electrode and an Orion 5 Plus Benchtop meter, with the lowest detectable concentration of 0.2 ppm and reproducibility of 2%.

High Pressure Injection (HPI) system

The blowout well had the same design and hydraulic properties of the tracer injection well. However, it was designed to deliver water into the beach until failure. The tip of the blowout and injection wells was composed of a Prepak well screen (Supplementary Figure 4, left panel), specially ordered from ECT (www.ectmfg.com). The wells were made of PVC Schedule 40, and they were 1.5 cm long and 5 cm in diameter. The tip had slots that are 0.254 mm and the well was surrounded by silica sand (20x40) that was held in place by a 60X60 stainless steel mesh that was clamped on the PVC pipe using stainless steel clamps. (Note that 20x20, 40x40, 60x60 meshes have the openings of 0.8636 mm, 0.381mm, and 0.2286 mm, respectively). After burying the system in the ground, a 10 cm thick layer of bentonite (clay) was placed 30 cm below the surface in a 60 cm radius around the injection point as shown in Supplementary Figure 4 (right panel). The bentonite acts as a sealing blanket, keeping the injection from short circuiting around the pipe and anchoring it in the ground, especially when under pressure.

Two months were allowed before any measurements or tests were conducted. For the tests, a pressure transducer (Mini-Diver, dataLogger) was dropped in the PVC pipe (i.e., at the bottom of the pipe) and used to record the pressure during injection. In addition, a pressure gauge (McMaster Carr, #4066K712) with a reading dial was connected to the hose near the entrance to the well. It was used to monitor the injection in the field. The connection of the wells to the injection system was achieved using braided tubings. On that system, various flow meters and diaphragm pumps were used. Each tank had a valve for controlling its condition, along with a main ball valve for the entire system. This setup is shown in Supplementary Figure 5, where 4 tanks were used at this beach.

The pumps used allowed continuous pumping of a 12V battery from 0 to 1.5 GPM (0 to 5.7 LPM). Only one pump was needed at either the blowout well or the injection well. The flow meters allowed us to set the flow to more or less constant values over the desired periods.

For the interpretation of the concentration measurements from the monitoring wells, there is a need to assign a concentration value that delineates the edge of the plume. Assigning large value, such as 50% of the maximum, implies that concentration of 30% or 20% of the maximum are too small to be treated as part of the plume, which does not seem reasonable. Assigning a small value, such as 0.1 percent of the maximum would overestimate the spread of the plume. For this reason, we elected to use 10% of the maximum as the edge of the plume. Such a value seems realistic and measurable from an engineering point of view. It is, for example, used to delineate the extent of the hyporheic zone in streams (Ge and Boufadel 2006; Harvey and Fuller 1998). In addition, if one were to inject dissolved oxygen in the water to deliver to the oil, the concentration of oxygen would supersaturated, reaching around 100 to 120 mg/L. Therefore, by simply relying on dilution, the 10% would give a concentration at the observation wells of 10-12 mg/L. However, it is expected that the oxygen will get depleted moving away from the well due to uptake by the hydrocarbons and naturally occuring organic matter. Therefore, the oxygen concentration would be less than 10 mg/l at the observation wells. Nothing that around 2.0-3.0

mg/L in the bulk pore water is needed for aerobic biodegradation of hydrocarbons, we belive that using 10% of the maximum tracer concentration of 100 mg/L to delineate the edge of the plume provides a sufficient safety factor.

RESULTS

We report first the results of the blowout experiment, followed by those of the injection experiment. Figure 2 shows the variation of the water pressure as function of time while the flowrate was changed. For the first 10 hours, the flowrate was set at 1.0 L/min (0.26 gpm). The total head (the sum of pressure head and elevation) was around 4.0 m until around the time t=4.0 hour when it increased to 5.4 m and followed the tide closely until t=8.0 hour, where it returned to 4.0 m when the tide dropped to below 4.0 m. This means that at the flow rate of 1.0 L/min, the pressure head was controlled by the tide during high tide. The flow was then increased to 2.0 L/min at which time, the head at the well increased above the value of 5.4 (the maximum head due to tide). Due to a malfunction in the pumping system, the flow dropped to zero, but the pressure remained higher than 5.4 m, which indicates that the increase in pressure was not due to head losses at the screen, because in that case, the pressure would have returned to 4.0 m. Therefore, one concludes that the rise of pressure was due to the buildup of water pressure in the sediment volume surrounding the well. The decrease in pressure upon pump stoppage reflects migration of water away from the well. The flow was then increased to 2.5 L/min at which time the pressure increased to around 18 m. When the flow was increased to 3.0 L/min (around 0.8 gpm), the pressure started decreasing. The pressure decreased further when the flow was increased to 4.9 L/min and to 5.7 L/min. This indicates that the blowout flow is somewhat around 3.0 L/min.

The decrease in pressure indicates that water emanating from the well found a low-resistance zone through the lower layer into the upper layer whose hydraulic conductivity is large. An explanation of this behavior is given in the Discussion section. Therefore, the continuous injection of chemicals, the flowrate has to stay below the "blowout" value of 3.0 L/min (around 0.80 gpm).

The injection of the tracer was conducted based on the results of the blowout well; in essence, the flow had to be less 3.0 L/min. Figure 3 reports the flow rate during tracer injection along with the total head at the well. The flow was set at 1.0 L/min (0.26 gpm) for 8 hours, and the pressure increased immediately to 2.0 m. The pressure fluctuated with the tide until t=14 hours, after which it behaved independently of the tide. Between t=20 hours and t=25 hours, the flow was set at 2.0 L/min. At time t=25 hours, the flow rate was reduced to 1.5 L/min, and the concentration was reduced to 0.0 mg/L to simulate the flushing of the tracer, which is needed in future modeling studies to better describe well hydrodynamics. The continuous increase in pressure indicates that this well is still functioning correctly.

The design was to have the concentration constant at 100 mg/L for 25 hours and then to change it suddenly to 0.0 mg/L. Due to logistic challenges, it was not possible to ensure that the concentration remains at 100 mg/L. However, 32 measurements of the concentration in the tanks gave an average concentration of 93 mg/L with a standard deviation of 13 mg/L, which is sufficiently small in comparison with the overall change (from 100 mg/L to 0.0 mg/L).

Figure 4 shows that the concentration of lithium increased from zero to around 80 mg/L at the first sampling event, which occurred around 7 hours after the beginning of injection. Earlier sampling was not possible because the well InjSea was submerged by the tide. The concentration at SP_B (shallow) appears to be affected by the tide, and it tended to decrease with a dropping tide, as one notes at t=8 hours and t=21 hours. In contrast, the concentration at the deep sensor SP_A increased steadily with time until reaching the value of 92 mg/L at t ≈ 24 hours. At the next sampling event, t≈30 hours, the concentration of SP_A decreased to 82 mg/L, probably as a result of the decrease of the injection concentration from around 100 mg/L to 0.0 mg/L. The concentrations at the SBs were close to each other and they were smaller than those obtained from the ports. The difference in concentration between the SBs and the SPs is due to a variety of non-exclusive reasons. The two mains reasons are: 1) the SPs represent point measurements and are therefore more accurate than the SBs. The readings from the SBs represent the concentration in a 200 mL volume that could have been filled from any side. In particular, if the SB is in contact with a high permeability soil volume, it would fill up from that location. Nevertheless, we used the SBs as a backup and in situations where no SP measurements were available. Thus, the primary measurements are from the SPs, and we reported those of the SBs for completeness. 2) The discrepancy between the SPs and the SBs is local heterogeneity, which is present in all natural settings. As more sampling took place, the concentration in the SBs increased, approaching those from the sampling ports. At t≈24 hours, the concentration at all the sensors was between 50 and 95 mg/L indicating that the tracer is more or less uniformly spread along the depth of Well InjSea.

From Figure 4 one deduces that the travel time for the injected water to Well InjSea is between 5 and 7 hours, and this is based on the rise of concentration at earlier times and based on the fall of concentration at times greater than t=24 hours. As the distance is around 2.5 m, the travel speed is 10 m/day in the seaward direction.

Figure 5 shows that the tracer reached Well InjLand within 24 hours and it was around 10 mg/L, which is around 10% of the injection concentration. Therefore the travelling speed of the plume in the landward direction is approximately 1.6 m/day. The concentration at the deep SB increased to around 6 mg/L at t≈24 hours, before it dropped to around 4 mg/L at t≈31 hours, probably because the injection concentration was decreased to 0.0 mg/L. Figure 5 indicates that the tracer reached a considerable depth (0.74 m) at 1.6 m landward of the injection well. It is obvious based on mass conservation that continuous injection would (at least) sustain this concentration. In fact, preliminary modeling that we conducted indicates that continuous injection would increase this concentration up to 30% of the injected concentration.

Chemicals move in the cross-shore (seaward-landward) directions due to the action of tide (Boufadel 2000; Boufadel et al. 2006; Brovelli et al. 2007). Therefore, the observations at Wells InjSea and InjLand do not clearly explain the effect of injection, which would be best ascertained by tracking the tracer in the along-shore direction, namely at wells InjLeft and InjRight.

Figure 6 reports the variation of the tracer at well InjLeft as function of time. At t=9.0 hours, the tracer reached 2.0 mg/L at SP_B and reached around 1.0 mg/L at SB Shallow (scale does not show such values). These values are small and should not considered as representative of the bulk of the tracer plume. However, they do suggest a certain mobility of the tracer due to pumping. The concentration reached 25 mg/L at SB Deep and 70 mg/L at SB Shallow at t=30 hours. The concentration dropped later, most likely due to the decrease in concentration from around 90 mg/L to 0.0 mg/L of lithium. Therefore, one concludes that the travel time to Well InjLeft is between 20 and 30 hours, which gives a travelling speed of approximately 2.0 m/day.

Figure 7 reports the variation of the tracer at well InjRight as function of time. At t=9.0 hours, the tracer reached around 2.0 mg/L (scale does not allow this value to show), which is close to the values reached at well InjLeft at the same time. At t=24 hours, the concentration of the tracer reached around 100 mg/L. It dropped then sharply to around 3 mg/L, which is probably due to dilution from the tide. The concentration rose again reaching 60 mg/L at t≈30 hours. The decrease that followed is due to the change of the injection concentration from 90 mg/L to 0.0 mg/L at t=25 hours. Figure 7 suggests that the travelling speed of the plume in the longshore right direction is around 1.5m/20 hours=1.8 m/day.

To give the reader a feel for the spread of the plume with time, we computed the contours of the plume as follows: At each observation well, the maximum concentration from all SPs and SBs was obtained and plotted as a function of time. Then, the software SURFER was used to obtain contours at times t=6.5 hours and 21 hours based on the concentration at the four observation wells InjSea, InjLand, InjLeft, and InjRight and at the injection well. Figure 8 shows the contours as percentage of the injection concentration (93 mg/L). It shows that the rate of spreading of the plume (delineated by 10% of the maximum) was large initially (t=6.5 hour). However, the subsequent spreading rate was not as large, which is probably due to dilution as a result of two complementary factors: 1) The tracer is moving away from the source and thus would tend to disperse and dilute upon interaction with “clean” water; and 2) the radial geometry due to injection results in less tracer mass per unit peripheral length as one moves away from the source. In other words, in the absence of a radial geometry, the tracer would still dilute, but the radial geometry exacerbates the dilution.

Discussion

Hydraulic injection tests were conducted to evaluate the feasiblity of delivering dissolved chemicals to the oil zone on Beach EL056C of Eleanor Island in Prince William Sound. The movement of water in the pore space could be imagined as occurring in tubes or micro-channels. Most of the flow occurs along the shortest path of the flow and the water velocity (or flux) decreases as the pathways deviate from the shortest path. When the flow is increased, the shortest path cannot deliver all of the excess water and thus, the velocity in the longer paths increases. In other words, the longer paths get activated. We believe this activation bring the needed chemicals to regions in the pore space that are considered “sheltered” or the oil in them is considered “sequestered” (Atlas and Bragg 2009a; Atlas and Bragg 2009b). In the tracer experiment, we noted, that samples taken prior to injection at the monitoring wells were clean but those taken 7 hours later contained sheens of oil, which suggests that new pathways through the oil layer are activated.

The natural movement of chemicals in the beach can be estimated as the product of the hydraulic conductivity and the seaward hydraulic gradient. Li and Boufadel (2010) found the hydraulic conductivity of the lower layer to be around 5.0E-5 m/s. Taking the hydraulic gradient to be

10% (i.e., parallel to the surface) one obtains a seaward speed of about 0.50 m/day, which is 20 folds smaller than the 10 m/day found in this study. Therefore, the enhancement of the hydraulic conveyance is another indicator that the HPI of nutrients and dissolved oxygen would likely enhance biodegradation of oil (if oil biodegradation is limited by nutrient and oxygen availability).

We found that the maximum discharge that could be injected into the lower layer (i.e., deep injection) was around 3.0 L/min and the associated (blowout or failure) pressure was 20 m. As it is highly unlikely for the water to go upward through the 10 cm-thick bentonite layer (Supplementary Figure 4, right panel) we believe that, at the critical flow of 3.0 L/min, the sudden and continual decrease in pressure after increasing the flow suggests that there is an irreversible process that occurred within the sediments. This process is the enlargement of the diameters of some tubes in a process that can be described as hydraulic fracturing occurring at the millimeter scale. The increase in the number of micro-channels at failure is not likely, because we do not think that the increase would cause the dramatic decrease in pressure at high flow. It is more likely due to the enlargement of certain micro-channels as the pressure drop is inversely proportional to the square of the diameter of the channel (Clark 1996). In addition, the increase in the number of channels would not result in an irreversible behavior, as observed in Figure 2.

The high pressure buildup prior to failure suggests that, despite its heterogeneity, the beach can still be treated as a homogeneous system from a hydraulics point of view. Had the heterogeneity been too large, as stipulated by Atlas and Bragg (2009a,b) for the beaches of Prince William Sound, then failure would have occurred at much lower pressure, say 5m.

It was found that the concentration of the tracer reached the shallow sensors first followed by the deep sensors. As it is unlikely that the tracer moved downward from the shallow sensors to the deep sensors within the time frame under consideration, we conclude that, at any particular moment, the tracer plume resembled an inverted cone. This implies an upward transport of applied chemicals. Considering that the oil layer on this beach is around 30 cm below the surface (see Supplementary Figure 3), the deep injection, as conducted herein, would bring needed chemicals to the oil layer from below, which makes bioremediation more promising for the following two reasons: 1) As the porosity in the lower layer is small (Li and Boufadel 2010), the injected chemicals would not dilute as much when they are applied in the upper layer. In addition, they would be sheltered from dilution with the incoming tides and waves that occur at the beach surface. Thus, the needed mass of chemicals would be small. And 2) As the movement of water in the beach in the mid to lower intertidal zone is outward of the beach (Li and Boufadel 2010), the only way that the needed chemicals (nutrients, dissolved oxygen) would move to the oil layer is by applying them below that layer. Applying them above the oil layer would, most likely, cause them to be washed out to the sea.

The plume of the tracer (delineated as 10% of the maximum) covered an area of 12 m^2 centered at the injection well within 24 hours. The diameter of the influence of the well is around 3.0 m (10 feet), which is much larger than the diameter of the confining bentonite layer was (1.0 m). The large diameter of influence indicates that chemicals' delivery via injection is logistically feasible. Based on our work on this beach, Beach EL056C, we estimate the area of the oil patch to be around 25 m^2. Therefore, if biodegradion of oil is limited by the nutrient and/or oxygen availability, 2 to 3 injection wells on this beach would ensure complete spatial coverage for successful bioremediation.

AKNOWLEDGMENTS

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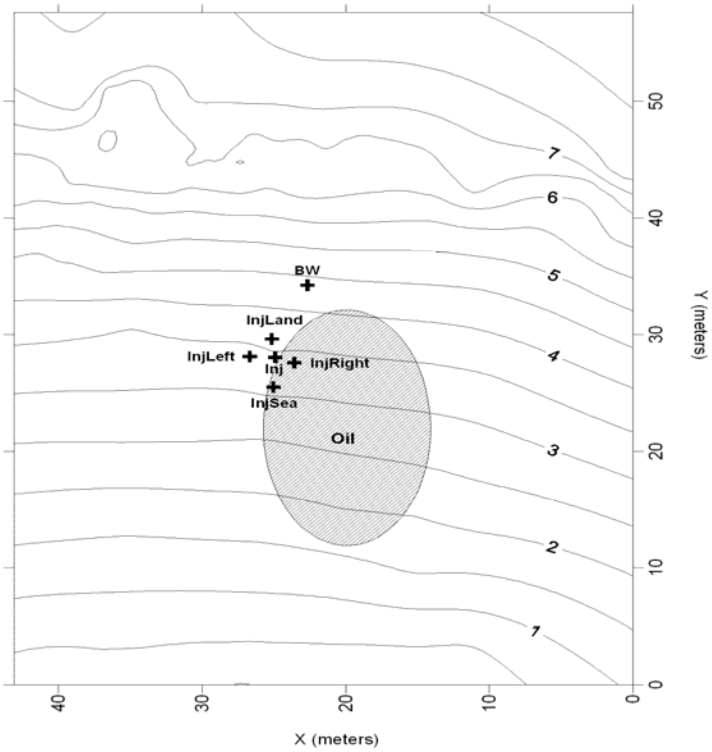


Figure 1: Top view showing the topographic contours of Beach EL056C. The Injection well (labeled Inj) is at the approximate location x=25 m; y=28 m. It is surrounded by four observation wells: On the landward side (InjLand), on the seaward side (InjSea), on the left (InjLeft) and on the right (InjRight). The blowout well (BW) is landward, at the location (x=22 m, y=35 m).

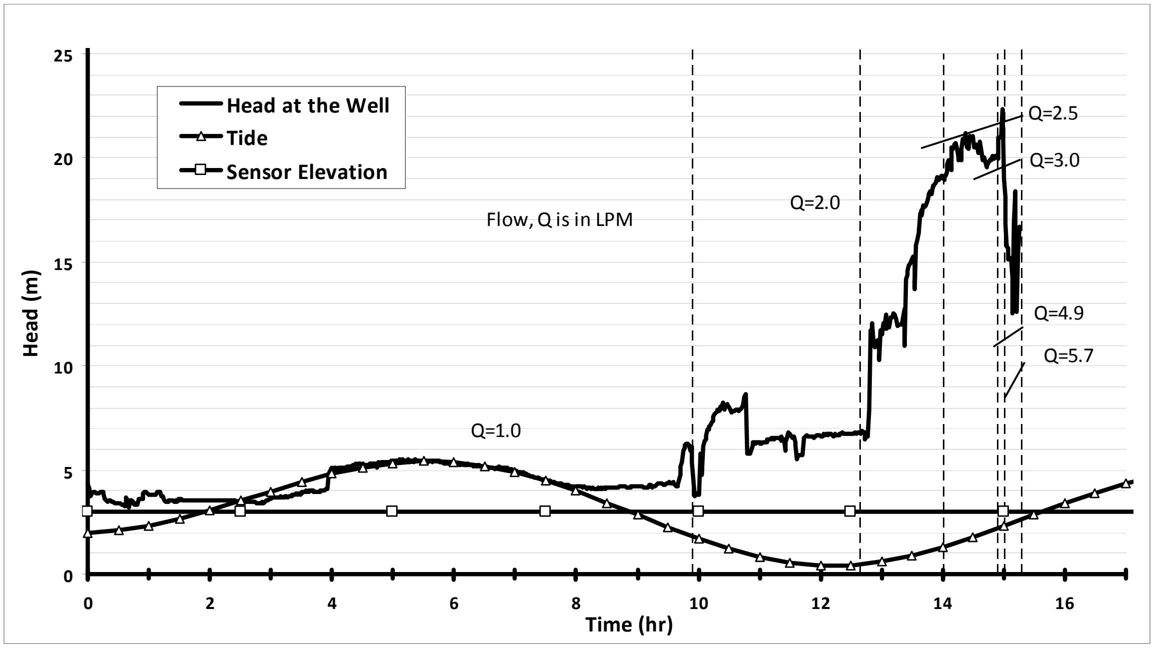


Figure 2: Variation of the total head as function of time as the injection flow rate (in L/min) was changed.

