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Laboratory model of a petroleum migration barrier in Arctic Alaska

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Abstract

Child's Pad is a gravel construction pad that was contaminated with petroleum during oil-field service operations in Deadhorse, AK. As part of a remedial action plan, a buffer strip of uncontaminated sandy gravel was placed along certain sections of the pad boundary. A peroxygen formulation manufactured by Regenesis©, sold as Oxygen Release Compound (ORC®), was placed in the buffer strips. The ORC was intended to supply oxygen to aerobic microorganisms capable of degrading petroleum. Tests were conducted in a 1/2 scale laboratory cell to determine the oxygen release characteristics of the ORC when subjected to expected subsurface flow rates of up to 0.02 l/s (6.9 m/day). In laboratory tests, a zone of enhanced oxygen concentration was formed down-gradient from the ORC socks. Only during periods when the flow rate was less than 0.01–0.015 l/s (3.5–5.2 m/day) was ORC-oxygen observed at monitoring points up-gradient or directly cross-gradient of the ORC. Conclusions from the laboratory study were that ORC may provide an aerobic zone in the Child's Pad barrier as far as 1 m directly down-gradient of the sock during periods of high flows (6.9 m/day).

Keywords: Bioremediation; Petroleum; Biological barrier; Oxygen

1. Introduction

Child's Pad is a gravel pad covering approximately 0.03 km^2 in Deadhorse, AK (see Fig. 1). The pad consists of sandy gravel 1–2 m thick overlying frozen tundra.

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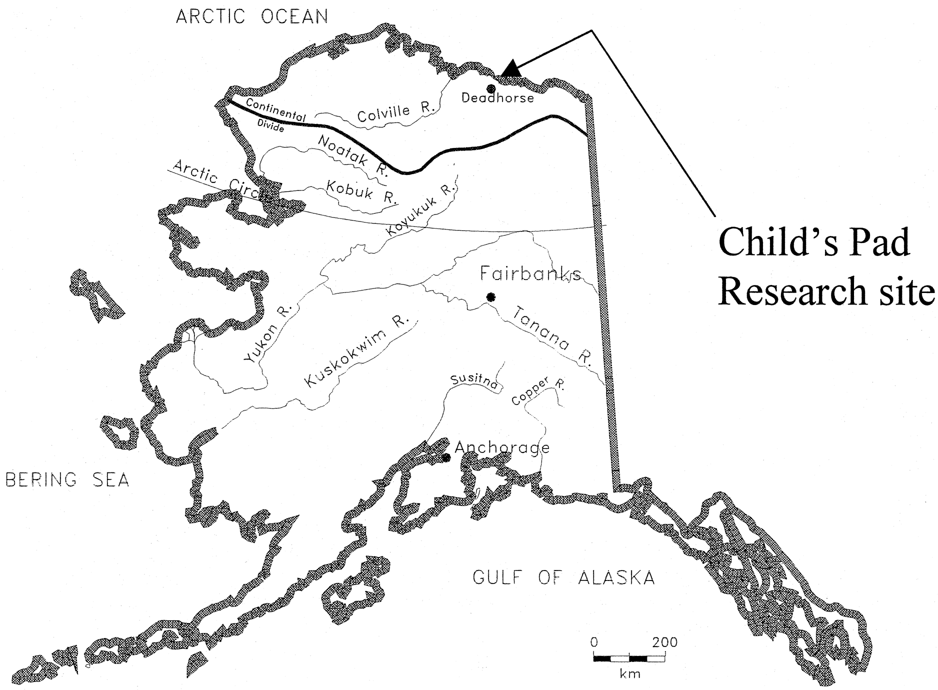

Fig. 1. Map of Alaska showing the location of Child's Pad, AK.

Permafrost extends from approximately 1 m below the gravel surface to over 500 m below ground. Beginning in June, the top 1 m of the pad thaws allowing a 'perched water table' to form in the unfrozen gravel.

