UNIVERSITY OF CALGARY

The Influence of Macropores on Flow and Transport to Subsurface Drains in Low

Permeability, Salt Affected Soils

by

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**Abstract**

The use of subsurface tile drains in conjunction with surface irrigation is proposed as a method for remediating salt affected soils, which are a major environmental issue for the oi l a nd gas i ndustry. U nderstanding t he i nfluence m acropores ha ve on t he effectiveness o f th e tile d rains in r emoving s alts f rom th e s oil is r equired f or future development of similar remediation sites. A multi-year study using conservative benzoic acid groundwater tracers was performed at a field site located in central Alberta in order to examine the affect macropores have on fluid flow and solute transport to subsurface tile d rains th rough lo w p ermeability s alt affected s oils. R egular s urface ir rigations occurred during the 2009 and 2010 f ield s easons ove r a $20 \times 20$ m t est pl ot a nd w ere combined w ith de tailed temporal m onitoring of t ile dr ain di scharge r ates a nd e ffluent tracer concentrations. The spatial distribution and concentration of the tracers were also monitored using soil and pore water sampling. Results were then used to construct a dual permeability flow and transport model using the software package HYDRUS to aid in the understanding of flow a nd t ransport d ynamics oc curring on s ite. T he t racer breakthrough t o t he t ile dr ains oc curred 46.75 hours a fter application to t he g round surface. A fter two field seasons, 7% of the initial applied tracer mass was recovered in the tile drains and 32% of the initial mass was accounted for in soil core extractions taken from directly below the plot which indicates solute flushing is occurring under the plot. The t ile dr ains w ere a ble t o c apture 5.9% a nd 5 1% of t he applied i rrigation ( including precipitation) w ater vol ume i n 2009 and 2010 r espectively. T he l arge di screpancy between t he t ile dr ain c apture vol umes i s t hought t o be a f unction of t he a ntecedent conditions in 2009 and 2010. Initial modeling results were successful at simulating the

tile drain discharge, but were less successful in matching the effluent tracer concentrations. Field observations and simulation results suggested that although macropores accounted for the majority of the fluid and solute transport, flushing of tracer from the soil to the tile drains was still occurring.

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## List of Symbols

| Symbol | Definition |
|---|---|
| h | Pressure Head |
| $\rho_b$ | Dry Bulk Density $(M/L^3)$ |
| $K_{sat}$ | Saturated Hydraulic Conductivity (L/T) |
| $K_{sf}$ | Saturated Hydraulic Conductivity of the Macropores (L/T) |
| $\theta_r$ | Residual Water Content of the Matrix $(L^3/L^3)$ |
| $\theta_{rf}$ | Residual Water Content of the Macropores $(L^3/L^3)$ |
| $\theta_s$ | Saturated Water Content of the Matrix $(L^3/L^3)$ |
| $\theta_{sf}$ | Saturated Water Content of the Macropores $(L^3/L^3)$ |
| $\alpha_m$ | Measure of the Inverse of the Air Entry Pressure in the Matrix (1/L) |
| $\alpha_f$ | Measure of the Inverse of the Air Entry Pressure in the Macropores (1/L) |
| $n_m$ | Empirical Parameter Describing the Pore-Size Distribution of the Matrix (unitless) |
| $n_f$ | Empirical Parameter Describing the Pore-Size Distribution of the Macropores (unitless) |
| $S_m$ | Matrix Sink Term $(T^{-1})$ |
| $S_f$ | Macropore Sink Term $(T^{-1})$ |
| $\Gamma_w$ | Transfer Rate of Water between Domains $(T^{-1})$ |
| $\omega$ | Volume of the Macropore System Relative to the Total Rock or Soil Volume (unitless) |
| $\alpha_w$ | Fluid Mass Exchange Coefficient $(L^{-1}T^{-1})$ |
| $a$ | Characteristic Half Width of a Matrix Block (L) |

| | |
|---|---|
| $\beta$ | Dimensionless Geometry Coefficient (unitless) |
| $\gamma_w$ | Dimensionless Scaling Factor (unitless) |
| $K_{as}$ | Effective Hydraulic Conductivity of the Interface between Matrix and Macropore Domains (L/T) |
| $D$ | Dispersion Tensor (L$^2$/T) |
| $q$ | Darcian flux (L/T) |
| $\varphi$ | Reaction Parameter (M/L$^3$T) |
| $\Gamma_s$ | Solute Mass Exchange Parameter (T$^{-1}$) |
| $\alpha_s$ | Solute Mass Transfer Coefficient (L$^{-1}$) |
| $C$ | Specified Concentration in the Respective Pore System (M/L$^3$) |
| $D_a$ | Effective Dispersion Coefficient (L$^2$/T) |
| $\alpha_L$ | Lateral Dispersivity (L) |
| $\alpha_T$ | Transverse Dispersivity (L) |
| $K_d$ | Distribution Coefficient (L$^3$/M) |

**CHAPTER ONE: INTRODUCTION**

When t he Leduc N o. 1 w ell di scovered c rude oil i n 1947, oi l a nd g as exploration a nd pr oduction i n A lberta be came one of t he l argest i ndustries i n t he province. In Alberta there are currently 275,000 jobs directly and indirectly linked to the oil a nd g as i ndustry a s of 2011 ( Government of A lberta, 2011) . T he i ncreased development a nd e xpansion of oi l a nd g as f acilities i n A lberta ha s resulted i n a n increased risk to the environment. These hazards can include the occurrences of industrial spills th at h ave t he p otential to r elease la rge v olumes o f h armful c hemicals ( metals, volatile or ganic c ompounds), h ydrocarbons a nd produced w ater ( brine c ontaining hi gh levels of dissolved ions, produced along with oil and gas) at the ground surface. One of the mo re c ommon and di fficult e nvironmental i ssues t o de al w ith i n oi l a nd gas production facilities is release of produced water. Produced water spills have the ability to a lter t he g eochemistry of t he a ffected s oils d ue t o t he a ddition of l arge vol umes o f chloride, calcium, magnesium and various other ions. This can result in both sodic (high sodium c ontent, hi gh pH , hi gh s odium a dsorption r atio ( SAR)) a nd s aline ( high s alt content, low pH, low SAR) soil conditions (Government of Alberta, 2010). The impact these spills has on the affected area can decrease the infiltration capacity of the soils and alter th e s oil s tructure; all o f w hich c an p otentially result in a ma jor r eduction in s oil fertility and crop production potential.