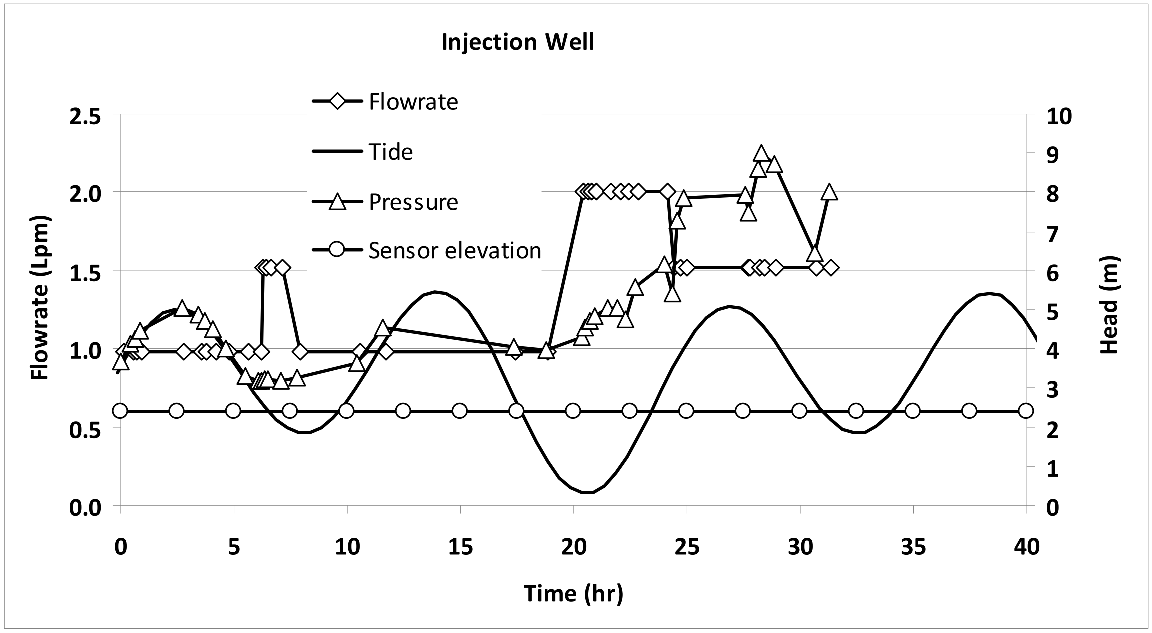


Figure 3: Variation of the flowrate and pressure during tracer injection. The injection occurred until t=33 hours. The average injection concentration between 0 and 25 hours was 93 mg/L. It was reduced suddenly to 0.0 mg/L at t=25 hours.

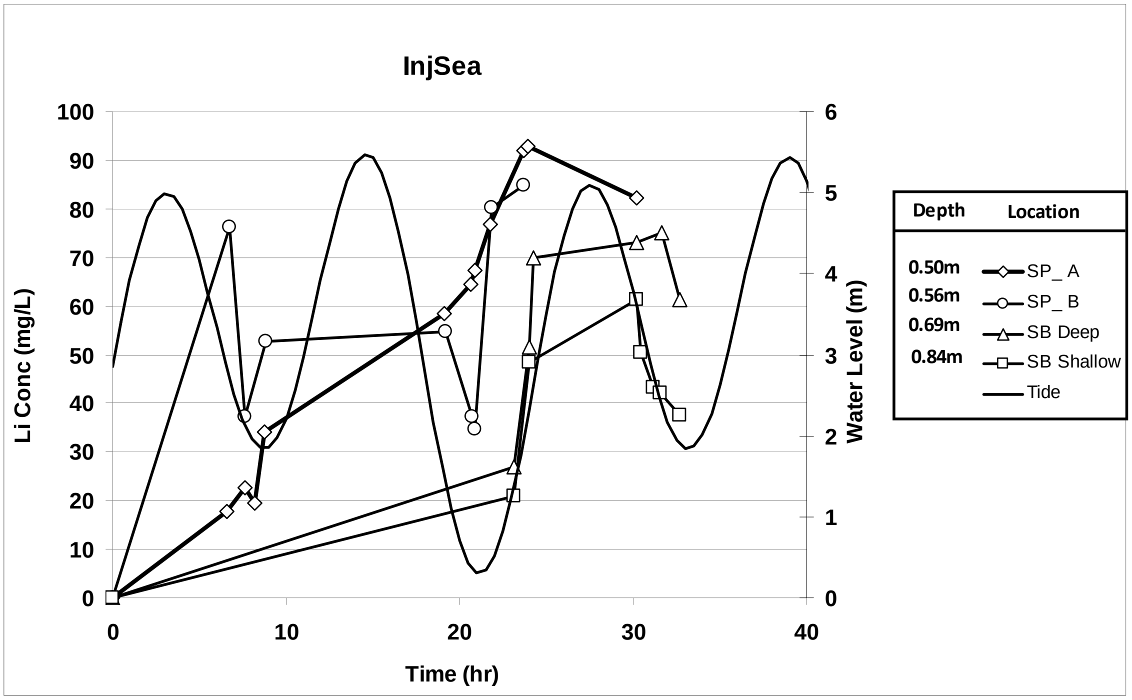


Figure 4: Variation of the concentration at various vertical locations at InjSea (Figures 1, 2, and 5), which is 2.5 m seaward of the injection well. The depth is reported in the frame on the bottom right of the figure.

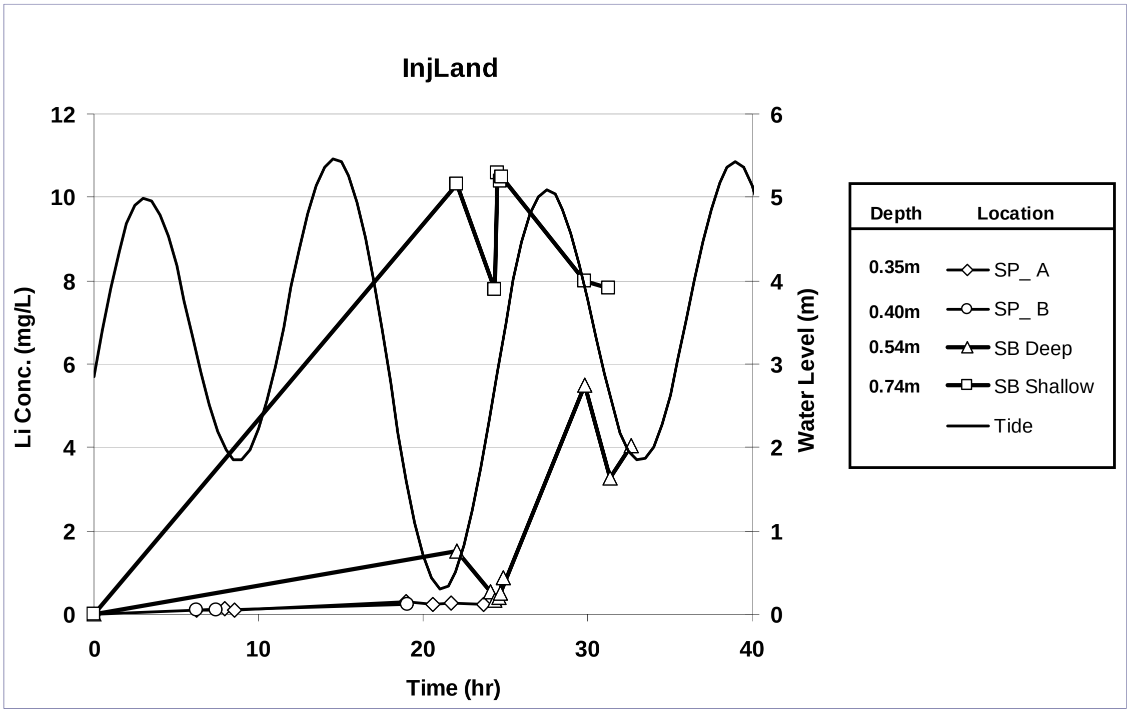


Figure 5: Variation of the concentration at various vertical locations at InjLand (Figures 1, 2, and 5), which is 1.6 m landward of the injection well. The depth is reported in the frame on the bottom right of the figure.

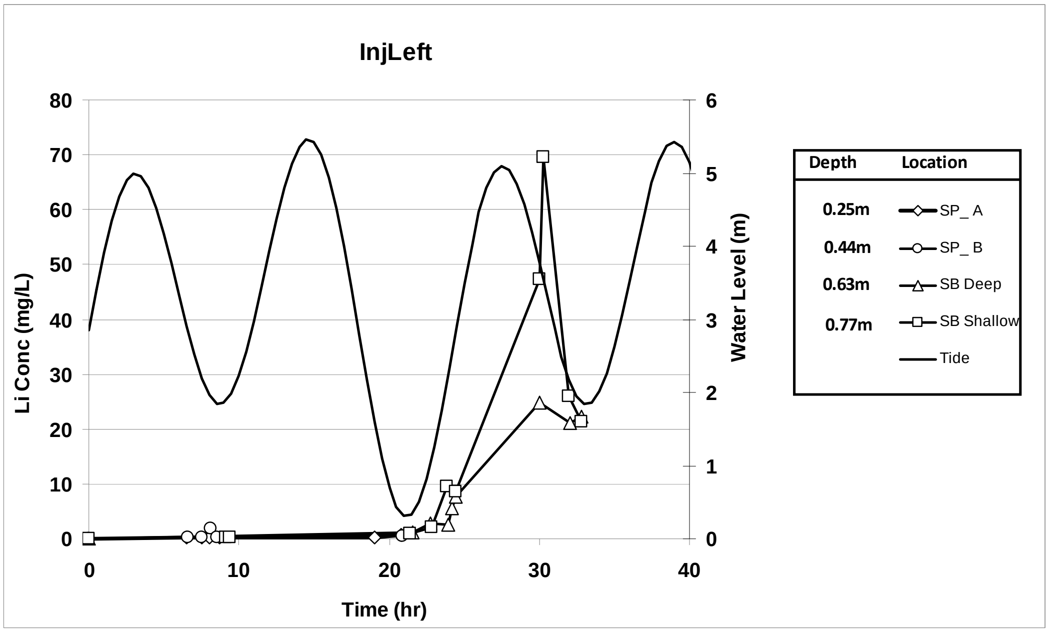


Figure 6: Variation of the concentration at various vertical locations at InjLeft (Figures 1,2, and 5), which is 1.7 m left (looking landward) of the injection well. The depth is reported in the frame on the bottom right of the figure.

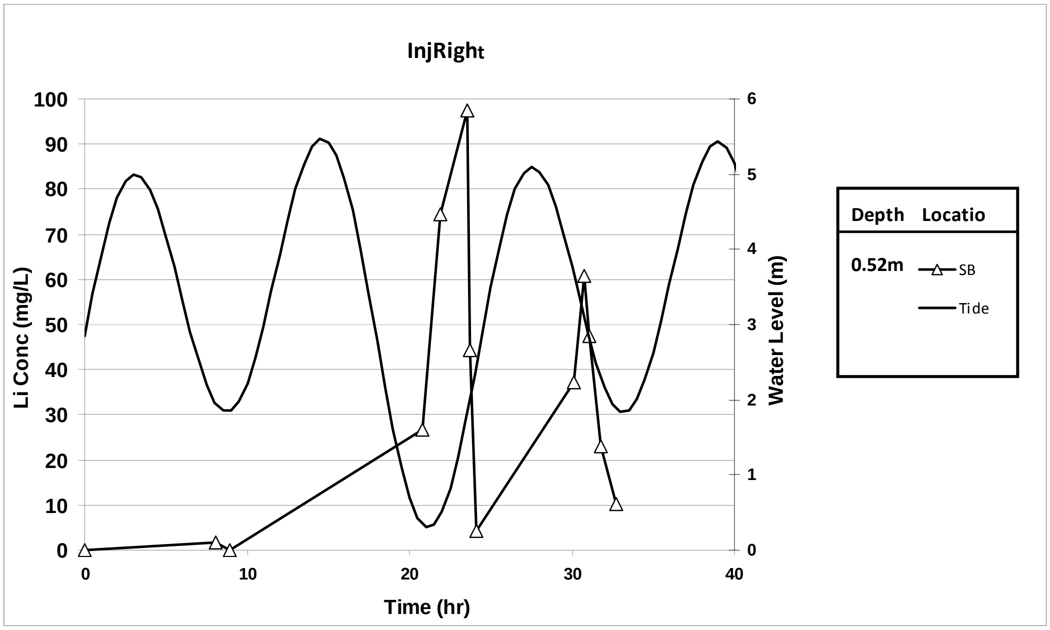


Figure 7: Variation of the concentration at various vertical locations at InjRight (Figures 1, 2, and 5), which is 1.5 m right (looking landward) of the injection well. Only a sampling box (SB) placed at the depth of 0.52 m was used.

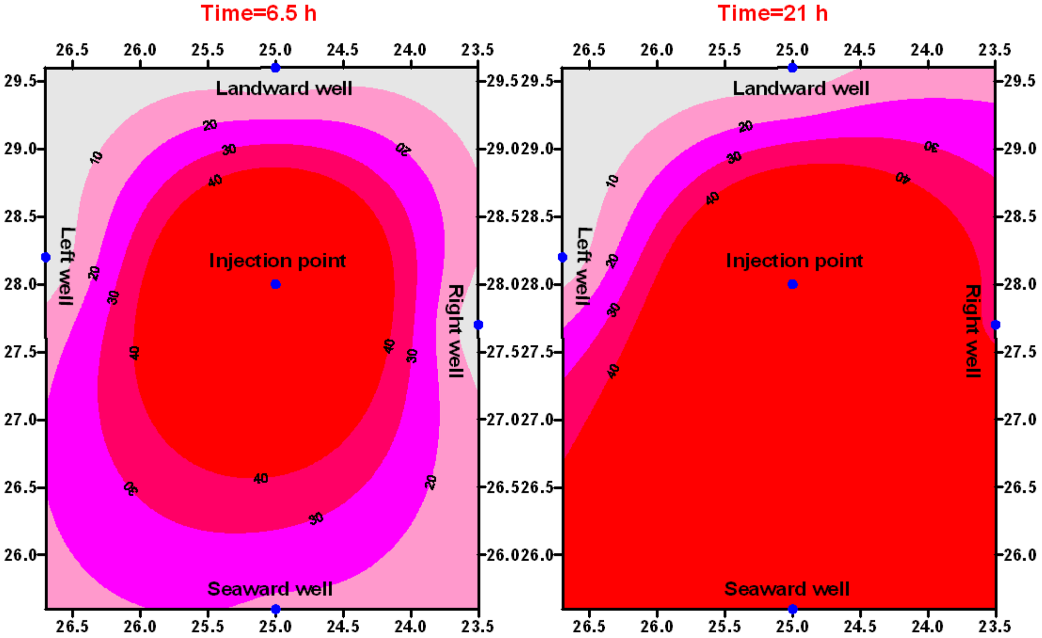
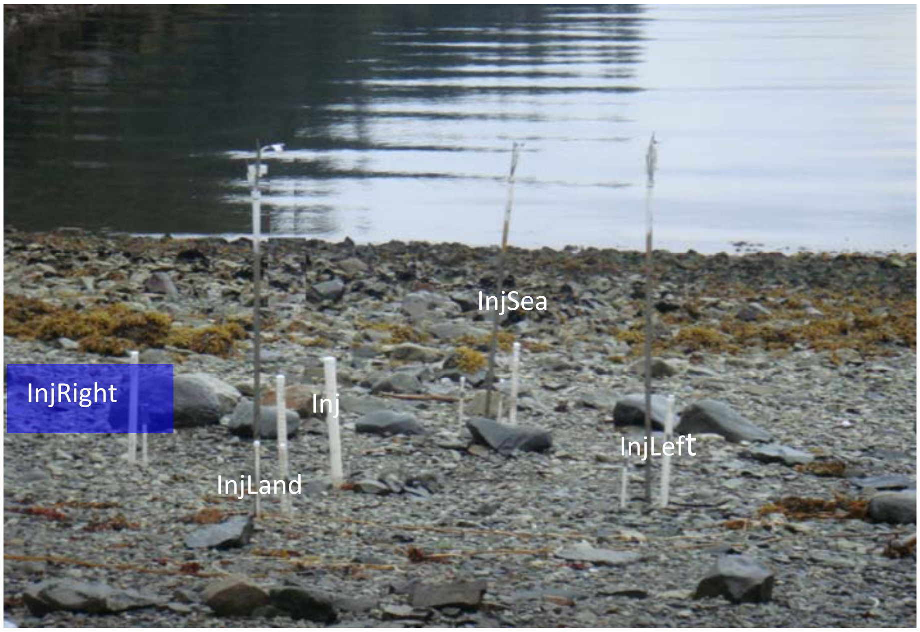
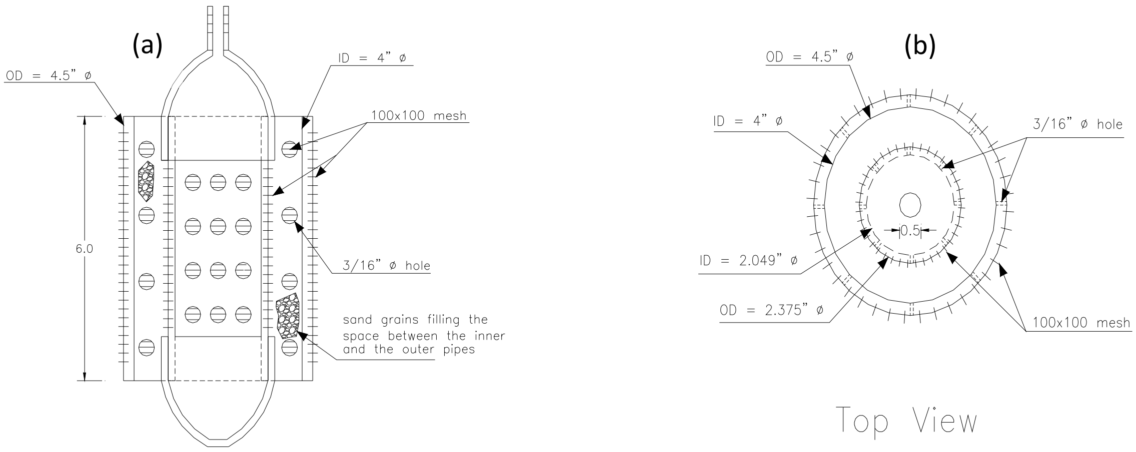


Figure 8: Empirical contours of lithium concentration as percentage of the maximum at two different times, 6.5 hours and 21 hours. The edge of the plume was delineated where the concentration is 10% of the maximum. The figure indicates that at t=21 hours, the injected plume occupies an approximate area of 12 m^2 (4.0 m cross shore X 3.0 m along shore).

