Use of Drains for Passive Control of Flow Through a Permeable Reactive Barrier.

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Abstract

Permeable reactive barrier technology is a cost effective means of treating near surface groundwater contaminant plumes. However, current reactive barrier technology lacks the capacity to manipulate flow rates and thus hydraulic retention time (HRT) within the barriers in order to maximize the effectiveness and longevity of the media. This study examines the effectiveness of tile drains as passive controls on the flow rate of ground-water through an existing wood particle media permeable reactive barrier treating agricultural nitrate. The use of upgradient and downgradient tile drains allowed HRT to be increased from 4.5 to 10 days in one trial and then to be decreased from 11.1 to 0.8 days in a second trial. Influent groundwater NO_3-N concentrations of ~100 mg/L were attenuated to detection limit (0.02 mg/L) only 12% of the 4 m long barrier with HRTs of 4.5 to 10 days. During the second trial, HRT was decreased to 0.8 days and NO_3-N penetrated to the downgradient edge of the PRB at 1.8 mg/L. The behaviour of SO_4 in the PRB was also affected by flow rate. SO_4 entered the PRB at 60 to 71 mg/L during the first trial. Under a HRT of 10 days it was depleted to detection limit after traveling through only 13% of the barrier. When HRT was decreased to 4.5 days, SO_4 was able to penetrate the downgradient edge of the PRB at concentrations from 4 to 6 mg/L. With a 0.8 day HRT SO_4 reduction was highly restricted as calculations showed 90% of available carbon in the PRB was being used to reduce NO_3-N, compared to 7.5% being used for SO_4 reduction at that time. In comparison, at the 10 day HRT, 61% of carbon being used for NO_3-N reduction, 8.7% for SO_4 reduction, 0.7 for dissolved oxygen and 29% was lost through DOC leaching. These calculations suggest that barrier efficiency can be greatly enhanced by manipulation of HRT through use of tile drains.

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1.0   Introduction

1.1   The Problem

Over the past two decades, permeable reactive barriers (PRBs) have been established as an effective and economical method of treating groundwater impacted by contaminants such as Fe, volatile organic carbons (VOCs), NO_3 and trace metals (Benner et al., 1997; O'Hannesin and Gillham, 1998; Robertson et al., 2000; Wilkin et al., 2002). PRB construction involves the placement of labile solids in the shallow groundwater zone in order to intercept a plume of contaminated groundwater. As contaminated groundwater passes through a PRB, the media in the PRB will react with the target contaminants while allowing the groundwater to continue its normal flowpath (Fig 1). The advantage of this technology is primarily related to the passive nature of the treatment system. This is in contrast to other remediation technologies, such as pump and treat, air sparging and soil vacuum extraction, which require ongoing maintenance until the contamination source and plume are removed (Doty and Davis, 1991; Bass et al., 2000; Thomson and Flynn, 2000). In contrast, once a reactive wall has been installed, it normally requires only occasional monitoring in order to confirm proper function.

However, a problem exists due to the inability to control groundwater flow rates through conventional PRBs. This is a concern as contaminants may pass through the reactive media at higher than optimal groundwater velocities allowing breakthrough of contaminants as a result (O'Hannesin and Gillham, 1998). Additionally, at other sites where groundwater flow rates are too low, hydraulic retention time (HRT) may be excessive, resulting in undesirable secondary reactions (Wilkin et al., 2002). Furthermore, as PRBs age, the

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reactive materials in these barriers may become depleted or less effective because of the presence of reaction products (Blowes et al., 2000; Wilkin et al., 2002). In these cases, an increased HRT could solve the problem. PRB technology has always struggled with the problem of less than ideal barrier flow rates.

Benner et al. (1997) were the first to install a reactive wall to treat acid mine drainage at the nickel rim mine site near Sudbury, Ontario. This reactive wall used a carbon source (leaf compost and woodchips) to initiate sulfate reduction (Eq. 1.1), which contributed to the precipitation of aqueous Fe^{2+} as iron sulfide (Eq. 1.2, Benner et al., 1997).

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \qquad (1.1)$$

$$Fe^{2+} + H_2S \rightarrow FeS_{(s)} + 2H^+ \qquad (1.2)$$
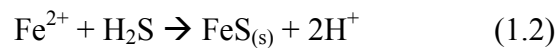
Benner et al. (1997) noted that in order for the effluent leaving the PRB to have a near neutral pH, Eq. 1.1 and 1.2 required that for every mole of SO_4 reacted, a mole of Fe must also be reacted. However, influent concentrations of SO_4 and Fe were not equal, with molarities of ~25 mmol/L of SO_4 and ~4 mmol/L of Fe (SO_4 >2400 mg/L, Fe >250 mg/L) (Fig 2a), this suggested that the estimated groundwater velocity of 4.4 cm/day would require ongoing manipulation to ensure that the variable concentration influent would have a HRT long enough to completely remove the acid producing Fe, but then leave ~84% of the influent SO_4 untreated.

The use of PRBs to treat VOC compounds such as tetrachloroethene (PCE) and trichloroethene (TCE) was first implemented by O'Hannesin and Gillham (1998) at CFB Borden in Ontario. While the experiment proved successful at reducing the concentration of PCE and TCE, from 268,000 to 23,350 µg/L and 58,000 to 10,970 µg/L respectively, there was a problem with the flow rate of the reactor not being slow enough (velocity of ~9

cm/day) to deplete the daughter products (dichloroethlene (DCE) and vinyl chloride (VC)).
It was recommended by O'Hannesin and Gillham (1998) that the groundwater needed a
longer exposure time to the zero-valent iron in order to fully deplete DCE and VC (Fig 2b)
by the following reaction pathways (Gillham and O'Hannesin, 1994):

$$PCE \rightarrow TCE \rightarrow DCE \rightarrow VC \rightarrow Ethene \qquad (1.3)$$
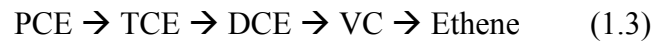
Increasing the size of the PRB to increase HRT would raise installation costs.
However, another option would be to manipulate the HRT within the barrier in order to
optimize the treatment of VOC compounds. This latter option would also provide flexibility
given the tendency of granular iron PRBs to develop secondary mineral precipitates which
reduce hydraulic conductivity (K) over time (Jeen, 2005).

Wilkin et al. (2002) installed a zero-valent iron PRB treating groundwater Cr^{6+}
contamination at Elizabeth City, North Carolina. This reactive layer was installed in 1996 in
order to intercept a groundwater chromate plume (>10 mg/L) from a plating shop, and
convert the hazardous hexavalent chromium in the plume to the less harmful trivalent form:

$$Cr(VI) + Fe(II) \rightarrow Cr(V) + Fe(III) \qquad (1.4)$$
$$Cr(V) + Fe(II) \rightarrow Cr(IV) + Fe(III) \qquad (1.5)$$
$$Cr(IV) + Fe(II) \rightarrow Cr(III) + Fe(III) \qquad (1.6)$$
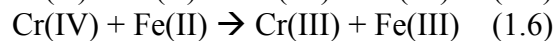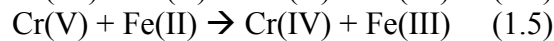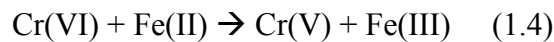
(Fendorf and Li, 1996)

Wilkin et al. suggested that secondary mineral build up combined with a poor
understanding of groundwater flow rates and microbial bio-fouling caused groundwater
velocities in the PRB that were too slow (0.15 m/day) to fully utilize the treatment capacity
of the media (Wilkin et al., 2002). In fact, Cr and DCE concentrations appeared to be
depleted before reaching the reactive wall (Fig 2c). It was speculated that during installation,
some mixing of zero-valent iron occurred in the adjacent upgradient portion of the aquifer,
and consequently the barrier itself was not actively treating contaminants.

Robertson and Cherry (1995) implemented a reactive wall using wood particles as a carbon source to promote NO_3 removal in a sewage plume at Long Point, Ontario. This labile carbon source promoted denitrification (Eq. 1.7, Delwiche, 1981):

$$5CH_2O_{(s)} + 4NO_3^-{}_{(aq)} \rightarrow 5CO_{2(g)} + 2N_{2(g)} + 3H_2O_{(l)} + + 4OH^-{}_{(aq)} \qquad (1.7)$$

In addition to reducing NO_3, it was noted that the organic carbon was also being depleted by SO_4 reduction (Eq. 1.1). Furthermore, excess dissolved organic carbon (DOC) was being leached into the downgradient groundwater zone from the reactive media. Robertson and Cherry (1995) recognized that the additional consumption of reactive media by such secondary reactions and excess leaching of DOC was detrimental to barrier longevity. Blowes et al. (2000) also noted that as reactors age, the HRT within the barrier may increase due to physical changes such as decreases in porosity and permeability. The possibility of flow manipulation provides a potential solution to the problem of non-productive barrier media depletion.

Having a system in place capable of proactively manipulating groundwater flow rates within a PRB could be advantageous at many sites. Ideally, such a system should not involve pumping, as it is desirable to maintain the passive characteristics of PRBs where possible.

1.2 Previous work

An early modified PRB design referred to as the "funnel-and-gate", used impermeable walls to funnel water from a larger spatial area into a localized zone of reactive media (Starr and Cherry, 1994). Unfortunately, flow through funnel-and-gates can be problematic because deterioration or heterogeneities within the reactive media can lead to

"short circuiting" through the wall. Additionally, modeling and field tests showed that water could be diverted around or under the walls if permanent deterioration occurred (Benner et al., 2001; Schipper et al., 2004). These obstacles were addressed in a modified funnel-and-gate design implemented by Lee et al. (1998). In this design, tile drains were placed downgradient of a wall of granular zeolite (clinoptilolite), used to adsorb ^{90}Sr, but in front of a solid sheet pile wall (Fig 3). A hydraulic head level control manhole, connected the PRB to the drainage lines. By manipulating the elevation of the outlet drain in the manhole, it was possible to change the head conditions within the wall, and thus vary the width of the upgradient capture zone. Aquifer K at this site ranged from10^{-3} to 10^{-2} cm/s (Killey and Munch, 1987), while the zeolite K was measured at $7x10^{-3}$ and $9x10^{-2}$ cm/s (Lee and Hartwig, 2005). Assuming uniform groundwater flow, it was estimated that the size of the capture zone could be altered up to three times its natural size when the barrier drain was lowered ~1m below the ambient water table elevation (Lee, 2007). The 11m wide wall thus captured a 33m wide flow zone.

1.3   The Zorra site reactive barrier

The Zorra study site, located in Zorra Township in southwestern Ontario, near the city of London, is located on an unconfined aquifer system which interacts with the Thames River. The aquifer system is composed of glaciofluvial outwash sands and gravels of the Wisconsinan age (Cowan, 1971, Robertson and Schiff, 2007). The upgradient farms are used for corn production, and a 2 ha portion of the upgradient field is used for poultry manure composting (Fig 4). Poultry manure has a relatively high N content (e.g. 3.6 dry wt %,

Liebhardt et al., 1979) and was also expected to contribute to the NO_3-N loading at this site. During a previous study at this site (Roberston et al., 2007) a PRB was installed to treat NO_3-N enriched groundwater at concentrations of 6 to 99 mg/L occurring in the shallow aquifer. The Zorra PRB was used for the principle experiment undertaken in this study.

The Zorra PRB was installed in August 2004 and was successful in attenuating NO_3 in the groundwater. The barrier is 8 m long by 4 m wide by 0.6 m thick, was installed into the shallow water table at 0.9 to 1.5 m depth, and was constructed of coarse woodchips (Robertson et al., 2007). After 11 months of operation it was noted that NO_3 was essentially depleted by the first monitoring point in the PRB which was located only 1.1 m from the upgradient edge of the ~4m wide PRB (Fig 5). This indicated that the HRT within the barrier was much longer than required for optimal barrier efficiency. The mean flow velocity within the Zorra barrier was determined in the previous study (Robertson et al., 2007). Using borehole dilution tests Robertson et al. (2007) observed PRB flow velocities of 29 +/- 7 cm/d (n = 4) compared to 25 +/- 26 cm/d (n = 4) in the adjacent shallow aquifer.

1.4   Research Objectives

The objective of this study was to demonstrate a passive technique for controlling the flow rate, and hence the ensuing redox environment, within a PRB to optimize the flow and concentration of NO_3-N into the PRB. The technique used involved the installation of a set of tile drains positioned upgradient and downgradient of the PRB, and directly connected to the PRB (Fig 4). The amount of additional flow entering or exiting the PRB through the tile drains was controlled by valves which were either completely open or closed during the

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experiments. In this study a large scale field test was undertaken at the Zorra site to demonstrate the utility of this technique in controlling flow through a PRB. Two distinct configurations were tested; configuration 1 used a downgradient tile line only. Under this configuration, all PRB effluent was presumably pulled into the downgradient tile and reactor system, effectively enhancing flow. Configuration 2 used both upgradient and downgradient drainage tiles to enhance flow. However, this configuration had the disadvantage of introducing a contrasting source of water from the upgradient tile into the barrier, which complicated geochemical interpretations. Despite this, use of the upgradient tile had the advantage of delivering the larger flow rates desired.

2.0   Zorra site enhanced flow rate experiment

2.1   Methods

2.1.1   Reactor and Drainage Tile Design

The Zorra PRB is composed of coarse grained woodchips and is positioned at the upgradient edge of a 100m wide riparian zone that separates an adjacent manure composting yard from the Thames River. The upgradient and downgradient edges of the reactor were modified in this study by the installation of perforated tile drains (Fig 6), which were intended to augment flow through the reactor.

The downgradient tile is composed of two sections. The first is a perforated section of 10 cm diameter PVC pipe, which was installed in contact with the down gradient edge of the reactor. Washed pea gravel, with an estimated K of 1 to 10^{-2} cm/s (Fetter, 2001) was placed around the tile line. This perforated segment extends 5 m southwestward to monitoring well PU 84. Extending southeasterly from PU 84 is a second solid (non-perforated) segment of tile ~30m in length (10 cm diameter Big-O™ flexhose) which ends at PU 85 (Fig 6), where it is connected to a second woodchip trench. The second trench, also referred to as the down gradient barrier (Fig 6), was installed to provide a permeable media for rapid drainage and also to offer additional denitrification capacity if required. This trench system consisted of a series of 3 cells 8 m x 1.5 m x 0.5 m in dimension and was composed of the same woodchip media found in the upgradient barrier (Fig 6). The downgradient trench system was not studied in this project. During the August flow manipulation event,

which occurred prior to the installation of the upgradient tile, flow through the downgradient tile line was terminated by plugging the tile at the monitoring well PU 84 location. Stopping flow to the downgradient tile, in this way, maintained the PRB in a natural flow condition.

The upgradient tile lines were installed in October 2006. The southwesterly tile was ~55 m in total length, and split into two sections. The first section consisted of an 8 m long, 10 cm diameter, perforated PVC pipe placed in contact with the upgradient edge of the PRB (Fig 6). The tile line was covered in washed pea gravel. A second perforated segment ~41 m in length extended westward from the PRB to well PU 91 (Fig 4). These two perforated sections are joined together by a 10 m length of solid (non-perforated) tile, which extends southwestward from PU 93 (Fig 6). A second upgradient tile line extending ~110 m northward from the PRB (Fig 4), was also installed at this time, but was not used in this study due to low NO_3-N concentrations (~0.2 mg/L as N) that were present in this tile line segment.

2.1.2 Monitoring Network and Flow Path Determination

Hydrogeological and geochemical conditions in the area near the barrier were monitored using a series of wells and multi-level piezometer bundles (Fig 7) most of which were installed in the previous study (Robertson et al., 2007). These were constructed of 0.6 to 0.3 cm diameter polyethylene tubing attached to a central pipe of 1 cm diameter PVC pipe. Samples were also taken from PU 93, a 10 cm diameter monitoring well, which was connected to the upgradient tile line (Fig 6). Eight monitoring points that had generally similar Cl^- concentrations were considered to the best available representation of the principle flow path through the reactor. These points were selected for detailed sampling

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during this study (Fig 7). Piezometer point PU 2-7 (Fig 7) was selected as being

representative of the upgradient groundwater, because shallower locations at nest PU 2

showed SO_4 and Cl^- concentrations which were lower than those found in the PRB (Table 1,

Fig 8). An average of numerous upgradient piezometers, such as PU 2-5 to 2-7, was not

considered appropriate representation of influent groundwater because concentrations of Cl-,

SO_4 and NO_3-N would have been too low, leading to higher error in normalization

calculations. Furthermore, previous flow modeling of the Zorra PRB (Robertson et al., 2007)

indicated that groundwater flowlines would converge upward into the PRB because of its

high-K characteristic (K of 1.2 cm/s, Fig 9), thus use of the deeper monitoring point (PU 2-7,

2.8 m depth) as being representative of the upgradient groundwater is reasonable, despite PU

2-7's close proximity to the silt layer beneath it, as observed by Robertson et al. (2007).

   Although PU 2-7 had higher levels of Cl^- (~30 to 40 mg/L) than the monitoring

points above this piezometer, the Cl^- concentration here was still not as high as those found

within the barrier (40 to 80 mg/L). If additional Cl^- found within the barrier is a function of

Cl^- being released from the labile woodchip media composing the barrier, then the amount of

Cl in the PRB should be a function of the DOC leached in the barrier. Cl concentration in

wood used in the Zorra barrier typically ranges from 0.3 to 19 mg/kg (Rowell, 1984).

Assuming 25 kg of DOC is leached per year, this would correspond to 7.5 to 475 mg of Cl^-.

Thus, the breakdown of wood media within the reactor cannot explain the elevated

concentrations of Cl^- in the PRB.

   Monitoring points along the downgradient portion of the PRB were selected within

the barrier, rather than underneath. Downgradient monitoring points were kept within the

PRB because a zone of stagnant groundwater flow was determined beneath the PRB during

previous nodeling study (Robertson, 2007). While this region of the aquifer appears to be

part of the down gradient depleted NO_3-N plume (Fig 5), Robertson (2007) determined

groundwater flow here was so slow that the groundwater leaving the PRB was predominantly

exiting the downgradient edge of the PRB, rather than the bottom of the PRB (Robertson,

2007).

2.1.3 Groundwater Sampling

Groundwater samples for major ion analyses were collected using a peristaltic pump

and were filtered (0.45 μm) prior to collection in two 20 mL plastic vials. One of the vials

was preserved by acidification to pH < 2 with HCl for cation analyses, while the second vial

was untreated for anion analysis. NO_3-N, SO_4-S and Cl^- analysis were generally completed

in the Earth & Environmental Sciences Dept., University of Waterloo using a Dionex ICS-90

ion chromatography system. Analyses of DOC, NH_4, Ca, K, Mg and Na were generally

conducted at the University of Guelph, Soil and Nutrient Laboratory. Analysis of trace

metals (Fe, As and Mn) were conducted in the Earth & Environmental Sciences Dept.,

University of Waterloo. As was analysed on a Perkin Elmer 4000 Atomic Absorption

Spectrophotometer, with a Varian VGA-76 vapour generator. Fe and Mn were analysed on a

Portable Datalogging Spectrophotometer Hach DR/2010. Some additional analyses were

also completed at The Geography Dept., Wilfrid Laurier University (SO_4-S, NO_3-N and Cl^-),

the University of Guelph Soil and Nutrient Laboratory (NO_3-N and Cl^-), and Maxxam

Analytics Inc. in Waterloo, ON (SO_4). Electrical conductivity (EC), Eh and pH

measurements were recorded in the field. EC was recorded using a Oakton conductivity

meter (model WD-35607-10), which was temperature corrected. Eh and pH were measured using Barnant model 20 field portable meters. Eh values were adjusted to the standard hydrogen electrode value and were checked against Zobell solution (Nordstrom, 1977). The pH electrode was calibrated to buffers of 7 and 4 at the beginning of the sampling run, and re-calibrated after ~ every six samples.

2.1.4   Flow Rate Manipulation

Flow rates in the Zorra PRB were manipulated on a number of occasions during the course of this study using the upgradient and downgradient tile lines (Fig 10). Two detailed flow enhancement trials occurred (August 11-18, 2006 and November 22-29, 2006) which represent the focus of this project: 1) The August flow enhancement trial (herein referred to as the August event) was started after the down gradient tile line had been open for an extended period (since August 7, 2006). This allowed for the best estimate of equilibrium in a system with a highly variable gradient. For this event the transect was first sampled in detail, then flow through the downgradient tile was stopped by plugging the tile drain at PU 84. This eliminated flow through the downgradient tile line, thus it was expected that the flow in the barrier would return to natural flow conditions. 2) The November flow enhancement trial (herein referred to as the November event) commenced with both the upgradient and downgradient tile lines closed. After detailed sampling, the upgradient and downgradient tile lines were opened, which caused enhanced flow through the PRB.

Changes in flow rates resulted in modified HRTs within the barrier. HRT was calculated as follows:

$$HRT = \frac{V_{PRB} * \eta}{Q_{Vol}} \qquad (2.1)$$

Where:

V_{PRB} = Volume of PRB (August event = 8 m x 0.6 m x 4 m = 19.2 m^3, November event = 8 m x 0.6 m x 3.75 m = 18 m^3; difference due to removal of some PRB material during construction of upgradient tile line in Oct. 2006)

η = Porosity of PRB (0.7, from van Driel et al., 2006a)

Q_{Vol} = Volumetric flow rate through PRB (in most cases considered equivalent to the flow rate measured in the downgradient tile line)

2.1.5 Borehole Dilution Tests

Flow rates within the PRB were determined using three methods: borehole dilution tests, tracer tests and use of an electromagnetic flowmeter. Three 5 cm diameter wells, which fully penetrated the reactive barrier, were installed in May, 2006 for borehole dilution testing (Fig 11). However, only the downgradient well (Fig 11, PU-BD3) was used for most testing in order to prevent contamination of the PRB porewater from the NaCl tracer solution used during testing. While the borehole dilution tests were the only tests which directly measured flow velocities in the PRB, these tests were given lesser preference when tile drain flow rate data was available due to errors associated with borehole dilution testing. Detailed description of the borehole dilution testing methodology and flow rate calculations are given in Appendix A.

2.1.6 Tracer Tests

Tracer tests, using a salt tracer injected into the downgradient tile line, were used to determine flow velocities within the downgradient tile (between PU 85 and PU 86). It was

assumed that all water leaving the down gradient edge of the PRB was being captured by the tile drain. This assumption was deemed valid because measurements in Δ hydraulic head between the upgradient edge of the PRB (PU 2-1.3) and PU 84 in the downgradient tile drain remained strong through the experiment (Appendix Table C2). Tracer tests to prove non-flowing conditions were also conducted between PU 85 and PU 86 when the tile drain was closed. Detailed description of the tracer test methodology and flow rate calculations are given in Appendix A.

2.1.7 Electromagnetic Flowmeter Tests

A Marsh-McBirney Flowmate 2000™ electromagnetic flow meter was used for tile groundwater velocities which were too fast for salt tracer testing. Use of the flow meter involved lowering the instrument head down monitoring points PU 85, 93 and 94 (10 cm diameter PVC pipe), into the middle of the completely water-filled, non-perforated tile line, then recording the flow velocity. Detailed description of the electromagnetic flowmeter test methodology and flow rate calculations are given in Appendix A.

2.1.8 Reaction Rate Calculations

Varying amounts of denitrification and sulfate reduction were observed in the barrier during this study. Reaction rates, assuming zero order kinetics, were calculated using Eq. 2.2 (van Driel et al., 2006a):

$$\text{Rate} = (C_{IN} - C_{OUT})/\text{HRT} \qquad (2.2)$$

Where:

C_{IN} = influent concentration (mg/L)
C_{OUT} = effluent concentration (mg/L)
HRT = Hydraulic Retention Time (days)

Rates were expected to be temperature dependant (Sutton and Murphy, 1974; Gillespie et al., 1986; Robertson, et al., 2000; van Driel, 2006a), however temperatures remained relatively consistent during the August and November events (14.5 to 16.5 ºC).

2.1.9 Geochemical modeling

Mineral saturation indices for several minerals which were expected to be influenced by changes in pH and redox conditions within the PRB (calcite, siderite, rhodochrosite and gypsum) were determined using the chemical speciation model PHREEQCI version 2.13.2 (Parkhurst, 2007). During modeling, C was only represented by dissolved inorganic carbon (DIC), values for DOC were not used. The input of DOC values would have added additional model complications due to complexation of DOC with metallic ions. Because of the possibility of DOC complexation, the cation values used in the modeling study may have overstated the activity of those cations.

2.1.10 Anion Normalization

In order to calculate reaction rate and carbon depletion values during the November event, an estimate had to be made regarding the expected concentration of an anion along the reactive barrier transect if no anion reduction was occurring.

Water chemistry in the upgradient tile (PU 93) varied greatly from the natural PRB influent (PU 2-7), these differences allowed for a Cl⁻ based normalization of anions (Table 4, Eq. 2.3). Expected, or normalized, values were then calculated based on this Cl- ratio (Eq. 2.4)

$$\text{(Actual PRB Cl}^- \text{ conc. - Natural Upgradient Cl}^- \text{ Conc.) /}$$
$$\text{(Upgradient Tile Cl}^- \text{ Conc. - Natural Upgradient Cl}^- \text{ Conc.) =}$$
$$\text{Cl}^- \text{ ratio} \qquad\qquad (2.3)$$

$$\text{(Cl}^- \text{ Ratio * Anion Upgradient Tile Conc.) +}$$
$$\text{((1-Cl}^- \text{ ratio) * Anion Natural Upgradient Conc.) =}$$
$$\text{Expected Anion Conc.} \qquad\qquad (2.4)$$

The difference between the expected and actual concentration of anions in the PRB allowed for determining the amount of anion loss required to carry out both reaction rate carbon depletion calculations during the November event.

2.2   Results

2.2.1   August Event

2.2.1.1 Hydraulic Response

The hydraulic gradient at the site fluctuates significantly over the year (Fig 12), but groundwater flow is predominantly southeastward from the upgradient farm fields toward the Thames river (Fig 13).

August event flow rates were measured using both tracer tests and borehole dilution tests (Table 2). When the downgradient tile was open, flow rates of 1.4 to 2.2 L/min were

measured in the downgradient tile between days -3 to 0 (Fig 14). Borehole dilution tests for

groundwater velocity within the reactive barrier were also performed during the August

event, which indicated a flow rate of 0.9 m/day on Day -1 (downgradient tile line open) and

0.4 m/day on Day 1 (downgradient tile line plugged, Table 2, Fig 15). Based on the tracer

and borehole dilution tests, the HRT for the August event was estimated to be ~ 4.5 days on

Day -1 and ~ 10 days on Day 1.

2.2.1.2 Anion Behavior

NO_3

Prior to the August event with the down gradient tile line open, groundwater NO_3-N

within the barrier was routinely reduced from ~100 mg/L to <1 mg/L before the first barrier

monitoring point (PU 2A, 0.05 m from the upgradient edge of the PRB) was encountered

(Fig 16a). As expected, after the down gradient tile was closed, and the HRT in the barrier

increased from 4.5 to 10 days between days -1 and 1 (note that borehole dilution testing on

Day 0 indicated an HRT of 7.2 days, Table 2), NO_3 was still depleted to < 1 mg/L before the

barrier monitoring point, PU 2B (0.15 m into the barrier). Reaction rates for denitrification

could not be determined, in this case, because they occurred too rapidly for the limited

monitoring network.

SO_4

Immediately prior to the August event, with the down gradient tile open, SO_4

penetrated the entire length of the reactive barrier (Fig 16b). SO_4 entered the PRB at > 60

mg/L and persisted at the down gradient edge at a concentration of 5.7 mg/L (Day -1, HRT

4.5 days). When the down gradient tile line was closed (HRT increased to 10 days), SO_4 in the reactive barrier declined to < 1 mg/L by monitoring point PU 2C (0.54 m from the up gradient edge of the PRB).

2.2.1.3 Trace metal and Cation Behaviour

Throughout the experiment, concentrations of As remained below the detection limit of ~4 ppb, with only one instance of As appearing on Day 6 at a concentration of 4.1 ppb (Fig 17b). Fe concentration within the barrier remained relatively consistent throughout the August event, increasing from 0.02 to 1.58 mg/L at the upgradient edge to 5.06 to 7.2 mg/L at the downgradient edge (Fig 17c).

2.2.1.4 Eh and pH Behaviour

Eh

Eh data collected during the August event shows oxidizing water with an average Eh of 351 mV entering the PRB. As the water passes through the barrier, Eh declined to ~ -30 mV. This occurred rapidly before reaching monitoring point PU 2C, located only 0.54 m from the up gradient edge of the PRB was reached (Fig 17a). Eh values during the entire August event remained relatively stable even though a the HRT increased from 4.5 to 10 days.

pH

The pH within the PRB was not substantially affected by the flow rate change between Day -1 and Day 1. The pH consistently decreases from ~7.2 to 6.2, between the

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upgradient and downgradient edges of the PRB, during flow through the barrier (Fig 18a). However, by days 4-6, a slightly lower pH of ~6.0 was measured at the downgradient edge of the barrier.

2.2.2 November Event

2.2.2.1 Hydraulic Response

The November event commenced with both the upgradient and downgradient tile lines closed. Borehole dilution tests were performed on the upgradient reactor before and after the valves at PU 85 and 93 were opened (0.47 to 0.73 m/d, Table 2, Fig 15). After the tile lines were opened, the electromagnetic flowmeter, measuring flow rates in the tile lines, was the primary method used to evaluate the flow rate in the PRB (Table 2). Flow in the tile line was 2.3 L/min on Day 1 after the valves were opened, but then slowly diminished to 1.0 L/min by Day 7.

2.2.2.2 Anion Behaviour
NO_3

During the November event, before the tile line valves were opened, NO_3 in the reactive layer behaved similarly to the August event. NO_3-N entered the reactive barrier at ~ 100 mg /L and was rapidly reduced to < 0.02 mg/L, before the first monitoring point (PU 2C) was reached (Table 4, Appendix Table B3). After the valves at PU 85 and 93 were opened (The north upgradient tile line was not opened due to lack of NO_3-N in upgradient tile, Table

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3, Fig 6), the HRT was lowered from 11.1 days on Day 0 to 0.8 days on Day 1 (Table 2). This then caused NO_3 to completely penetrate the 4 m long PRB on Day 1, at which time a NO_3-N concentration of 1.8 mg/L remained at the down gradient edge of the PRB. Day 1 was the only day in which NO_3-N fully penetrated the barrier. In all subsequent days, NO_3-N was reduced to < 1 mg /L within 2.7 m into the barrier (monitoring point PU 5-1.3, Fig 19) as tile flow rates slowly diminished and HRT values increased (Table 2).

SO_4

Prior to the tile lines being opened during the November event, SO_4 entered the PRB at a concentration of 88.6 mg/L and diminished to a concentration of 0.1 mg/L after traveling 2.7 m into the PRB (Fig 19b). Immediately after the tile lines were opened, SO_4 depletion was lessened by the flow rate increase (0.3 m/day on Day 0 increased to 4.8 m/day on Day 1), which led to a decrease in HRT from 11.1 days on Day 0 to 0.8 days on Day 1 (Table 2). Note however, that after the tile lines were opened, flow within the barrier became a mixture of inflow from the upgradient tile plus natural groundwater flow. The chemical composition of these two influent components contrasted considerably (Tables 3,4). To assist in determining the amount of SO_4 reduction that was occurring, SO_4 content was normalized to the values expected based on the ratio of flow from the upgradient groundwater versus that from the upgradient tile inflow. This was done by comparing Cl^- concentrations in the upgradient tile (Table 3) to those in the PRB, then determining the percent of tile-related flow (Table 4, Fig 20). Typically, C/Co for SO_4 stayed above 0.8 over the entire length of the PRB, during the higher flow rate days (2.1 to 4.8 m/day), compared to a C/Co of 0.0 on Day

0, at monitoring point PU 5-1.3 (2.68 m into the PRB), when the flow rate was only 0.3 m/day.

