

**Radial Movement of a Passively Released Gas from a Monitoring
Well**

by

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ABSTRACT

In order to preserve groundwater as a viable source of drinking water, remedial measures must be applied where appropriate. The application of the various remedial technologies is site and contaminant dependent. Differing geology, subsurface soil, groundwater geochemistry, type of contaminant present, cost and even accessibility to the site are all considerations when selecting an appropriate remedial system. At many sites oxygen is a limiting factor for aerobic degradation of many organic compounds like methyl tert butyl ether (MTBE) and hydrocarbons found in diesel and fuel oil, etc. (Nyer et al, 2002).

Mechanisms limiting the success of getting the oxygen out of the passive release well include:

- Slow chemical diffusion of oxygen in water;
- Limited cross section of the groundwater flowing into the well and advecting oxygenated water back into the aquifer; and
- Generally weak transverse dispersion, both horizontal and vertical, during subsequent advection of the oxygenated water in the porous media.

These issues must be recognized even in the design of a passive release well remediation system. For example, a typical remedial objective is to deliver dissolved oxygen across the width and vertical extent of a contaminant zone in an aquifer. The width of the oxygen plume around the injection well defines how many oxygen-release wells are required to create a curtain of oxygen. Cost-effective design dictates fewer wells, while effective coverage may dictate more wells placed closer together. Thus, understanding the transverse width over which significant oxygen is passively released to the aquifer (the “radius of influence”) is a critical design parameter and the focus of this thesis. Due to the difficulty in getting a passively released dissolved oxygen plume to transversely encompass the total width of a contaminant plume, other more efficient means of introducing oxygen into the subsurface are required. Injecting amended water directly into a release well would increase the transverse distance in which dissolved oxygen would spread.

A series of experiments were conducted at CFB Borden to assess the efficacy of an oxygen releasing technology called the iSOC™. The experiments were all conducted in the same manner, by connecting a tank of oxygen to the iSOC™ unit, which then was placed in a release well and allowed to run in experiment 1 for 103 days, experiment 2 for 132 days and experiment 3 for 29 days.

Dissolved oxygen concentrations were measured at varying time intervals throughout each experiment using an Orion dissolved oxygen probe. Results of each of the three experiments were very similar in that dissolved oxygen was only detected in a very narrow plume (10 cm to 25 cm in width) within 1 m of the release well.

The presence of BTEX, BOD and COD within the groundwater and soil at the site were investigated to assess if presented a significant enough sink for the oxygen and thereby limiting the transverse growth of the dissolved oxygen plume. Groundwater results indicated that while dissolved oxygen was utilized for BTEX degradation and to overcome the natural oxygen demand (both BOD and COD) at the site, the amount of oxygen released into the aquifer would have satisfied both of these processes. The COD of the soil at the site presented a higher oxygen demand than the groundwater and presented a greater limiting factor to the transverse growth of the oxygen plume.

By releasing oxygen passively with the iSOC™ only a small transverse portion of the Borden aquifer was likely influenced. This limitation has been noted in general for passive release technologies (Wilson & Mackay, 1995). While the iSOC™ technology develops very high oxygen levels in the groundwater in the release well, it does not overcome the hydrogeological constraint of limited transverse dispersion. Thus, a high oxygen concentration is delivered to a very narrow segment of the aquifer.

Overall, transverse dispersion has a minimal impact on a passively release oxygen plume, particularly in close proximity to the release well, but once the plume has migrated a distance away from the release well the effect of transverse dispersion increases. The oxygen demand of an aquifer can also limit the effect of transverse and longitudinal dispersion. If a site has a high chemical or biological oxygen demand the released gas will be consumed before dispersion can have an effect on the plume. By injecting nutrient rich water into a release well the water will forcibly overcome any influence transverse dispersion will have in and around a release well, thereby relying on longitudinal dispersion to create a larger area for contaminant degradation to occur.

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DEDICATION

This thesis is dedicated to my husband Jeff and my Family, whose love, support and encouragement was boundless.

TABLE OF CONTENTS

LIST OF TABLES.....	x
LIST OF FIGURES.....	xi
1.0 Introduction and Background	1
1.1 Remedial Technologies	1
1.1.2 Passive Release Technologies.....	1
1.2 iSOC™	3
2.0 Release Well Zone of Influence	6
2.1 Effect of Flow through the Well Screen	6
2.2 Effect of Dispersion	7
2.3 Well Spacing.....	8
3.0 Field Experiments	12
3.1 Summary of Experiments	12
3.2 Site Installations	13
3.3 Analysis and Methodology	16
3.3.1 SF ₆	16
3.3.2 Dissolved oxygen (DO)	17
3.3.3 Biological Oxygen Demand/Chemical Oxygen Demand.....	18
3.3.4 Total BTEX	18
3.3.5 Bromide.....	19
3.3.6 pH	19

3.3.7 Total Iron.....	19
3.3.8 Alkalinity.....	20
4.0 Field Experiment 1	21
4.1 Oxygen Results	21
4.2 Factors Effecting Release	23
4.2.1 COD Results	23
4.2.2 BOD and BTEX Results	25
4.2.3 Bromide Results.....	25
4.3 Findings of Experiment 1	26
5.0 Oxygen Release Field Experiment #2.....	27
5.1 SF ₆ Tracer Test	27
5.1.1 Operation.....	27
5.1.2 Findings.....	27
5.1.3 Discussion	29
5.2 Oxygen Release.....	29
5.2.1 Operation.....	29
5.2.2 Findings.....	30
5.2.3 Discussion	30
6.0 Oxygen Release Field Experiment 3	34
6.1 Findings.....	34
6.1.1 Oxygen Release.....	34

6.1.2 Effect of BTEX – Mass Balance.....	37
6.1.3 Alkalinity Changes.....	40
6.1.4 Iron	43
6.1.5 Findings of Experiment 3.....	44
6.2 Summary and Conclusions of Passive Release Field Trials.....	45
7.0 Injection of Oxygenated Water.....	47
7.1 Injection Experiment 1: Injection of 210L.....	48
7.1.1 SF ₆ Tracer Results.....	49
7.2 Injection Experiment 2: Injection of 600L.....	51
7.2.1 SF ₆ Tracer Results.....	52
7.3 Summary of Discussion of Injection Experiments.....	57
8.0 Modeling of Passive Release from a Well.....	59
8.1 Modeling simulations.....	59
8.1.1 Simulation 1 - Results	60
8.1.2 Simulation 2 - Results	63
8.1.3 Discussion	66
9.0 Summary and Conclusions	72
References.....	74
Appendices	74

LIST OF TABLES

Table 1. Dissolved gas concentrations (mg/L) with depth.....	4
Table 2 Maximum dissolved oxygen concentrations Experiment 1.....	23
Table 3 Oxygen required to overcome oxygen demand at Borden Field Site.....	24
Table 4 Calculations of Oxygen required to overcome soil COD for various plume sizes.....	24
Table 5 Potential sources of dissolved oxygen demand Experiment 1.....	25
Table 6 Average BTEX concentrations ($\mu\text{g/L}$) in row 1 and row 2.....	39
Table 7 Volumes of injected water based on different radii.....	48
Table 8 Assumptions for Simulation 1 and 2 using Hydrogeosphere.	59

LIST OF FIGURES

Figure 1. iSOC™ unit and cross section of microporous fibres	3
Figure 2. Groundwater flow in and out of a 5 cm diameter well screen	7
Figure 3. Natural hydraulic capture of an unpumped well at a steady state.	9
Figure 4 Modeling results of a released amendment through different well spacing configurations.	11
Figure 5 API Gasoline Spill site location in GMT gate.....	13
Figure 6 iSOC™ Oxygen Release Well Layout for Experiment 1&2.....	14
Figure 7 Site Layout Experiment 3.....	15
Figure 8 Cross section of release site along groundwater flow.	16
Figure 9 Maximum dissolved oxygen concentrations (mg/L) Experiment 1.....	22
Figure 10 Borehole dilution tests.....	26
Figure 11 Distribution of SF ₆ (µg/L) on Day 17 of the SF ₆ tracer test.....	28
Figure 12 Plan view of DO concentrations in iSOC™ Experiment 2.....	32
Figure 13 Cross Section of dissolved oxygen concentrations	33
Figure 14 Maximum dissolved oxygen concentrations, day 29, Experiment 3.	35
Figure 14 (continued) Maximum dissolved oxygen concentrations, day 29, Experiment 3.	36
Figure 14 (continued) Dissolved oxygen concentrations, day 29, Experiment 3.....	37
Figure 15 Plan View of maximum BTEX concentrations.....	38
Figure 16 Maximum BTEX concentrations (µg/L) from Experiment 3.	40
Figure 17 Maximum alkalinity concentrations (mg/L) from Experiment 3.	41
Figure 18 Maximum pH results from Experiment 3.....	42

Figure 19. Plot of Alkalinity and BTEX concentrations from Experiment 3.....	43
Figure 20 Total iron results from Experiment 3.....	44
Figure 21 Radi of different volumes of injected water.....	47
Figure 22 SF ₆ results of 210 L injection.....	50
Figure 22 (continued) SF ₆ results of 210 L injection.....	51
Figure 23 Maximum SF ₆ Tracer Results for the 600L injection.....	53
Figure 23 (continued) Maximum SF ₆ Tracer Results for the 600L injection.....	54
Figure 24 Maximum dissolved oxygen results for the 600 L injection.....	56
Figure 24 (continued) Maximum dissolved oxygen results for the 600 L injection.....	57
Figure 25 Simulation 1 results, with no decay.....	62
Figure 26 Simulation 2 results, with decay.....	65
Figure 27 Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 1 (no decay).....	67
Figure 27 (continued) Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 1 (no decay).....	68
Figure 28. Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 2, with decay.....	69
Figure 28 (continued) Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 2, with decay.....	70
Figure 29 Maximum transverse distance between release wells, based on >10 mg/L dissolved oxygen boundary.....	71

1.0 Introduction and Background

A series of experiments were conducted to evaluate the radial movement of a passively released gas as it migrates out of a well and to observe the maximum horizontal width of the resulting plume of dissolved gas within a few metres of the release well. The experiments were conducted in an unconfined, rather homogeneous sand aquifer at the University of Waterloo's research site on Canadian Forces Base Borden. Modeling was also completed to determine the effect transverse dispersion has on a plume within a few meters of the release well and the role oxygen demand has on the transverse width of a released oxygen plume.

1.1 Remedial Technologies

In many parts of the world groundwater is the only source for drinking water, household and industrial use. In many places groundwater is becoming unusable as a drinking water source due to long-term contamination from industry, agricultural practices and overuse (Bayer and Finkel, 2006). In order to preserve groundwater as a viable source of drinking water, remedial measures must be applied where appropriate. The application of the various remedial technologies is site and contaminant dependent. Differing geology, subsurface soil, groundwater geochemistry, type of contaminant present, cost and even accessibility to the site are all considerations when selecting an appropriate remedial system.

Some of the more common types of groundwater remedial technologies are pump and treat systems (P&T) (Bayer and Finkel, 2006), permeable reactive barriers (PRB) (Blowes et al, 2000), monitored natural attenuation (MNA) (Wiedemeier et al, 1999), air sparging (Johnson et al, 1993), and passive in situ bioremediation (Chapelle, 1999) (van Cauwenberghe and Roote, 1998). Each technology has its benefits but due to differing hydrogeologic and geochemical conditions at a site, some technologies may be more appropriate and effective than others. The remedial technology should be selected on a site by site basis.

1.1.2 Passive Release Technologies

Technologies deemed passive are systems which, once installed, involve no active work (i.e. pumping) (Bayer and Finkel, 2006). Typically, an additive is passively released and allowed to move with the natural groundwater gradient. Once the contaminated groundwater comes into contact with the additive a biological or chemical reaction occurs, resulting in at least reduced concentrations of the contaminant. These passive technologies typically provide the factor (electron

acceptor, nutrient, etc.) which is lacking in the subsurface system and is a requirement in order to degrade a contaminant. At many sites oxygen is a limiting factor for aerobic degradation of many organic compounds like methyl tert butyl ether (MTBE) and hydrocarbons found in diesel and fuel oil, etc. (Nyer et al, 2002).

There are many in situ technologies like Oxygen Releasing Compound™ (ORC), Waterloo Emitter™ and iSOC™ available which passively introduce dissolved oxygen into the aquifer. ORC is a proprietary formulation of magnesium peroxide (MgO₂) (Bianchi-Mosquera et al. 1994), and is supplied in an inert filter sock containing approximately a 50:50 mixture of ORC and #90 silica sand (Chapman et al. 1997). The socks are lowered into a well and a chemical reaction between the ORC and groundwater releases oxygen upon contact (Bianchi-Mosquera et al. 1994). Technologies like the Waterloo Emitter™ and iSOC™ are units which are connected to gas canisters and are inserted into wells. They rely upon diffusion of oxygen gas across a permeable membrane to release dissolved oxygen into the groundwater (Wilson and Mackay, 2002) (www.isoc.com). Each technology is able to introduce varying amounts of oxygen from approximately 16 – 25 mg/L (ORC and the Waterloo Emitter™) (Chapman et al 1997 and Wilson and Mackay, 2002) to concentrations greater than 45 mg/L (iSOC™) (www.isoc.com).

When using oxygen addition as a part of a remediation system a number of issues need to be considered. As Nyer (2003) points out: “We have found that getting the oxygenated water out of the well and into the aquifer is probably the controlling factor in using oxygen as part of your remediation plans.”

Mechanisms limiting the success of getting the oxygen out of the passive release well include:

- Slow chemical diffusion of oxygen in water;
- Limited cross section of the groundwater flowing into the well and advecting oxygenated water back into the aquifer; and
- Generally weak transverse dispersion, both horizontal and vertical, during subsequent advection of the oxygenated water in the porous media.

These issues must be recognized even in the design of a passive release well remediation system. For example, a typical remedial objective is to deliver dissolved oxygen across the width and

vertical extent of a contaminant zone in an aquifer. The width of the oxygen plume around the injection well defines how many oxygen-release wells are required to create a curtain of oxygen. Cost-effective design dictates fewer wells, while effective coverage may dictate more wells placed closer together. Thus, understanding the transverse width over which significant oxygen is passively released to the aquifer (the “radius of influence”) is a critical design parameter and the focus of this thesis. Due to the difficulty in getting a passively released dissolved oxygen plume to transversely encompass the total width of a contaminant plume, other more efficient means of introducing oxygen into the subsurface are required. Injecting amended water directly into a release well would increase the transverse distance in which dissolved oxygen would spread.

1.2 iSOC™

A series of experiments were conducted at CFB Borden to determine efficacy of a passive release device (iSOC™), the specific purpose of the experiment is to determine the radial dispersion of oxygen from an injection well when the oxygen is delivered by a novel iSOC™ system.

The iSOC™ is a passive release technology created by inVentures Technologies Inc. The unit infuses high concentrations of dissolved gases into liquids in a bubble-less manner (Figure 1), this is accomplished by maintaining a gas pressure lower than the surrounding liquid pressure.

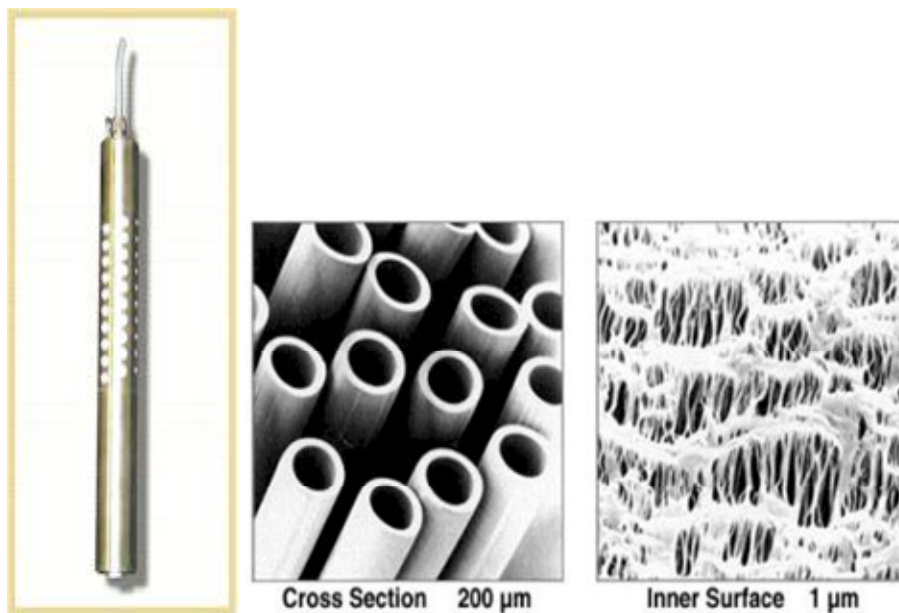


Figure 1. iSOC™ unit and cross section of microporous fibres

(www.isocinfo.com).

The technology is based on the mass transfer of a gas through a hydrophobic micro-porous hollow fibre to the surrounding liquid (Figure 1). The microporous fibres provide a large interfacial area (~ 7000 m²/m³) for gas transfer. The amount of dissolved gas released into the groundwater is dependent upon Henry's Law whereby the weight of any gas that will dissolve in a given volume of liquid, at a constant temperature, is directly proportional to the pressure that the gas exerts above the liquid (www.isocinfo.com). Laboratory trials completed by inVentures indicate that, with greater depth (greater confining hydrostatic pressure), a higher concentration of dissolved gas will be released into the water. A number of different dissolved gases can be used with the iSOC™, depending on the remedial system requirements. Table 1 illustrates the potential dissolved gas concentrations with depth for oxygen, methane, propane, ethane and hydrogen.

Gas Type	Water Column Depth in Meters				
	1.5	3	4.5	6	15
Oxygen	42	55	62	69	11
Methane	22	30	33	37	59
Propane	66	88	99	110	175
Hydrogen	2	2	3	3	5
Ethane	57	75	85	95	150

Table 1. Dissolved gas concentrations (mg/L) with depth (www.isocinfo.com).

The iSOC™ will delivery 41 mg/L of dissolved oxygen per atmosphere of head pressure on the unit (www.isocinfo.com). Standard atmospheric pressure at sea level is 101 kPa (14.7 psi) and decreases to approximately 69 kPa (10 psi) at 3048 m (10 000 ft) elevation. Based on this range of pressures, an iSOC™ with 6 m of water above it, will result with 69 mg/L of dissolved oxygen delivered to the well. This is dependent on an atmospheric pressure of 101 kPa plus the water head pressure of 108 kPa creating a total pressure of 206 kPa (www.isocinfo.com).

As the oxygen passively releases from the iSOC™ into the well water the groundwater within the well will become saturated with dissolved oxygen. As the oxygen saturated groundwater flows out of the well screen into the aquifer, the oxygen begins to exsolve out of solution to below saturated concentrations. The time required for the level of oxygen saturation to change from saturated to below solubility concentrations is its half-life. inVentures claims that it would require in a 3 m by 5 cm diameter column, 7 days for the saturated water to be reduced by one-half (www.isocinfo.com). A 7 day half-life is also confirmed by Berry-Sparks (1987) who conducted microcosm studies which monitored the usage of dissolved oxygen for BTEX degradation. The results indicated that within an approximately 7 day time period dissolved oxygen concentrations were reduced by half (Berry-Sparks, 1987).

A specialized head distributor is attached to a low flow regulator which controls the flow of gas from the pressurized tank to the iSOC™. A 6.35 mm polyurethane tubing connects the head distributor to the iSOC™, via barbed fittings. The outside casing is stainless steel and measures 4 cm wide and 38.1 cm long. The stainless steel casing houses 700 microporous microfibers with an internal flow controller set at a minimum of 15 cc/min (50 psi) but will adjust itself depending on the depth of the unit. Once the iSOC™ is connected to the pressurized tank it is ready to be lowered into the well for use. On average one iSOC™ unit will use approximately 28 L of oxygen per day (www.isocinfo.com).

2.0 Release Well Zone of Influence

Oxygen may be transferred from the well to the groundwater by two mechanisms:

- The high concentrations in the well establishes a concentration gradient into the groundwater, driving mass out by the process of diffusion; or
- Groundwater flowing through the well screen can become infused with dissolved oxygen from the iSOC™ unit and advection of the oxygenated water into the aquifer.

Unless groundwater flow is almost nil, the latter mechanism will dominate.

2.1 Effect of Flow through the Well Screen

In order to estimate the flux of oxygenated water out of the well screen, the flow in and out of a well screen must be understood. In the late 1960's scientists were conducting experiments on point and borehole dilution methods to determine direction of groundwater flow and filtration velocities (Drost et al., 1968 and Halevy et al., 1967). From reviewing other researchers work on the principles of dilution, Halevy et al. (1967) compiled all of the information available at that time concerning the use of borehole dilution to obtain direct measurements of filtration velocities, in aquifers under natural or induced hydraulic gradients. Due to the typical heterogeneity in the subsurface and in recharge, groundwater flow direction can shift. The addition of boreholes further distorts horizontal flow patterns of groundwater by creating a semi-impermeable barrier. Groundwater will still be able to flow through the well screen but at different rates than in the surrounding subsurface material. Other factors like changing velocities inside the well due to vertical flow, differences in head, density currents and flow due to artificial mixing in the borehole itself (Halevy et al. 1967) will have an effect on how groundwater enters and exits a well.

Drost et al. (1968) discusses laboratory experiments and computer modeling conducted to determine the groundwater velocity using the borehole dilution technique. Before this could be done accurately, understanding of the distortions caused by permeability differences in an aquifer, in the gravel pack surrounding a well and in the well screen were required. Through their investigations it was determined that horizontal flow through the well screen area, has a greater impact on how groundwater flows in and out of a well than vertical flow inside of the well screen. Therefore the width of the well screen determines the groundwater flow velocity in and out of the

well. It was determined that one could expect to groundwater to flow in and out of the well at twice its well screen diameter (Figure 2).

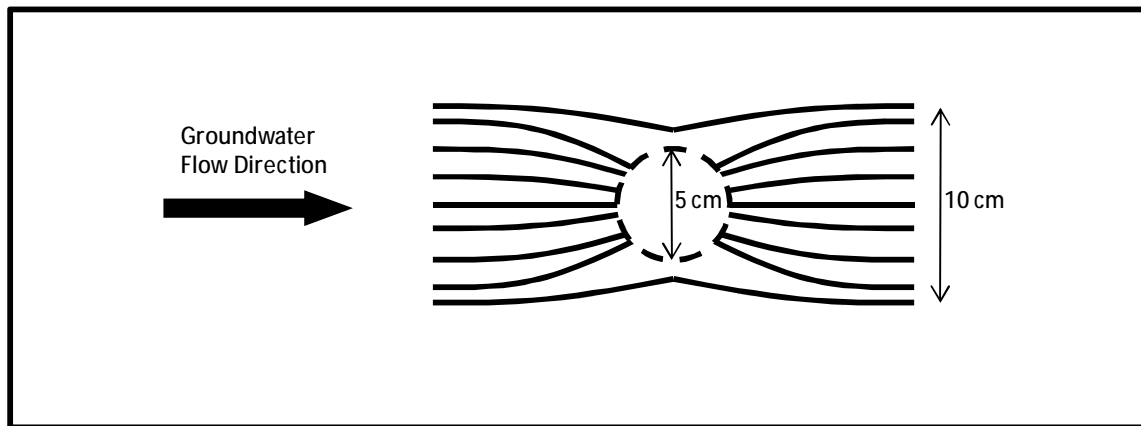


Figure 2. Groundwater flow in and out of a 5 cm diameter well screen

(after Drost et al, 1968).

By continuing with this theory one would expect to see the same pattern as groundwater saturated with oxygen exits a well screen. For example, a 5 cm dia. release well, theoretically would produce a 10 cm wide oxygen plume directly down gradient of the injection well (Figure 4). This has been observed in the field by Wilson et al (2002) in sandy aquifers at two sites using passive diffusive emitters to deliver oxygen. Once the oxygen laden groundwater has moved away from the screen, processes like transverse dispersion, biological or chemical oxygen utilization will affect the width and length of the oxygen plume.

2.2 Effect of Dispersion

One of the main conclusions in Halevy et al. (1967), Drost et al. (1968) and Wilson et al. was that dispersion is the main control of the transverse spreading of a plume and that advection is mainly longitudinally, whether it is from a contaminant spill, passive release or from a buried source. Dispersion is defined as the mixing of a solute and uncontaminated water as it flows through the subsurface porous media; becoming reduced in concentration with distance from the source (Fetter, 2001). The spreading of solute along the groundwater flow path is longitudinal dispersion; while the spreading of solute perpendicular to the groundwater flow path is transverse dispersion (Freeze and Cherry, 1979). In most cases it has been observed that longitudinal dispersion has a greater effect on the spatial distribution of a solute than transverse dispersion (Freeze and Cherry,

1979). Many tracer tests have been performed to observe the role dispersion has on the spreading of a tracer in heterogeneous porous media. Sauty (1980) observed that the heterogeneity of the soil media will have an effect on the transverse dispersivity. The greater the heterogeneity the greater the effect transverse dispersion will have on a plume within 1 m of the source well. The observation was reinforced by Gelhar (1979) who also observed that the effect of longitudinal dispersion increased with distance while the process of transverse dispersion had a reduced effect on the solute distribution.

A natural gradient tracer test was performed in the homogeneous aquifer at CFB Borden, to investigate how spilled solutes or contaminants released from buried sources would be spatially distributed and to be able to predict arrival times of hazardous contaminants (Sudicky et al 1983). A chloride tracer solution was injected into the aquifer in five injection wells and samples were collected from a monitoring network consisting of 69 multi-level bundles and 17 mini-piezometers, covering an area approximately 15 m long, 5 m wide and 5 m deep. Groundwater samples were collected over a 121 day period. The results indicated that the spatial distribution of the chloride plumes could be characterized as long and thin plumes. Much like what Sauty and Gelhar observed in their tracer tests, there was a distinct increase in longitudinal dispersion values with distance away from the source. However, Sudicky et al. also observed an increase in the transverse dispersivity from 0.0125 m to 0.075 m over the 120 days and 15 m travel distance.

Sauty (1980) observed a ratio of 20 between the longitudinal and transverse dispersion. The ratio between the longitudinal and transverse dispersion calculated by Sudicky et al. (1983) was less than 5. This contrast could be attributed to the fact that Sauty's experiment was performed in a more heterogeneous porous media. We can conclude from their experiments that: 1) advection and longitudinal dispersion will be the main driving force in the shape of a solute plume and 2) while that transverse dispersion will increase with time and distance, its effect on a plume will remain much less than that of longitudinal dispersion.

2.3 Well Spacing

Wilson et al (1997) used a 2-Dimensional finite element modeling program (Sudicky, 1990) which applied the findings of Halevy et al (1967) and Drost et al (1968) to the passive release of nutrients in a series of wells for the remediation of contaminants. In order to effectively capture and treat contaminant plumes via an array of unpumped wells; the distance between each well (well spacing)

must be carefully selected. If remediation is to occur inside of the well, then the spacing between release wells are required to be < 1 well diameter. Longitudinal transverse dispersion would increase the spreading of the released nutrients, thereby allowing remediation to occur further downgradient of the release well (Figure 4).

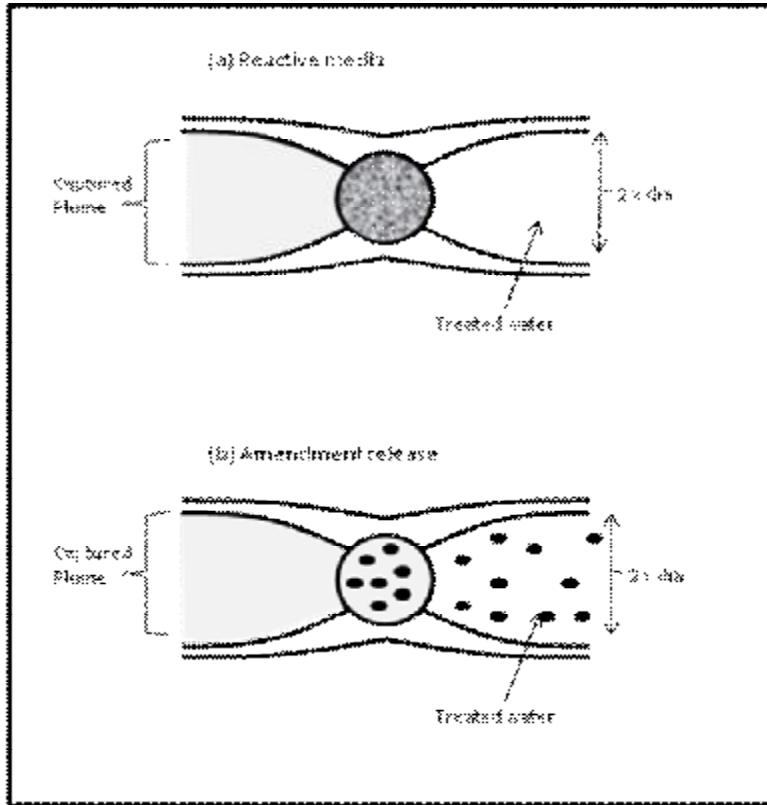


Figure 3. Natural hydraulic capture of an unpumped well at a steady state.

(a) Treatment of contaminant occurs inside the well using a highly permeable reactive media. (b) Treatment occurring downgradient of a release well with a nutrient additive released from a passive device, which does not interfere with the natural flow of groundwater through the well screen (after Wilson et al, 1997).