Soil on Child's Pad is presently being land-farmed to treat gasoline and diesel fuel contamination. To prevent migration of petroleum contaminants, two migration barriers were designed for portions of the pad border. Migration barriers consist of a strip of uncontaminated sandy gravel separating the pad from the adjacent tundra. The first barrier is 3.1 m wide, 81 m long and 0.6 m deep. One hundred ORC® socks (0.3 m tall and 0.15 m in diameter) were placed upright in the barrier 0.3 m below grade. Two rows of socks were placed in a staggered arrangement (see Fig. 2). The second barrier is 3.1

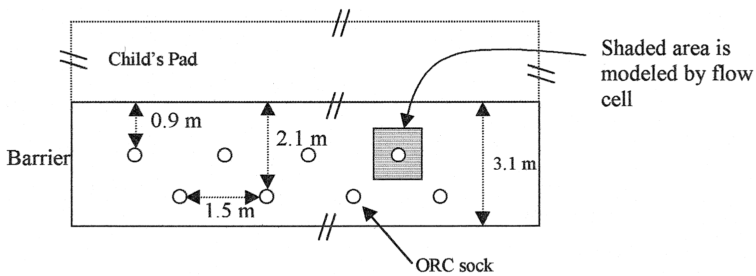

Fig. 2. Top view of a Child's Pad barrier section.

m wide, 91 m long, 0.6 m deep and contains 120 ORC socks in the same staggered arrangement of two rows.

The research described herein was designed to evaluate the directional movement of oxygen released from an ORC sock into the barrier. Tests were conducted using a 1/2 scale model of a section in the actual barrier. The area the model was designed to simulate is shaded in Fig. 2. The depth of the gravel in the flow cell and the geometric dimensions of the sock placed in the flow cell were 0.5 times the size of those in the field.

2. Background

2.1. Solid phase oxygen

Solid phase oxygen (SPO) refers to a suite of solid compounds with the potential to release oxygen when in contact with moist soil. A number of companies manufacture a product containing SPO in the form of a simple peroxide or peroxyhydrate for use in bioremediation. The SPO used in this research was a formulation of magnesium peroxide (MgO_2) and phosphate ions produced in a patented process under the trade name ORC (Regenesis). The stoichiometric conversion of a metal (M) peroxide to oxygen and a metal hydroxide is generally thought to occur by two reactions [1]:

$$2MO_2 + 4H_2O \rightarrow 2H_2O_2 + 2M(OH)_2 \quad (1)$$

$$2H_2O_2 + \text{catalyst} \rightarrow 2H_2O + O_2 + \text{catalyst} \quad (2)$$

Farone [2] proposed that for magnesium peroxide, however, the conversion occurs in the single reaction:

$$2MgO_2 + 2H_2O \leftrightarrow O_2 + 2Mg(OH)_2 \quad (3)$$

Although preliminary research on peroxides and peroxyhydrates found that oxygen was released too quickly to be of practical use in bioremediation [3], the divalent metal peroxides were found to be more stable. In addition, treatment of peroxides with phosphoric acid or phosphate salts has been used to slow the release of oxygen [4]. Phosphate ions are used in a patented intercalation process to produce ORC [5].

2.2. Gravel pad hydrology

On Alaska's North Slope, the ground is frozen year-round with the exception of a shallow surface layer (< 1 m) that thaws in the summer. If the surface of the tundra is warmed, the frozen ground melts and the surface becomes unstable. All North Slope construction, therefore, occurs on gravel pads approximately 1–2 m thick, built directly on the tundra. The gravel pad insulates the frozen ground from the heat of buildings. In abandoned gravel pads, or in the exposed areas of active-use pads, permafrost will inundate the pad from the bottom. Precipitation then freezes in the interior of the pad forming an 'ice-island' and a hydraulic high at the center of the pad [6]. Water applied to gravel pads will flow away from the center of the pad or into the thawed depressions left by buildings. Unless removed, contamination in the gravel will gradually leach into the surrounding tundra.

3. Materials and methods

3.1. Cell construction

The flow cell was constructed of 0.6 cm thick Plexiglas and supported by a wood frame. The seams of the Plexiglas were fused with acrylic cement and fastened with small metal screws. A bead of silicon was applied along the interior seams to prevent water or air from escaping. Three large access ports were cut near the center of the removable Plexiglas cover. The access ports also had covers that could be removed and resealed. Fig. 3 is a schematic diagram of the flow cell. Two interior baffle walls were constructed to create inlet and exit chambers. The baffle walls were constructed of 0.6 cm perforated Plexiglas sheets. Cheesecloth and wire screens were placed over the baffle walls to restrict movement of fine-grained materials. Water was introduced into the cell through a threaded nozzle in the bottom of an entry chamber. Water was removed from the cell through a port in the bottom of the exit chamber. In order to prevent channeling of water in the flow cell, a 0.6 cm raised plastic grid was fused to all interior Plexiglas surfaces.

