Ground Water Monitoring&Remediation

Feasibility of High Pressure Injection of Chemicals into the Subsurface for the Bioremediation of the Exxon Valdez Oil

by Michel C. Boufadel and Adane M. Bobo

Abstract

Delivery of dissolved chemicals to bioremediate 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 196 kPa. 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 h. The tracer plume traveled at the average speeds of 10 m/d in the seaward direction and 1.7 m/d in other directions. The rapid movement under HPI and the large diameter of influence (3.0 m) indicated that bioremediation of the Exxon Valdez oil on this beach via injection of chemicals is logistically feasible.

Introduction

The 1989 Exxon Valdez oil spill polluted around 2000 km of rocky intertidal shorelines within Prince William Sound and western Gulf of Alaska (Bragg et al. 1994; Neff et al. 1995). Recent studies by scientists from the National Oceanic and Atmospheric Administration (Short et al. 2004, 2006) estimated that between 60 and 100 tons of subsurface oil persists in many initially polluted beaches along Prince William Sound. The persistence of oil was noted by other studies (Michel and Hayes 1999; 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; Anyakora 2007). Short et al. (2006) reported that sea otters and ducks would encounter subsurface lingering Exxon Valdez oil spills in the northern Knight Island, while foraging there the external surface of these animals might become contaminated, and oil ingestion may follow during preening.

The response for dealing with the persistent Exxon Valdez oil on this beach ranges from vigorous mechanical removal of contaminated sediments (Etkin and Tebeau 2005; Owens et al. 2005; Taylor and Owens 2005) 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. 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 lack of nutrients such as nitrate and phosphate on this beach was noted early on during clean-up of the spill (from 1989 through 1992). This led to a major effort where around 55 tons of nutrients were applied on beaches of PWS (Bragg et al. 1994). A recent study (Eslinger et al. 2001) found that the maximum concentration of nutrient in PWS is less than 0.20 mg-N/L, an order of magnitude smaller than the minimum needed for optimal (70%) biodegradation of hydrocarbons (Boufadel et al. 1999; Du et al. 1999; Zhu et al. 2001).

This study addresses remediation of persistent oil 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 approximately 40 m and an across-shore length of approximately 50 m. The sediments are coarse ranging from gravel (a few millimetres) to pebbles and cobbles (10 to 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 subjected to extensive treatment (Taylor and Reimer 2008). However, oil persists on this beach at the amount considered to be heavy oil

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residue 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 (Figure S1). The left (looking landward) 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 (Boufadel et al. 2010) 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 underlain by a layer that has 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-d injection test with Bromide and Boron and Lithium isotopes in sandy aquifer to assess the behavior 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 multiborehole 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 article 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 a 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

There are several intrusive and nonintrusive ways of putting sensors underground for measuring soil physical properties. However, it is practically impossible to drive sensors into this beach for two main reasons: (1) geology of the beach, the top 30 to 60 cm depth of the beach is composed of sand, gravel, pebble, and cobble varying in size from 0.25 to 300 mm. These are intertwined between boulders (up to 100 cm) typically spaced by a few meters. Beyond the first 40 to 50 cm depth, the beach is highly compacted and hard to push any sensors down. (2) Apart from measuring soil physical properties and water level, for collecting water samples, one needs to place specially designed water sample collecting devices at different depths. Therefore, it is necessary to excavate pits to place the sensors and water sampling device 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 to 28 and the second was August 18 to 29 when the measurements were conducted.

In total, six pits were dug for the purpose of delivery of evaluating chemicals. 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 (BW) 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 (Figure 1 and Figure S1). 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 (Figure 1 and Figure S1). The HPI was considered promising on this beach because the beach has a bedrock around 2.0 to 3.0 m, which is deep enough to allow for this approach.