2.2.2.3 Trace Metal and Cation Behaviour

Both before and after the tile lines were opened, Mn concentration increased from < 0.1 mg/L in the upgradient groundwater to 2 to 3 mg/L within the barrier (Fig 21b). However, a consistent decrease in Mn of 0.5 to 1 mg/L was noted within the first 3 m of the barrier while tile lines were open. Fe exhibited similar behaviour, increasing from 0.1 mg/L in the upgradient groundwater to 6 to 9 mg/L at the downgradient edge of the barrier (Fig 21c). Although several points decreased in concentration when flow increased (PU 4-1.6, 5-1.3), several other points increased (PU 2C, 3-6, 6-2). As expected, Ca, Mg, K and Na also appeared to be relatively unaffected by the flow rate changes, as concentration changes remained generally consistent with the mixing ratio changes between tile water and natural back ground water (Figs 21, 22).

2.2.2.4 Eh and pH Behaviour

Eh

At the beginning of the November event, water entered the barrier at an Eh of ~ +475 mV, then decreased to ~ +60 mV at the downgradient edge of the barrier (Fig 21a). However, this decrease was abrupt and occurred by the first monitoring point on Day 0, whereas the decrease occurred more uniformly through the barrier after the flow was increased (Fig 21a).

pH

At the beginning of the test when all tile valves were closed, influent groundwater

had a pH of 7.3, while the PRB effluent groundwater had a pH of 6.4 (Fig 22). These

observations are similar to those seen during the August event. After the valves were opened,

the decreasing pH trend disappeared, and the pH became relatively consistent at ~6.8 +/-

0.25, similar to the tile value of 6.9 +/- 0.07 (Fig 22a).

2.3   Modeling of Mineral Precipitation in the Zorra Barrier

The concentrations of major anion, cations, Eh and pH, measured on Day 7 of the

November event along the main transect, were input into PHREEQCI for determination of

the mineral saturation indices (Fig 24). Input data are given in Appendix B Table B4.

Results show that gypsum and calcite remain slightly to moderately undersaturated

throughout the entire PRB. Thus, it is unlikely that these minerals will precipitate in the

reactor. However, rhodochrosite and siderite show significant SI increase along the barrier

transect. Rhodochrosite SI increases from -0.8 in the upgradient groundwater to 0.4

immediately downgradient of the PRB, while siderite SI increases from -2.2 in the upgradient

groundwater to 0.62 immediately downgradient of the PRB. Thus, it is possible that these

minerals are precipitating in the PRB. Pyrite was not included in the modeling because the

required values for $H_2S_{(g)}$ in the model were not collected during the experiment.

2.4   NO$_3$ Disappearance in Upgradient Tile

The sampling events of November 20 to 29, 2006 showed NO$_3$-N values of 17.3 to 38.8 mg/L in the up gradient tile line (PU 93), but then much lower values of < 0.02 mg/L were consistently measured the following spring (May-June, 2007, Fig 25a, Table 3). Additionally, NH$_4$-N values in the upgradient tile line remained low throughout this period (1.4 to 2.2 mg/L, Fig 25), indicating that lack of NH$_4$ nitrification was not the reason for the lower nitrate values. The Total Kejldahl Nitrogen (TKN) value of the tile was only 4.4 mg/L on June 28, 2007 (Table 3). This indicates a disappearance of 15 to 35 mg/L of total N in the tile flow between the time of the November 2006 enhanced flow experiment and subsequent sampling in spring 2007.

2.5 Discussion

2.5.1 Flow Rate Manipulation

The flow rate data collected using a variety of methods (Table 2) demonstrated that substantial flow rate changes were achieved during the August and November manipulation events. During the August event, the HRT increased from 4.5 to 10 days, and during the November event HRT decreased from 11.1 to 0.8 days. These observations indicate that it is possible to passively manipulate HRT in a PRB using a simple valved tile drain system. Furthermore, this study demonstrated that existing PRBs can be easily retro-fitted with upgradient and downgradient tile drains that can then enhance the flow rate. If slower flow rates are desired, other PRB design modifications would have to be considered, such as expanding the length of the PRB.

This study also illustrated flow manipulation problems arising from the inability to control the natural gradient. During summer months, the hydraulic gradient across the Zorra site typically diminishes from 0.007 to essentially nil (Fig 12b). When hydraulic gradients were very low (e.g. July 2006), it was not possible to manipulate flow. This problem was compounded by occasional rain events which quickly increased the hydraulic head of the Thames river, while leaving the hydraulic head of upgradient regions unchanged. Furthermore, intense rain events caused flooding of the riparian zone, which on several occasions completely eliminated the horizontal hydraulic gradient across the entire study site. These are problems common to many PRB sites routinely affected by drought or variable precipitation. Thus, at

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many other sites, flow rate manipulation using drains would have been easier than at the Zorra site.

Data from borehole dilution testing was typically given less preference over flow rates calculated from the velocity of groundwater in the tile drains. Robertson et al. (2005) found that spatially varying borehole dilution tests were highly variable (33 to 749 cm/day) in a PRB consisting of similar woodchip media. Furthermore, the non-linear semi-log C/Co vs. time relationship (Fig 15) suggests an error in the borehole dilution tests. The large differences in flow rate, combined with the woodchip media being presumably more permeable than the well screen and bio-fouling of the well screen may have resulted in the incorrect selection of the formation factor used in calculations ($\alpha = 2$, Eq. A1). Thus, assuming that essentially all flow leaving the PRB enters the downgradient tile drain, the tracer and electromagnetic tests would give more representative values of flow PRB rate, and were thus given preference, where available.

2.5.2 NO$_3$ Response

Complete NO$_3$-N removal (<0.02 mg/L) typically occurred prior to the groundwater reaching the first monitoring points in the PRB (PU 2A to PU2C) during the August event, thus exact NO$_3$-N reaction rates could not be determined at that time. When groundwater flow rates increased to >1.5 m/day, during the November event, NO$_3$-N penetrated beyond the first monitoring point and average normalized NO$_3$-N reaction rates of 115 and 77 mg/L/day were determined at PU 3-6 and 5-1.3 respectively (Days 1 to 7, Table 5). These reaction rates are dissimilar to those reported previously in other PRBs containing coarse wood particle media

(~3 to 20 mg/L/day, Robertson et al. 2000; van Driel et al. 2006a,b). This brings the validity of the normalized rates into question. With the normalization procedure, expected NO_3-N concentrations, without denitrification, are higher leaving the PRB than entering the PRB (Table 4, Table 5).

Influent groundwater temperature for the August and November events remained fairly consistent at 14.5 to 16.5 °C. However, if temperatures had fluctuated, reaction rates would have changed (van Driel et al., 2006a). Diminished reaction rates with lower temperatures would have led to higher concentrations of NO_3 migrating farther into the reactor. This suggests a necessity of changing the flow rate in PRBs on a seasonal basis, particularly at shallow locations where greater seasonal temperature changes occur.

A possible explanation for the disappearance of NO_3 in the upgradient tile during May to June 2007 is that the source of the upgradient groundwater has changed. Between November, 2006 and May to June, 2007, the Cl^- values in the upgradient tile dropped from generally 140 to 190 mg/L to 52 to 89 mg/L (Fig 25b). Fe in the tile drain also changed, as concentrations increased from 0.14 mg/L (November 29, 2006) to 6.1 mg/L (May 23, 2007, Table 3). However, the lower 2007 tile Cl^- values remain consistent with the other groundwater source zones at the site, all of which had NO_3-N values generally above 10 mg/L (Robertson and Schiff, 2007). Thus, a differing source does not explain the absence of NO_3.

Groundwater DOC concentration in the upgradient tile may have also contributed to loss of NO_3-N through conventional denitrification (Eq. 1.7). During the November event, DOC in the upgradient tile was observed between 75 to 96 mg/L. However, on June28, 2007, the concentration of DOC in the same tile line drops to 18 mg/L. It is possible that the concentration of DOC has been lowered due to consumption of carbon by the denitrification

process. Unfortunately, Eh values in the upgradient tile were not collected during the Spring of 2007 due to equipment malfunction in the field, as a result redox environment in the upgradient tile could not be determined and denitrification could not be confirmed.

Another possible explanation for the disappearance of NO_3 in the tile line is the recently revealed "anammox" process. This reaction was first identified by Mulder et al. (1995) and involves the coupled removal of NH_4 and NO_3 together under anaerobic environments (Mulder et al., 1995).

$$3NO_3^- + 5NH_4^+ \rightarrow 4N_2 + 9H_2O + 2H^+ \qquad\qquad 2.5$$
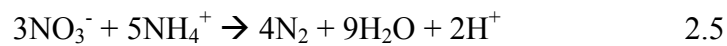
If such a reaction were taking place certain conditions would have to be met. High levels of both NH_4^+ and NO_3^- would have to co-exist in the upgradient aquifer (Van de Graaf, 1997). As well, the aquifer or tile drain must remain anoxic (Strous et al., 1997), and temperature must also be kept between 20 to 43ºC (Van de Graaf, 1997). However, the possibility of this reaction occurring at lower groundwater temperatures has not been fully explored and it is possible that all of these conditions could occur beneath the compost site by the mixing of recharge from different areas of the compost yard.

2.5.3   NO₃ and SO₄ Interaction

Under natural slower flow conditions, SO_4 reduction in the barrier took place at similar rates of between 14 to 34 mg/L/day during both the August and November events (Table 5). These rates pertain to barrier environments which were largely devoid of NO_3-N. After the tile lines were opened for the November event, the flow rate increased and NO_3-N rich water (>2 mg/L) penetrated throughout the barrier. Since SO_4 reduction is typically inhibited in the

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presence of NO_3 (Appelo and Postma, 2005, Fig 19a,b), the PRB was potentially converted from a SO_4 reducing environment to a NO_3 reducing environment (Brock et al., 1984). This is seen in the reaction rate response of SO_4 in the PRB. At piezometer PU 3-6 (where NO_3-N is present), the reaction rates for SO_4 between days 1 to 7 ranged from 0 to 31 mg/L/day; while at PU 5-1.3 (where NO_3-N was reduced) reaction rates for SO_4 between days 1 to 7 ranged from 17 to 63 mg/L/day. This would suggest that SO_4 reduction had been slowed in the portion of barrier where NO_3-N was >1 mg/L. However, this statement remains weak due to uncertainty associated with the normalization procedure (i.e. data scatter, daily changes in tile contribution and flow rate, the highly contrasting influent SO_4 concentrations, the 0.5 to 1 day time lag for influent groundwater to reach the principle monitoring points). Also, because of the short duration of the experiment (7 days) and the time lag required for bacteria to adjust to changes in redox conditions, equilibrium conditions may not have been achieved.

Minimizing SO_4 reduction would be advantageous in this case because additional carbon is consumed and an undesirable reaction product (H_2S) is generated (Eq. 1.1). During the August event, the decreased flow rate allowed the fraction of carbon being depleted from NO_3 reduction to decrease from 75 to 62% (Table 6), indicating a less efficient use of the carbon media under the slower flow rate. However, under the decreased flow rate, 88 kg less C would be used annually, as less NO_3 and SO_4 mass would enter the PRB (Table 6). Assuming the dry density of the bulk woodchip media in the Zorra PRB is 300 kg/m^3 (Robertson, 2007), that 58% of the wood mass is C (University of Guelph Soil and Nutrient Lab) and that all the carbon in the PRB is equally labile, the 3100 kg of carbon in the 8 m x 3.75 m x 0.6 m Zorra PRB would last 18 years at an average flow rate of 2.1 L/min, and 36 years at 0.95 L/min if reaction rates were maintained. Although the slower flow rate contributes to increased

longevity, it is less efficient because 38% of C is lost through the SO_4 reduction and excess DOC leaching. Furthermore, under this slowest studied flow rate, the least amount of NO_3-N is removed. Under higher flow rates during the August event, the PRB treats ~2.5 times more NO_3-N per year (123 kg/yr compared to 49 kg/year), demonstrating that the PRB is more efficient when the flow rate is increased. Estimates of C-depletion during the November event are problematic due to the difference in influent tile groundwater geochemistry compared to the natural influent groundwater (Table 6, Appendix Table B3). However, after normalization of the groundwater chemistry, the higher flow rates during the November event contribute to even greater PRB efficiency. Calculations from Day 7 of the November event (4.9 L/min, 2.1 m/day) indicate that 90% of the carbon depletion in the PRB is being used for denitrification. Furthermore, only 166 kg of C-media is required to treat 155 kg/yr of NO_3-N annually at this flow rate (4.9 L/min, 2.1 m/day). Thus, the PRB should last 17 years under the enhanced flow condition. Also of note is that the concentration of DOC in the upgradient tile line is higher than that leaving the PRB at PU 6-2 (Actual values of 58 mg/L compared to 36 mg/L respectively). This is beneficial to the PRB, as the amount of DOC material lost through leaching is minimized, and supplementary upgradient tile DOC will also contribute to denitrification, which should increase the barrier longevity.

2.5.4   Cation Response

The response of Fe and Mn during the enhanced flow November event was not as expected. An increase in redox potential should have resulted in a decrease in Fe and Mn within the barrier due to oxidation of Fe^{2+} and Mn^{2+} and subsequent mineral precipitation

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reactions (Stone and Morgan, 1984 a, b; Lovley and Phillips, 1986; Lovley, 1987; Stone, 1987a, b; Hering and Stumm, 1990). However, concentrations of Fe and Mn stayed relatively consistent even though the redox environment changed. This may suggest that the precipitation of Fe and Mn are being controlled internally within the PRB, and is not solely affected by reductive dissolution of hydroxide minerals. Blowes et al. (1994) noted that discrimination in PRB carbon source material could control levels of Fe(II) and Mn(II) being released into a PRB, as the degradation of wood media would likely release both Fe and Mn into solution. This could be occurring at the Zorra site. Concentration of Fe and Mn in wood chips typically ranges from 10 to 14 mg/kg and 20 to 140 mg/kg respectively (Rowell, 1984). Therefore, it is possible that the persistent concentrations of Fe and Mn in the barrier are a function of degradation of the wood chip media.

The reduction of SO_4 may also affect the concentrations of Fe and Mn. While the redox environment within the PRB during the November event was somewhat low (+13 to +335 mV), it does not appear to be within the stability field for FeS_2 at the pH ranges observed (below Eh values of ~ -150 mV, pH of 6.4 to 7.3, Appelo and Postma, 2005). However, Appelo and Postma (2005) note that under sulfate reducing conditions, the production of HS^- will cause FeS_2 mineral precipitation to occur (Eq. 1.2).

$$FeS + S^0 \rightarrow FeS_2 \qquad\qquad (2.6)$$

(Appelo and Postma, 2005)

Furthermore, the Eh environment of the Zorra PRB is within the 0 to +400 mV Eh range observed at the Nickel Rim site in Sudbury, Ontario (Bain, 1996), where pyrite and iron sulphide was actively precipitating.

2.5.5 Other Redox Indicators

During the August event, values for Eh, pH and DOC remain steady in the barrier (Fig 16a, 22a, 21c), because the HRT change was smaller (increased from 4.5 to 10 days). Changes in redox conditions during the November event were more pronounced however, because the change in HRT was more abrupt decreasing from 11.1 to 0.8 days. In particular Eh increased from +20 to +335 mV at PU 2C (Fig 20a), which presumably indicated a changing redox environment from SO_4 reducing to NO_3 reducing (despite some SO_4 reduction being still evident under enhanced flow rates). Consequently, on Day 1 after the flow increased, NO_3-N penetrated through the entire barrier. Thus, HRT manipulation can play an important role in controlling the redox environment in a wood-particle reactor such as this.

2.5.6 Normalization Error

Unfortunately the normalization procedure holds a substantial amount of error. This is most evident in the unusually high NO_3-N reaction rates determined during the November event. This is caused by three main sources of error: the first, is that the normalization procedure utilizes a Cl^- ratio, which is based off Cl^- concentrations which are somewhat variable (Figs 15, 18).

The second source of error is in the selection of piezometer point PU 2-7 as the natural upgradient monitoring point. Cl^- concentrations at PU 2-7 typically ranged from 31 to 37 mg/L, with lower concentrations commonly found closer to ground surface (Fig 8). However, Cl^- concentrations in the PRB varied between 38 to 84 mg/L. Ideally, a monitoring point at the

immediate upgradient face of the PRB would be better suited to describe the influent water chemistry, as there would be fewer sources of temporal or spatial related error. However, limitations in the monitoring network and a poor understanding of the heterogeneity of the aquifer, combined with the resulting difficulty in determining exact flowlines of groundwater into the PRB, prevented the use of such a point. Thus, PU 2-7 was selected as the best available representation of upgradient water chemistry.

The third source of error is the large difference between chemistry in the tile drain and the natural upgradient groundwater. This is of particular importance to NO_3-N, as concentrations range from 90 to 108 mg/L in the natural upgradient groundwater, compared to only 17 to 21 mg/L in the upgradient tile. Essentially, the error associated with the Cl^- ratio will be amplified by this large difference in influent NO_3-N, as an incorrect estimation of percent of flow from each of the upgradient influent sources will cause greater changes in estimated NO_3-N concentrations in the PRB.

Effectively, calculations requiring normalized anion values, such as reaction rates and carbon depletion estimates, are somewhat flawed. Thus, any statements made using these calculations are not entirely conclusive.

2.5.7 PRB Transience and Microbial Equilibrium

Manipulation of flow rates in the Zorra PRB was expected to increase the transience of water chemistry and redox values. This effect was likely maximized during the November event, where prior to the upgradient and downgradient valves being opened, the PRB was dominated by natural groundwater flow (0.3 m/day). When the HRT was decreased from 11.1

to 0.8 days, NO_3-N enriched water was carried to the downgradient regions of the PRB.

Upgradient microorganisms in the PRB were likely unaffected by the increase in NO_3-N

concentration, as NO_3-N was not uncommon in the region, however microorganisms in the

downgradient region of the PRB would have been significantly affected by the sudden change

in groundwater chemistry. Prior to the November flow enhancement event, between

piezometer points PU 5-1.3 and 6-2, concentrations of SO_4 ranged from 0.3 to 0.6 mg/L (Table

4), thus the sudden increase in NO_3-N and SO_4 in this portion of the PRB would have

significantly affected the redox and microbial equilibrium. Scholten et al. observed that

cultured acetate using nitrate reducing bacteria typically took 4 to 6 weeks of incubation to

reach maximum populations in a controlled lab environment, however acetate using sulfate

reducing bacteria required 9 to 10 months of incubation to reach maximum populations (2002).

If the response of acetate using microorganisms can be assumed to be similar to those found in

the Zorra PRB, the continually variable groundwater chemistry in the PRB (Appendix Tables

B1,B2,B3,B4) may suggest that a true microbial equilibrium is never reached. This problem is

further compounded by the highly variable natural gradient on site (Figure 11), which will

affect the distance NO_3-N and SO_4 are able to penetrate into the PRB. Thus, even under natural

gradient induced flow conditions, microbial equilibrium in the Zorra PRB is questionable.

While flow rates were not kept constant in this study, stricter control of flow rate may help

promote microbial equilibrium in an environment such as the Zorra PRB.

2.5.8   Effect of Carbon Compound Variety on Reaction Rates

Plant matter is typically composed of the following components (Paul and Clark, 1989):

2-20%	sugars and soluble carbohydrates,
15-60%	cellulose,
10-30%	hemicellulose,
5-30%	lignin,
2-15%	protein.

In a denitrifying PRB, the sugars and soluble carbohydrates are the first sources of labile carbon to be consumed; this is followed by hemicellulose (structurally dissimilar to cellulose) and eventually cellulose (Vogan, 1993). Plant matter most resistant to break down is the lignin fraction, which is compose of highly branched polymers of aromatic carbon units (Vogan, 1993). Reaction rates during the early stages of a reactive layer's lifespan will be higher than those later on due to the availability of more soluble carbohydrates in the reactive media (Vogan, 1993). Effectively, reaction rates in the Zorra PRB, during this study, should not be affected by the carbon media, since the barrier was ~1.3 years old at the beginning of the experiment, and presumably exhausted of the more labile carbon fractions.

3.0   Longevity of Wood Particle Barriers Treating Groundwater Nitrate

3.1   Introduction

Investigation of the long-term treatment capacity of wood particle barriers is of interest because the requirement for frequent media replenishment could make costs associated with this technology uncompetitive. To further assess longevity, two PRBs were investigated for their long-term treatment effectiveness. The Woodstock and Zorra barriers were chosen as both have been in operation for a similar length of time (3 to 4 years), treating groundwater NO_3 contamination. Both use high-K woodchip media which causes groundwater at depth to converge into the barrier (Robertson et al., 2005; Robertson et al., 2007). Previous longer term studies (Robertson et al., 2000; Schipper and Vojvodic-Vukovic, 2001; van Driel et al., 2006a) have not considered reactive barrier configurations using the coarser media.

3.2   Barriers

Woodstock reactive barrier

The Woodstock reactive barrier was installed in September 2003 near Woodstock, Ontario (Robertson et al., 2005). The pit for the reactor was trenched to ~ 2 m below ground surface, into the shallow water table zone, with a backhoe. It was speculated that such high K-layers near the water table would cause groundwater flow from depth to converge into the high K zone (Robertson et al., 2005). A plywood box was then installed to ~ 0.4 m below the water table to prevent sloughing. The box was then filled with ~ 0.4 m^3 of coarse wood particle media. Before the reactor was backfilled, the up and down gradient plywood walls were

removed, in order to allow for lateral flow through the wood media. HRTs in the barrier were

generated using flow rate data from borehole dilution tests. While the borehole dilution

velocities varied considerably between 0.33 to 7.49 m/d (Robertson et al., 2005), an average

hydraulic retention time of ≈ 0.6 days was determined. More detailed explanation of

experiment construction and design is provided by Robertson et al. (2005).

Zorra reactive barrier

The installation and description of the Zorra reactive barrier has been presented

previously (Section 1.3).

3.3   Results and Discussion

Woodstock Barrier

The initial sampling event (3 months after start up) indicated an influent concentration

of ~10 mg/L NO_3-N entering the barrier (Robertson et al., 2005). After passing through the

PRB, a down gradient plume of low NO_3-N groundwater (< 1 mg/L) occurred (Fig 26a). The <

1 mg/L NO_3-N plume that has developed down gradient of the reactive layer has remained

consistent for 3.8 years after installation (Fig 26b,c), demonstrating that the PRB is still

functioning.

Zorra Site

Upgradient groundwater NO_3-N concentrations at this site have ranged from 5 to >100

mg/L, with the highest NO_3 levels found at depths of 1 to 3 m below the water table. As the

high-K layer of the PRB diverts water from depth into the PRB, a plume of NO_3-N depleted

water is generated down gradient. By year 0.3 the plume of NO_3-N reduced water was still displacing the NO_3-N rich background water out of the local transect shown (Fig 27a). Sampling in year 0.9 indicated that the downgradient NO_3-N was completely displaced out of the transect at that time (Fig 27b). The down gradient plume remained similar, within this local zone, in year 2.3 (Fig 27c), confirming that the reactor is still functioning properly.

3.4   Conclusions

Based on the consistency of the plumes of nitrate attenuated groundwater at both the Woodstock and Zorra sites, over 2 to 4 years of operation, it appears that there has been no deterioration in PRB treatment performance at either of these sites over this time period.

4.0 Summary and Conclusions

4.1 Conclusions

4.1.1 Zorra site experiment

By changing the head conditions at the edges of the PRB using upgradient and downgradient tile drains, these experiments have demonstrated that it is possible to manipulate flow rates, and hence the hydraulic retention times in the reactor. Consequently, this technique has important implications for determining the redox environment within a PRB. While the ability of the tile drains to inhibit SO_4 reduction was somewhat uncertain in this case, the use of tile drains may allow larger capture areas to be remediated using a local scale PRB. At the Zorra site, natural flow through the barrier was insufficient to fully utilize the treatment capacity of the reactor for NO_3. With subsequent use of the tile drain system, more optimal NO_3 treatment conditions were periodically achieved during these experiments, allowing for more efficient use of barrier reactive materials. Flow enhancement increased the proportion of C being depleted by NO_3-N reduction from 62% at flow rates of 0.2 m/day, to 90% at flow rates of 2.1 m/day. Another implication is that the valve system could increase the seasonal treatment efficiency of the reactor. During the warm summer months, tile valves could be opened to accommodate for the higher reaction rates available, while the valves could be closed in the winter months to accommodate lower reaction rates.

4.1.2 Barrier longevity

This study demonstrated that wood-particle barriers composed of coarse woodchips, such as those at the Woodstock and Zorra sites, are capable of treating NO_3 contaminated groundwater for time spans of at least 2 to 4 years without media replenishment. Downgradient plumes at both sites indicate that there has been little or no deterioration of the treatment performance of the reactors over this time period.

4.2 Further Research

The choice of reactive media may play some role in the release of metallic ions in the PRB. Further study on the rate at which these metals are released from wood-particle PRB environments should be undertaken in order to understand the impact construction materials play in the geochemical evolution of downgradient plumes. If degradation of wood media contributes to the release of undesirable trace metals, wood-particle PRBs could potentially contribute to groundwater contamination.

One aspect of the enhanced flow rate system which was not addressed in this study was the degree to which modifying flow rates affects the down gradient plume shape. This could be assessed at the Zorra site through the installation of additional piezometers around the tile drain inlets and outlets and through further flow manipulation experiments.

Continued study of wood-particle PRB longevity should also be undertaken. In particular, the question of how flow enhancement effects PRB longevity should be more fully

addressed through continued operation of the Zorra site PRB and through additional C-depletion calculations.

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Tables

Table 1. Geochemistry along PRB detailed monitoring transect prior to August Event used for flow path determination (down gradient tile line open).

	Cl⁻ (mg/L)	NO3-N (mg/L)	SO4 (mg/L)	EC (µS)	Eh (mV)	pH
09-Aug-06						
PU 2-2	42.7	1.01	41.3	684	316	6.89
PU 2-3	35.2	3.36	26.6	644	336	6.98
PU 2-4	32.7	3.20	22.2	585	336	7.1
PU 2A	70.1	1.35	78.3	919	218	7.02
PU 2B	82.3	0.42	85.4	1058	60	6.81
PU 2C	86.8	< 0.02	53.6	1123	-36	6.54
PU 3-6	65.9	< 0.02	21.2	1050	20	6.5
PU 4-1.6	88.6	< 0.02	35.0	1141	-39	6.25
PU 5-1.3	66.3	< 0.02	13.1	996	-20	6.2
PU 6-2	48.0	0.02	4.1	985	19	6.09
11-Aug-06						
PU 2-5				859	318	7.15
PU 2-6				1238	349	7.12
PU 2-7	31.8	110.9	60.4	1566	323	7.07
PU 2A	48.6	0.28	49.3	811	247	7.12
PU 2B	60.3	< 0.02	49.4	990	61	6.86
PU 2C	85.6	< 0.02	47.6	1174	-13	6.63
PU 3-6	71.8	< 0.02	25.3	1049	-35	6.52
PU 4-1.6	81.6	< 0.02	24.4	1215	-22	6.35
PU 5-1.3	62.6	< 0.02	10.3	961	-23	6.28
PU 6-2	55.6	< 0.02	5.7	959	53	6.19

Table 2. Flow rate measurements. BHD is Borehole dilution test in barrier; Tracer is a salt tracer test in tile lines (Aug 11- Nov 29, 2006); EM is flow rate measured within the drainage tiles using a magnetic flow meter.

	Date	Event Day	Test Type	Flow in Tile (L/min)	Barrier Flow Velocity (m/day)	HRT (days)	Valve
August Event	7-Aug-06	Day -5	Tracer	4.1	1.7	2.3	open
	8-Aug-06	Day -4	Tracer	2.0	0.9	4.6	open
	8-Aug-06	Day -4	BHD		0.8	5.2	open
	9-Aug-06	Day -3	Tracer	2.7	1.2	3.5	open
	10-Aug-06	Day -2	Tracer	1.9	0.8	4.8	open
	11-Aug-06	Day -1	Tracer	2.1	0.9	4.5	open
	12-Aug-06	Day 0	BHD		0.6	7.2	open
	12-Aug-06	Day 0	Tracer	1.4	0.6	6.9	open
	13-Aug-06	Day 1	BHD		0.4	10	closed
November Event	22-Nov-06	Day 0	BHD		0.3	11.1	closed
	23-Nov-06	Day 1	BHD		0.5	7.3	open
	23-Nov-06	Day 1	EM	11.1	4.8	0.8	open
	25-Nov-06	Day 3	EM	8	3.4	1.1	open
	27-Nov-06	Day 5	EM	5.9	2.5	1.5	open
	29-Nov-06	Day 7	EM	4.9	2.1	1.8	open

Table 3. Geochemistry of upgradient tile. Values taken from PU 93, unless otherwise stated.

	Day	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	NH$_4$-N (mg/L)	EC (µS)	pH	Fe (mg/L)	Mn (mg/L)	TKN (mg/L)	DOC (mg/L)
20-Nov-06 *	Day -2	249.1	0.15	107	8.66						161
20-Nov-06	Day -2	418.4	38.8	112	2.65						96.2
23-Nov-06	Day 1	177.7	16.9	149							
25-Nov-06	Day 3	141.0	17.3	143		880	6.79				
27-Nov-06	Day 5	193.4	19.2	153		224	6.92				
29-Nov-06	*Day 7*	*160.8*	*20.7*	*171*		*936*	*6.86*	*0.14*	*1.5*		*75*
23-May-07		65.7	<0.002	108	1.4	2880	7.17	6.1	4		
14-Jun-07		89	< 0.002		1.4	3150	6.94				
19-Jun-07		51.8	< 0.002		1.5	1883	7.05				
26-Jun-07		65.8	0.46		1.4						
28-Jun-07										4.4	18.2

* Values denote chemistry from second (north) upgradient tile.

Table 4. Data used for November event reaction rate calculations.