The well spacing issue was illustrated by Wilson et al. through the following simulations. Using aquifer parameters, similar to those of the aquifer at CFB Borden, Ontario (from Mackay et al 1986; Sudicky 1986) three simulations were produced using nitrate as the desired amendment to degrade a BTEX plume. The following assumptions were applied to all three simulations:

- all of the demand for the introduced amendment is satisfied,
- the amendment was released at a steady state throughout the run,

- amendment release was done via an in well emitter (emitter will occupy only a small fraction of the internal well volume), the aquifer had a uniform hydraulic conductivity (K) of 8.42 m/day, and the well K was 100 times that of the aquifer (Wilson et al 1997).

All of the simulations were for a 75 day experiment and the nitrate release concentration was set for three times the consumption rate of 15 mg/L for BTEX degradation via nitrate. The first simulation (Figure 4a) assumed a single row of 20 cm diameter wells spaced 1.2 m apart. The nitrate formed pinstripes plumes, with no transverse blending. The second simulation was a single row of wells 0.8 m apart and the third was two rows of staggered wells; each well was 1 m apart and the rows (center to center was 0.5 m apart (Wilson et al 1997), unlike in figure 4b, where the 0.33 m contours from all three wells blend into one large nitrate plume creating a continuous zone in which remediation could occur. In the third simulation two rows of wells were used. Figure 4c shows that with the wells in close proximity a greater blending of the nitrate was achieved and at a higher concentration, therefore potentially increasing the rate of BTEX degradation. While these results show that blending of amendment released plumes can occur, it is highly dependent on sites hydrogeologic parameters, especially dispersivity (longitudinal and transverse).

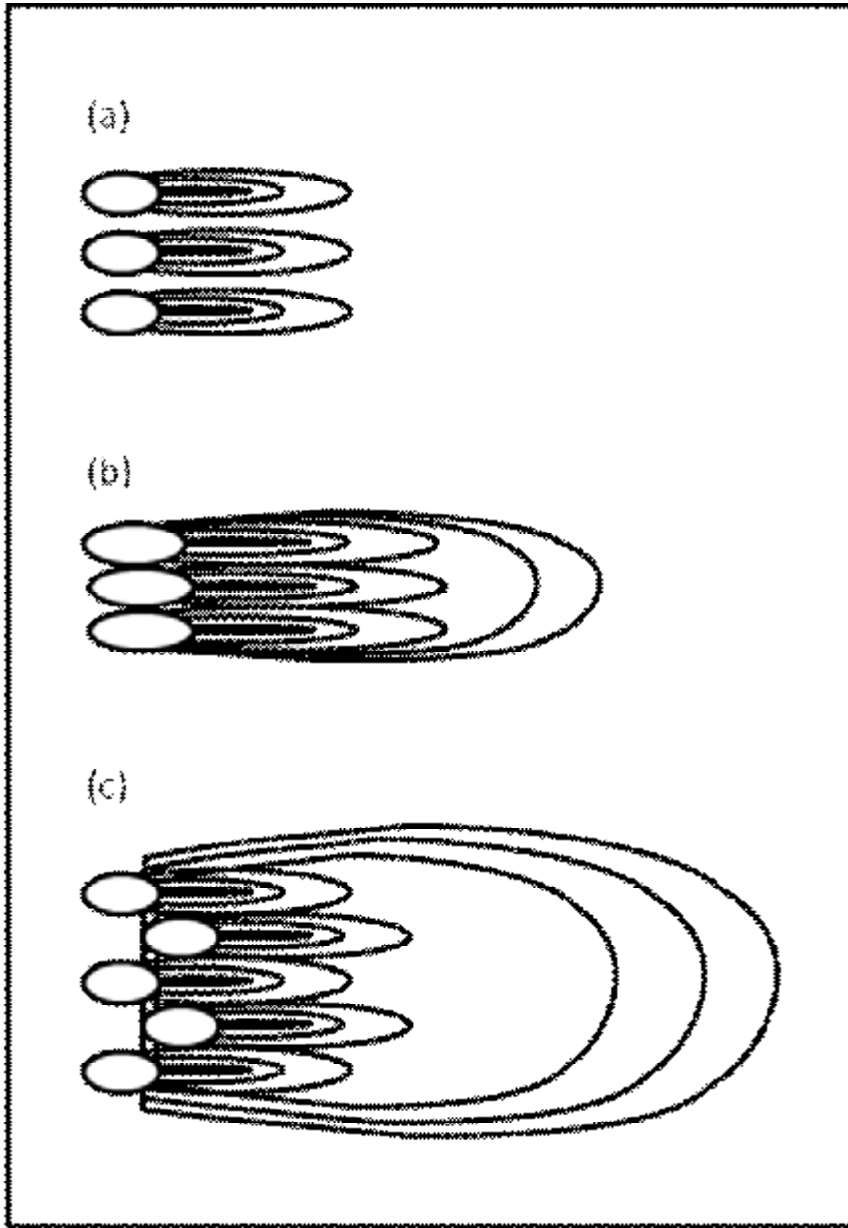


Figure 4 Modeling results of a released amendment through different well spacing configurations.

(a) 20 cm diameter wells spaced 1.2 m apart. (b) 20 cm diameter wells spaced 0.8 m apart. (c) Two rows of 20 cm diameter wells spaced 1 m apart and the rows are 0.5 m apart (after Wilson et al, 1997).

3.0 Field Experiments

3.1 Summary of Experiments

In total, three field trials were completed in an attempt to determine the area that passively release dissolved oxygen effects when it exits the release well. To further investigate the radial distribution of dissolved oxygen, to experiments were conducted by injecting different volumes of nutrient amended water in the release well. The injection experiments are further detailed in Section 7.0. All of the field experiments were conducted at the same experimental site in the “API Barn” at CFB Borden (Figures 5 and 6). There were some minor changes to the monitoring well layout between experiments. As seen in Figure 7 the release well was relocated for the second experiment. During experiment #1 the iSOC™ became lodged in the release well and the only means of removing it for refurbishment was to remove the entire well; it was impossible to re-install the release well in the same location so the same well was reinstalled approximately 1 m to the west of the original location (Figure 6). In order to more closely define the downgradient dissolved oxygen plume width a series of stainless steel drivepoints were installed on either side of O-12 and R4-2 during experiment 3.

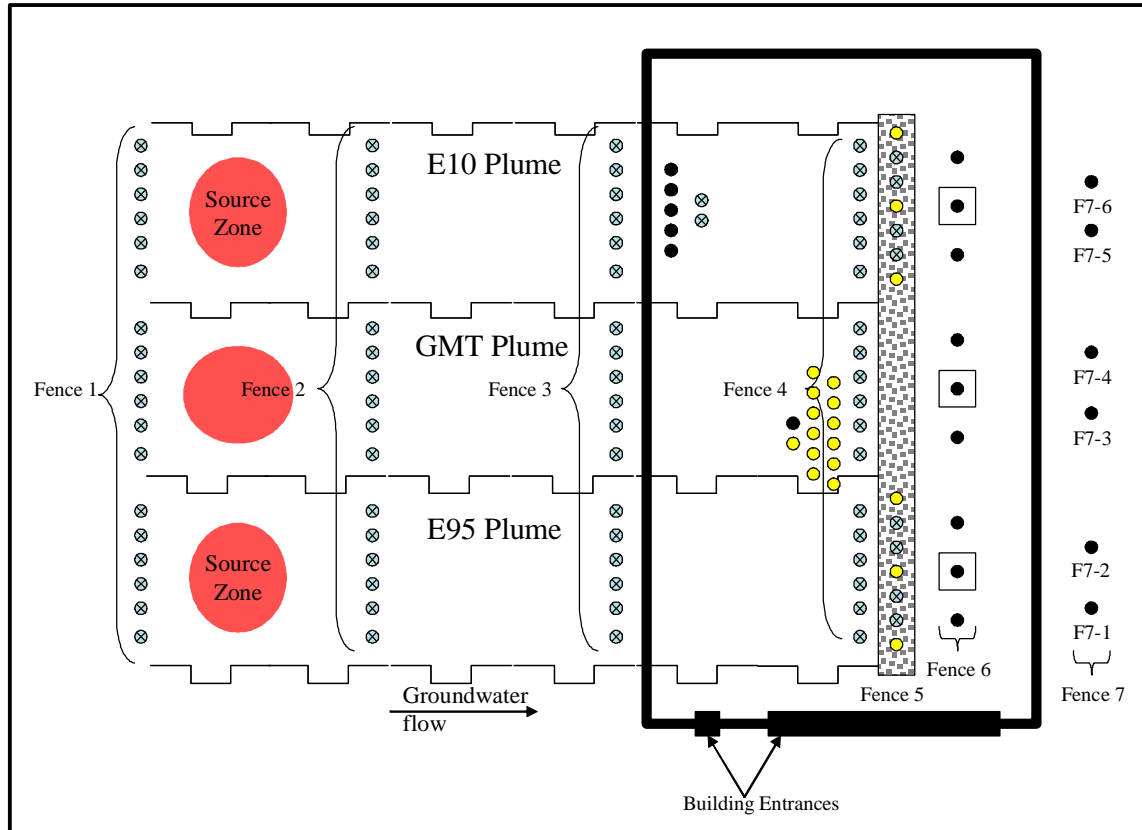


Figure 5 API Gasoline Spill site location in GMT gate.

The iSOC™ was installed in a 5 cm diameter well, and was positioned at approximately 30 cm from the bottom of the well at 4 m bgs, allowing for at least 6 m column of water above it. A “T” sized tank of laboratory grade oxygen was used for all of the experiments and the iSOC™ pressure was set at 379 kPa (55 psi) for a projected dissolved oxygen concentration of 45 mg/L in the release well.

3.2 Site Installations

The site is located in the API Barn in the sandpit site at CFB Borden. In January, 2004 sheet-piling was installed to create 3 open ended “gates”; in which 3 different types of gasoline blends were spilled and the resulting dissolved plumes studied by Mocanu (M Sc, 2007) (Figure 5).

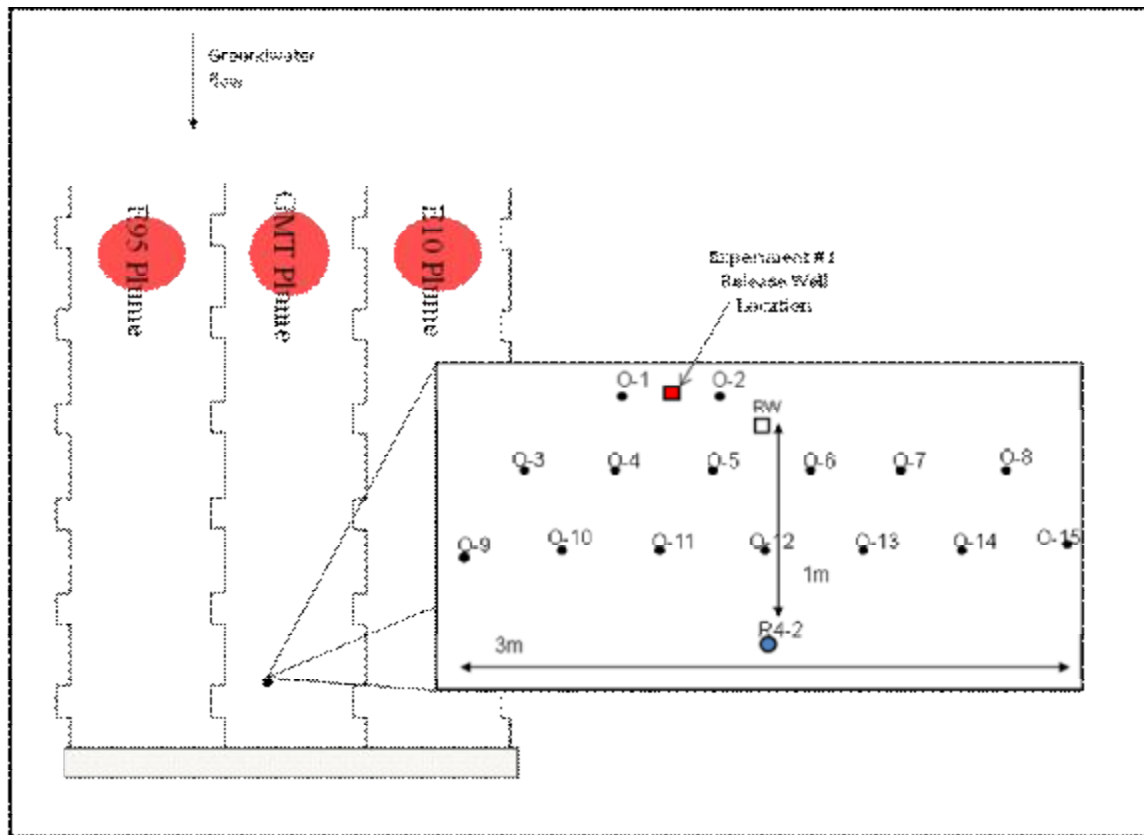


Figure 6 iSOC™ Oxygen Release Well Layout for Experiment 1&2.

The red square box is the original location of the release well in experiment 1. The release well for experiment 2 is labeled as RW. Wells labeled O are screened monitoring wells and R4-2 is a multilevel sampling well. See text for details about the O wells.

The iSOC™ experiments were conducted in the middle gate, termed GMT, in which a mixture of gasoline, Methyl tert-Butyl Ether (MTBE) and tert-Butyl Alcohol (TBA) was spilled (Figure 5). In the downgradient end of the middle gate, an oxygen-release well and a series of monitoring wells were installed in two, staggered rows (Figure 6 and 7). The rows are 50 cm apart and the wells in each row are also spaced 50 cm apart. All wells are installed to 4.3 m bgs: the 5 cm ID injection well is fully screened from 0 m bgs to 4.5 m bgs while the 2.5 cm ID monitoring wells are screened from 1-4 m bgs, followed by a 14 point multi-level (sample points distributed between 2-4 m bgs, with 18 cm intervals) (Figure 8). A series of 2.5 cm ID monitoring wells were used in the experiment to simulate the type of monitoring wells which would be used outside of a research environment.

Experiment one was started before the injected hydrocarbons had advanced into the experimental zone, downgradient of fence 3 (Figure 5). The gasoline was injected on the 8th to 13th of October 2004, with a groundwater velocity ranging from 9-10 cm/day the bulk of the hydrocarbon plume would have arrived in the test area 145 days into the oxygen release experiment. Approximately 103 days into the experiment, low levels of hydrocarbons and MTBE was detected in the iSOC™ experiment zone (Table 2).

For Experiment 2, the release well (RW-1) was reinstalled 1 m directly upgradient of multi-level well R4-2 as RW in Figure 6. At the start of the second experiment the hydrocarbon plume was well established, with the plumes outer most boundary located between R4-2 to R4-5 (located 3m east of R4-2) (Figure 15) . Thus encompassing the release well and monitoring wells O-6, 7, 8, 12, 13 and 14.

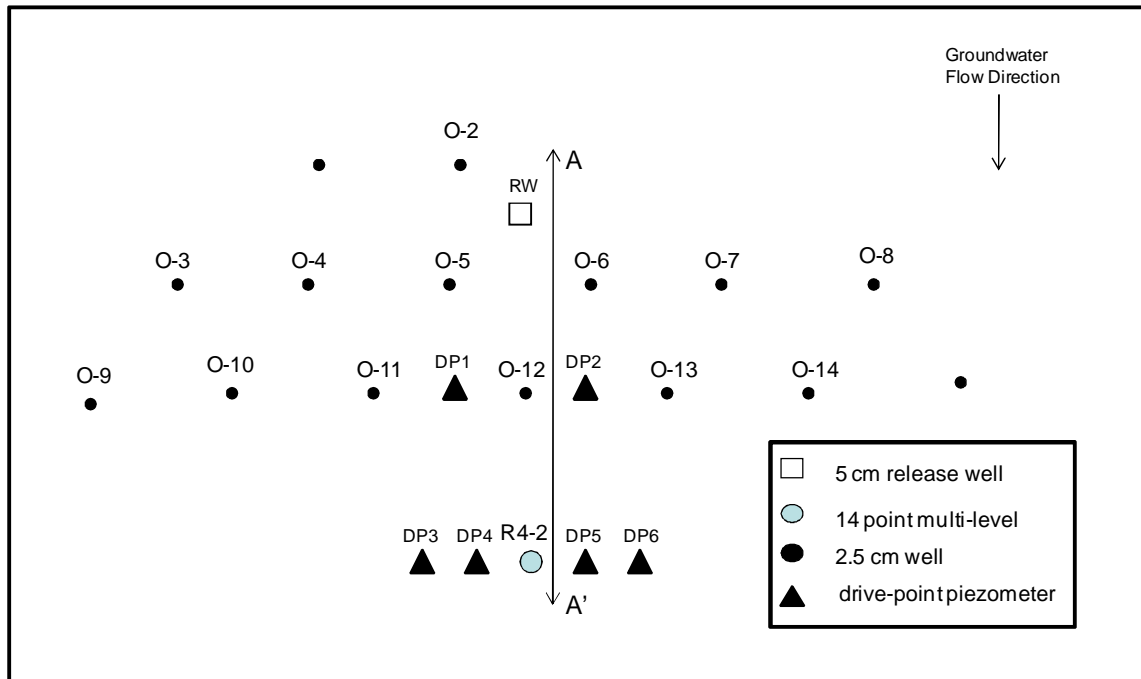


Figure 7 Site Layout Experiment 3.

Experiment 3 was conducted in the same manner as experiment 1 and 2, with mixture of oxygen and SF₆ gas passively released using an iSOC™ unit. Six stainless steel drive points were installed to further delineate the width of the dissolved oxygen plume (Figure 7). Two drive points were installed 25 cm east and west of O-12 (the drivepoints are labeled DP-1 and DP-2) and four more drivepoints were installed 25 cm and 50 cm east (DP-3, DP-4) and west (DP-5, DP-6) of R4-2 to a

depth of 260 cm below ground surface. The length of the experiment was shortened to only 1 month. As observed in experiment 2, the horizontal distribution of dissolved oxygen did not change over extended lengths of time. Dissolved oxygen was measure in the field while groundwater samples for SF₆, BTEX, total iron, alkalinity and pH analysis were collected and brought back to the laboratory for analysis. The above listed parameters were collected approximately every 7 days.

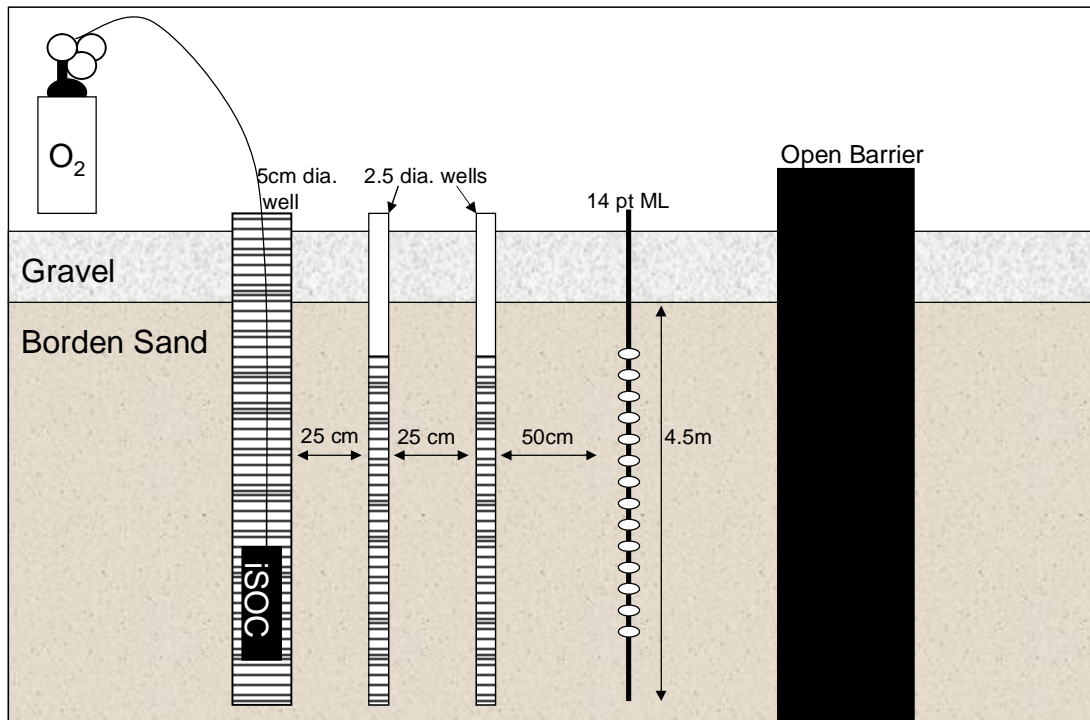


Figure 8 Cross section of release site along groundwater flow.

2.5 cm diameter wells are projected onto the section. See text for details of well construction.

3.3 Analysis and Methodology

3.3.1 SF₆

Background groundwater samples were taken before the SF₆ release and within the first few hours of the release. Subsequent groundwater samples were taken over a 17 day period. Water samples were collected from the monitoring wells through polyethylene tubing using a Masterflex™ peristaltic pump with a vacuum seal sampling cap, in a clear glass 40 mL VOA bottle with a fitted Teflon-lined septa screw cap. Samples were taken in duplicate from each well at depths bgs of 1.5 m, 3 m and 4 m. To prevent loss of volatile SF₆, water was pumped from the well at a slow rate to

reduce bubbling. The VOA bottles were capped with no headspace and were stored inverted. No chemical preservative was added as SF₆ is inert. Samples were kept cold in the field, brought back to the University of Waterloo's Organic Geochemistry lab for analysis and stored at 4°C in the laboratory for less than 7 days before analysis.

For analysis, a 10 mL aliquot was taken from the 40mL VOA bottle and transferred into a 30 mL glass barrel syringe along with 10mL of air. If dilution was required a 2 mL aliquot was taken using a 10 mL glass syringe and 8 mL of air was also added. The syringe was then shaken and allowed to equilibrate for 1 hour. A 4 µL aliquot of the gas phase from the syringe was taken in a gas tight syringe and manually injected into a Shimadzu GC-9A gas chromatograph fitted with an electron capture detector (ECD) with a Restek, Molecular Sieve 5A Plot Column (30 m x 0.53 mm), nitrogen was used as the carrying gas at 20 mL/min. The SF₆ detection limit was <1.0 µg/L. The GC was calibrated by an external standard method. A range of SF₆ concentrations are prepared by spiking small volumes (100 – 2 µL) of SF₆ gas into 1 L glass bottles filled with water. Concentrations of dissolved SF₆ in the collected groundwater samples were calculated based on the assumption that 100% partitioning of the gas into the headspace occurred.

3.3.2 Dissolved oxygen (DO)

Samples were collected at three different depths within wells (1.5 m, 3 m and 4 m bgs) to capture the vertical distribution of dissolved oxygen. This assumes that groundwater flowing through the wells is not significantly mixed vertically. DO was analyzed in the field using an Orion Dissolved Oxygen Probe # 083010 with Meter (model 835). In order to reduce the creation of gas bubbles which might introduce a negative bias, water was slowly pumped by the peristaltic pump into a flow through cell housing the probe. In this way groundwater was continuously drawn across the probe until readings stabilized. Results are given in mg of O₂/L. In the lab the probe's detection limit is typically 0.1 mg/L at room temperature. Due to the entrainment of oxygen via the sampling method in the field, readings of below 1 mg/L in the field are considered to be no different than zero. During the first experiment sampling and analysis for dissolved oxygen was done about every two weeks for the first month. Thereafter, sampling conducted was monthly. For the second experiment sampling for dissolved oxygen was conducted every few weeks and for the third experiment was conducted approximately every 7 days.

3.3.3 Biological Oxygen Demand/Chemical Oxygen Demand

Samples were collected from the release well and sent to ALS Laboratories, Waterloo, Ontario for analysis of biological and chemical oxygen demand. Groundwater was collected into two 500 mL nalgene bottles, no chemical preservatives were added, and samples were kept cold (4°C). Analysis for the biological oxygen demand (BOD) was done using the analytical method reference APHA 5210 B (detection limit of 2mg/L) and for the chemical oxygen demand (COD) the APHA 5220 D method (detection limit of <10 mg/L) was used. COD on the aquifer solids was also done, aquifer cores were collected in the sandpit upgradient of the research site in an area not impacted by hydrocarbons. The cores were homogenized and subsampled. Aquifer COD was completed by Xu X, from the Civil and Environmental Engineering Department using a dichromate digestion method (Xu and Thomson, 2008).

3.3.4 Total BTEX

Groundwater samples were collected in standard clear glass 40 mL VOA bottles, using a stainless steel screw cap sample head attached the sampling tubing (low density polyethylene, LDPE) and connected the pump head of a Masterflex™ peristaltic pump. The sampling cap is placed before the pump head to prevent contact with the pump tubing whereby desorption of contaminants from the tubing can occur. All samples were collected with no headspace, and preserved with 0.4 mL of Sodium Azide (10% W/V solution). Samples were then stored at 4°C for a maximum of 14 days before analysis.

Samples were analyzed at the Organic Geochemistry Laboratory at the University of Waterloo by a solvent microextraction gas chromatographic technique. All samples and standards are equilibrated to room temperature before extraction. The micro-extraction techniques begins with the removal of 5 mL of the sample, which was discarded using a glass barrel syringe and 2 mL of methylene chloride (containing internal standards m-fluorotoluene and fluorobiphenyl (25 mg/L)) was injected into the sample bottle. The vial was resealed and agitated on its side at 350 rpm on a platform shaker for 20 minutes. After shaking the bottle was inverted and allowed to sit for 30 minutes to allow the water and solvent phases to separate. Approximately 0.7 mL of the solvent was removed using a gas tight glass syringe, through the septum of the sample bottle. The aliquot of solvent removed was placed in a Teflon sealed autosampler vial, which was loaded onto a HP7673A autosampler for injection into the gas chromatograph.

Samples were then analyzed with a HP 5890 capillary gas chromatograph, with a flame ionization detector (FID). Three microliters of the solvent was injected in a splitless mode (purge on 0.5 minutes, purge off 10 minutes) onto a 0.25 mm x 30 m length, DB5 capillary column with a stationary phase film thickness of 0.25 µm. The total run time was 10 minutes; data integration was completed with a HP 3398A integrator. All results are reported in µg/L.

3.3.5 Bromide

Analysis was completed using an Orion Bromide ion specific probe with meter. A 15 mL aliquot of sample is transferred into a 20 mL glass bottle with stir bar and placed on a stirrer. The bromide probe is lowered into the bottle; the sample was continuously stirred until a stable reading was achieved. All readings were measured in mV, and the results were converted in mg/L by using a standard calibration. All results are presented in Appendix B

3.3.6 pH

pH analysis was done in the laboratory, samples were collected in the field in 25 mL clear glass vials. 10 mL of the sample was used for the total iron analysis so a headspace was left to prevent the sample from becoming anaerobic. The samples were stored at 4°C until analysis could be done using an Orion pH probe with meter. A 15 mL aliquot of sample was transferred into a 20 mL glass bottle with stir bar and placed on a stirrer. A pH probe is lowered into the bottle; the sample is continuously stirred until a stable reading was achieved.

3.3.7 Total Iron

Groundwater was collected for total iron analysis in a 25 mL glass bottle with headspace to prevent the sample from becoming anaerobic. Samples were stored at 4°C until analysis could be completed and then was allowed to warm up to room temperature. Total Iron analysis was completed using a portable HACH DR/2400 colour spectrophotometer; a US EPA approved Method 8008 was used for total iron analysis of water. The FerroVer® Method (0.02 to 3.00 mg/L) requires 10 mL of groundwater to be placed into an optically ground vial, in which a powder pillow containing a premeasured amount of Ferro Ver Iron Reagent was added to the sample. The vial was swirled to allow the reagent to dissolve and a three minute timer was set to let the reagent react with the iron in the sample. After 3 minutes the sample turned orange in colour if iron was present. The sample was inserted into the spectrophotometer for analysis. All results are in mg/L.

3.3.8 Alkalinity

Samples collected for alkalinity analysis in 250 mL or 500 mL nalgene bottle, depending on what was available. Due to time constraints all of the samples were collected and then brought back to the lab for analysis and not analysed in the field. The samples were stored at 4°C and then brought to room temperature for analysis. A HACH digital titrator was used; 250 mL of groundwater was removed from the sample bottles and placed into a 500 mL glass volumetric flask. A premeasured pillow of bromphenol blue indicator powder pillow was added to the sample and then was swirled around until the reagent was dissolved, then bromocresol green – methyl red powder pillow was added and again the flask was swirled around until the second reagent was dissolved. Then a 5 minute timer was set to allow the reagents to react with the groundwater sample. After 5 minutes a 1.600 N mg/L solution of sulphuric acid was slowly added to the sample using the digital titrator. The acid was added in small aliquots until the sample turned a light pink. The number on the digital titrator reflects the concentration of alkalinity in the groundwater sample in mg/L.