Contaminated, Child's Pad soil was placed in the flow cell to a depth of 0.3 m. The soil was sandy gravel with a diesel contamination of approximately 500 mg/kg. Just prior to the start of testing, a 1/2 scale ORC sock (0.08 m diameter × 0.15 m tall) was buried in the upright position in the center of the cell. The flow cell cover was then sealed and remained sealed until the end of testing.

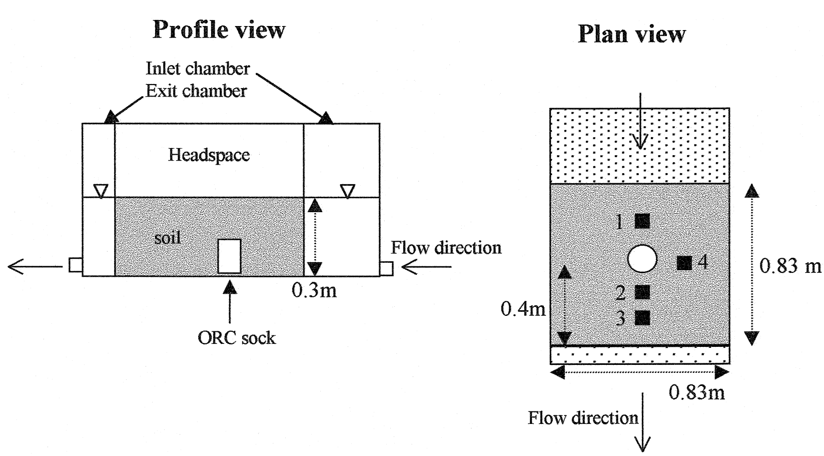

Fig. 3. Plan and profile views of the laboratory flow cell.

The hydraulic head across the flow cell was controlled by raising or lowering a 76 l equalization tank connected to the inlet chamber of the cell. De-ionized water flowed from the faucet to the top of the equalization tank and from the bottom of the tank to the flow cell. A constant head was created by allowing excess water from the faucet to drain through an overflow spout located near the top of the equalization tank. During testing, the water level inside the flow cell was adjusted so the entire 0.3 m of soil was saturated, leaving 0.3 m of sealed headspace above the soil.

3.2. Sampling

Fig. 3 shows the flow cell with the position of the ORC sock and the four sample locations. Water samples were removed through Tygon tubing installed in the soil and passing through sealed apertures in a sidewall of the flow cell. Sampling position #1 was located 0.27 m directly down-gradient from inlet baffle and 0.15 m directly up-gradient of the ORC sock. Sampling position #2 was located 0.15 m directly down-gradient of the ORC sock. Sampling position #3 was located 0.15 m down-gradient of position #2. Sampling position #4 was located 0.15 cm cross-gradient from the ORC sock. To draw the water samples, sampling tubes were siphoned with a large syringe. The samples were tested for dissolved oxygen using a YSI Model 5739 dissolved oxygen probe and meter. A gas phase oxygen sensor (Dataright) was mounted in the headspace of the flow cell.

3.3. Testing conditions

Three flow regimes were tested based on conditions that might be encountered in the field. A varying flow test served to evaluate the behavior of the ORC sock when subjected to rapidly changing flow rates, as might occur before, during and after precipitation events. A constant flow test was designed to simulate spring drainage when the snowmelt creates a constant flow through the barrier for a period of days. A static test was intended to simulate the condition during which the ORC sock is submerged and no flow passes through the barrier. This condition occurs after snowmelt when the tundra surrounding the pad is submerged.