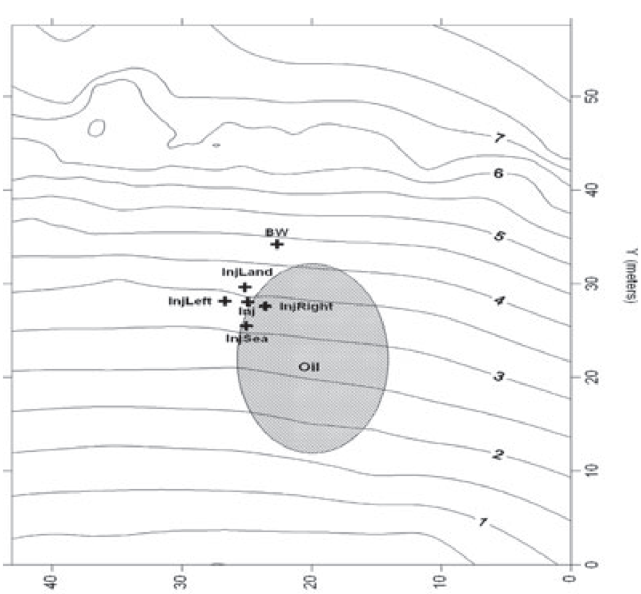

Figure 1. Top view showing the topographic contours of Beach EL056C. The injection well (labeled Inj) is at the approximate location $x = 25$ m, $y = 28$ m. It is surrounded by four observation wells: on the landward side (InjLand), on the seaward side (InjSea), on the left (InjLeft), and on the right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

The overall approach was to place in each pit a 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, dataLogger) 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 (Figure 2). 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 SB consisted of two perforated concentric cylinders made of PVC Schedule 40 (Figure S2). The chamber between them was filled with sand. 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 100 × 100 steel screen. The diameter of the inner cylinder was 5 cm (2 inches) and 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. Seven SBs were designed and build as a backup for taking water samples in case the SPs were clogged. The depth of SPs and SBs for the observation wells is plotted in Figure 2.

Lithium in a technical grade anhydrous (ReagentPlus® grade, assay >%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) 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, 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

