

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 dissolved chemicals to potentially bioremediate oil from the Exxon Valdez oil spill was investigated at Smith Island, Prince William Sound, Alaska. Two transects for tracer application were installed: one at a clean area and another at an oiled area. Tracer delivery occurred under ambient pressure through manifolds. Lithium in LiBr/sea water solution was the inert tracer, and the solution (82.6 mg/L of lithium) was released at a flow rate of 0.23 L/min for 58.5 h. While maintaining the flow rate, the solution was switched to sea water (i.e., 0.0 mg/L of lithium) for 16 h. The results show that the tracer moved landward with rising tides and seaward with falling tides. The plume got deeper moving landward and shallower moving seaward of the manifold. Thus, in situations where oil biodegradation is limited by the availability of nutrients or oxygen, applying these chemicals by this technique would allow them to reach entrapped oil seaward of the manifold from below. The seaward plume traveling speed (around 2.0 m/d) 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 (PWS), 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, 2006) estimated that between 60 and 100 tons of subsurface oil persists in many initially polluted beaches in PWS. The persistence of oil was noted by other studies (Michel and Hayes 1999; Page et al. 2008; Taylor and Reimer 2008; Li and Boufadel 2010). Short et al. (2004) found that the oil contains a relatively high percentage of polycyclic aromatic hydrocarbons 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 (Card and Meehan 2005; Mauseth et al. 2005a, 2005b; Michel and Benggio 2005; Thumm et al. 2005) and in situ bioremediation (Lindstrom et al. 1991; Prince 1993, 1997; Venosa et al. 1996; Wang et al. 1998; Margesin and Schinner 1999). 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 cleanup 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). Recently, Eslinger et al. (2001) found that the maximum concentration of nutrients is less than 0.20 mg N/L. A more recent study by Atlas and Bragg (2009) on the beach under study in this article 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).

Sharifi et al. (2011) conducted measurements at depths varying from 0.50 to 1.0 m at this beach and found an average concentration in the beach similar to that found by Atlas and Bragg (2009), that is, around 0.20 mg N/L. They also

measured the dissolved oxygen concentration in the oiled area of this beach and found it to be less than 1.0 mg/L. They concluded that oxygen limitation could be the major factor preventing further biodegradation of the oil. Atlas and Bragg (2009) noted that the ratio of nitrogen to nonpolar hydrocarbons (Bragg et al. 1994) is high and concluded that adding nutrients to the beach would not enhance the biodegradation of oil. In addition, 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 this to be a valid argument that could only be addressed through a pilot study of bioremediation where chemicals, such as nutrients and oxygen (maybe biosurfactants), 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 such chemicals, and based on the movement of the tracer, one could design pilot studies for bioremediation. We sought our objective by releasing a conservative tracer, lithium in a lithium bromide solution made of sea water, and we monitored its movement in the beach. The tracer was released at the depths of 0.60 and 0.45 m on the right and left sides (looking landward) of the beach under ambient conditions. We labeled 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, Massachusetts, to study the chemical reaction and transport of selected chemicals in a field setting. Kloppmann et al. (2009) conducted a 38-d 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 East Yorkshire, UK. To explain how pink salmon eggs in PWS became contaminated by Exxon Valdez oil, Carls et al. (2003) investigated groundwater movement between oil-contaminated intertidal beaches and salmon streams by the release of fluorescent tracer dyes (Liquid rhodamine WT dye) in Sleepy Creek and Junction Creek, PWS, 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

Field Setup

The study took place in a beach 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 (Page et al. 2008; Taylor and Reimer 2008). However, oil persists on this beach at the amount considered to be heavy oil residue 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 and Figure S1, Supporting Information). 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 to 20 cm) interspersed between boulders (up to 100 cm). The geology consists of basalts and pillow basalt features similar to nearby Knight Island (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.

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 are needed for this to occur. For this reason, we designed the field study in 2009 to have 9 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 to 28 and the second was August 18 to 29 when the measurements were conducted.

Two trenches were dug in the cross-shore direction (i.e., landward-seaward) to conduct the 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 S1).



Figure 1. Photograph of the beach 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 APR of the tracer are shown.