Several d ifficulties a rise w hen d eveloping a r emediation s trategy for s alt affected s oils. T hese i nclude t he l ocation of t he s pill ( remote o r c entered i n a hi ghly congested a rea), s ize o f s pill ar ea ( $m^2$ − $km^2$), s pill c omposition ( non-reactive, h ighly

reactive and harmful) and composition of affected soils (low permeability, presence of fractures, high permeability). One remediation method for treating saline/sodic soils is the installation of subsurface tile drains used to leach the salts from the soil and drain them away from the affected area. The effectiveness of the drains depends primarily on the permeability of the soil, tile drain spacing and the total volume of water passing through the soil. Closer drain spacing typically results in larger volumes of water removed from the soil, thereby increasing the leaching rate of the salts (Kladivko et al., 1999). Another factor that may influence the tile drain effectiveness is the presence of macropores (fractures, root holes), which have the ability to transport infiltrating water straight to or beyond the installed tile drains and reduce the efficiency of salt flushing from the soil profile. Preferential flow along macropores causes large volumes of water to bypass sections of soil matrix, reducing the amount of salt being flushed.

## 1.1 Objectives

In 2008, a research project was initiated to determine the effectiveness of subsurface drains (tile drains) for the removal of salts from low permeability, fractured soils and to examine whether surface applied irrigation could enhance the leaching of salts from the soils into the tile drains. Due to the large scope of the research, several projects were created with the intent of contributing to the overall research goal. The primary objective of this research project is aimed at furthering the understanding of how macropores influence solute transport to subsurface tile drains in low permeability, salt affected soil. This was accomplished by completing two tracer experiments over an irrigated, tile drain plot. The results from the tracer experiments were then used to

construct a calibrated 2-dimensional, dual permeability numerical flow and transport model using the HYDRUS software package. The numerical model will help quantitatively determine the influence macropores have on tile drain flow dynamics and solute transport through the low permeability soils.

## 1.2 Thesis Outline

This chapter introduces the scope of the research problem as well as the main objectives of the completed research. Chapter 2 will introduce the research site including its historical development and a discussion of previous and current research being conducted at the site by the University of Calgary. Chapter 3 is a literature review that discusses the occurrence and treatment of salt affected soils, the use of tile drains as a remediation strategy, macroporosity and their impacts, the use of benzoic acids as groundwater tracers and variably saturated flow and transport modeling. Chapter 4 describes the fieldwork and laboratory methodology used to characterize flow and tracer transport at the site. The development and calibration of the numerical flow and transport model are discussed in Chapter 5. Chapter 6 presents the results and discussion of the benzoic acid tracer experiments and the flow and transport simulations. Chapter 7 contains the final conclusions of the research along with recommendations for future work.

## CHAPTER TWO: RESEARCH SITE BACKGROUND

### 2.1 Historic Site Development

The research site under investigation is located southwest of Edmonton, Alberta in a region used primarily for agriculture (Figure 2.1). The site was originally used as an oil and gas battery to facilitate oil and gas production activities in the region. Air photos of the property show that development of the site as an oil and gas production facility was established prior to 1962 (Komex International, 1999). Ongoing development occurred from the early 1960's through until the 1980's. Throughout the history of the site, multiple small releases of produced water occurred, negatively impacting the soil conditions. During the mid 1980's (exact date unknown) a pipeline spill on site released an unknown volume of hydrocarbons and produced saline water (Komex International, 1997). Removal of 6085 $m^3$ of hydrocarbon contaminated soil in 2001 left approximately 27000 $m^3$ of shallow, salt affected soil on site (Komex International, 2005). The addition of calcium soil amendments along with the installation of subsurface tile drains in 2003 acted as an in-situ remediation strategy with the intent to remove salt from the soil via flushing to the tile drains (Komex International, 2003). Drains were installed in locations of high salinity at a depth of approximately 2.1 meters below ground surface in a west – east direction with 10 meter separation (Figure 2.2). All drains are connected to main lines that discharge into a wet well located on the south edge of the property. A summary of work completed by various environmental consulting firms between 1998 and 2006 is as follows (Smith, 2008)

- Four electromagnetic (EM) surveys completed between 1998 and 2004
- Seven shallow (approx. 3-5 meters) monitoring wells installed in 1998 and re-installed in 2004; three deep (below 5 meters) monitoring wells installed in 1999
- Monitoring well sampling in 1998 and 2004 for groundwater chemical analysis.
- Excavation of hydrocarbon impacted soils in 2001
- Soil sampling and analysis in 1998, 1999 and 2004
- Installation of subsurface tile drain system and application of calcium amendments in 2003

## 2.2 Summary of Previous and On-Going Research Projects

Research done by the University of Calgary on the site began in the mid 2000's with multiple near surface geophysical surveys being conducted (Electrical Resistivity Tomography (ERT), EM and push tool electrical conductivity (EC)). Multiple ERT surveys were run in two separate locations on the property (south and western edge), both of which were used to characterize and monitor the depth of the salt impacted soil over time. Additional site wide EM and push tool electrical conductivity surveys were conducted to determine the spatial extent of the salt impacted soil as shown in Figure 2.2. Numerical models were developed by Smith (2008) to estimate the time required to remove salt from the soils under natural climatic conditions and to determine what effect the tile drain spacing had on salt flushing. The models developed were also used to investigate the role density dependent flow had on salt transport in variably saturated conditions. Results from the simulations suggested that surface irrigation over the tile drain area could enhance the salt production in the tile drains. Additional experiments were conducted in 2008 using tension infiltrometers and Guelph permeameters to examine the variance of surface hydraulic conductivities under varying soil conditions (tilled, irrigated, natural).

A s econd pha se of t he monitoring pr ogram investigating th e e ffectiveness o f subsurface tile drains for remediation of salt affected, low permeability soils was initiated in 2008. The 2008 p rogram bui lt on t he previous monitoring w ork with the completion of several push tool conductivity surveys performed throughout the full site coupled with soil core analysis. S ix additional full site EM surveys were completed in 2010 that were used t o de termine i f m easureable c hanges ha ve been obs erved i n t he s alt di stribution compared to previous surveys and to ultimately determine the total mass of salt residing on site.

Furthermore, an experimental irrigation test plot and control plot were constructed in 2008 to ex amine w hether surface i rrigation could enhance s alt flushing from th e s oil into the tile drains. The experimental and control plots were constructed in areas of high salinity ( Figure 2.2) s o that gr eater d ecreases i n s oil s alinity c ould b e o bserved. T he experimental plot (Plot A) w as o utfitted w ith drip line irrigation s ystem and monitoring equipment, while the control plot (Plot B) was left without irrigation. In the experiment, irrigation w ater w as r egularly applied t o t he s urface of t he pl ot a long w ith r outine measurements of tile drain effluent chemistry (chloride). Additional monitoring focused on c hanges i n s oil geochemistry a nd di fferences observed i n t he E RT a nd EM s urveys, which c ould be us ed t o m easure and m onitor t he pe rformance o f t he t ile dr ains. Observed decreases in the soil's electrical conductivity would indicate a removal of salts. ERT surveys were completed over the experimental plot (Plot A) throughout the course

of t he research p rogram t o t rack t he changes i n s oil el ectrical co nductivity o ver an d between the tile drains.