SUPPLEMENTARY FIGURES



Supplementary Figure 1: The cluster of wells in the center represents the Tracer Injection well along with the observation wells around it. On the landward side (InjLand), on the seaward side (InjSea), on the left (InjLeft) and on the right (InjRight).



Supplementary Figure 2: The sampling box (SB) used for water sampling. a) A vertical cross section of the SB, b) a horizontal cross section at mid height.

Supplementary Figure 3: Picture of the pit for the injection well facing landward. Note the oil layer at the depth of 20-30 cm.

Supplementary Figure 4: The left panel shows the screen that covered the tip of the injection well and the blowout well. The right panel shows the injection well along with surrounding wells (the sea is to the left in this figure).

Supplementary Figure 5: The tanks used for injection, each has a boiler drain type valve, with a ball valve controlling the flow (not visible).

Feasibility of deep nutrients delivery into a Prince William Sound beach for the bioremediation of the Exxon Valdez oil spill

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ABSTRACT

Delivery of nutrients and dissolved oxygen to potentially bioremediate oil from the Exxon Valdez Oil Spill was investigated using tracer studies at Beach SM006C of Smith Island, Prince William Sound, Alaska. Two transects of wells for tracer application were installed in the beach, one at the right (clean) side of the beach, and one at the left side that was polluted with heavy oil residue. The tracer delivery occurred under ambient pressure from manifolds 0.60 and 0.45 m deep at the right and left transects respectively. Lithium in a lithium bromide solution made with seawater was used as the inert tracer. The solution was released for 58.5 hours at an average concentration of 82.6 mg/L of lithium at a constant flow rate of 0.23 LPM. The application was then switched to seawater-only for 16 hours at the same flow rate. The tracer was monitored at multiple depths at locations seaward and landward of the manifolds. The results show that the tracer fluctuated with the tidal cycle, moving landward with rising tides, and seaward with falling tides. The plume got deeper as it moved landward and shallower as it moved seward of the maniford. As the oil is entrapped in the top 10 cm on this beach, applied nutrients and dissolved oxygen by this technique would reach the entrapped oil from beneath as they travel seaward of the manifold. Therefore, in situations where biodegradation is limited due to nutrients and/or dissolved oxygen, this techniqure of delivery would enhance oil biodegradation. The large travelling speed of the plume in the seaward direction (around 1.5 to 2.0 m/day) suggests that this technique is logistically feasible from a hydraulic point of view.

INTRODUCTION

The 1989 Exxon Valdez oil spill polluted around 800 km of intertidal shorelines within Prince William Sound, Alaska [*Bragg et al.,* 1994; *Neff and Stubblefield,* 1995; Neff et al., 1995]. Recent studies by scientists from the National Oceanic and Atmospheric Administration (NOAA) [*Short et al.,* 2004; *Short et al.,* 2006] estimated that between 60 and 100 tons of subsurface oil persists in many initially-polluted beaches in Prince William Sound (PWS). The persistence of oil was noted by other studies [*Michel and Hayes,* 1999; *Taylor and Reimer,* 2008; Page et al., 2008, *Li and Boufadel,* 2010]. *Short et al.* [2004] found that the oil contains a relatively high percentage of Polycyclic Aromatic Hydrocarbons (PAH) known to be toxic to the fauna and flora [*Carls et al.,* 2001]. *Short et al*. [2006] reported that sea otters and harlequin ducks foraging the beaches in northern Knight Island would encounter subsurface lingering Exxon Valdez oil.

Possible responses for dealing with the persistent Exxon Valdez Oil in the subsurface of beaches of PWS range from vigorous mechanical removal of contaminated sediments [*Etkin and Tebeau,* 2005; *Owens et al.,* 2005; *Taylor and Owens,* 2005; Michel et al., 2006] to “natural attenuation” (or no-action), passing by intermediate approaches such as hot water injection [*Michel and Benggio,* 2005; *Mauseth et al.,* 2005a; *Mauseth et al.,* 2005b; *Card and Meehan,* 2005; *Thumm et al.,* 2005] and in-situ bioremediation. The latter is particularly appealing because it does not require displacement of beach sediments or oil; it simply relies on delivering needed chemicals, namely nutrients and dissolved oxygen, to the oiled zone.

The low concentration of nutrients, such as nitrate and phosphate was noted early on during clean-up of the spill (from 1989 through 1992), and led to a major effort where around 55 tons of nutrients were applied on some of the beaches of PWS [*Bragg et al.,* 1994]. More recently, *Eslinger et al*. [2001] found that the maximum concentration of nutrients is less than 0.20 mg-N/L. A recent study by Atlas and Bragg (2009) on the beach under study in this paper found an average nutrient concentration of 0.24 mg-N/L. Therefore, the nutrient nitrogen concentration is an order of magnitude smaller than the minimum needed for optimal biodegradation of hydrocarbons, which ranges from 2.0 to 10 mg/L [*Boufadel et al.,* 1999; *Du et al.,* 1999; *Zhu et al.,* 2001]. Atlas and Bragg (2009) noted that the ratio of nitrogen to non-polar hydrocarbons (Bragg et al., 1994) is high, and they concluded that adding nutrients to the beach would not enhance the biodegradation of oil. Atlas and Bragg (2009) and Owens et al. (2008) argued that the oil is sequestered within the sediments, and is thus inaccessible to pore water nutrients. We believe that the ratio is important from a stoichiometric point of view but may not be as important from a kinetics point of view, where the micro-organisms need to witness high concentrations (i.e., 2 to 10 mg/L). Oil sequestration is an important issue. However, it can be only addressed through a pilot study of bioremediation where nutrients are added to the beach and the biotransformation of oil is monitored.

The purpose of our investigation herein is to evaluate the transport of a tracer simulating nutrients delivery for a potential bioremediation study of the oil. The study took place on Beach SM006C located on Smith Island at the coordinates 147° 24’ 13.84” W, 60° 31’ 10.30” N. The beach was heavily polluted from the Exxon Valdez oil spill and was subject to extensive treatment [*Taylor and Reimer,* 2008; Page et al., 2008]. However, oil persists on this beach at the amount considered to be Heavy Oil Residue (HOR) according to the ASTM F1687-97, 2003 classification (see also [*Short et al.,* 2004]), and it is located on the left side of the beach between the mid-tide line and the low-tide line (Figure 1). The right side of the beach is clean. The beach faces north, and is subjected to waves developed over a fetch of 60 km, as they travel southwest.

The sediments throughout the beach are coarse, ranging from gravel (a few millimeters) to pebbles and cobbles (10-20 cm) interspersed between boulders (up to 100 cm). The geology consists of basalts and pillow basalt features similar to nearby Knight Island in the Prince William Sound [*Lethcoe,* 1990]. Page et al. (2008) classified this beach as "exposed bedrock/rubble". The left side of the beach is exposed to waves while a tombolo (protruding rock formation) shelters the right side of the beach below the mid tide level. An armor layer of worked pebbles and clasts covers most of the left side of the beach and the mid to upper tide region of the right side of the beach. As one moves seaward, that layer disappears and a higher percentage of boulders emerges, and possibly an outcrop of the bedrock. Twenty nine sediment samples were obtained at various depths (from 30 cm to 90 cm) throughout the beach and were sieved in the lab to generate the grain size distribution. The average effective grain size (d_{10}) was 0.7 mm, the average grain size (d_{50}) was 7.2 mm, and the average coefficient of uniformity (d_{60}/d_{10}) was around 15, the latter suggests a poor sorting (i.e, a wide distribution).

Our recent measurements at a depth of 0.80 m at this beach (*Sharifi et al.,* 2010, manuscript in preparation) confirmed the low concentrations of nutrients reported by Atlas and Bragg (2009) and throughout the Sound. We also measured the dissolved oxygen concentration in the oiled area of this beach and found it to be less than 1.0 mg/L. Therefore, not only is the concentration of nutrients small, but also the concentration of dissolved oxygen. Nevertheless, the objective of this study is to investigate the delivery of dissolved chemicals into the beach, and such chemicals could be nutrients, dissolved oxygen, or biosurfactants, depending on the adopted bioremediation. We sought our objective by releasing a conservative tracer, lithium in a lithium bromide solution made of seawater, and we monitored its movement in the beach. The tracer was released at the depths of 0.60 m and 0.45 on the right and left sides of the beach beach under ambient conditions. We labelled such a release Ambient Pressure Release (APR). The APR was chosen for this beach due to its shallow bedrock in the oiled area. Although no oil was present on the right side of the beach, the release at that side was intended to use as a control.

Tracer studies in aquifers is a common technique; *Fox et al.* [2010] performed injection test in distinct biogeochemical zones of sand and gravel aquifer in Cape Cod, MA, to study the chemical reaction and transport of selected chemicals in a field setting. *Kloppmann et al.* [2009] conducted a 38 day injection test with Bromide and Boron and Lithium isotopes in a sandy aquifer to assess the behavior of emerging chemical pollutants. *Hartmann et al.* [2007] studied a multi-borehole radial tracer test in a confined aquifer of E.Yorkshire, UK. To explain how pink salmon eggs in Prince William Sound became contaminated by Exxon Valdez oil, *Carls et al.* [2003] investigated groundwater movement between oil-contaminated intertidal beaches and salmon streams by release of fluorescent tracer dyes (Liquid rhodamine WT dye) in Sleepy Creek and Junction Creek, Prince William Sound, Alaska. However, we are not aware of any study evaluating the spreading of solutes following deep release of a tracer into a beach subjected to tide.

METHODS

As it is practically impossible to drive sensors into the beach, one needs to excavate pits to place the sensors in them and then refill the pit. However, one needs to provide sufficient time for the sediments to recover after excavation (i.e. to return to the original natural configuration). Otherwise, the measurements from sensors deep into the beach would be “contaminated” by water coming down from the shallow zone of the sediment column. We found, based on the measurements conducted in 2008, that a few weeks is needed for this to occur. For this reason, we designed the field study in 2009 to have 8 weeks between the task of excavation and placement of sensors and the task of conducting measurements. This required two field trips in the Summer of 2009. The first was June 16-28 and the second was August 18-29 when the measurements were conducted.

Two trenches were dug in the cross-shore direction (i.e., landward-seaward) to conduct the Ambient Pressure Release (APR): One in the clean area of the beach (right side facing landward) and another in the oiled area of the beach (left side) (Figures 1 and 2). While the material of the Right Trench were unconsolidated material (Figure 3), that of the Left (oiled) Trench consisted mostly of large boulders with small spacing between them (Figure 4). The excavation was extremely difficult in the (left) oiled trench requiring the usage of a hand-held 64 lb jackhammer (Brute^{TM} Breaker Hammer, Bosch) and a 71 lb auger (General 330 H 5HP Two-Man Auger). A manifold was placed in each trench in the along-shore direction and observation “wells” or “pits” were placed landward and seaward of it. At each of the observation wells, sensors were placed at various depths. The trenches were then re-filled and two months were allowed to pass before the tracer (lithium) experiment was started. During the experiment, water samples were taken from the sensors in the wells, and they were later analyzed in the lab for lithium concentration.

For sampling the movement of the tracer, the overall approach was to place in each pit, a PVC pipe, a multiport sampling well, and two Sampling Boxes (SB). The PVC pipe had an inner diameter of one inch and was slotted across over the whole length to allow water passage. A pressure transducer (Mini-Diver, dataLogger) was placed at the bottom of the PVC pipe to record the water pressure at an interval of 10 minutes. The barometric pressure, monitored by an air-pressure sensor (BaroLogger, DL-500, Schlumberger), was subtracted from the readings of the pressure transducers to obtain the water level. No rainfall occurred during the field measurement period in August.

The multiport sampling wells were made of stainless steel and contained sampling ports (SP) at various levels. The sampling ports were spaced at the interval of 0.20 m and were labeled A, B, C, and D from the bottom up. Each port was connected via a tubing that extended to the top of the pipe. A tygon tube was placed on each of the tubings, and it was connected to a luer lock three-way valve. To prevent blockage by fine sediments and to guarantee good hydraulic connection between the beach pore water and the water inside the well, the ports were wrapped with fine stainless-steel screen.

The Sampling Boxes (SBs) were used as backup in case the SPs got clogged. Each SB (Figure 5), consisted of two perforated concentric cylinders made of PVC schedule 40. The chamber between them was filled with Sand #16 from Alaska Sand and Gravel Co.

(http://www.anchsand.com/). The diameter of the sand grains ranged from 0.21 to 1.41 mm with an average size of 0.88 mm. The uniformity coefficient d_{60}/d_{10} was 1.68, which reflects a rather uniform sand. Both cylinders were covered with a 100X100 steel screen. The diameter of the inner cylinder was 5 cm (2 inches) the length was 15 cm (6 inches), which results in a volume of 300 mL. The inner diameter of the outer cylinder was 10 cm (four inches), and the spacing between the cylinders was around 1.5 cm. Twelve SBs were used for this study.

Lithium in a technical grade anhydrous (ReagentPlus (Registered) grade, assay >%99) LiBr (Sigma-Aldrich Co., St. Louis, MO) was used as the conservative tracer in these experiments. It was used successfully in previous beach tracer studies [*Wrenn et al.,* 1997b; *Wrenn et al.,* 1997a]. It was applied in a lithium bromide solution at the approximate concentration of 5,000 mg/L. Water samples (approximately 100 mL) were collected with 50-mL luer lock syringes from the multiport sampling wells and placed in 125-mL polyethylene bottles (Fischer Scientific, Fairlawn, NJ) shipped to the laboratory at Temple University in Philadelphia, PA for analysis (of Lithium) by atomic absorption spectroscopy with an air-acetylene flame at 670.8 nm. To provide an idea of the movement of the tracer in the field, the bromide was sampled using a Thermo Scientific (Beverly, MA) Bromide electrode and an Orion 5 Plus Benchtop meter, with the lowest detectable concentration of 0.2 ppm and reproducibility of 2%.

Ambient Pressure Release (APR)

The Ambient Pressure Release (APR) implemented was designed to release the tracer solution through a manifold (Figure 3) along shore (i.e., perpendicular to the seaward-landward direction). The manifold was made of a 0.5 inch soaker hose enclosed with a 1 inch perforated

PVC pipe wrapper with a 60x60 mesh having an opening width of 0.009 inches. The perforations in the pipe had the diameter of 0.0016 m and were spaced by approximately 0.1 m. It was connected to a 0.5 inch polypropylene tube that protruded from the surface. The manifold was at the depth of 0.60 m in the Right Trench and at the depth of 0.45 m in the Left Trench. The injection tanks were placed next to each other landward of the high tide line (Figure 6).

Two months were allowed before any measurements or tests were conducted. The connection of the wells to the injection system was achieved using braided tubing. Various flow meters and diaphragm pumps were used. Each tank had a valve for controlling its condition, along with a main ball valve for the entire system. This setup is visible in Figure 6, where 8 tanks were used at this beach.

The experimental design required a flow of 0.23 LPM, (around 0.06 GPM) and a concentration of 100 mg/L of lithium for a duration of 58.5 hours, after which, the concentration was switched to 0.0 mg/L of lithium while the flow was kept constant for 16 hours. The switch to low concentration was intended to understand the flushing of the tracer from the beach, needed for modeling studies. The pumps (SHURflo #8050-305-526) allowed continuous pumping off of a 12V battery from 0 to 5.6 LPM (0-1.5 GPM). The flow meters (King Instruments Company Inc, 0.7-7 GPH) allowed us to set the flow to an essentially constant value over the desired period. Due to logistical challenges, it was not possible to ensure that the concentration remained at 100 mg/L. However, 12 measurements of the concentration in the tanks over the 58.5 hour duration gave an average concentration of 82.6 mg/L with a standard deviation of 6.3 mg/L. The latter is sufficiently small in comparison with the overall change (from 82.6 mg/L to 0.0 mg/L) such that one can assume the existence of a plateau of concentration in the tanks until t=58.5 hours when the concentration was reduced suddenly to 0.0 mg/L (by emptying the tanks and refilling them with seawater) for another 16 hours.

For the interpretation of the concentration measurements from the monitoring wells, there is a need to assign a concentration value that delineates the edge of the plume. Assigning large value, such as 50% of the maximum, implies that concentration of 30% or 20% of the maximum are too small to be treated as part of the plume, which does not seem reasonable. Assigning a small value, such as 0.1 percent of the maximum would overestimate the spread of the plume. For this reason, we elected to use 10% of the maximum as the edge of the plume. Such a value seems realistic and measurable from an engineering point of view. It is, for example, used to delineate the extent of the hyporheic zone in streams [*Harvey and Fuller,* 1998; *Ge and Boufadel,* 2006]. In addition, if one were to release dissolved oxygen in the water to deliver to the oil, the concentration of oxygen would be supersaturated, reaching around 130 mg/L. Therefore, by simply relying on dilution, the concentration at the observation wells would reach 13 mg/L. As it is expected that the oxygen will get depleted moving away from the well due to uptake by the hydrocarbons and naturally occuring organic matter, the oxygen concentration would decrease. We determined that if the decrease is up to 80%, then the concentration would still be larger than 2.0-3.0 mg/L, the minimum concentration needed for aerobic biodegradation of hydrocarbons. Therefore, it is realistic to use the 10% of the maximum tracer concentration of 82.6mg/L to delineate the edge of the plume. We report first the results of the Right Transect (clean).

RESULTS

Right Transect: The Clean Transect

Figure 7 shows the measured tracer concentration at W3_1, which is 0.75 m landward of the manifold at W3_M (Figure 2). For t < 60 hours, the tracer concentration at Sampling Port A (SP_A) increased with an increase in the tide level and decreased when the tide decreased. This indicates that each tidal cycle was displacing the tracer landward. The tank concentration was switched to 0.0 mg/L at t=58.5 hours, and Figure 7 shows that the concentration at SP_A for t between 70 and 74 hours was lower than those at 58.5 hours or 48 hours. Thus, continuous tracer release is needed to sustain the concentration high enough at 0.75 m landward of the manifold.

In terms of the bulk of the plume delineated by the 10% value (i.e., 8.0 mg/L), the tracer migrating with the tide reached a concentration of 10% of the maximum at 23 hours at SP_A, indicating a travel speed of 0.75 m/23 hours ≈ 0.80 m/day. A value of 10% was reached at t=2 hours which is relatively fast. We have considered and ruled out many possibilities for this sudden rise. However, the low values at t=10 hours suggest that such a value should be treated as an "outlier", probably because of the complex pathways due the combined effects of tidal hydraulics and subsurface heterogeneity.