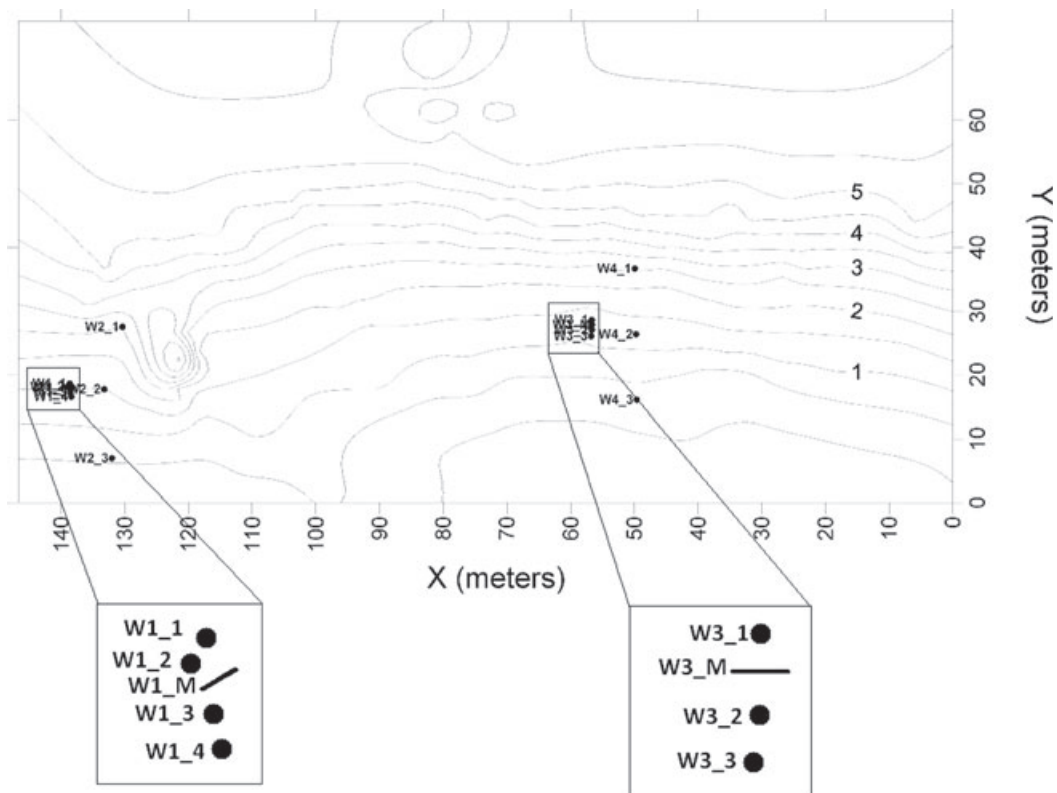


Figure 2. Top view showing the topographic contours of beach and the emplacement of the two trenches for the APR. The two trenches were at an approximate elevation of 1.5 m. The black circles are observation wells and the black lines are the manifold in the trench.

The excavation was extremely difficult in the (left) oiled trench requiring the usage of a handheld 64-pound jackhammer (Brute™ Breaker Hammer, Bosch, Mount Prospect, Illinois) and a 71-pound auger (General 330 H 5HP Two-Man Auger, General Equipment Company, Owatonna, Minnesota). 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 refilled using the same material which is excavated from them. During the experiment, water samples were taken from the sensors in the wells and were later analyzed in the laboratory for lithium concentration.

Sampling and Tracer

For sampling the movement of the tracer, the overall approach was to place in each pit, a polyvinyl chloride (PVC) pipe, a multiport sampling well, and two sampling boxes (SBs). The PVC pipe had an inner diameter of 1 inch and was slotted across over the whole length to allow water passage. A pressure transducer (Mini-Diver Data-DL501, Schlumberger, New York) was placed at the bottom of the PVC pipe to record the water pressure at an interval of 10 min. 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 (SPs) at various levels. The SPs were spaced at an interval of 0.20 m and were labeled A, B, C, and D from the bottom up. Port D was above the ground in all wells and hence it was not used for analysis. Each port was connected via a tube that extended to the top of the pipe. A tygon tube was placed on each of the tubes 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.



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.