4.0 Field Experiment 1

4.1 Oxygen Results

This initial test was completed in the GMT gate prior to the arrival of oxygenates/hydrocarbons in the experimental zone. The set up is shown in Figure 6. For 77 days (11/04/04 - 1/20/05) oxygen concentrations in the iSOC™ release well were approximately 42 mg/L, but minimal dissolved oxygen was detected in any downgradient well. Low concentrations of dissolved oxygen, between 1 and 2 mg/L, were detected at wells O-3, O-4 and O-5 throughout the experiment, but these concentrations were comparable to the background dissolved oxygen concentrations measured prior to the start of the experiment (Figure 9). Therefore, the detection of dissolved oxygen between 1 and 2 mg/L throughout the experiment cannot be directly attributed to the presence of a dissolved oxygen plume created by the iSOC™ unit.

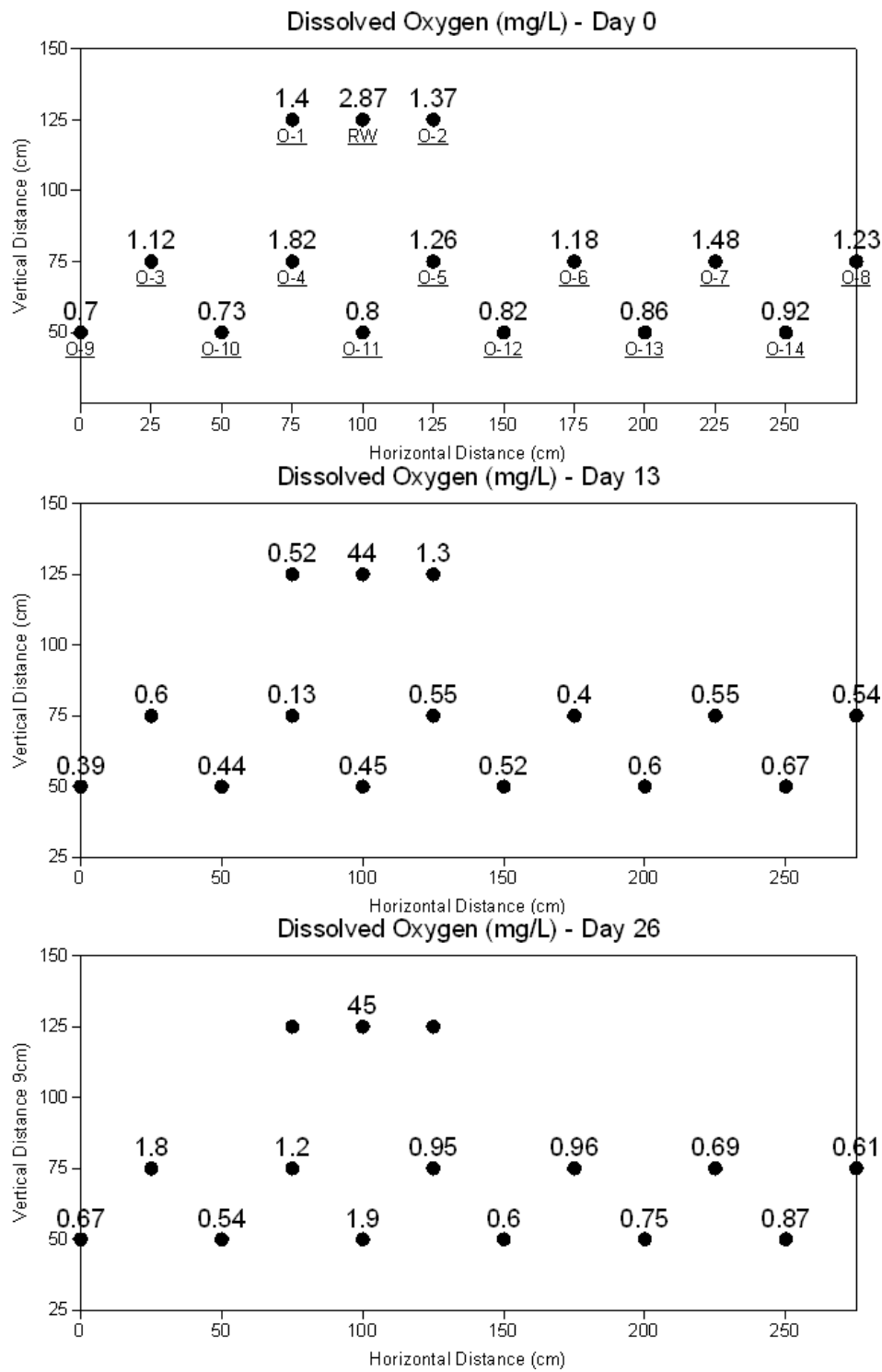


Figure 9 Maximum dissolved oxygen concentrations (mg/L) Experiment 1.

Between days 77 and 89 the O₂ tank emptied, flooding the iSOC™ and rendering it useless. Starting on day 89 and until day 98 oxygen was seen downgradient only in well O-11 at concentrations up to 5.8 mg/L (Table 2). This suggests a narrow oxygen plume, less than 10 cm wide, was created in the aquifer.

Well ID	O2 (mg/L)									
	t=0 11/4/04	t=8 11/12/04	t=13 11/17/04	t=18 11/22/04	t=26 11/30/04	t=77 1/20/05	t=89 2/1/05*	t=91 2/3/05	t=98 2/10/05	t=103 2/15/05
O-1	1		1	1		1	0			
INJ-A	3		44	39	45	42	2	2	2	2
O-2	1		1	2		3	2	2	2	2
O-3	1	1	1	2	2	0	0	1	1	1
O-4	2	1	0	2	1	2	1	1	2	1
O-5	1	1	1	1	1	3	1	2	3	1
O-6	1		0	1	1		0	2	1	1
O-7	1		1	1	1		0	0	1	1
O-8	1		1	1	1		0	0	0	1
O-9	1		0	1	1		0	0	1	1
O-10	1		0	1	1		0	0	1	1
O-11	1		0	1	2		4	6	2	1
O-12	1		1	1	1		0	0	1	1
O-13	1		1	1	1		0	0	1	
O-14	1		1	1	1		0	0	0	
O-15	BLOCKED									
background										
*tank blew out										

Table 2 Maximum dissolved oxygen concentrations Experiment 1.

4.2 Factors Effecting Release

4.2.1 COD Results

A number of calculations and tests were done in order to determine why so little oxygen was seen downgradient and why > 2 mg/L oxygen was only detected after 77 days. One thought was that there was significant oxygen demand in the groundwater/aquifer. Elsewhere in the Borden aquifer, it has determined that the upper value of COD in the aquifer sand, to be 1.90 +/- 0.12 g O₂/kg (Sra, 2008; personal communication), but in actuality one can expect to see a COD of approximately 0.95 g O₂/kg. The COD of the soil can have a significant impact on the spatial distribution of the dissolved oxygen. If 1.9 g of O₂ per kg sand is required to satisfy the oxygen demand, than within a 10 cm wide by 1 m long by 3 m high plume, the approximately 543 kg of soil would require 1030 g of oxygen to satisfy the COD. A simple calculation can be done to determine the oxygen demand of the soil for differing plume widths by multiplying the bulk soil density of Borden sand (1.81 g/cm³) by the volume of the aquifer (soil + pores) in a plume (Table 4).

With the COD value of 1.90 g O₂/kg is correct we can compare the COD of Borden soil to the maximum mass of oxygen released into the aquifer. By assuming that the groundwater in each of the calculated plume volumes in Table 3 was at the maximum level observed in the release well (45 mg/L) we can calculate if the “potential” dissolved oxygen released by the iSOC™ exceeds the oxygen required to overcome the oxygen demand of the soil. This can be done by multiplying the observed oxygen concentration by the volume of soil for the different plumes sizes in Results are shown in Table 3.

Volume of Soil (cm ³)	O ₂ (g) Required at Borden Field Site
1	4.5x10 ⁻⁵
3*10 ⁵	13
1.5*10 ⁶	67.5
3*10 ⁶	135

Table 3 Oxygen required to overcome oxygen demand at Borden Field Site.

The results indicate that a concentration of 45 mg/L of oxygen may not overcome the chemical oxygen demand of the Borden aquifer, and one might not expect to see any oxygen 1 m downgradient of the release well over the 10 cm wide assumed plume width. In the second experiment described in the next section, dissolved oxygen is detected in wells downgradient of the release well suggesting that either the oxygen demand was satisfied during experiment 1 or that the COD of the Borden aquifer is actually lower than 1.90 g O₂/kg.

Length*Width*Height (cm)	Volume of Soil (cm ³)	Mass of Soil (Density*Volume) (kg)	O ₂ Required (g)
1*1*1	1	0.00181	3.4*10 ⁻³
100*10*300	3*10 ⁵	543	1032
100*50*300	1.5*10 ⁶	2700	5130
100*100*300	3*10 ⁶	5430	10317

Table 4 Calculations of Oxygen required to overcome soil COD for various plume sizes.

4.2.2 BOD and BTEX Results

Samples were collected for BTEX and BOD analysis, to assess if they could attribute to the oxygen demand of the groundwater. BTEX samples were sent to the University of Waterloo's Organic Geochemistry Laboratory for analysis, which is detailed in Section 3.34. The BOD samples were sent to ALS Laboratories for analysis. Results indicated that the concentrations of dissolved BTEX and BOD were not a significant sink for oxygen released by the iSOC™ (Table 5).

	BTEX (ug/L)	Sulfate (mg/L)	BOD (mg/L)	COD (water, mg/L)
RW	6	19	2	2
O-8	111	9		
O-11	111	3		
O-13	125	6		

Table 5 Potential sources of dissolved oxygen demand Experiment 1.

4.2.3 Bromide Results

A borehole dilution test using a sodium bromide slug was completed on the release well to determine whether or not the screen was biofouled and thus preventing the oxygen from exiting the well. A sodium bromide solution consisting of a mixture of 7 L of deionized water and 8.2 g of sodium bromide was slowly injected in the middle of the release well screen and was monitored over approximately 55 hours. Samples were initially collected from the release well every 5 minutes for the first hour, every 20 minutes for 11 hours and then every hour until the completion of the experiment at hour 55. The samples were collected by pumping approximately 20 mL of water from each well into a plastic scintillation vial. All samples were stored at 4°C and brought to room temperature before analysis.

Results from the first bromide injection indicated (Appendix B) that the velocity through the well screen was 0.009 cm/hr, which was slower than anticipated. If the groundwater was flowing unimpeded through the well screen, a velocity of approximately 0.45 cm/hr should be observed. As discussed in Section 3.1 the iSOC™ unit became lodged in the well and in order to extract the unit the entire well was removed and then reinstalled in a new location. A second bromide tracer test was performed on the well screen after it was reinstalled to ensure that groundwater was flowing through the well screen. The second bromide tracer test was conducted in the same manner as the first one, the well screen was not cleaned in between the first and second tracer test. The results from the second tracer test indicated that groundwater was flowing through the well screen at a rate of 0.43 cm/hr, which is a much higher rate than measured during the first tracer test of

0.009 cm/hr (Figure 10 a & b). This indicates that the well screen was either clogged with sediment from the surrounding soil or was biofouled through the growth of naturally present microbes preventing the groundwater from flowing into and out of the well screen.

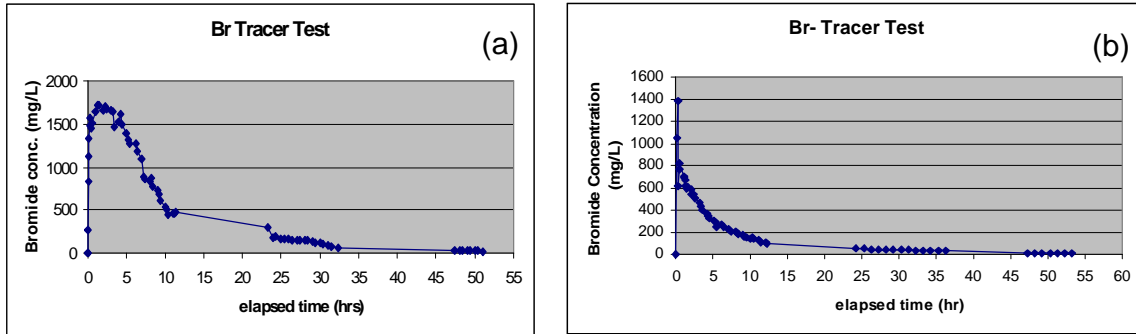


Figure 10 Borehole dilution tests.

(a) Borehole dilution test done at the end of Experiment 1. (b) Borehole dilution test done before Experiment 2.

4.3 Findings of Experiment 1

Very little oxygen was found in the groundwater. The significant COD of the soil could have limited the development of a dissolved oxygen plume. Fouling of the well screen could have prevented the oxygen from migrating out of the well and into the aquifer.

5.0 Oxygen Release Field Experiment #2

5.1 SF₆ Tracer Test

Before the release of oxygen in Experiment 2, a gas tracer test was conducted to:

- determine if the well has been properly developed,
- provide an ambient groundwater flow direction and velocity in this area, and
- estimate the extent of transverse spreading of a non-reactive, non-retarded chemical.

Sulfur Hexafluoride (SF₆) was selected as the tracer because it is chemically and biologically inert; in natural groundwater systems its background concentration is negligible; it is nontoxic at high concentrations; and it can be detected at very low concentrations (Wilson and Mackay, 1993). It is a neutral molecule and therefore will not be affected by electrostatic interactions by positive or negative charged materials in the subsurface (Watson et al, 1997) SF₆ is a dense gas (6.602 g/L) at room temperature. It is highly volatile and will strongly partition from water into the vapour phase (Lide, 1991). Wilson and Mackay (1993) evaluated the behavior of SF₆ in a column test using Borden sand as the media. Results from the test indicated that SF₆ would behave in a similar manner as bromide in a saturated sandy media. While SF₆ and oxygen will not diffuse and migrate within the aquifer in the exact same manner, the release of a SF₆ gas can provide an estimate of the direction of flow and the transverse spreading of the dissolved oxygen plume.

5.1.1 Operation

A mixture of 5% SF₆ and 95% oxygen was passively release into the well using the Waterloo Emitter™. The Waterloo Emitter™ was employed because previous tests using an iSOC™ did not effectively emit SF₆. Since both the iSOC™ and Waterloo Emitter™ are passive release systems it was assumed that SF₆ emitted would have the same hydrogeological interaction with the groundwater as would an inert gas from the iSOC™. Due to a faulty regulator the tracer release was short-lived (~ 20 hours).

5.1.2 Findings

Results indicate that the slug of SF₆ followed a narrow flow path. After 17 days the SF₆ slug was only detected in the release well (RW) and in wells O-6, O-12 and R4-2 in sample point 7 only (2.6 m bgs) (Figure 11). SF₆ was detected in O-6 only on days 4 and 7 of the test; for the last 10 days the

concentrations were non-detect (Appendix C). This could either reflect the short time in which the SF₆ was released or the presence of a preferred pathway created by a zone of higher conductivity. No SF₆ was found in the wells on either side of O-6 and O-12, indicating that the slug remained no greater than 50 cm in width. The highest concentration (2260 µg/L) was found in the release well on day 2 of the test. Concentrations detected in the downgradient wells were much lower, 20-58 µg/L (all SF₆ data is in Appendix A and C). The reason for the large decrease between the release well and downgradient well concentrations is unknown. It is possible that the high concentrations passed between wells O-11 and O-12 or between O-12 or O-13 and that well O-12 received only the dilute, dispersed edge of the SF₆ plume.

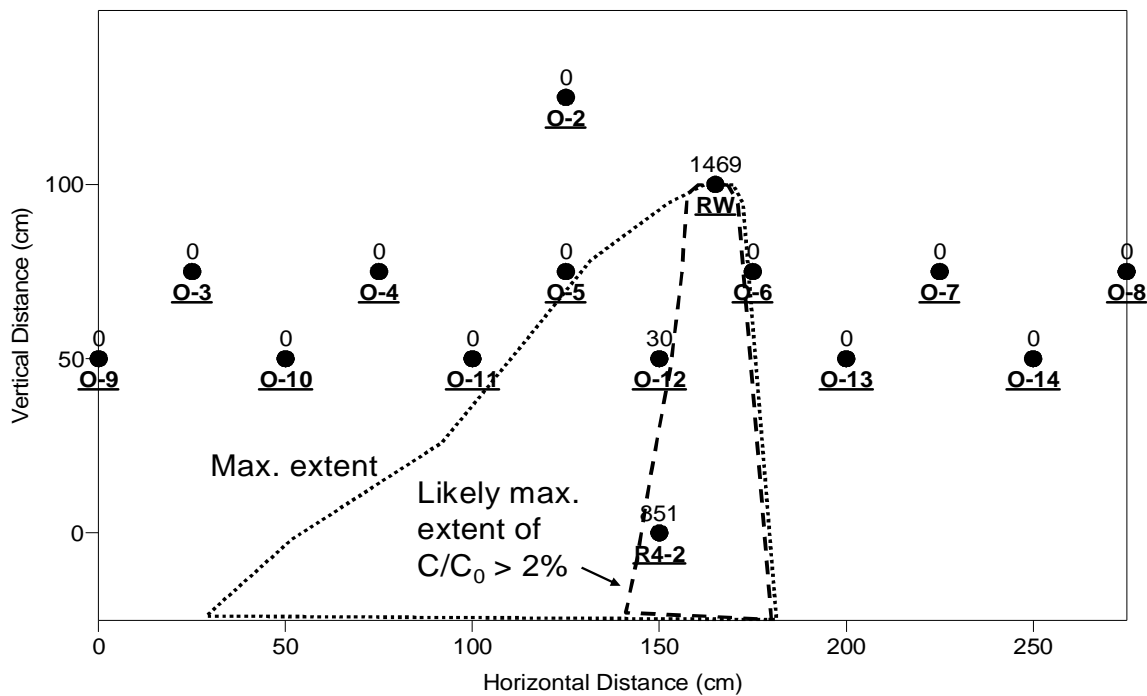


Figure 11 Distribution of SF₆ (µg/L) on Day 17 of the SF₆ tracer test.

Maximum concentration in each well is shown. See Appendix C for data. Well labels are shown below solid well symbol. The “maximum extent” of tracer (dotted line) is inferred as the greatest width between non-detect wells. The much more “likely maximum extent of $C/C_0 > 2\%$ ” is also shown as dashed line, based on significant detected SF₆ concentrations and reasonably symmetrical transverse spreading.

5.1.3 Discussion

While the tracer test was not a long-term release as intended, we can infer from the SF₆ distribution (Figure 11) that inert chemicals when passively released from a well will not be spread widely transverse to flow. The tracer was detected in only 2 downgradient wells and so it could be as narrow as a few centimeters. The likely maximum width of the SF₆ plume (i.e., with concentrations > 2% of those in the injection well) was approximately 14 cm at about 1.25 m downgradient of the release well. This is consistent with the low apparent transverse dispersivities in the Borden aquifer, typically 0.03 – 0.04 m horizontally (Sudicky et al., 1983; Freyberg, 1986) as deduced from chloride tracer experiments with 11 and 60 m plume advection. Apparent vertical transverse dispersion is even weaker, and is likely due mainly to diffusion (Sudicky et al., 1986). At Borden and in general, horizontal transverse dispersivities are at least an order of magnitude smaller than longitudinal values and, further, vertical transverse dispersivities are some 1 to 2 orders of magnitude smaller than horizontal transverse dispersivities (Gelhar et al., 1992). The narrow tracer plume generated by passive release of tracer in a well is consistent with this weak transverse dispersivity of the Borden aquifer. The flow direction of the SF₆ tracer is taken as the direction of groundwater flow and so was used to locate downgradient monitoring wells.

5.2 Oxygen Release

5.2.1 Operation

During the second iSOC™ release experiment concentrations of total aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene and trimethylbenzene isomers, and naphthalene) were entering the test area at row 3, well 2, 7 m directly upgradient of R4-2) at 60 mg/L and leaving at R4-2 at 50 mg/L (Figure 16). There was no MTBE and TBA detected in the system; both contaminants had already migrated through the gate (Mocanu, 2007).

Due to the use of a mixture of SF₆ and oxygen in the tracer test prior to the iSOC™ release test, dissolved oxygen (DO) concentrations taken prior to the SF₆ tracer test were used as background levels for the oxygen release which started a few weeks later. All wells had DO concentrations below 1 mg/L.

A refurbished iSOC™ was pressure tested and then installed on July 17, 2006 in the new release well, with the oxygen pressure set at 3.5 kg/cm² (50 psi). The oxygen release was continued for a total of 132 days.

5.2.2 Findings

Within 24 hours, the release well DO concentrations had reached 46 mg/L. By day 14 the dissolved oxygen plume had reached multi-level R4-2 only at point 7 (2.58 m below ground surface). Over the 132 day test, the dissolved oxygen was only detected in well O-12, 50 cm directly downgradient of the release well (see Figure 12) and in R4-2 only in points from 2.04 m to 2.9 m bgs. In O-12 the oxygen concentration was more evenly distributed vertically with concentrations of 8-9 mg/L throughout the screened area of 2-4 m bgs (Figure 12). Oxygen was not detected in either of the wells located 25 cm east and west of the release well (wells O-5 and O-6, respectively; see Figure 12; data in Appendix D). Oxygen was never detected in the downgradient wells O-11 or O-13 (wells that are 50 cm on either side of O-12 at a distance of 50 cm); see Figure 14 (data in Appendix D).

5.2.3 Discussion

The dissolved oxygen detections mirrored that of the SF₆ tracer. The DO was again detected in only 2 downgradient wells and the DO plume might be as narrow as a few centimetres. Figure 12 shows the same “maximum extent” limits and the same “likely maximum extent limits”; the later constrained by requiring some plume symmetry. Given that DO in well O-12 was very significant, it is possible that the groundwater flow has shifted somewhat and so the “rotated likely maximum extent” plume is shown, constrained by flow direction from RW through O-12 and again the need for some plume symmetry. In the “rotated” case, the DO plume could be 100 cm wide at about 125 cm downgradient of the release well. In order to achieve a 100 cm wide DO plume the transverse dispersion would have to be unrealistically large and therefore it is highly unlikely.

SF₆ and oxygen were first detected in point 7 in multi-level R4-2 rather than at the nearer O12; the tracer was initially detected at this point on day 10 of the tracer test as opposed to day 14 for the oxygen (Figure 13 and Appendix C for SF₆ data). A delay in the oxygen plume arrival could reflect the need to overcome the background COD or background BOD of 2 mg/L and/or to degrade hydrocarbons which were now present in the test area. Consumption of this BOD may also explain the reduced DO concentrations at R4-2 (< 10 mg/L), 1 m downgradient of the release well. For example, in August, 2005 (during the first iSOC™ experiment), upgradient multilevel well R3-2 in Row 3 had a few points containing about 1 mg/L aromatic hydrocarbons having an oxygen demand of 6 mg/L. Degradation of these would reduce the DO level in the release well from about 46 mg/L to about 40 mg/L. Clearly, even if BOD as aromatic hydrocarbons was entering the release well, the water in the release well would retain a very high DO level (40 mg/L). Further reduction of DO through consumption of dissolved aromatics as released water dispersed with plume water

transverse to flow would only reduce the narrow DO plume fringe to below detection. The released water DO concentrations far exceed the groundwater BOD and so residual DO should remain in a plume downgradient of the release well. So, the reduced DO in points of R4-2 does not seem to reflect consumption of BOD. Alternatively, the DO plume might have been centered to either side of R4-2, with only the dispersed edge passing through R4-2. The lack of significant DO in the lower points of R4-2 could reflect groundwater flow/dispersion whereby flow at the greater depth simply bypasses R4-2 to the east or west.

The maximum possible horizontal width of the dissolved oxygen plume in the monitoring network was between 25 and 50 cm. Oxygen was not detected in either of the wells located 25 cm west of the release well (well O-5) and 10 cm east of the release well (well O-6; see Figure 9) during the 132 day oxygen release period (data in Appendix D). A possible reason why dissolved oxygen was not detected in the well closest to the release well (O-6) was because it is in the dispersed edge of the dissolved oxygen plume. Oxygen was detected in O-12, 50 cm directly downgradient of the release well, at about $\frac{1}{4}$ of the release well concentration, but was never detected in the adjacent downgradient wells O-11 or O-13 (wells that are 50 cm on either side of O-12 at a distance of 50 cm downgradient, see Figure 8) (data in Appendix D). This is consistent with the SF₆ distribution, except that low concentrations of SF₆ were also detected periodically in O-6. As stated previously the oxygen was detected 1m downgradient of the release well at the multi-level well R4-2 after 14 days. One hypothesis is that the iSOC™ release well produced a dissolved oxygen plume similar in horizontal distribution to the SF₆ plume created with a Waterloo Emitter™ from the same well. This is consistent with the performance of a passive release well expected from Drost et al. (1968). The other is that a broader DO plume was generated but was consumed by natural BOD resulting in a much narrower residual DO plume. In the rather homogeneous Borden sand aquifer, it appears that oxygen or any additive passively released into groundwater via a well will have a small radial foot print creating a narrow plume downgradient of that well.

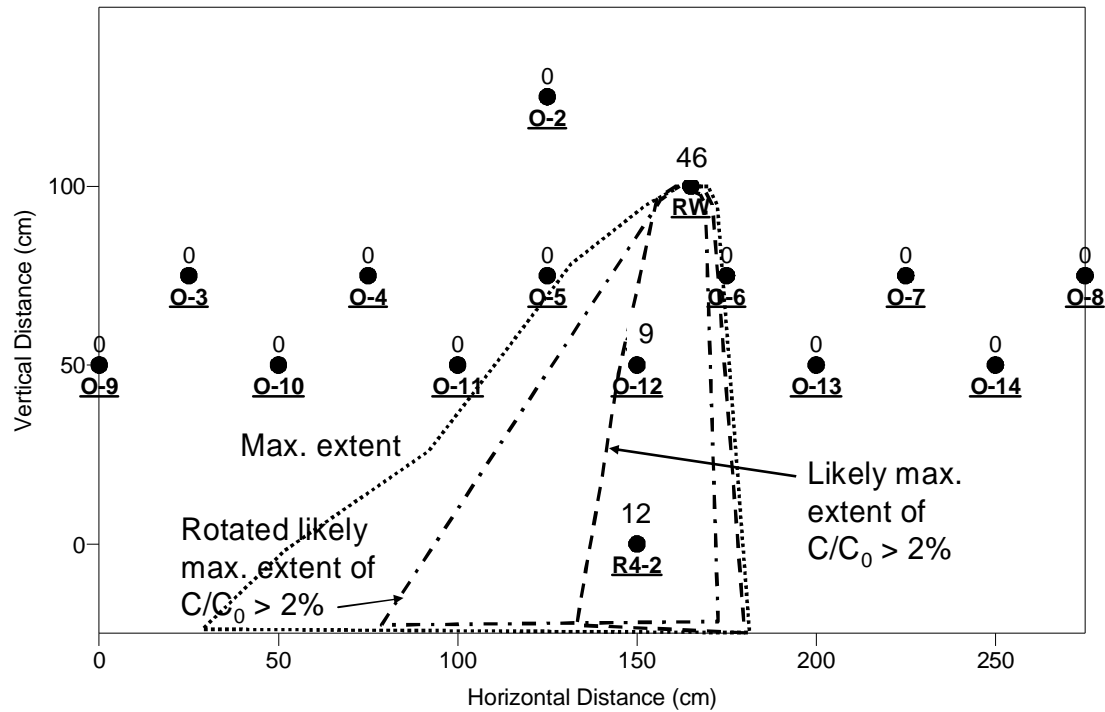


Figure 12 Plan view of DO concentrations in iSOC™ Experiment 2.

Maximum concentrations in a well are shown. See Appendix D for data. The “maximum extent” of tracer (dotted line) is inferred as the greatest width between non-detect wells. The much more “likely maximum extent of $C/C_0 > 2\%$ ” is also shown as dashed line, based on significant detected DO concentrations and reasonably symmetrical transverse spreading. Since it is also possible that flow direction could have changed, a “rotated likely maximum extent of $C/C_0 > 2\%$ ” is shown as a dashed-dotted line. This assumes flow from RW through O-12 and reasonable symmetry of dispersed plume.