In Figure 7, one notes a slight increase in the concentration of the shallow SB at t=46 hours. This value is much smaller than those observed at SP_A. The high concentration at SP_A does

not seem to reach the shallow SB (at 0.35 m deep), which indicates that the tracer remained in the deeper portion of the beach. Therefore, applying chemicals deep into the beach would not result in them being carried to shallow depths at locations landward of the application.
The seaward wells, W3_2 and W3_3 (Figure 8) show that the tracer concentration increased more rapidly with time than the landward well W3_1. This is not surprising as tidal hydraulics results in a net seaward movement of chemicals [*Wrenn et al.,* 1997b; *Boufadel et al.,* 2007]. The plume reached W3_2 at approximately t=10 hours and reached W3_3 at approximately t=25 hours. This seems reasonable as the distance of W3_3 to the manifold (W3_M) is around double that of W3_2 to W3_M. The travel speed was around 1.90 m/day for W3_2 and 1.8 m/day for W3_3.

For W3_2, the earlier arrival of the plume (t=2 hours) reflects the ease of the pore water to move out towards the sea with the tide. Due to the large number of samples that were taken at that particular time, we are inclined to accept these readings as representative of the physics. Note that, unlike W3_1 where the concentration reached more than 10% in less than two hours, the concentration at W3_3 remained less than 5%. The concentration at both SP_A and SP_B had an increasing trend until t=50-60 hour (depending on the availability of measurements) and it was always lower at t=70 hours, 11.5 hours after switching to injection of 0.0 mg/L of lithium (i.e., only saltwater).

For W3_2, the concentration at SP_A (which is at 59 cm depth) was larger than that at SP_B (which is 35 cm deep). However, they were relatively close at W3_3. This indicates that the tracer moves upward (i.e., toward the surface). In other words, the ratio of concentration of SP_B to SP_A increased indicating a shift of the mass of the plume upward. In general, the concentrations along Transect 3 were higher at W3_2 in comparison with other wells, W3_1 and W3_3. This is not surprising due to the fact that W3_1 was landward of the manifold and W3_3 was seaward, but farther, from the manifold, W3_M, than W3_2.

Left Transect: The Oiled Transect

The trench contained large boulders (Figure 4), and the manifold was 0.45 m deep. There were four monitoring wells: two landward of the manifold location and two seaward of it.

Figure 9 reports the concentration of the tracer landward of the manifold (Figure 2). The lower panel contains the results of well W1_2 located 0.85 m landward of the manifold. There is a slight increase in concentration at SP_B and the shallow SB. However, the concentration at SP_A seems to increase at 25 hours and continue to rise, with some fluctuations, until reaching the maximum at 58.5 hours. The concentration of SP_A dropped sharply afterwards, which could be due to tidal hydraulics (i.e, dilution by the tide). The decrease at t=70 hours seems attributed to stoppage of high concentration injection and the conversion to injection of seawater (0.0 mg/L of lithium). The concentration at SP_B and the shallow SB increased starting at t=35 hours and continued until t=58.5 hours. The concentration at these sensors (SP_B and shallow SB) became almost zero at times greater than 70 hours. One concludes that the tracer plume moved 0.85 m in 40 hours, which gives a landward travelling speed of 0.50 m per day.

The upper panel of Figure 9 contains the concentration of two SBs at well W1_1, located 1.40 m landward of the Ambient Pressure Release (APR) manifold. Measurements from the Sampling Ports (SP) were not available. The tracer was higher in the deep SB, which was noted in well W1_2 of this trench and W3_1 (located landward of the injection manifold at the Right Trench). This suggests that the tracer does not propagate much upward in this trench. Based on the fact that the concentration reached 12 mg/L at t=58.5 hours, one may conclude that the travel speed of the plume is around 0.50 m per day, which is, interestingly, very close to the landward speed obtained based on the data of W1_2 (note end of previous paragraph).

Figure 10 reports the concentration at wells W1_3 and W1_4, located 0.80 m and 1.60 m seaward of the manifold W1_M (Figure 2). The upper panel (W1_3) shows that the concentration of the lithium tracer increased first at the deep sensors, SP_A and deep SB. The concentrations of these sensors were relatively close for the period that they overlapped. The concentration of both sensors was close to the maximum at t=35 hours. Afterward measurements were obtained only from SP_A and they show that the concentration reached that of the source (83 mg/L) at 58.5 hours, before dropping to below 10 mg/L at time greater than 70 hours. The concentration at the shallow SB increased steadily, with a small drop for times between 45 and 50 hours. It increased again to reach 42 mg/L, which is around 50% of the maximum, at t=58.5 hours. It dropped below 10 mg/L at times greater than 70 hours. Based on this panel, the tracer plume moved a distance of 0.80 m in 10 hours, an approximate speed of 2.0 m/day in the seaward direction.

The lower panel of Figure 10 shows the tracer concentration as obtained from two SBs at well W1_4, located 1.60 m seaward of the manifold (Figure 2). The concentration at the deep SB increased first, reaching 17 mg/L at t=10 hours. The concentration at the shallow SB reached 11 mg/L as the same time. At around t=35 hours, there was a reversal in the order of concentrations with that of the shallow SB becoming higher. This indicates upward migration of the plume where more of the mass of the plume is at the upper sensor. This is particularly noted for well W1_3 (upper panel of Figure 10) where the concentration of the shallow SB was one third of that of the deep SB for the majority of the time. Based on the concentration at t=10 hours, the plume travelled 1.60 m in 10 hours, which gives an average seaward migration speed of 3.50 m/day, a large value that should be considered as an approximation considering the uncertainty in delineating the plume (i.e., 10% of the maximum).

DISCUSSION

A tracer, lithium bromide, was released under ambient pressure conditions in manifolds 0.60 and 0.45 m deep at two transects of Beach SM006C that ran landward-seaward. The Right Transect was clean and the Left Transect contained oiled at the concentration of Heavy Oil Residue (HOR). The concentration of the tracer at the source was around 83 mg/L and the flow rate was 0.23 liter per minute (around 4 cc per second) and it was deliverd through a one inch (ID) 0.82 m long manifold placed perpendicular to the transects. After 58.5 hours of Ambient Pressure Release (APR), the concentration was changed to 0.0 mg/L for another 16 hours while maintaining the flow rate.

The migration speed of the tracer in the landward direction was 0.8 m/day at the Right (clean) Transect and 0.5 m/day at the Left (oiled) Transect. In the seaward direction, the migration speed was around 2.0 m/day at both Transects. Many factors affect the movement of the plume, such as the location with respect to the tidal cycle, the topography, and the permeability of the beach. The travel speeds should be treated as approximate values, as the plume was delineated by the 10% concentration (of the maximum). We estimate the uncertainty in estimating these values to be around 50%.

As the plumes at both transects moved landward, the ratio of the concentration at shallow sensors to that at deep sensors decreased. The same ratio increased as the plumes moved seaward. This indicates that the plumes sank into the beach as they migrated landward, and rose toward the surface as they migrated seaward. This finding is represented in Figure 11 which shows the edge of the plume (the 10%) as interpolated from sensors at t=58.5 hours. As noted in tidal studies [*Li and Boufadel,* 2010; *Boufadel,* 2000; *Boufadel et al.*, 2006], seawater fills the beach on the landward side during high tides and travels seaward within the beach during low tides. The flow becomes upward when the water exits the beach surface, because the submerged beach surface is an equipotential and velocity vectors are perpendicular to it [*Boufadel,* 2000].

In the oiled transect, the upward motion as the plume travels seaward suggests that if nutrients are limiting, one could apply dissolved nutrients deep into the beach and rely on tidal hydraulics to carry them to the upper portion of the beach (say at depths smaller than 0.30 m) where the oil was observed [*Short et al.,* 2004; *Short et al.,* 2006]. Therefore, oil entrapped within the sediments seaward of the manifold and at shallower depths than the manifold would be exposed to high concentration of nutrients moving upward from below it. Conversely, it is highly unlikely that the landward motion would be deliver any nutrients applied through the manifold to the oiled layer.

The experiments showed that relatively high tracer concentrations arrive at distances up to 1.5 m from the release manifold, which suggests that dilution, while being present, does not prevent the delivery of chemicals at the approximate distance of 1.5 m from the release manifold. The small dilution is due to the small pore space in the lower layer as a result of the small porosity value [Page et al., 2008]. Therefore, after the pulse displaces the existing water, it does not get diluted much. This demonstrates further the superiority of delivering the needed chemicals (nutrient and dissolved oxygen) deep into the beach rather applying them at the surface, where they get diluted by the incoming tide in the high permeability and high porosity upper layer.

This field project was conducted as a hydraulic feasiblity study for potential bioremediation of the *Exxon Valdez* oil spill. The fast movement of the tracer in the seaward direction along with its upward movement suggests that if bioremediation of the *Exxon Valdez* oil spill is limited by nutrient availability, delivering the nutrients by the technique adopted here is logistically feasible. Based on our work on this beach, we estimate the area of the oil patch located on the left side of the beach to be around 70 m^2 (7 m along shore X 10 m across shore). Therefore, 2 to 3 injection manifolds, each of them around 7.0 m long and each placed at depths of 0.30 m to 0.45 in the oiled Transect would ensure complete spatial coverage of the oil by the nutrients.

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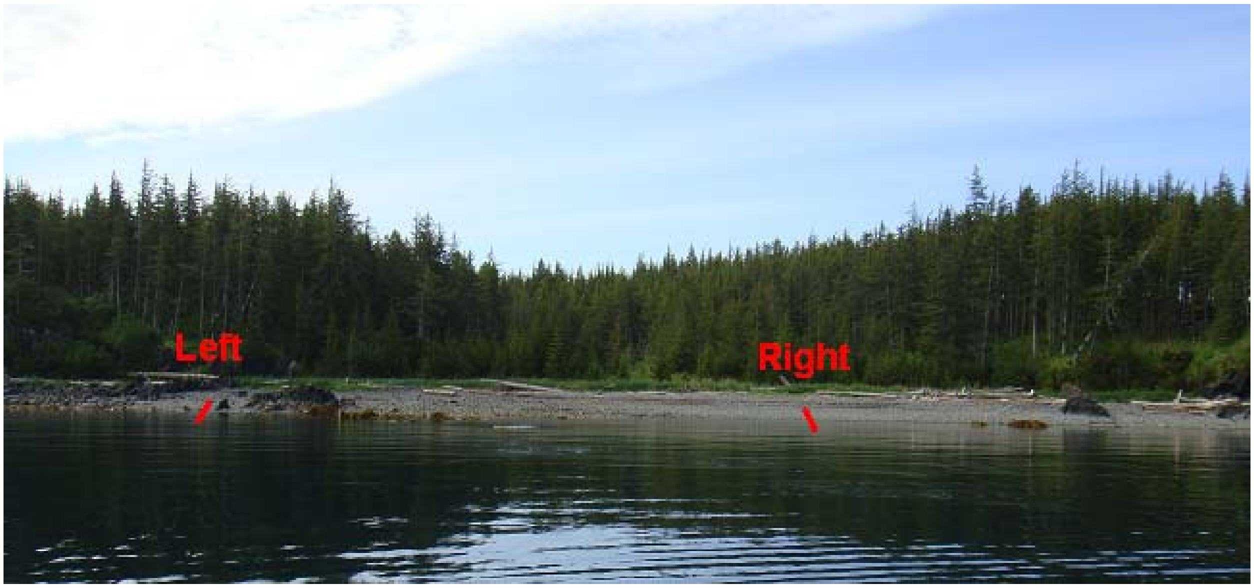


Figure 1: Photograph of SM006C during the Summer of 2009. Oil is entrapped on the left side of the beach (to the left of the rock formation). The approximate locations of the transects where the Ambient Pressure Release (APR) of the tracer are shown.

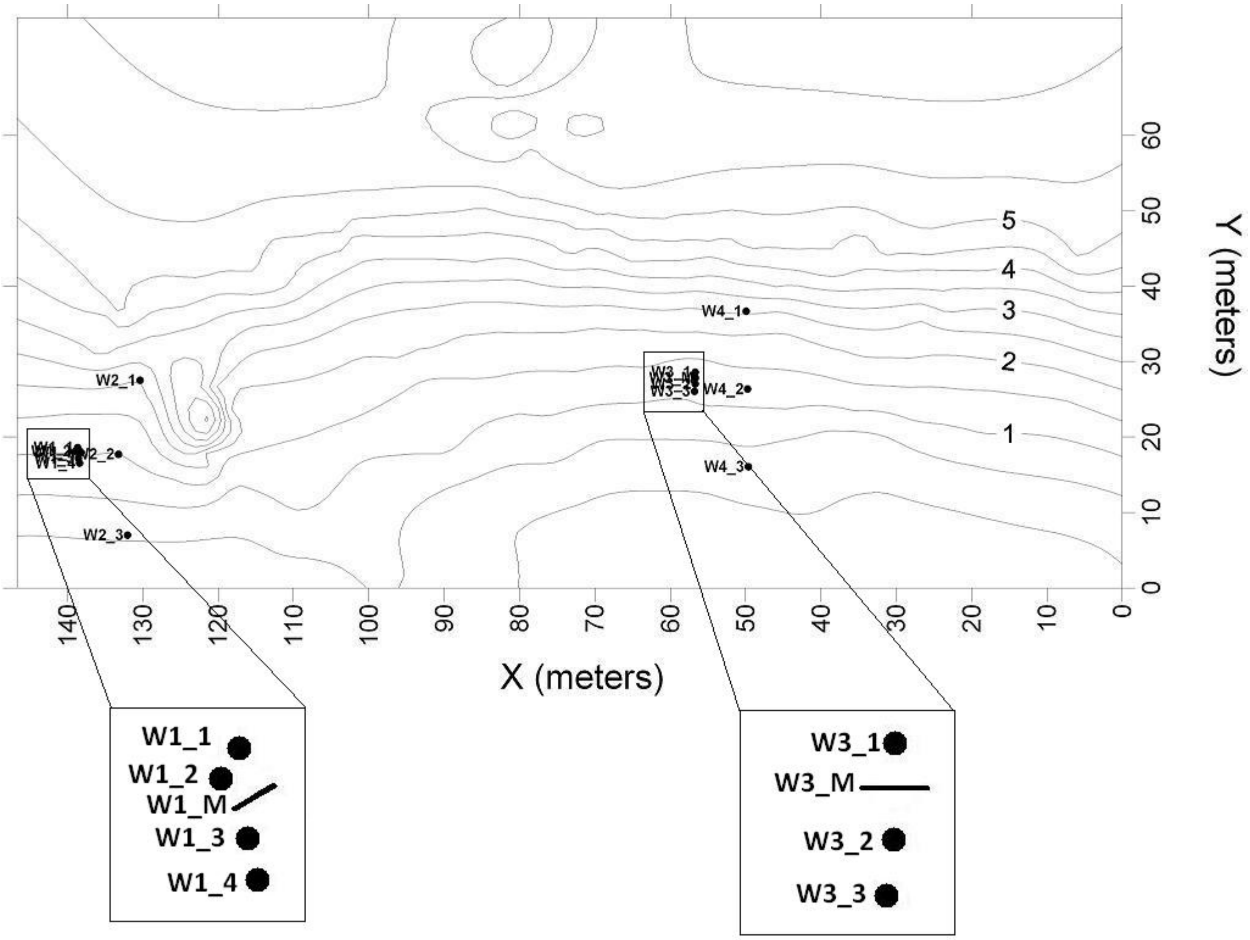


Figure 2: Top view showing the topographic contours of Beach SM006Cand the emplacement of the two trenches for the Ambient Pressure Release (APR). The two trenches were at the approximate elevation of 1.5 m.

Figure 3: Photo of the Right (clean) Trench with the manifold placed across before refilling the trench. Note that the sediments were gravel and pebbles. The cobbles were mostly from the beach surface.

Figure 4: Picture of Left Trench (oiled) facing landward. Note the extent of oiling and the presence of large boulders.

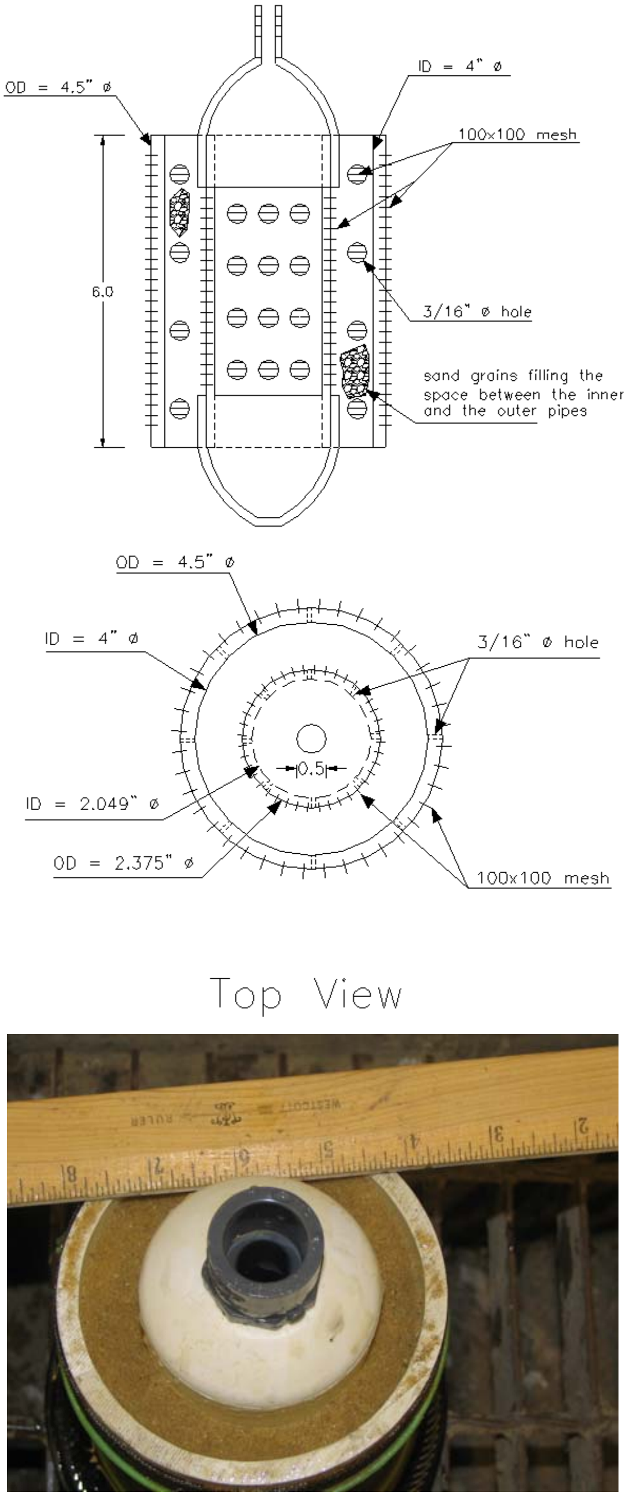


Figure 5: The sampling box (SB) used for water sampling. a) A vertical cross section of the SB, b) a horizontal cross section at mid height, c) photo of the SB showing the sand between the concentric cylinders

Figure 6: The eight tanks used for injection, each has a boiler drain type valve, with a ball valve controlling the flow to the pump (not visible).