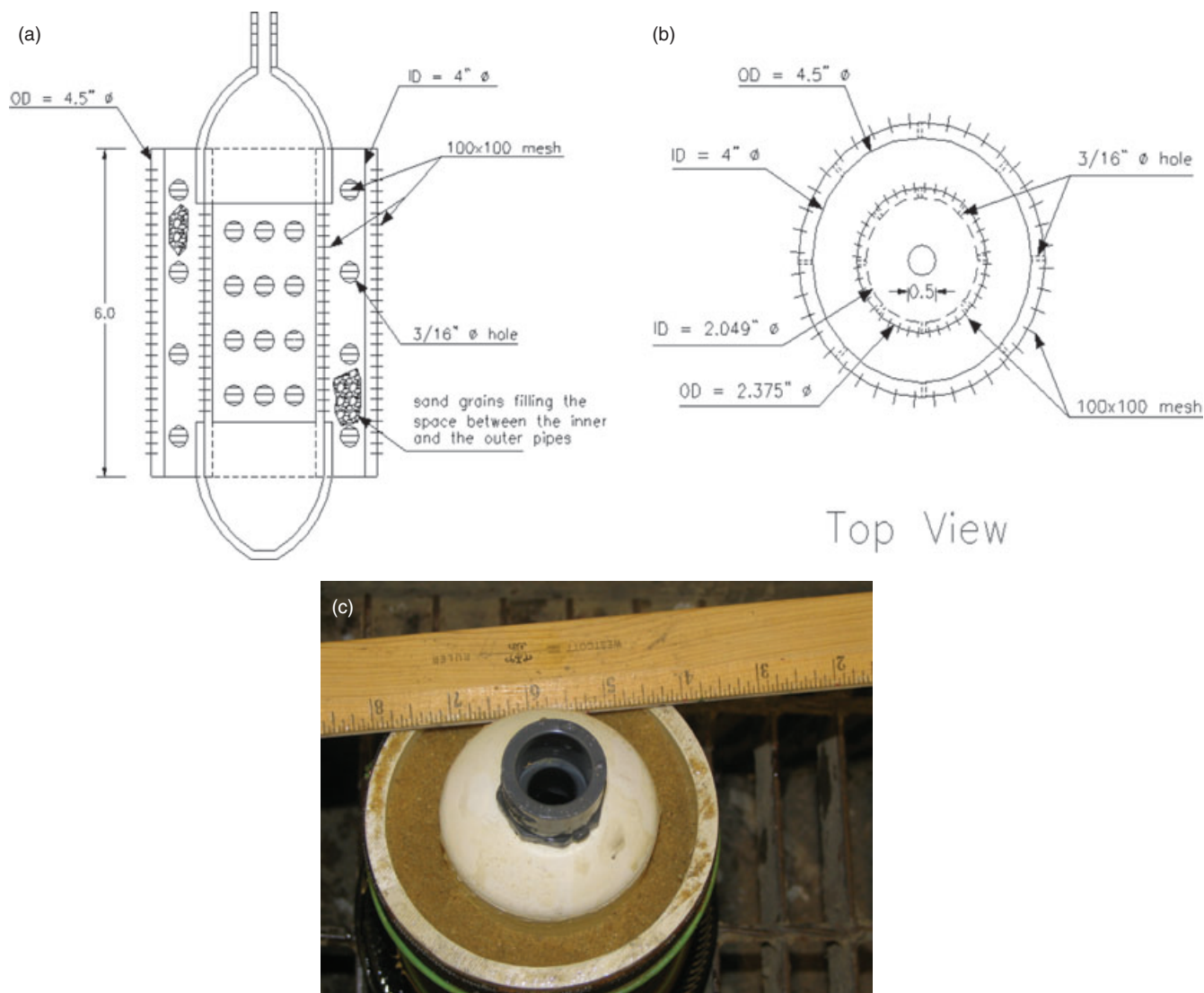


Figure 4. The SB used for water sampling. (a) A vertical cross section of the SB, (b) a horizontal cross section at mid-height, and (c) photo of the SB showing the sand between the concentric cylinders.

The SBs were used as backup in case the SPs got clogged. Each SB (Figure 4) 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 100×100 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 (4 inches) and the spacing between the cylinders was around 1.5 cm. Fourteen SBs were used for this study.

For sampling from SBs, we used a long tygon tubes sent all the way down to the SBs through the PVC pipes and the water samples were extracted using the 60-mL syringes. To remove the water samples stayed in the SB, the first five samples ($5 \times 60 \text{ mL} = 300 \text{ mL}$, equivalent to the volume of the SB) were disposed and the sixth sample was kept.

Sampling from various wells was dependent on the logistics, man power, and the tide level.

Lithium in a technical grade anhydrous (ReagentPlus® grade, assay more than 99%) LiBr (Sigma-Aldrich Co., St. Louis, Missouri) was used as the conservative tracer in these experiments. It was used successfully in previous beach tracer studies (Wrenn et al. 1997a, 1997b). It was applied in a lithium bromide solution at an approximate concentration of 5000 mg/L. Water samples (~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, New Jersey) shipped to the laboratory at Temple University in Philadelphia, Pennsylvania 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 a lowest detectable concentration of 0.2 ppm and reproducibility of 2%.

Ambient Pressure Release

The 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 60 × 60 mesh having an opening width of 0.009 inches. The perforations in the pipe had a 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 a depth of 0.60 m in the Right Trench and at a 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 S2).

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 S2, where eight tanks were used at this beach.

The experimental design required a flow of 0.23 L/min (around 0.06 gal/min) and a concentration of 100 mg/L of lithium for a duration of 58.5 h, after which, the injection solution was switched to sea water (~0.0 mg/L of lithium) while the flow was kept constant for 16 h. The switch to sea water 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 12-V battery from 0 to 5.6 L/min (0 to 1.5 gal/min). The flow meters (King Instruments Company Inc., Garden Grove, California, 0.7 to 7 gal/h) allowed us to set the flow to an essentially constant value over the desired period.

Owing to the 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-h 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 to 0.0 mg/L) such that one can assume the existence of a plateau of concentration in the tanks until $t = 58.5$ h when the concentration was reduced suddenly to 0.0 mg/L (by emptying the tanks and refilling them with sea water) for another 16 h.

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 is too small to be treated as part of the plume, which does not seem reasonable. Assigning a small value, such as 0.1% 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, the oxygen will get depleted moving away from the well, so the oxygen concentration decreases. We determined that if the decrease is up to 80%, then the concentration would still be larger than 2.0 to 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 82.6 mg/L to delineate the edge of the plume. But to have a feeling about migration of half of the tracer concentration, the “Results” section also reports the 50% of the maximum tracer concentration in each well. We report first the results of the Right Transect (clean).