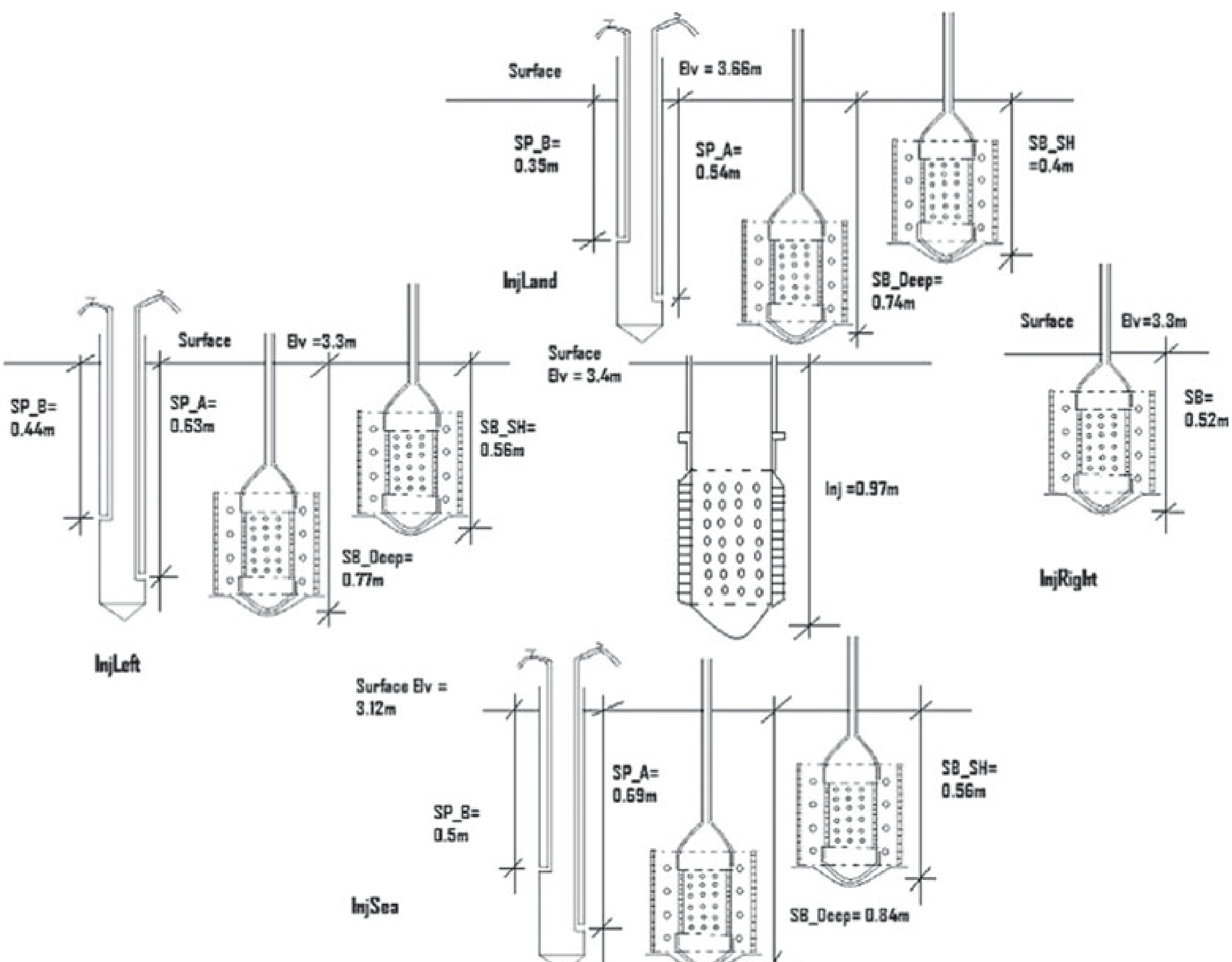

Figure 2. Depth of SBs and SPs from the surface for InjLand, InjLeft, InjRight, and InjSea observation wells. The figure is not on scale.

tracer in the field, the bromide was sampled using a Thermo Scientific (Beverly, Massachusetts) Bromide electrode and an Orion 5 Plus Benchtop meter, with the lowest detectable concentration of 0.2 ppm and reproducibility of 2%.

HPI System

The BW 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 (Figure S4, 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 (20 × 40) that was held in place by a 60 × 60 stainless-steel mesh that was clamped on the PVC pipe using stainless-steel clamps. (Note that 20 × 20, 40 × 40, and 60 × 60 meshes have the openings of 0.8636, 0.381, 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 Figure S4 (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.

To record the pressure during injection, a pressure transducer (Mini-Diver, dataLogger) was dropped in the PVC pipe (i.e., at the bottom of the pipe). 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 Figure S5, where four tanks were used at this beach.

The pumps used allowed continuous pumping of a tracer/seawater with a flow rate which varies from 0 to 1.5 gpm (0 to 5.7 lpm) using a 12 V battery. Only one pump was needed at either the BW or the injection well. The flow meters allowed us to set the flow to more or less constant values over the desired periods.

Results

We report first the results of the blowout experiment, followed by those of the injection experiment. Figure 3 shows the variation of the water pressure as function of time while the flow rate was changed. For the first 10 h, the flow rate was set at 1.0 L/min (0.26 gpm). Considering the lowest low-tide point as a datum, the total head (the sum of pressure head and elevation) was around 4.0 m until around the time $t = 4.0$ h when it increased to 5.4 m and followed the tide closely until $t = 8.0$ h, 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 0, 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.