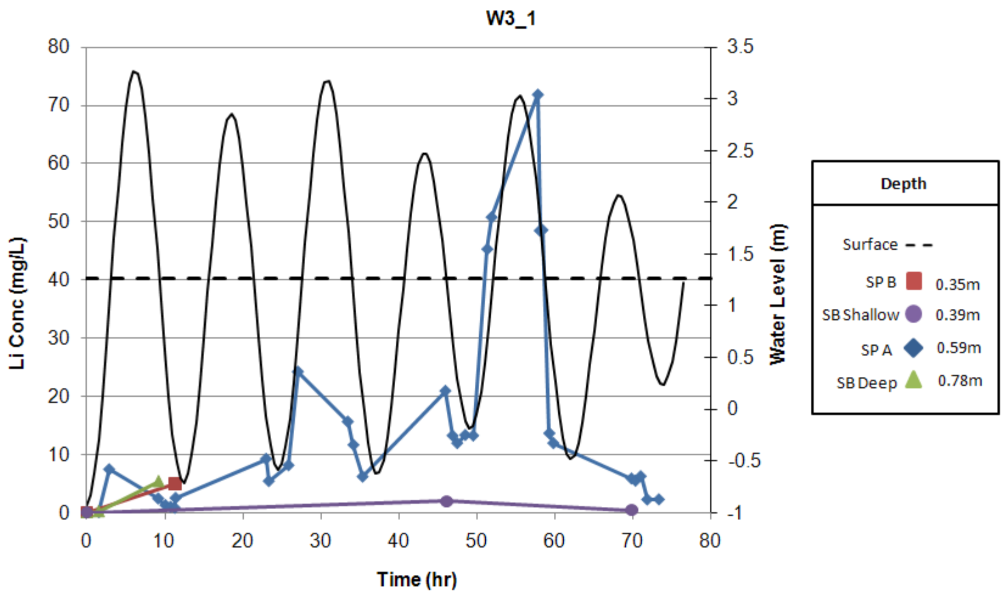


Figure 7: Lithium concentration as function of time at multiple sensors at Well W 3_1 well located 0.75 m landward of the W3_M. The tide level is also reported and should be read on the secondary axis. The depths of the sampling points are displayed in the legend. The injection concentration was 83 mg/L from 0 until 58.5 hour and then it was reduced to 0.0 mg/L for times greater than 58.5 hour.

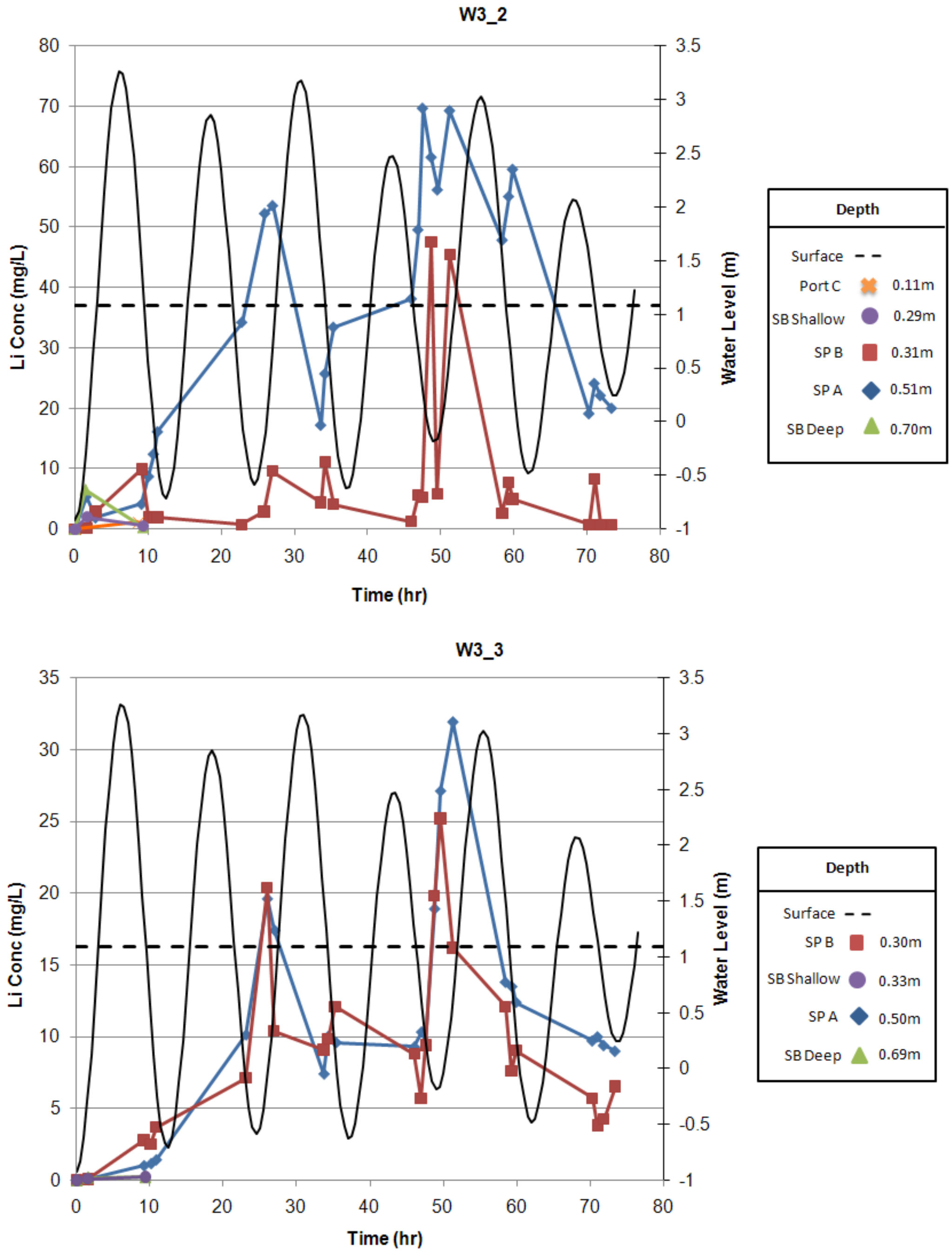


Figure 8: Tracer concentration at seaward monitoring wells. W3_2 located 0.80 m seaward of W3_M and W3_3 located 1.8 m seaward of W3_M, respectively.

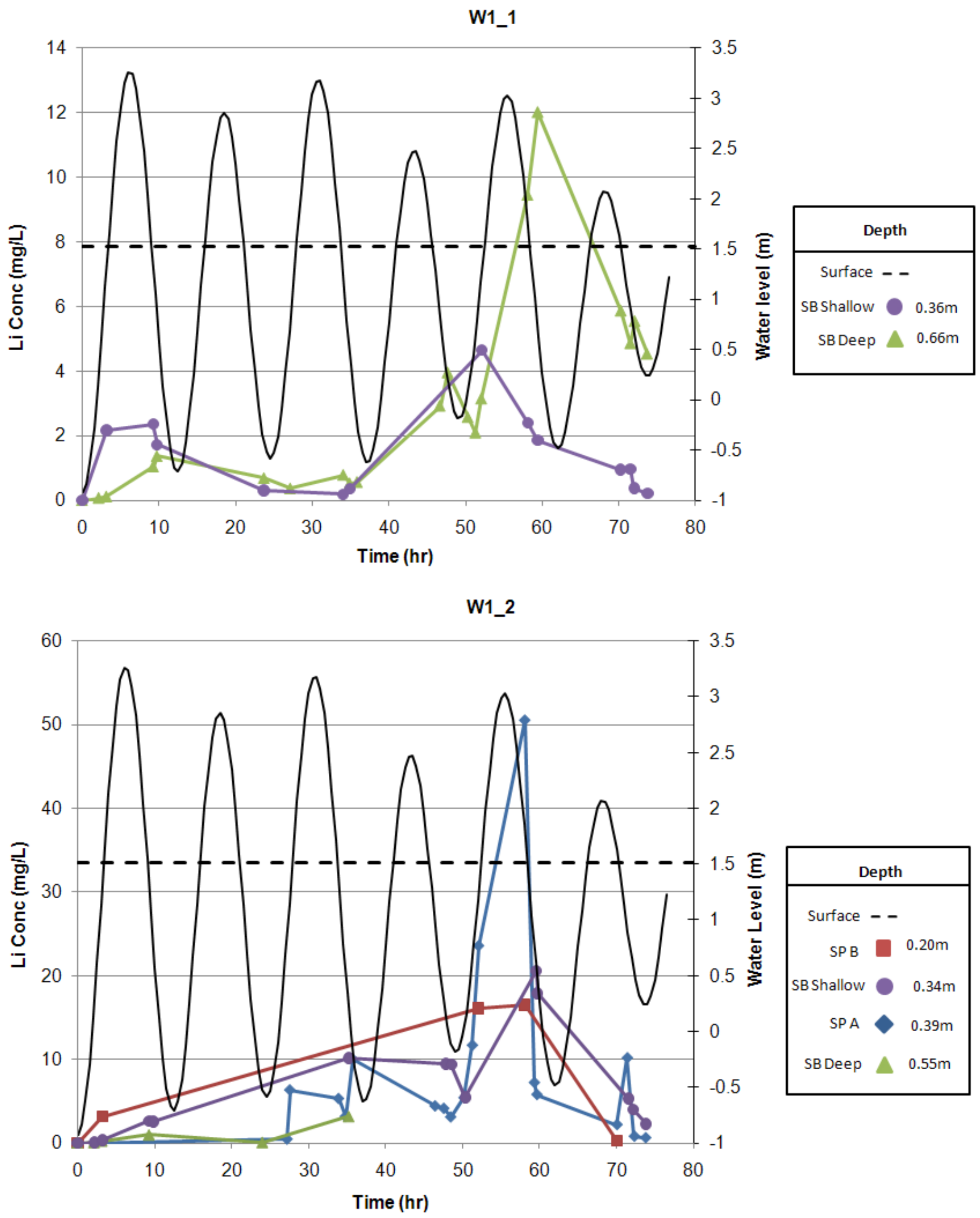
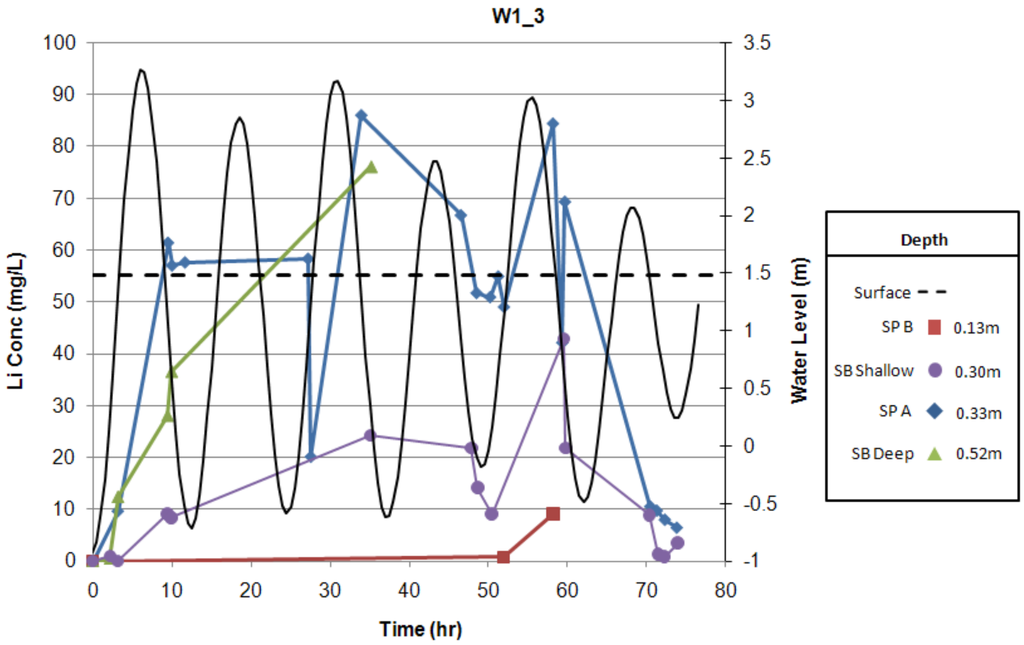


Figure 9: Lithium concentration and tidal level as function of time at wells W1_1 and W1_2 located respectively 0.85 m and 1.40 m landward of the manifold in the left transect (Figure 2).



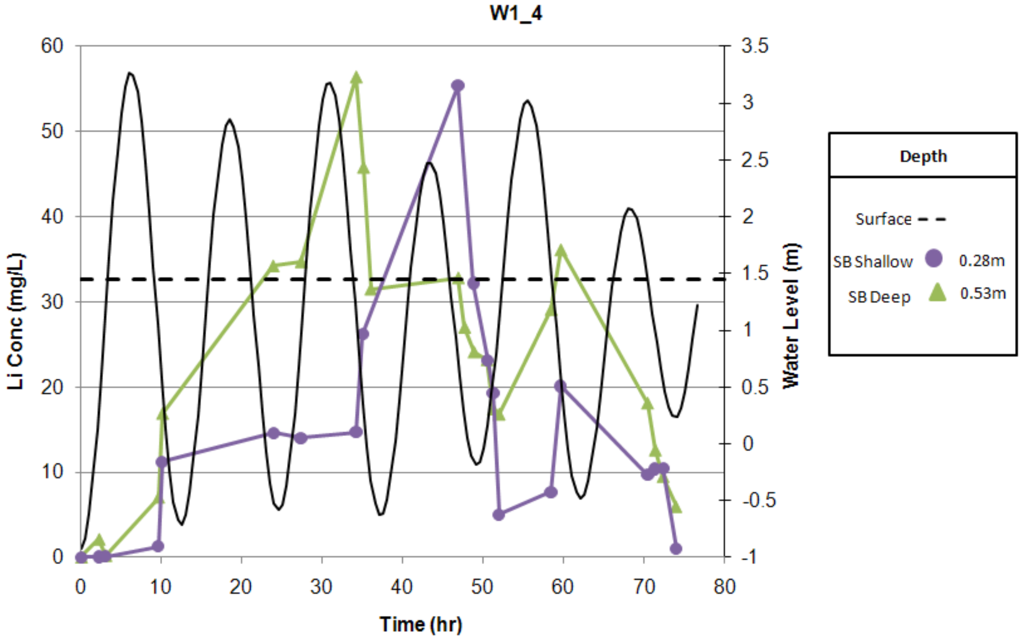


Figure 10: Concentration at two wells, W1_3 and W1_4 located 0.80 m and 1.60 m seaward of the manifold (Figure 2).

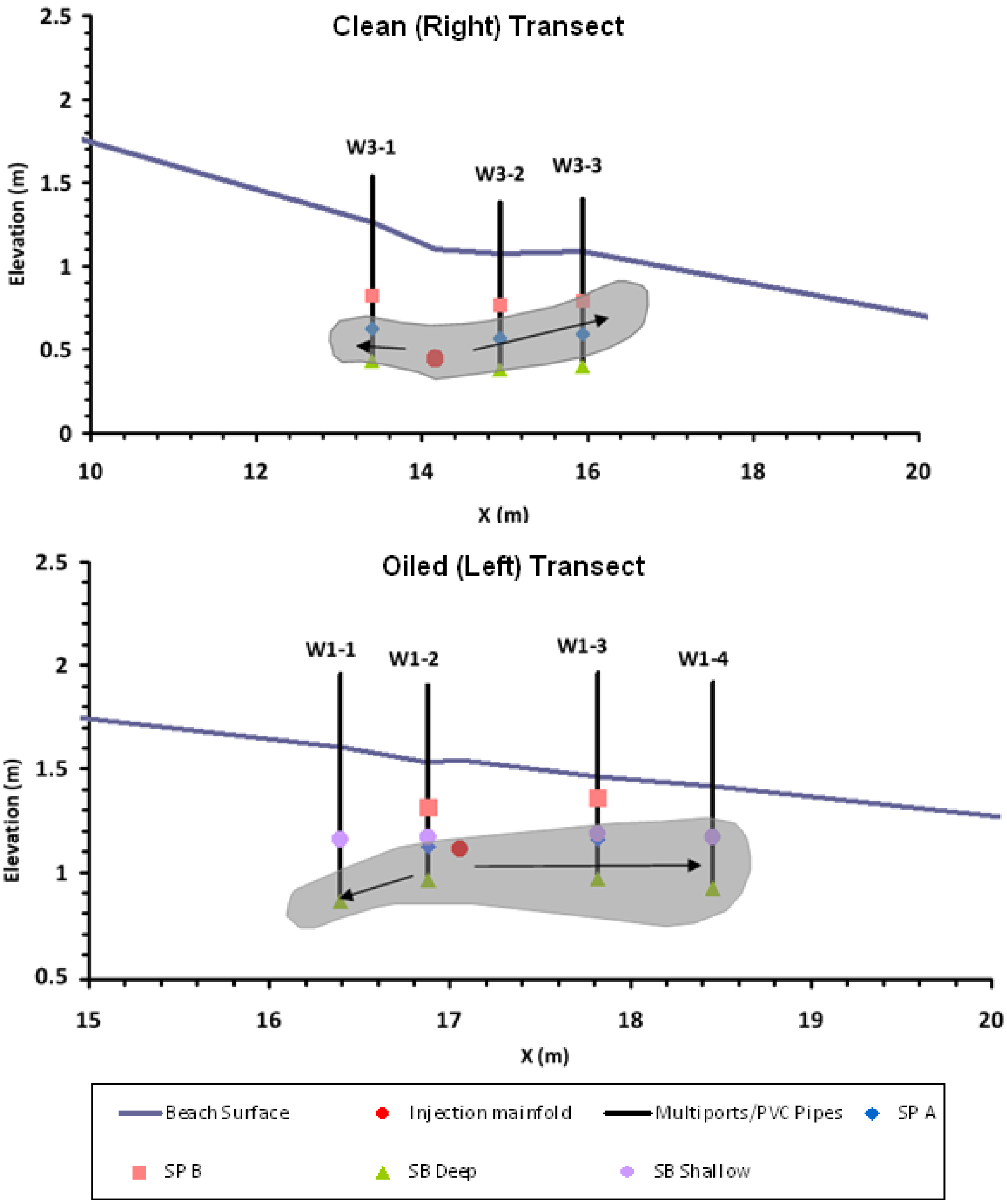


Figure 11: Plume location delineated as 10% (about 8.3 mg/L) of the initial tracer concentration at time 58.5 hours and re-constructed movement in a) the clean (right) transect and b) the oiled (left) transect). In both situations, the plume sank as moving landward and rose as moving seaward of the manifold. For bioremediation purposes, nutrients and oxygen should be applied landward and deeper of the oil layer (top 10 cm in this beach)

Nutrient and oxygen concentrations within the sediments of an Alaskan beach polluted with the Exxon Valdez oil spill

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Abstract

Measurements of the background concentrations of nutrients, dissolved oxygen (DO), and salinity were obtained from a beach that has oil from the Exxon Valdez oil spill in 1989. Two transects were set across the beach, one passed through an oil patch while the other transect was clean. Three pits were dug in each transect and they ranged in depth from 0.9 m to 1.5 m. The DO was around 1.0 mg/L at oiled pits and larger than 5 mg/L at clean pits. The average nutrient concentrations in the beach were 0.39 mg-NL^{-1} and 0.020 mg-PL^{-1}. Both concentrations are lower than optimal values for oil biodegradation (2 to 10 mg-NL^{-1} and 0.40 mg-PL^{-1} to 2.0 mg-PL^{-1}), which suggests that they are both limiting for biodegradation. The lowest nitrate values were found in the oiled pits, and noting the low DO at these pits, one concludes that denitrification was probably occurring in the oiled zone and that oil consumption by microorganisms is probably occurring under anoxic conditions. This explains the slow biodegradation rate reported in various studies.