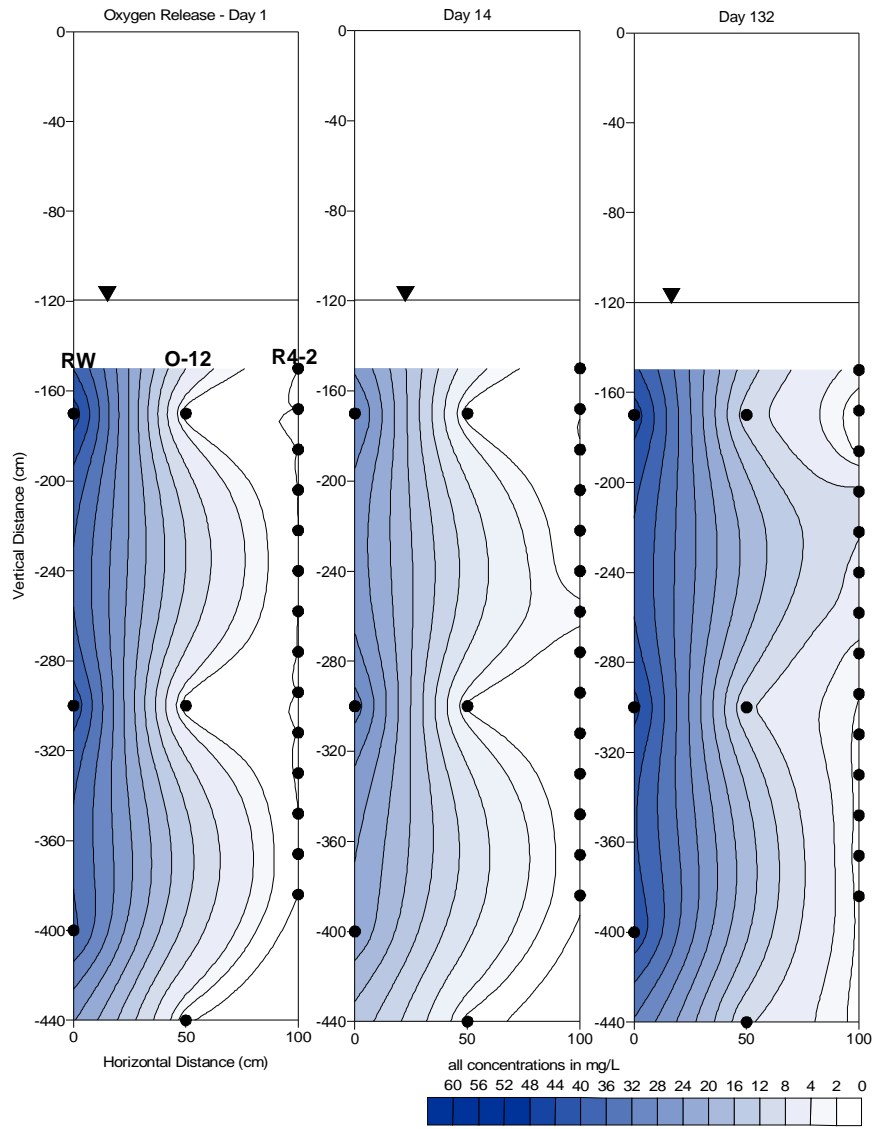


Figure 13 Cross Section of dissolved oxygen concentrations

Release well (RW), O-12 and R4-2 (multilevel) Day 1, 14 and 132.

6.0 Oxygen Release Field Experiment 3

A third oxygen release experiment was completed to determine the effect of BTEX in the groundwater on the development of an oxygen plume. This experiment was operated in the same manner as experiment 2 with the exception of the installation of six additional stainless steel drive points (as described in section 3.1) and the total duration of the experiment was only 29 days. Samples for total BTEX, pH, alkalinity and total iron were collected along with dissolved oxygen on days 0, 7, 17, 24 and 29. All collection and analysis methodology was described in Sections 3.3.1 through 3.3.7.

6.1 Findings

6.1.1 Oxygen Release

The dissolved oxygen results mimicked the results gathered in the previous passive release experiment. Oxygen was detected in the release well at the start of the experiment at a concentration of 27.5 mg/L and continued to increase to a concentration of 44 mg/L (day 29). Over the 29 day duration of the experiment oxygen was only detected in well O-12 and in various sampling points in R4-2 multilevel. No oxygen was detected in any of the drive points installed on either side of O-12 or R4-2 (Figure 14), indicating that the oxygen plume remained very thin in width.

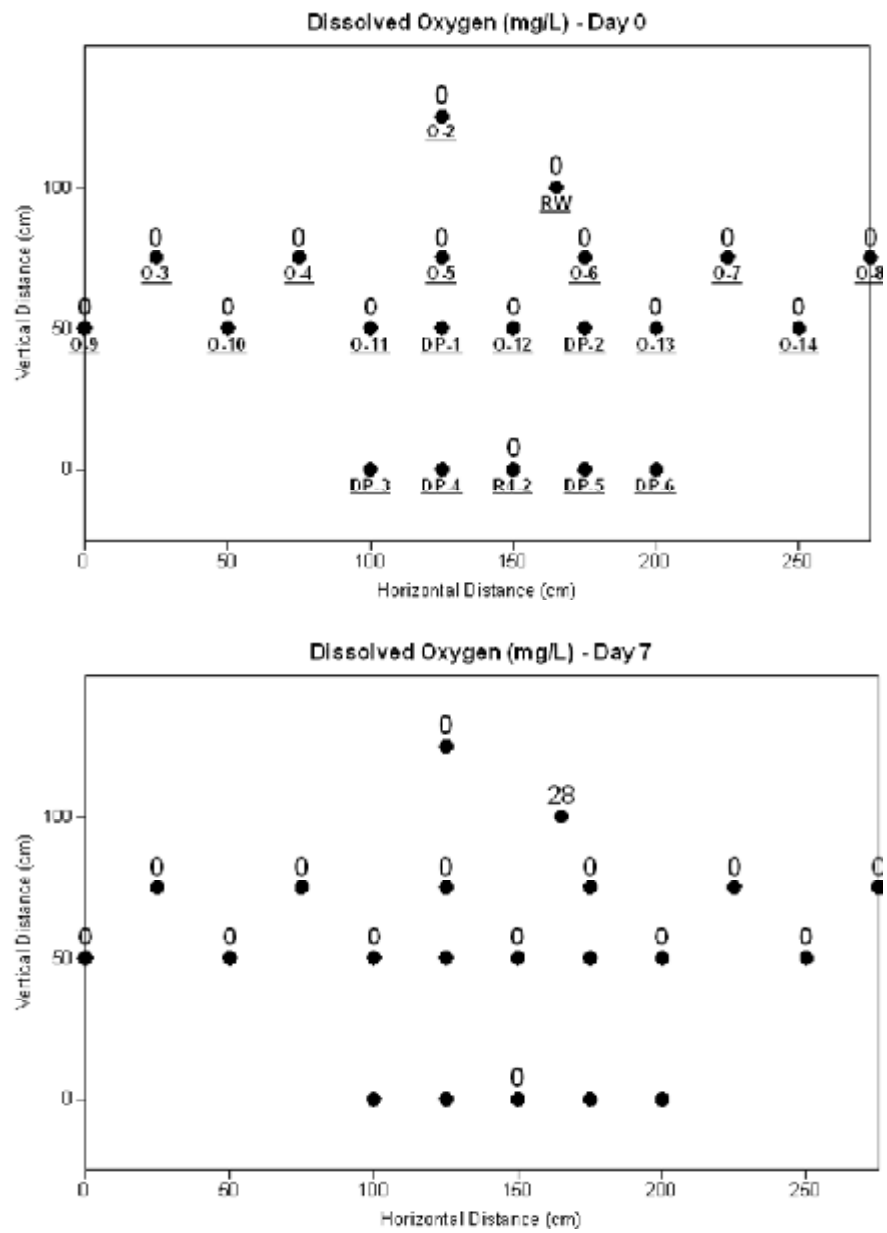


Figure 14 Maximum dissolved oxygen concentrations, day 29, Experiment 3.

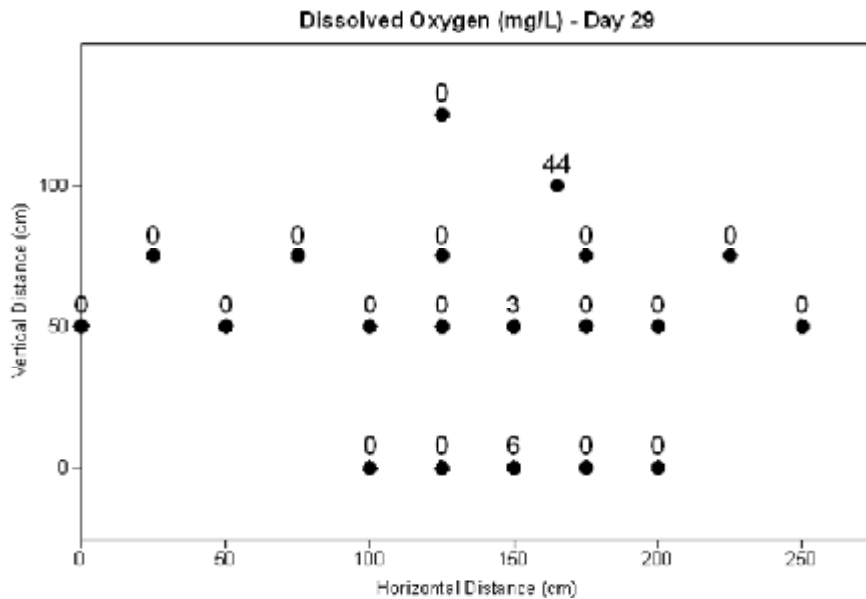


Figure 14 (continued) Dissolved oxygen concentrations, day 29, Experiment 3.

In section 5.2.3, the outcome of the second passive release experiment was that the maximum horizontal width lied somewhere between 25 to 50 cm. With no DO detected at any of the drive points located 25 cm to either side of O-12 and at O-6 which is approximately 10 cm to the west of the release well, we can conclude that within a distance of 50 cm from the release well the maximum horizontal distance lies between 10 and 25 cm. Drive points were also installed 1 m downgradient of the release well 25 and 50 cm on either side of R4-2. No oxygen was detected at the drive points but oxygen was detected at various points on R4-2, ranging in concentration from 1.7 to 5.9 mg/L. This indicates that the maximum horizontal width of the oxygen plume remained within a 10 to 25 cm width, 1 m downgradient of the release well. A plume width ranging between 10 and 25 cm would be consistent with Borden transverse dispersivity within a 1 m travel distance of a release well.

6.1.2 Effect of BTEX – Mass Balance

Groundwater samples were collected prior to oxygen release to determine background concentrations. The dissolved gasoline plume (as described in section 3.2) has been in place since 2004. The BTEX plume flowed directly down the middle of the gate and concentrations were temporally variable due to differing rates of dissolution of BTEX components from the dissolved source located approximately 17.5 m upgradient (Figure 15).

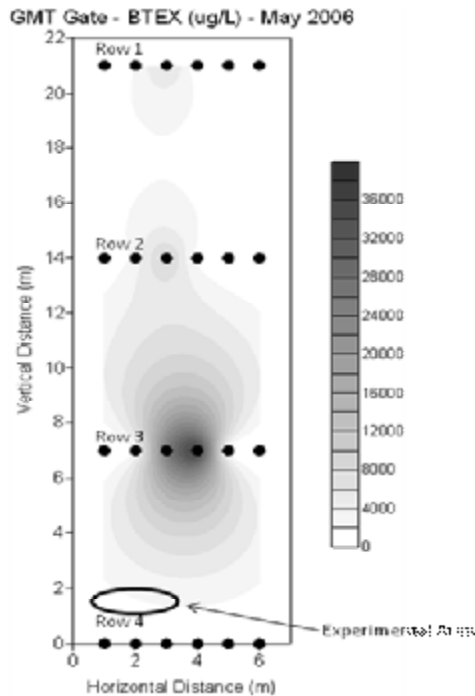


Figure 15 Plan View of maximum BTEX concentrations

In the multilevel wells in the GMT Gate during experiment 3.

BTEX concentrations prior to the start of the third experiment ranged from 11 $\mu\text{g/L}$ to 241 $\mu\text{g/L}$ (Figure 16) with the highest concentrations detected at the wells located closer to the middle of the gate (O-7, O-8, O-13 and O-14). It was difficult to determine if BTEX degraded during the experiment due to fluctuating BTEX concentrations entering the treatment area. Therefore, only the BTEX results from the release well and R4-2 will be discussed. From day 0 to day 24 BTEX concentrations ranged from 6 to 107 $\mu\text{g/L}$ in the release well. Downgradient concentrations at monitoring point (R4-2) ranged from 0 to 2 $\mu\text{g/L}$ in the same period of time. This indicated that degradation of BTEX was occurring. Oxygen concentrations during that time in the release well ranged from 27 to 43 mg/L and at R4-2 ranged from 0 to 5 mg/L. This large reduction in oxygen concentration likely reflects its usage in the degradation of BTEX. By calculating the average BTEX concentration of each row, we can further see if there was any BTEX degradation occurring. Table 6 summarizes the average BTEX results from the third experiment. Within 7 days the average BTEX concentrations in the first row (wells O-3 to O-8) reduced from 52 to 30 mg/L and in the second row (O-9 to O-14) the average BTEX concentrations reduced from 45 to 31 mg/L. By day 17 the average BTEX concentrations in both rows further reduced to 26 and 25 mg/L. After 17 days the

rate of BTEX reduction slowed and eventually BTEX concentrations remain fairly constant, in both rows until the end of the experiment. An inverse relationship between the dissolved oxygen and BTEX concentrations can be observed. When dissolved oxygen concentrations increase there is a decrease in BTEX concentrations, but as the dissolved oxygen concentrations decrease so does the rate of BTEX degradation.

	t=0	t=7	t=17	t=24	t=29
WELL ID	22/10/07	29/10/07	08/11/2007	15/11/07	20/11/07
O-3 to O-8	52	30	26	20	23
O-9 to O-14	45	31	25	25	28

Table 6 Average BTEX concentrations ($\mu\text{g/L}$) in row 1 and row 2.

This can be further studied by looking at the mass balance of BTEX. It requires approximately 3 mg/L of oxygen to degrade 1 mg/L of BTEX (Wilson et al. 1997). Since the highest concentration of BTEX observed during the field experiments was 107 $\mu\text{g/L}$ in the release well, there should be more than enough oxygen present for utilization in the aquifer. At times BTEX was detected at R4-2 at concentrations no higher than 5 $\mu\text{g/L}$ and dissolved oxygen concentrations of 12 mg/L. Therefore there was sufficient dissolved oxygen present in the groundwater to degrade the BTEX within the test area and to overcome the high soil chemical oxygen demand which was determined in section 4.2.1 to be present at the Site.

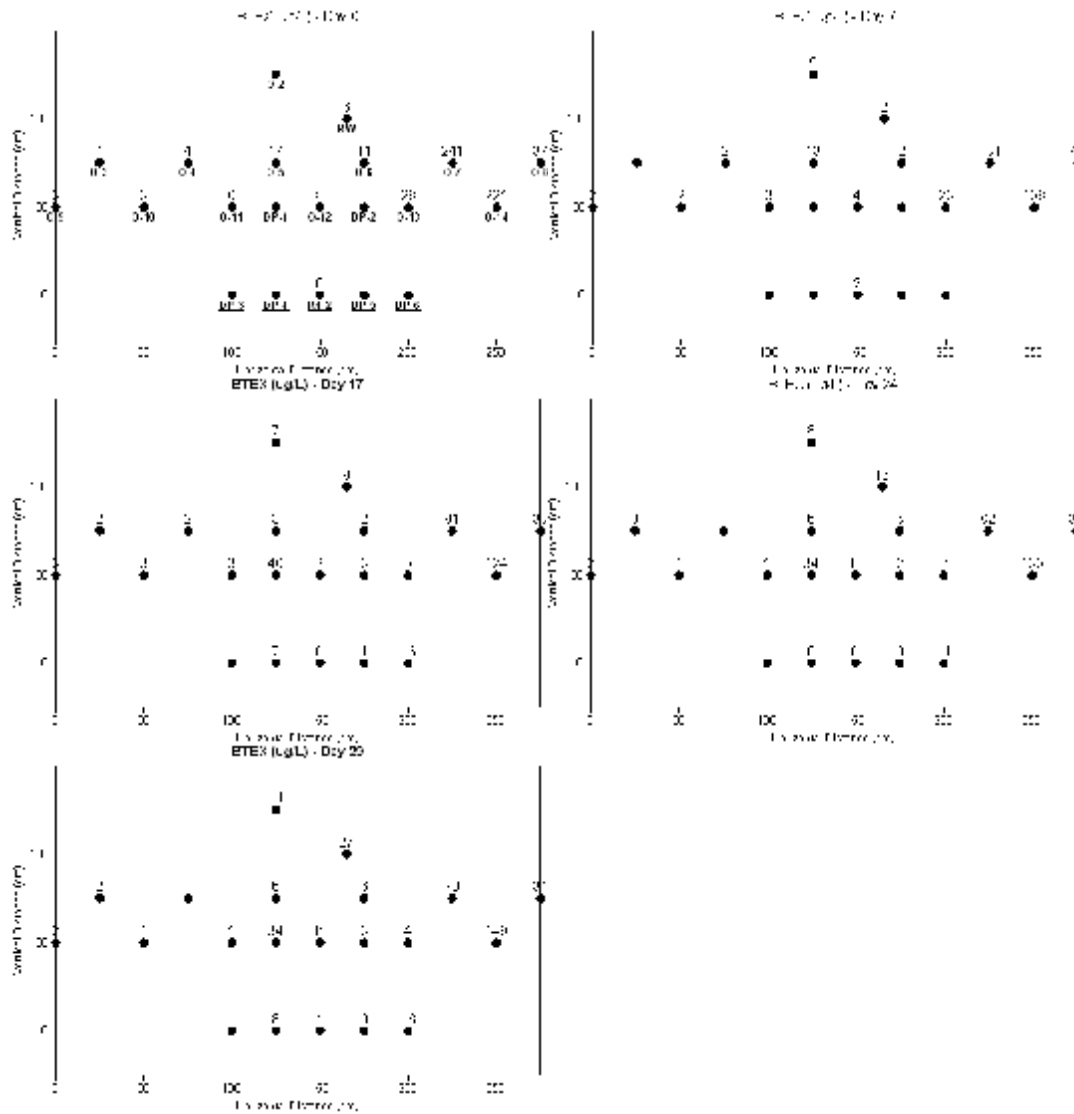


Figure 16 Maximum BTEX concentrations ($\mu\text{g/L}$) from Experiment 3.

6.1.3 Alkalinity Changes

Figure 17 shows the alkalinity results for this third experiment. Background alkalinity at the site ranged from 111 to 138 mg/L. At day 7, the overall alkalinity increased at all sampling locations, ranging from 130 to 155 mg/L. By day 17 the alkalinity analysis indicated that there was increased carbon dioxide produced in locations where oxygen was present, at the release well, O-12 and R4-2. This trend was observed for the duration of the experiment. Generally, as alkalinity concentrations increase an increase in pH can also be observed. The pH results did not alter significantly throughout the experiment (Figure 18). Background pH was approximately 7.6, where oxygen was observed a 0.2 decrease in pH was observed (~ 7.4). This slight decrease in pH observed over time

at 0-12 and R4-2 is within the probe's specifications. Anomalous high pH of approximately 8 was detected at RW-2 on day 7 and at O-10 on day 17, this is not considered significant, it was noted that the sample was very silty and could have interfered with the probe. In this case the relationship between increasing alkalinity and pH is not conclusive.

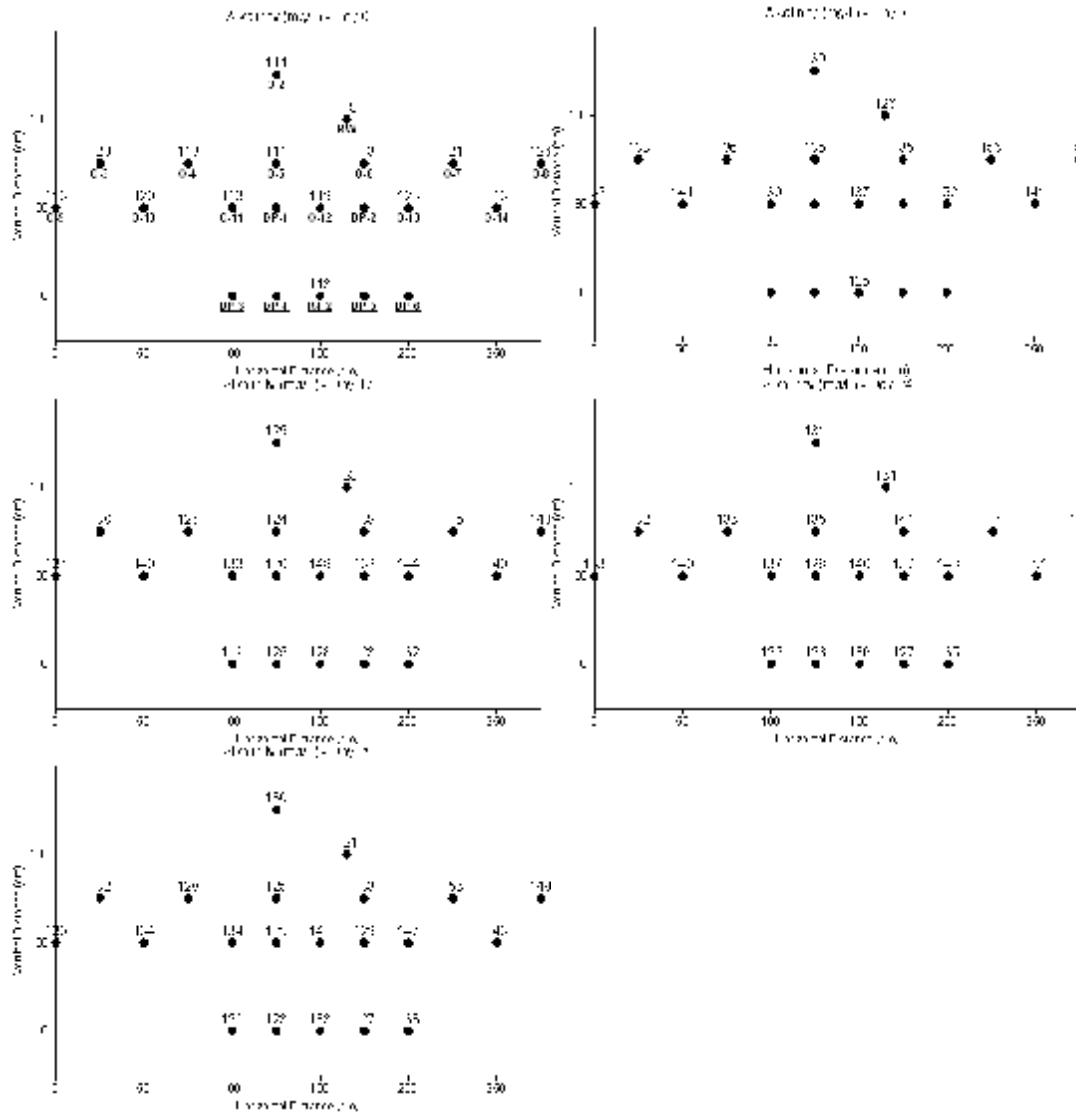


Figure 17 Maximum alkalinity concentrations (mg/L) from Experiment 3.

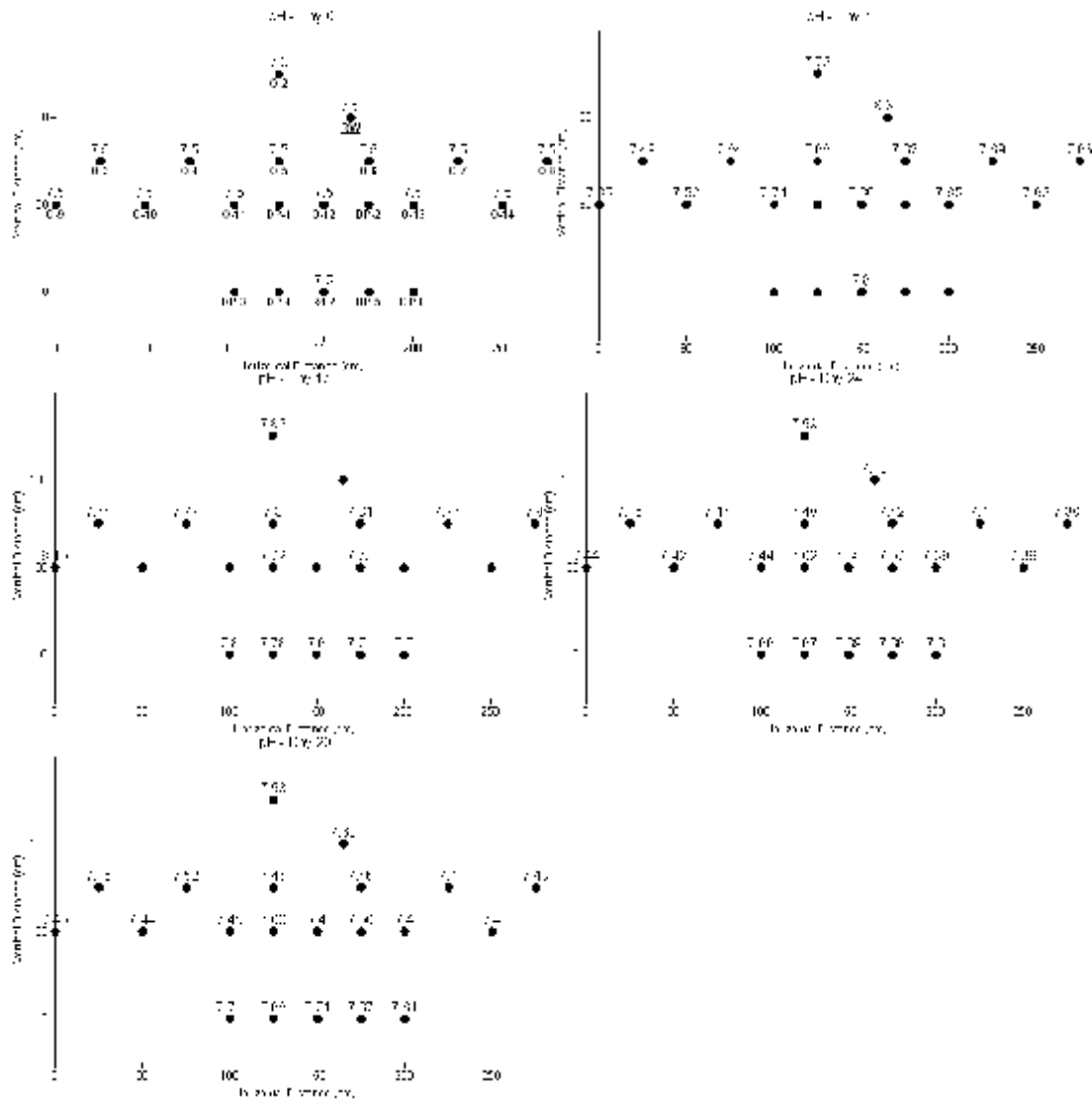


Figure 18 Maximum pH results from Experiment 3.

High alkalinity was also observed at well O-7, O-8, O-13 and O-14, which is where the highest concentrations of BTEX were observed. When comparing the average alkalinity and BTEX concentrations for rows 1 and 2 we see an inverse relationship (Figure 19). As BTEX concentrations decreased, alkalinity concentrations increased, indicating that carbon dioxide is being produced as a byproduct of aerobic biodegradation of the BTEX.

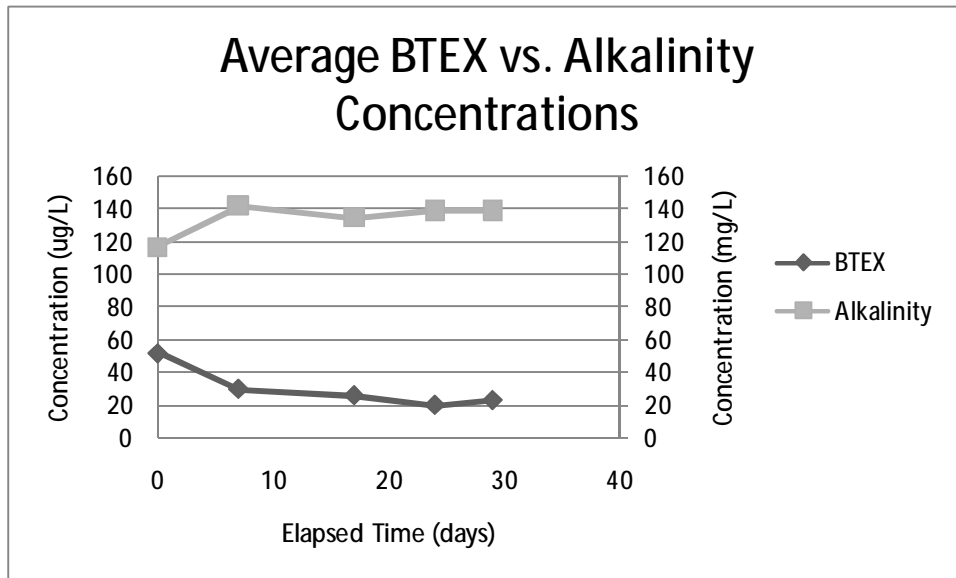


Figure 19. Plot of Alkalinity and BTEX concentrations from Experiment 3.

6.1.4 Iron

Total iron concentrations were very low throughout the entire experiment (Figure 20). Background concentrations ranged from 0 to 0.14 mg/L at 0-9. The high iron concentrations detected at 0-9 is likely due to the wells close proximity to the metal sheet-pile wall. Well 0-9 is only approximately 50 cm way from the sheet-pile. Over time, oxidation of the sheet-pile will occur, resulting in an increase in iron concentrations along the length of the wall. Also, some higher total iron concentrations (~1 mg/L) were observed sporadically at various wells throughout the experiment. On average the background total iron concentration in the monitoring network was 0.02 mg/L (Figure 20). This is not considered to represent a general increase in the total iron. Iron in the subsurface is not considered a sink for the dissolved oxygen as total iron concentrations remained fairly constant throughout the experiment.