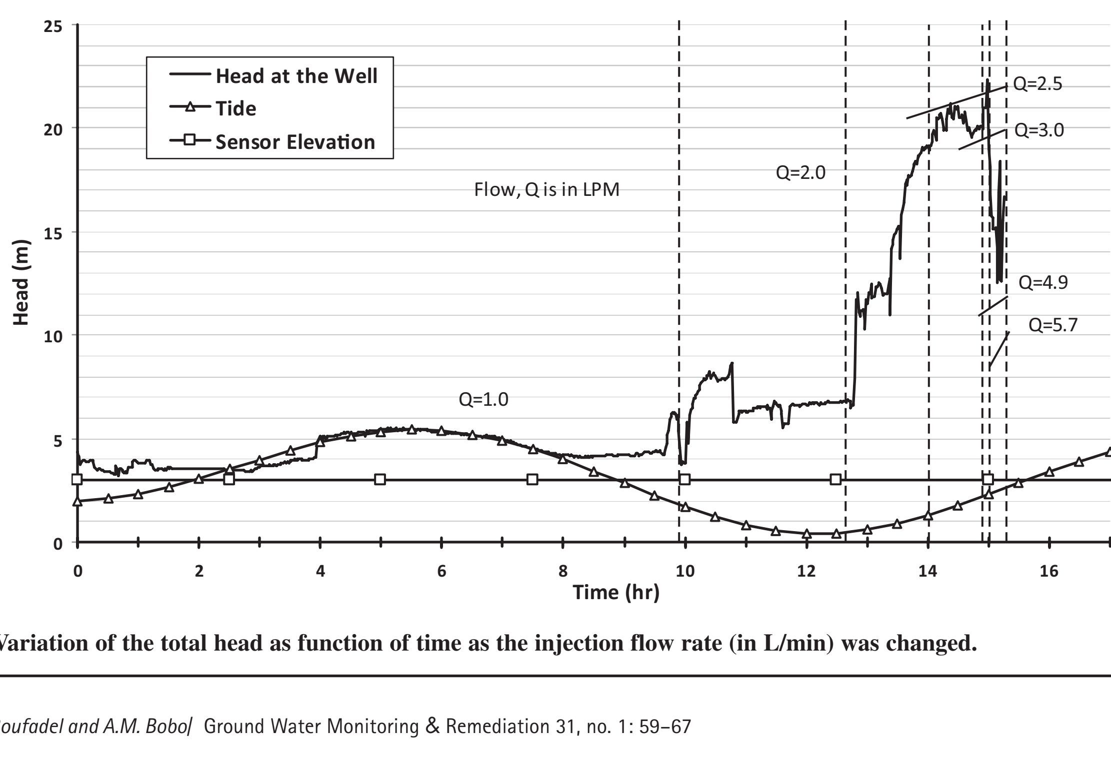

Figure 3. Variation of the total head as function of time as the injection flow rate (in L/min) was changed.

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, for the continuous injection of chemicals, the flow rate 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 BW; in essence, the flow had to be less than 3.0 L/min. Figure 4 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 h, and the pressure increased immediately to 2.0 m. Starting from $t = 12$ h, the injection puts more pressure on the sediment than due to tide. The pressure fluctuated with the tide until $t = 20$ h, after which it behaved independently of the tide. Between $t = 20$ h and $t = 25$ h, the flow was set at 2.0 L/min. At time $t = 25$ h, 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 h 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 to 0.0 mg/L).

Figure 5 shows that the concentration of lithium increased from 0 to around 80 mg/L at the first sampling event, which occurred around 7 h 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 $t = 8$ h and $t = 21$ h. In contrast, the concentration at the deep sensor SP_A increased steadily with time until reaching the value of 92 mg/L at $t \approx 24$ h. At the next sampling event, $t \approx 30$ h, the concentration of SP_A decreased to 82 mg/L, probably as a result of the decrease of the injection concentration from around 100 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 nonexclusive reasons. The two main 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 SPs. At $t \approx 24$ h, 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 5 one deduces that the travel time for the injected water to Well InjSea is between 5 and 7 h, and this is based on the rise of concentration at earlier times and based on the fall of concentration at times greater than $t = 24$ h. As the distance is around 2.5 m, the travel speed is 10 m/d in the seaward direction.

Figure 6 shows that the tracer reached Well InjLand within 24 h and it was around 10 mg/L, which is around 10% of the injection concentration. Therefore, the traveling speed of the plume in the landward direction is approximately 1.6 m/d. The concentration at the deep SB increased to around 6 mg/L at $t \approx 24$ h, before it dropped to around 4 mg/L at $t \approx 31$ h, probably because the injection concentration was decreased to 0.0 mg/L. Figure 6 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