		Tile	PU 2-7	PU 2C	PU 3-6	PU 4-1.6	PU 5-1.3	PU 6-2
Day 0	22-Nov-06	0		0	0	0	0	0
Day 1	23-Nov-06	1		0.85	0.76	0.68	0.45	0.35
Day 3	25-Nov-06	1		0.94	0.79	0.63	0.56	0.54
Day 5	27-Nov-06	1		0.64	0.39	0.36	0.28	0.32
Day 7	29-Nov-06	1		0.80	0.68	0.73	0.46	0.43
		NO_3-N Measured (mg/L)						
Day 0	22-Nov-06	--	106.5	0.0	0.0	0.1	0.0	
Day 1	23-Nov-06	16.9	107.5	13.8	11.8	7.6	3.9	
Day 3	25-Nov-06	17.3	91.4	12.4	10.2	4.4	0.4	
Day 5	27-Nov-06	19.2	91.7	14.1	11.3	1.6	0.0	
Day 7	29-Nov-06	20.7	90.1	11.0	7.7	3.7	0.0	
		NO_3-N Expected (Co) based on fraction of tile flow (mg/L)						
Day 1	23-Nov-06	16.9	107.5	30.3	38.5	45.8	67.1	
Day 3	25-Nov-06	17.3	91.4	21.7	32.6	44.7	49.5	
Day 5	27-Nov-06	19.2	91.7	45.5	63.4	65.9	71.7	
Day 7	29-Nov-06	20.7	90.1	34.6	43.1	39.7	58.1	
		SO_4 Measured (mg/L)						
Day 0	22-Nov-06	0.0	88.6	17.4	22.1	9.0	0.3	0.6
Day 1	23-Nov-06	149.3	90.5	141.8	129.1	103.2	83.2	58.0
Day 3	25-Nov-06	143.3	87.0	150.0	132.3	116.5	95.6	95.0
Day 5	27-Nov-06	152.7	79.0	147.6	98.9	102.1	82.1	83.0
Day 7	29-Nov-06	171.3	85.1	153.4	132.1	112.2	100.7	93.5
		SO_4 Expected (Co) based on fraction of tile flow (mg/L)						
Day 1	23-Nov-06	149.3		140.6	135.2	130.5	116.7	111.1
Day 3	25-Nov-06	143.3		139.9	131.6	122.4	118.8	117.3
Day 5	27-Nov-06	152.7		125.9	107.8	105.3	99.3	102.4
Day 7	29-Nov-06	171.3		154.1	143.5	147.7	124.8	122.2
		DOC Measured (mg/L)						
Day 7	29-Nov-06	75.0	3.2	57.7	47.9	37.6	34.9	35.7
		DOC Expected (Co) based on fraction of tile flow (mg/L)						
Day 7	29-Nov-06	--	--	60.6	51.8	55.4	36.3	34.1

Fraction of tile flow based on Cl⁻ ratio

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Table 5. Reaction rates of NO_3-N and SO_4 for August and November events. a) August event reaction rates, Rate = (Concentration In – Concentration Out)/ HRT, b) November event reaction rates, (Anion loss)/HRT. November rates normalized based on Cl^- mixing ratio between upgradient natural groundwater and tile influent, where anion loss is the difference between expected and actual anion concentrations.

a)

					SO₄				
Piezometer Pair	Day	Flow in Tile (L/min)	Barrier Flow Velocity (m/day)	Distance HRT measured over (m)	HRT (days)	Raw Conc. In (mg/L)	Raw Conc. Out (mg/L)	Difference Measured (mg/L)	Raw SO₄ Reaction Rate (mg SO₄/L/day)
				August Event					
PU 2A, 3-6	Day -1	2.1	0.9	1.05	1.1	49	10	-39	34
	Day 0	1.4	0.6	1.05	1.8	51	15	-36	20
	Day 1		0.4	1.05	2.6	42	3	-39	15
				November Event					
PU 2C, 4-1.6	Day 0	--	0.3	2	5.6	88	9	--	14

b)

						NO₃-N				
						November Event				
Piezometer	Day	Flow in Tile (L/min)	Barrier Flow Velocity (m/day)	Distance HRT measured over (m)	HRT (days)	Raw Conc. (mg/L)	Tile Flow Fraction	Expected Conc. In (mg/L)	Anion Loss (mg/L)	Normalized NO₃ Reaction Rate (mg N/L/day)
PU 3-6	Day 1	11.1	4.8	0.95 a)	0.2	12	0.76	39	-27	139
	Day 3	8	3.4	0.95	0.2	10	0.79	33	-22	93
	Day 5	5.9	2.5	0.95	0.4	11	0.39	63	-52	145
	Day 7	4.9	2.1	0.95	0.4	8	0.68	43	-35	82
PU 5-1.3	Day 1	11.1	4.8	2.68	0.5	3.9	0.45	67	-63	117
	Day 3	8	3.4	2.68	0.7	0.4	0.56	50	-49	73
	Day 5	5.9	2.5	2.68	1.0	0.0	0.28	72	-72	71
	Day 7	4.9	2.1	2.68	1.2	0.0	0.46	58	-58	48
						SO₄				
						November Event				
Piezometer	Day	Flow in Tile (L/min)	Barrier Flow Velocity (m/day)	Distance HRT measured over (m)	HRT (days)	Raw Conc. (mg/L)	Tile Flow Fraction	Expected Conc.(Co, mg/L)	Anion Loss (mg/L)	Normalized SO₄ Reaction Rate (mg SO₄/L/day)
PU 3-6 (NO₃-N present)	Day 1	11.1	4.8	0.95	0.2	129	0.76	135	-6	31
	Day 3	8	3.4	0.95	0.2	132	0.79	132	0	0
	Day 5	5.9	2.5	0.95	0.4	99	0.39	108	-9	25
	Day 7	4.9	2.1	0.95	0.4	132	0.68	144	-12	28
PU 5-1.3 (NO₃-N not present)	Day 1	11.1	4.8	2.68	0.5	83	0.45	117	-34	63
	Day 3	8	3.4	2.68	0.7	96	0.56	119	-23	34
	Day 5	5.9	2.5	2.68	1.0	82	0.28	99	-17	17
	Day 7	4.9	2.1	2.68	1.2	101	0.46	125	-24	20

Table 6. PRB carbon consumption during varying flow rates. August event influent data from PU 2C, effluent data from PU 6-2. November event calculations based on difference between normalized and expected values at PU 6-2. Values for dissolved oxygen (DO) on August event Day 4 and November event Day 7 were estimated from appendix B data. Flow rate value for August event Day 4 was estimated based on the change in HRT between valve open and closed conditions (from 4.5 days to 10.0 days respectively).

	Concentration (mg/L)			Δ (g/day)	C consumed		% of Total C Consumed
	Influent (PU 2C)	Effluent (PU 6-2)	loss (Δ)		(g/day)	(kg/year)	
August Event Day -1 (Flow 2.1 L/min, vel. ~0.9 m/day)							
NO_3-N	111	< 0.02	-111	-336	360	131	75.4
SO_4	60	5.7	-54	-164	41	15	8.6
DO	3	< 0.1	-3	-9	3	1	0.7
DOC	14	38	24	73	73	26	15.2
					Total	174	100.0
August Event Day 4 (Flow ~0.95 L/min, vel. ~0.2 m/day)							
NO_3-N	99	< 0.02	-99	-135	145	53	61.6
SO_4	60	0.1	-60	-82	20	7	8.7
DO	3	< 0.1	-3	-4	2	1	0.7
DOC	4	54	50	68	68	25	29.0
					Total	86	100.0
November Event Day 7 (Flow 4.9 L/min, vel. ~2.1 m/day)							
	Concentration (mg/L) (PU 6-2)			Δ (g/day)	C consumed		% of Total C Consumed
	Expected	Actual	Anion loss (Δ)		(g/day)	(kg/year)	
Normalized Values							
November Event Day 7 (Flow 4.9 L/min, vel. ~2.1 m/day)							
NO_3-N	60	< 0.02	-60	425	455	166	89.5
SO_4	122	93.5	-29	203	51	18	9.9
DO	3	< 0.1	-3	21	8	3	1.6
DOC	34	35.7	+2	-11	-4	-2	--
					Total	185	100.0

Figures
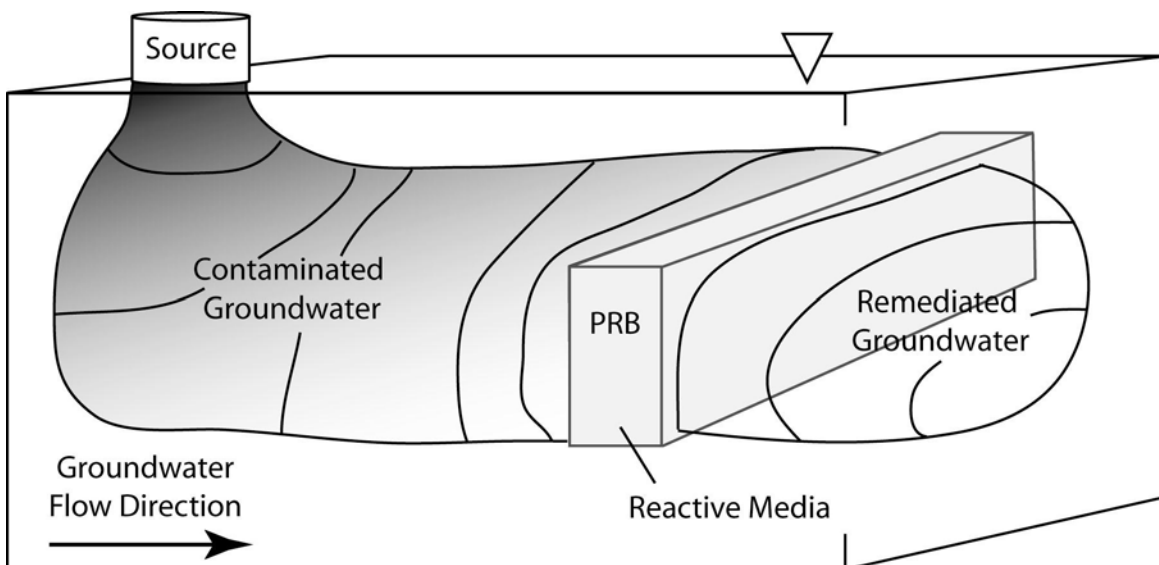
Figure 1. Conceptual diagram of a permeable reactive barrier. Contaminated groundwater is transported through the permeable reactive barrier and treated passively by barrier materials which either degrade, precipitate or adsorb target contaminants and allow the remediated water to exit the downgradient edge of the barrier.
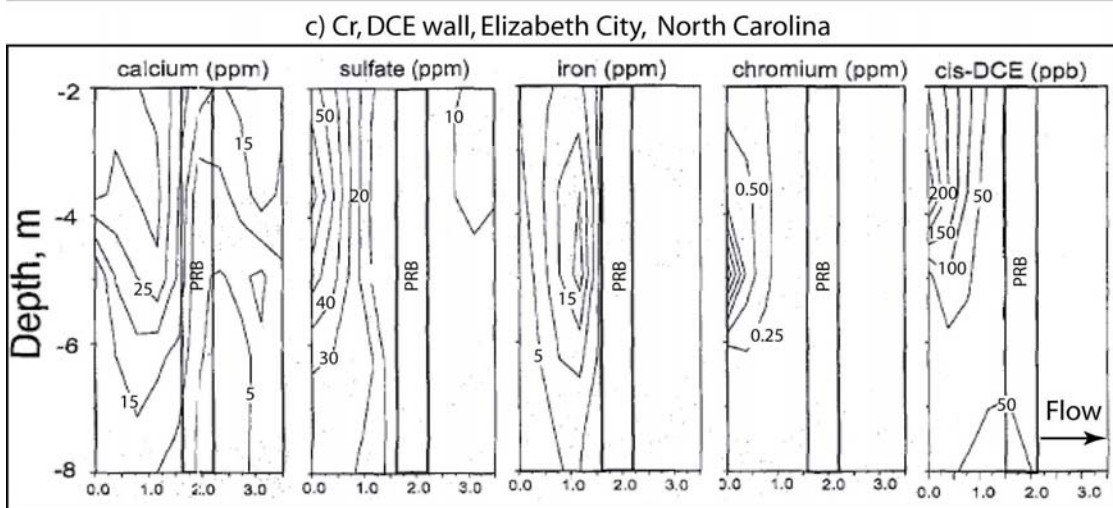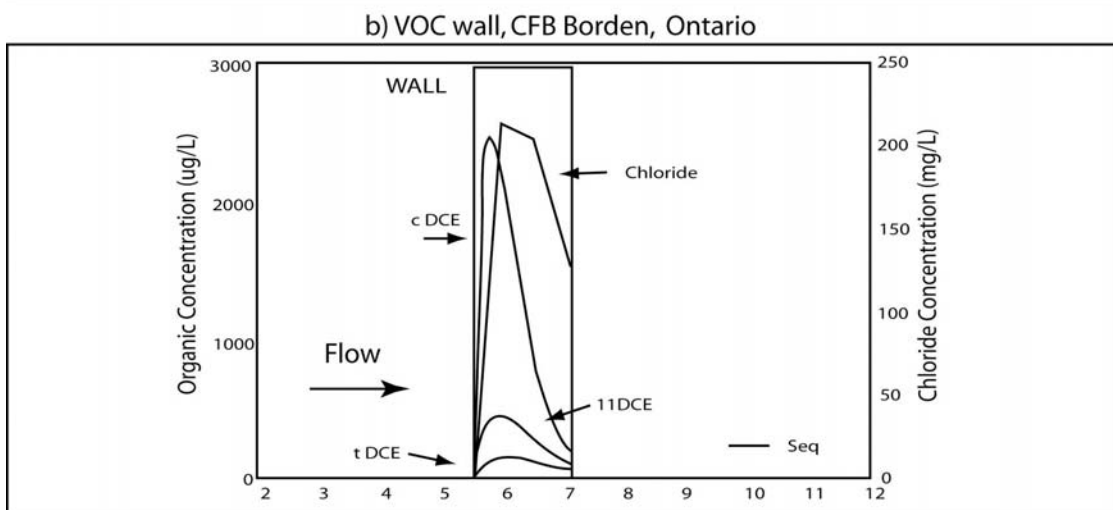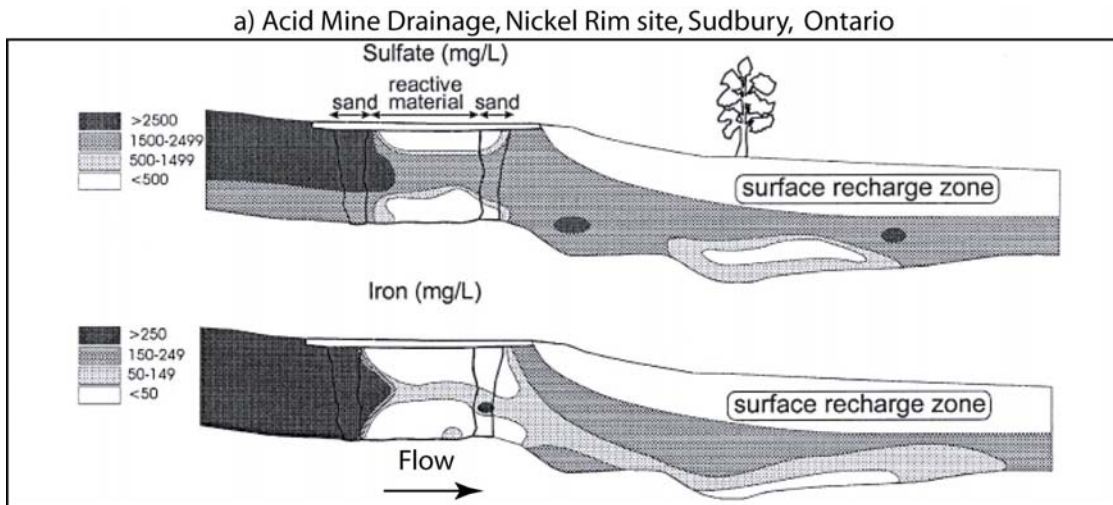
Figure 2. Examples of PRBs with non-optimal flow rates: a) organic carbon (mulch and woodchips) barrier treating acid mine drainage, Nickel Rim mine site, Sudbury, Ontario, from Benner et al. (1997) b) zero-valent iron wall treating VOC compounds, CFB Borden, Ontario from O'Hannesin and Gillham (1998), c) zero-valent iron wall treating Cr and DCE, Elizabeth City, North Carolina from Wilkin et al. (2002).
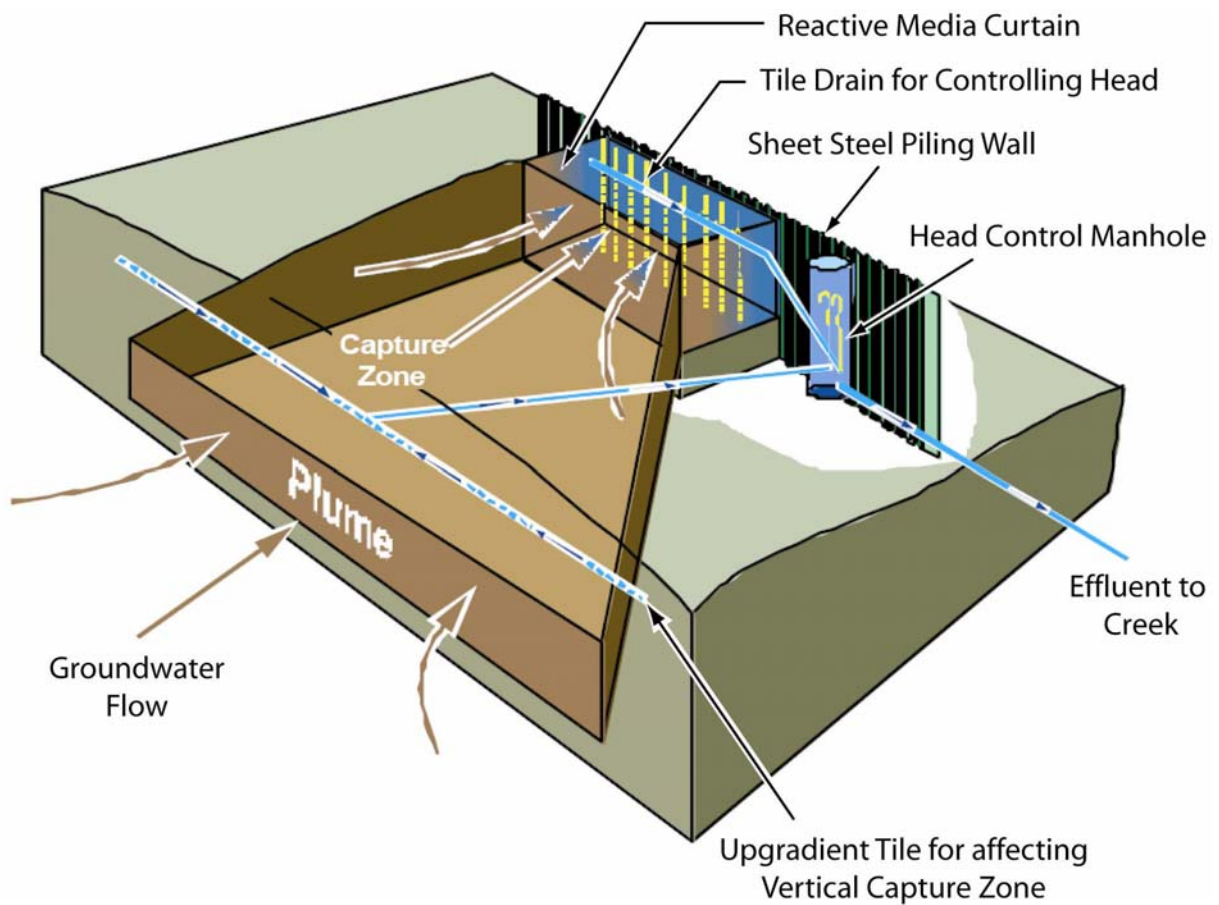
Figure 3. AECL's ^{90}Sr sorbing Wall-and-Curtain. ^{90}Sr contaminated water upgradient of the wall is drawn into the adsorbing curtain by the tile drain and vertical perforated well system installed in the adsorbing material. When the tile line removing the effluent water from the adsorbing wall is lowered inside the adjacent manhole, the hydraulic head in the curtain is affected. The sheet piling behind the curtain is necessary in order to prevent interaction between the curtain and the downgradient wetland. Figure adapted from Lee and Hartwig (2005).
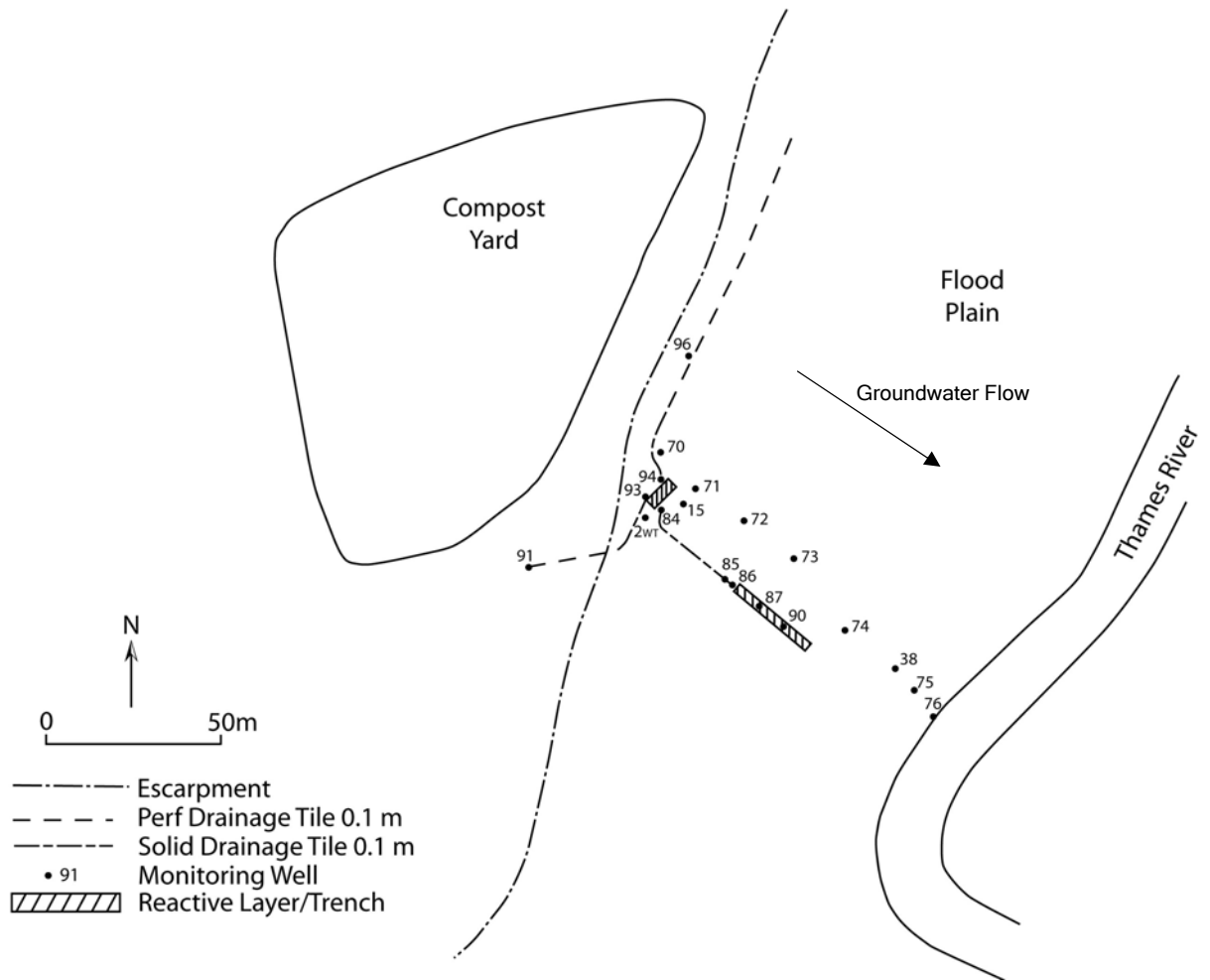
Figure 4. Site sketch of Zorra Site. See Figure 7 for PRB main transect points.

Figure 5. NO$_3$ distribution along Zorra reactive barrier transect, 4 months after layer installation (from Robertson et al., 2007).
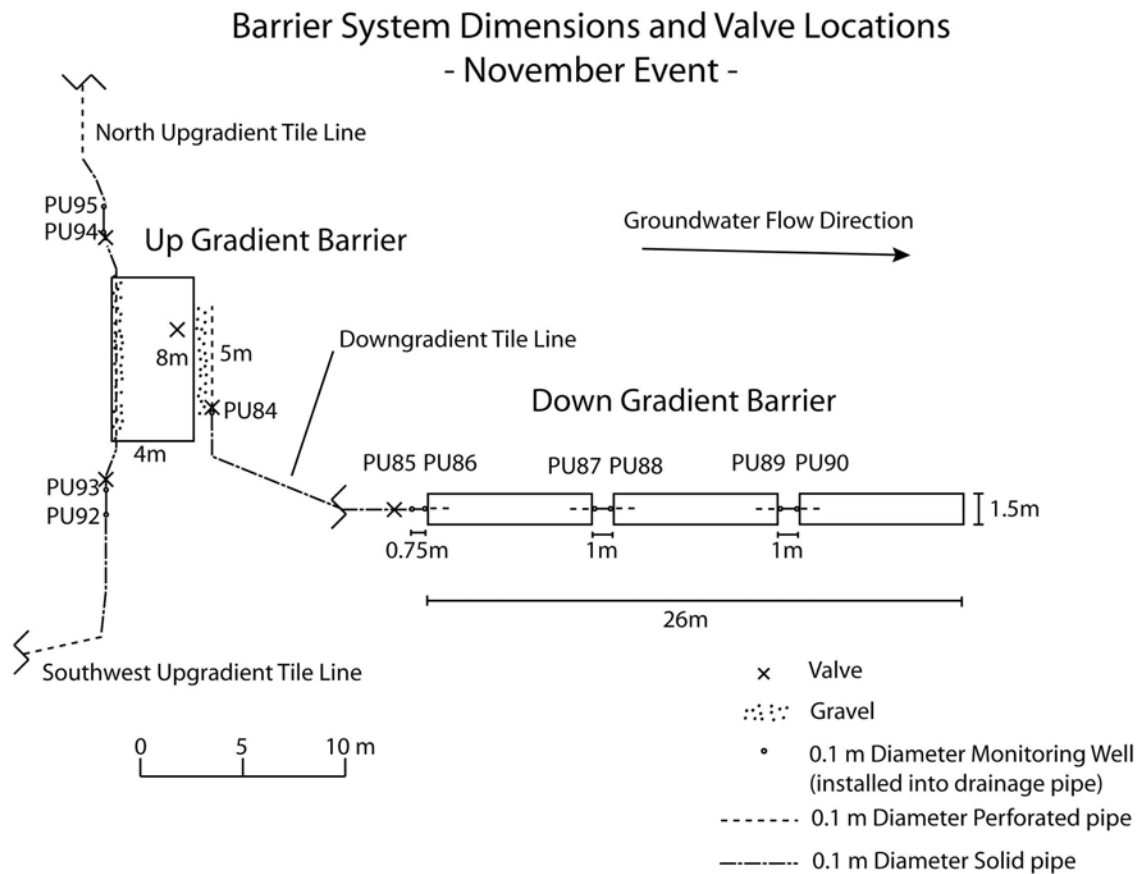
Figure 6. Sketch of Zorra PRBs showing up and down gradient tile lines and valve locations. The up gradient barrier is approximately 0.55 m in depth, and the down gradient barrier is about 0.6 m in depth. During the August 2006 event, only the down gradient tile line was in place. The upgradient tile lines and monitoring wells 91-96 were installed September 25-26, 2006.
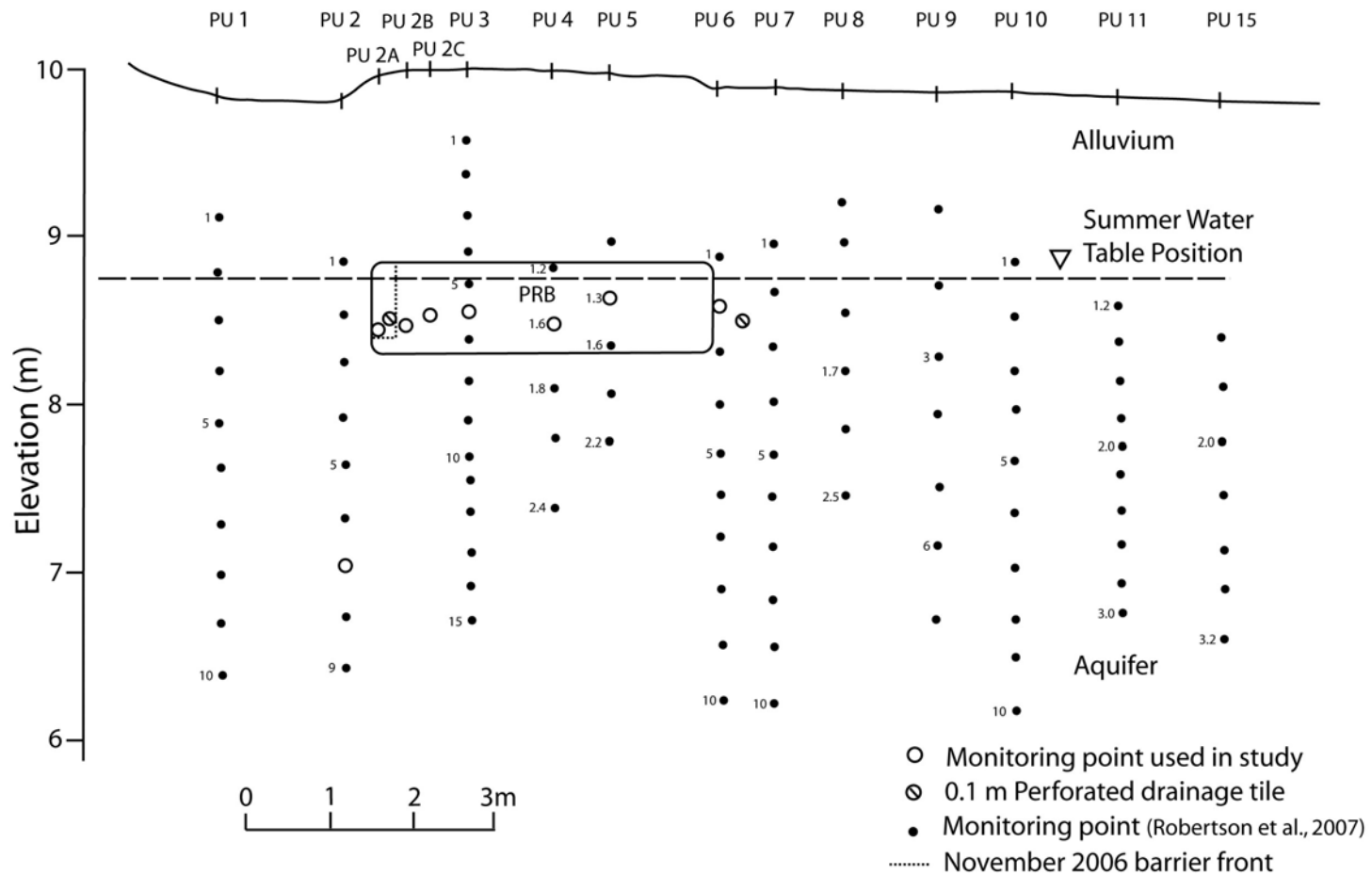
Figure 7. Monitoring network transect through Zorra reactive barrier showing principle monitoring points used in this study, and piezometer bundles installed in a previous study (Robertson et al, 2007). Piezometer locations along transect are indicated in the text by the first number, followed by a hyphen with depth to tip as the second number (i.e. PU 2-7, PU 5-1.3).