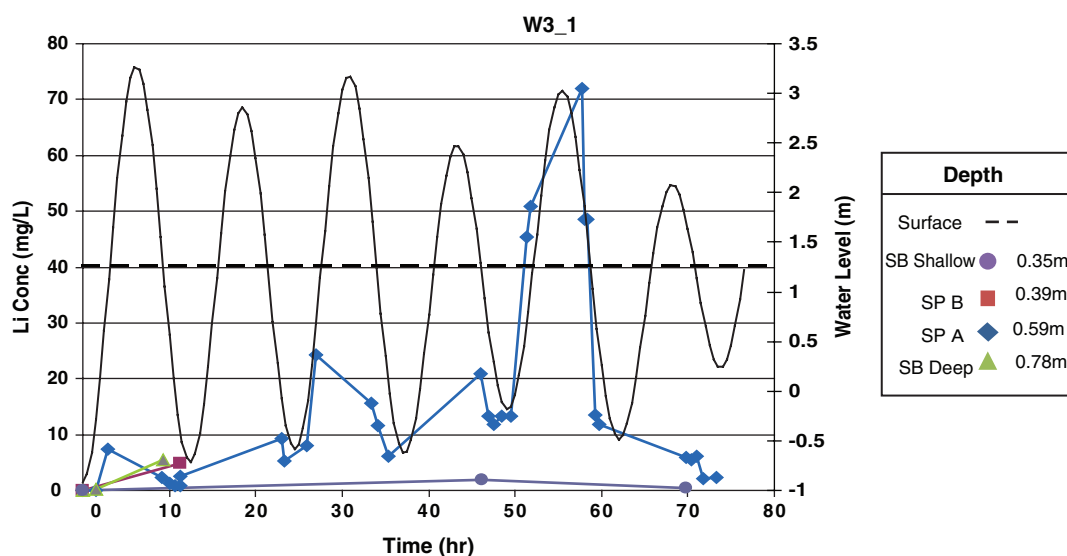


Figure 5. Lithium concentration as a function of time at multiple sensors at well W3_1 located 0.75 m landward of the W3_M. The tide level is also reported and should be read on the secondary axis. The depths of the sampling points are displayed in the legend. The injection concentration was 83 mg/L from 0 until 58.5 h and then it was reduced to 0.0 mg/L for times greater than 58.5 h. Owing to logistic problem, we were not able to continue sampling for SP_B and deep SB beyond $t = 10$ h.

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 $t < 60$ h, 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 $t = 58.5$ h, and Figure 5 shows that the concentration at SP_A for t between 70 and 74 h was lower than those at 58.5 or 48 h. Thus, the injection should be continued to sustain the concentration high enough at 0.75 m landward of the manifold.

The tracer concentration of 50% of the maximum reached at 51 h at SP_A. 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 h at SP_A, indicating a travel speed of $0.75 \text{ m}/23 \text{ h} \approx 0.80 \text{ m/d}$. A value of 10% was reached at $t = 2$ h which is relatively fast. We have considered and ruled out many possibilities for this sudden rise. However, the low values at $t = 10$ h suggest that such a value should be treated as an “outlier,” probably because of the complex pathways due to the combined effects of tidal hydraulics and subsurface heterogeneity.

In Figure 5, one notes a slight increase in the concentration of the shallow SB at $t = 46$ h. 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.