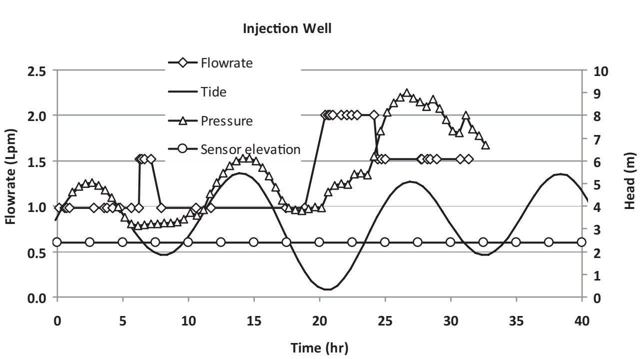

Figure 4. Variation of the flow rate and pressure during tracer injection. The injection occurred until $t = 33$ h. The average injection concentration between 0 and 25 h was 93 mg/L. It was reduced suddenly to 0.0 mg/L at $t = 25$ h.

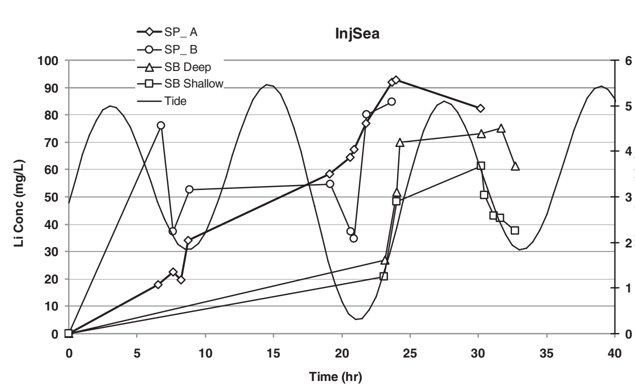

Figure 5. Variation of the concentration at various vertical locations at InjSea (Figures 1, 2, and 5), which is 2.5 m seaward of the injection well. The depth of each SPs and SBs is reported in Figure 2.

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.

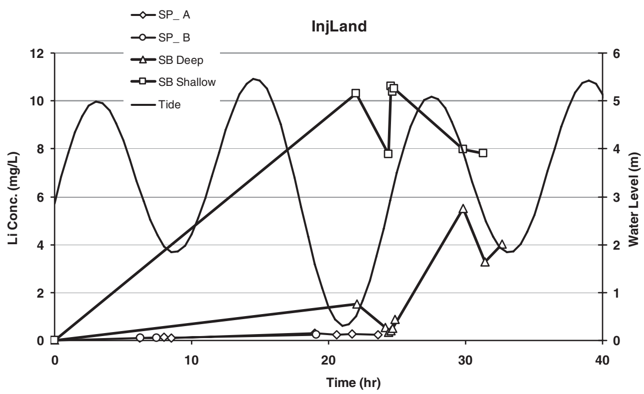

Figure 6. Variation of the concentration at various vertical locations at InjLand (Figures 1, 2, and 5), which is 1.6 m landward of the injection well. The depth of each SPs and SBs is reported in Figure 2.

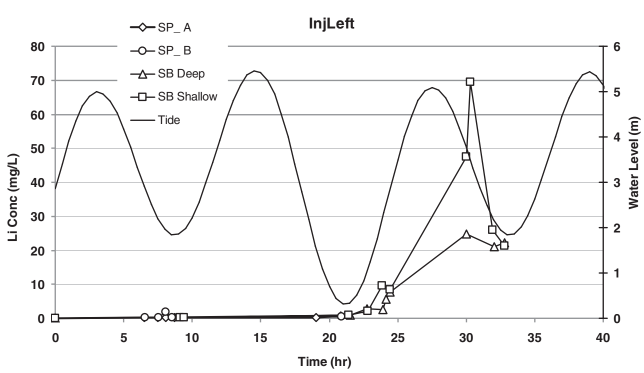

Figure 7. Variation of the concentration at various vertical locations at InjLeft (Figures 1, 2, and 5), which is 1.7 m left (looking landward) of the injection well. The depth of each SPs and SBs is reported in Figure 2.

Figure 7 reports the variation of the tracer at well InjLeft as function of time. At t = 9.0 h, 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 be 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 h. The concentration dropped later, most likely due to the decrease in concentration from around 90 to 0.0 mg/L of lithium. Therefore, one concludes that the travel time to Well InjLeft is between 20 and 30 h, which gives a traveling speed of approximately 2.0 m/d.