Increasing ev idence ha s s hown t he i nfluence m acropores ha ve on pr eferential flow a nd t ransport i n s oils ( Bouma, 1981; B even a nd G ermann, 1982; J arvis, 2007 ). Initial r esults f rom t he 2008 i rrigation s eason, te nsion in filtrometer me asurements a nd analysis o f s oil co res indicated that p referential flow p athways were affecting th e flow and transport o f water a nd s alts in the soil on s ite. Analysis of s oil c ores recovered on site and observations made during excavation of the tile drains confirmed the presence of macropores ( fractures a nd r oot hol es) ( Figure 2.3). To te st th e influence macropores have on s olute flow a nd t ransport, t wo t racer e xperiments w ere conducted i n 2009 a nd 2010. R esults f rom t he t racer ex periments w ere t hen u sed t o co nstruct a cal ibrated numerical flow and transport m odel that could help quantify the role m acroporosity h as on tracer transport to the tile dr ains. This m odel c ould then be a dapted in the future t o examine other salt flushing issues (e.g., soil swelling, geochemical alterations) and assess alternative remedial design options.

Full Site Area

**Figure 2.1.  Airphoto of site.**
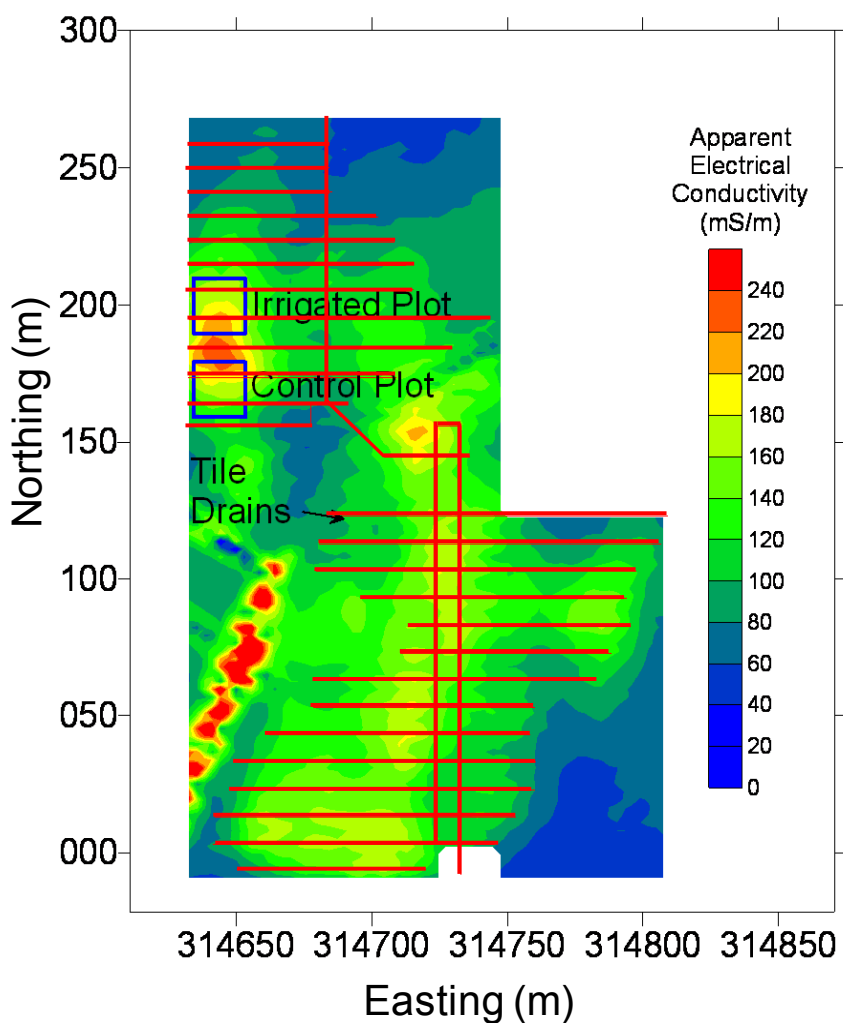
**Figure 2.2. Site map showing spatial distribution of apparent electrical conductivity with the installed tile drain layout (red lines running west – east). High levels of electrical conductivity (warm colours) correspond to high levels of in-situ salt. Distribution of installed tile drains focus primarily in high electrical conductivity regions.**
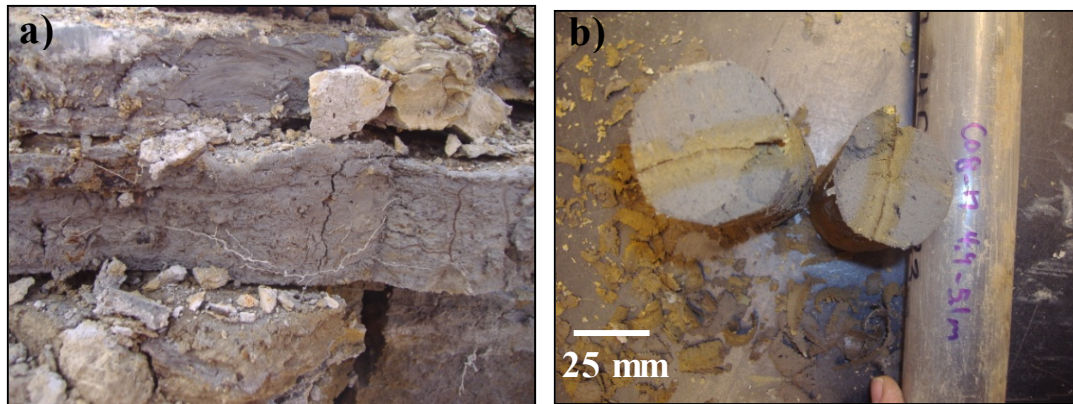
**Figure 2.3.  Photos of a) fractures and roots observed during site excavation and b) fractures observed in recovered soil cores.**

## CHAPTER THREE: LITERATURE REVIEW

### 3.1 Salt Affected Soils

In A lberta, a pproximately 1.6 millio n a cres o f land suffers f rom complications associated w ith hi gh salt concentrations resulting in a reduced c rop yield of up t o 2 5% (Alberta A griculture, 19 91). Salt af fected s oils ar e characterized b y higher a mounts of soluble salts that can cause negative impacts on crop yields (Abrol et al., 1988). They can be caused b y the us e of s aline g roundwater f or i rrigation, excessive ir rigation in a rid regions, poor subsurface drainage, or result from industrial spills releasing large volumes of brine over the land surface (Abrol et al., 1988). There are two main classifications for salt a ffected s oils: s aline a nd s odic. Common c haracteristics f or s aline s oils in clude having a pH less than 8.2 in the saturated paste test (Abrol et al., 1988) and an electrical conductivity greater t han 4 dS /m a t 25°C. Saline s oils tend t o e xhibit w hite p atches o f precipitated s alts, es pecially i n el evated areas w here ev aporation o ccurs ( Tanji, 1 990). Generally, the permeability of the soil is not impacted by the increased salinity. Common characteristics of s odic s oils i nclude ha ving a pH g reater t han 8.2 i n the s aturated pa ste test, i ncreased l evels of sodium relative to th e levels of calcium and magnesium, and at times a n e lectrical conductivity greater t han 4 dS /m a t 25°C ( Abrol e t a l., 1988) . Visually, s odic s oils w ill di splay a br own c rust and h ave a lo wer in filtration c apacity caused by the swelling and dispersion of clay minerals due to an increased proportion of sodium ions (Tanji, 1990). The increase in sodium ions causes the clay particles to repel each other, decreasing the pore size of the clay, which in turn decreases the permeability of the soil (Appelo and Postma, 2005).