During the varying, constant and static tests, the concentration of dissolved oxygen was measured at each monitoring point over periods of 10, 5 and 6 days, respectively. The concentration of dissolved oxygen (DO) that would be expected from microbial respiration and inorganic reactions was based on a measured oxygen uptake rate (OUR). To obtain the OUR, soil samples were taken from the four sampling points in the flow cell, weighed, and diluted with 250 ml of distilled water. A YSI probe was placed into the slurry and the flask was filled to the top with distilled water and sealed with parafilm. A magnetic stir plate provided mixing. Dissolved oxygen readings were taken periodically over two or three days to obtain an average OUR. The expected DO profile due to microbial respiration and inorganic reactions (without the influence of an ORC sock) was termed, ‘theoretical DO’.

The flow cell was operated at 22°C. The summer soil temperature at Child’s Pad may range from 22°C at the surface to 0°C 1 m below grade (i.e. at permafrost). A previous study was conducted to determine the effects of temperature on oxygen release from ORC in barrier soil [7]. The oxygen evolution rate from ORC was between 2 and 3 times lower at 7°C than at 21°C. Previous studies have shown that microbial activity also drops by 2–3 times for a similar drop in temperature [8].

The influent DO for the flow cell was generally between 5 and 6 mg/l. The DO of water passing through the barrier would likely be depleted in oxygen since the flow would have already passed through the microbially active pad. In the flow cell, semi-oxygenated influent conditions were maintained in order to observe both oxygen consumption and/or accumulation in the barrier soil.

4. Results

The average OUR for soil recovered from positions #1–#4 was 1 mg/kg wet soil/h. This OUR was used to calculate the theoretical DO at all positions in the flow cell for all tests.

During the varying flow test, the DO at position #1 was approximately 3.5 mg/l at the start of study (see Fig. 4). The measured DO exceeded the theoretical DO during periods when the flow rate was less than 0.015 l/s (5.2 m/d). As shown in Fig. 5, the measured DO at position #2 stayed between 3 and 6 mg/l throughout the test, always exceeding the theoretical DO. In contrast, the water reaching position #3 (see Fig. 6) retained very little of the DO present in the influent (i.e. theoretical DO). The measured DO, however, was consistently higher than the theoretical DO and never fell below 1

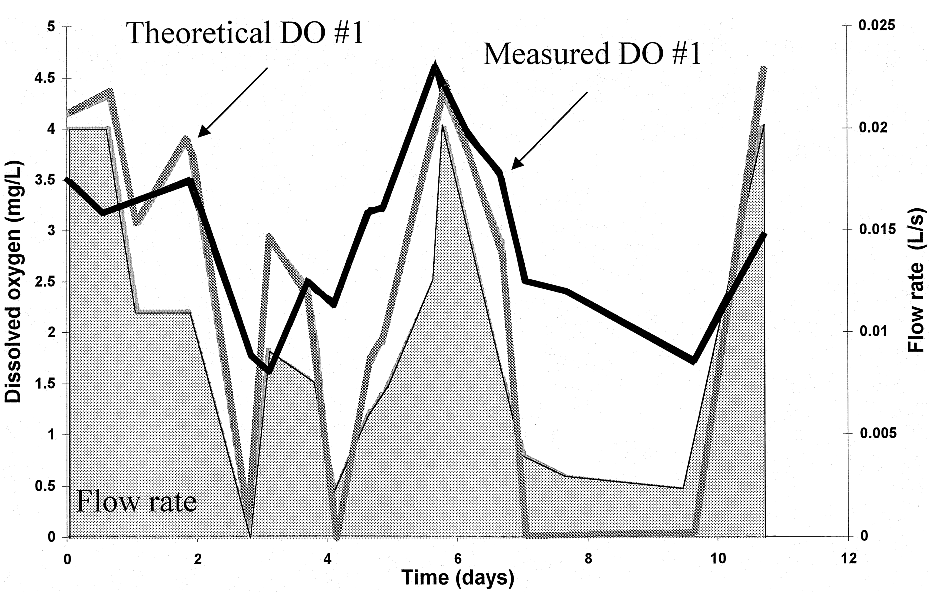

Fig. 4. Dissolved oxygen and flow profiles in the flow cell at position #1.