Figure 8 reports the variation of the tracer at well InjRight as function of time. At t = 9.0 h, 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 h, 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 $t \approx 30$ h. The decrease that followed is due to the change of the injection concentration from 90 to 0.0 mg/L at t = 25 h. Figure 8 suggests that the traveling speed of the plume in the longshore right direction is around 1.5 m/20 h = 1.8 m/d.

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 h and 21 h based on the concentration at the four observation wells InjSea, InjLand, InjLeft, and InjRight and at the injection well. 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 concentrations 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% of the maximum would overestimate the spread of the plume.

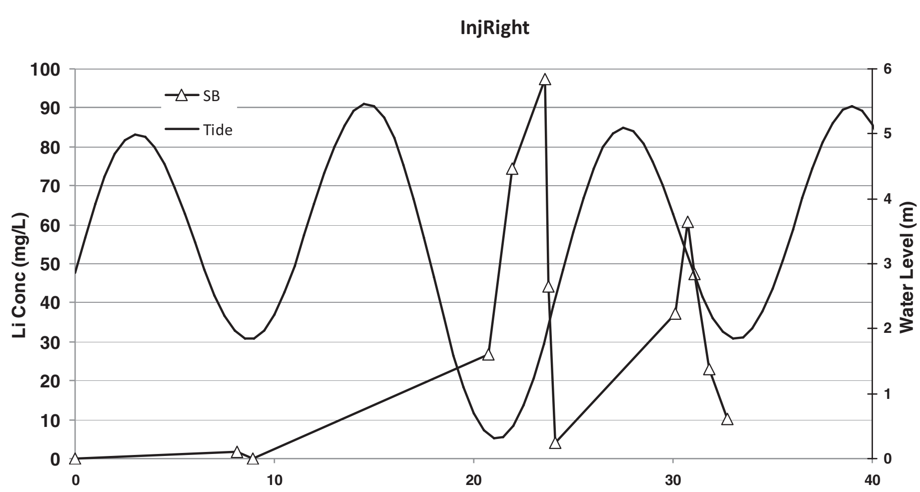

Figure 8. Variation of the concentration at various vertical locations at InjRight (Figures 1, 2, and 5), which is 1.5 m right (looking landward) of the injection well. Only a SB placed at the depth of 0.52 m was used.

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. In addition, if one were to inject dissolved oxygen in the water to deliver to the oil, sufficient concentration of oxygen would reach the observation wells. Nothing that around 2.0 to 3.0 mg/L of oxygen 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. Figure 9 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 h). 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 microchannels. 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 brings 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, 2009b). In the tracer experiment, we noted that samples taken prior to injection at the monitoring wells were clean but those taken 7 h later contained sheens of oil, which suggests that new pathways through the oil layer are activated.

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 196 kPa. As it is highly unlikely for the water to go upward through the 10-cm-thick bentonite layer (Figure S4, 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 microchannels 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 microchannels 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 3.