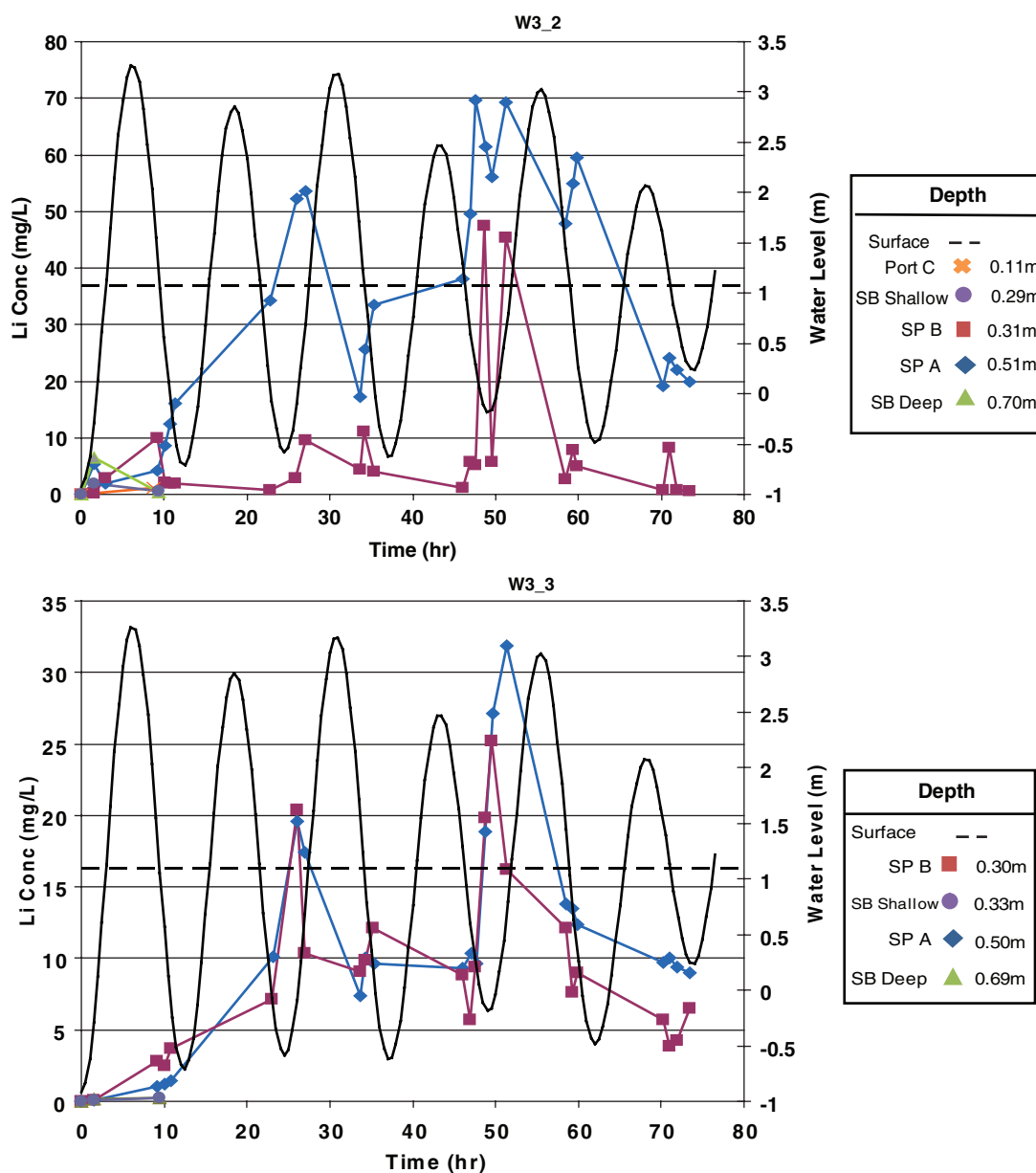


Figure 6. Tracer concentration at seaward monitoring wells. W3_2 located 0.80 m seaward of W3_M and W3_3 located 1.8 m seaward of W3_M.

The seaward wells, W3_2 and W3_3 (Figure 6), 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 and W3_3 at approximately the same time; however, the concentration at W3_3 was always about half that of W3_2. However, using the same concentration as a basis, say 40 mg/L, one concludes that tracer arrived at W3_2 in 10 h and to W3_3 in 24 h. 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 thus around 1.90 m/d for W3_2 and 1.8 m/d for W3_3.

For W3_2, the earlier arrival of the plume ($t = 10$ h) reflects the ease of the pore water to move out toward the sea with the tide. Owing 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 10 h, the concentration at W3_3 remained less than 5% until $t = 24$ h. The concentration at both SP_A and SP_B had an increasing trend until $t = 50$ to 60 h (depending on the availability of measurements) and it was always lower at $t = 70$ h, which represent a time period of 11.5 h after switching to injection of 0.0 mg/L of lithium (i.e., only salt water). The tracer concentration at W3_3 never reached more than 32 mg/L in any ports or SBs, but at W3_2 the tracer concentration reached 50% the maximum at $t = 26$ h and $t = 49$ h at SP_A and SP_B, respectively.

For W3_2, the concentration at SP_A (which is 0.50 m deep) was larger than that at SP_B (which is 0.30 m 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 Right Transect 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