Cl⁻ Concentrations along Zorra site main transect

a) Year 0.9 – June 27, 2005
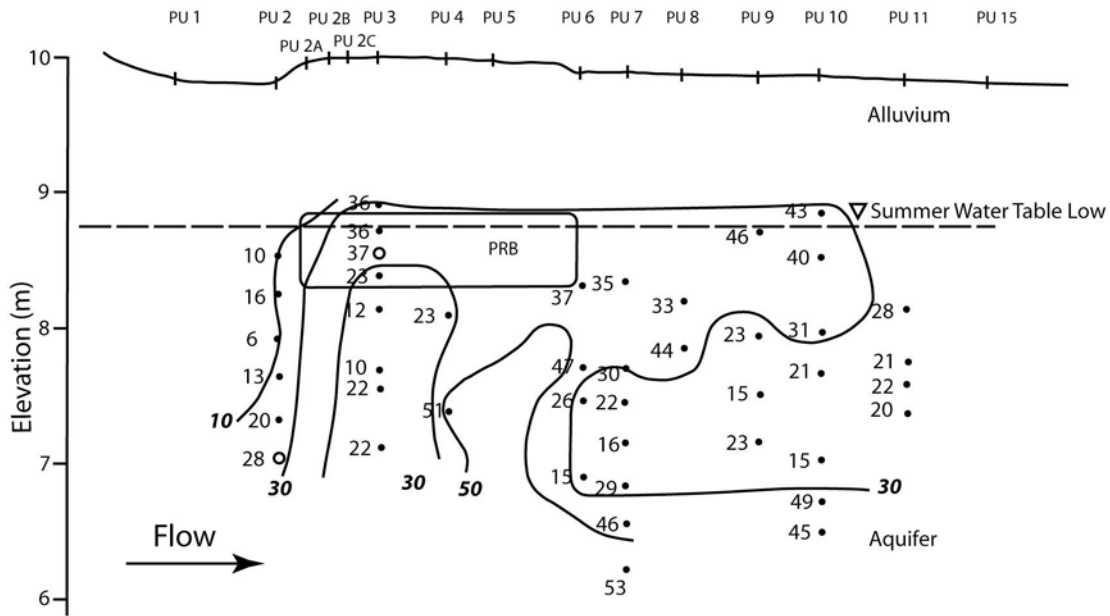
b) Year 2.3 – November 22, 2006
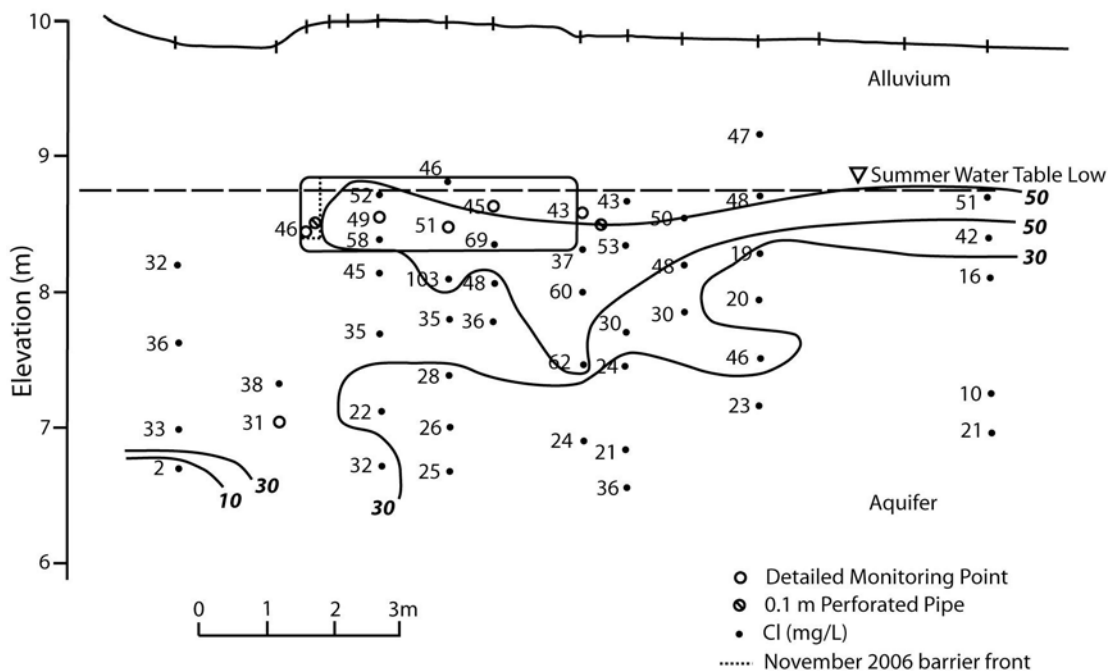
Figure 8. Concentration of Cl⁻ along Zorra barrier transect 0.9 and 2.3 years after installation. Distribution of elevated Cl⁻ in plume for 2.3 year cross section has been affected by input concentrations from the tile drain during valve tests at the up gradient 0.1 m perforated pipe (Cl⁻ in tile drain = 141-178 mg/L).

Flow modeling of Zorra site PRB
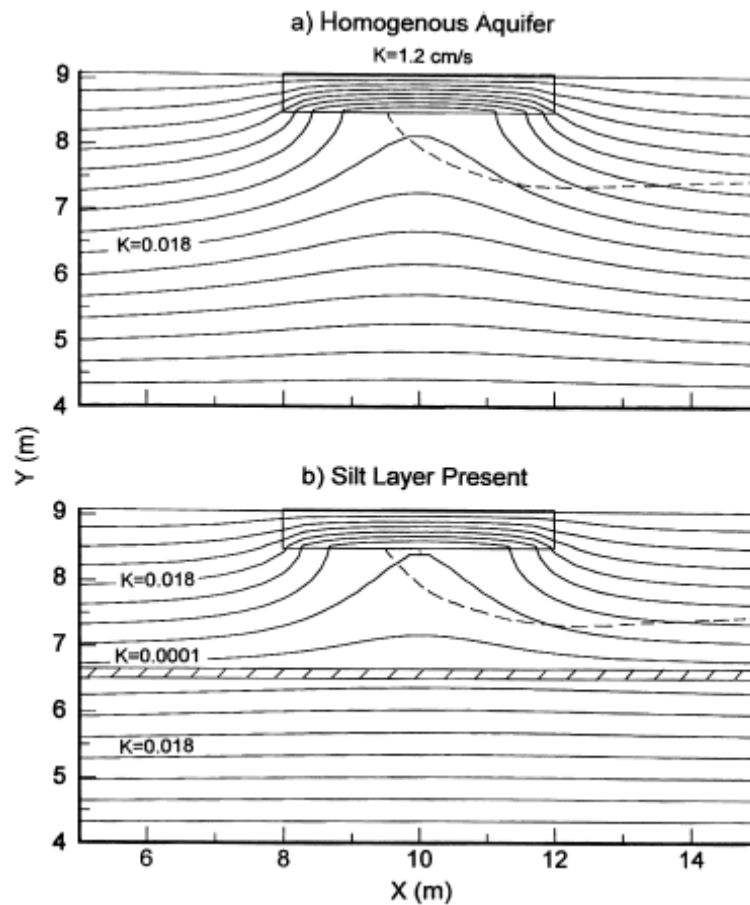
Figure 9. Numerical simulation of groundwater streamlines associated with Zorra PRB. a) representation of a homogenous aquifer system with a high K layer present representing the PRB. b) water flow path with known silt lens beneath Zorra barrier. Dashed lines represented 30 mg/L NO_3-N contours at Zorra site. Model domain extends from x = 0 to 20 m and y = 4 to 9 m, from (Robertson et al., 2007).

August, 2004	Zorra reactive barrier installed. (PRB flow = 0.3 m/day)
September, 2005	Downgradient tile and (second) reactive barrier installed. Downgradient valve left closed.
April, 2006	Sampling sweeps of entire PRB transect during valve closed conditions conducted.
May 2, 2006	Downgradient tile drain opened. Frequent sampling of valve open conditions begins. (PRB flow = 0.7 m/day)
July 19, 2006	Downgradient valve is temporarily closed then re-opened to test flow and valve capabilities. (PRB flow = 0.2 to 0.7 m/day)
July 20, 2006	Downgradient tile closed until August 7, 2006. (PRB flow ~0.2 m/day)
August 7, 2006	Background sampling for August event begins, with downgradient valve left open. (PRB flow = 1.7 m/day)
August 11, 2006	August event commences, downgradient valve is closed. (PRB flow = 0.9 m/day)
August 18, 2006	August event concludes, downgradient tile left closed. (PRB flow < 1 m/day)
October, 2006	Upgradient tile lines are installed.
November 14, 2006	Valves in upgradient tile lines are temporarily opened and closed again to test valves. (PRB flow = 3.3 m/day)
November 22, 2006	November event commences, upgradient and downgradient valves are opened. (PRB flow = 0.3 m/day)
November 29, 2006	November event concludes, upgradient and downgradient tile lines are left open. (PRB flow = 2.1 m/day)
May 23, 2007	Barrier transect and upgradient tile lines are sampled for chemistry and flow rates. Tile lines are open. (PRB flow ~2.5 m/day)
June 28, 2007	Last day of sampling for this project. All tile lines are left open. (PRB flow ~ 1.9 m/day)

Figure 10. Chronology of construction and flow manipulation events affecting PRB chemistry and equilibrium at Zorra research site. More detailed information on valve state and flow rates in Appendix Table A1. August 2004 flow rate from Robertson et al. (2007).
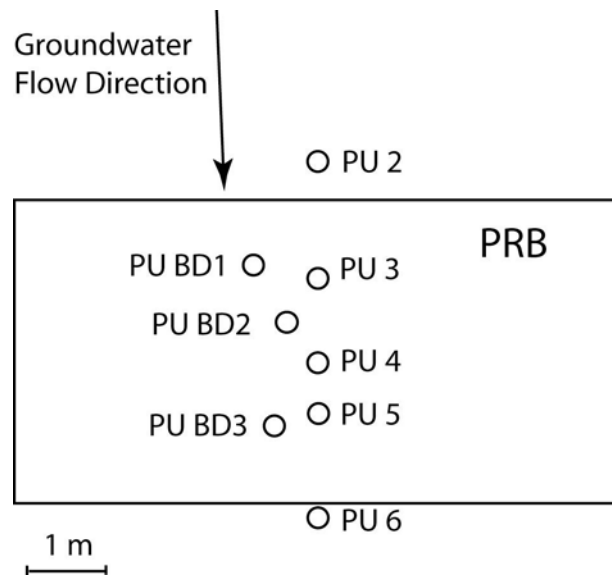
Figure 11. Location sketch of 5-cm diameter wells used for borehole dilution testing.

Hydrograph
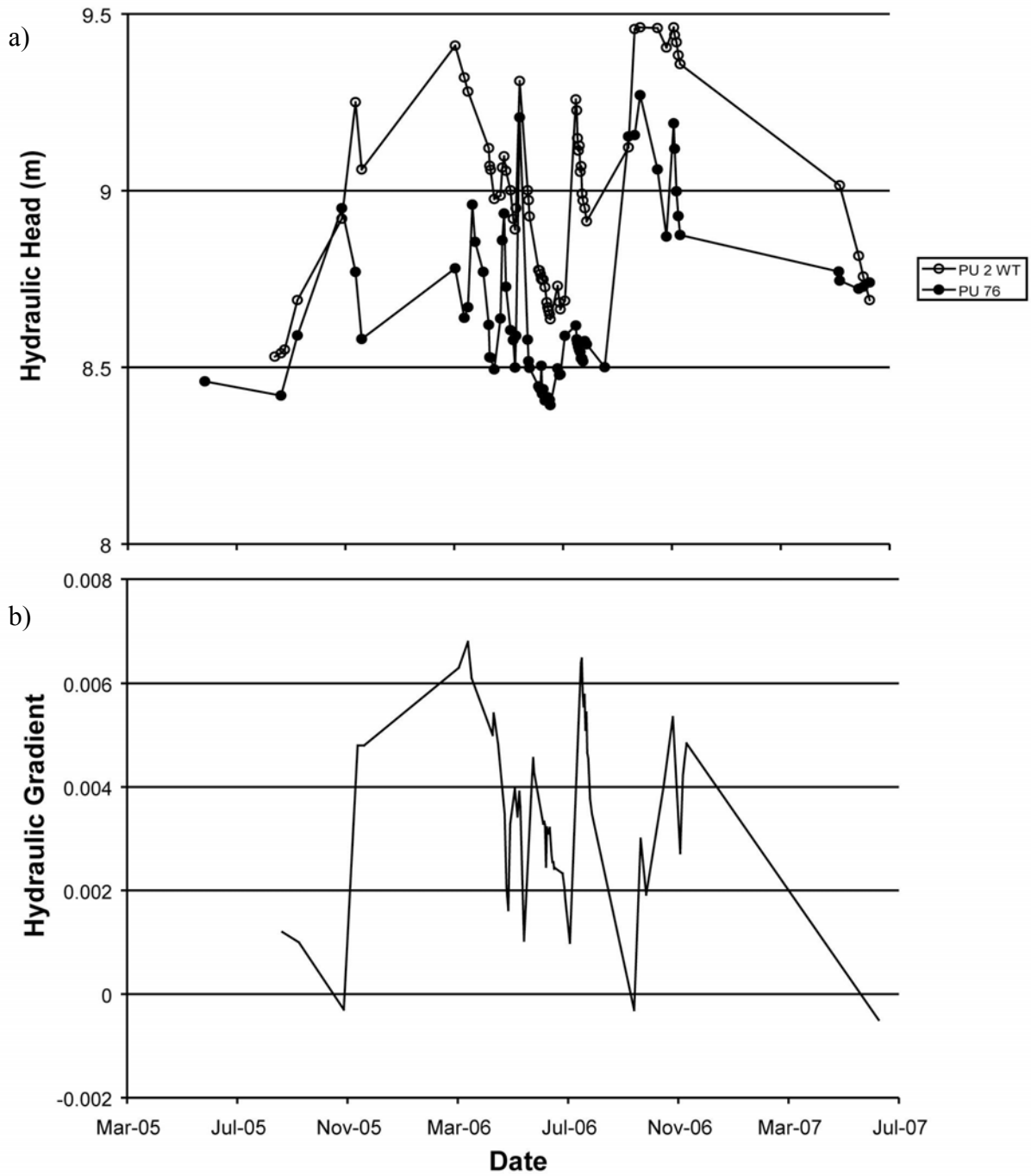
Figure 12. Hydrograph of Zorra site water table elevation and horizontal hydraulic gradient. Head values are relative to arbitrary datum; a) Comparison of water table elevations at monitoring wells PU 2WT and PU 76, site flooded where lines cross; b) Hydraulic gradient between PU 2WT and PU 76 (distance between points is 100m, Fig 4).

Water Table during August and November Enhanced Flow events
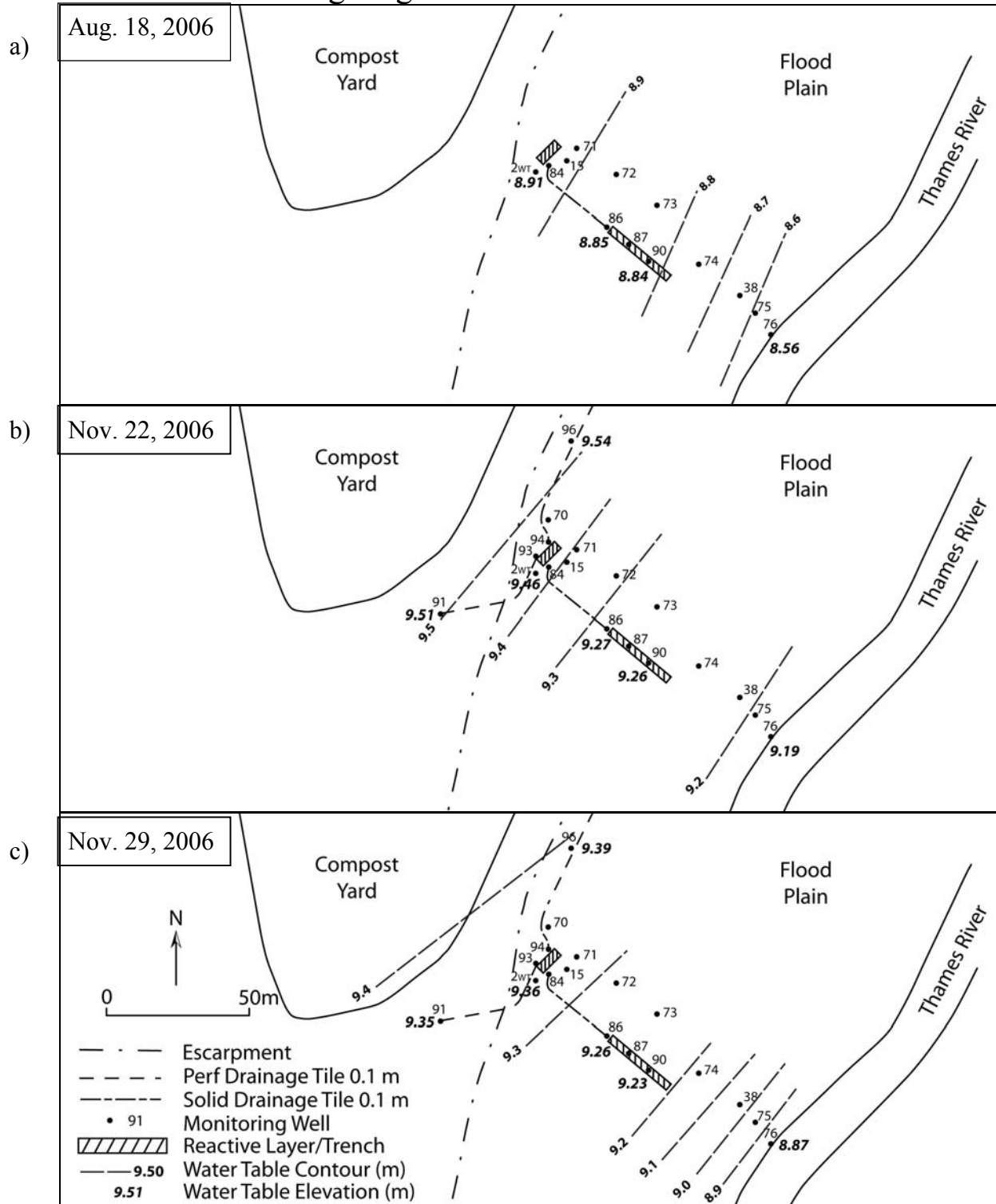
Figure 13. Water table map during: a) August event (valve closed), b) November event (valves closed), c) November event (valves open).

August Event Tracer Tests

August 10, 2006	August 11, 2006
(Day -2 – Valve Open)	(Day -1 – Valve Open)

Test 1
Q = 2.0 L/min

Test 1
Q = 2.0 L/min

Test 2
Q = 1.9 L/min

Test 2
Q = 2.2 L/min

Test 3
Q = 2.0 L/min
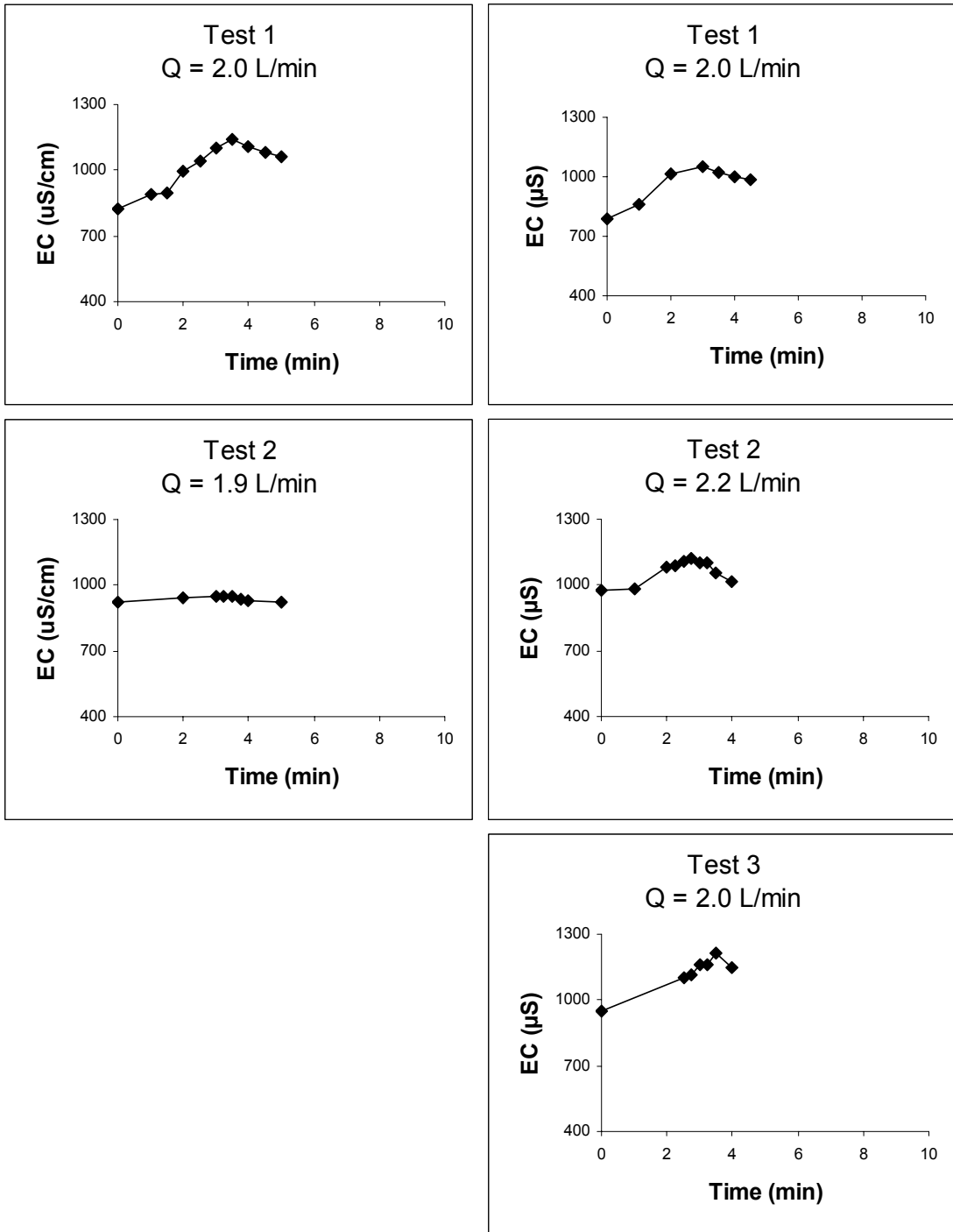
Figure 14. Tracer tests performed between monitoring points PU 85-86 in the down gradient tile line (0.75m travel distance). Tests on August 10-12 indicate flow rate in the down gradient tile line prior to the barrier being plugged after the Aug 12 flow rate testing. Tests for August 16 and 18 illustrate no flow conditions in the down gradient tile. EC variability reflects variation in NaCl amounts used in tests. See Figure C1 for diagram showing experiment setup.

August Event Tracer Tests

August 12, 2006	August 16, 2006
(Day 0 – Valve Open)	(Day 4 – Valve Closed)
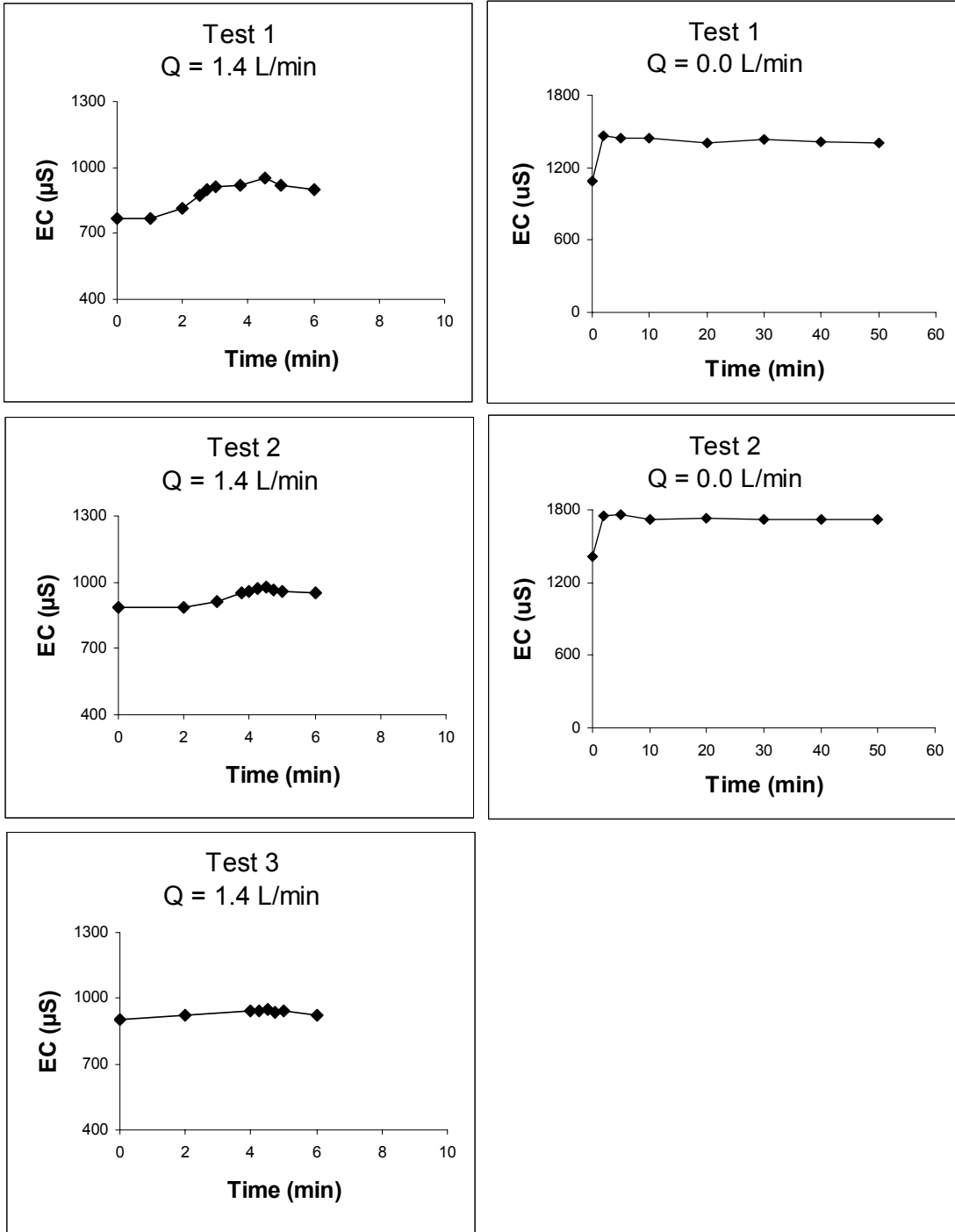
Figure 14 (continued)

August Event Tracer Tests

August 18, 2006
(Day 6 – Valve Closed)
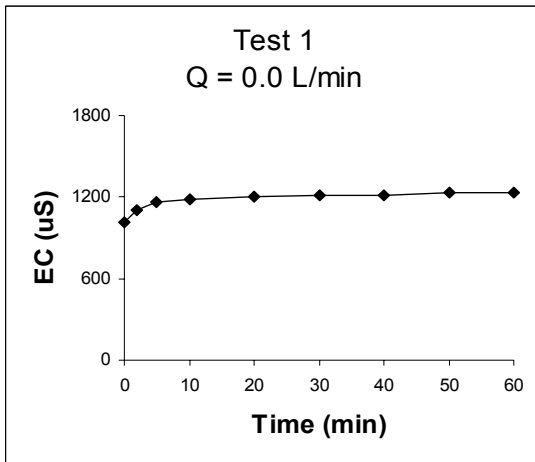
Figure 14 (continued)
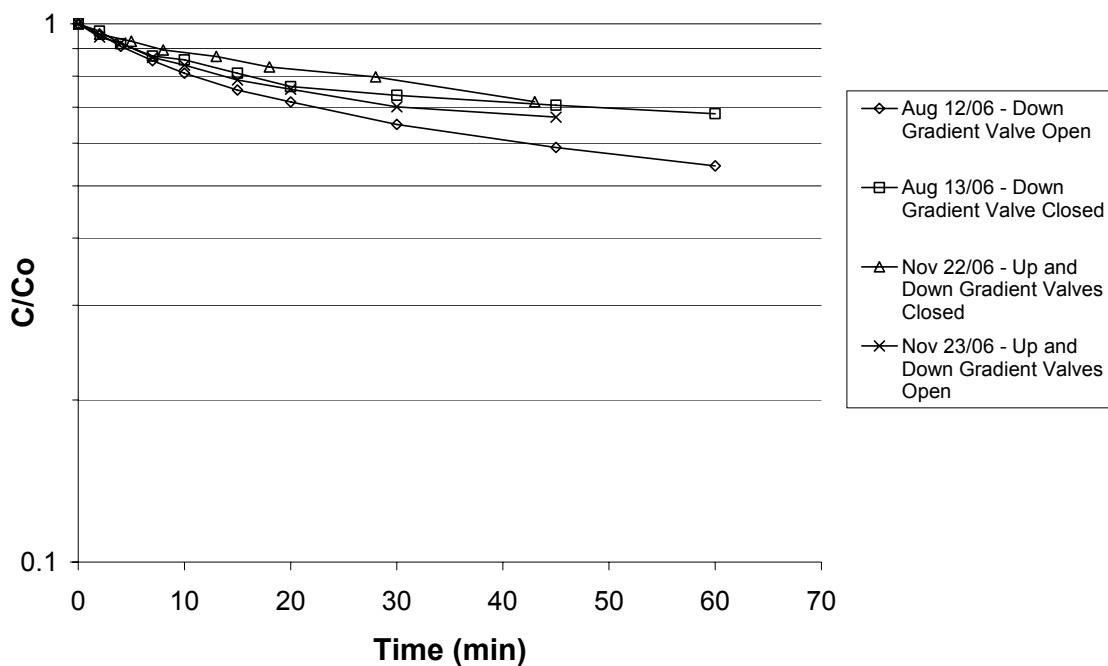
Figure 15. Borehole dilution test results for August and November events. C/Co is normalized EC, where C is the EC at the time of measurement and Co is the EC at the beginning of the test. Background EC varied between days, with values of 1090, 1210, 890 and 1260 µS on each date respectively. Initial EC at start of test was 4260, 3570, 1472, 3280 µS on each date respectively.

Figure 16. Major anions along PRB transect during August decreased flow event: a) NO$_3$-N, b) SO$_4$, c) Cl$^-$. Solid lines are days when down gradient perforated pipe was open. Dashed line days are representative of natural flow conditions with the downgradient tile line closed.