Remediation strategies used to treat salt affected soils include the addition of a soil amendment (e.g., gypsum), scraping of precipitated surface salts, planting salt tolerant crops, physical excavation and removal of the affected soils, or leaching the salts from the soil with the aid of subsurface drains (Abrol et al., 1988). The addition of gypsum ($CaSO_4 \cdot 2H_2O$) acts to replace sodium on cation exchange sites by supplying sufficient quantities of the divalent calcium ion (Tanji, 1990). The sodium – calcium ion substitution aids in decreasing the clay particle repulsion, preventing clay mineral dispersion and the reduction of soil permeability. Another strategy used is the leaching of salts with subsurface drains. This allows for salts to pass through the soil column and into the drains, removing the salts from the affected area. This technique can potentially lower the soil salinity of the affected area quicker if used in conjunction with surface irrigation when compared to soil flushing under natural climatic conditions although soil sodicity issues may arise as a result of poor irrigation water quality (high TDS).

## 3.2 Tile Drains

Subsurface tile drains can be a useful remediation method for the reclamation of contaminated sites. Traditionally, tile drains have been used in agricultural practice as a method for regulating the water table and improving subsurface drainage. In contaminated sites, they act as a tool to enhance the flushing and removal of harmful solutes from the affected area. The efficiency of tile drains in site remediation is dependent on tile drain spacing, magnitude and frequency of irrigation, time of initial irrigation after solute application, soil structure, and contaminant mobility (Balasubramanian et al., 1973; Kladivko et al., 2004). It is thought that tile drain fields

with a close spacing will naturally collect more solute/contaminant than a tile drain field with wider tile drain spacing. Furthermore, managing the irrigation rates and volumes applied can be important to ensure the right soil moisture conditions exist for leaching of potential contaminants. A study performed by Balasubramanian et al. (1973) found that nitrate transport rates to tile drains were influenced by the timing of intermittent irrigation (surface flooding) events following application of nitrate to the ground surface. The study suggested that the management of irrigation rates and fertilizer application can help reduce nitrate losses to subsurface drains. Allowing the nitrate time to migrate from the more permeable macropores into the less permeable matrix after aplication reduced nitrate losses in comparison to quickly irrigating after nitrate application. This has implications in salt flushing scenarios in which irrigations using large volumes of water shortly after salt application should enhance the salt removal to subsurface drains by not allowing the salt to migrate from the macropores into the less permeable matrix.

Several other issues can be encountered with the use of subsurface drains that can negatively impact the surrounding environment. Drain outlets generally discharge into surface waters, which can have an adverse impact on surface water quality. Levels of nitrate and fecal bacteria exceeding drinking water guidelines have been measured at tile drain discharge outlets in studies completed by Jaynes et al. (2001) and Jamieson et al. (2002). This is not likely a major issue for remediation schemes as the tile drain effluent in generally not discharged into surface water bodies, but is instead treated or disposed of after collection.

Low permeability soils such as the glacial sediments found throughout Alberta, can increase the time required for solute removal using tile drains. The low permeability soils decrease the speed at which fluids and solutes can travel through the soil, increasing the required remediation time. The effectiveness of tile drains as a remediation strategy for reclaiming saline-sodic soils in Southern Alberta was investigated by Van Schaik and Milne (1961). The researchers found that tiles installed at a relatively shallow depth (0.76 meters) in low permeability glacial tills were able to successfully flush the soils after 3 years while applying a total of 1.8 meters of irrigation water (roughly 6 pore volumes). A decrease in salt concentration was also observed beneath the drains suggesting that the tile drains were able to flush soils underlying the drains. Another study that focused on tile drain usage in low permeability glacial sediments in Alberta found that a decrease in salinity was observed only within the top 30 cm of the soil profile after 2 years of irrigation (Paterson and Brook Harker, 1980). Both of these studies indicate that although remediation times may be lengthy and variable due to the low permeability soils, tile drains can be a useful technique for flushing salts.

## 3.3 Variably Saturated Flow in Macroporous Soils

Flow and transport in variably saturated conditions is a function of a soil's ability to retain and drain water due to the dependence between hydraulic conductivity ($K$) and pressure head (h) (Freeze and Cherry, 1979). In conditions of h < 0, the soils will be under tension, causing preferential draining of the larger pores, reducing the effective hydraulic conductivity of the soil. As h << 0 and the tension placed on the soil increases, the remaining smaller saturated pores begin to drain further reducing the soil's

hydraulic c onductivity. T he c omplex na ture of t he r elationship be tween h ydraulic conductivity, pr essure he ad a nd m oisture content l eads t o nonl inear flow equations t hat are not subject to easy solutions (Fetter, 2001).

Furthermore, t he pr esence of m acropores a dds t o t he c omplexity of variably saturated f low a nd transport. The t erm m acroporosity can b e given t o an y l arge continuous soil por es that i nfluence t he flow a nd t ransport of fluids a nd s olutes ( Beven and Germann, 1982). Although there is much debate among researchers on how large the opening m ust be t o be deemed a " macropore" ( Bouma, 1981), m ost c an a gree on t he influence macropores have on pr eferential flow and transport in the subsurface (Bouma, 1981; Beven and Germann, 1982; Jarvis, 2007). These preferential flow paths are most often generated in t he s oil due t o de siccation or pr evious s tress, r oot hol es, a nimal burrows or natural soil pipes (Beven and Germann, 1982). Under unsaturated conditions, fluid f low i n macropores is initiated or "turned on" onc e t he s oil ha s r eached n ear saturation and the large radius macropores are able to fill up and transmit water (Weiler and N aef, 2 003). R apid t ransport o f s olutes i s generally a ch aracteristic behaviour of macropores. Macropores have been found to decrease the breakthrough time of solutes to tile dr ains, due t o t hese preferential flow p athways a cting as a "short cut" t o the dr ains (Kung et al., 2000; Kohne and Gerke, 2005; Stone and Wilson, 2006). T he majority of flow in the soil is channelled through the macropores, while only a small fraction of the soil matrix is exposed to any infiltrating water. This can be troublesome when attempting to completely flush a solute (i.e. salt) from the soil matrix as only portions of soil matrix will be exposed to infiltrating fresh water.

Understanding t he d ynamics be tween t he m atrix a nd m acropore dom ains i s important when studying the influence macropores have in a low permeability soil. Fluid and solute transfer between the matrix and macropore region is a highly complex process that can depend on va riables such as macropore geometry, the hydraulic conductivity of the matrix a nd m acropore r egions, s oil m oisture c ontent a nd the s olute c oncentrations present in the matrix and macropore domains (Gerke and van Genuchten, 1996).