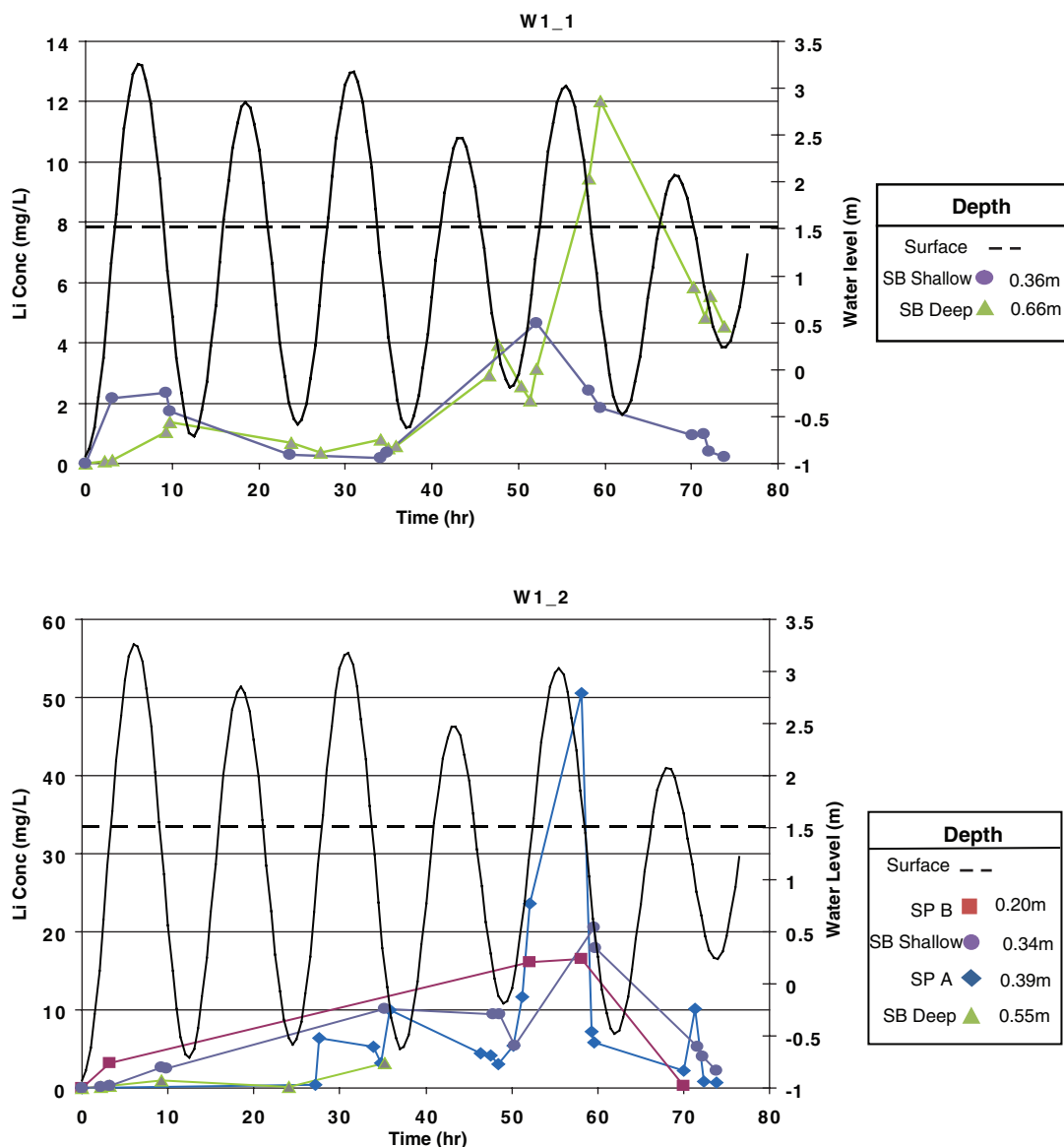


Figure 7. Lithium concentration and tidal level as function of time at wells W1_1 and W1_2 located, respectively, 0.65 and 0.20 m landward of the manifold in the left transect (Figure 2).

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 S1) 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 7 reports the concentration of the tracer landward of the manifold (Figure 2). The lower panel contains the results of the well W1_2 located 0.20 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 h and continues to rise, with some fluctuations, until reaching the maximum at 58.5 h (which is close to 50% of the maximum tracer concentration). The concentration of SP_A dropped sharply afterward, which could be due to tidal hydraulics (i.e., dilution by the tide). The decrease at $t = 70$ h is due to the stoppage of high concentration injection and the conversion to injection of sea water (0.0 mg/L of lithium). The concentration at SP_B and the shallow SB increased starting at $t = 35$ h and continued until $t = 58.5$ h. The concentration at these sensors (SP_B and shallow SB) became almost zero at times greater than 70 h. Considering the value of 10 mg/L at 35 h (for shallow SB), one concludes that the tracer plume moved 0.2 m in 35 h, which gives a landward traveling speed of 0.14 m/d. The samples for W1_2 deep SB were not taken beyond $t = 35$ h and it is hard to compare with other SPs or SBs, but for time $t < 35$ it behaves almost the same as SP_A.

The upper panel of Figure 7 contains the concentration of two SBs at well W1_1, located 0.65 m landward of the APR manifold. Measurements from the SPs 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. The maximum tracer concentration observed in well W1_1 was not more than 12 mg/L and it is not even 15% of the maximum. On the basis of the fact that the concentration reached 12 mg/L at $t = 59.5$ h, one may conclude that the travel speed of the plume is around 0.26 m/d, which is, relatively, very close to the landward speed obtained based on the data of W1_2 (note the previous paragraph).

Figure 8 reports the concentration at wells W1_3 and W1_4, located 0.80 and 1.40 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 their measurements overlapped. The concentration of both sensors was close to the maximum at $t = 35$ h. Subsequent measurements were obtained only from SP_A and they show that the concentration reached that of the source (83 mg/L) at 58.5 h, before dropping to below 10 mg/L at time greater than 70 h. The concentration at the shallow SB increased steadily, with a small drop for times between 45 and 50 h. It increased again to reach 42 mg/L, which is around 50% of the maximum, at $t = 58.5$ h. It dropped below 10 mg/L at

times greater than 70 h. On the basis of this panel, the tracer plume moved a distance of 0.80 m in 10 h, an approximate speed of 2.0 m/d in the seaward direction. Even though SP_A (0.33 m) and shallow SB (0.30 m) have a comparable depth, they behaved differently (Figure 8). The difference in concentration between the SBs and the SPs could be due to a variety of nonexclusive reasons. The two main reasons are (1) the SPs represent point measurements and are therefore more accurate than the SBs and (2) the readings from the SBs represent the concentration in a 300-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.

The lower panel of Figure 8 shows the tracer concentration as obtained from two SBs at well W1_4, located 1.40 m seaward of the manifold (Figure 2). The concentration at the deep SB increased first, reaching 17 mg/L at $t = 10$ h. The concentration at the shallow SB reached 11 mg/L at the same time. As well W1_4 was covered by the tide, it is hard to tell exactly when 50% of the maximum tracer concentration reached to the well, but it is between 27 and 34 h for deep SB and between 35 and 46 h for shallow SB. At around $t = 35$ h, there was a reversal in the order of concentrations with that of the shallow SB becoming higher. This indicates the 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 8) where the concentration of the shallow SB was one-third of that of the deep SB for the majority of the time. On the basis of the concentration at $t = 10$ h, the plume traveled 1.40 m in 10 h, which gives an average seaward migration speed of 3.40 m/d, a large value that should be considered as an approximation considering the uncertainty in delineating the plume (i.e., 10% of the maximum).

Discussion

Slow-release chemical oxidation (chemox) method has become a common method for environmental remediation. In chemox, highly reactive chemicals are slowly injected into the subsurface where the oxidants rapidly react to oxidize and breakdown subsurface contaminants to less harmful by-products. The most commonly used oxidants include peroxide, ozone, and permanganate. The method provides in situ efficient remediation technology that stimulates the natural biodegradation of aerobically degradable contaminants in soil. Slow-release chemox was successfully implemented to remediate subsurface contaminant such as unsaturated aliphatic and aromatic compounds (Luster-Teasley and Onochie 2009). However, we are never aware of any studies regarding APR of required chemicals to remediate deep stranded oil in tidally influenced gravel beach. This study, therefore, deals with way of delivering needed chemical and/or oxygen for the first time using APR tracer for potential biodegradation of the subsurface oil in the beach.