August Event (Tile Closed on Day 0)
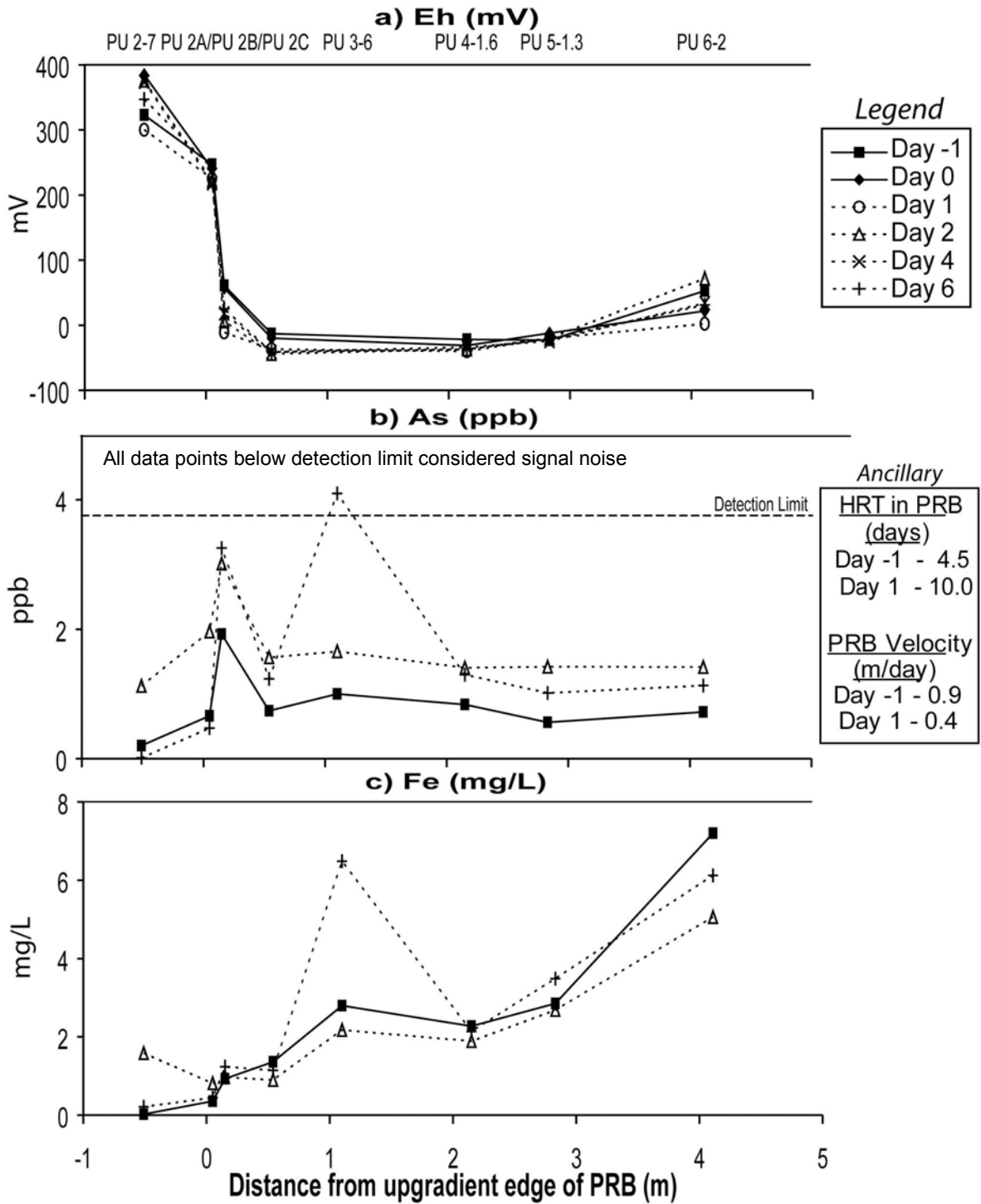
Figure 17. Eh and trace metal concentrations along PRB transect during August decreased flow event: a) Eh, b) As, c) Fe. Solid lines are days when down gradient perforated pipe was open. Dashed line days are representative of natural flow conditions with the downgradient tile line closed.
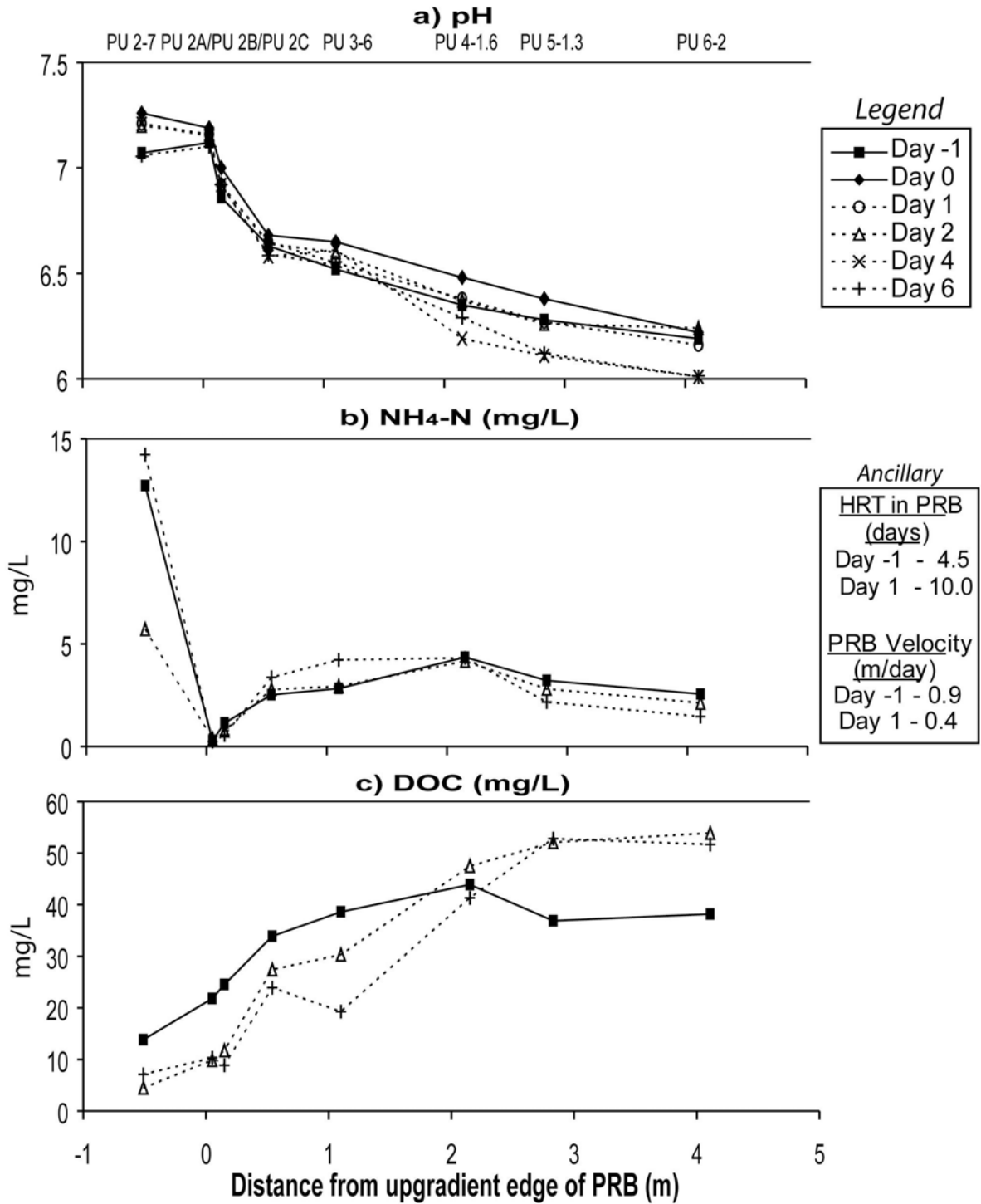
Figure 18. pH, NH$_4$-N and DOC along PRB transect during August decreased flow event. a) pH, b) NH$_4$-N, c) DOC. Solid lines are days when down gradient perforated pipe was open. Dashed line days are representative of natural flow conditions with the downgradient tile line closed.

November Event (Tiles Opened on Day 0)
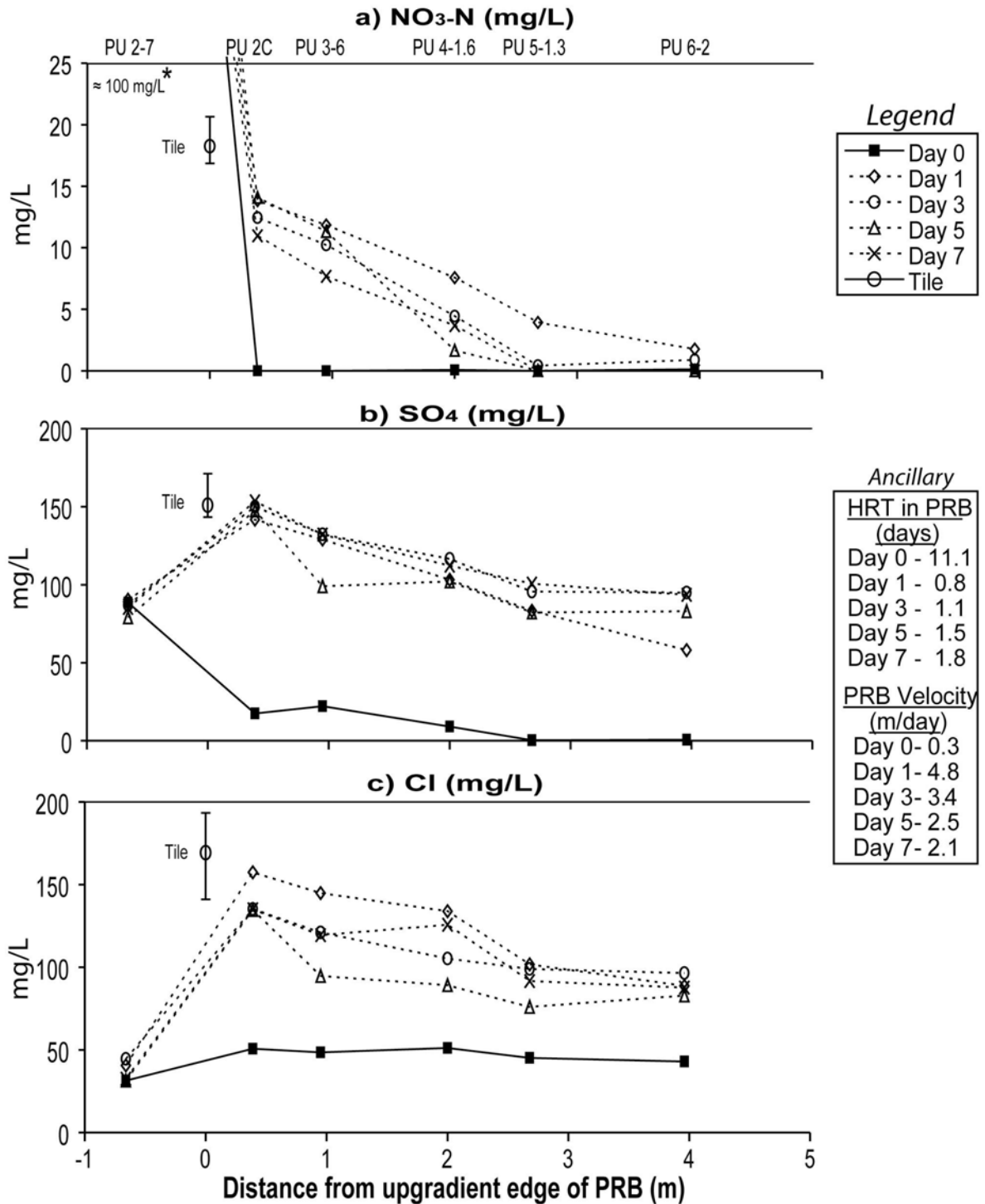
Figure 19. Major anions along PRB transect during November enhanced flow event: a) NO$_3$-N, b) SO$_4$, c) Cl$^-$. Solid lines represent natural flow conditions, with all perforated tile lines closed. Dashed lines represent days when both the upgradient and downgradient tile drains were open. * value represents NO$_3$-N concentration at PU 2-7.

November Event
(Both Tile lines Opened)

a)

PU 93 PU 2C   PU 3-6   PU 4-1.6   PU 5-1.3   PU 6-2

Fraction Tile Flow

— ■ — Day 0
··◇·· Day 1
··○·· Day 3
··△·· Day 5
··✕·· Day 7

b)

SO_4 C/Co

Distance from upgradient edge of PRB (m)

HRT in PRB
(days)
Day 0 - 11.1
Day 1 - 0.8
Day 3 - 1.1
Day 5 - 1.5
Day 7 - 1.8

Velocity
(m/day)
Day 0- 0.3
Day 1- 4.7
Day 3- 3.4
Day 5- 2.5
Day 7- 2.1
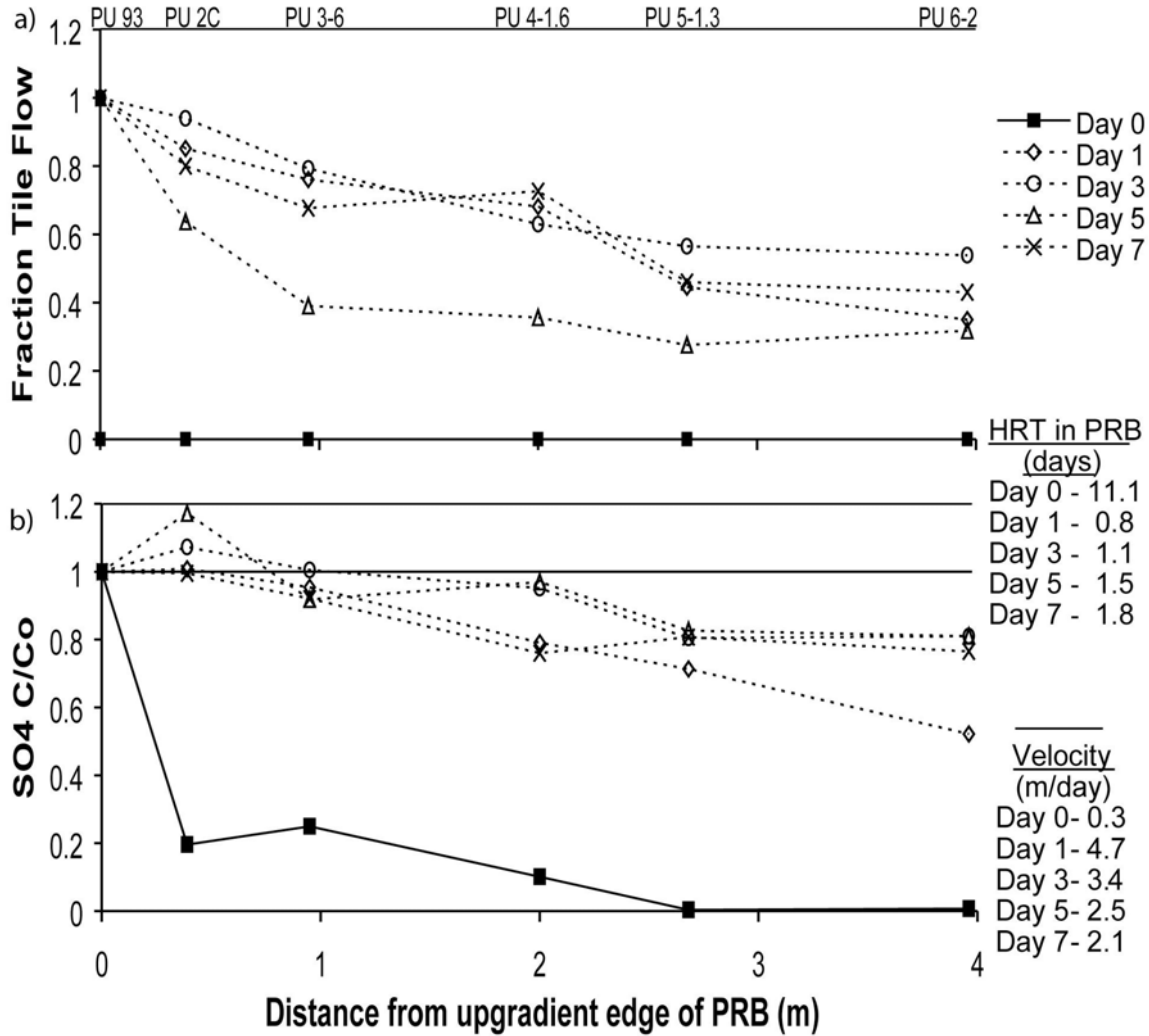
Example Calculation of SO_4 C/Co for Day 3 at PU 3-6 (Nov 25/06):

% tile flow (from Cl^- ratio) = (121-45)/(141-45) =0.79

Tile SO_4 (PU 93) = 143 mg/L

Background SO_4 (PU 2-7) = 87 mg/L

SO_4 concentration at PU 3-6 = 132

Co = (0.79*143.3)+[(1-0.79)*87.0]

= 132

C/Co = 132/132

= 1

Figure 20. a) Mixing ratio of tile and natural water in reactive barrier based on Cl^- ion ratio along flow path. Ratio value describes the contribution of tile water at a given monitoring point; b) Normalized SO_4 in barrier for November enhanced flow event. Data from Table 4.

Figure 21. Eh and trace metal concentrations along PRB transect during November enhanced flow event: a) Eh, b) Mn, c) Fe. Solid lines represent natural flow conditions (tile lines closed). Dashed lines represent days when both the upgradient and downgradient tile drains were open.

Figure 22. pH and major cations along PRB transect during November enhanced flow event: a) pH, b) Ca, c) Mg. Solid lines represent natural flow conditions (tile lines closed). Dashed lines represent days when both the upgradient and downgradient tile drains were open.

Figure 23. Misc. cations and DOC along PRB transect during November enhanced flow event:
a) K, b) Na, c) DOC. Solid lines represent natural flow conditions (tile lines closed). Dashed
lines represent days where both the upgradient and downgradient tile drains were open.
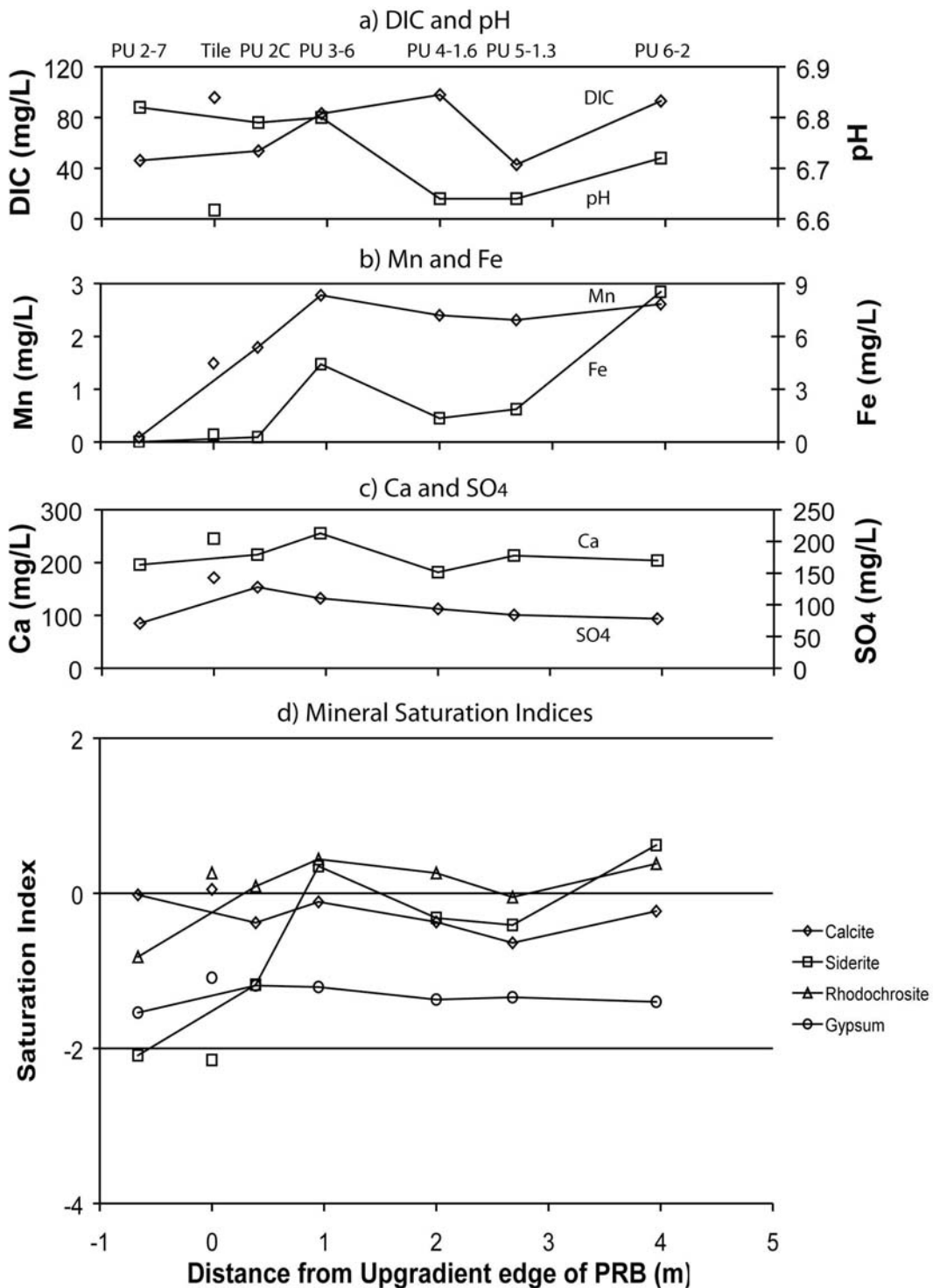
Figure 24. Geochemistry of Zorra PRB on November 29, 2006 (Day 7 November enhanced flow event). a) DOC and pH, b) Mn and Fe, c) Ca and SO_4, d) mineral saturation indices for calcite, siderite, rhodochrosite and gypsum along barrier transect. Values shown not on the trend lines represent upgradient tile values. Mineral saturation indices calculated using the chemical speciation model PHREEQCI (Parkhurst, 2007).

Geochemical History of Upgradient Tile
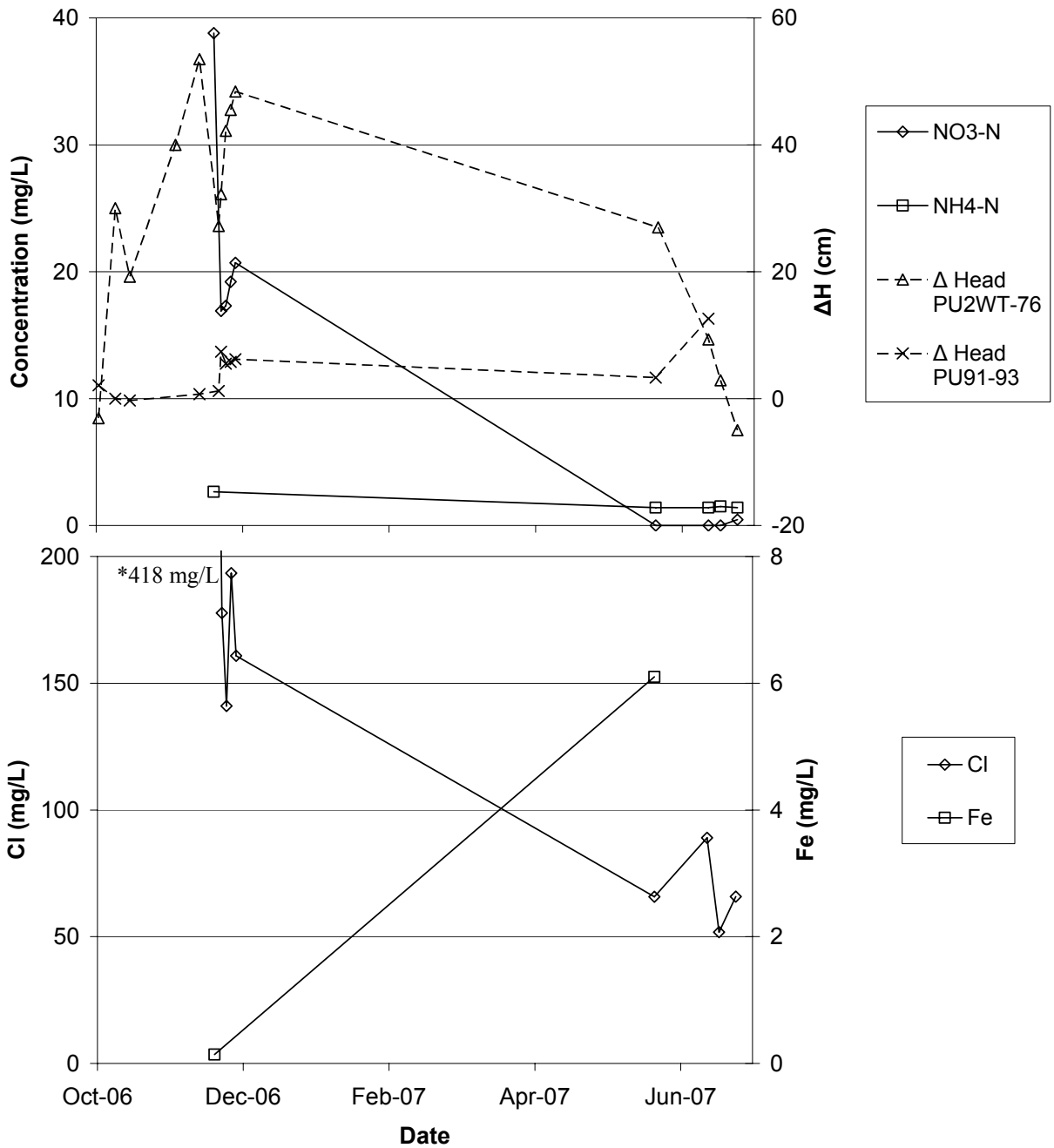
Figure 25. Geochemical history of upgradient tile as sampled from PU 93. a) NO_3-N and NH_4-N in upgradient tile with head changes across research site (PU 2 to PU 76). b) Cl^- and Fe in upgradient tile. Valve at PU 93 closed until Nov 22.

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Woodstock Site
NO$_3$-N
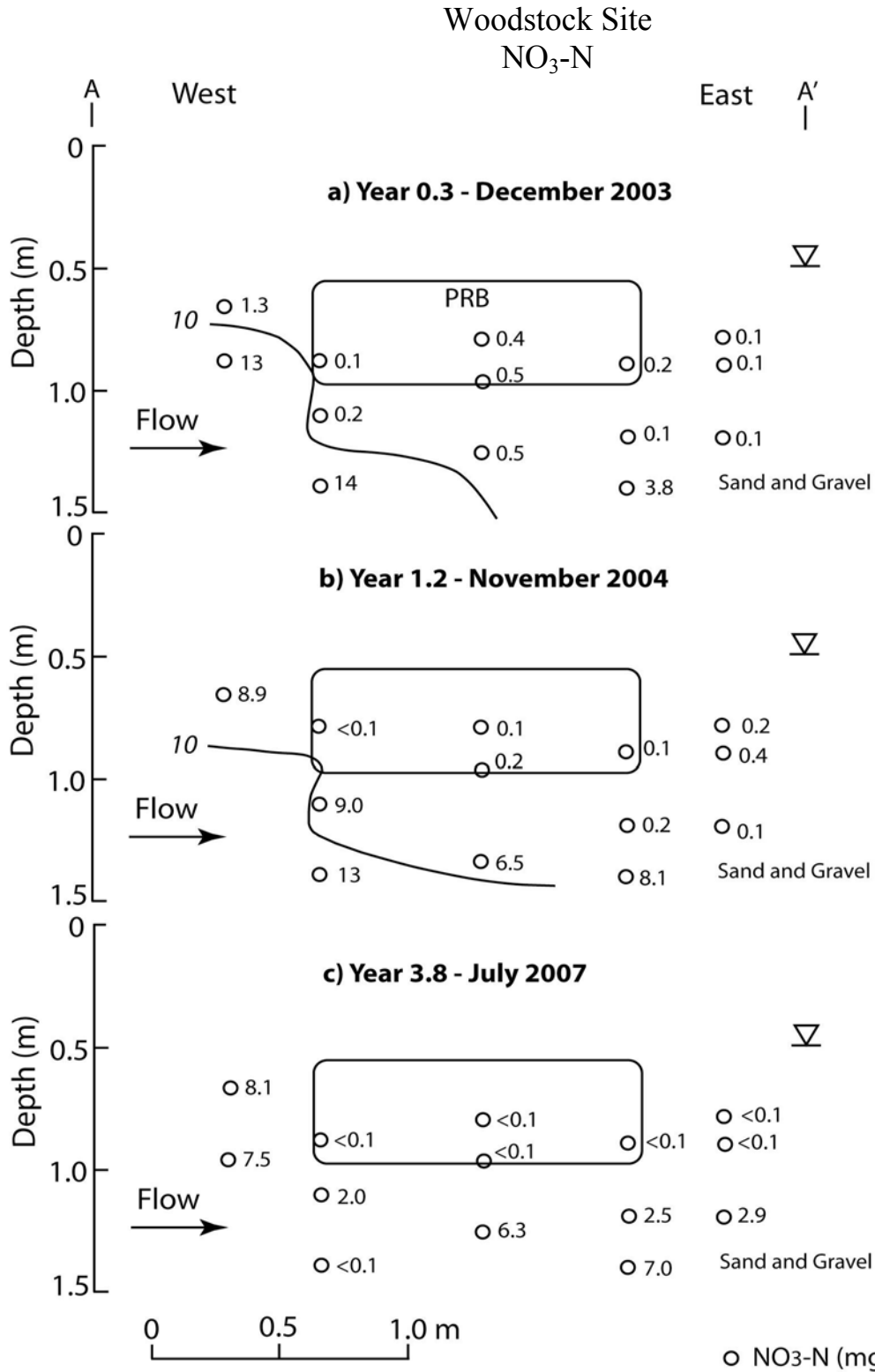
Figure 26. NO$_3$-N concentration along A to A' transect of Woodstock wood-particle barrier. a) 0.3 years after installation (adapted from Robertson et al., 2005) b) 1.2 years after installation and c) 3.8 years after installation.
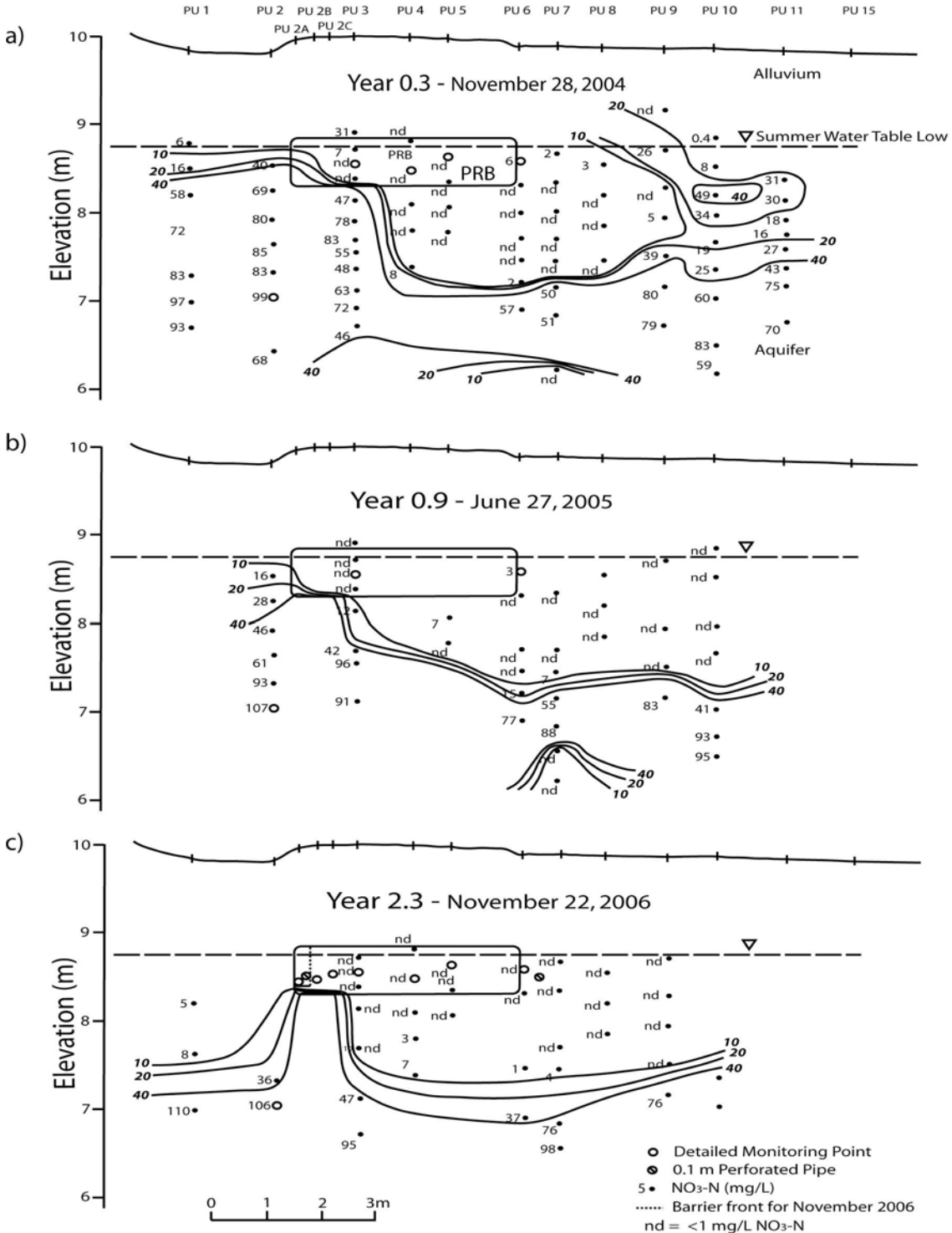
Figure 27. History of NO$_3$-N concentrations through Zorra reactive barrier transect, a) 0.3 years after installation (from Robertson et al., 2007), b) 0.9 years after installation and c) 2.3 years after installation. nd = not detected (NO$_3$-N < 1 mg/L). Data values are given in Appendix B.

Appendix A

Flow rates within the tile lines and barrier.

(Measured using borehole dilution tests, with salt tracer tests and electromagnetic flow meter readings to determine flow rate in tile lines at Zorra site, April 2006 to June 2007)

Borehole Dilutions tests; Field procedure

Flow rate data was collected in the barrier using three wells constructed of 5 cm PVC pipe which fully penetrated the PRB, offset 0.4-0.85 m from the main monitoring transect (Front, middle and rear Borehole dilution wells, Fig 11). The borehole dilutions were carried out by packing off the monitoring well at the top of the well screen with a packing device consisting of tightly wrapped tape, which fit snuggly into the monitoring well. Water with elevated EC (approximately 2-3 times background) was circulated through the borehole with the use of a peristaltic pump. The decay in EC was monitored until C/Co was approximately equal to 0.5 or until a clear trend in EC decay was established. Horizontal groundwater velocity was determined from the duration time of the EC recovery using Eq. A1 (Drost et al., 1968):

$$v = -W/(\alpha A \eta t) \ln (EC/EC_o) \qquad (A1)$$

Where:
  W = Volume of space between packer and the bottom of the fully screened well
  A = Cross-sectional area of the packed off section of well, perpendicular to flow;
  EC/EC_o = normalized ratio of elevated EC at any given time compared to the initial EC, when $t = 0$ for the test
  t = Measurement of time passed since the test commenced
  η = porosity of the formation being tested
  α = adjustment factor dependant on the well screen and filter pack.