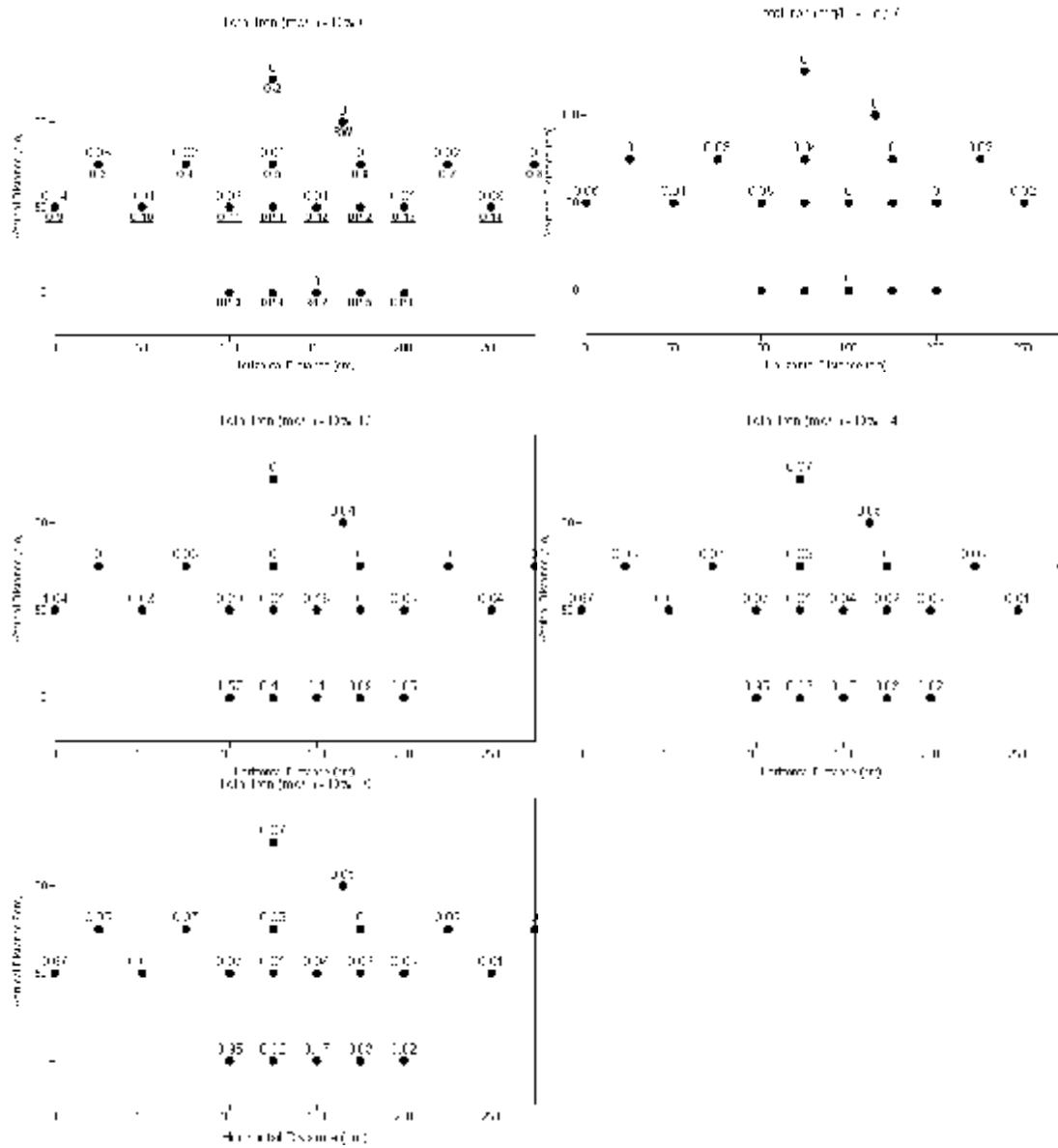


Figure 20 Total iron results from Experiment 3.

6.1.5 Findings of Experiment 3

The results of the BTEX, total iron, pH and alkalinity analysis during the third experiment indicated that only a portion of the dissolved oxygen plume was being consumed for BTEX degradation, as DO was detected at the downgradient multi-level R4-2. As indicated in Section 4.0, oxygen is initially utilized to satisfy the natural oxygen demand of the aquifer before the dissolved oxygen can be available for utilization for contaminant degradation.

Total iron concentrations were measured to assess if the dissolved oxygen was being utilized for iron oxidation. Low total iron concentrations were detected throughout the experiment, with the exception at well O-9, which is likely attributed to oxidation of the nearby sheet-pile wall. These results indicate that any available dissolved oxygen was not utilized for iron oxidation and therefore at this site iron cannot be a limiting factor in the growth of the dissolved oxygen plume.

The effect of BTEX in the groundwater as a limiting factor on the development of an oxygen plume was also assessed. There appears to be a significant depletion of BTEX in the oxygenated zone. The results indicated that when there is excess dissolved oxygen in the aquifer only a small portion of the DO was utilized for BTEX degradation. The dissolved oxygen concentrations remained low downgradient of the release well, while decreasing average BTEX concentrations and increasing average alkalinity concentrations across the Site indicate that BTEX degradation was occurring. Dissolved oxygen was still detected 1 m downgradient of the release well at R4-2 after 29 days. This indicates that BTEX degradation was a factor in limiting the maximum extent of the dissolved oxygen plume.

6.2 Summary and Conclusions of Passive Release Field Trials

Due to equipment failure not much can be concluded from the first passive release experiment, only that there are many processes in the subsurface which will act as an oxygen demand outside of biodegradation. In order for oxygen utilization by subsurface microbial populations to occur the natural biological, chemical and total solid oxygen demand must be overcome before any of the oxygen can be utilized for remedial purposes.

The second experiment focused on determining the possible maximum horizontal width of the oxygen plume. Dissolved oxygen was released for a total of 132 days, in that time oxygen was detected in a very limited area. From these observations we could conclude that the maximum horizontal width of the oxygen plume could range from 25 to 50 cm. A narrow dissolved gas plume was observed from the results of a SF₆ tracer test done prior to the oxygen release using the Waterloo Emitter™. The dissolved oxygen plume had a similar horizontal distribution to that of the SF₆ distribution, again less than 25 to 50 cm. A more detailed monitoring network and investigation into other oxygen utilization processes would be required to make a more accurate estimation of the plume width.

The final passive release experiment focused on the usage of the released oxygen for BTEX biodegradation purposes. With the installation of drive points 25 cm on either side of O-12 and R4-2 we were able to conclude that the oxygen plume created was less than 25 cm in width. When all of the pH, total iron, alkalinity, BTEX and dissolved oxygen results are combined it is apparent that some of the released oxygen is being utilized for the degradation of BTEX which has limited the oxygen plume's downgradient concentration.

In all three experiments the maximum width of the dissolved oxygen plume remained between 10 and 25 cm, indicating that within 1 m of a release well the width of a plume is limited by transverse dispersion and likely also by oxygen utilization for COD and BTEX oxidation.

7.0 Injection of Oxygenated Water

To further investigate the radial distribution of introduced dissolved gases two additional experiments were conducted. These experiments involved sparging an oxygen/SF₆ blend gas into a known volume of water and then injecting it into the aquifer via the release well. It is presumed that if a slug of water is injected into a well it will displace or push the native groundwater a certain distance away from the release well. Assuming the presence of horizontal flow, the injected water would move with the natural gradient, amending a greater volume of groundwater than by a passive release (Figure 21a and 21b).

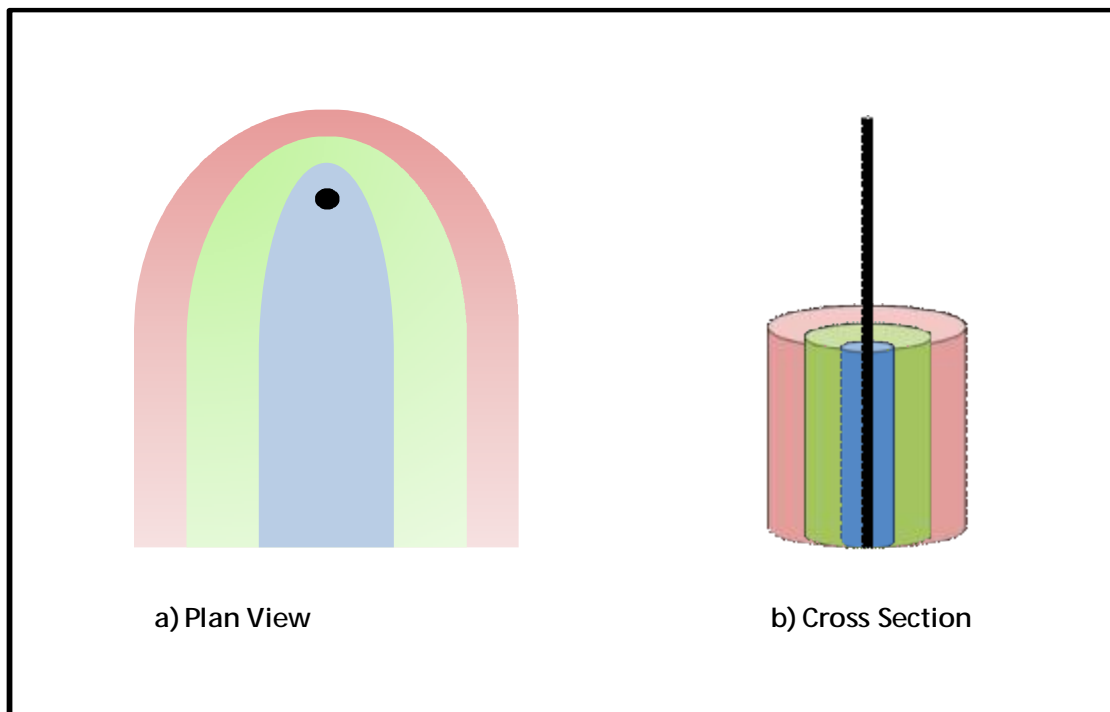


Figure 21 Radi of different volumes of injected water.

Simple volumetric calculations were completed (Table 7) to determine the volume of injected water (the “slug”) required to extend the slug a specific distance from the well screen. The calculations were done using the length of the well screen (4.26 m) as the height of the injected slug, and various radii. For example, in order to push groundwater into the aquifer 25, 50 or 200 cm, one would have to inject 210, 840 or 13 400 L of water, respectively. Due to layering and the typical heterogeneity of the subsurface geology preferential pathways or vertical movement of the injected water can occur, resulting in an unsymmetrical injection imprint.

Injecting water has potential drawbacks, such as raising of the water table. If the contaminant of concern is a light non-aqueous phase liquid (LNAPL), like gasoline, it could be spread vertically or smeared by the rising water table. Also, mounding could locally increase the horizontal gradient and so could “drive” free or mobile LNAPL away from the injection well, the contaminant plume or even bring it to the surface. The total injection time is also a factor to consider when injecting water amended with dissolved gases. If the injection time is long then the remedial gases could come out of solution before the amended water is injected into the aquifer, resulting in the injection of water with no tracer gas. A balance between preferred size of treatment area and time is required.

Diameter (cm)	Radius (cm)	Volume (L)
5	2.5	9
25	12.5	210
30	15	302
40	20	536
42	21	591
50	25	839
200	100	13405

Table 7 Volumes of injected water based on different radii.

To insure detection of the tracer in the well closest to the release well (O-6), injectate diameters of 25 and 42 were targeted for the field trials. The injection experiments were performed in the same experimental site as the iSOC™ passive release oxygen trials, prior to the installation of the additional drivepoints as described in section 3.1.

7.1 Injection Experiment 1: Injection of 210L

Approximately, 210 L was collected into a plastic above ground storage tank and was sparged with an oxygen/SF₆ blend gas for 2 hours. To prevent raising the water table and the possibility of the sparged water from overflowing in the release well, the sparged water was slowly injected into the release well using a Masterflex™ peristaltic pump; at a maximum rate of 1 L/min over 3.5 hours. Samples of the injected water were collected before and close to the end of the injection to insure that the SF₆ did not volatilize during the injection period. This injection was repeated on day 3. Samples were collected on days 1, 2, 3, 4, 7 and 10, using the sample method described in section 3.3.1. All samples were stored at 4°C and analyzed within 14 days of collection.

7.1.1 SF₆ Tracer Results

The results are shown in Figure 22. They indicate that within 1 day SF₆ was detected at a distance of approximately 50 cm, which is double the distance anticipated. Concentrations in the release well and well O-6 ranged from approximately 2200 µg/L to 2700 µg/L. Fifty centimeters downgradient of the release well in O-7, SF₆ was detected at a concentration of 7 µg/L. By day 3, SF₆ was detected at approximately a diameter of 1 meter around the release well. A second injection was done on day 3 in the same manner as before, and before SF₆ samples were collected. The day 3 samples indicated that, with a second injection, an injectate diameter of 1 meter was achieved. By day 4 we begin to see the gradual decrease in SF₆ concentration in the release well, while concentrations 1 m downgradient of the release well in R4-2 begin to increase. Also on day 4 the treatment area returned to a diameter of 50 cm, indicating that if treated water is injected every few days a larger horizontal area of treated water can be maintained.

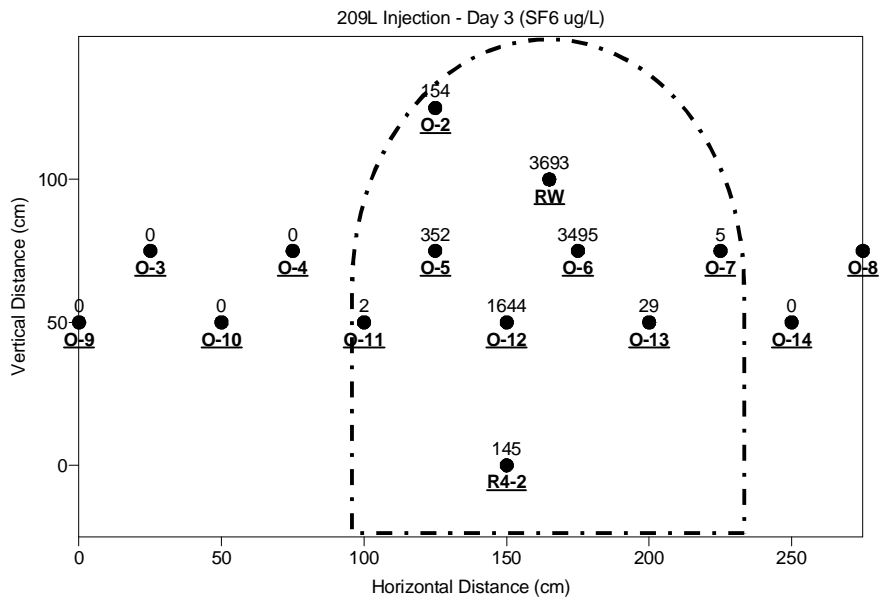
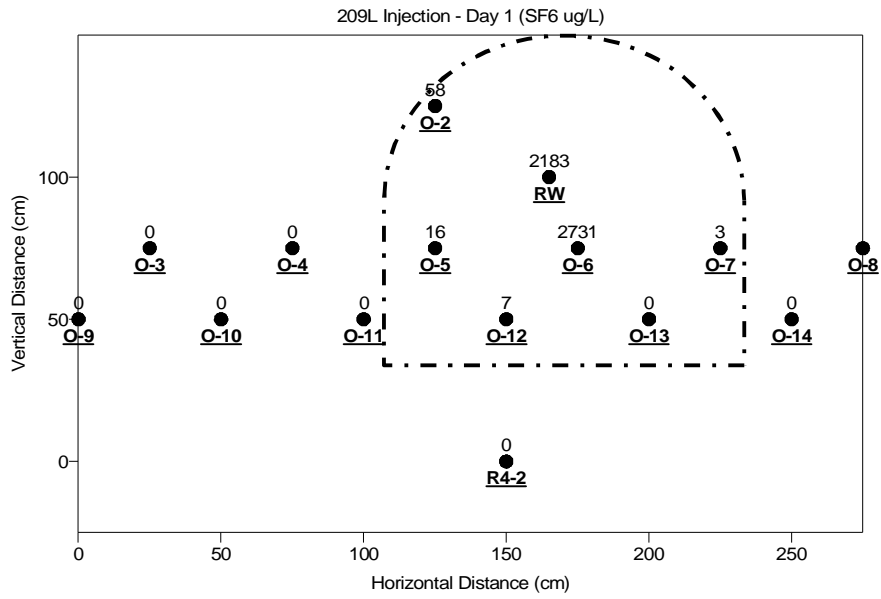


Figure 22 SF₆ results of 210 L injection.

The dashed line indicates the estimated maximum extent of the SF₆ plume.

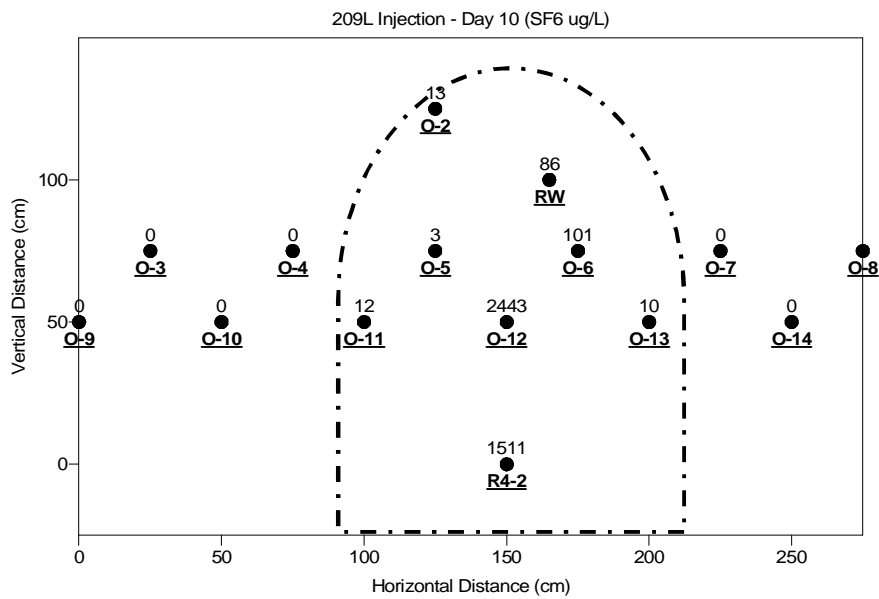
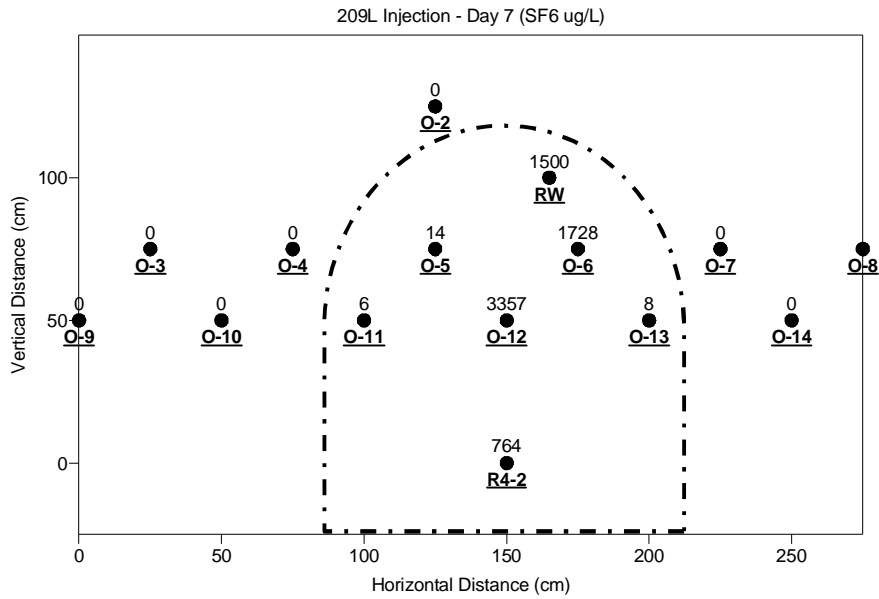


Figure 22 (continued) SF₆ results of 210 L injection.

The dashed line indicates the estimated maximum extent of the SF₆ plume.

7.2 Injection Experiment 2: Injection of 600L

Two months after the first injection of 210 L of SF₆ amended water a second tracer injection was completed. The purpose for the second injection was to increase the treatment area from 24 cm to 42 cm, by injecting approximately 600 L of water. If the same injection rate of 1 L/min was used it

would take roughly 10 hours to inject all of the water, resulting in the dissolution and volatilization of the SF₆ tracer. A larger Masterflex™ peristaltic pump was used which injected the water at a rate of 6.4 L/min. The injection of 600 L took 90 minutes. To monitor the level of the water table, water levels were measured in the release well every 10 minutes for the duration of the injection. Before the injection started the water level was approximately 1.169 m below ground surface (m bgs). During the injection the water table increased to 0.803 m bgs, raising the water table by 0.366 m bgs. Groundwater samples were collected on days 1, 2, 5, 7 and 9; all samples were collected in the same manner as described in section 3.3.1.

7.2.1 SF₆ Tracer Results

The results are shown in Figure 23. On day 1, SF₆ was detected in a 2 m wide by 0.5 m long area, which is greater than the 42 cm diameter distance anticipated. Initial concentrations in the release well and O-6 (25 cm downgradient of the release well) are approximately 1200 µg/L, and SF₆ was detected at wells O-4 and O-7, which define the tracer plume borders, at concentrations of only 6 µg/L. By day 2 the width of the SF₆ plume has reduced in size to a width of approximately 1 m. On day 5 the release well concentration begins to decrease while SF₆ concentrations at downgradient wells begin to increase, indicating that the tracer plume is moving with the groundwater flow. Day 9 was the last sampling event, the width of the plume remained at approximately 1 m, and the highest SF₆ concentration was detected at well O-12 which is 50 cm downgradient of the release well.

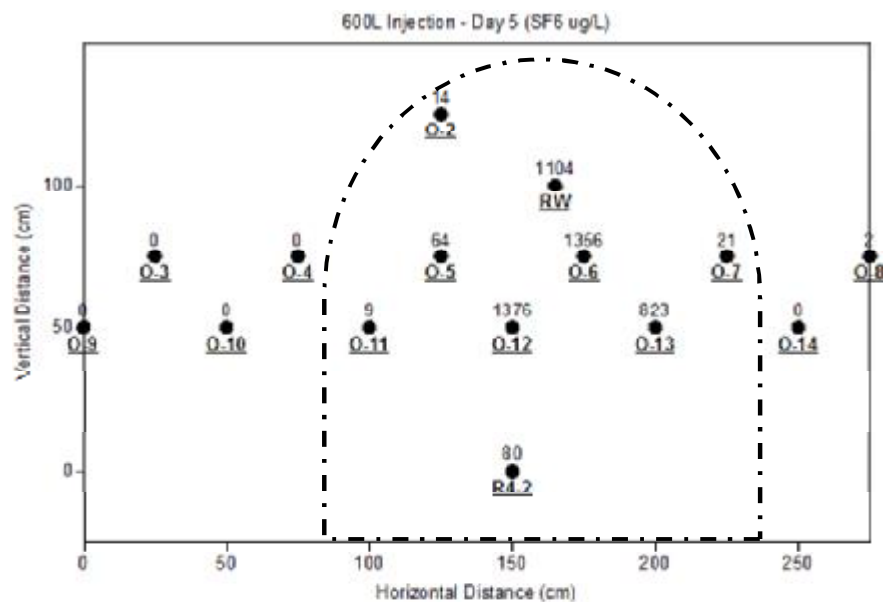
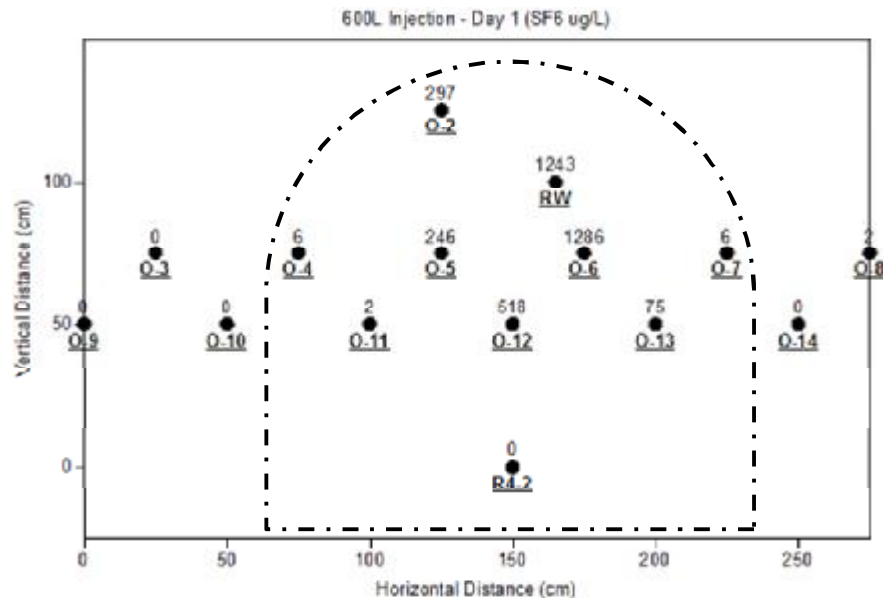


Figure 23 Maximum SF₆ Tracer Results for the 600L injection.

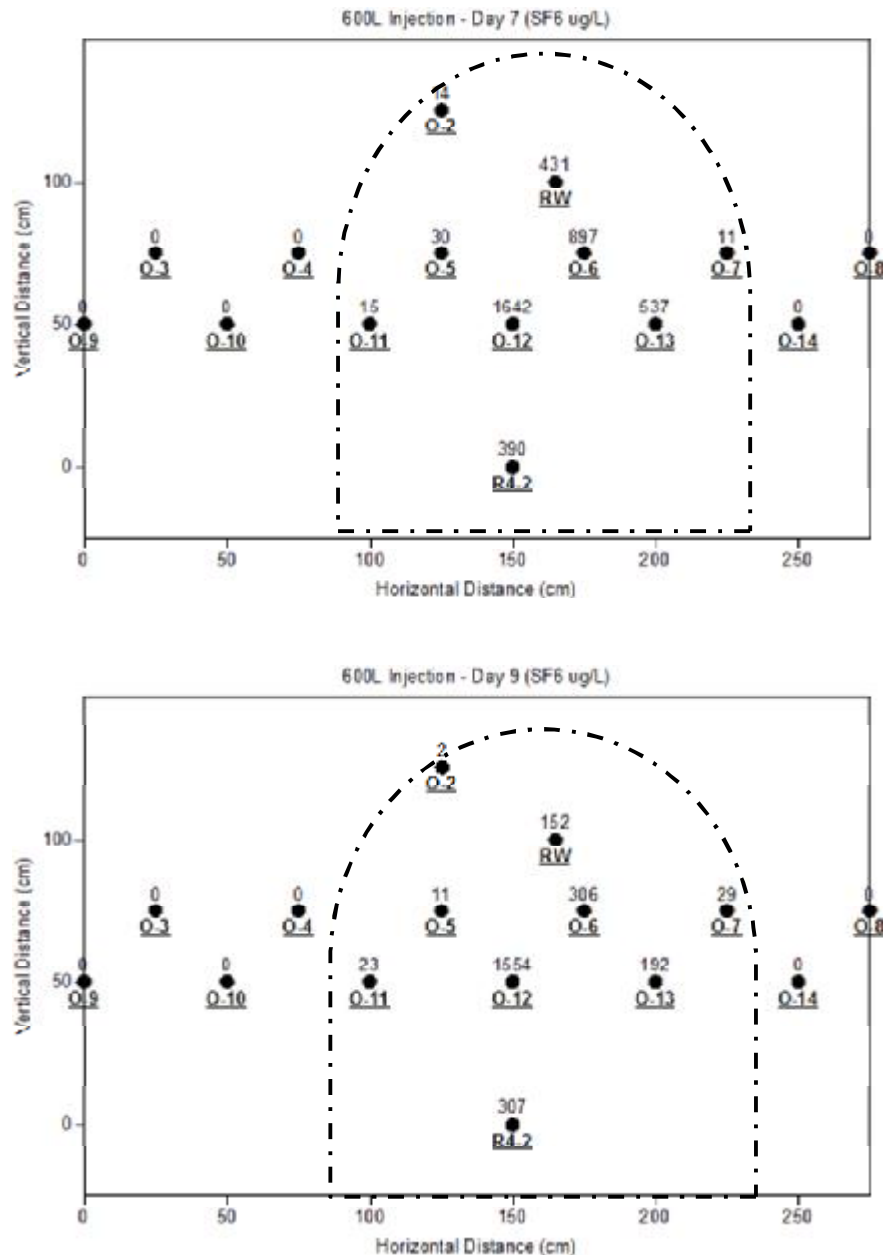


Figure 23 (continued) Maximum SF₆ Tracer Results for the 600L injection.

Dissolved oxygen concentrations were also collected during this experiment to observe how the dissolved oxygen would move throughout the system. As in the previous passive release experiment background concentrations of dissolved oxygen were collected from the wells in the monitoring network and no dissolved oxygen was detected in any of the wells. On day 1 dissolved oxygen concentrations ranged from 19 mg/L in the release well to 3 mg/L in R4-2 (1 m downgradient) (Figure 24). The width of the dissolved oxygen plume was approximately 50 cm.

Over the course of the experiment (9 days) the approximate width of the dissolved oxygen plume remained the same but the concentration of dissolved oxygen quickly decreased. By day 5, a concentration in the release well was 5 mg/L, while at R4-2 it remained at 3 mg/L. On day 9 dissolved oxygen concentrations were below detection limits. The rapid decrease in concentrations could indicate utilization by subsurface microbial populations for degradation of hydrocarbons present within the monitoring next work, as discussed in section 6.3.