The migration speed of the tracer in the landward direction was 0.8 m/d at the Right (clean) Transect and 0.2 m/d at the Left (oiled) Transect. In the seaward direction, the migration speed was around 2.0 m/d at both the Transects. The center of the plume moved on average 1.8 and 0.8 m to

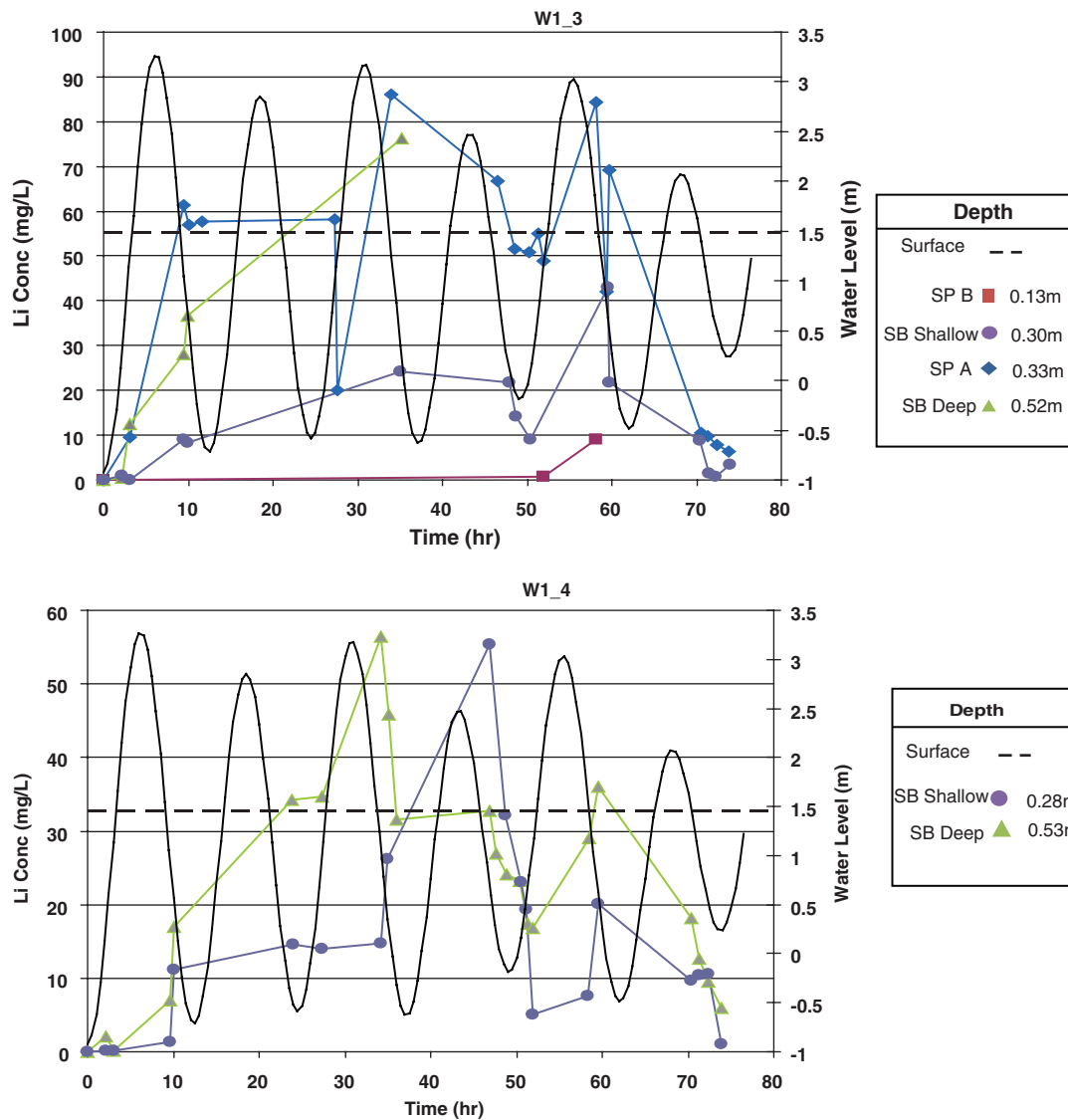


Figure 8. Concentration at two wells, W1_3 and W1_4, located 0.80 and 1.40 m seaward of the manifold, respectively (Figure 2). Multiport was not installed at this well and hence SPs' data are not available.

seaward in clean and oiled transect, respectively (Figure S3). The seaward migration of the plume was sometimes slowed down due to tidal cycle. From clean transect, one can easily see the overall upward movement of the centroid of the plume, but in oiled transect it traveled both directions (Figure S3). 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. Migration speed difference among the clean and oil transect is mainly due to two possible reasons: (1) variation in the physical properties of the two transects, which includes porosity and/or hydraulic conductivity. As we can see from Figure 1 and Figure S1, the oiled transect has cobbles and boulder in and around the observation wells (which hinder the ease of flow) while the clean transect has gravel sediment. (2) The outcropped bedrock on landside of oiled transect (Figure 1) possibly blocked the flow of water or landside recharge which keeps the groundwater table high enough specially during low tide and speeds up the transport of added tracer in oiled transect. The travel speeds should be treated as approximate values,

as the plume was delineated by the 10% concentration (of the maximum).