For this study, an α value of 2 was used in all tests, which is appropriate for a permeable well screen installed without a filter pack (Drost et al. 1968). Porosity was assumed to be 0.7, based on the work done by van Driel (2004), who constructed a similar PRB using the same construction materials.

Tracer Tests

Salt tracer tests were conducted by lowering a length of 0.6 cm diameter tubing (fixed to a 2.5 cm PVC pipe) equal in length to that of the monitoring well down monitoring well PU 85 (10 cm in diameter, Fig A1). The end of the 0.6 cm diameter tubing was positioned in the middle of the horizontally running, non-perforated, tile line running from PU 84 to 86. A similar device was installed at PU 86 (0.75 m down gradient from PU 85), but had two lengths of 0.6 cm tubing connected to each side of the 2.5 cm PVC pipe. The 2.5 cm pipe was oriented so that each of the 0.6 cm tubes attached would be equidistant from monitoring well PU 85. The tubing was then connected to a flow through conductivity cell, which measured EC of the water in the tile line. Flow was circulated through the tubing using a peristaltic pump. Once a background reading for EC was established in the tile line, a 10 mL concentrated pulse of NaCl solution was injected into the tubing at PU 85. A series of EC measurements were then taken at PU 86 to establish a breakthrough curve. The time taken for a maximum EC reading to travel from PU 85 to 86 was used to determine the flow rate within the tile line. The maximum flow rate this test method was capable accurately recording was ~6 L/min (1.3 cm/s). This method was also used to illustrate no flow conditions in the down gradient tile line when the tile line was plugged at PU 84. The salt pulse was injected at PU 85 and EC readings were recorded at PU 86 for approximately 1 hour to ensure there was no peak to the EC readings. Flow rate readings in the down gradient tile were converted to volumetric flow by multiplying the flow rate by the cross sectional area (81 cm^2) of the tile line. Volumetric flow was then converted to HRT using Eq. A2.

$$HRT = (V_{PRB} * \eta)/R_{Tile} \qquad (A2)$$

Where:

V_{PRB} = volume of the PRB (August event = 8 m x 4 m x 0.6 m = 19.2 m^3, November event = 8 m x 3.75 m x 0.6 m = 18 m^3; difference due to removal of some PRB material during construction of upgradient tile line in Oct. 2006)

η = porosity of the reactive medium (0.7)

R_{Tile} = flow rate of water moving in the down gradient tile, which was assumed to be fully capturing flow leaving the down gradient edge of the PRB.

Magnetic Flow meter

The other methods used to monitor flow rate in the drainage tiles included a Marsh-McBirney Flow-Mate 2000$^®$ magnetic flow meter. Use of the flow meter involved lowering the instrument head down monitoring points PU 85, 93 and 94 (10 cm diameter PVC pipe), into the middle of the completely water-filled non-perforated tile line, then recording the flow velocity. The flow meter was not able to measure rates <1.5 L/min (0.3 cm/s).

Table A1 – Flow rate data at Zorra site. Test types include EM: Magnetic flow meter at PU 85;

Tracer: Salt tracer test at PU 85-86; BHD: Borehole dilution in barrier.

Date	Test Type	PU 85 Flow in down-gradient tile (L/min)	Volumetric Barrier flow (m³/d)	(Equivalent) Barrier flow velocity (m/d)	Barrier HRT (days)	Valve State
10-Apr-06	EM	3.0	4.3	1.3	3.1	open
2-May-06	EM	3.0	4.3	1.3	3.1	open
3-May-06	EM	1.5	2.2	0.7	6.1	open
4-May-06	EM	1.5	2.1	0.6	6.3	open
8-May-06	EM	0.7	1.0	0.3	13.3	open
15-May-06	Tracer	2.1	3.0	0.9	4.5	open
29-May-06	Tracer	2.4	3.5	1.0	3.9	open
1-Jun-06	Tracer	1.2	1.7	0.5	8.1	open
15-Jun-06	Tracer	2.2	3.2	0.9	4.2	open
27-Jun-06	BHD		2.2	0.6	6.2	open
7-Jul-06	BHD		1.0	0.3	13.3	closed
9-Jul-06	BHD		0.6	0.2	21.1	open
19-Jul-06	BHD		0.5	0.2	26.0	closed
19-Jul-06	Tracer	1.6	2.2	0.7	6.0	open
19-Jul-06	BHD		0.9	0.3	15.0	open
25-Jul-06	BHD		0.6	0.2	22.8	closed
6-Aug-06	BHD		0.6	0.2	22.6	closed
7-Aug-06	BHD		1.2	0.4	11.3	open
7-Aug-06	Tracer	4.1	5.8	1.7	2.3	open
8-Aug-06	Tracer	2.0	2.9	0.9	4.6	open
8-Aug-06	BHD		2.6	0.8	5.2	open
9-Aug-06	Tracer	2.7	3.9	1.2	3.5	open
10-Aug-06	Tracer	1.9	2.8	0.8	4.8	open
11-Aug-06	Tracer	2.1	3.0	0.9	4.5	open
12-Aug-06	BHD		1.9	0.6	7.2	open
12-Aug-06	Tracer	1.4	1.9	0.6	6.9	open
13-Aug-06	BHD		1.3	0.4	10.0	closed
16-Oct-06	Tracer	>18.2	>26.3	>9.4	< 0.4	open
14-Nov-06	EM	7.8	11.2	3.3	1.1	open
22-Nov-06	BHD		1.1	0.3	11.1	closed
23-Nov-06	BHD		1.7	0.5	7.3	open
23-Nov-06	EM	11.1	16.0	4.8	0.8	open
25-Nov-06	EM	8.0	11.5	3.4	1.1	open
27-Nov-06	EM	5.9	8.5	2.5	1.5	open
29-Nov-06	EM	4.9	7.1	2.1	1.8	open
27-May-07	EM	5.9	8.5	2.5	1.5	open
14-Jun-07	EM	7.1	10.2	3.0	1.2	open
19-Jun-07	EM	4.5	6.4	1.9	2.0	open

Table A2 – Flow rates in PU 85 and 93 after installation of up gradient tile line. Measurements taken using electromagnetic flow meter. Tile valves were open in all cases unless otherwise indicated.

	L/min
14-Nov-06	
PU85 (closed)	<1.5
PU93 (closed)	<1.5
PU85 (open)	7.8
PU93 (open)	4.2
23-Nov-06	
PU85	11
PU93	7.4
25-Nov-06	
PU85	8.0
PU93	4.2
27-Nov-06	
PU85	5.9
PU93	1.5
29-Nov-06	
PU85	4.9
PU93	2.2
27-May-07	
PU 85	5.9
PU 93	3.0
14-Jun-07	
PU 85	7.1
PU 93	4.5
19-Jun-07	
PU 85	4.5
PU 93	1.5
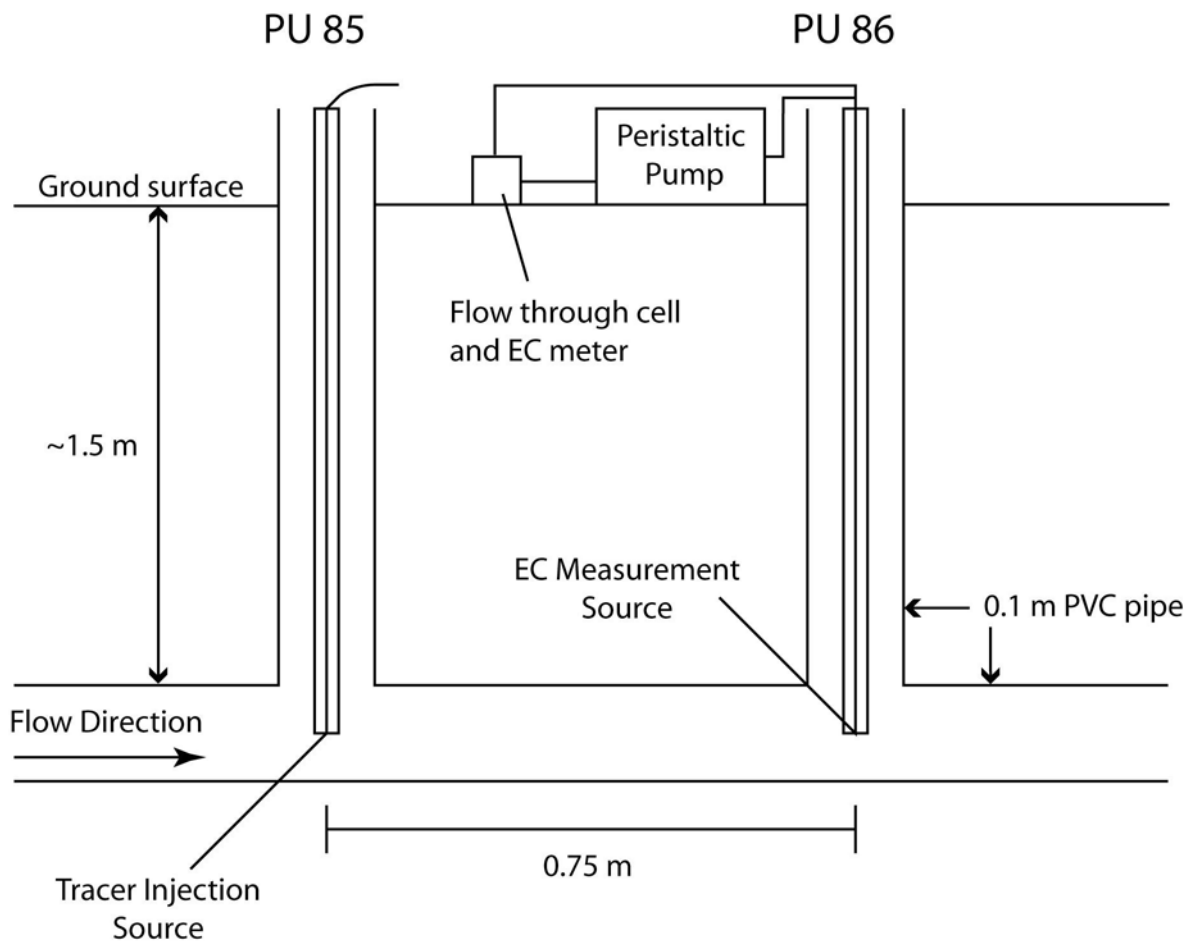
Figure A1 – Set up of salt tracer test at Zorra site. Test interval between PU 85-86. Salt tracer injected into PU 85, while EC monitored at PU 86 using flow through EC cell.

PU 85-86 (Downgradient tile line)
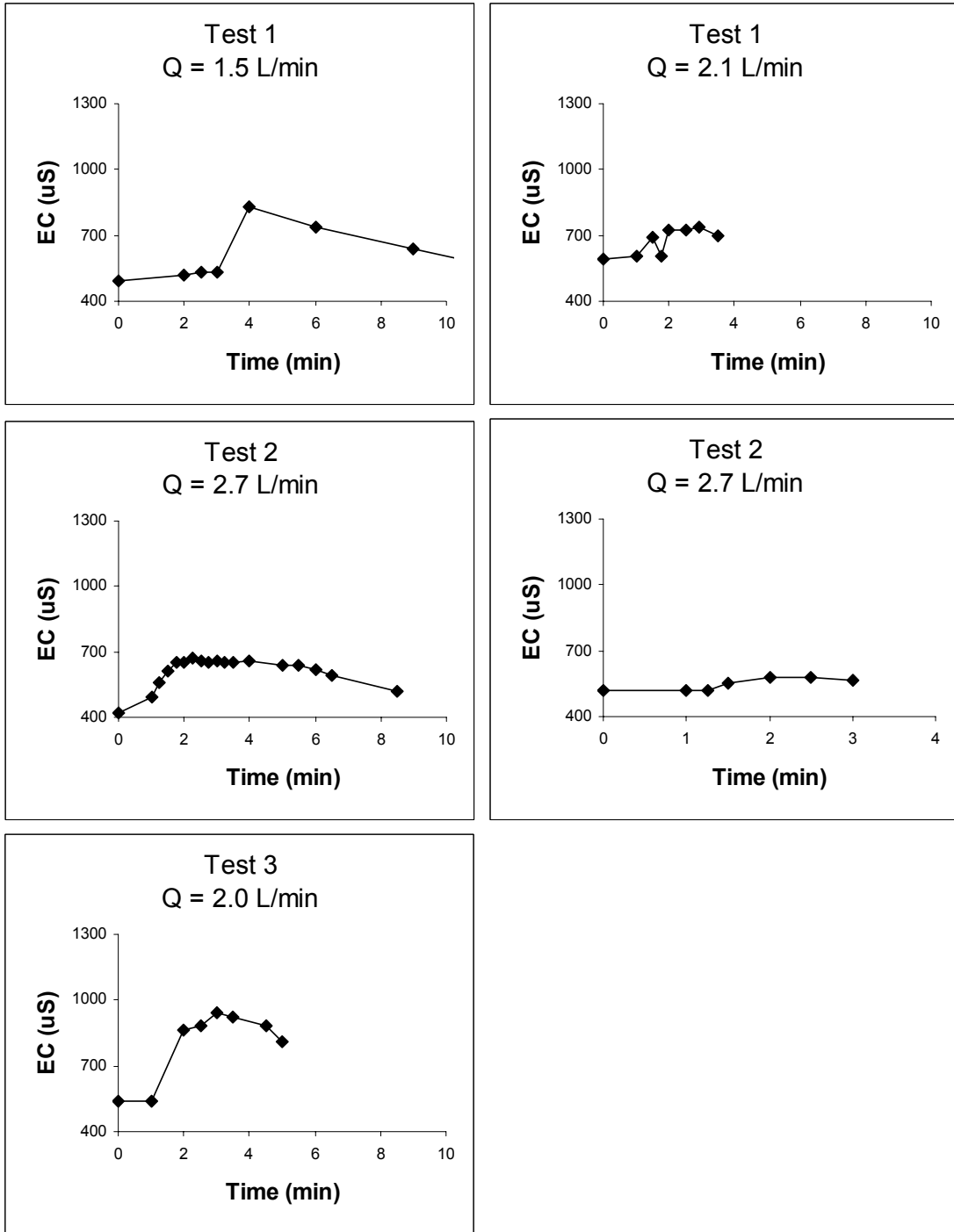
Figure A2: Salt tracer tests for flow rate determined in downgradient tile line up to and including August 2006 enhanced flow rate experiment. The distance between PU 85 and PU 86 is 0.75m, with EC measurements taken from PU86 (Fig C2). Tracer tests were performed with valve open conditions, excluding the "No-flow" tests on August 16th and 18th, 2006. Q values were obtained by recording the time taken for peak EC in PU 86 to travel from PU85-86, dividing this by the 0.75m distance and converting to volumetric flow.

PU 85-86 (Downgradient tile line)

June 1, 2006 (Valve Open)   June 15, 2006 (Valve Open)

Test 1
Q = 1.2 L/min

Test 1
Q = 1.7 L/min

Test 2
Q = 2.4 L/min

Test 3
Q = 2.4 L/min

Figure A2 (con't)

90
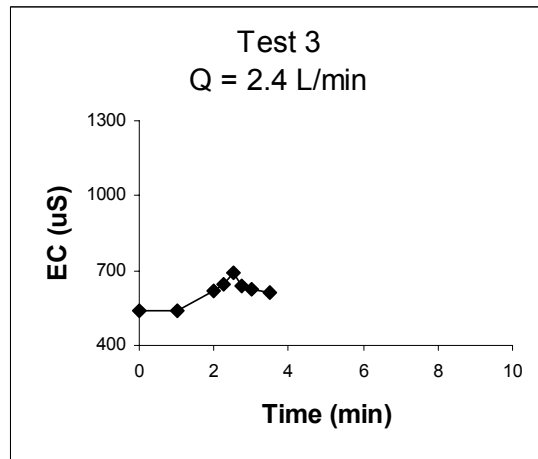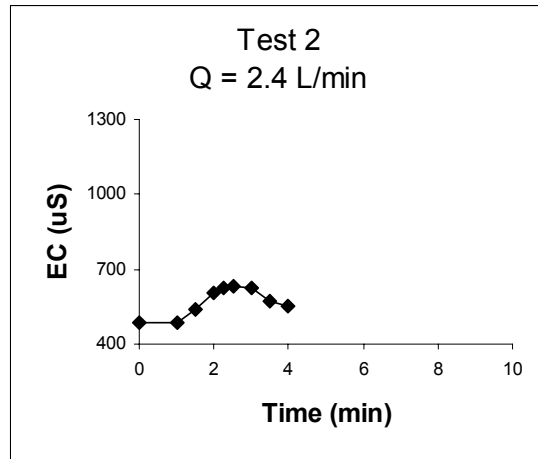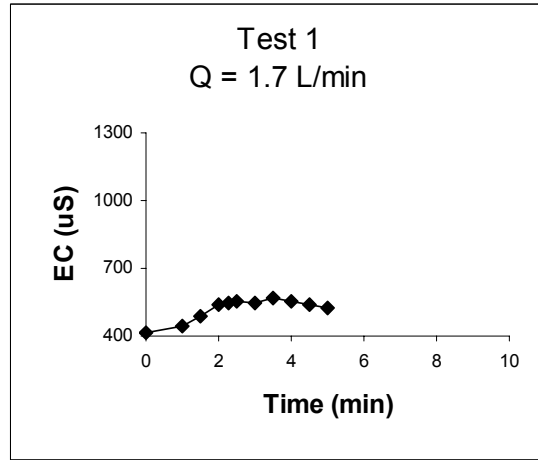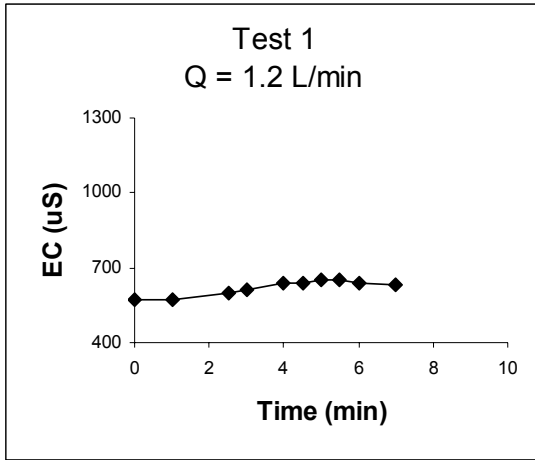
PU 85-86 (Downgradient tile line)

July 19, 2006 (Valve Open)
(Downgradient tile opened 5 mins before Test 1)
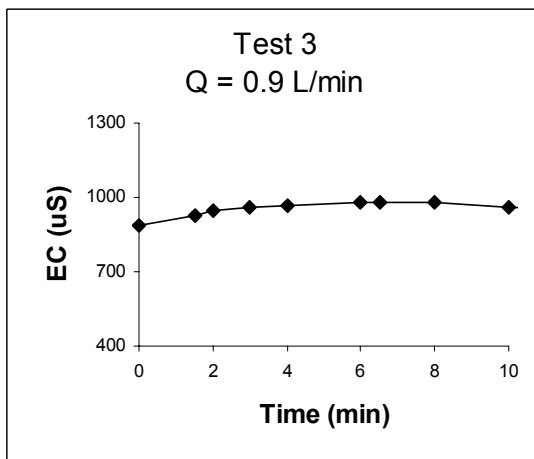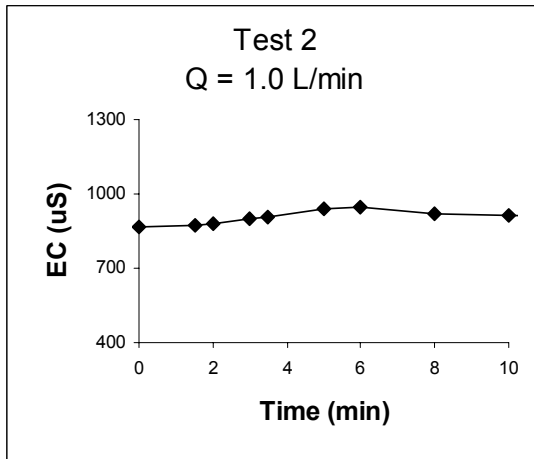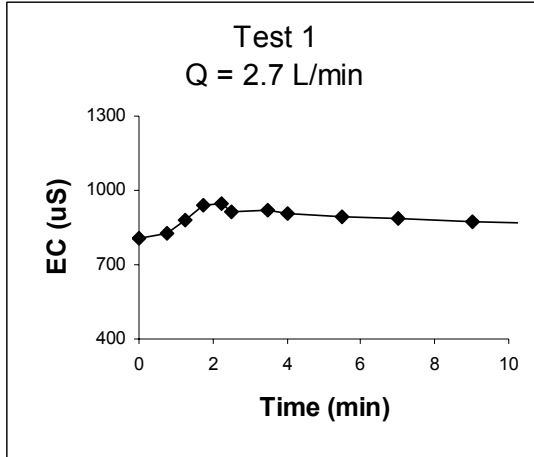
Figure A2 (con't)

PU 85-86 (Downgradient tile line)
August 7, 2006 (Valve Open)
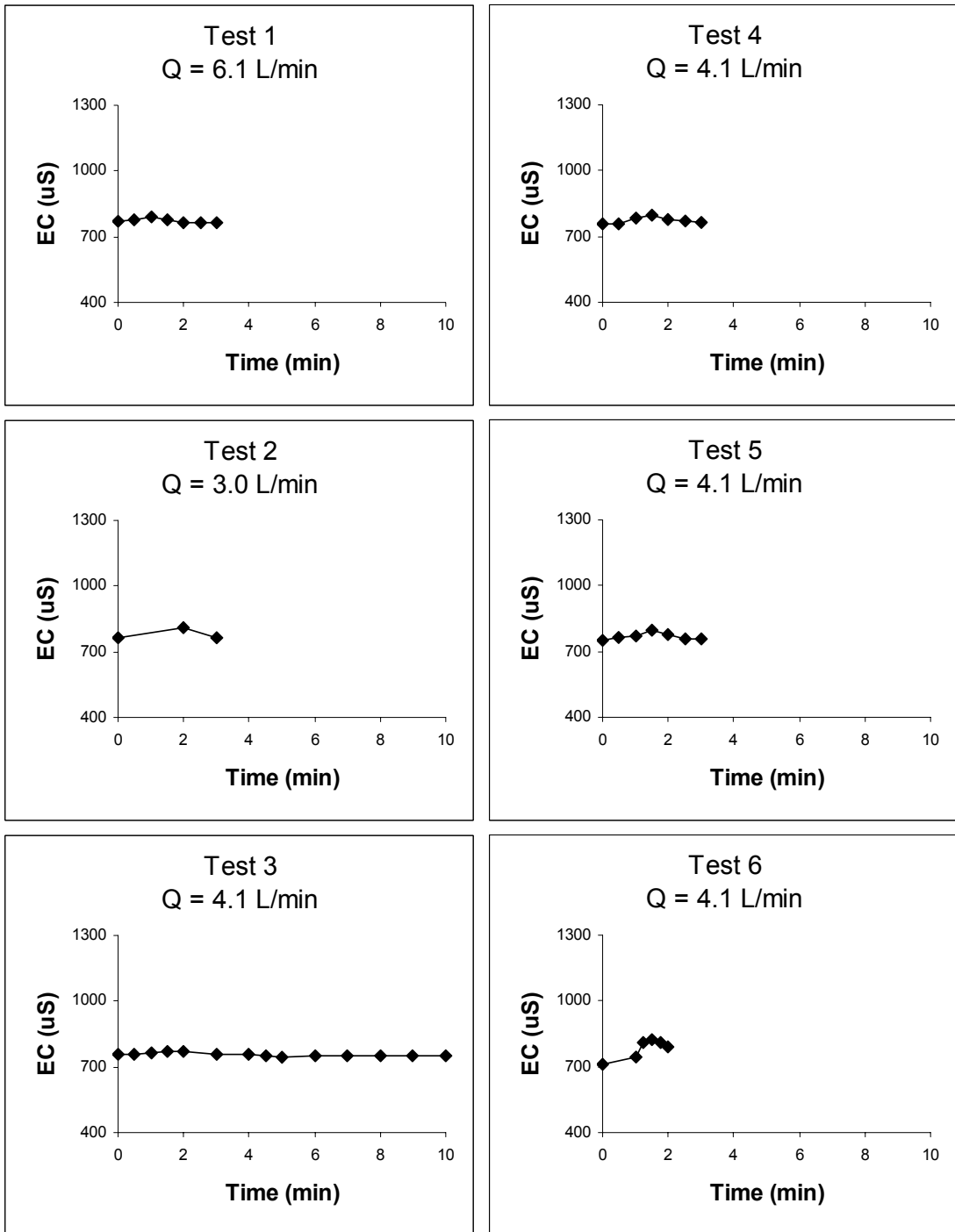
Figure A2 (con't)

PU 85-86 (Downgradient tile line)

August 8, 2006 (Valve Open)   August 9, 2006 (Valve Open)
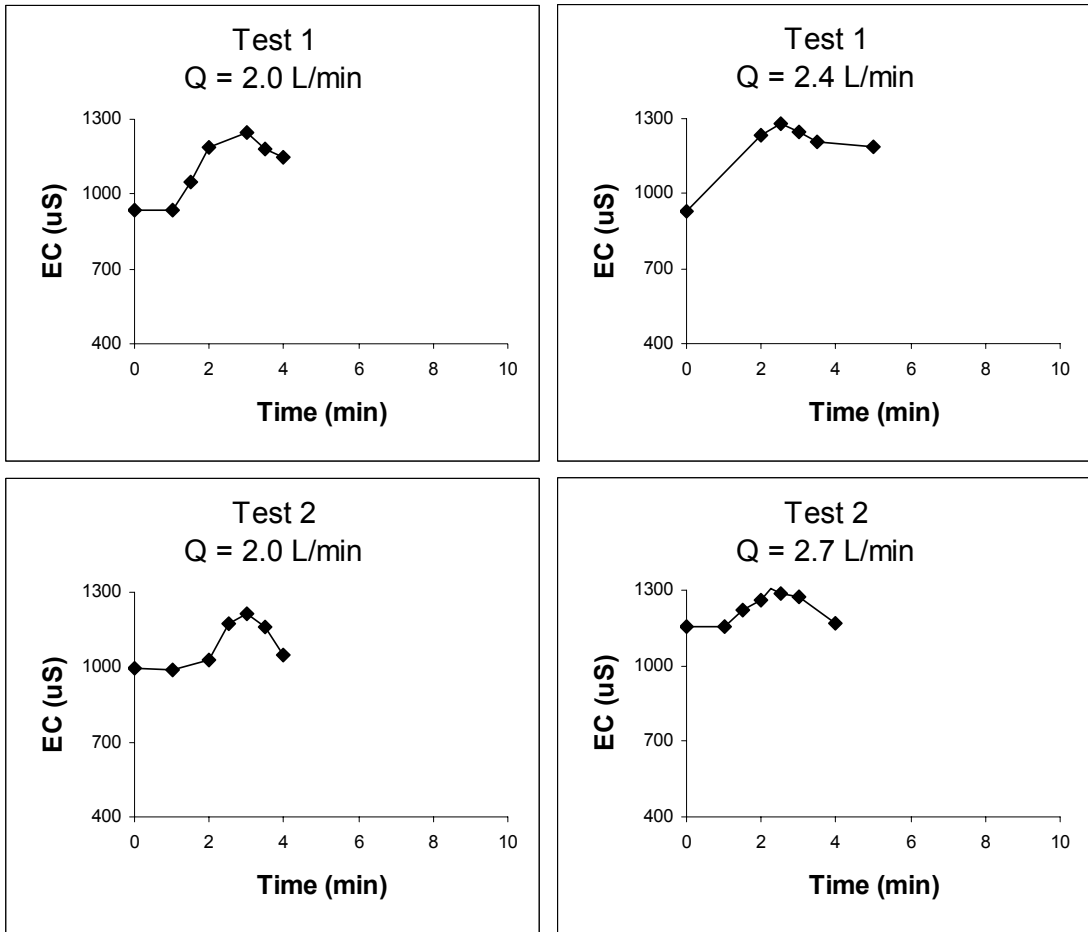
Figure A2 (con't)

PU 85-86 (Downgradient tile line)

August 10, 2006
(Event Day -2 – Valve Open)

August 11, 2006
(Event Day -1 – Valve Open)
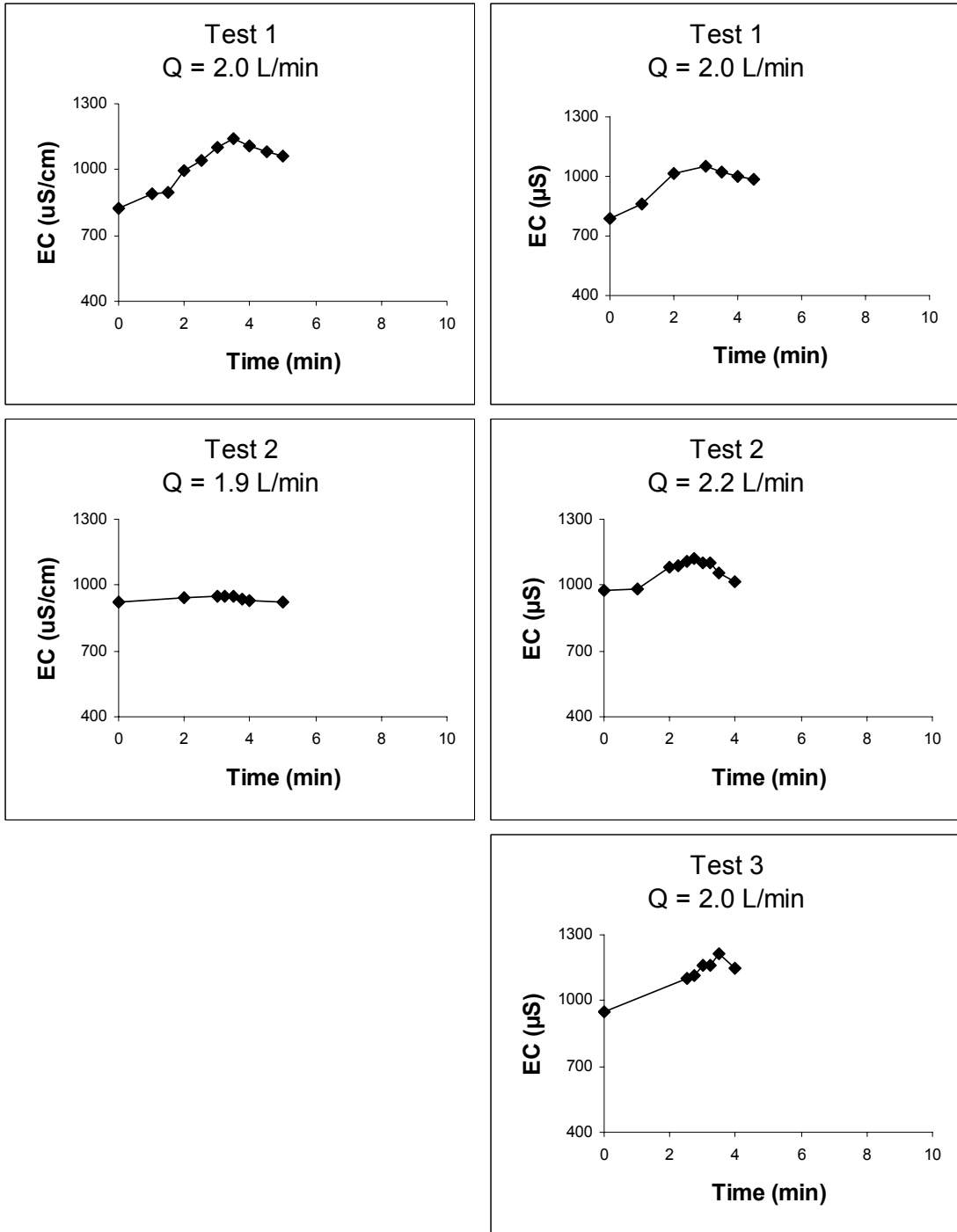
Figure A2 (con't)