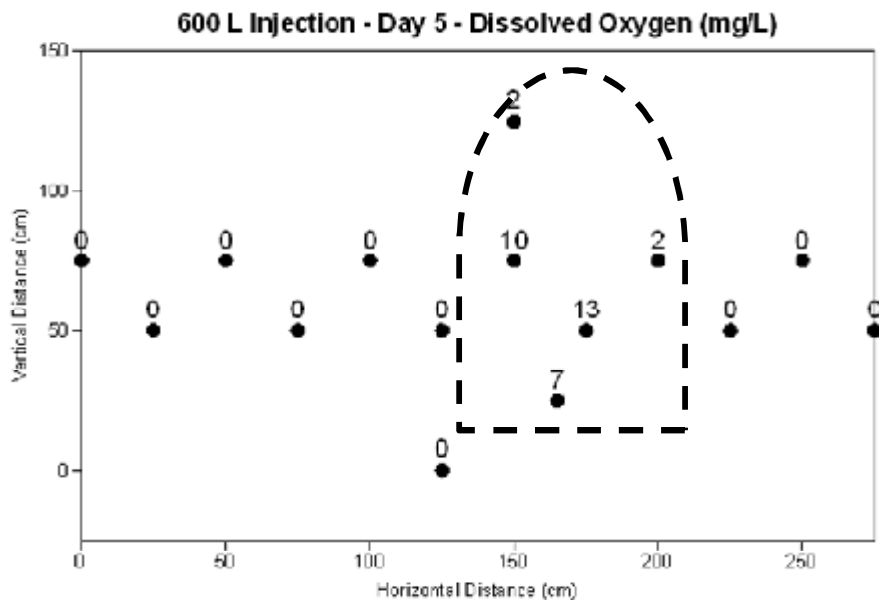
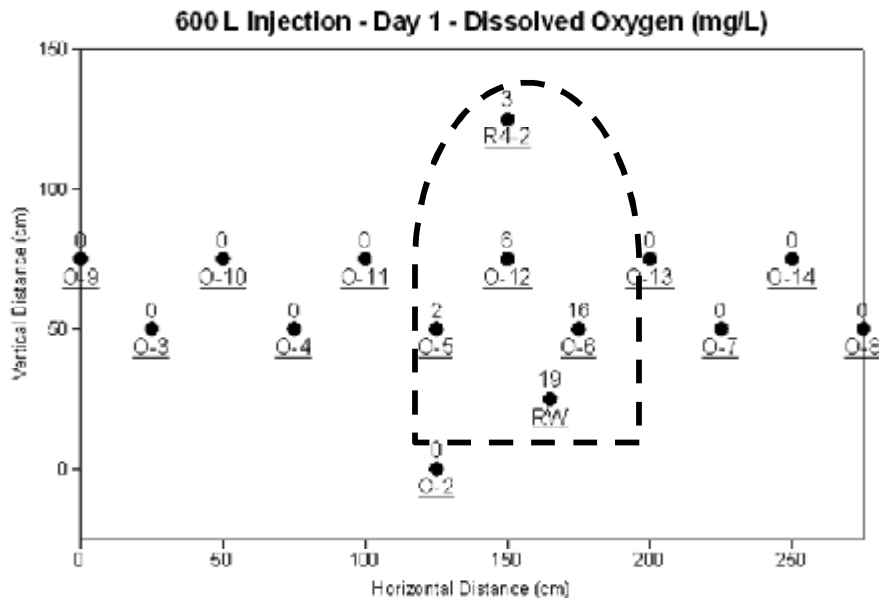


Figure 24 Maximum dissolved oxygen results for the 600 L injection.

Dashed line indicates the maximum extent of the dissolved oxygen plume.

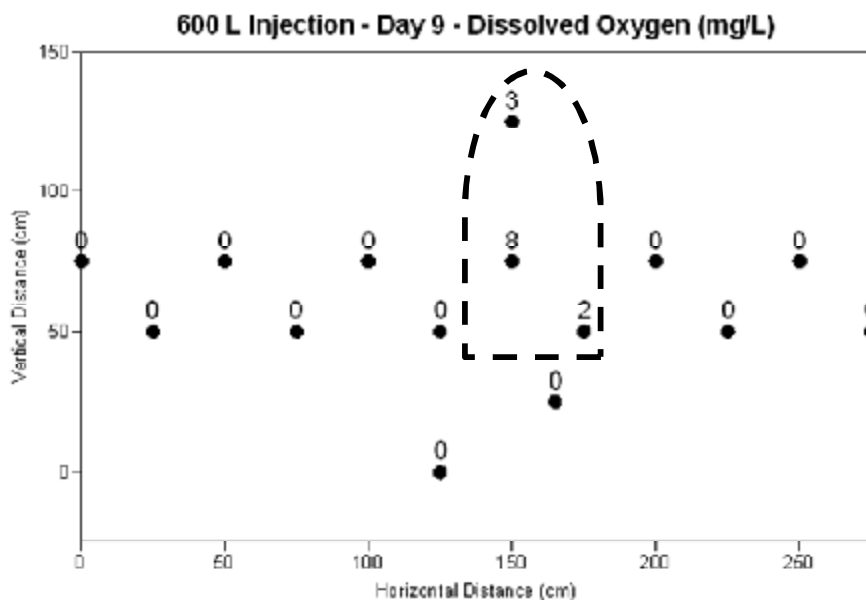
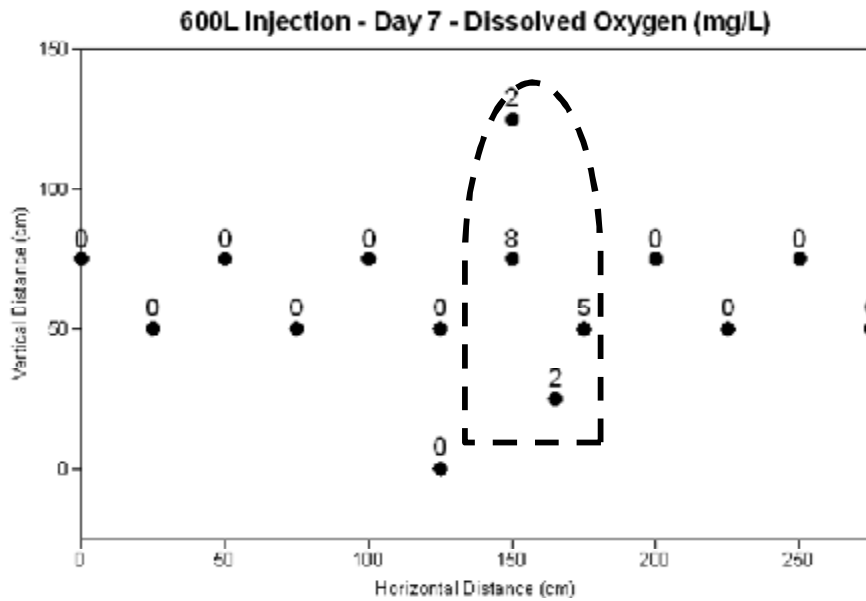


Figure 24 (continued) Maximum dissolved oxygen results for the 600 L injection.

Dashed line indicates the maximum extent of the dissolved oxygen plume.

7.3 Summary of Discussion of Injection Experiments

The injected SF₆ tracer was detected beyond the target diameters of 24 and 42 cm, which reflects the simplistic volumetric calculations shown in Table 7. Clearly, heterogeneities allowed some tracer water to migrate further than anticipated based on a homogenous aquifer model. It is

unknown why the SF₆ was detected at double and triple the distance away from the release well. It was observed that once stabilized, the width of the tracer plume did not change with time. As the tracer plume migrated with the groundwater, the tracer plume width remained the same but the concentrations decrease with distance.

During the first injection experiment, a second slug of 210 L was injected on day 3, resulting in an increase in the SF₆ plume width. By the next day the width reduced to its previous size, indicating that a greater area could be targeted through periodic injections of amended water and thus treating a greater volume of contaminated groundwater. Periodic injections of amended water (whether it is a gas or nutrient) would maintain a more constant concentration of oxygen in a wider area than by a single injection or by passive release of gases.

The effective diameter of dissolved oxygen plume created during the 600 L injection was approximately 50 cm (radius of 25 cm) which is ¼ the size of the SF₆ plume. According to Table 7 one would have to inject approximately 840 L to obtain a radius of 25 cm. If a greater radius is desired either consecutive injections need to be conducted or greater volumes of dissolved oxygen amended water would have to be injected.

8.0 Modeling of Passive Release from a Well

Results from the passive release experiments 2 and 3 were very similar. In each experiment very narrow plumes of oxygen were observed within 1 m of the release well. A definitive maximum horizontal distance of the plume was impossible to determine, due to restrictions on well placement and the presence of BTEX in the test area. Borden field parameters were applied in a numerical modeling program called Hydrogeosphere (Therrien and Sudicky, 2007.) to evaluate if the presence of BTEX could have hindered the horizontal growth of the oxygen plume (Table 8).

Hydrogeosphere is a 3-D modeling program which simulates flow and contaminant transport in the subsurface (Therrien and Sudicky, 1996). It incorporates advection, dispersion, and diffusion into the formulas and allows for flow in both the porous matrix and in fractures. It uses the Newton-Raphson linearization technique which enables the program to model situations in which the hydraulic properties vary by a number of orders of magnitude and also applies the standard time-marching Galerkin method as a part of the solute transport equation (Therrien and Sudicky, 1996).

8.1 Modeling simulations

The first simulation is based upon the assumption that there is no utilization of the released oxygen. The aquifer is a homogeneous medium fine sand, oxygen saturation is 45 mg/L at an average groundwater temperature of 13 °C and Borden hydrogeological parameters are as detailed in Table 6. The monitoring well network use in the simulation is identical to the network used for the field experiments at CFB Borden. The simulation was run for the same length of time as the field trials, 132 days. Results are presented in Figures 25 and 26.

Velocity	9 cm/day
Hydraulic Gradient	0.0043
Porosity	0.33
Longitudinal Dispersivity	0.08 m
Transverse Dispersivity	

* all parameters from Freyburg (1986)

Table 8 Assumptions for Simulation 1 and 2 using Hydrogeosphere.

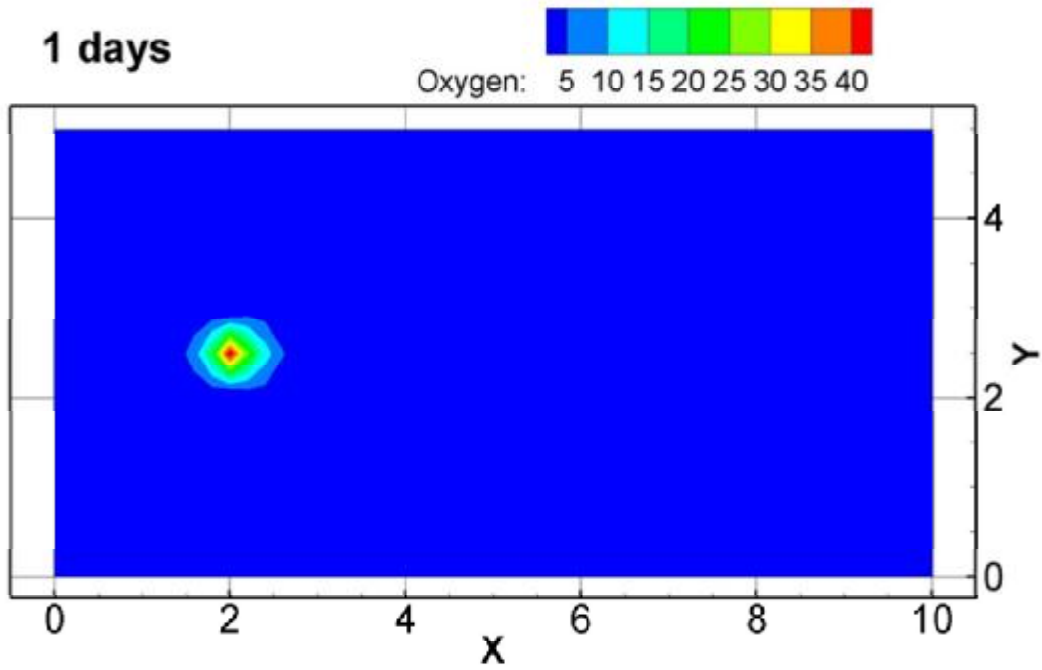
The second simulation introduces the utilization of the oxygen during biodegradation. Hydrogeosphere has a half-life formula which can be applied to the model to factor in the usage of the released dissolved oxygen into the aquifer system. This half-life formula allows the model to present the effect of degradation on a growing plume in a simple manner. As discussed in Section 1.3 a half-life of up to 7 days is demonstrated to reduce the saturated oxygen concentrations the groundwater by half, if 45 mg/L of dissolved oxygen is being released, after 7 days the concentration would be reduced to 22.5 mg/L. Therefore a dissolved oxygen half-life of 7 days was assumed for this simulation. All other assumptions concerning the oxygen saturation, temperature and hydrogeologic parameters remain the same as in the first simulation.

8.1.1 Simulation 1 - Results

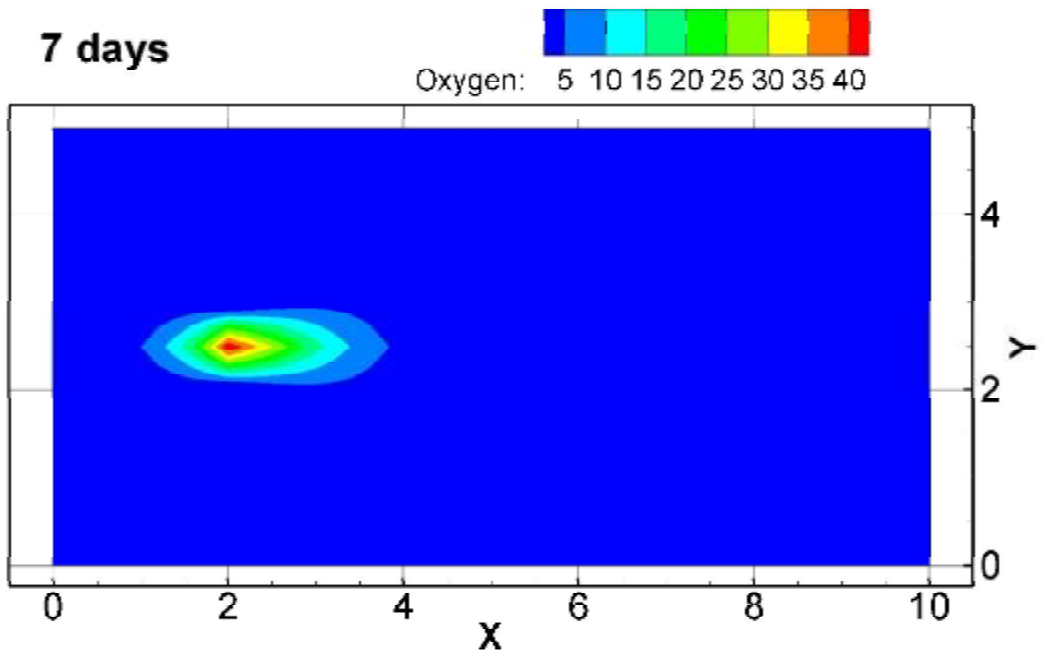
The distribution of oxygen from simulation 1 on days 1, 7, 14 and 132 days are presented in Figure 26. On day one, oxygen concentrations in the release well were approximately > 40 mg/L and at the monitoring points in O-6 only, at between 5-10 mg/L. The DO plume is approximately 50 cm in length and 30 cm in width. After 7 days, the DO concentration in well R4-2, located 1 m downgradient from the release well, were at >5 mg/L, at monitoring well O-6 and O-12 at concentrations of 25 mg/L to 30 mg/L and 15 mg/L to 20 mg/L, respectively. The maximum width of the plume was approximately 75 cm at R4-2, but the width in and around the release well remained the same at approximately 50 cm. The total length of the plume, measured from the release well to the most downgradient tip of the plume is approximately 2 m. Results for day 14 are similar to day 7 with the exception that the DO concentrations increased at wells O-6, O-12 and R4-2 and that the DO plume has migrated past the monitoring network to an approximate length of 5 m. At day 132 the DO plume is well outside of the simulation area but the width of the plume in and around the release well has remained the same at approximately 50 cm. At R4-2 the plume width has increased to approximately 1 m. The simulation estimates that at 8 m downgradient of the release well the DO plume would have a maximum width of approximately 1.5 m.

If we compare the simulation to the field experiment results we can see major discrepancy in the lengths of the plumes. Also, if the simulations are reasonable representations, the SF₆ plume would have been greater than the 10 to 25 cm width observed during the field experiments. The simulation results suggest that there are other limiting factors other than nutrient utilization occurring, which will effect plume size.

1 days



7 days



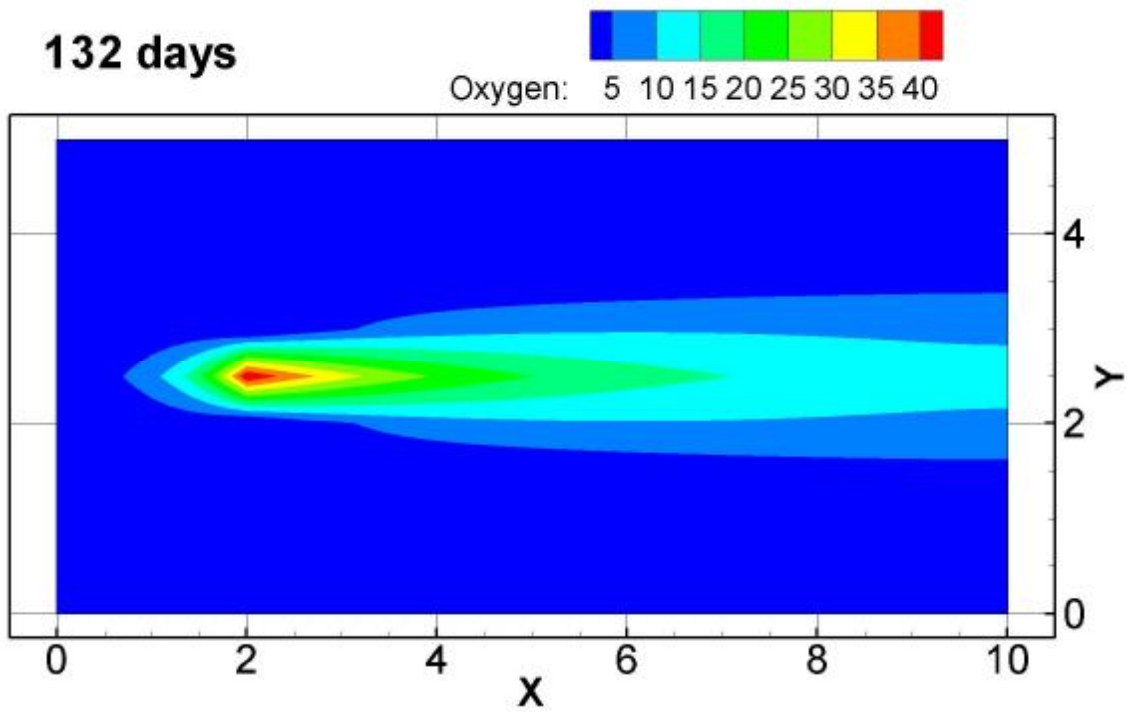
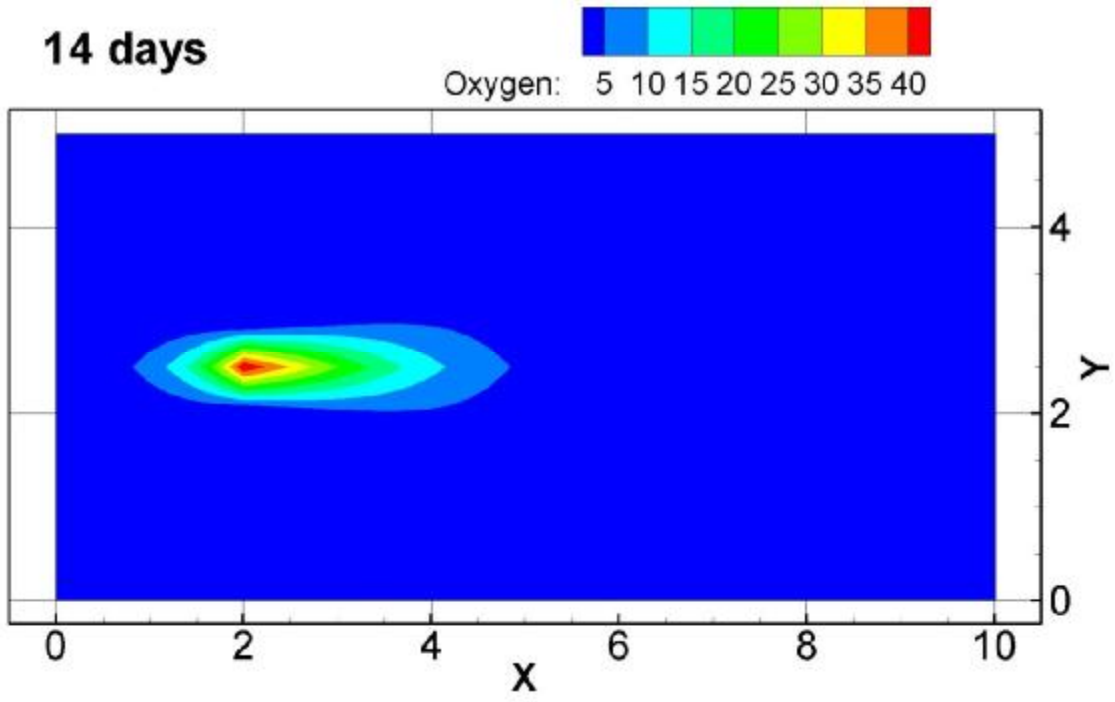
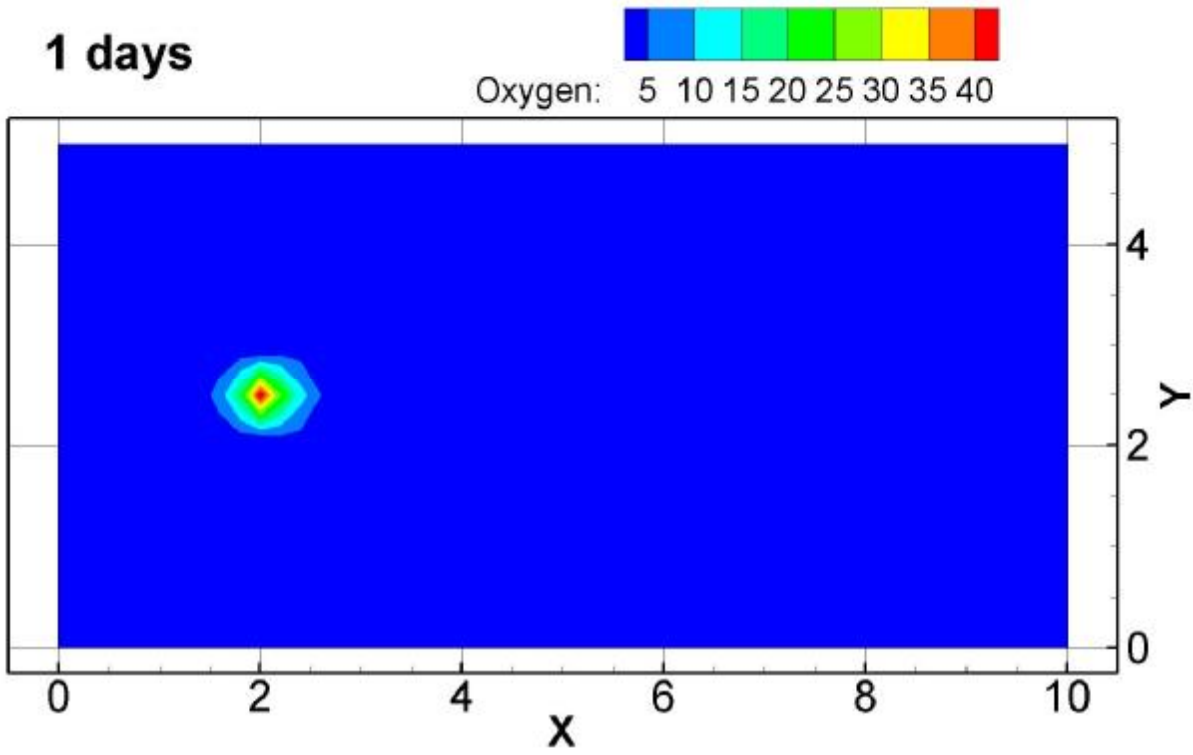


Figure 25 Simulation 1 results, with no decay.

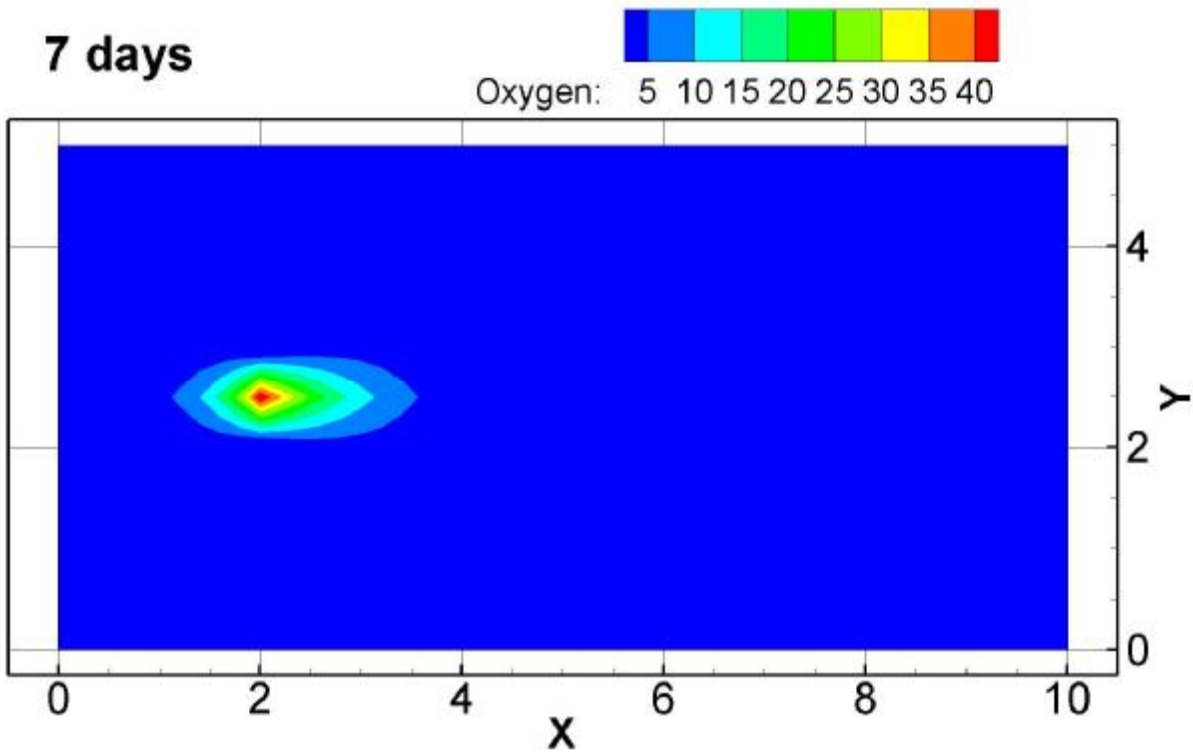
8.1.2 Simulation 2 - Results

The results of the second simulation on days 1, 7, 14 and 132 days are presented in Figure 26. On day one dissolved oxygen concentrations in the release well were at > 40 mg/L and at the first monitoring fence at well O-6 at 10 to 15 mg/L. The DO plume is approximately 50 cm in length and 50 cm in width. After 7 days, the DO plume at R4-2 was at a concentration ranging from 5 to 10 mg/L. DO was also at monitoring wells O-6 (at a concentration of approximately 25 mg/L to 30 mg/L) and at O-12 (at a concentration of 10 mg/L to 15 mg/L). The width of the DO plume at R4-2 was approximately 75 cm but the width of the DO plume at the release well remained at approximately 50 cm. The length of the DO plume (from the release well to the most downgradient tip of the plume) is approximately 1.5 m. Results for day 14 are similar to those on day 7 with the exception that higher concentrations of DO at monitoring wells O-6, O-12 and R4-2, the width of the entire plume is 50 cm (even at R4-2, which on Day 7 had a width of approximately 75 cm) and the total length of the plume increased to approximately 2 m. Day 132 results are very similar to those of Day 14. The width of the DO plume remains at approximately 50 cm and the DO is still only present in the release well, O-6, O-12 and R4-2 at the same concentrations as detected at Day 14. The only change between Day 14 and 132 would be that the DO plume increase to a total length of 2.5 m.