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 9 which shows the edge of the plume (the 10%) as interpolated from sensors at $t = 58.5$ h. As noted in tidal studies (Boufadel 2000; Boufadel et al. 2006; Li and Boufadel 2010), sea water 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

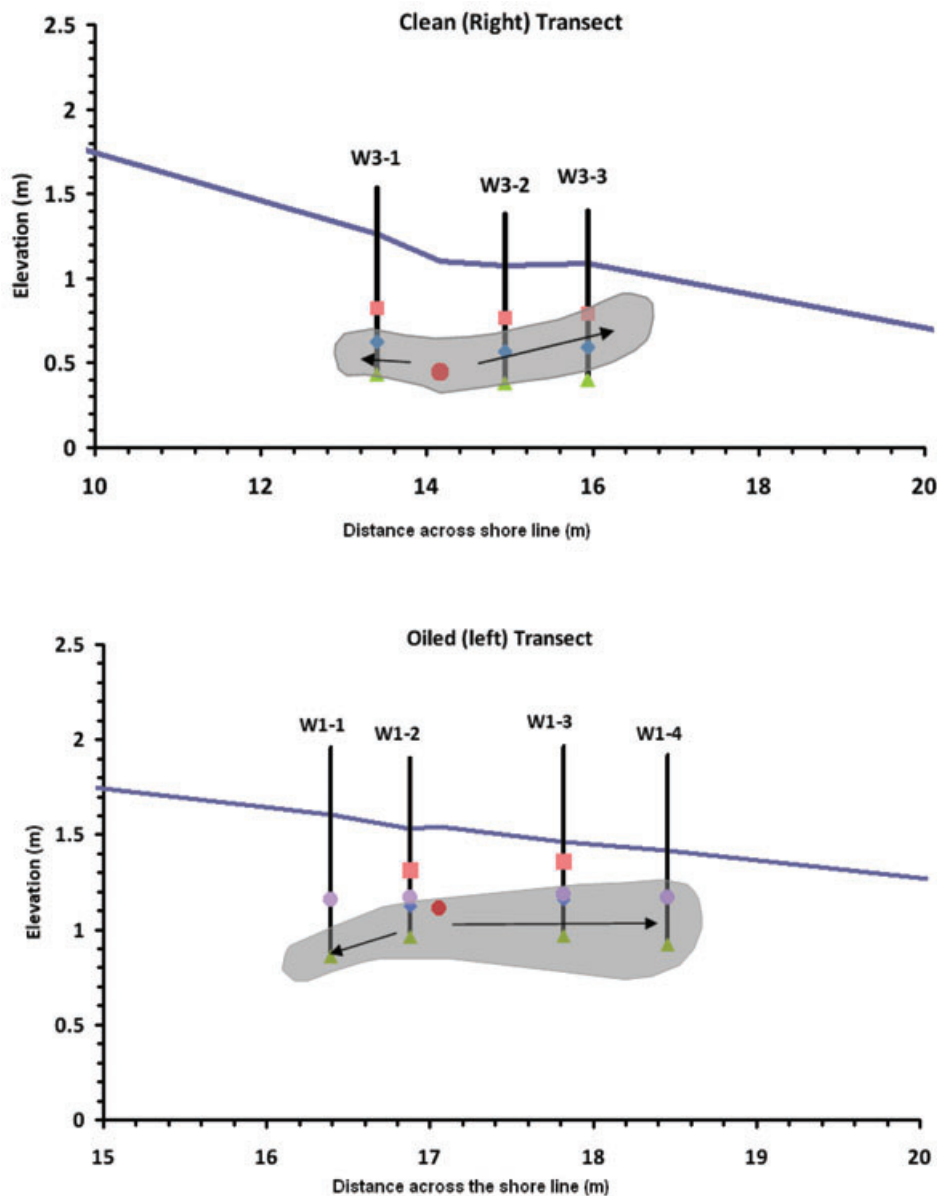


Figure 9. Plume location delineated as 10% (about 8.3 mg/L) of the initial tracer concentration at time 58.5 h and reconstructed movement in (a) the clean (right) transect and (b) the oiled (left) transect. In both situations, the plume sank moving landward and rose moving seaward of the manifold. For bioremediation purposes, nutrients and oxygen should be applied landward and deeper of the oil layer. Note that for the purpose of clarity, the location of the wells was recalculated considering the value 35 and 42 m in y axis (across shore line) as zero for left and right transects, respectively.

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, 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 chemicals (nutrients, oxygen, and biosurfactants) moving upward from below. Conversely, it is highly unlikely that the landward motion would deliver any chemicals 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 an 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; Li and Boufadel 2010). Therefore, after the pulse displaces the existing water, it does not get diluted much. This demonstrates further the superiority of delivering the needed chemicals deep into the beach rather than 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 feasibility 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 availability of chemicals, delivering them by the technique adopted here is logistically feasible. On the basis of 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 m² (7 m along shore × 10 m across shore). Therefore, two to three injection manifolds, each of them around 7.0 m long and each placed at depths of 0.30 to 0.45 m in the oiled transect would ensure complete spatial coverage of the oil by the required chemicals.

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Supporting Information

The following supporting information is available for this article:

Figure S1. Picture of Left Trench (oiled) facing landward. Note the extent of oiling and the presence of large boulders.

Figure S2. 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 S3. Temporal variation of coordinates of plume centroid for left and right transects; increase in X_G indicates seaward movement; decrease in Z_G indicates downward movement.

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