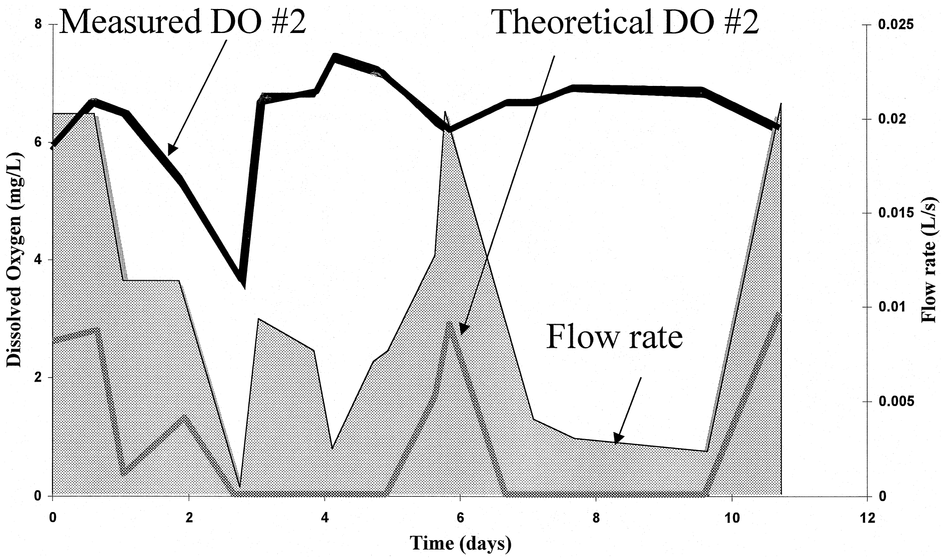

Fig. 5. Dissolved oxygen and flow profiles in the flow cell at position #2.

mg/l. The measured DO at position #4 (see Fig. 7) mirrored those measured at position #1.

During the 5-day constant flow test, the DO at positions #2 and #3 were 2 mg/l above the theoretical DO while the DO at positions #1 and #4 were at or slightly below the theoretical DO. During the 6-day static test, the DO dropped, but was maintained at

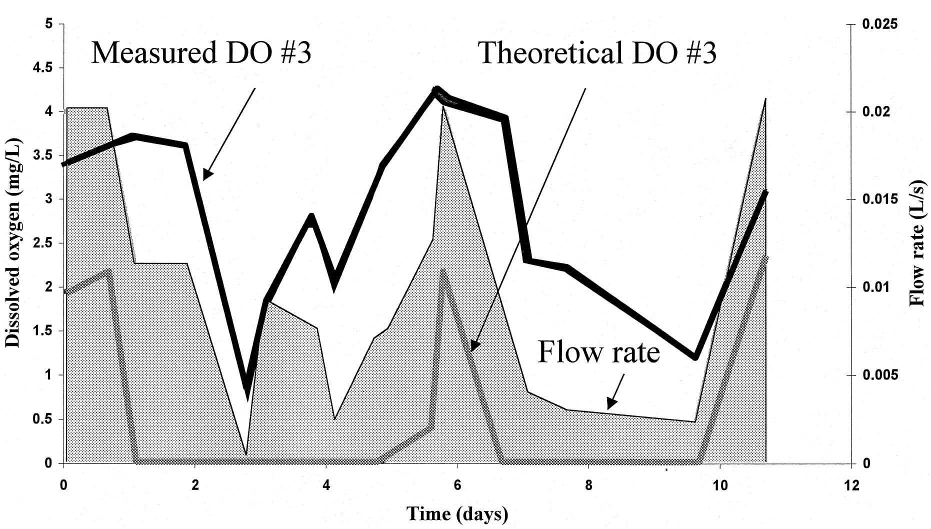

Fig. 6. Dissolved oxygen and flow profiles in the flow cell at position #3.