## 3.4 Vadose Zone Hydrologic Tracers

The a bility t o i dentify t he i nfluence s oil m acropores ha ve on flow a nd solute transport is commonly accomplished with the use of conservative tracers. Monitoring the breakthrough to subsurface monitoring locations allows physical measurements of travel time and velocities to be made. A dditionally, studying the spatial distribution of tracers within th e s oil c olumn helps unde rstand t he i nfluence he terogeneities have on flow. Multiple natural tracers exist in the form of isotopes ($^{3}$H, $^{14}$C, $^{36}$Cl, $^{18}$O), all of which can help calculate r echarge, infiltration r ates and tr ansport time s o f groundwater (Allison et al., 1994). The anions chloride and bromide are commonly used as conservative tracers because t hey do not de grade, r eact or adsorb in the s ubsurface, are co st efficient, and easily d etectable at l ow co ncentrations. O ne p otential s etback i s b oth ch loride an d bromide a re not e ffective t racers i n a reas w ith hi gh pr e-existing c oncentrations (i.e. salt affected soils).

Recently, the use of benzoic acids as groundwater tracers has become increasingly popular. Multiple studies have examined whether benzoic acids could be used as suitable non-reactive t racers i n t he s ubsurface. T hese studies have s hown t hat t wo s pecific benzoic aci ds, 2,6-Difluorobenzoic acid ( DFBA) a nd P entafluorobenzoic a cid (PFBA), act similar to br omide i n that t hey h ave t he s ame m easureable b reakthrough t imes a nd show no s igns of s orption (Bowman, 1984 a; B owman, 1984b; J aynes, 1994) . Commonly, DFBA and PFBA are analyzed using High Precision Liquid Chromatography (HPLC), which is a ble to s imultaneously d etect b oth a cids a t r elatively lo w concentrations an d o ffers a r elatively precise and a ccurate m easurement t echnique (Bowman, 1884a; M cCarthy et al., 2000; D ahan a nd R onen, 2001) . Both D FBA and PFBA ha ve be en us ed i n several f ield s tudies a s c onservative gr oundwater t racers a nd have b een t ypically a pplied on t he s oil s urface, or i njected a t de pth (Bowman a nd Gibbens, 1992; Jaynes, 1994; Kung et al., 2000). A series of laboratory column tests, soil batch e xperiments, a quifer a nd va dose t ests w ere pe rformed b y Bowman and G ibbens (1992) and found that both DFBA and PFBA showed no s igns of d egradation, sorption and e ach recorded br eakthrough t imes s imilar t o t hat of br omide. O ther experiments performed by Kung et al. (2000), Dahan and Ronen (2001) and Johnson et al. (2003) all found t hat bot h D FBA and P FBA a cted s imilar t o br omide a nd c hloride unde r f ield conditions in that they showed no d egradation or sorption. An experiment completed by Jaynes ( 1994) di d not o btain f ull r ecovery of D FBA i n s oils s aturated with a know n concentration of D FBA ove r a 60 d ay pe riod. T he l ab ba tch t est m easured a t otal decrease i n D FBA concentration of 0.6 m g/L from a n i nitial c oncentration of 2 m g/L over the s tudy p eriod. No m easureable d ecrease i n c oncentration w as noted f or P FBA

under the same conditions.  It was noted that the decrease in mass in not necessarily due to the degradation of the benzoic acid but could be due to a decrease in the recovery of DFBA from the solution over time.  Another study by Hu and Moran (2005) supported the findings of Jaynes (1994) in that the transport of the benzoic acid tracers could be retarded by changes in the pH of the soil, presence of organic matter, iron oxide content and clay mineralogy.

## 3.5 Variably Saturated Flow and Transport Modeling

When numerically defining flow and transport in variably saturated media, a mathematical relationship termed the soil water characteristic model must be developed to describe the dependence among hydraulic conductivity, water content, and the applied pressure head.  One method for describing the unsaturated hydraulic properties for an individual soil is the van Genuchten model (van Genuchten, 1980).  The relation between pressure head (h) and soil water content (Equation 3.1) or hydraulic conductivity (Equation 3.2) is as follows:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{\left[1 + |\alpha h|^n\right]^m} \qquad (3.1)$$

$$K(h) = \frac{\left\{1 - (\alpha h)^{n-1}\left[1 + (\alpha h)^n\right]^{-m}\right\}^2}{\left[1 + (\alpha h)^n\right]^{\frac{m}{2}}} \qquad (3.2)$$

where $\theta_r$ is the residual water content ($L^3/L^3$), $\theta_s$ is saturated water content ($L^3/L^3$), $\alpha$ (1/L) is the measure of the inverse of the air entry pressure, n (unitless) is an empirical parameter describing the pore-size distribution and $m = 1 - \frac{1}{n}$ (Wise et al., 1994).  The

van Genuchten – Mualem model predicts how a specific soil's water content reacts to changing negative pressures (or tensions) allowing for unsaturated hydraulic conductivities to be calculated for a specific soil tension or water content.

The use of numerical flow and transport models has become an important part of hydrogeological studies due to their ability to provide useful information on how a subsurface flow system operates, and how that system will behave when exposed to varying forcing factors (Fetter, 2001). Simulating fluid flow and solute transport in a variably saturated system can be accomplished using Richards' equation for a single matrix domain. When soil heterogeneities in the form of macropores begin to influence flow and transport, a single domain model is no longer useful in representing the physical processes occurring. Macropores are often represented in numerical simulations either discretely or using dual continuum formulations. Modeling macropores discretely requires that each macropore be represented by a group of model elements with a specific geometry, hydraulic conductivity and storage capacity. To accurately represent such a system, a large amount of information on the geometric distribution and connectivity of the macropores is needed. Using the software program HydroGeoSphere, this is accomplished numerically by representing discrete fractures with 2-dimensional planes of connected nodes that form part of a 3 dimensional grid. The matrix and macropore domains are then coupled by their collocation (Weatherill et al., 2008). Generally, large numbers of nodes are needed to simulate flow through discrete macropores. Alternatively, the dual continuum method represents the matrix and macropores as two separate, but overlapping domains. This allows for flow to occur in both domains with

fluid and solute transfer occurring between them. This typically decreases the number of elements needed because the full spatial distribution of macropores does not need to be defined, thus reducing simulation times.