PU 85-86 (Downgradient tile line)

August 12, 2006	August 16, 2006
(Event Day 0 – Valve Open)	(Event Day 4 – Valve Closed)
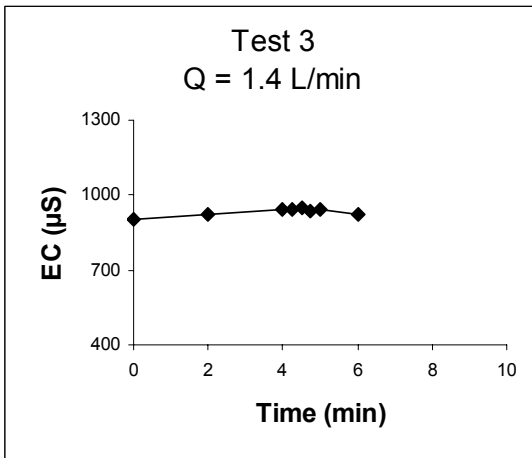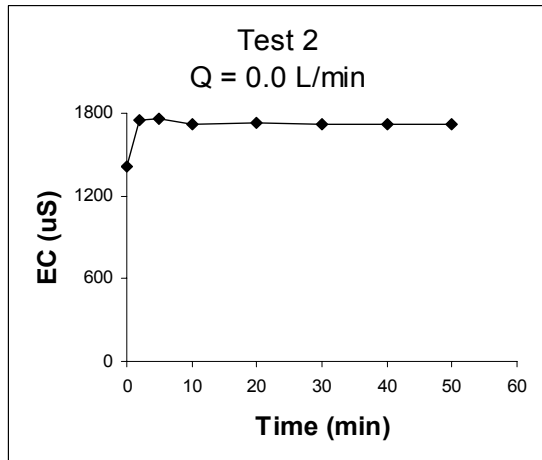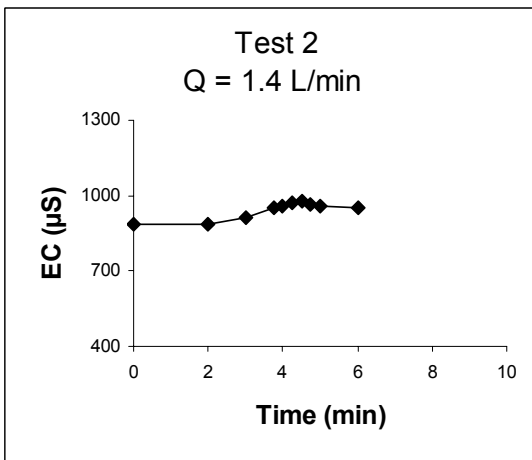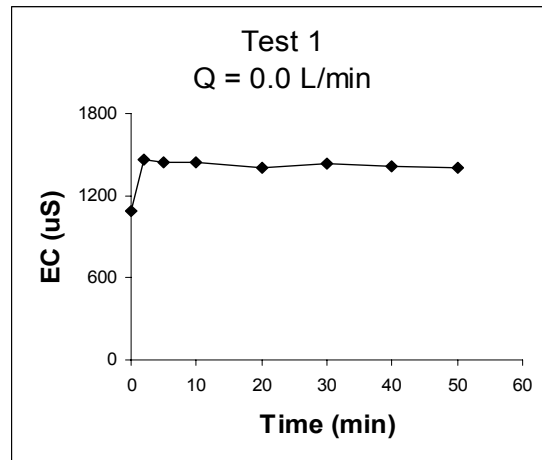
Figure A2 (con't)

PU 85-86 (Downgradient tile line)
August 18, 2006
(Event Day 6 – Valve Closed)

Test 1
Q = 0.0 L/min

EC (uS) vs Time (min)
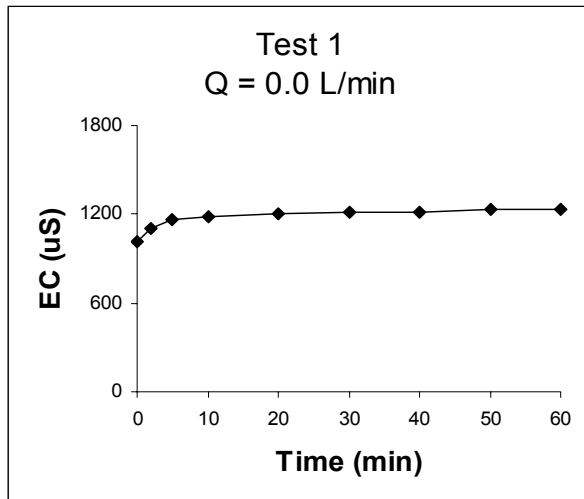
Figure A2 (con't)

Appendix B

Detailed geochemistry along the Zorra barrier principal flow path,
November 28, 2004 to November 29, 2006.

Table B1: Geochemistry along the Zorra barrier transect on days not part of enhanced flow experiments. Downgradient tile line was opened May 2, 2006 and remained open unless otherwise stated. "Cmt" values were collected using Chemets colourimetric field test kits.

	Cl⁻ (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH_4-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO_3 (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
10-Apr-06															
PU 1-4	30.1	11.6	19.8	300	435	6.95							> 5	5.5	< 0.1
PU 2-3	29.9	6.53	23.4	309	397	7.07							> 5	5	< 0.1
PU 2-4	11.5	7.10	14.3	276	413	7.06							2	4	< 0.1
PU 3-4	31.7	< 0.02	2.8	340	33	6.74							< 0.1	4	1.5
PU 5-1.3	32.9	< 0.02	2.5	344	2	6.74							< 0.1	3	0.9
14-Apr-06															
PU 11-2.2	28.3	8.04	29.2	367	198	6.73							> 5	2.5	< 0.1
PU 10-2	39.0	< 0.02	38.2	315	145	6.78							< 0.1		5.5
PU 9-2	15.8	< 0.02	35.0	316	76	6.55							< 0.1	< 1	> 10
PU 4-1.6	45.0	< 0.02	0.4	252	25	6.76							< 0.1	< 1	0.8
PU 6-2	34.4	1.63	2.6	298	90	6.65							< 0.1	< 1	3
PU 7-4	15.9	12.1	29.8	331	150	6.78							4	< 1	< 0.1
PU 8-1.2	17.4	2.12	34.6	408	82	6.69							< 0.1	< 1	< 0.1
PU 8-1.7	17.7	3.06	47.1	319	118	6.77							0.15	< 1	< 0.1
17-Apr-06															
PU 2-5	11.5	31.5	39.6	499											
PU 2-6	28.4	< 0.02	71.8	863											
PU 2-7	29.5	< 0.02	57.2	907											
PU 3-1	55.4	0.24	44.6	653											
PU 3-2	56.2	0.18	46.4	677											
PU 3-3	49.3	0.02	27.0	633											
PU 3-5	41.1	< 0.02	3.3	420											
PU 3-6	40.5	0.66	2.1	611											
PU 3-7	31.5	2.10	22.1	354											
PU 3-8	33.5	5.22	22.7	344											
PU 3-10	19.2	10.1	18.3	325											
PU 3-11	11.5	18.7	24.2	378											
PU 3-13	23.9	< 0.02	58.8	702											
PU 3-14	28.1	< 0.02	55.6	789											

Table B1 (con't)

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
PU 3-15	34.0	< 0.02	66.8												
PU 4-1.2	32.8	0.11	0.3	416											
PU 4-1.8	43.6	< 0.02	5.8	439											
PU 4-2.1	17.0	13.6	16.9	395											
PU 4-2.4	25.7	11.6	19.5	381											
PU 5-1.6	36.3	< 0.02	0.4	432											
PU 5-1.8	16.4	5.68	26.0	344											
PU 5-2.2	12.3	11.6	21.5	382											
PU 8-0.7	2.8	2.54	4.6	605											
PU 8-1.0	56.1	< 0.02	32.5												
PU 8-1.4	24.0	< 0.02	44.8	424											
PU 9-3	14.4	0.07	52.5	446											
PU 9-4	23.1	1.60	16.4	593											
PU 9-5	19.0	28.7	44.2	509											
PU 9-6	24.9	81.4	54.1	770											
PU 6-3	34.5	0.85	4.5	461											
PU 6-4	16.9	2.11	39.5	411											
PU 6-5	6.8	14.3	22.7	405											
PU 6-6	23.8	1.97	28.9	423											
PU 6-7	22.8	13.9	25.5	417											
PU 6-8	19.4	64.3	61.1	689											
PU 6-9	0.4	0.09	0.09	888											
PU 7-2	34.6	0.03	36.6	868											
PU 7-3	17.2	4.12	32.7	593											
PU 7-6	27.4	6.60	26.5	605											
PU 7-8	22.2	< 0.02	51.5	972											
PU 7-9	33.9	< 0.02	65.4	1211											
PU 7-10	45.8	44.4	67.2	1232											
PU 10-1	46.9	0.04	33.9	750											
PU 10-3	20.1	< 0.02	45.1	626											

Table B1 (con't)

	Cl$^-$ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
PU 10-4	27.1	0.07	2.9	975											
PU 10-5	25.5	0.02	0.2	1148											
PU 10-6	22.8	14.7	34.9	691											
PU 10-7	22.2	70.9	57.4	985											
PU 10-8	30.6	81.0	62.0	1100											
PU 10-9	48.5	< 0.02	65.5	1179											
PU 11-1.0	29.1	0.85	31.1	1000											
PU 11-1.2	36.4	0.18	24.9	860											
PU 11-1.4	16.4	< 0.02	32.4	681											
PU 11-1.6	18.6	< 0.02	20.6	767											
PU 11-1.8	29.6	0.41	31.6	761											
PU 11-2.0	28.3	0.60	34.3	738											
PU 11-2.2	26.3	11.4	31.0	683											
PU 11-2.4	16.4	41.0	35.0	702											
PU 11-2.6	27.8	38.3	48.7	821											
PU 11-2.8	35.3	< 0.02	73.1	1098											
PU 15-1.2	61.3	0.04	36.8	568											
PU 15-1.5	37.9	< 0.02	52.7	676											
PU 15-1.8	24.8	< 0.02	48.2	720											
PU 15-2.1	19.8	< 0.02	8.2	671											
PU 15-2.4	10.0	23.0	26.7	569											
PU 15-2.7	24.2	69.1	63.9	1014											

Table B1 (con't)

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
26-Apr-06															
PU 1-3	17.7	9.00	15.2	453	382				<0.02	3.42	3.42	0			
PU 1-4	27.9	10.1	20.9	468	459				<0.02	5.07	4.75	0.317		5	> 0.1
PU 2-2	27.6	9.72	22.2	433	261				<0.02	3.05	3.05	0			
PU 2-3	31.0	7.83	23.3	434	306				<0.02	3.64	3.01	0.625		5	> 0.1
PU 3-5	37.6	< 0.02	5.3	861	96				0.98	26.8	26.8	0		1.5	0.8
PU 3-6	40.4	< 0.02	2.1	963	94				0.82	9.76	9.76	0			
PU 3-7	29.9	1.44	15.7	735	100				0.64	7.21	6.83	0.381			
PU 4-1.6	37.5	< 0.02	1.2	909	80				<0.02	72.4	72.4	0		< 1	2
PU 5-1.3	34.1	< 0.02	0.8	919	83				0.03	70.6	70.6	0			
PU 5-1.6	36.9	< 0.02	0.3	937	80				<0.02	60.6	60.6	0			
PU 6-2	31.7	< 0.02	0.4	955	124				<0.02	67.7	66.4	1.24			
PU 7-2	38.6	< 0.02	26.8	1086	136				1.8	8.04	8.04	0			
PU 7-3	16.9	< 0.02	45.0	830	160				0.05	3.84	3.84	0			
PU 8-1.4	28.2	< 0.02	39.4	846	130				0.65	5.18	5.18	0			
PU 9-2	22.9	< 0.02	35.3	708	136				0.61	3.72	3.72	0			
PU 9-3	17.0	< 0.02	48.3	903	132				0.4	4.72	4.39	0.321			
PU 10-1	42.2	< 0.02	30.5	1128	155				<0.02	4.2	4.2	0			
PU 10-2	36.2	< 0.02	37.0	816	139				0.3	4.08	3.76	0.321			
PU 10-3	21.3	< 0.02	40.7	816	165				0.52	3.74	3.74	0			
PU 11-1.2	25.8	< 0.02	31.7	1016	137				0.25	5.14	5.14	0			
PU 11-1.4	24.4	< 0.02	34.2	892	144				0.37	5.63	5.17	0.46			
PU 15-1.5	32.7	< 0.02	60.4	1022	148				0.88	5.85	4.59	1.26			

Table B1 (con't)

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
2-May-06															
PU 1-3	20.2	8.23	16.5	468	301								< 0.1	3	2.25
PU 1-4	28.1	9.70	20.3	470	357								< 0.1	3	3
PU 2-1.3	26.6	10.0	21.6	422	421								< 0.1	7	> 5
PU 2-2	26.6	11.0	20.8	424	426								< 0.1	4	> 5
PU 3-5	34.4	< 0.02	1.0	607	43								4.5	< 1	< 0.1
PU 3-6	34.6	< 0.02	0.9	651	38								3	< 1	< 0.1
PU 3-7	27.6	3.28	19.9	504	69								0.8	< 1	< 0.1
PU 4-1.2	31.4	< 0.02	0.14	611	42								3	< 1	< 0.1
PU 4-1.6	35.5	< 0.02	0.6	649	47								3	< 1	< 0.1
PU 5-1.3	31.0	< 0.02	0.5	662	45								2	< 1	< 0.1
PU 5-1.6	35.0	< 0.02	0.3	682	37								8	< 1	< 0.1
PU 6-2	29.0	< 0.02	0.05	676	116								5		< 0.1
PU 6-3	32.2	< 0.02	0.2	866	133								>> 10		< 0.1
3-May-06															
PU 2-1.3	30.9	8.73	22.7	440	441	7.39							2.25	8	< 0.1
PU 2-2	27.5	10.4	22.4	465	441	7.39							3	8	< 0.1
PU 3-5	36.4	0.07	3.6	639	105	6.81							< 0.1	3	1
PU 3-6	36.3	< 0.02	3.6	690	46	6.84							< 0.1	< 1	3
PU 3-7	27.9	5.93	21.5	502	168	7.26							2	1.5	1.5
PU 4-1.2	29.5	< 0.02	0.2	588	37	6.75							< 0.1	< 1	2
PU 4-1.6	32.8	< 0.02	0.8	610	17	6.69							< 0.1	< 1	2
PU 5-1.3	31.8	< 0.02	0.6	628	22	6.6							< 0.1	< 1	2
PU 5-1.6	34.6	< 0.02	1.4	681	23	6.61							< 0.1	< 1	8
PU 6-2	29.5	< 0.02	0.2	706	125	6.74							< 0.1	< 1	2
PU 6-3	29.5	< 0.02	8.1	774	120	6.84							< 0.1	< 1	>> 10

Table B1 (con't)

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
4-May-06															
PU 2-1.3	29.0	7.11	21.7	425	363	7.59								5	
PU 2-2	31.3	8.39	22.0	431	395	7.61								4	
PU 3-5	38.9	< 0.02	10.6	586	59	6.93								2.5	
PU 3-6	39.0	< 0.02	10.0	607	5	6.93								< 1	
PU 3-7	28.4	5.04	23.3	465	165	7.39								3	
PU 4-1.2	30.7	< 0.02	2.9	532	13	6.81								< 1	
PU 4-1.6	33.5	< 0.02	4.7	552	4	6.77								< 1	
PU 5-1.3	30.1	< 0.02	4.7	542	4	6.7								< 1	
PU 5-1.6	36.1	0.02	7.1	630	20	6.7								< 1	
PU 6-2	27.8	0.03	0.6	629	120	6.76									
PU 6-3	30.4	0.04	15.0	684	120	6.96									
8-May-06															
PU 2-1.3	33.5	10.1	23.2	355	439	7.61							> 5	5.5	
PU 2-2	29.2	8.01	23.2	360	446	7.59							> 5	5	
PU 3-5	35.2	0.03	8.5	423	72	6.98							< 0.1	1.5	1
PU 3-6	34.8	0.02	7.2	435	-6	6.97								< 1	
PU 3-7	21.5	7.98	21.1	372	86	7.34							1	< 1	
PU 4-1.2	30.0	0.02	2.0	394	18	6.74								< 1	2
PU 4-1.6	32.3	< 0.02	3.2	415	-1	6.74								< 1	
PU 5-1.3	28.4	0.02	2.8	380	-10	6.75								< 1	
PU 5-1.6	33.6	0.04	2.2	473	1	6.66								< 1	8
PU 6-2	31.7	0.06	1.3	456	106	6.75									2.5
PU 6-3	37.2	0.06	31.1	560	95	7									>> 10

Table B1 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
15-May-06															
PU 2-1.3	26.9	17.0	23.4	395	455	7.59									
PU 2-2	30.1	13.0	22.4	382	455	7.6									
PU 3-5	32.1	< 0.02	6.0	432	-21	6.95									
PU 3-6	33.4	< 0.02	3.3	471	-30	6.96									
PU 3-7	13.3	12.7	20.3	396	61	7.34									
PU 4-1.2	27.6	0.02	1.4	425	0	6.72									
PU 4-1.6	30.0	< 0.02	2.7	425	-13	6.65									
PU 5-1.3	25.6	< 0.02	1.8	381	-11	6.74									
PU 5-1.6	31.8	< 0.02	2.1	468	5	6.64									
PU 6-2	31.3	0.06	7.5	437	89	6.77									
PU 6-3	41.2	0.29	39.1	484	98	7.09									
17-May-06															
PU 2-1.3	n.d.	16.3	23.9	422	418	7.6									
PU 2-2	31.8	14.5	23.1	436	430	7.36									
PU 3-5	33.4	0.02	3.4	500	-3	6.93									
PU 3-6	33.3	< 0.02	2.5	520	7	6.92									
PU 3-7	13.3	13.2	22.1	442	63	7.32									
PU 4-1.2	25.9	0.03	1.0	479	9	6.71									
PU 4-1.6	30.1	< 0.02	2.2	483	-18	6.63									
PU 5-1.3	24.1	0.02	1.3	450	-21	6.71									
PU 5-1.6	33.3	< 0.02	7.3	543	-5	6.65									
PU 6-2	31.3	< 0.02	5.6	505	67	6.84									
PU 6-3	39.2	< 0.02	38.4	533	161	7.11									

Table B1 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
19-May-06															
PU 2-1.3	23.7	14.0	21.1	436	380	7.54									
PU 2-2	24.5	13.1	21.6	443	390	7.52									
PU 3-5	30.5	< 0.02	3.2	507	-34	6.9									
PU 3-6	30.2	< 0.02	2.8	512	6	6.93									
PU 3-7	11.6	11.3	19.1	459	88	7.33									
PU 4-1.2	28.0	< 0.02	1.3	545	32	6.73									
PU 4-1.6	29.3	< 0.02	2.3	514	0	6.57									
PU 5-1.3	24.4	< 0.02	2.1	478	-4	6.65									
PU 5-1.6	31.7	< 0.02	2.9	556	14	6.65									
PU 6-2	27.5	< 0.02	6.1	521	74	6.9									
PU 6-3	35.9	< 0.02	38.5	541	79	7.17									
21-May-06															
PU 2-1.3	20.3	11.7	20.1	426	428	7.45									
PU 2-2	19.4	10.9	19.7	423	419	7.6									
PU 3-5	27.8	0.03	1.2	476	-35	6.88									
PU 3-6	27.1	< 0.02	0.3	536	4	6.92									
PU 3-7	11.8	13.2	19.9	444	118	7.31									
PU 4-1.2		0.07	0.2	494	-26	6.64									
PU 4-1.6		0.07	0.2	516	-29	6.52									
PU 5-1.3	24.3	< 0.02	0.9	477	-42	6.62									
PU 5-1.6	31.1	< 0.02	2.1	573	-21	6.63									
PU 6-2	27.0	< 0.02	3.4	526	50	6.82									
PU 6-3	34.6	< 0.02	39.2	521	64	7.11									

Table B1 (con't)

	Cl⁻ (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH_4-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO_3 (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
29-May-06															
PU 2-1.3	12.5	10.0	18.5	376	378	7.58									
PU 2-2	17.7	11.7	20.3	345	413	7.57									
PU 3-5	22.0	< 0.02	1.6	379	-19	6.95									
PU 3-6	23.8	< 0.02	2.0	421	-4	6.9									
PU 3-7	11.2	16.5	22.4	432	90	7.28									
PU 4-1.2	21.4	< 0.02	0.2	440	26	6.64									
PU 4-1.6	26.1	< 0.02	1.1	419	10	6.53									
PU 5-1.3	22.7	< 0.02	0.2	419	-17	6.55									
PU 5-1.6	30.1	< 0.02	0.7	503	-1	6.59									
PU 6-2	24.6	< 0.02	0.6	450	88	6.73									
PU 6-3	26.8	0.24	34.4	487	88	7.16									
14-Jun-06															
PU 2-1.3	23.3	< 0.02	4.5	421	254	7.74									
PU 2-2	22.0	1.16	9.7	390	375	7.65									
PU 3-5	31.0	< 0.02	0.4	556	11	6.77									
PU 3-6	31.3	< 0.02	0.7	597	78	6.83									
PU 3-7	18.1	1.45	13.3	466	115	7.15									
PU 4-1.2	34.4	< 0.02	0.7	715	49	6.46									
PU 4-1.6	34.6	< 0.02	1.2	655	11	6.55									
PU 5-1.3	36.3	0.03	0.5	697	15	6.35									
PU 5-1.6	31.7	< 0.02	1.5	656	7	6.56									
PU 6-2	31.7	< 0.02	1.7	657	98	6.51									
PU 6-3	19.7	< 0.02	37.8	595	88	7.08									

Table B1 (con't).

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
15-Jun-06															
PU 2-1.3	19.2	2.41	11.9	295	247	7.7									
PU 2-2	18.3	5.92	18.3	317	333	7.76									
PU 3-5	29.9	0.06	0.5	426	11	6.78									
PU 3-6	29.2	< 0.02	0.6	463	65	6.82									
PU 3-7	18.6	1.88	15.2	383	93	7.13									
PU 4-1.2	32.5	< 0.02	0.9	515	31	6.45									
PU 4-1.6	32.7	< 0.02	0.6	479	-7	6.53									
PU 5-1.3	35.5	0.04	0.2	512	-1	6.33									
PU 5-1.6	31.9	< 0.02	0.7	498	-11	6.57									
PU 6-2	34.4	< 0.02	1.5	506	92	6.55									
PU 6-3	15.6	< 0.02	42.2	459	76	7.09									
16-Jun-06															
PU 2-1.3	15.3	4.88	17.6	322	288	7.66									
PU 2-2	18.9	8.65	22.3	340	326	7.71									
PU 3-5	28.4	< 0.02	0.2	424	47	6.74									
PU 3-6	29.0	< 0.02	0.2	418	94	6.76									
PU 3-7	18.1	2.68	15.6	400	145	7.04									
PU 4-1.2	32.5	< 0.02	0.7	502	77	6.36									
PU 4-1.6	32.3	< 0.02	0.2	497	28	6.45									
PU 5-1.3	35.7	< 0.02	0.2	554	42	6.24									
PU 5-1.6	31.9	< 0.02	1.0	544	40	6.46									
PU 6-2	31.8	< 0.02	1.3	360	114	6.49									
PU 6-3	15.1	< 0.02	41.2	485	107	6.96									
26-Jun-06															
PU 2-2	16.3	10.3	21.3	472	359	7.46									
PU 3-6	20.2	0.28	0.7	525	88	6.73									
PU 6-2	22.7	< 0.02	0.3	636	135	6.41									

Table B1 (con't)

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (μS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
27-Jun-06															
PU 2-2	16.3	10.3	20.7	447	406	7.61									
PU 3-6	19.9	< 0.02	0.2	502	70	6.81									
PU 6-2	23.5	0.02	0.3	647	38	6.3									
28-Jun-06															
PU 2-2	17.8	10.5	21.6	447	420	7.53									
PU 3-6	20.2	< 0.02	0.2	500	62	6.79									
PU 6-2	27.1	< 0.02	0.2	586	59	6.27									
29-Jun-06															
PU 2-2	15.2	13.1	22.2	547		7.55									
PU 3-6	21.3	0.09	0.3	626		6.85									
PU 6-2	25.4	0.02	0.2	718		6.3									
30-Jun-06															
PU 2-2				481	416	7.53									
PU 3-6				635	56	6.94									
PU 6-2				684	43	6.24									
1-Jul-06															
PU 2-2				482	436	7.6									
PU 2-3				591	441	7.46									
PU 2-4				693	441	7.31									
PU 3-5				566	-4	6.72									
PU 3-6				596	67	6.89									
PU 3-7				576	79	7.12									
PU 4-1.2				612	17	6.33									
PU 4-1.6	25.8	< 0.02	0.3	613	-7	6.41									
PU 5-1.3	27.0	< 0.02	0.3	650	17	6.24									
PU 5-1.6	35.1	< 0.02	0.5	748	14	6.47									
PU 6-2	14.4	< 0.02	0.2	662	64	6.26									
PU 6-3				668	67	6.98									

Table B1 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
05-Jul-06															
PU 2-2 July 5	3.6	1.92	4.7	483	390	7.5									
PU 2-3	15.8	18.6	23.8	544	450	7.42									
PU 2-4	3.2	12.4	14.5	724	482	7.3									
PU 2A	26.9	12.9	22.8	744	285	7.94									
PU 2C	22.2	0.03	0.8	712	74	6.63									
PU 3-6		0.17	1.4	601	60	6.79									
PU 3-7	28.0	0.24	7.5	583	66	7									
PU 4-1.2	14.3	0.03	0.4	620	19	6.24									
PU 4-1.6	21.0	0.04	0.2	673	5	6.31									
PU 5-1.3	24.9	0.06	0.4	694	13	6.16									
PU 5-1.6	27.8	< 0.02	0.3	799	22	6.44									
PU 6-2	23.2	0.05	0.5	718	93	6.2									
PU 6-3	19.3	0.38	40.0	709	101	6.88									
06-Jul-06															
PU 2-2	15.7	9.80	20.4	507	347	7.45									
PU 2-3	15.0	18.8	23.3	579	355	7.44									
PU 2-4	6.3	36.9	36.8	763	376	7.28									
PU 2A	22.9	16.2	26.8	620	361	7.6									
PU 2B	28.1	3.02	14.9	753	237	7.22									
PU 2C	20.5	0.24	0.9	802	90	6.75									
PU 3-6	21.2	0.05	0.8	678	90	6.81									
PU 4-1.2	19.7	< 0.02	1.4	676	11	6.29									
PU 4-1.6	20.5	0.05	0.2	717	-16	6.32									
PU 5-1.3	22.8	0.05	0.2	729	5	6.18									
PU 5-1.6	26.0	< 0.02	0.2	827	35	6.38									
PU 6-2	22.3	0.04	0.4	766	58	6.14									
PU 6-3	18.9	0.13	30.0	779	56	6.87									

Table B1 (con't)

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
07-Jul-06															
PU 2-2	15.7	9.93	21.1	460	405	7.44									
PU 2-3	15.0	20.1	24.6	530	433	7.38									
PU 2-4	6.2	38.0	37.6	706	448	7.3									
PU 2A	23.6	17.1	28.3	651	384	7.3									
PU 2B	29.1	3.00	19.3	627	292	7.39									
PU 2C	19.6	0.07	0.8	700	59	6.78									
PU 3-6	20.7	0.06	0.6	662	50	6.75									
PU 3-7	26.7	0.23	5.4	620	44	7.02									
PU 4-1.2	16.9	0.02	0.6	693	32	6.32									
PU 4-1.6	16.0	< 0.02	0.4	708	15	6.37									
PU 5-1.3	23.4	0.06	0.5	715	8	6.14									
PU 5-1.6	22.7	0.03	0.7												
PU 6-2	21.1	< 0.02	17.7	761	14	6.15									
PU 6-3	15.3	10.3	21.5	814	45	6.8									
08-Jul-06															
PU 2-2	15.4	9.69	20.4	525	414	7.45									
PU 2-3	14.3	23.2	24.1	608	402	7.46									
PU 2-4	6.0	47.2	37.7	783	381	7.33									
PU 2A	23.7	17.6	26.2	682	360	7.39									
PU 2B	27.1	11.0	26.7	770	397	7.59									
PU 2C	24.4	0.19	1.0	787	88	6.97									
PU 3-6	23.5	0.04	0.6	714	60	6.79									
PU 4-1.2	14.0	< 0.02	0.4	670	38	6.33									
PU 4-1.6	22.3	< 0.02	0.4	726	14	6.38									
PU 5-1.3	29.4	< 0.02	0.5	742	-6	6.17									
PU 6-2	28.8	< 0.02	0.5	800	52	6.26									
PU 6-3	21.4	< 0.02	22.1	808	45	6.84									

Table B1 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (μS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
09-Jul-06															
PU 2-2	19.5	10.7	20.5	492	336	7.5									
PU 2-3	14.6	24.5	24.8	588	373	7.44									
PU 2-4	6.1	48.3	39.5	772	399	7.31									
PU 2A	22.6	19.8	27.9	698	364	7.3									
PU 2B	22.0	2.64	11.8	703	50	6.94									
PU 2C	23.4	< 0.02	1.5	692	0	6.76									
PU 3-6	20.9	< 0.02	0.7	672	57	6.67									
PU 4-1.2	16.3	< 0.02	0.5	1007	42	6.44									
PU 4-1.6	22.0	< 0.02	0.4	723	13	6.36									
PU 5-1.3	24.3	< 0.02	0.3	746	32	6.17									
PU 6-2	25.6	< 0.02	0.4	791	56	6.19									
PU 6-3	19.4	< 0.02	32.4	756	59	6.92									
17-Jul-06															
PU 2-2				385	347	7.36									
PU 2-3				571	432	7.33									
PU 2-4				761	445	7.28									
PU 2A				647	296	7.24									
PU 2B				807	65	6.62									
PU 2C				748	-3	6.51									
PU 3-6				482	-1	~6.5									
PU 4-1.2				660	32	~6									
PU 4-1.6				609	-17	~6									
PU 5-1.3				828	-9	~6.25									
PU 6-2				844	10	~6.25									

Table B1 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
19-Jul-06 Downgradient Valve Closed															
PU 2-2	7.2	4.45	16.7	480	374	6.71									
PU 2-3	12.3	24.5	24.5	610	381	7.19									
PU 2-4	6.0	48.6	41.6	798	409	7.23									
PU 2A	17.6	11.4	24.1	617	315	7.28									
PU 2B	19.6	1.87	6.7	775	20	6.73									
PU 2C	17.8	< 0.02	0.2	845	5	6.55									
PU 3-6	18.5	< 0.02	0.2	830	49	6.62									
PU 4-1.6	17.6	< 0.02	0.2	854	-11	6.37									
PU 5-1.3	22.5	0.06	0.2	870	4	6.18									
PU 6-2	24.4	0.09	0.2	883	17	6.19									
PU 6-3				924	47	6.73									
19-Jul-06 Downgradient Valve Open															
PU 2-2	6.8	4.45	16.3	484	386	6.87									
PU 2-3	11.7	24.0	23.9	603	405	7.03									
PU 2-4	5.9	< 0.02	40.7	808	413	7.02									
PU 2A	17.2	10.3	23.4	639	355	7.07									
PU 2B	19.8	3.11	10.6	733	113	6.5									
PU 2C	17.9	0.07	0.8	808	57	6.31									
PU 3-6	17.3	< 0.02	0.6	876	110	6.47									
PU 4-1.6	18.0	0.03	0.6	879	31	6									
PU 5-1.3	21.6	0.02	0.14	908	40	5.81									
PU 6-2	24.0	< 0.02	0.14	905	46	5.86									

Table B1 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
20-Jul-06															
PU 2-2				498	365	6.93									
PU 2-3				653	399	7.18									
PU 2-4				854	423	7.26									
PU 2A				664	323	7.32									
PU 2B				792	60	6.78									
PU 2C				844	4	6.53									
PU 3-6				845	18	6.44									
PU 4-1.6				915	-8	6.24									
PU 5-1.3				944	-11	6									
PU 6-2				964	30	6.01									
25-Jul-06															
PU 2-2					368	6.88									
PU 2-3					417	7.03									
PU 2-4					426	7.11									
PU 2A					283	7.17									
PU 2B					150	6.82									
PU 2C					78	6.34									
PU 3-6					97	6.34									
PU 4-1.6					48	6.08									
PU 5-1.3					42	5.81									
PU 6-2					66	5.88									

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Table B1 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (μS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH$_4$-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO$_3$ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
06-Aug-06															
PU 2-2	57.4	1.57	53.4		335	7.13									
PU 2-3	31.5	2.91	23.5		360	7.31									
PU 2-4	29.5	2.69	19.1		363	7.32									
PU 2A	48.9	0.09	52.6		269	7.38									
PU 2B	69.4	< 0.02	70.9		169	7.22									
PU 2C	149.3	< 0.02	120.5		16	6.68									
PU 3-6	82.4	< 0.02	39.6		28	6.58									
09-Aug-06															
PU 2-2	42.7	1.01	41.2	684	316	6.89									
PU 2-3	35.2	3.36	26.5	644	336	6.98									
PU 2-4	32.7	3.20	22.2	585	336	7.1									
PU 2A	70.1	1.35	78.0	919	218	7.02									
PU 2B	82.3	0.42	85.2	1058	60	6.81									
PU 2C	86.8	< 0.02	53.5	1123	-36	6.54									
PU 3-6	65.9	< 0.02	21.1	1050	20	6.5									
PU 4-1.6	88.6	< 0.02	34.9	1141	-39	6.25									
PU 5-1.3	66.3	< 0.02	13.0	996	-20	6.2									
PU 6-2	48.0	0.02	4.1	985	19	6.09									
10-Aug-06															
PU 2-2	37.0	0.57	35.9	630	383	6.52									
PU 2-3	33.4	2.58	24.1	608	395	7.06									
PU 2A	55.4	0.75	59.7	805	243	7									
PU 2B	67.6	< 0.02	63.3	956	46	6.86									
PU 2C	85.8	< 0.02	47.7	1132	-28	6.54									
PU 3-6	68.6	< 0.02	20.2	1006	-3	6.42									

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Table B2: Detailed geochemistry of Zorra barrier transect during August decreased flow experiment. Downgradient tile was closed on August 11-12, 2006 and open August 13-18, 2006. "Cmt" values are data collected using Chemets colourimetric field test kits.