1 days



7 days



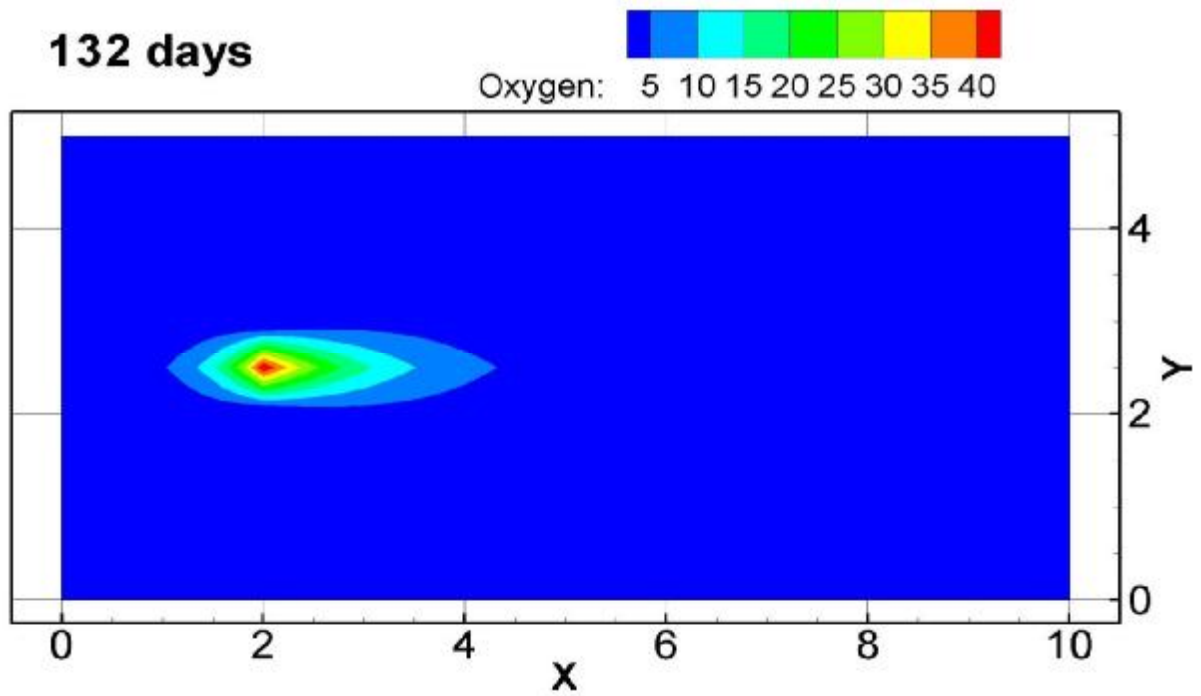
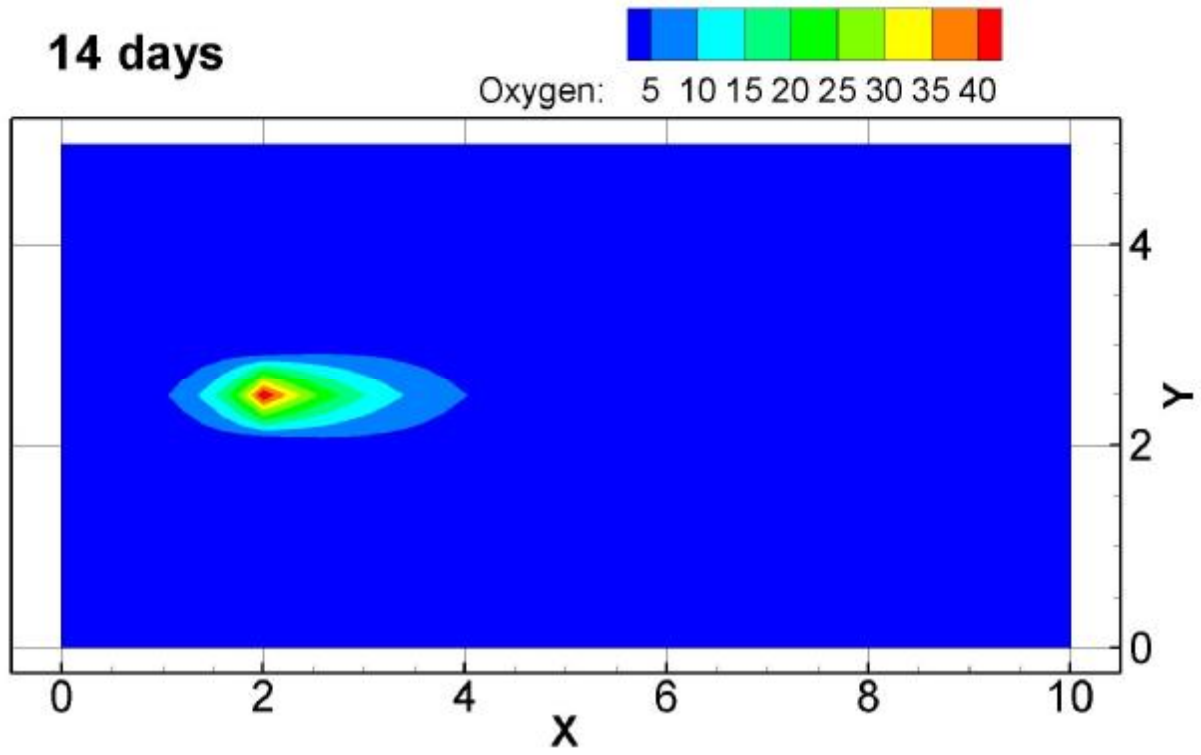


Figure 26 Simulation 2 results, with decay.

8.1.3 Discussion

When comparing the two simulations a few conclusions can be made. Both simulations indicate that the dissolved oxygen will migrate with the groundwater in a similar manner, in that within 1 m of the release well, the DO plume can only reach a maximum transverse extent of 50 cm. In the first simulation in which there was no demand for the oxygen, the DO plume extended to greater than 10 m in length and at the downgradient end the width of the plume reached approximately 2 m. In the second simulation whereby a half-life of 7 days was applied to the DO utilization, DO only extended approximately 2.5 m downgradient of the release well and had a maximum width of 50 cm. It would appear that the presence of an oxygen demand, whether it is either chemical or biological, will limit the length and width of the DO plume.

The simulation results correlated well to the data collected in the passive release field trials detailed in Sections 4.0, 5.0 and 6.0. As with the model simulations no dissolved oxygen was present beyond the width of 50 cm. In fact, during the third field trial where six drive point piezometers were installed at 25 cm intervals away from monitoring wells O-12 and R4-2 with no oxygen present in the drive points after a 29 days of operation. Figures 28 and 29 depict the observed dissolved oxygen concentrations from experiment 2 with simulation 1 and 2 results superimposed. The simulations predicted a larger maximum area of extent than what actually occurred in the field. This could be attributed to the fact that in the field there were low levels of hydrocarbons present at the site, increasing the demand of oxygen, which was not factored into the model. The utilization of the injected nutrient, in this case oxygen has a enormous effect on plume development. Therefore, if there was no oxygen demand at the field site a much larger (in width and in length) with higher concentrations of dissolved oxygen would be observed. But this does not account for the discrepancy between the simulation results and the tracer experiment.

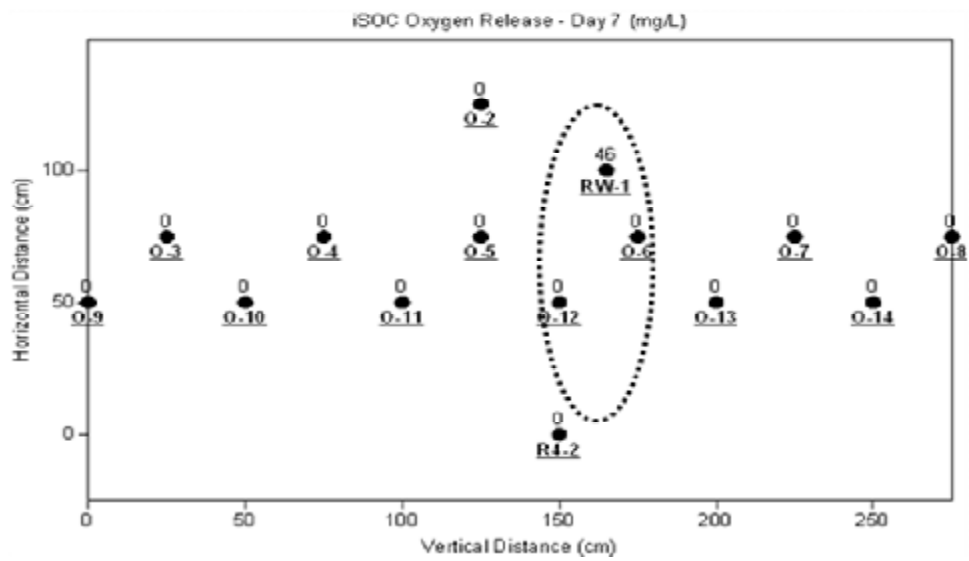
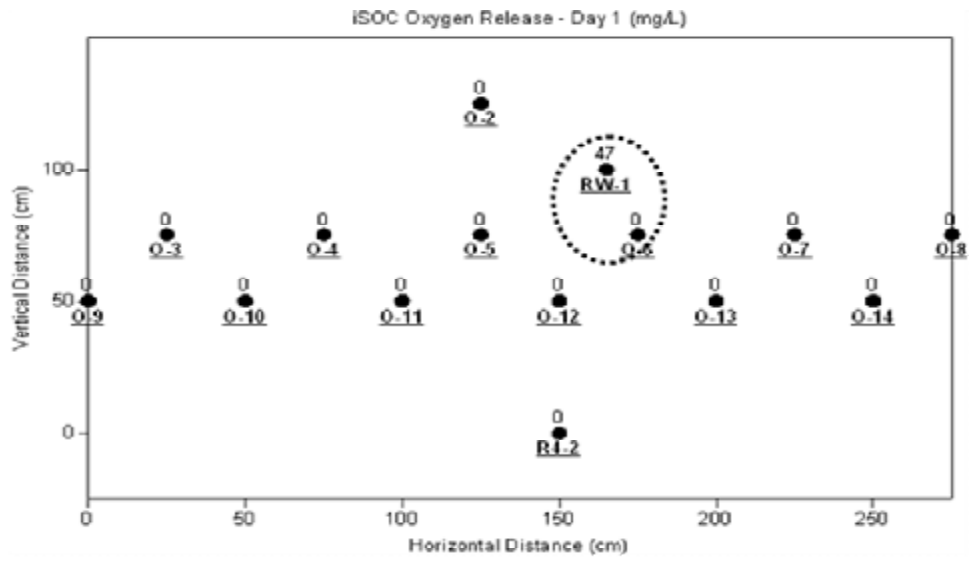


Figure 27 Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 1 (no decay).

The dashed line is the estimated maximum extent of the dissolved oxygen plume.

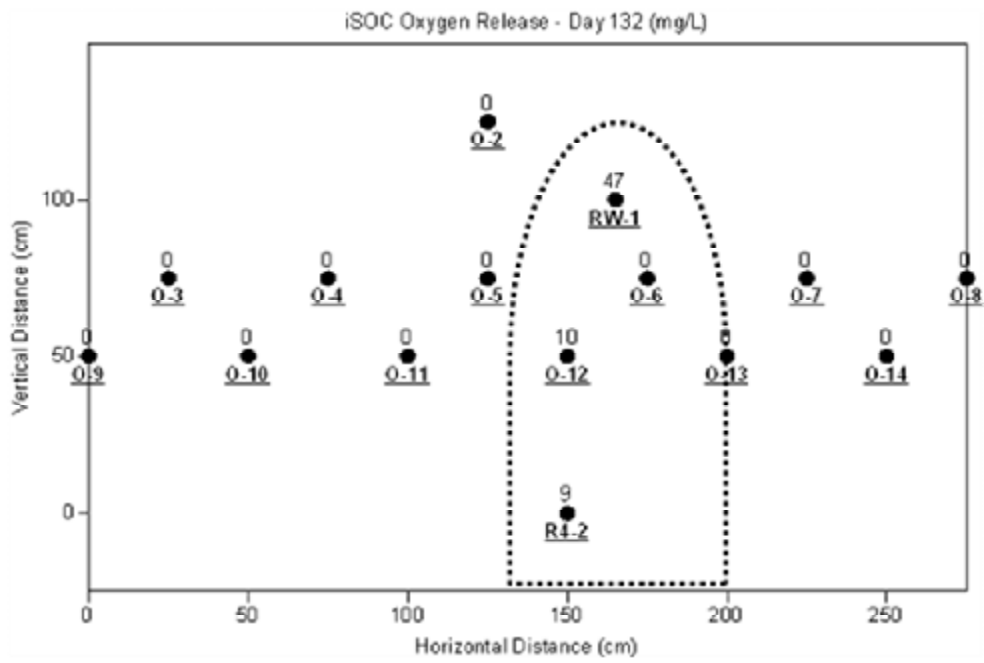
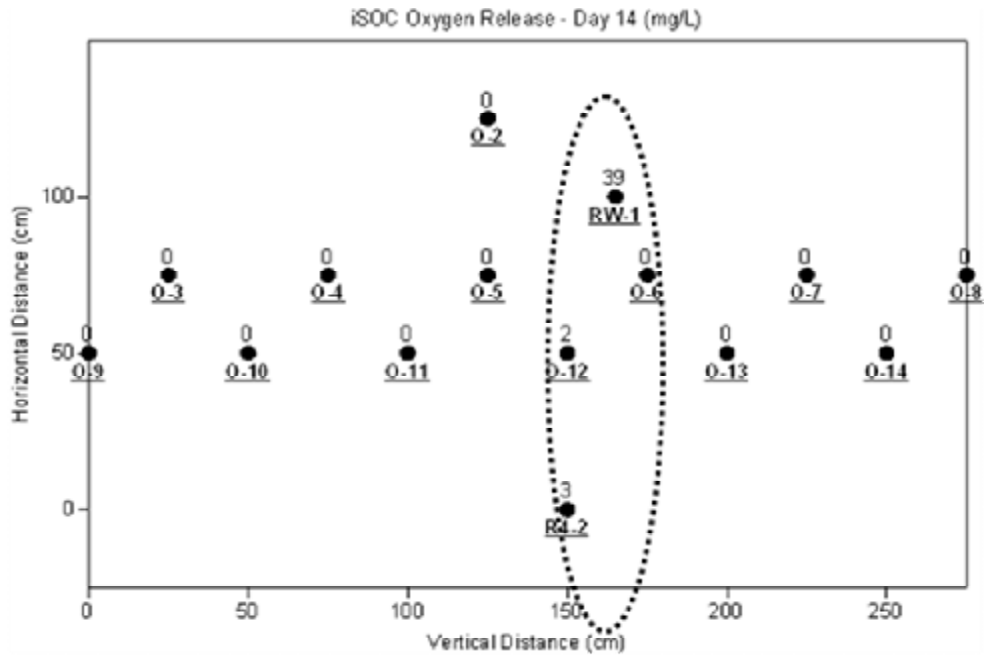


Figure 27 (continued) Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 1 (no decay).

The dashed line is the estimated maximum extent of the dissolved oxygen plume.

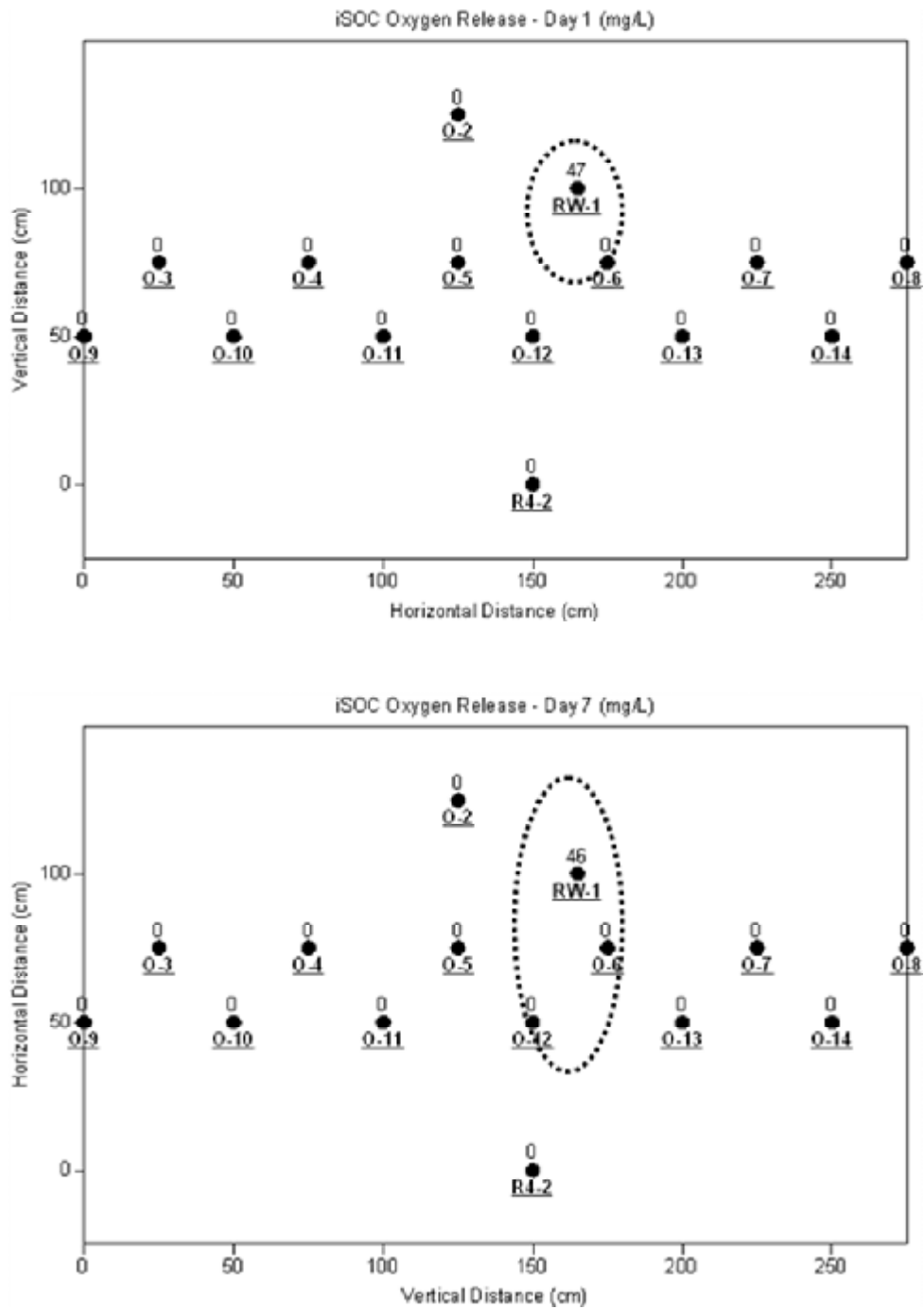


Figure 28. Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 2, with decay.

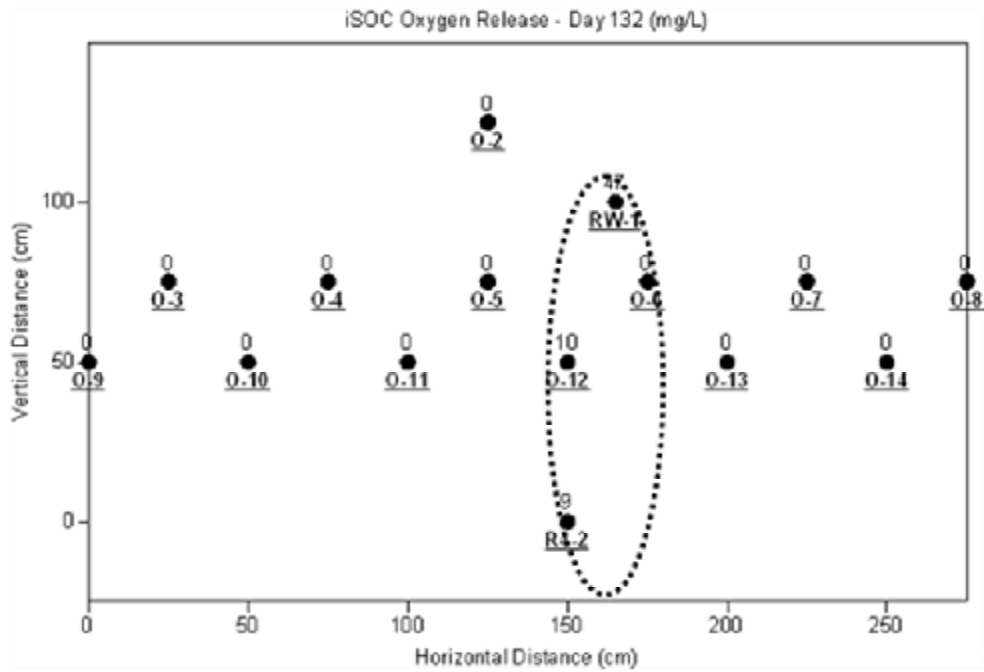
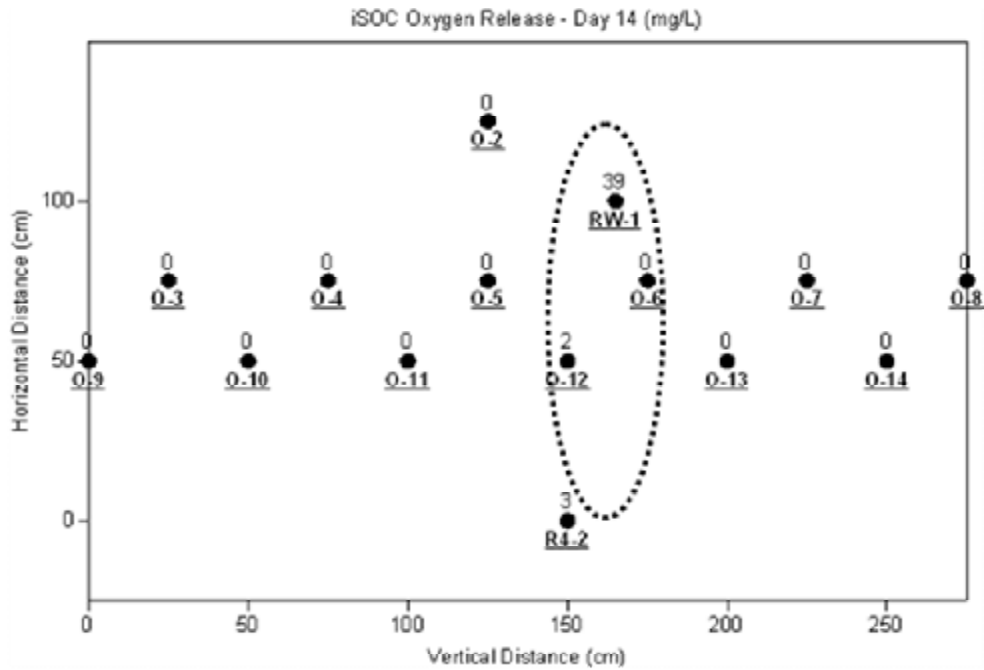


Figure 28 (continued) Experiment 2, dissolved oxygen results with the maximum width boundary from simulation 2, with decay.

If we superimposed the 10 mg/L boundary on to the monitoring network from the field experiment we can observe the number of release wells required to provide > 10 mg/L dissolved oxygen across the Site. Using day 132 results from simulation 1 we would require 6 release wells spaced a 1.5 m intervals (Figure 29). Therefore the minimum spacing between release wells for a plume in at the Site at CFB Borden should be 1.5 m.

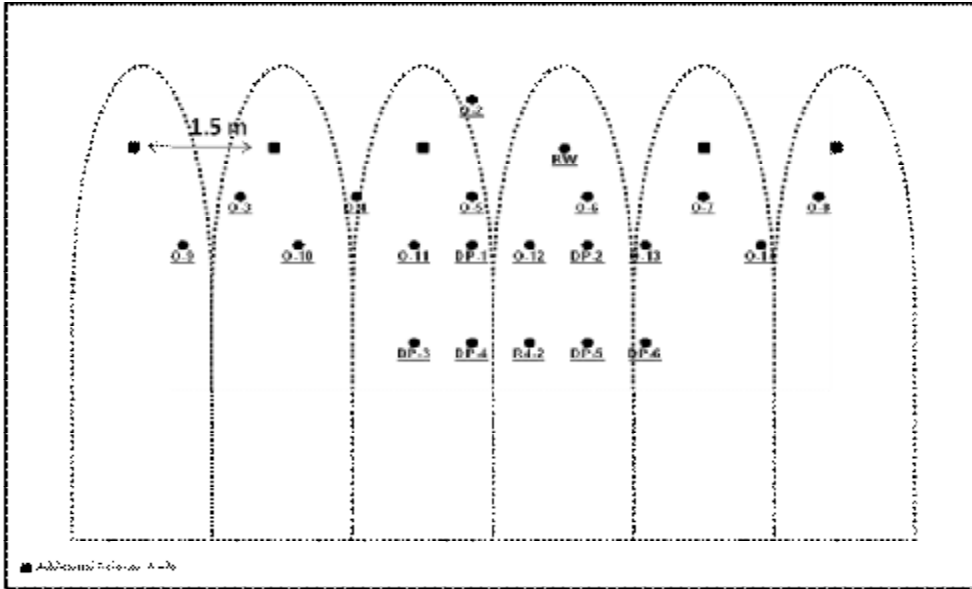


Figure 29 Maximum transverse distance between release wells, based on >10 mg/L dissolved oxygen boundary

Based on day 132 results from simulation 1.

9.0 Summary and Conclusions

By releasing oxygen passively with the iSOC™ only a small transverse portion of the Borden aquifer was likely influenced. This limitation has been noted in general for passive release technologies (Wilson & Mackay, 1995). While the iSOC™ technology develops very high oxygen levels in the groundwater in the release well, it does not overcome the hydrogeological constraint of limited transverse dispersion. Thus, a high oxygen concentration is delivered to a very narrow segment of the aquifer. The original purpose of these experiments was not to determine how effectively the iSOC™ is able to treat groundwater contaminated with gasoline but to determine what kind of a radial impact a passive release technology has around a release well. Due to the unfortunate circumstances which occurred in the first experiment gasoline eventually did impact the results. In order to establish how much of the oxygen was consumed via biodegradation a short third experiment was completed, this experiment lasted 29 days and sampling occurred on a weekly basis for alkalinity, pH, dissolved oxygen, BTEX and total iron. Extra drive-point piezometers were installed to aid in further determining the maximum extend of the dissolved oxygen plume. Results indicated that the dissolved oxygen plume had a maximum width of no greater than 25 cm, but the presence of BTEX degradation limited the area enhanced by oxygen.

Modeling was completed using Hydrogeosphere™, which a 3-D modeling program which is able to simulate flow and contaminate transport within an aquifer system by incorporating processes like advection, dispersion and diffusion. The results from the first and second simulations (with no oxygen demand, a half-life of 7 days for the oxygen) both indicated that within the first meter of flow the maximum width of the dissolved oxygen plume would be no greater than 50 cm. The first simulation also indicated that transverse dispersion does widen the non-reactive plume but has a greater effect the further it has migrated from the release well. The second simulation also indicated that when there was an oxygen demand the length of the plume is limited, but the width is not seriously restricted. This reduction in the length of the plume also further reduces the volume of contaminated groundwater the oxygenated water can treat.

By superimposing the day 132, 10 mg/L boundary from simulations 1 and 2 we can observe that the difference in area covered by the two simulations is not that different. Therefore in order to cover the entire BTEX plume at the experimental Site at CFB Borden, a minimum transverse distance between release wells would be approximately 1m.

In situ passive release technologies are more cost effective than more active remediation systems as they incur minimal operation and maintenance costs and do not require the establishment of large infrastructures at the site. But, a greater oxygen demand will limit the area in which a contaminant plume will be aerobically enhanced. This implies that when in well passive release technologies are considered as a method for remediation one must consider that a number of wells and passive releasing devices will be required to create a large enough oxygenated area to encompass the entire width of a contaminant plume.

It is suggested that by injecting oxygen rich water into the release well, that the dissolved oxygen will be pushed wider (i.e., transverse to flow). The hydraulic concept is simple and well understood (see Devlin & Baker, 1994): the injection of water from a screened well into a reasonably homogeneous aquifer, with the radius of injected water dependent mainly on the hydraulic conductivity of aquifer layers and to a lesser degree upon the groundwater flow. Use of multiple injection/pumping wells or permeable barriers could provide better control and optimization of spreading of oxygenated water transverse to groundwater flow (e.g., Devlin & Barker, 1996).

It must be noted that the injected, oxygenated water just displaces contaminated groundwater and so the enhanced aerobic biodegradation being sought will only occur through dispersive mixing of injected oxygenated water and contaminated groundwater downgradient of the injection site. This is the same process limiting the performance of the iSOC™. However, the mixing process is now longitudinal dispersion, which is typically an order of magnitude stronger than transverse dispersive mixing. In order to maximize the transverse extent of the oxygenated water, multiple injections on a regular basis will be required.

Overall, transverse dispersion has a minimal impact on a passively release oxygen plume, particularly in close proximity to the release well, but once the plume has migrated a distance away from the release well the effect of transverse dispersion increases. The oxygen demand of an aquifer can also limit the effect of transverse and longitudinal dispersion. If a site has a high chemical or biological oxygen demand the released gas will be consumed before dispersion can have an effect on the plume. By injecting nutrient rich water into a release well the water will forcibly overcome any influence transverse dispersion will have in and around a release well, thereby relying on longitudinal dispersion to create a larger area for contaminant degradation to occur.