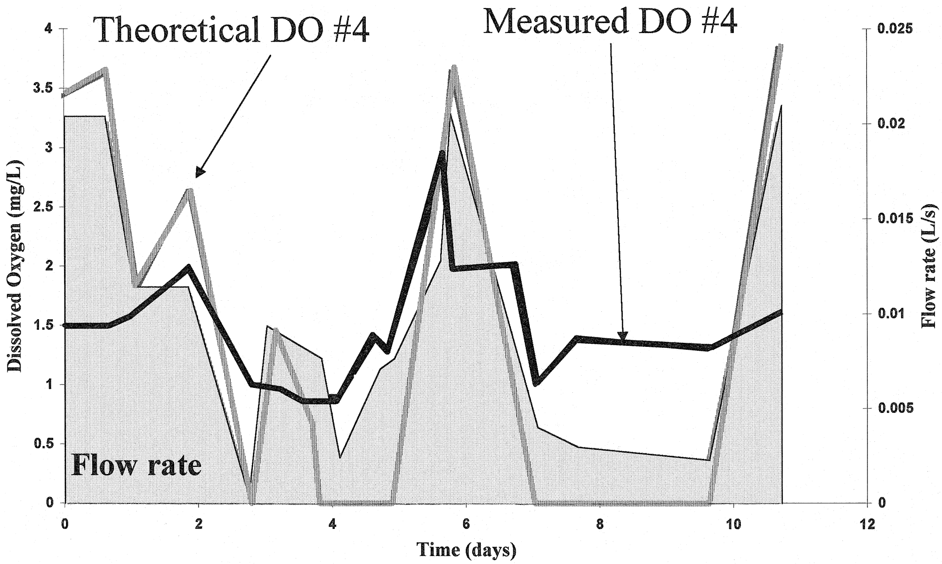

Fig. 7. Dissolved oxygen and flow profiles in the flow cell at position #4.

1 mg/l or greater at all positions for the duration of the test. The theoretical DO was zero within one day of the static test.

5. Discussion

Oxygen can be transported throughout the flow cell by advection and/or dispersion. Advection is the transport of a material by a fluid. Dispersion occurs by two processes, molecular diffusion and mechanical dispersion. Mechanical dispersion is a function of the dispersivity of the porous medium and the flow velocity, but is unrelated to concentration gradients. In contrast, molecular diffusion is governed only by the concentration gradient. If the mean velocity of the fluid is high, dispersion is dominated by mechanical dispersion. Molecular diffusion is only dominant in stagnant systems where advection and mechanical dispersion are absent. The ORC sock could influence the DO at positions #1 and #4 only if molecular diffusion dominated oxygen movement. Since positions #2 and #3 were directly down-gradient from the ORC sock, the DO at each position could be effected by ORC-oxygen transported by advection, mechanical dispersion and molecular diffusion.

The observations at position #1 suggest that at flows below 0.01–0.015 l/s (3.5–5.2 m/d), the ORC sock acted to increase the DO at position #1. Under low or no flow conditions, oxygen could be driven in the direction of position #1 from the ORC sock by diffusion only. At high flow rates, however, advective transport should have dominated oxygen movement and no effect from the ORC sock was expected or measured. At times when the sock should have had no effect on the measured DO at position #1, the measured DO and theoretical DO should have been equal. The fact that the measured DO was below the theoretical DO for flow rates above 0.01–0.015 l/s illustrates that the OUR was slightly higher than measured in the oxygen uptake tests.

The ORC sock had an obvious impact on the DO at position #2 at all flow rates. Rapid changes in the flow rate were reflected by rapid changes in the theoretical DO, but not the measured DO. The inflation observed in the dissolved oxygen concentration resulted from the excess oxygen being supplied by the ORC sock. Since the oxygen could travel from the ORC sock to position #2 by advection, mechanical dispersion and molecular diffusion, the DO was under the influence of the ORC oxygen at all times. The only significant drop in measured DO occurred when the flow rate was reduced to zero.

At position #3, further from the ORC sock than position #2, the influence of the ORC sock was reduced, but still evident. As with position #2, the measured DO exceeded the theoretical DO at all times. The effect of the rapidly changing flow rates on measured DO were more evident at position #3 than position #2, however, particularly during periods when the flow rate fell below 0.01–0.015 l/s (3.5–5.2 m/d). This probably resulted from the fact that position #3 was twice as far from the ORC sock as position #2. The influence of the sock was expected to be greatest at position #3 when advection dominated since water transports oxygen directly down-gradient of the sock.

During periods of low or no flow, molecular diffusion causes oxygen to travel equally in all directions. This is confirmed by the fact that the DO at position #4 was only above the theoretical DO when flow rates were less than 0.01–0.015 l/s (3.5–5.2 m/d). As expected, the same result was observed for position #1. The theoretical and measured DO were less at position #4 than at position #1 due to the slightly longer flow path to position #4 and greater exposure to microbial and inorganic oxygen consumption. In all other respects the curves representing DO at positions #1 and #4 behaved the same.