Introduction

Large residues of spilled oil from the tanker vessel Exxon Valdez in 1989 are still found within the beaches of Prince William Sound (PWS). The subsurface oil (SSO) is observed in the middle and lower intertidal zones, which are habitat for foragers. The contaminated beaches were investigated extensively and subsurface oiling conditions are reported in various works (Short et al., 2004; Owens et al., 2008; Taylor and Reimer, 2008). These studies showed that the oil is still not weathered and contains high concentrations of polycyclic aromatic hydrocarbon (PAHs) known to be harmful to the marine and coastal ecosystem (Carls et al., 2001; Peterson et al., 2003). The oil is typically located under a layer of gravel, pebbles, and cobbles in a low porosity layer 5 to 50 cm below the surface. The average thickness of the oil layer is about 10 cm, but it could reach up to 22 cm (Michel et al., 2006).

One remediation strategy attempted after the spill was bioremediation (Bragg et al., 1994), which relies on enhancing the biodegradation of oil. Biodegradation of hydrocarbons has been extensively studied and is known to occur fast under aerobic conditions. Potential limitation to the process includes low concentrations of oxygen (O_2, electron acceptor) and nutrients such as nitrogen (N) and phosphorous (P). In an attempt to overcome the low levels of N and P in Prince William Sound beaches, large amounts of fertilizers (approximately 50,000 kg of nitrogen and 5,000 of phosphorous) were added to 300 miles of contaminated shorelines over the summers of 1989 to1992 (Pritchard et al 1991;

Claxton et al 1991; Bragg et al 1994). Nevertheless, large amounts of oil (60 to 100 tons) still persist in the beaches (Short et al., 2004, 2006).

More recently, Atlas and Bragg (2009a; 2009b) conducted measurements in PWS beaches, and reported for the beach studied in this paper, EL056C on Eleanor Island (Fig. 1) an average nitrate concentration of 0.36 of mg-N/L and DO values larger than 5.0 mg/L. Li and Boufadel (2010) found that the beach consists of two layers, an upper layer with high permeability, overlaying a low permeability layer, where the oil could be trapped with limited exchange with upper layer. They also found that the low permeability zone is anoxic. This was a new finding as it was traditionally assumed that the levels of oxygen in beach sediments are large enough for bioremediation (Page et al., 2008).

The objective of this study is to provide detailed measurements of nutrient and dissolved oxygen concentration deep into the beach and to evaluate the impact of these values on oil biodegradation.

Site description

Our investigation was conducted on beach EL056C on Eleanor Island. This beach was a single pocket beach with along-shore width of about 40 m and an across-shore length of about 50 m. The coordinates of the beach were 147° 34’ 17.42” W and 60° 33’ 45.57” N. The sediments of the beach are coarse ranging from gravel (a few millimeters diameter) to pebbles and cobbles (10 to 20 cm diameter) and the beach has a low exposure to the wave energy. The beach was heavily oiled after the Exxon Valdez oil spill in 1989, but latter studies found that one side (right) of the beach had heavy oil residue (HOR), according to the ASTM F1687-97 (2003) classification (see also Short et al., 2004) while the other side (left) was completely clean. The oil was located at lower to middle intertidal zone on the right of the beach (Short et al., 2004; Taylor and Reimer, 2008; Atlas and Bragg, 2009a; Atlas and Bragg, 2009b; Li and Boufadel, 2010). The persistence of oil on the right side was explained by Li and Boufadel (2010) as due to a water table that drops into the lower layer at low tide. The upper (high permeability) layer on the left side of the beach was much deeper and high freshwater recharge sustained the water table in it (i.e., a low freshwater recharge would have resulted in water table dropping into the lower layer).

Site preparation

As it is practically impossible to drive sensors into the beach, one needs to excavate pits to place the sensors in them and then refill the pit. However, if the concentration in the lower layer is sought, then one needs to provide a sufficient time for the sediments to "heal" after excavation (i.e. to return to the original two-layer configuration). Otherwise, the sensor measurements from the lower layer would be "contaminated" by water from the upper layer. We found, based on the measurements conducted in 2008, that a minimum period of 6 weeks is needed for this to occur. For this reason, we designed the field study in 2009 to have 8 weeks between the task of excavation and placement of sensors and the task of conducting measurements. This required two field trips in the summer of 2009. The first was June 16-28 and the second was August 18-29 when the samples were taken.

In total, six pits were dug for the purpose of evaluating chemicals delivery, three on the left transect which was clean and three on the right transect which crossed the oil zone. (Fig.s 1 and 2). The surface elevation of the wells, on both transects was selected in a way that there would be one well in the upper tidal zone, one in the intermediate zone, and one in the lower intertidal zone. The tidal range on this beach varied from -0.1 m to 5.7 m which was just landward of the wells W1_1 and W2_1.

The overall approach was to dig the pits to about 5 feet deep and place a polyvinyl chloride (PVC) pipe, a multiport sampling well (SP), and two sampling boxes (SB) in the pits. The PVC pipe had an inner diameter of one inch, and was slotted across over the whole length to allow water passage. A pressure transducer (Mini-Diver DataLogger, Schlumberger, Sugar Land, TX) was placed at the bottom of each PVC pipe to record the water pressure at 10 minutes interval. The barometric pressure, monitored by an air-pressure sensor (DL-500 BaroLogger, Schlumberger, Sugar Land, TX), was subtracted from the readings of the pressure transducers to obtain the water level. No rainfall occurred during the field measurement period in August 2009.

The multiport sampling wells were made of stainless steel and contained sampling ports (SP) at various levels. The ports were spaced at the interval of 0.19 m and were labeled A, B, C, and D from the bottom up. Each port was connected via a steel tubing that extended to the top of the pipe. A 1/8 inch inner diameter Tygon tube (Cole-Parmer, Vernon Hills, IL) was placed on each of the steel tubings, and it was connected to a Luer-

Lok three-way valve (Cole-Parmer, Vernon Hills, IL). To prevent blockage by fine sediments and to guarantee good hydraulic connection between the beach pore-water and the water inside the well, the ports were wrapped with fine stainless-steel screen.

The sampling box (SB) consisted of two perforated concentric cylinders made of PVC schedule 40 (Fig. 3). The chamber between them was filled with Sand #16 from Alaska Sand and Gravel Co. (Anchorage, AK, http://www.anchsand.com/). The diameter of the sand grains ranged from 0.21 to 1.41 mm with an average size of 0.88 mm. The uniformity coefficient was 1.68, a low value that indicates a uniform sand. Both cylinders were covered with a 100×100 (opening per square inch) steel screen. The diameter of the inner cylinder was 5 cm (2 inches) the length was 15 cm (6 inches), which results in a volume of 200 mL. The inner diameter of the outer cylinder was 10 cm (4 inches), and considering the thickness of the inner cylinder wall, the spacing between the cylinders was around 1.5 cm. Twelve SBs were designed and built for the dual purpose of measuring the dissolved oxygen (DO) of pore-water and as a backup for taking water samples in case the sampling ports (SPs) were clogged.

Sampling Methods

It was desired to measure DO, nutrient and salinity of the pore-water samples in this study. The sampling procedure for each parameter was different. The DO samples were measured in the field where the nutrient concentration and salinity were determined in the lab.

Dissolved Oxygen Measurements

Dissolved oxygen (DO) was measured in the field using a Thermo Scientific, RDO optical probe and an ORION 4 Plus handheld meter. The water was pumped from the sampling boxes into a measuring chamber using a peristaltic pump (Masterflex, Cole-Parmer, Vernon Hills, IL) and the water was allowed to overflow from the measuring chamber. The measuring chamber was a 6.0 cm long and 5.0 cm (2 inch) (ID) PVC pipe Schedule 40. The volume was thus around 120 ml. To the top and bottom of the pipe were glued half inch thick fiberglass plates. Silicon glue was used to ensure no water or air leakage at the contact of the pipe and the fiberglass plates. One hole (5/8 inch ID) was drilled in each of the top and bottom plates for the water to flow in and out of the chamber. Inflow to the chamber was from the bottom plate and the outflow was from top. Brass pipes and connections were used at the connections and all of the connections were sealed with Teflon tape. In addition, another hole (3/4 inch ID) was drilled in the middle of the top plate and threaded so that the DO probe would be screwed in to the measuring chamber. A Teflon tape was rolled around the DO probe to seal the probe in the place.

For sampling, one end of the Masterflex tubing (peristaltic pump tubing, Masterflex, Cole-Parmer, Vernon Hills, IL) was lowered to the bottom of the sampling box and the other end was connected to the inflow of the measuring chamber (Fig. 4). Then the peristaltic pump was started and flow rate was adjusted to have a steady flow with no air bubbles. It was assumed that the steady state was achieved 10 minutes after running the pump, the first reading was taken and considered the representative value for the pore water.

Pore-Water Sampling, Shipping and Handling for Nutrient and Salinity

Nutrient samples were collected from different ports of the multiport sampling wells (SP) and at different times, depending on accessibility (due to tide level) and resources. The water samples were collected using sterilized 60 ml syringe (BD Luer-Lok, Fisher Scientific, Pittsburgh, PA) each time. The persons taking the samples wore disposable lab gloves (nitrate free). The sampling started from the port closest to the surface and moved to the deeper ports. The samples were put in 30 ml high density polypropylene bottles (Nalgene, Fisher Scientific, Pittsburgh, PA). All the bottles were acid washed (in 10 percent HCl acid bath for 18 hours) and rinsed 3 times with DI water prior to the field sampling. The first volume (60 mL in the syringe) taken from each port was wasted. An additional volume of 25 ml was used to rinse the bottles. Once the rinsing was finished, the remaining water in the syringe was disposed, and new water sample was taken from the port using the same syringe and emptied into the rinsed bottle. The bottles were filled up to the neck to leave enough room for expansion during freezing. All bottles were labeled indicating the beach/pit/depth, time and date of sampling. The samples were kept cooled in ice filled cooler on the beach and they were immediately frozen in -5 °C freezer on board (US Environmental Protection Agency, 1983). The samples were air shipped to Temple University in Dry Ice to keep the samples frozen all the time during the shipping. Once in the lab, the samples were kept in a dark, -20 °C freezer prior to the analysis (Dore et al., 1996). Six measurements were made in the lab. They were for ammonia (NH_3,), Nitrite (NO_2,), Nitrite/Nitrate (NO_2/NO_3,), Phosphate (PO_4), Silicate (SiO_2) and salinity.

Nutrient and Salinity Analysis of the Pore-Water Samples

The nutrient compounds were measured using AutoAnalyzer3 (Seal Analytical, Mequon, WI). The frozen samples were defrosted and kept in the fridge (below 4 °C) in batches of 76 samples, at the time of analysis the samples were taken out of the fridge, hand shaken for 15 seconds and passed through 0.45 micron PTFE membrane filters (Puradisc^{TM}, Whatman, Florham, NJ) into the AutoAnalyzer3 cups. The segmented flow method was used in Autoanalyzer3 and the concentrations were detected by colorimetric analysis. Ammonia in seawater was measured using the Berthelot reaction where a blue-green colored complex was formed which was measured at 660 nm wavelength. Nitrate in the solution was reduced to nitrite by a copper-cadmium reactor column (Grasshoff et al., 1999; Seal Analytical, 2008).The nitrite was then reacted with sulfanilamide under acid condition to form a purple azo dye. The color was detected in 550 nm wavelength (Grasshoff et al., 1999; Seal Analytical, 2008). Phosphate was measured following the Murphy and Riley method until a blue color was formed by reaction of orthophosphate, molybdate ion and antimony ion followed by reduction with ascorbic acid at a pH<1. The blue complex was read at 880 nm wavelength (Grasshoff et al., 1999; Seal Analytical, 2008). The soluble silicate was determined in this method based on reduction of siliconmolybdate in acidic solution to molybdenum blue by ascorbic acid. The complex was read at 820 nm wavelength (Grasshoff et al., 1999; Seal Analytical, 2008).

The salinity of the same pore-water samples was measured using a digital refractometer (Salinity-300035, Sper Scientific, Scottsdale, AZ). The samples were filtered and about 1.5 mL of sample was poured into the measuring cup of the instrument and the salinity was determined based on the refraction index of the sample. The refractive index of the samples was affected by the density of each sample which was different for various salinities.

Analytical Methods Quality Assurance

For each nutrient compound a four point calibration curve was obtained. In order to check the precision of the procedure, each 10th sample was re-analyzed. Drift and carry-over errors were also accounted for by checking the calibrants every 24 samples. In addition, every 36 samples, quality control cups (DI water cup and one highest calibrant cup) were placed with samples to control the analytical measurements.

The DO probe was calibrated using the water-saturated air calibration method. The zero calibration was conducted in zero oxygen solution. A 60 g L^{-1} solution of sodium sulfite was prepared, the already calibrated DO probe was then placed in the solution and zero calibration was achieved. The water-saturated air calibration was performed daily in the field prior to sampling.

The refractometer was calibrated using DI water. The refraction index of DI water was between 1.3329 and 1.3331. Different salinity control solutions (10, 20, 35 and 50 g L^{-1}) were made to check the instrument accuracy. DI water and one of the salinity control solution were measured after every 10 sample measurements.

The minimum detection limits of different analytical methods and instruments used for measuring the DO, salinity and nutrients are reported in Table 1.

Results and Discussion

Li and Boufadel (2010) analyzed the water motion within this beach and found that the beach fills with seawater through the beach surface near the high tide line (landward of W1_2 and W2_2 in Fig. 1) during high tide and to fill from the landward aquifer during the rest of the tidal cycle. They also found that the beach drains to sea through the beach surface in the seaward portion of the intertidal zone (at and seaward of W1_3 and W2_3), especially at low tide. Therefore, water moves seaward within the beach and exits near the low tide line. This has consequences on the biotransformation of nutrients and depletion of DO as they move within the beach.

Fig. 5 reports the DO measurements. The wells on the left (clean) side of the beach, W1_1 and W1_2, showed the highest DO concentrations (around 7 mg L^{-1}), which could be explained by landward recharge and high exchange with seawater. The DO concentration decreased moving seaward to W1_3 (around 5 mg L^{-1}), which could be a sign of oxygen depletion within the beach due to microbial activity. Although the DO concentration decreased, it did not cause the system to become anoxic (< 1 mg L^{-1}).

On the right transect, the DO concentration at W2_1 (landward) was around 5 mg L^{-1} which could be an indication of groundwater recharge and seawater mixing. Moving seaward to the oily wells (W2_2 and W2_3), the DO concentration decreased drastically, reaching 0.8 mg L^{-1} at W2_2 and 1.25 mg L^{-1} at W2_3. The paired two tailed student's *t*-test was used to compare the means of the observed values in the beach. The null hypothesis (H_0) was defined as the means of the observed data are the not significantly different. The alternative hypothesis (H_1) was assumed that there is evidence that the means are significantly different. The level of significance was 95% ($\alpha = 0.05$). The statistical analysis showed that the mean of DO in the oily wells are significantly different than the rest of the wells in the beach, ($P(t) = 0.0003 < P(T) = 0.05$).

Fig. 6 represents the nitrite/nitrate-N (NO_2/NO_3-N) levels in the beach. The NO_2/NO_3-N concentrations on left transect (clean) were about 0.11 – 0.14 mg-N L^{-1} with a slight increase moving seaward. However, the differences between the mean values of the three wells were not statistically significant (5% level of significance). On the contrary, the concentration of nitrate-N on the right (oily) transect was highest at W2_1 (0.5 mg-N L^{-1}), and then decreased significantly (an order of magnitude) moving seaward to W2_2 and W2_3 to about 0.05 – 0.06 mg-N L^{-1} ($P(t) = 0.03 < P(T) = 0.05$). These two values were the lowest in the beach. The seawater samples were taken from the boat away from the beach to eliminate possible contamination from shore run off and fish spawning. The nitrate-N concentration of these samples (0.048 mg-N L^{-1}) was lower than the concentrations in the beach but close to the seawater values found in other studies in Prince William Sound (Eslinger et al., 2001) and in the Delaware Bay (Ullman et al., 2003). The high average concentration of nitrate detected on the beach (0.139 mg-N L^{-1}) could be due to nitrogen fixation in the beach either through bacteria in the beach sediments (e.g., cyanobacteria) Postgate (1998, p10) or through the groundwater recharge to the beach enriched with nitrogen-fixing *Frankia* sp. from vegetation type (mainly alder trees) covering inland of the upper intertidal zone of the beach (Cooper, 1942; Atlas and Bragg, 2009b). Nitrogen inputs to groundwater result as a consequence of leaching from soil organic matter, biological nitrogen fixation through conversion of atmospheric nitrogen to ammonia by nitrogenase enzyme (Postgate, 1998, p12)

The ammonia concentrations (Fig. 7) on the left transect decreased from 0.255 mg-N L^{-1} at W1_1 to 0.115 mg-N L^{-1} W1_2 and then increased again to 0.236 mg-N L^{-1} W1_3. On the oily transect, the concentration of the ammonia increased from 0.200 mg-N L^{-1} at W2_1 to 0.32 mg-N L^{-1} at W2_2 and then decreased to 0.227 mg-N L^{-1} at W2_3. The highest concentration of ammonia was observed at the well with the highest oil concentration. However, the differences between mean ammonia concentrations throughout the beach were not significant ($P(T) = 0.05 < P(t) = 0.3$). The ammonia concentration of the seawater (0.169 mg-N L^{-1}) was lower than most of the concentrations in the beach, which is probably due to the generation of nitrogen in the beach, as discussed regarding nitrate (Fig. 6). The high level of ammonia in the oily well (i.e., 0.32 mg-N L^{-1} at W2_2) is consistent with the detection of anoxic conditions, as high concentrations of groundwater ammonia are commonly observed under anoxic conditions (Ullman et al., 2003; Slomp and Van Capellen, 2004).

Fig. 8 shows that the concentration of phosphate-P was essentially the same for the left two left transect wells W1_1 and W1_2 (0.01 mg-P L^{-1}), but almost doubled when moving seaward to W1_3. On the right transect, the phosphate concentration at W2_1 was relatively close to the value observed for W1_1 and W1_2, but increased at W2_2 (0.034 mg-P L^{-1}) and W2_3 (0.024 mg-P L^{-1}). In general, the phosphate concentration of the pore-water samples was approximately one order of magnitude lower than the average reported in the literature (Ullman et al., 2003). The phosphate concentration in seawater was 0.014 mg-P L^{-1}, comparable to average values in the literature on PWS (Eslinger et al., 2001) and the Delaware Bay, 0.035 mg-P L^{-1} (Ullman et al., 2003).