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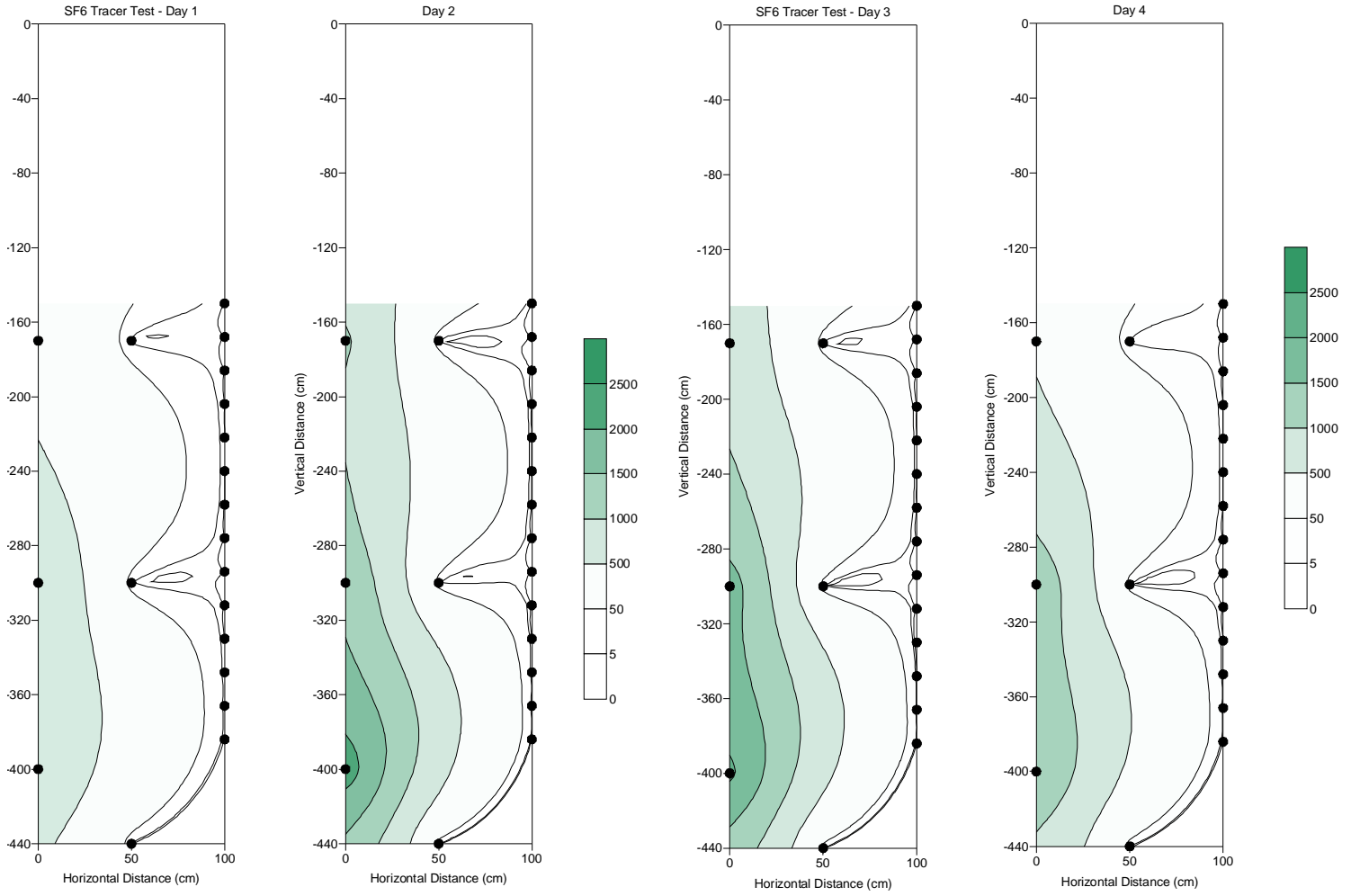
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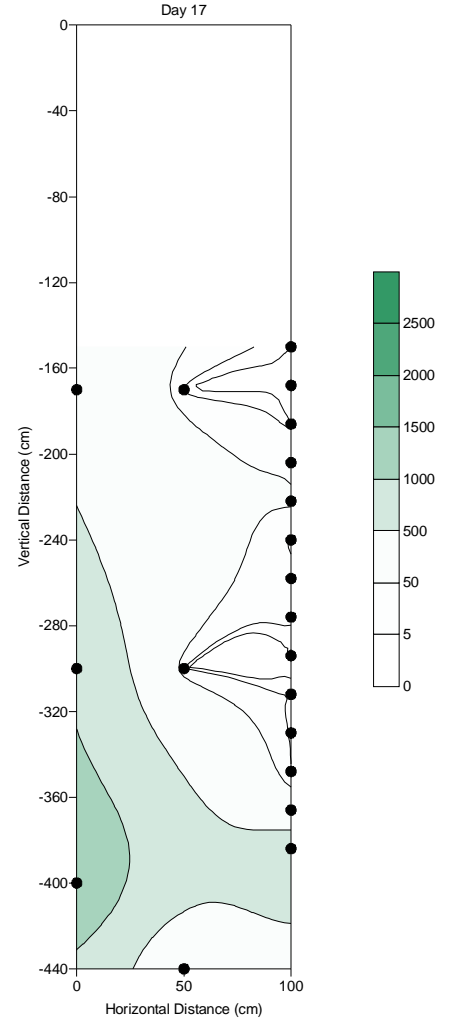
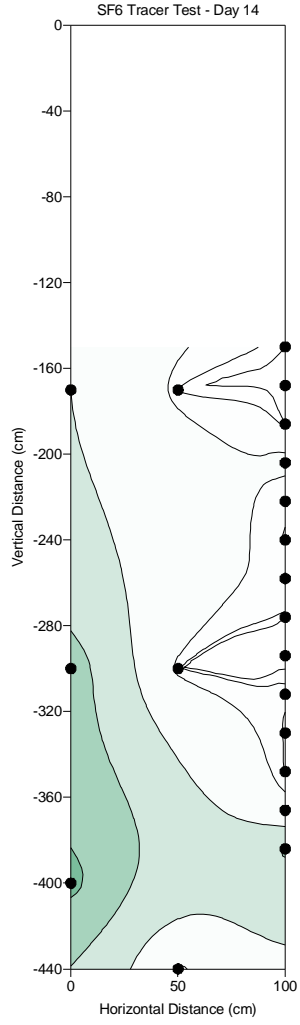
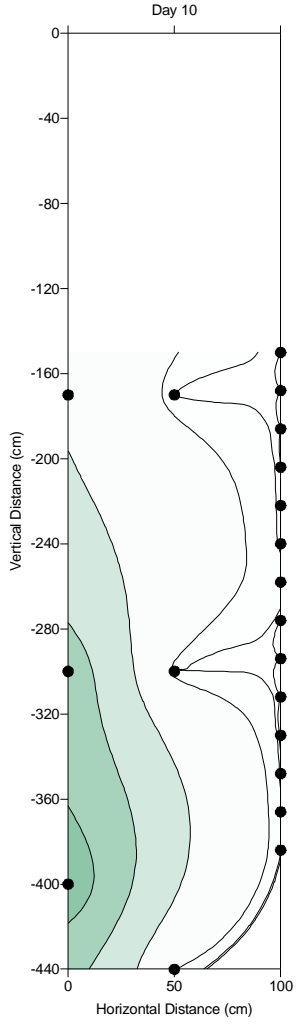
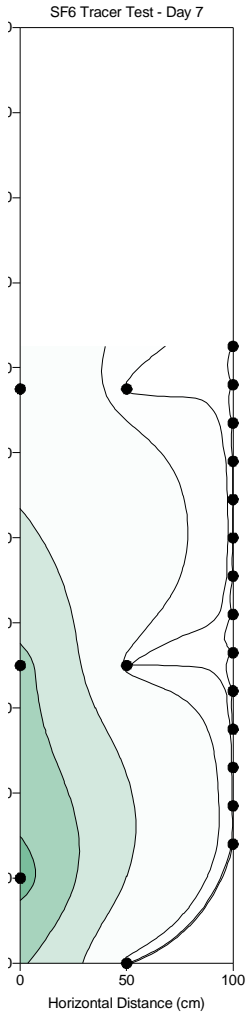
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Appendix A

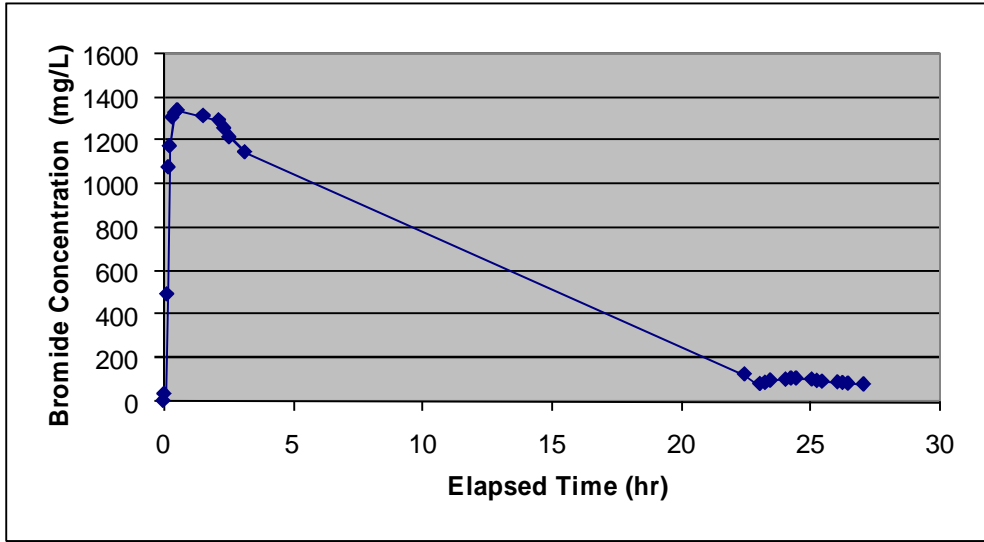
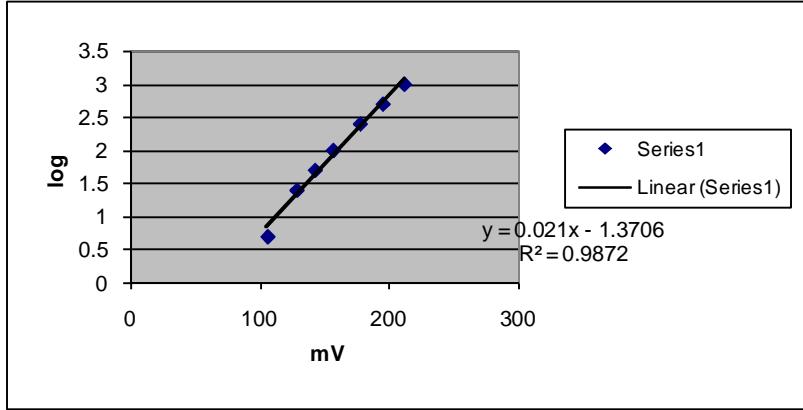
SF₆ Cross – Section Plots (μg/L), Experiment 1.





Appendix B

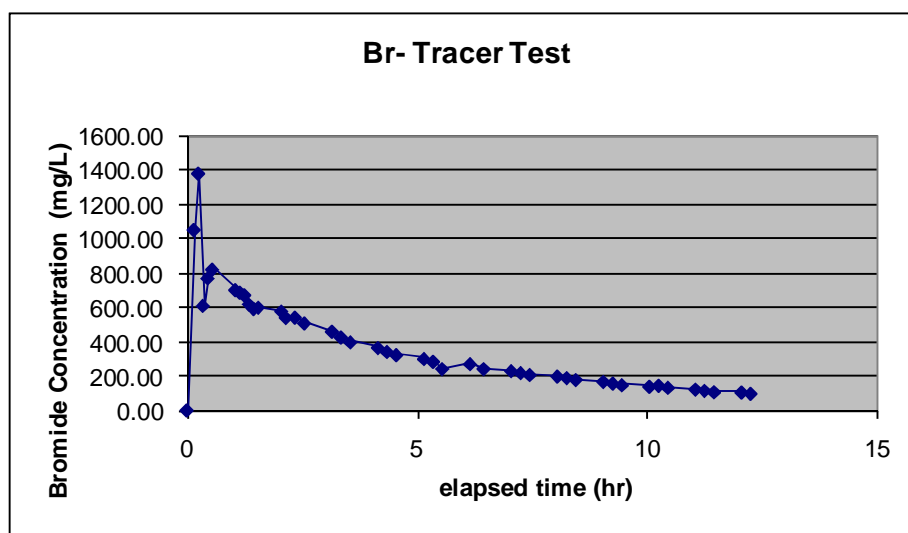
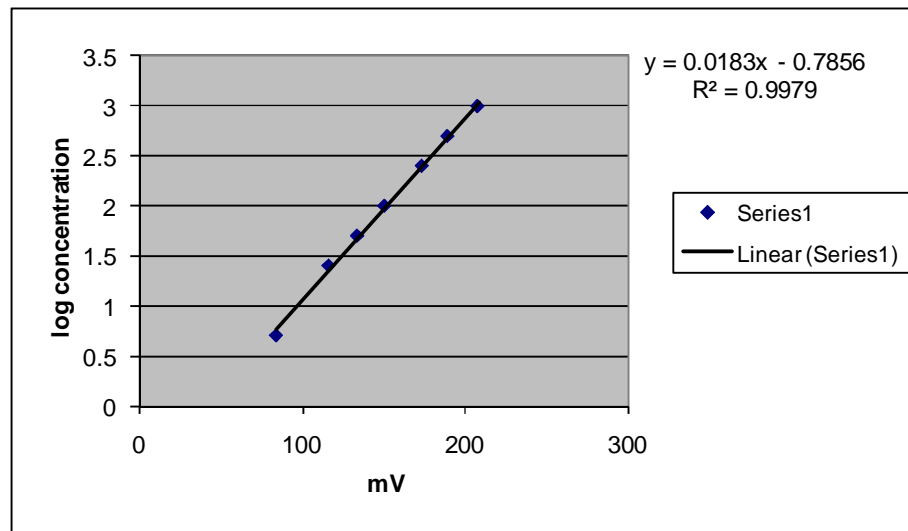
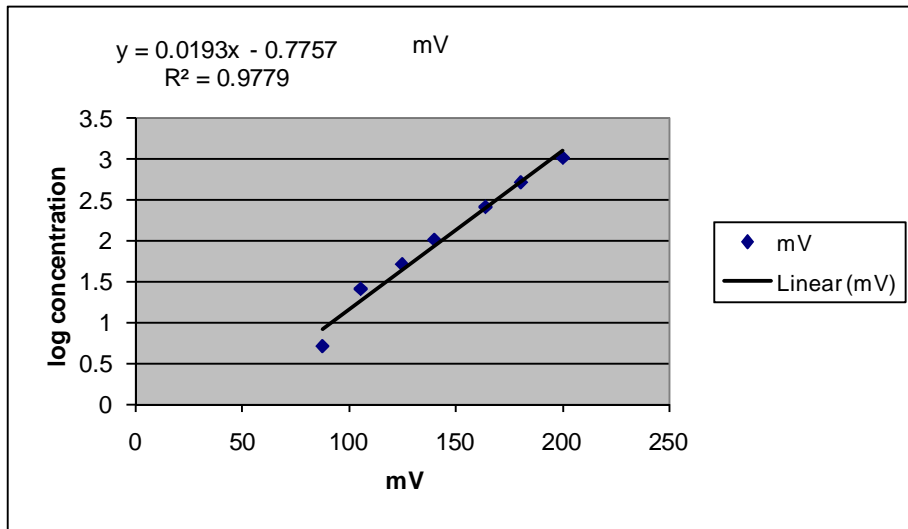
Bromide Samples - Feb. 15-16, 2005				
Borehole Dilution				
Standards (mg/L)	log	mV	mV	
1000	3	215.1	211.5	
500	2.7	199	195	
250	2.4	186.1	177.5	
100	2	168.2	156.5	
50	1.7	159.7	142.5	
25	1.4	157	128.3	
5	0.7	160	105.7	
Feb. 15/05		elapsed time (hr)	mV	concentration (mg/L)
1	12:14	0	97	4.64
2	12:18	0.04	140.1	37.28
3	12:30	0.15	193.6	495.45
4	12:35	0.2	209.7	1079.20
5	12:40	0.25	211.5	1177.33
6	12:50	0.35	213.7	1309.48
7	13:00	0.45	214	1328.62
8	13:10	0.55	214.2	1341.53
9	14:00	1.55	213.8	1315.83
10	14:20	2.15	213.5	1296.88
11	14:40	2.35	212.9	1259.80
12	15:00	2.55	212.2	1217.87
13	15:20	3.15	211	1149.21
1	11:00	22.45	165.4	126.71
2	11:20	23.05	156.5	82.39
3	11:40	23.25	157.8	87.74
4	12:00	23.45	160.1	98.06
5	12:20	24.05	161	102.42
6	12:40	24.25	162.1	108.02
7	13:00	24.45	161.9	106.98
8	14:00	25.05	161.2	103.42
9	14:20	25.25	159.8	96.65
10	14:40	25.45	159	92.98
11	15:00	26.05	158.2	89.45
12	15:20	26.25	157.6	86.90
13	15:40	26.45	156.8	83.60
14	16:00	27.05	156	80.43



Nov. 2-4, 2005

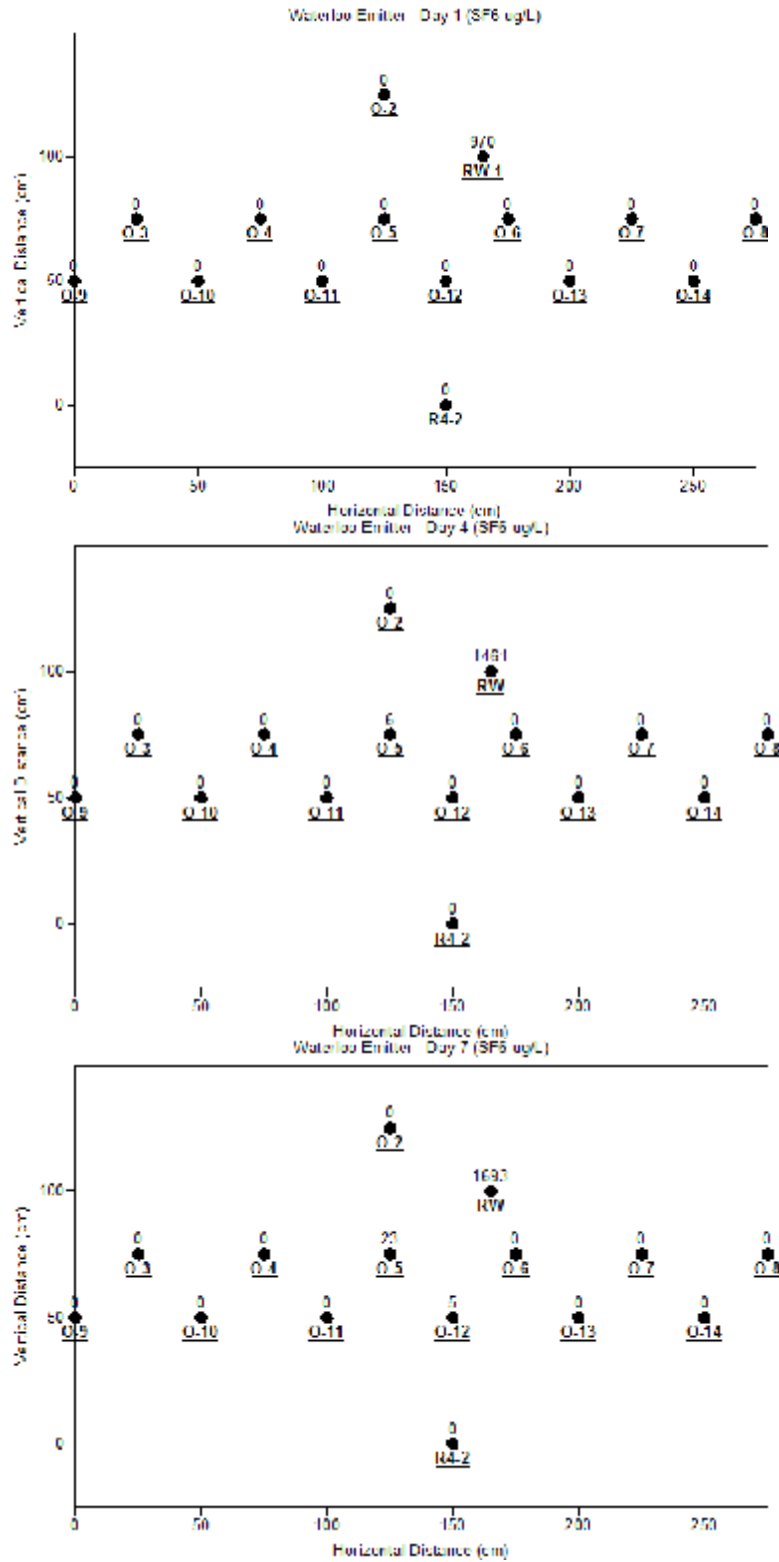
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500	2.7	180.8	189.3	179.9	187.2	188	189.7	191.2	
250	2.4	164.1	173.1	164.4	172.2	172.1	173.9	175	
100	2	140.1	149.6	139.6	152.2	151.3	150.8	150.5	
50	1.7	125	133.5	127.1	139.8	138.1	134.1	134	
25	1.4	105.5	114.8	117.2	126	124.9	116.5	115.5	
5	0.7	87.6	88.2	113.1	113.2	111.7	84.2	81.3	

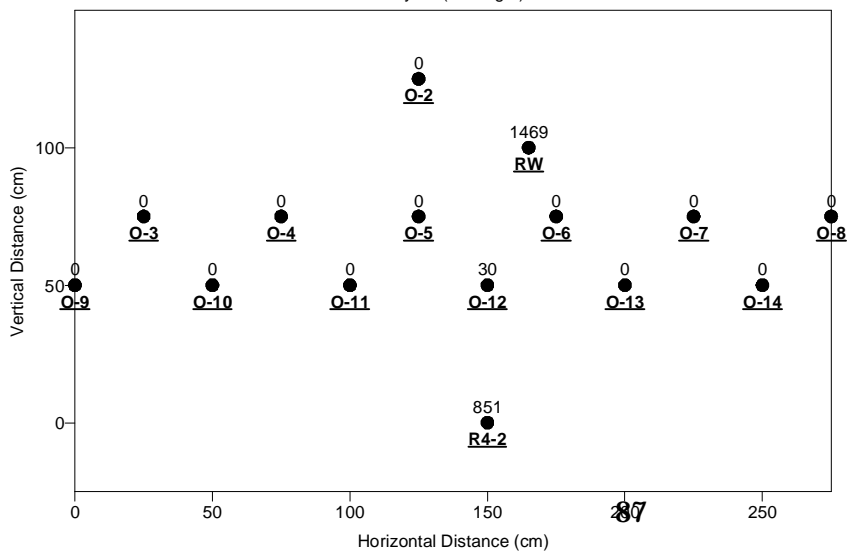
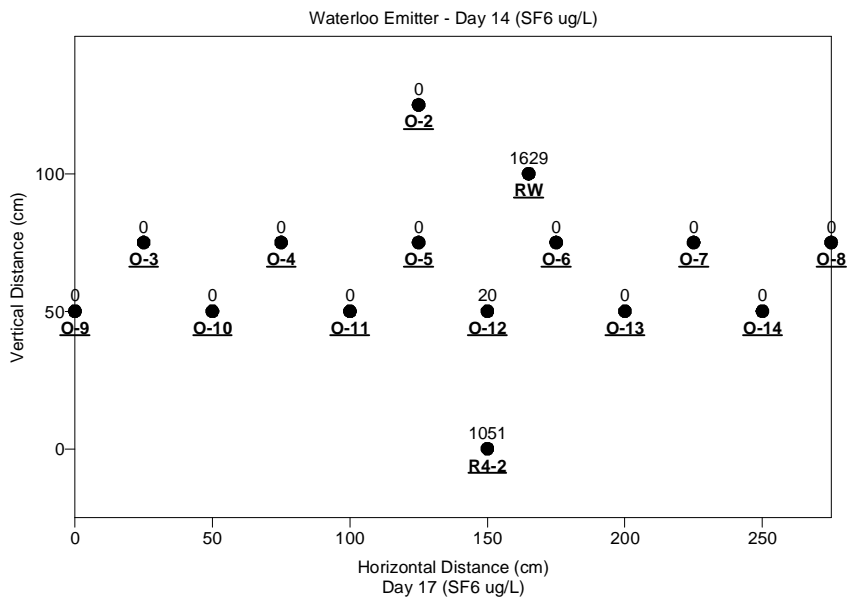
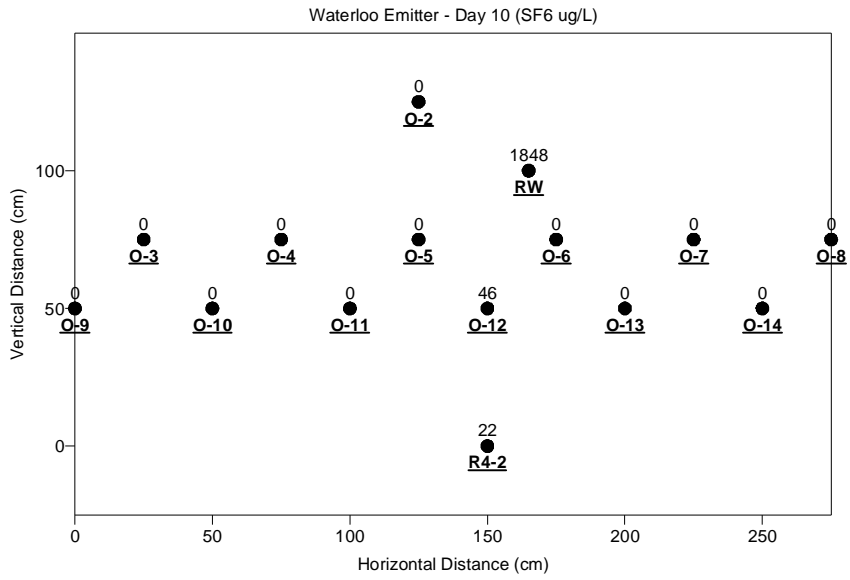
date	time	elapsed time (hr)	mV	concentration	date	time	elapsed time (hr)	mV	concentration	
	bg	0	66.1	3.16						
Nov. 2	10:00	0.15	208.1	1053.49	Nov.3	10:00	24.25	138.2	55.39	
	10:10	0.25	214.5	1379.59		11:00	25.25	136.4	51.35	
	10:20	0.35	195.2	611.73		12:00	26.25	135	48.41	
	10:30	0.45	200.7	771.28		13:00	27.25	133.2	44.87	
	10:40	0.55	202.2	821.60		14:00	28.25	133.3	45.06	
	10:50	1.05	198.5	702.99		15:00	29.25	132.1	42.84	
	11:00	1.15	198	688.34		16:00	30.25	130.6	40.21	
	11:10	1.25	197.5	673.98		17:00	31.25	129.5	38.39	
	11:20	1.35	195.5	619.51		18:00	32.25	128.5	36.81	
	11:30	1.45	194.5	593.95		19:00	33.25	126.4	33.69	
	11:40	1.55	194.8	601.51		20:00	34.25	125.1	31.90	
	11:50	2.05	193.9	579.12		21:00	35.25	124.5	31.10	
	12:00	2.15	192.3	541.36		22:00	36.25	123.3	29.57	
	12:20	2.35	192.4	543.65		Nov.4	9:00	47.25	106.5	14.57
	12:40	2.55	190.9	510.35			10:00	48.25	104.8	13.56
	1:00	3.15	188.5	461.26			11:00	49.25	104.9	13.62
	1:20	3.35	186.7	427.57			12:00	50.25	103.5	12.84
	1:40	3.55	185.1	399.70			13:00	51.25	102.7	12.41
	2:00	4.15	183.1	367.39			14:00	52.25	101.9	12.00
	2:20	4.35	181.5	343.44			15:00	53.25	100.2	11.17
2:40	4.55	180.2	325.13							
3:00	5.15	178.5	302.66							
3:20	5.35	177.2	286.52							
3:40	5.55	173.4	244.13							
4:00	6.15	176	272.40							
4:30	6.45	173.4	244.13							
4:40	7.05	172.2	232.09							
5:00	7.25	171	220.65							
5:20	7.45	169.8	209.77							
5:40	8.05	168.7	200.27							
6:00	8.25	167.7	192.00							
6:20	8.45	166.3	181.00							
6:40	9.05	164.8	169.92							
7:00	9.25	163.3	159.51							
7:20	9.45	161.8	149.74							
7:40	10.05	160.3	140.57							
8:00	10.25	161.4	147.24							
8:20	10.45	159.4	135.34							
8:40	11.05	157.6	125.45							
9:00	11.25	156.1	117.77							
9:20	11.45	154.4	109.63							
9:40	12.05	154.1	108.25							
10:00	12.25	152.4	100.77							



Appendix C

SF₆ Release (µg/L) Plan View Experiment 2.





Appendix D

Oxygen Release (mg/L) Plan View Experiment 2.