There are two main types of dual continuum models currently in use: dual porosity and dual permeability models. The dual porosity model assumes flow and solute transport occurs only through the macropores, making fluid in the matrix immobile while still allowing fluid and solute transfer between the matrix and fracture domains (Simunek et al., 2003) (Figure 3.1a). Mass exchange between the two domains is determined by a combination of the hydraulic head, soil moisture or concentration gradients and varying mass exchange parameters (Gerke and van Genuchten, 1993a; Jarvis, 1995). Commonly the dual porosity model requires fewer input parameters when compared to the dual permeability model, and is generally more stable numerically and requires less time to generate a solution. Alternatively, the dual permeability model allows fluid and solute flow in both matrix and fracture domains, which are coupled to allow mass transfer between domains (Simunek et al., 2003) (Figure 3.1b). Numerically, flow within the domains is described using Richards' equation for both the matrix and macropores. Transfer between each domain is accomplished with the use of a coupling term. Solute transport in each domain is determined with the use of the advection-dispersion equation. Similar to fluid flow, solute mass transfer between domains is accomplished with the use of a coupling term which accounts for solute transfer via diffusion and advection.

**a) Dual Porosity Model**

Matrix Domain    Macropore Domain

**Water**

No Flow          Flow

*Mass Exchange*

**Solute**

No Transport     Transport

*Mass Exchange*
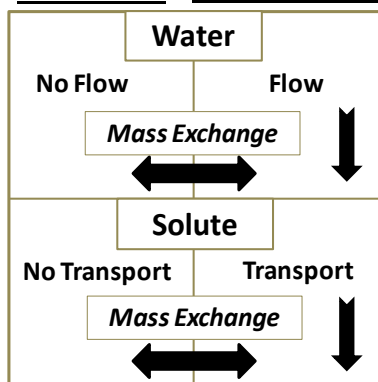
**b) Dual Permeability Model**

Matrix Domain    Macropore Domain

**Water**

Flow             Flow

*Mass Exchange*

**Solute**

Transport        Transport

*Mass Exchange*
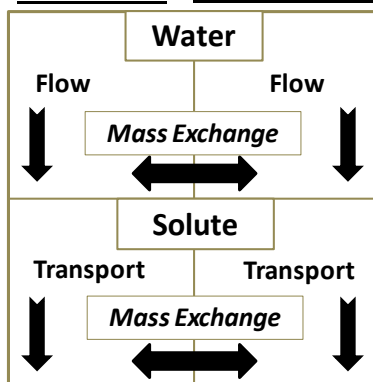
**Figure 3.1. Schematic depicting a) flow and solute transport in a dual porosity domain and b) flow and solute transport in a dual permeability domain. Modified from Simunek and van Genuchten, 2008.**

## CHAPTER FOUR: METHODS AND MATERIALS

### 4.1 Physiographic Setting

#### *4.1.1 Regional Setting and Climate*

The research site is located approximately 10 km southwest of Devon, Alberta at XX-XX-50-26 W4M on an abandoned oil and gas satellite. Located in the arid region of central Alberta, th e n earby to wn o f C almar (approximately 2 k m s outh) h istorically receives 5 21 m m o f an nual p recipitation an d reaches an nual average maximum an d minimum temperatures of 9.3°C and -3.5°C, respectively (Environment Canada, 2011). Located w ithin t he P arkland N atural E co-region, t opography can b e c haracterized as gently u ndulating w ith n o s ignificant to pographic r elief ( Natural R egions C ommittee, 2006).

#### *4.1.2 Lithology*

The r egion i s l ocated e ast of t he front ranges o f t he C anadian R ockies a nd h as been heavily influenced lithologically by previous glaciations. Prior to the glaciations the topography was characterized by broad north-east to southeast trending valleys (Mossop and Shetsen, 1994). R egionally, glaciations occurred at least five times with the earliest likely 1.8 million years ago (Mossop and Shetsen, 1994). Each glacial advance deposited high l evels of glacial a nd non -glacial s ediments in l akes a nd de pressions (Mossop a nd Shetsen, 1994) . R egionally, t he s urficial s ediments r est upon t he t op of t he U pper Horseshoe C anyon formation. T hese s urficial s ediments c an r each thicknesses of up t o 300 m in some locations. Locally, the top of the Upper Horseshoe Canyon formation is located 20 m below ground surface (Mossop and Shetsen, 1994).

Analysis of soil cores show that the site is underlain by a layer of top soil roughly 0.20 m thick, followed by a low permeability glaciolacustrine silt layer with a thickness of 2.2 m extending to a depth of 2.4 m below ground surface. Below the glaciolacustrine silt unit exists a fractured dense glacial till unit extending below 7.0 m that is interrupted by two fine to medium sand units at depths of 4.0 m and 6.0 m with thicknesses of approximately 0.5 m (Figure 4.1).

*4.1.3 Soil Properties*

Particle size distribution, dry bulk density, porosity and cation exchange capacity were analyzed for the top soil, glaciolacustrine, glacial till and the B series sand unit. Particle size distribution for the glaciolacustrine and glacial till units were measured using the Mastersizer 2000 (Malvern Instruments). Particle size distribution of the B series sand unit was completed by sieve analysis. Particle size classifications for each material were taken from The Canadian System of Soil Classification (Haynes, 2005). Cation exchange capacity of the glaciolacustrine and glacial till units was calculated using the procedure found in Amrhein and Suarez (1990). A summary of the soil properties can be found in Table 6.1

**4.2 Plot Construction and Monitoring Equipment**

In 2003, site wide subsurface tile drains were installed 2.1 meters below ground surface at 10 m spacings in areas shown to be highly affected by salts. Each tile drain was originally installed resting on top of a 1.0 meter wide by 0.35 meter thick

gravel pack. All tile drains were installed by excavating a trench causing a large zone of disturbed s oil a bove t he t ile dr ains ( Figure 4. 1). D imensions of t he t rench w ere constructed at a 1:1 ratio, meaning the depth of the trench corresponds to the width of the trench m easuring f rom the c enter out t o t he e dge. P revious m odeling c ompleted b y Smith (2008) suggested that s urface i rrigation c ould e nhance t he flushing of s alts from the s oil an d d ecrease the time r equired for remediation. In or der to t est t his, t wo pl ots were constructed on t he w estern edge of t he pr operty i n a l ocation w ith t he hi ghest measured e lectrical conductivity (Figure 2.2), w ith each pl ot constructed directly over a pair of tile drains. The experimental plot (Plot A) was constructed with surface irrigation drip lines while the control plot (Plot B) was constructed without drip lines. Throughout the c ourse of t he pr ogram, bot h pl ots w ere m onitored ( soil c ore s alinity, pus h t ool conductivity, ERT surveys) for changes in soil salinity. Furthermore, tile drains beneath the e xperimental p lot w ere d iverted in to a s ump, w hich a llowed mo nitoring o f th e tile drain effluent and discharge rates.

*4.2.1 Irrigation Plot (Plot A), Tile Drain and Sump Construction*

Construction of Plot A and B began in 2008. Both 20 m × 20 m plots were deep tilled, levelled, and surrounded by a compacted soil berm designed to limit any runoff or runon during i rrigation and pr ecipitation e vents (Figure 4.2). T he focus of t his study was Plot A, where irrigation was used to enhance salt leaching. To enable monitoring of flow and water quality in the tiles, the two tile drains (North and South) beneath Plot A were isolated from the surrounding tile drainage system. In 2009, a 3.5 m deep by 1.5 m diameter s ump w as in stalled a pproximately 1 5 meters e ast o f P lot A . Both tile d rain

discharge outlets were directed into the sump to allow for effluent monitoring (Figure 4.3). Discharge rates were monitored using tipping buckets (TB1L, Hydrological Services Pty Ltd) calibrated to 0.73 L/tip that allowed for a maximum flow rate of 25 L/min. Regular sampling every 3 – 8 hrs was conducted using ISCO (model 6712) automated samplers.