Higher concentrations of phosphate and ammonia observed at W2_2 (and to a lesser extent at W2_3) and low DO and nitrate values at these wells are consistent with the existence of anoxic conditions (Ullman et al., 2003; Slomp and Van Capellen, 2004). As phosphorus in groundwater is mostly present as inorganic dissolved phosphate, it precipitates rapidly by reaction with ferric iron forming iron phosphate under oxic conditions (Slomp and Van Cappellen, 2004). However, under anoxic conditions, phosphate removal is less efficient, resulting in higher concentrations (Slomp and Van Cappellen, 2004). The concentration of the phosphate at the two most seaward wells (W1_3, 0.023 mg-P L^{-1} and W2_3, 0.024 mg-P L^{-1}) were higher than most of the rest, This might be explained by the decomposition of algae residues or spawning fish at the lower intertidal zone of the beach (note that our seawater measurements were taken around a mile offshore). It is worth noting that the statistical analysis did not show a significant difference between the mean phosphate concentrations throughout the beach ($P(T) = 0.05 < P(t) = 0.1$

Silicate is a constituent of the sediments and the seawater, allowing one to trace the origin of the nutrients in a beach (Ullman et al., 2003). The silicate concentrations are given in Fig. 9. On the left transect, the silicate concentration decreased slightly from W1_1 (1.63 mg L^{-1}) to W1_2 (1.47 mg L^{-1}) and then increased moving seaward to W1_3 (2.32 mg L^{-1}). On the right transect, the highest concentration was at W2_1 (2.68 mg L^{-1}), and decreased moving seaward. In a beach, the upper and lower intertidal zones should have the highest silicate concentration (Ullman et al., 2003) which could be an indication of mixing of seawater and groundwater in different zones of the beach. This phenomena was observed on the left transect where the concentration decreased from W1_1 to W1_2 and then increased to W1_3. On the right transect the trend was not completed. It started with a high concentration and decreased at W2_2 but where it was expected to increase at W2_3 it decreased. The low value indicates a lack of water exchange between the sea and the beach at W2_3, which is also supported by the low dissolved oxygen at that well

The salinity of this beach is given in Fig. 10. The seawater salinity was found to be 25 parts per thousands (ppt). In both transects the salinity was highest in the mid-intertidal zone and decreased going landward and seaward. This configuration is due to tidal hydraulics (Wrenn et al., 1997; Ataie-Ashtiani et al. 1999; Boufadel, 2000) and it was demonstrated in detail for this beach by Li and Boufadel (2010). In essence, freshwater tends to be highest near the high tide line (see Fig. 1) due to proximity to the source (the landward aquifer or runoff). As the freshwater propagates into the beach, the rising tide pushes it downward causing the freshwater to propagate further seaward and to pinch out near the low tide (Boufadel, 2000). Li and Boufadel (2010) found that a large freshwater flow enters the beach through the Left Transect in comparison with the Right Transect. Therefore, the average salinity on the left transect was expected to be lower than the right transect. However, due to the high variability with tide of salinity, the statistical analysis did not show a significant difference between the salinity of the wells throughout the beach, (P(T)= 0.05< P(t)= 0.3). As our focus in this paper is on nutrients, we elect to investigate this issue in a future work using detailed modeling as conducted by Li and Boufadel (2010).

DISCUSSION

Atlas and Bragg (2009b) conducted measurements on this beach by driving piezotubes into the beach until reach the top of the oil layer. They reported an average nutrient concentration of 0.36 mg-NL^{-1}, and DO concentrations larger than 5.0 mgL^{-1}. The average nutrient value that they reported are comparable to our average of 0.392 mg-NL^{-1} (based on the nitrate and ammonia, Figs. 6 and 7). The largest discrepancy is in the DO measurements and could be due to two non-exclusive reasons. 1) For our results, we placed the sensors in the beach two months prior to taking samples to provide sufficient time for the beach to return to its natural state. When piezotubes are driven into this beach, as done by Atlas and Bragg (2009b), they would invariably hit cobbles in their way which would disturb the path, and we believe that one should allow a sufficient time for the sediments to return to their natural state, otherwise, the sampling at depth might be contaminated by water from shallower depths. Unfortunately, nor the time between driving the piezotubes and sampling nor the diameter of the piezotubes were provided by Atlas and Bragg (2009b). 2) Atlas and Bragg (2009b) measured the nutrient and oxygen concentrations above the oil layer, while our measurements were from below the oil layer, which, we argue, are more relevant for oil biodegradation considering the lithology and the hydraulics in this beach; Li and Boufadel (2010) found that this beach can be viewed as consisting of two layers, an upper layer with a high hydraulic conductivity (around 1.0 cm.s^{-1}) underlain by a layer whose hydraulic conductivity is 100 to 1000 times smaller. Based on comparison between the oil and clean transect, they concluded that oil resides a few centimeter below the layers' interface. This is illustrated in Fig. 11. Therefore, sampling above the oil zone would, most likely, provide high oxygen concentration due to the high conductivity in the upper layer (Fig. 11). In addition, due to tidal hydraulics, seawater (rich in DO) does not enter the beach near W2_3, on the contrary it leaves the beach through that location (Li and Boufadel, 2010). This implies that the net movement of water also opposes the molecular diffusion of oxygen from the sea. Tidal hydraulics therefore explains the findings by Atlas and Bragg (2009b) that the lower part of the oil layer is not weathered at all while the top part exhibits gradual weathering going toward the beach surface. The lower part of the oil layer is not weathered because the water that arrives there is deplete of oxygen, as our measurements at W2_2 and W2_3 showed (Fig. 5).

The nitrogen concentrations were about an order of magnitude lower than the required concentrations (2 to 10 mg-NL^{-1}) for optimal biodegradation of hydrocarbons (Venosa et al., 1996; Boufadel et al., 1999; Du et al., 1999; Zhu et al., 2001). Bragg et al. (2004) and Atlas and Bragg (2009a,b) use the ratio of non-polar hydro, and we believe it to be the correct approach for stoichiometry, but it might not be applicable for the kinetics, where the micro-organisms need to "see" the high nutrient concentration for them to thrive. In addition, the fact that the N:P ratios is this study are greater than the optimum ratio for biodegradation (around N:P=10) (Liebeg and Cutright, 1999) suggests that not only nitrogen is limiting but also phosphate.

We have found that the concentrations of nutrients and dissolved oxygen are limiting for the biodegradation of oil when compared to values reported in the literature. But it has been argued in some studies on the Exxon Valdez spill that the lack of oil biodegradation could be also due to lack of bioavailability, or mass transfer limitation due to sequestration of oil (Taylor and Reimer, 2008; Page et al., 2008; Atlas and Bragg, 2009a,b). We believe this to be a valid consideration that could be only addressed by a field remediation study where the nutrients and dissolved oxygen concentrations are increased through a delivery technique and the oil concentrations are monitored as function of time. Nevertheless, the near anoxic conditions along with denitrification at oiled wells indicate that the beach geochemistry at oiled areas is significantly different from the rest of the beach.

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Table 1: Detection limit of the different analytical methods used.

Measuring Method	Detection Limit
RDO probe (D.O.)	0.01 mg/L
Ammonia (NH_3)-N	0.56 µg/L
Nitrate (NO_2/NO_3)-N	0.21 µg/L
Phosphate (PO_4)-P	0.29 µg/L
Silicate (SiO_2)	1.8 µg/L
Refreactometer (salinity)	1 parts per thousands (ppt)

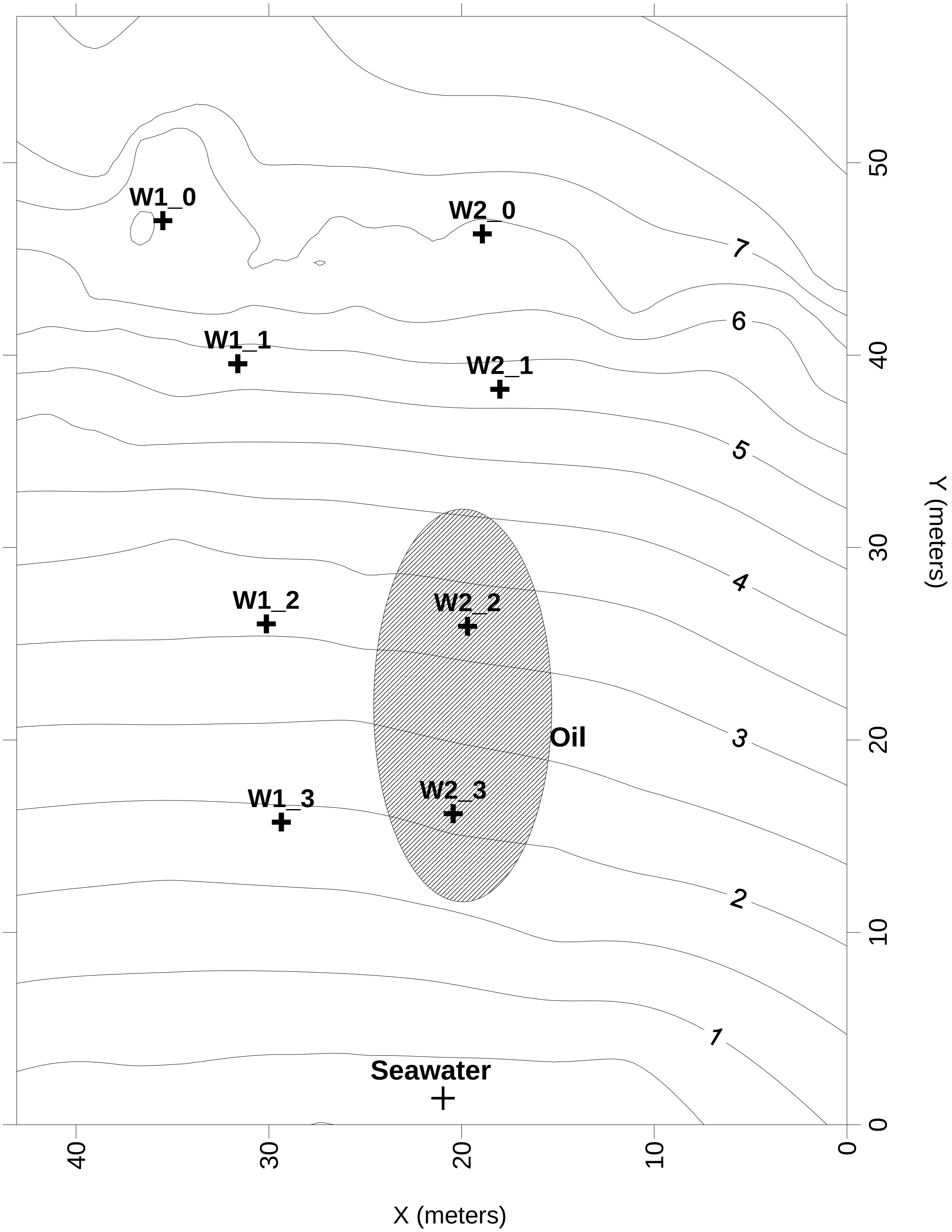

Figure 1: Topographic map of EL056C, showing the location of the sampling wells in each transect. The oil was observed at the right transect in W2_2 and W2_3.

Figure 2: A photo of the beach El056C, showing the two transects, each well is labeled.

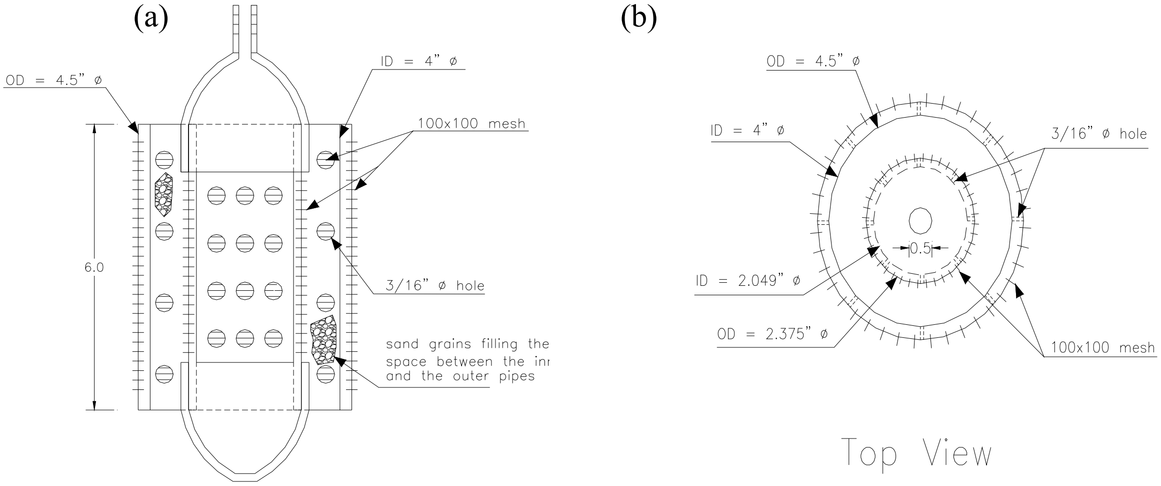

Figure 3: The sampling box (SB) used for water sampling. a) A vertical cross section of the SB, b) top view.

Figure 4: Dissolved oxygen measuring setup during operation. The DO probe (black) is immersed in the measuring chamber (transparent cylinder with red top and bottom).

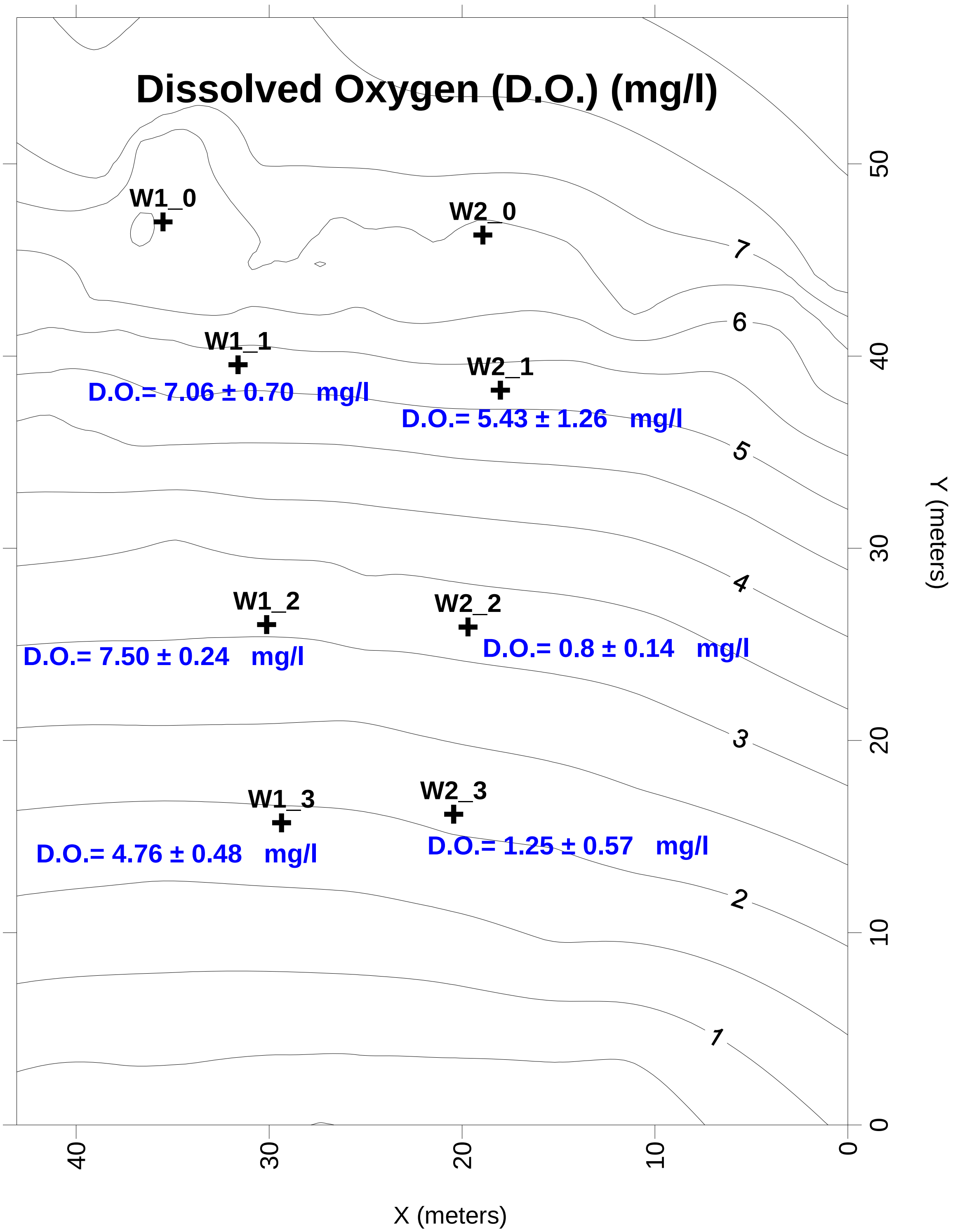

Figure 5: Dissolved oxygen (DO) in mg/L. Near anoxic conditions are noted at W2_2 and W2_3 where oil persisted (see Figure 1)

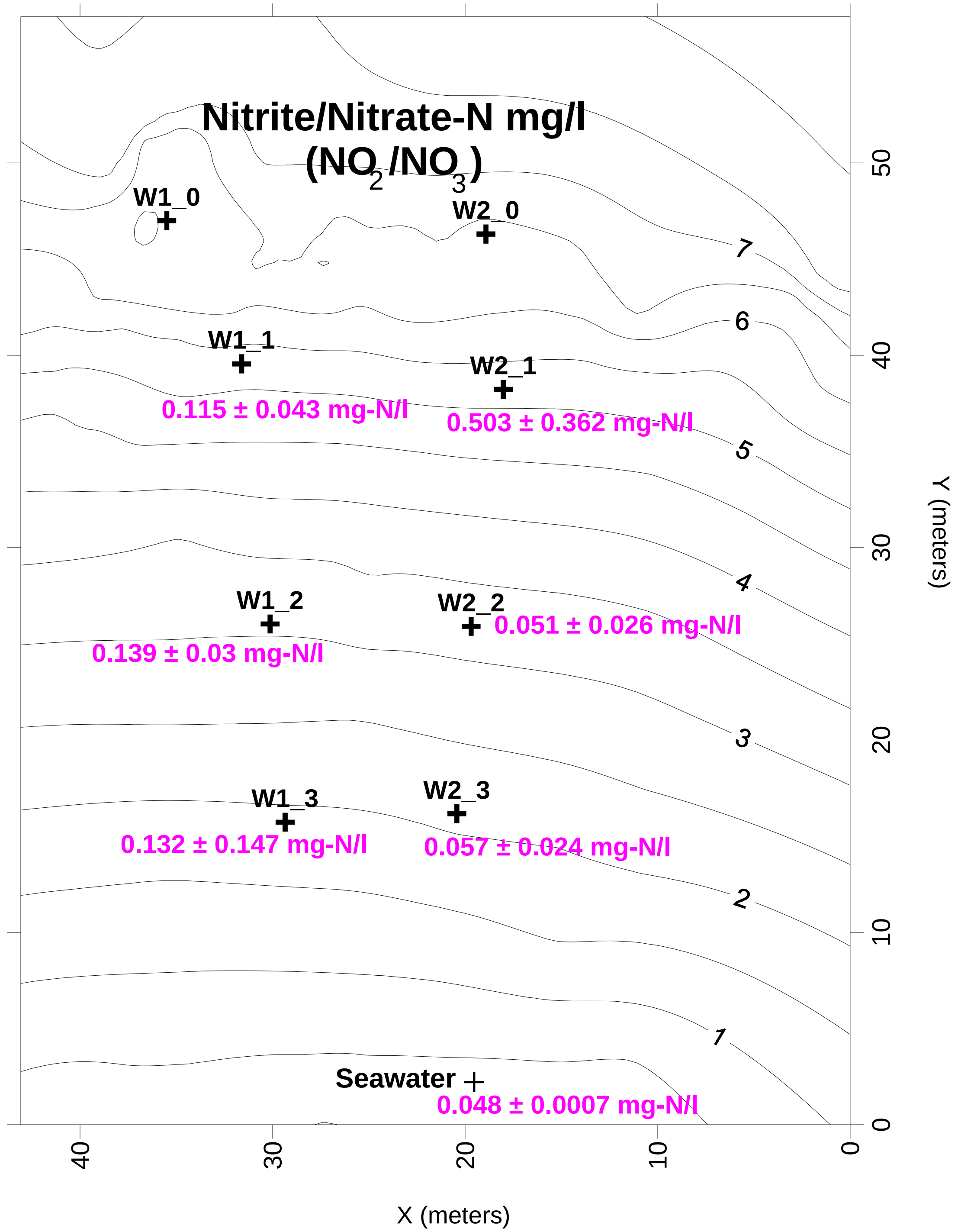

Figure 6: The average nitrite/nitrate-N results of the two deepest ports in mg-N/L. The concentrations at W2_2 and W2_3 (oily wells) were significantly different from the rest of the values.