In order to confirm the observation that no oxygen reached positions #1 or #4 during flow periods greater than 0.015 l/s (5.2 m/d), a test was conducted during which the flow rate was held constant 0.02 l/s (6.9 m/d) for 5 days. The DO at positions #1 and #4 were below the theoretical DO during the entire period while the DO at positions #2 and #3 was at least 2 mg/l greater than the theoretical DO. This result confirmed that at 0.02 l/s (6.9 m/d) no oxygen traveled up-gradient or cross-gradient from the ORC sock to positions #1 or #4 but oxygen from the ORC continuously impacted positions #2 and #3.

One additional test was conducted to confirm that molecular diffusion drove oxygen from the ORC sock to all positions when flow was below 0.01 l/s (3.5 m/d). At the end of the constant flow test, the flow was stopped. After allowing the flow cell to equilibrate for 3 h, measurements were recorded with no flow for six days. The theoretical DO dropped to 0 within one day while the measured DO remained above 1 mg/l at all positions for the six day test. This result indicated that oxygen from the ORC sock reached all subsurface monitoring points. Although no tests were conducted to prove that the oxygen reaching the subsurface was from the ORC sock and not the flow cell headspace, a gas phase oxygen sensor in the sealed reactor headspace recorded no measurable drop in oxygen concentration.

Based on the DO at position #2, the ORC sock produced enough oxygen to maintain a concentration of 2 to more than 6 mg/l greater than the theoretical DO. The contribution to the measured DO by the ORC sock at position #3 was consistently between 1 and 3 mg/l greater than the theoretical DO. If the DO evolved from the ORC sock were moved by advection alone, we would have expected the measured and theoretical DO differential to be the same at positions #2 and #3. Since the differential between the measured and theoretical DO was less at position #3 than at position #2, dispersion likely contributed to the movement of oxygen cross gradient in the flow cell.

It is generally accepted that 4–5 mg of oxygen are consumed per mg of petroleum consumed by microorganisms [9]. By contributing 2 to 6 mg/l of oxygen to the water crossing the barrier, the ORC sock contributes the potential to degrade approximately 1 mg/l of petroleum. The solubility of diesel fuel is 5 mg/l. Since the site does not contain free product, it is unlikely that the saturation concentration would be reached. As such, the concentration of oxygen produced by the ORC sock could be useful in this application.

Other studies have reported that addition of ORC in saturated soil resulted in increased concentrations of dissolved oxygen and enhanced biodegradation of dissolved contaminants [10–13]. Most other studies, however, were in situations where screened wells were filled with a series of ORC socks strung together. In these cases, a constant flow of groundwater passed through the socks. When comparing the Child's Pad research to other studies, it is important to take into consideration the unique conditions of a petroleum migration barrier in the Arctic. The Child's Pad barrier is a unique ORC application in that the entire thaw depth of the soil is little more than 500 cm. One sock placed upright occupies most of the thawed soil. The barrier soil is entirely frozen 9 months of the year, and in various stages of thaw the remaining 3 months. For example, in mid-July the ORC sock may be thawed at the top but still frozen at the bottom. In mid-September the sock is frozen at the top and thawed at the bottom. In addition, during the snow melt period before the ground thaws, surrounding tundra becomes ponded, creating saturated, static groundwater conditions. When the tundra drains, the barrier is subjected to far more rapid rates of 'groundwater' flow then those typically observed in aquifers. Following drainage, the barrier behaves like a typical vadose soil until the soil freezes for the winter.

6. Conclusions

Laboratory tests indicated that the ORC barrier would create an aerobic zone down gradient of the socks that may enhance microbial activity. Since no oxygen was observed directly cross-gradient from the sock, proper spacing of the socks and hydraulic control would be necessary to make an effective biological barrier. The oxygen uptake rate in the barrier soil was approximately 6 mg/l/m (at 0.02 l/s). Based on the OUR and flow rate of the laboratory set-up, the socks may provide aerobic conditions 0.5–1 m directly down-gradient of the ORC in the barrier at Child's Pad. This oxygenated zone is calculated for the space directly down-gradient of the ORC sock only.

Acknowledgements

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