	Cl^- (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH_4-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO_3 (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
11-Aug-06 - Day -1															
PU 2-5				859	318	7.15							5	1	<0.1
PU 2-6				1238	349	7.12							>5	3	<0.1
PU 2-7	31.8	110.9	60.2	1566	323	7.07	0.02	0.20	12.72	16.7	13.8	2.87	>>5		<0.1
PU 2A	48.6	0.28	49.1	811	247	7.12	0.36	0.66	0.3	21.8	21.8	0	1	<1	
PU 2B	60.3	< 0.02	49.2	990	61	6.86	0.93	1.92	1.14	25.5	24.5	0.997	<<1		1.5
PU 2C	85.6	< 0.02	47.4	1174	-13	6.63	1.36	0.74	2.53	34.3	33.9	0.455		<1	1.5
PU 3-6	71.8	< 0.02	25.2	1049	-35	6.52	2.79	1.00	2.83	39	38.6	0.387			2.5
PU 4-1.6	81.6	< 0.02	24.3	1215	-22	6.35	2.27	0.84	4.36	44.3	43.9	0.355			3
PU 5-1.3	62.6	< 0.02	10.3	961	-23	6.28	2.85	0.56	3.22	36.9	36.9	0			3
PU 6-2	55.6	< 0.02	5.7	959	53	6.19	7.20	0.72	2.56	38.5	38.2	0.313			10
12-Aug-06 - Day 0															
PU 2-6	26.7	72.3	90.1	1236	408	7.16									<0.1
PU 2-7	37.2	89.3	70.7	1423	385	7.26									<0.1
PU 2A	50.7	< 0.02	50.8	800	240	7.19									
PU 2B	53.1	< 0.02	39.6	875	57	7									1
PU 2C	82.5	< 0.02	31.5	1102	-20	6.68									2
PU 3-6	75.1	< 0.02	14.7	1032	18	6.65									
PU 4-1.6	84.3	< 0.02	13.7	1115	-31	6.48									3
PU 5-1.3	62.7	< 0.02	2.3	964	-12	6.38									3
PU 6-2	56.6	< 0.02	4.2	954	22	6.22									>10
13-Aug-06 - Day 1															
PU 2-6	28.0	76.6	96.4	1289	315	7.17							>>5	2	
PU 2-7	37.4	97.2	59.8	1504	300	7.21							>>5		<0.1
PU 2A	43.2	< 0.02	41.3	778	225	7.16							<0.1	<1	
PU 2B	50.6	< 0.02	25.8	869	-11	6.92									1
PU 2C	73.4	< 0.02	2.8	1053	-37	6.65									
PU 3-6	70.9	< 0.02	2.5	1002	7	6.55									10
PU 4-1.6	82.6	< 0.02	7.5	1087	-40	6.38									
PU 5-1.3	61.0	< 0.02	1.2	951	-20	6.27									3
PU 6-2	55.5	< 0.02	0.2	903	2	6.16									

Table B2 (con't)

	Cl⁻ (mg/L)	NO₃-N (mg/L)	SO₄ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	NH₄-N (mg/L)	DC (mg/L)	DOC (mg/L)	DIC (mg/L)	Cmt NO₃ (mg/L)	Cmt DO (mg/L)	Cmt Fe (mg/L)
14-Aug-06 - Day 2															
PU 2-6	28.8	83.5	102.6	1294	381	7.1									
PU 2-7	37.3	102.4	70.6	1411	376	7.2									
PU 2A	47.2	0.61	45.6	787	222	7.16									
PU 2B	50.3	< 0.02	26.0	845	6	6.92									
PU 2C	70.6	< 0.02	0.7	985	-44	6.64									
PU 3-6	69.2	< 0.02	0.8	956	12	6.6									
PU 4-1.6	82.3	< 0.02	4.6	1068	-37	6.37									
PU 5-1.3	62.3	< 0.02	1.4	947	-20	6.26									
PU 6-2	54.3	< 0.02	0.08	881	72	6.24									
16-Aug-06 - Day 4															
PU 2-7	32.5	99.4	60.2	1387	374	7.21			5.71	4.46	4.46	0			
PU 2A	41.2	0.74	38.6	800	218	7.15			0.37	16.6	9.84	6.72			
PU 2B	49.2	0.05	28.1	828	18	6.92			0.77	14.2	11.7	2.49			
PU 2C	66.3	< 0.02	0.9	975	-41	6.58			2.78	27.8	27.4	0.353			
PU 3-6	65.6	< 0.02	0.4	988	29	6.61			2.94	30.3	30.3	0			
PU 4-1.6	80.2	< 0.02	1.6	1066	-34	6.19			4.17	47.9	47.5	0.36			
PU 5-1.3	64.1	< 0.02	0.4	965	-24	6.11			2.81	52.1	52.1	0			
PU 6-2	54.5	< 0.02	0.14	881	34	6.01			2.13	54.5	53.9	0.605			
18-Aug-06 - Day 6															
PU 2-7	37.1	111.8	68.2	1461	347	7.06	0.22	0.01	14.23	7.1	7.1	0			
PU 2A	38.3	0.33	35.1	740	241	7.1	0.44	0.47	0.25	10.3	10.3	0			
PU 2B	45.1	< 0.02	27.0	825	25	6.92	1.24	3.26	0.57	9.34	8.85	0.495			
PU 2C	64.5	< 0.02	4.4	979	-41	6.59	1.15	1.23	3.37	24.4	23.9	0.457			
PU 3-6	65.6	< 0.02	1.5	962	26	6.54	6.49	4.10	4.22	19.7	19.3	0.349			
PU 4-1.6	81.7	< 0.02	4.6	1114	-37	6.29	2.13	1.30	4.32	41.7	41.3	0.408			
PU 5-1.3	63.0	< 0.02	1.5	995	-21	6.12	3.49	1.02	2.17	53.3	52.8	0.5			
PU 6-2	54.6	< 0.02	0.3	861	31	6.01	6.12	1.13	1.46	52.3	51.7	0.639			

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Table B3 – Detailed geochemistry of Zorra barrier transect during the November enhanced flow experiment. Upgradient and downgradient tile lines were closed for November 22, 2006 sampling and open on November 23-29, 2006 sampling. Data from November 29, 2006 used for PHREEQCI modeling.

	Cl⁻ (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)
22-Nov-06 - Day 0												
PU 2-7	31.4	106.5	88.3	784	475	7.28	0.000	0.12	171.37	<3.00	40.11	13.33
PU 2A	45.7	0.06	21.5	566	90	7.24	1.875	3.16	152.48	16.5	26.94	23.48
PU 2B	41.7	< 0.02	23.3	493	74	7.15	4.311	2.99	123.67	23.16	20.63	23.94
PU 2C	50.7	< 0.02	17.3	522	20	7.2	0.575	3.14	110.1	26.57	21.46	26.71
PU 3-6	48.5	< 0.02	22.0	533	110	7.23	3.384	3.27	104.45	26.03	18.3	24.36
PU 4-1.6	51.2	0.07	8.9	551	52	6.53	4.338	3.21	121.46	30.02	20.93	32.61
PU 5-1.3	45.1	< 0.02	0.3	518	61	6.42	5.629	2.89	184.6	24.3	21.19	27.74
PU 6-2	42.9	0.13	0.6	528	74	6.41	5.856	2.31	134.05	19.74	18.5	25.88
23-Nov-06 - Day 1												
PU 93	177.7	16.9	148.8									
PU 2-7	40.7	107.5	90.2	795	373	6.98						
PU 2A	102.1	8.82	96.8	724	245	6.82						
PU 2B	58.4	0.59	43.3	499	40	6.9						
PU 2C	157.4	13.8	141.3	904	245	6.76						
PU 3-6	144.9	11.8	128.6	777	164	6.98						
PU 4-1.6	134.0	7.57	102.9	776	64	6.8						
PU 5-1.3	101.7	3.93	82.9	694	13	6.73						
PU 6-2	88.7	1.77	57.8	664	61	6.44						
25-Nov-06 - Day 3												
PU 93	141.0	17.3	142.8	880	260	6.79	0.447	1.36	225.06	110.73	42.71	56.21
PU 2-7	44.6	91.4	86.7	729	474	7.17	0.147	0.07	198.57	<3.00	42.32	14.95
PU 2A	84.0	7.74	89.5	711	304	6.89	0.375	2.34	166.2	54.9	26.76	35.92
PU 2B	38.6	< 0.02	40.9	379	73	7.01	3.329	2.55	97.17	15.19	16.37	21.41
PU 2C	135.2	12.4	149.5	771	146	6.81	2.293	1.66	180.6	98.76	37.25	49.88
PU 3-6	121.1	10.2	131.9	786	129	6.82	4.565	2.37	223.26	86.8	37.09	48.37
PU 4-1.6	105.3	4.44	116.1	709	153	6.89	2.275	2.22	158.37	72.56	36.43	43.58
PU 5-1.3	99.0	0.41	95.3	642	27	6.85	3.202	2.74	145.15	58.2	30.53	40.16
PU 6-2	96.6	0.89	94.7	662	166	6.68	8.729	3.04	147.45	60.19	31.14	41.23
27-Nov-06 - Day 5												
PU 93	193.4	19.2	152.1	880	224	6.92						
PU 2-7	31.4	91.7	78.7	718	478	7.25						
PU 2A	116.0	8.93	138.9	689	353	6.98						
PU 2B	38.8	0.92	38.8	382	139	7.1						
PU 2C	134.6	14.1	147.1	799	254	6.95						
PU 3-6	94.7	11.3	98.6	786	186	6.95						
PU 4-1.6	89.2	1.65	101.7	688	230	7.04						
PU 5-1.3	76.1	< 0.02	81.8	628	66	6.98						
PU 6-2	82.9	< 0.02	82.7	659	25	6.8						

Table B3 (con't)

	Cl⁻ (mg/L)	NO$_3$-N (mg/L)	SO$_4$ (mg/L)	EC (µS)	Eh (mV)	pH	Fe (mg/L)	Mn (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	DOC (mg/L)	DIC (mg/L)
29-Nov-06 - Day 7														
PU 93	160.8	20.7	170.7	936	218	6.86	0.138	1.49	245.39	133.37	44.57	59.31	75.0	95.8
PU 2-7	32.6	90.1	84.8	713	510	6.82	0.011	0.09	163.33	<3.00	44.72	14.83	3.2	46.2
PU 2A	90.2	8.99	97.5	644	415	6.84	0.000	2.64	175.58	60.73	27.92	38.63		
PU 2B	43.9	2.57	47.3	426	289	6.93	3.338	2.41	112.33	16.17	18.66	22.53		
PU 2C	135.2	11.0	152.9	816	335	6.79	0.284	1.79	178.98	103.99	35.76	48.03	57.7	53.6
PU 3-6	119.4	7.68	131.7	814	265	6.8	4.420	2.78	212.67	88.76	34.04	45.93	47.9	83.1
PU 4-1.6	125.7	3.68	111.9	699	320	6.64	1.347	2.4	151.28	75.08	33.25	46.16	37.6	98.0
PU 5-1.3	91.6	< 0.02	100.4	640	45	6.64	1.865	2.31	177.66	65.84	31.53	41.54	34.9	42.9
PU 6-2	87.8	< 0.02	93.2	654	35	6.72	8.529	2.61	169.7	59.04	29.46	38.83	35.7	93.1

Table B4 – Geochemistry at Zorra site prior to April 2006. Some data from Robertson et al. (2007). All values are in mg/L, n.d. = not detected.

	November 28, 2004	December 1-4, 2004	December 16, 2004	December 21, 2004	January 29, 2005	June 27-28, 2005			May 3, 2005	July 7, 2005		September 1, 2005	
	NO$_3$-N					NO$_3$-N	Cl$^-$	SO$_4$	NO$_3$-N	NO$_3$-N	SO$_4$	NO$_3$-N	Cl$^-$
PU 1-2	6			17									
PU 1-3	16			1.4					7				
PU 1-4	58	1.3			13								
PU 1-5	72												
PU 1-6													
PU 1-7	83								85				
PU 1-8	97												
PU 1-9	93								110				
PU 2-1.3				10.2									
PU 2-2	40					16	9.8	5.3					
PU 2-3	69	0.8				28	16	8.3					
PU 2-4	80	1				46.4	5.5	9.4					
PU 2-5	85					61.2	13.3	20.2					
PU 2-6	83					93.3	19.8	19.4					
PU 2-7	99					106.8	27.8	22.6					
PU 2-8													
PU 2-9	68												
PU 3-4	31					0.02	36	0.6					
PU 3-5	7	0.2		0.3	0.31	0.11	35.5	0.5					
PU 3-6	0.3					0.01	36.5	0.3					
PU 3-7	0.1					0.01	23.2	0.8					
PU 3-8	47					11.7	12.1	6.1					
PU 3-9	78												
PU 3-10	83					41.8	9.7	14.4					
PU 3-11	55					95.6	22.4	21.8					
PU 3-12	48												
PU 3-13	63					91.1	23.5	19.4					
PU 3-14	77												
PU 3-15	46												

Table B4 (con't)

	November 28, 2004	December 1-4, 2004	December 16, 2004	December 21, 2004	January 29, 2005	June 27-28, 2005			May 3, 2005	July 7, 2005		September 1, 2005	
	NO$_3$-N					NO$_3$-N	Cl$^-$	SO$_4$	NO$_3$-N	NO$_3$-N	SO$_4$	NO$_3$-N	Cl$^-$
PU 4-1.1	0.2									0.01	0.4		
PU 4-1.4	0.1									0.01	0.06		
PU 4-1.7	0.1									0.01	0.05		
PU 4-2.0	0.1									11.9	26		
PU 4-2.3	8											12	
PU 4-2.6	58									17.5	20.9		
PU 4-2.9	13									47.6	59.7		
PU 5-1.3	0.1												
PU 5-1.6	0.1												
PU 5-1.9	0.1					6.7	23.2	9.9					
PU 5-2.2	0.1					<0.01	50.9	0.1					
PU 5-2.5	0.1											0.13	
PU 6-2	6		0.2		0.38	3.1	1.1	1.2					
PU 6-3	0.1	16				0.01	37.1	0.2					
PU 6-4	0.1												
PU 6-5	0.1					0.01	47.4	0.2					
PU 6-6	0.1					0.63	26.4	2.6					
PU 6-7	2					14.9		6.8					
PU 6-8	57					76.6	14.9	19.2					
PU 6-9													
PU 6-10												81.3	
PU 7-2	2												
PU 7-3	0.1				0.4	0.02	34.6	7					
PU 7-4	0.1												
PU 7-5	0.1					0.01	30	9.1					
PU 7-6	0.1					6.9	22.2	6.6					
PU 7-7	50					55	16	12.6					
PU 7-8	51					87.8	28.8	20.1					
PU 7-9						<0.01	46.4	2.9				91.6	
PU 7-10	0.4					<0.01	53.1	8					

Table B4 (con't)

	November 28, 2004	December 1-4, 2004	December 16, 2004	December 21, 2004	January 29, 2005	June 27-28, 2005			May 3, 2005	July 7, 2005		September 1, 2005	
	NO$_3$-N					NO$_3$-N	Cl$^-$	SO$_4$	NO$_3$-N	NO$_3$-N	SO$_4$	NO$_3$-N	Cl$^-$
PU 8-1.4	3	13	7.7		0.36								
PU 8-1.7	0.1					0.01	33.1	2.9					
PU 8-2.1	0.1				1.5	0.01	43.7	0.4					
PU 8-2.5	0.3												
PU 9-1	0.2												
PU 9-2	26					0.01	46.2	0.3					
PU 9-3	0.2				0.41								
PU 9-4	5					0.53	23.3	4.6					
PU 9-5	39					6.8	15.4	8.9					
PU 9-6	80					84.3	23.4	19.4					
PU 9-7	79												
PU 10-1	0.4					0.01	42.6	7.9					
PU 10-2	8				0.58	0.02	39.9	0.3					
PU 10-3	49												
PU 10-4	34				44	0.01	30.9	0.5					
PU 10-5	19					0.59	21.3	2.5					
PU 10-6	25											14.8	
PU 10-7	60					40.9	15.5	15.5					
PU 10-8						93.3	29.5	22.6					
PU 10-9	83					94.6	45.1	21.5					
PU 10-10	59												
PU 11-1.2													
PU 11-1.4	31				0.47								
PU 11-1.6	30					19	28.3	9.2					
PU 11-1.8	18												
PU 11-2.0	16					10.6	21.3	7.7					
PU 11-2.2	27	17			34.6	17.8	22.2	9.1					
PU 11-2.4	43					23.8	20.4	12					
PU 11-2.6	75												
PU 11-2.8													
PU 11-3.0	70												

Table B4 (con't)

	November 28, 2004	December 1-4, 2004	December 16, 2004	December 21, 2004	January 29, 2005	June 27-28, 2005			May 3, 2005	July 7, 2005		September 1, 2005	
	NO$_3$-N					NO$_3$-N	Cl$^-$	SO$_4$	NO$_3$-N	NO$_3$-N	SO$_4$	NO$_3$-N	Cl$^-$
PU 13-1.3	13				2.3								
PU 13-1.6	19		11.2		30.8								
PU 13-1.9	40												
PU 13-2.2	64												
PU 13-2.5	74												
PU 13-2.8	65												
PU 13-3.0	59												

Appendix C

Water level measurements, Zorra site, June 2005-May 2007.

Table C1 – Hydraulic head values at Zorra site during June 2005-May 2007, relative to arbitrary datum. Monitoring well locations are shown on Figs 4 and 7 * values originally from PU 76-1.3, which was washed away in a high water event. Point PU 2-1.3 is 1.3 m below ground surface.

Hydraulic Head (cm)												
	PU 2	PU 2-1.3	PU 2A	PU 76-3.2	PU 84	PU 86	PU 90	PU 91 4"	PU 91 1/2"	PU 93	PU 94	PU 96
23-Jun-05				846								
08-Sep-05	853											
15-Sep-05	854			840								
19-Sep-05	855											
03-Oct-05	869			857								
21-Nov-05	892			895								
06-Dec-05	925			877*								
13-Dec-05	906			858*								
26-Mar-06	941			878*								
05-Apr-06	932			864*								
09-Apr-06	928			867*								
14-Apr-06		937.5		896	929	917.5	916.5					
17-Apr-06		929		885.5	925	915.5	915					
26-Apr-06		927.5		885	925	915	914.5					
2-May-06 (2pm)	912	914		864	913	903.5	902.5					
3-May-06	907	907.1		860.5	903.7	903.9	903					
4-May-06	905.9	905.7		852.7*	904.2	904.5	903.8					
8-May-06	897.6	898.6		854.9	896.7	896.3	896.1					
15-May-06	898.6	899.3		866.4	898.4	898.6	897.7					
17-May-06	906.5	907		886.4	905.7	905.7	905.2					
19-May-06	909.7	909.8		892.9	909	909.1	908.1					
21-May-06	905.6	906		875.5	904.9	905.2	904.2					
26-May-06	900.1	899.7		861.7	898.5	898.7	897.7					
29-May-06	892	892.4		854.5	890.8	890.8	890.5					
31-May-06	889	889.6		854.2	887.8	888	887.4					
1-Jun-06	895	894.5		858.7	893.2	893.2	892.7					
5-Jun-06	931	928.4		917.2	923.9	923.8	921.6					
14-Jun-06	900.1	901.1		863.3	897.8	897.9	897					

Table C1 (con't)

Date												
15-Jun-06	897.3	898		858.4	894.7	894.8	893.8					
16-Jun-06	892.7	894.2		854.5	889.1	891.7	890.7					
26-Jun-06	877.5	878.5		846.6	877	876.9	876.7					
27-Jun-06	877.4	878.7		848.4	876.4	876.3	876.4					
28-Jun-06	876.4	877		846.4	877.9	875.1	875					
29-Jun-06	875	876.8		847.8	875.8	875.1	874.8					
30-Jun-06	874.7	875.8		845.6		873.5	874.8					
1-Jul-06	874.8	873.8		843.8		872.1	872.2					
3-Jul-06	872.7	870.8		843.1		869.3	868.9					
5-Jul-06	868.4	870.4		855.3		865.2	865.3					
6-Jul-06	867	870.4		842.4		864.2	863.9					
7-Jul-06	866	867.3		842		863.9	862.9					
8-Jul-06	865	866		841.8	864.4	864.5	864.4					
9-Jul-06	863.6	864.8		840.5	863.4	863.5	863.5					
17-Jul-06	873	874.4		853.2	873.9	871.9	872.7					
19-Jul-06 (9am)	868.4	869.6		848.8	868.4	865.7	865.9					
19-Jul-06 (3:30pm)	867.9	869		848.5	867.8	865.1	864.6					
19-Jul-06 (9pm)	866.7	867.9		847.8	866.3	867.1	866.5					
20-Jul-06	866.4	868.3		848	866.2	866.6	866.3					
25-Jul-06	868.8	870.4		858.8	869.4	868.9	869.2					
6-Aug-06	925.8	926.9		870.8	932.1	912.6	911.2					
7-Aug-06	922.7	922.2		867.3	924	906.7	905.7					
8-Aug-06	914.8	914.6		872.8	909.2	909.3	906.1					
9-Aug-06	911.3	911		867.7	905.6	905.7	903.4					
10-Aug-06	912.7	907.7		861.8	903.6	904.3	901.7					
11-Aug-06	905.3	904.5		860.2	898.5	898.4	897.2					
12-Aug-06	906.9	901.8		864.3	897.1	897.4	896.1					
13-Aug-06	899.1	900.9		857.6	890.9	890.9	890.2					
14-Aug-06	897.2	898.8		849.3	888.2	889.3	888.8					
16-Aug-06	895	895.5		858.2	887.2	886.2	885.8					
18-Aug-06	891.3	892.6		858.9	969	884.5	883.9					
7-Sep-06		879		850		867.5						
3-Oct-06	912.2		914	915.3	913.7	919.2	918.1	910.5	911.2	908.4	912.6	912.3
10-Oct-06	945.7		946.3	915.7	946.4	927	926.5	944.6	946.5	944.6	947.3	947.7
16-Oct-06	946.2		950.8	927	951.5	936.7	936.2	951.6	952.8	951.9	954	955.5

Table C1 (con't)

	PU 2	PU 2-1.3	PU 2A	PU 76-3.2	PU 84	PU 86	PU 90	PU 91 4"	PU 91 1/2"	PU 93	PU 94	PU 96
3-Oct-06	912.2		914	915.3	913.7	919.2	918.1	910.5	911.2	908.4	912.6	912.3
10-Oct-06	945.7		946.3	915.7	946.4	927	926.5	944.6	946.5	944.6	947.3	947.7
16-Oct-06	946.2		950.8	927	951.5	936.7	936.2	951.6	952.8	951.9	954	955.5
4-Nov-06	946		959	906	951	929.5	928.5				953	984
14-Nov-06	940.5		938.2	887	938.8	925.1	922.9	939.5	939.5	938.8	941	946.6
22-Nov-06	946.2		947.7	919	948	927.7	926	949	951.3	947.8	952.3	954
23-Nov-06	944		933	911.8	932.8	932.9	925.9	940.2	947.3	932.8	949.2	951.6
25-Nov-06	942		930	899.8	930.4	930.4	924.8	935.7	942	930.2	944.6	946.5
27-Nov-06	938.3		928	892.8	928.3	928.1	923.8	933.7	937.8	927.9	940.2	942.7
29-Nov-06	935.8		926.5	887.4	926.3	926.4	922.5	932.2	935.4	926	937.2	939.1
23-May-07			904.4	877.1	902.9	903	898.3	906.1	910.8	902.8	916.7	914.2
24-May-07	901.5			874.5	900	900.5				898		
14-Jun-07	881.5			872.2	878.9	878.3		893	893.1	880.4		889.5
19-Jun-07	875.7			872.8	874.2	875.3				874		884
26-Jun-07	869			874		948.5				867		

Table C2 – Difference in hydraulic head between monitoring points at Zorra site before installation of upgradient tile line. Point PU 2-1.3 is 1.3 m below ground surface.

Δ Head (cm)	PU 2-2 - 76	PU 84-90	PU 86-90	PU 2-1.3 - 86	PU 2-1.3 - 84	PU 2-76
14-Apr-06		12.5	1.0	20	8.5	
17-Apr-06		10.0	0.5	13.5	4	
26-Apr-06	50.5	10.5	0.5	12.5	2.5	
2-May-06 (2pm)	52.0	10.5	1.0	10.5	1	50
3-May-06	54.3	0.7	0.9	3.2	3.4	54.2
4-May-06	53.0	0.4	0.7	1.2	1.5	53.2
8-May-06	49.2	0.6	0.2	2.3	1.9	48.2
15-May-06	35.5	0.7	0.9	0.7	0.9	34.8
17-May-06	21.1	0.5	0.5	1.3	1.3	20.6
19-May-06	16.3	0.9	1.0	0.7	0.8	16.2
21-May-06	33.2	0.7	1.0	0.8	1.1	32.8
26-May-06	39.2	0.8	1.0	1	1.2	39.6
29-May-06	34.7	0.3	0.3	1.6	1.6	34.3
31-May-06	39.7	0.4	0.6	1.6	1.8	39.1
1-Jun-06	35.6	0.5	0.5	1.3	1.3	36.1
5-Jun-06	7.7	2.3	2.2	4.6	4.5	10.3
14-Jun-06	43.3	0.8	0.9	3.2	3.3	42.3
15-Jun-06	46.3	0.9	1.0	3.2	3.3	45.6
16-Jun-06	44.4	-1.6	1.0	2.5	5.1	42.9
26-Jun-06	33.9	0.3	0.2	1.6	1.5	32.9
27-Jun-06	34.6	0.0	-0.1	2.4	2.3	33.3
28-Jun-06	33.2	2.9	0.1	1.9	-0.9	32.6
29-Jun-06	26.4	1.0	0.3	1.7	1	24.6
30-Jun-06	33.3		-1.3	2.3		32.2
1-Jul-06	30.0		-0.1	1.7		31
3-Jul-06	30.2		0.4	1.5		32.1
5-Jul-06	28.9		-0.1	5.2		26.9
6-Jul-06	28.9		0.3	6.2		25.5
7-Jul-06	26.8		1.0	3.4		25.5
8-Jul-06	25.2	0.0	0.1	1.5	1.6	24.2
9-Jul-06	25.5	-0.1	0.0	1.3	1.4	24.3
17-Jul-06	24.7	1.2	-0.8	2.5	0.5	23.3
19-Jul-06 (9am)	21.8	2.5	-0.2	3.9	1.2	20.6
19-Jul-06 (3:30pm)	20.3	3.2	0.5	3.9	1.2	19.2
19-Jul-06 (9pm)	21.2	-0.2	0.6	0.8	1.6	20
20-Jul-06	20.3	-0.1	0.3	1.7	2.1	18.4
25-Jul-06	11.5	0.2	-0.3	1.5	1	9.9
6-Aug-06	65.1	20.9	1.4	14.3	-5.2	64
7-Aug-06	64.3	18.3	1.0	15.5	-1.8	64.8
8-Aug-06	57.7	3.1	3.2	5.3	5.4	57.9
9-Aug-06	55.2	2.2	2.3	5.3	5.4	55.5
10-Aug-06	52.8	1.9	2.6	3.4	4.1	57.8
11-Aug-06	50.2	1.3	1.2	6.1	6	51
12-Aug-06	49.3	1.0	1.3	4.4	4.7	54.4

Table C2 (con't)

13-Aug-06	48.4	0.7	0.7	10	10	46.6
14-Aug-06	47.1	-0.6	0.5	9.5	10.6	45.5
16-Aug-06	38.1	1.4	0.4	9.3	8.3	37.6
18-Aug-06	36.1	85.1	0.6	8.1		34.8
7-Sep-06	29.0			11.5		

Table C3 – Difference in hydraulic head between monitoring points at Zorra site after upgradient tile line installation.

Δ Head (cm)	PU 84-90	PU 86-90	PU 2A-86	PU 2A-84	PU 2-76	PU91-2A	PU 91-93	PU 91-2A
3-Oct-06	-4.4	1.1	-5.2	0.3	-3.1	-3.5	2.1	-1
10-Oct-06	19.9	0.5	19.3	-0.1	30	-1.7	0	0.8
16-Oct-06	15.3	0.5	14.1	-0.7	19.2	0.8	-0.3	6.6
4-Nov-06	22.5	1	29.5	8	40			
14-Nov-06	15.9	2.2	13.1	-0.6	53.5	1.3	0.7	-1
22-Nov-06	22	1.7	20	-0.3	27.2	1.3	1.2	5.1
23-Nov-06	6.9	7	0.1	0.2	32.2	7.2	7.4	3.3
25-Nov-06	5.6	5.6	-0.4	-0.4	42.2	5.7	5.5	0
27-Nov-06	4.5	4.3	-0.1	-0.3	45.5	5.7	5.8	-0.5
29-Nov-06	3.8	3.9	0.1	0.2	48.4	5.7	6.2	-0.4
23-May-07	4.6	4.7	1.4	1.5		1.7	3.3	
24-May-07					27			
14-Jun-07					9.3		12.6	11.6
19-Jun-07					2.9			
26-Jun-07					-5			