A meteorological station (Figure 4.2) located at the center of the plot contained a data logger (CR1000, Campbell Scientific) that recorded net radiation (NRLITE2, Campbell Scientific), surface temperature (SI-111, Campbell Scientific), and soil heat flux (HFT3, Campbell Scientific). The data logger was programmed to record measurements at 5 second intervals while recording the average value every 20 minutes. A second weather station (WatchDog Model 2900ET, Spectrum Technologies) was located at the south end of the site and was used to monitor precipitation, relative humidity, wind speed and direction, and air temperature. Measurements were taken using built in measurement devices recording average readings at 15 minute intervals.

### 4.2.2 Monitoring Wells

Three series (A, B, C) of monitoring wells were installed throughout the course of the research program (Figure 4.1). The A series wells have been installed to a depth of 2.0 – 2.5 meters below ground surface, in the glaciolacustrine sediments. These wells were installed to target the unit most affected by the salt. Additionally, the A series wells were completed shallow enough to enable accurate water table monitoring. The B series wells were installed at approximately 4.5 meters below ground surface and were

completed i n t he B s eries s and unit w hile th e C s eries w ells w ere in stalled a t approximately 6 m eters below ground surface in the C series sand unit. The wells were used to monitor water levels and solute concentrations (salt and tracers) in each unit.

In 2009 , twelve PVC 2.54 c m di ameter A s eries monitoring w ells (Figure 4.4) were in stalled manually using a s oil co re auger and s creened o ver a 0 .5 m eter i nterval with a 1 .0 meter s and p ack. Bentonite ch ips w ere placed i n t he bor ehole a nnulus from the top of the sand pack up to ground surface to seal the remaining hole. In 2010, 14 new PVC 2.54 a nd 5.08 c m A , B a nd C monitoring wells w ere in stalled (Figure 4.4) using either 4.45, 10.21 or 15.24 c m s olid s tem a uger. W ells w ere in stalled with a s creen length of 0.5 meters and a sand pack of 1 .0 meter. Similar to the 2009 w ells, bentonite chips were placed in the borehole above the sand pack and hydrated to seal the borehole annulus. Well logs of 11 of the monitoring wells can be found in Appendix E.

Hydraulic he ad m easurements i n t he m onitoring w ells w ere r ecorded us ing pressure t ransducers ( Level T roll 500 & 700, Level Logger G old). T he t ransducers recorded the water levels in the wells to the nearest millimetre every 20 minutes, starting in 2009 a nd c ontinuing unt il t he e nd of t he 201 0 s eason. T he Level T roll t ransducers were ve nted; t herefore no ba rometric pr essure correction w as ne eded. Level Logger Gold transducers were not vented; therefore a s eparate transducer was used to record the barometric pressure, allowing for corrections to be made during data processing. Manual water level measurements were also taken using a water level tape in order to ensure the pressure transducer data quality.

*4.2.3 Suction Lysimeter Installation*

Ten stainless steel single chamber suction lysimeters (Soil Measurement Systems Model SW-071) were installed in two locations on the site at the beginning of the 2010 field season, in the centre of Plot A and directly above the north tile drain. The lysimeters were used to sample in situ pore water at five sampling depths. Five lysimeters were installed above the north tile drain with sampling ports located at depths of 0.15, 0.30, 0.56, 0.72 and 1.46 m below ground surface. The remaining five lysimeters were installed at the center of the plot with sample ports located at 0.15, 0.30, 0.73, 0.88 and 1.38 m below ground surface. Lysimeters were installed using a 10.16 cm diameter solid stem auger for bore holes deeper than 30 cm and by a 5.08 cm diameter hand auger for holes shallower than 30 cm. Holes that were drilled with the 10.16 cm auger were stopped at a depth 20 cm shallower than the final borehole depth. The remaining portion of the borehole was dug using the smaller diameter hang auger to improve the contact between the lysimeter and the surrounding soil. Boreholes deeper than 30 cm were augered vertically. The shallower 15 and 30 cm boreholes were augered at a 30° angle from the ground surface to minimize potential for short circuiting from the ground surface directly to the sampling port. Once each hole was drilled, a slurry of water and silica flour was mixed and poured into the hole and the lysimeter was inserted with the remaining slurry poured into the hole until a tight seal was formed. Lysimeters were attached to a 2.54 cm PVC pipe that housed two plastic tubes, which extended to ground surface for sampler evacuation/pressurization and sample collection. Once the lysimeter was in place, a 10.16 cm PVC casing was inserted into the hole to a depth approximately

10 cm above the sampling port of the lysimeter (Figure 4.5). The PVC casing was capped and bentonite chips were used to seal the space between the borehole walls and casing in order to ensure no surface water infiltration occurred into the borehole.

**4.3 Plot A Irrigation**

Routine Plot A irrigation events occurred in summer and fall of 2009 and 2010. The purpose of the irrigation was to examine whether surface applied irrigation could enhance salt flushing. The plot was irrigated using 13.6 mm diameter polyethylene drip lines supplied by Rain Bird. Drip lines ran east – west and the irrigation lines were spaced 1.2 meters apart from each other covering Plot A (Figure 4.6). The irrigation lines were fed from a pump that was connected to a 10,000 L irrigation tank. Irrigation was applied manually using a gas pump for the early part of the 2009 field season. The remainder of the irrigation program used an automated system powered by solar panels. The system was programmed to apply a set volume of water beginning at a preset time. Irrigation frequency varied based on the amount of surface ponding observed and the amount precipitation received during the previous days. Irrigation events typically occurred every 1-2 days or at times longer depending on precipitation.

*4.3.1 2009 Irrigation Season*

Irrigation in 2009 began on July 9 and continued until October 1 with a cumulative irrigated water depth of 612 mm and 56 mm of precipitation making the cumulative water applied 668 mm (Appendix A). During irrigation of the plot it was noted water would preferentially pond in the northeast corner of the plot. In an attempt to

prevent this, irrigation volumes were applied to the plot in order to minimize the amount of ponding that occurred. Once any observable amount of ponded water began to form, irrigation was shut off. Irrigation would resume either the following day or the next scheduled irrigation session.

*4.3.2 2010 Irrigation Season*

Prior to the 2010 irrigation season, plot A was levelled by adding top soil to the surface in order to avoid surface ponding that was observed during the 2009 season. Irrigation of the plot began on May 2 and ended on October 5. A total of 385 mm of irrigation water was applied to the plot over 157 days. The total amount of precipitation that fell on the plot in the same time period was 293 mm making the cumulative amount of water applied to the plot 678 mm (Appendix A).