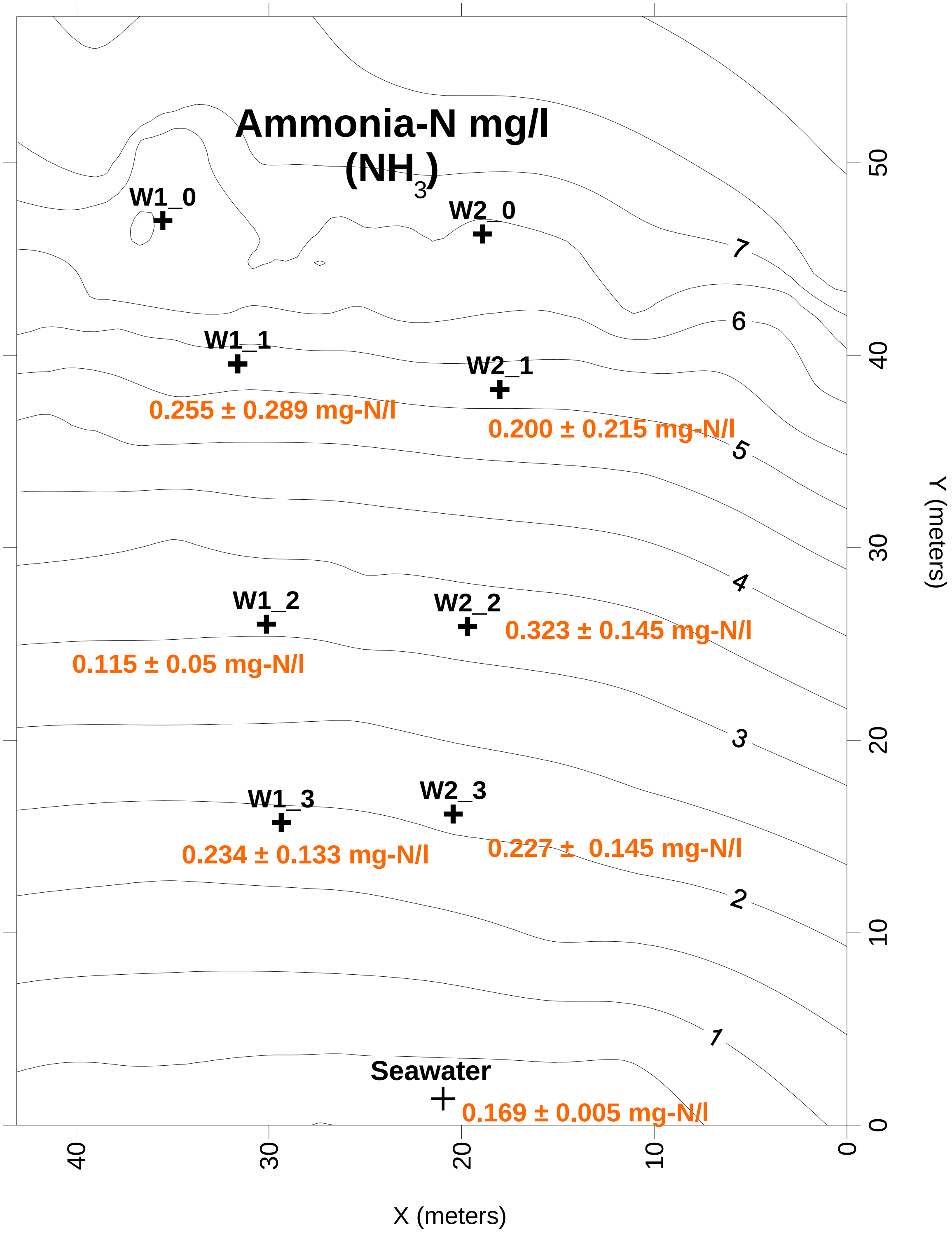

Figure 7: The average concentration of ammonia mg-N/L of the two deepest ports in mg-N/L. A higher concentration of ammonia was observed in the beach in comparison to the that in the sea. This could be due to nitrogen fixation in the beach.

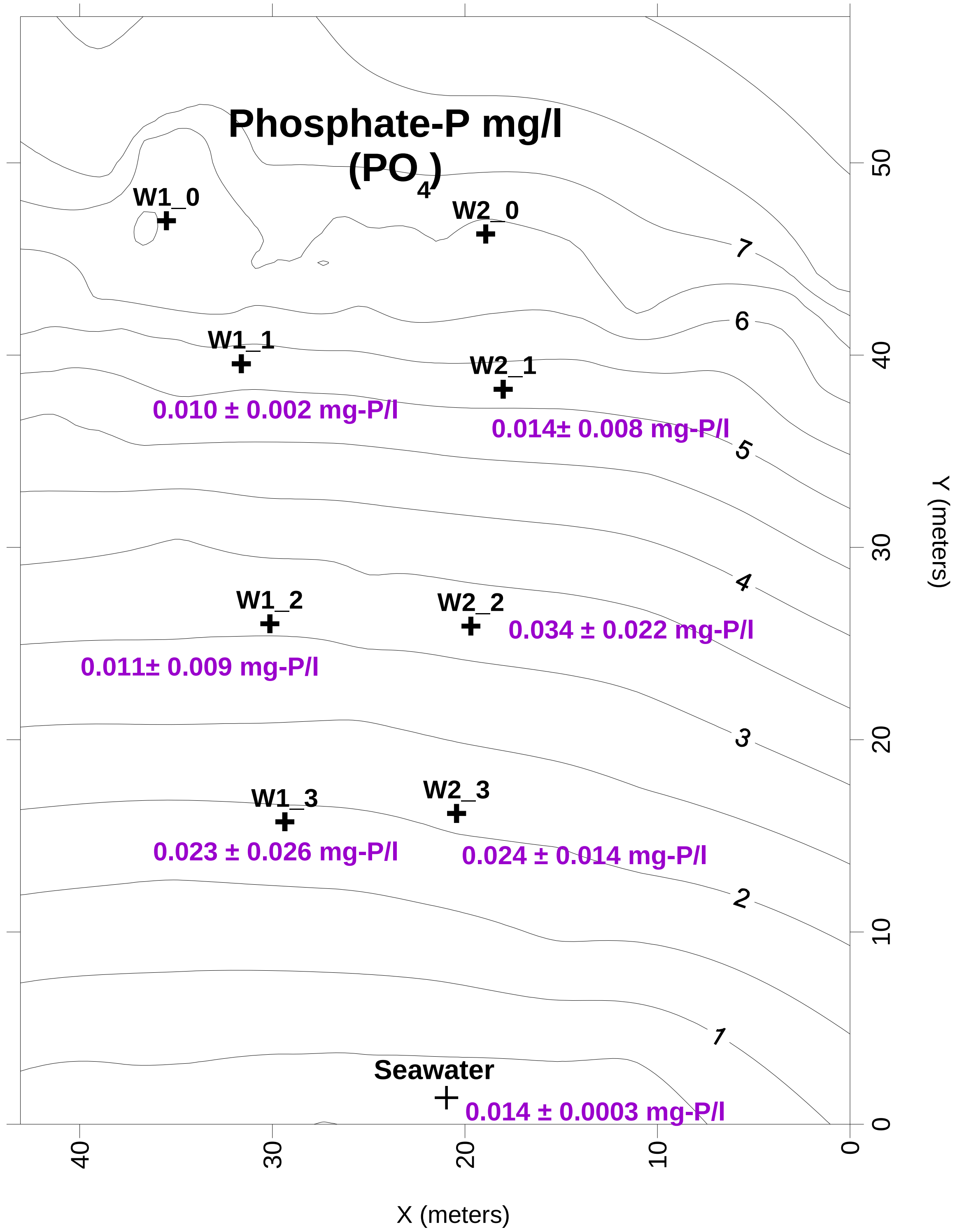

Figure 8: The average phosphate concentration mg-P/L of the two deepest ports. The highest concentrations were observed in the oily wells.

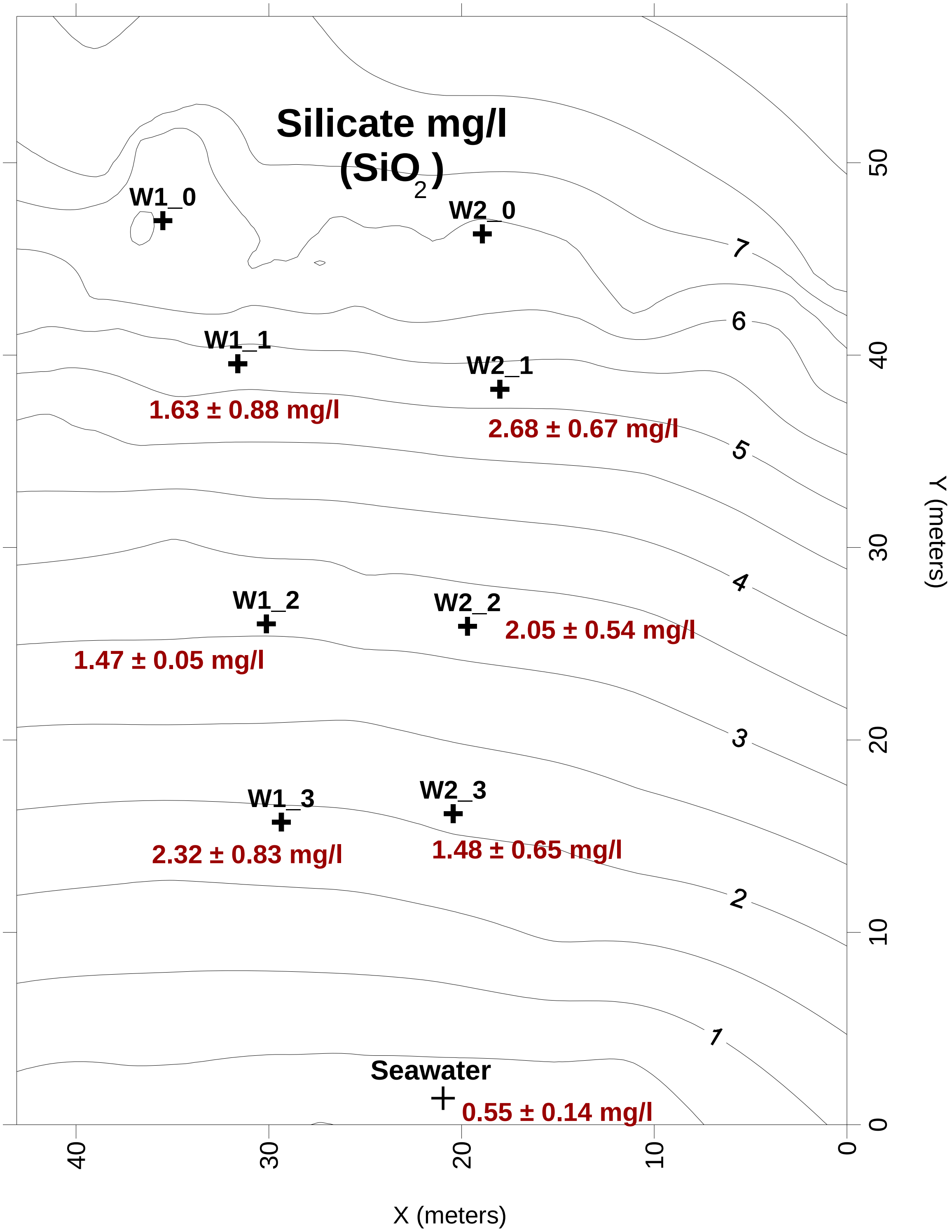

Figure 9: The average silicate concentration of the two deepest ports in mg/L.

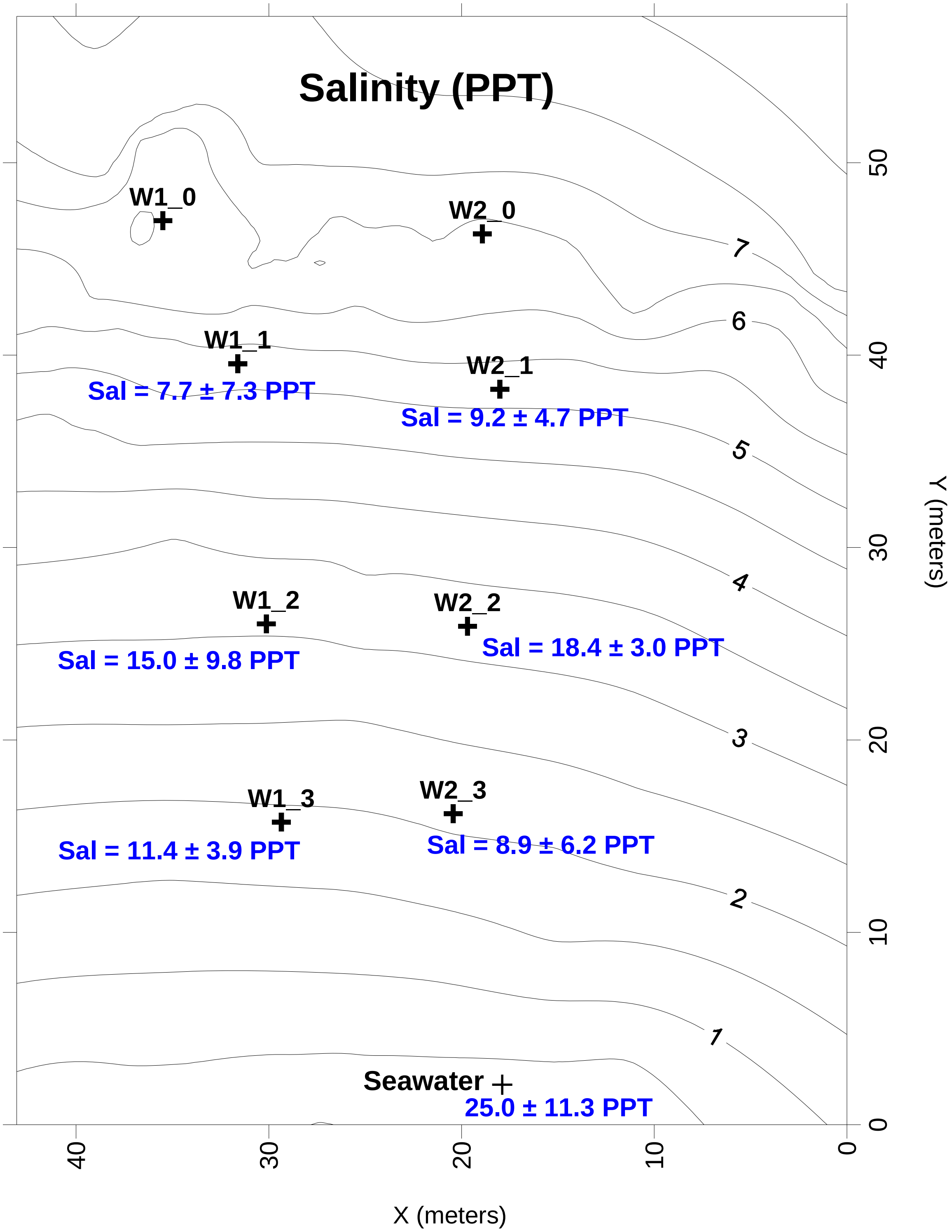

Figure 10: The average salinity of the two deepest ports in part per thousands (ppt). The values and trend in both transects were comparable.

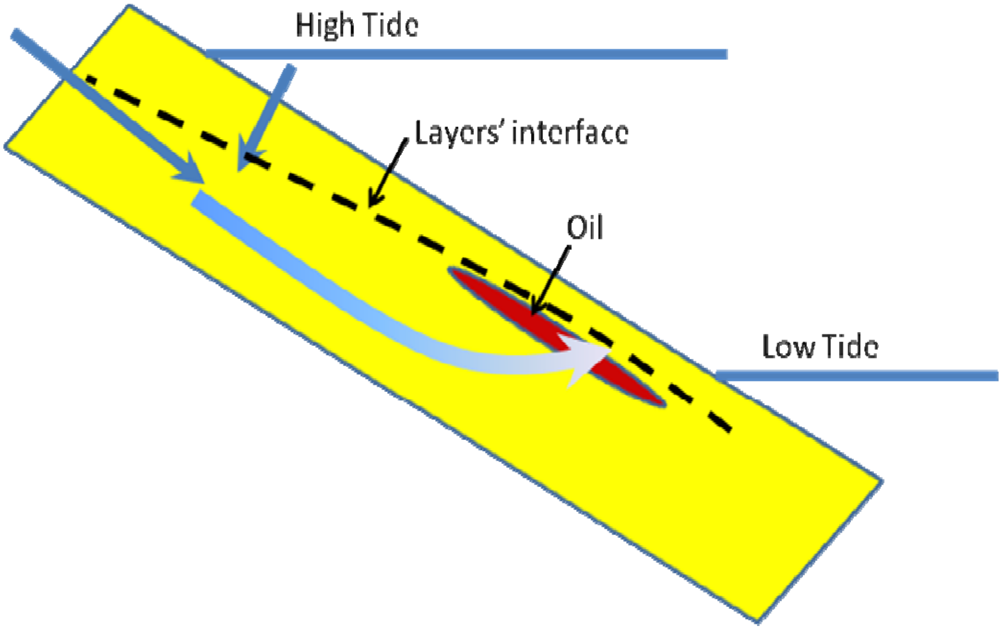

Figure 11: Schematic of water flow within the oiled transect (Right Transect, see Fig. 1). The beach fills from the landward side and from the sea near the high tide line (large blue arrows). As water moves seaward within the beach (curved arrow) it loses its dissolved oxygen and nitrate. Measurements above the oil layer in the upper layer would invariably provide high dissolved oxygen values to the large permeability of the upper layer.