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

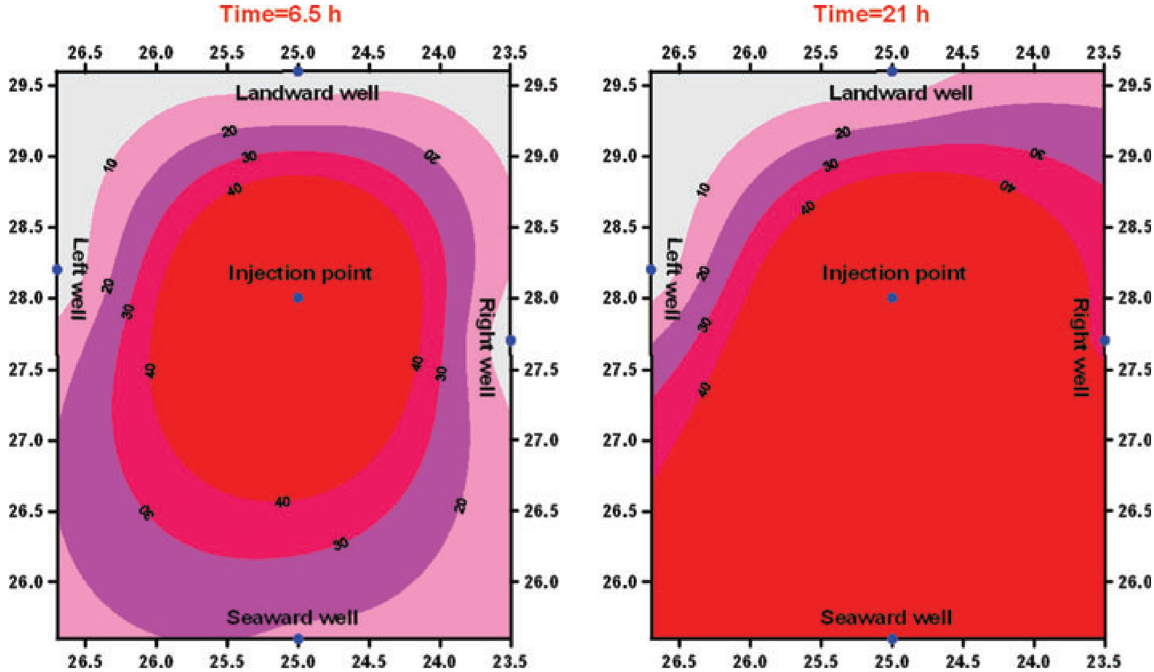

Figure 9. Empirical contours of lithium concentration as percentage of the maximum at two different times, 6.5 and 21 h. The edge of the plume was delineated where the concentration is 10% of the maximum. The figure indicates that at t = 21 h, the injected plume occupies an approximate area of 12 m^2 (4.0 m cross shore × 3.0 m along shore).

and Bragg 2009a, 2009b) for the beaches of Prince William Sound, then failure would have occurred at much lower pressure, say 5 m.

Li and Boufadel (2010) found that the hydraulic conductivity (K) of the beach is 1.0E-2 m/s for upper layer and 5E-5 m/s for lower layer. From our tracer study the tracer traveled with speed of 1.16E-4 m/s and 2E-5 m/s seaside and other sides, respectively. The seaside travel speed due to injection is faster than the previous study. One can see from these values that the lower layer permeability has significant effect on tracer transport than upper layer. To understand the effect of the injection on groundwater flow, one can easily calculate the Darcy flux with and without the injection. The hydraulic gradient ($\Delta H/L$) of the beach is fluctuated with tide. During high tide, the hydraulic gradient (HG) of the beach gets low value and vice versa during low tide. Without injection, HG ranges between 0 (during high tide) and 0.15 (during low tide) seaward of the injection point. With injection, the small flow rate values have minimal changes on HG, but during high flow rate injection, HG varies between 0.38 (during high tide) and 0.63 (during low tide). Therefore, the maximum Darcy flux ($q = -K(\Delta H/L)$) will be 7.3E-5 m/s and 7.5E-6 m/s with and without the injection, respectively. The flux is relatively high during the injection period, but it is still safe because the maximum pressure due to the injection (88 kPa) is way lower than the blowout pressure (196 kPa). This enhancement of the hydraulic conveyance is another indicator that the HPI of nutrients and dissolved oxygen would likely enhance biodegradation of oil.

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 chemicals. Considering that the oil layer on this beach is around 30 cm below the surface (see Figure S3), 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 tracer concentration fluctuated with tide, especially at the shallow sensors. However, the concentration increased with time during injection. 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 h. 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 bioremediation via injection of chemicals 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, two to three injection wells on this beach would ensure complete spatial coverage by the injected chemicals (dissolved oxygen and nutrients) for successful bioremediation.

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Supporting Information

The following supporting information is available for this article:

Figure S1. 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).

Figure S2. The sampling box (SB) used for water sampling. (a) A vertical cross section of the SB and (b) a horizontal cross section at mid height.

Figure S3. Picture of the pit for the injection well facing landward. Note the oil layer at the depth of 20 to 30 cm.

Figure S4. The left panel shows the BW. The right panel shows the injection well along with surrounding wells (the sea is to the left in this figure).

Figure S5. The tanks used for injection, each has a boiler drain type valve, with a ball valve controlling the flow (not visible).

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