**4.4 Tracer Application**

In order to characterize the influence macroporosity had on salt flushing to subsurface tile drains, two conservative benzoic acid tracers were used in experiments in plot A. The first tracer experiment occurred in 2009 and was designed to study to how solutes move throughout the subsurface in soils containing macropores. Breakthrough of the tracer into the tile drains was monitored in addition to monitoring the spatial distribution of the tracer in the soil profile at the end of the 2009 and 2010 field seasons. The second tracer experiment occurred in 2010 and was designed to help determine the hydraulic connection between the different lithological units present on site and aid in

understanding t he m acropore i nfluence  above  the t iles i n t he l ower  portion of  t he

glaciolacustrine unit.

*4.4.1 Benzoic Acid Tracer Descriptions*

The c onservative t racer us ed f or t he 2009 s  urface a pplication w as 2,6  –

Difluorobenzoic a cid ( DFBA) ( 98% pur ity,  Oakwood P roducts, W est C olumbia, S outh

Carolina).  P entafluorobenzoic a cid ( PFBA) ( 99% pur ity,  Oakwood  Products, W est

Columbia, South Carolina) was used as a  groundwater tracer for the second experiment

that took place in 2010.    A pplication of D FBA a nd P FBA a s conservative t racers i n

hydrogeological investigations initially began in the early 1980's (Bowman, 1984a) and

has become a p opular alternative to traditional groundwater tracers (bromide, chloride).

The two tracers are generally conservative in the subsurface (Bowman, 1984a), have low

measureable de tection l imits ( Bowman,  1984b ), and c an be  de tected w ithout a nalytical

interference u sing  HPLC ( Bowman a nd G ibbens, 1992;  K ung e t a l., 2000;  Dahan  and

Ronen, 2001).

*4.4.2 Tracer Applications*

4.4.2.1 DFBA Application

The surface a pplication of D FBA oc curred on A ugust 18 , 2009.   The pr ocedure

for the mixing and application of DFBA was adapted from previous studies (Kung et al.,

2000; Gish and Kung, 2007).    The dry DFBA powder was added to fresh irrigation water

and m ixed i n s mall b atches.  O nce t he D FBA w as co mpletely d issolved, pot assium

hydroxide (KOH) was added in small increments until the pH reached near neutral levels (6.5 – 7.5). In total, 4.5 kg of DFBA was added to 5200 L (13 mm equivalent depth) of water in the irrigation tank, which resulted in a DFBA solution with a concentration of 866 mg/L. Once all batches were added to the irrigation tank, the DFBA solution was then applied to the surface of the experimental plot via irrigation drip lines over a period of 1.5 hours. Sample collection from the tile drains to monitor DFBA breakthrough began immediately after DFBA application and continued for the remainder of the 2009 and 2010 field seasons.

## 4.4.2.2 PFBA Injection

Two PFBA injections occurred on July 20 and July 21, 2010. The first injection occurred July 20 and was located directly above the north tile at a depth of 1.72 m below ground. Two separate batches of PFBA were mixed prior to injection, both consisting of 10 L of deionized water mixed with 43 g each of PFBA making a solution of 4.3 g/L. Small portions of KOH were added to each mixture until a pH of approximately 7 was reached. The borehole previously used to house the 1.46 m lysimeter was used for the injection hole. The lysimeter was removed and purged of water prior to the PFBA injection. A total of 20 L of 4.3 g/L PFBA solution was injected over a one hour period. The injection was separated into two batches due to the length of time required for the acid to completely dissolve into solution. Monitoring the breakthrough of the PFBA into the north tile drain began immediately after the first injection.

Monitoring w ell M W09-13A wa s used as the l ocation of t he s econd i njection, which occurred on July 21. S imilar to the previous injection, two batches consisting of 43 g of PFBA each were mixed with 10 L of deionized water and KOH and the solution was injected into MW09-13A over a 2 hour time period. A pneumatic pressure slug (a device used to pressurize a well, forcing water out of t he well, into the formation) was required to inject th e full solution into the well due to th e relatively lo w permeability material surrounding the well screen. The breakthrough of the PFBA tracer in monitoring well M W09-13B w as o bserved b y s ampling imme diately a fter th e f irst in jection a nd continuing t o s ample a t e very 6 hour s f or t he ne xt 72 da ys.

## 4.5 Water Sampling

### 4.5.1 Tile Drain Effluent

Effluent samples from the tile drain were recovered via ISCO automated sampling devices. One sampler was dedicated to each of the north and south tile drains and was programmed to collect samples at regular time intervals between 3 and 8 hours. Samples were then transferred from the internal 1 L, plastic ISCO sampling bottles to clean 125 mL Nalgene sample bottles and placed into a cooler. ISCO sampling bottles were then rinsed with acetic acid followed by deionized water then returned back into the ISCO sampler. The ISCO was then reprogrammed to continue sampling. S amples w ere then placed i n a c ooler a nd t ransported ba ck t o t he U niversity o f C algary for an alysis. Electrical conductivity and temperature of each sample was measured in the lab.

*4.5.2 Monitoring Well Samples*

Monitoring well samples were collected at the beginning of every month (June – October) over a two day period using a peristaltic pump (Geotech, Geopump) connected to 5 mm diameter polyethylene sample tubing. Monitoring wells completed at 2 m (A series), and 6 m (C series) were purged dry the day prior to sample collection to ensure the sample collected was representative of the surrounding formation waters. B series monitoring wells (completed at 4.5 m) were completed in a slightly higher hydraulic conductivity unit; therefore, low flow sampling techniques were used (Puls and Barcelona, 1996). For low flow sampling the well was pumped at a low rate (to limit drawdown) while electrical conductivity, pH and temperature were monitored in a flow-through cell. Once the indicator parameters stabilized the sample was collected and placed into a clean 125 mL Nalgene sample bottle. Field parameters for all samples (electrical conductivity, pH and temperature) were recorded at the time of sample collection. Samples were placed in a cooler, transported back to the lab and stored in a refrigerator until analyzed.

*4.5.3 Suction Lysimeter Samples*

Lysimeter samples were collected monthly, five times (June – October) during the 2010 season. Sample collection required a two days to prepare and sample the lysimeters. On the first day, the lysimeters were purged dry and a suction of approximately 50 – 60 kPa was applied to each lysimeter by hand pump. After approximately a 24 hour period, samples were collected by releasing the applied suction and pumping the sample into a plastic flow through cell using a hand pump. Similar to

the monitoring w ells, f ield p arameters ( EC, p H an d t emperature) were r ecorded immediately after sample collection. Each sample was then placed in a clean, 125 mL Nalgene bottle and stored in a cooler until transported back to the university.

## 4.6 Soil Sampling

Soil samples were collected at the end of both the 2009 and 2010 field seasons to evaluate t he concentrations a nd s patial di stribution of s alt and t he DFBA t racer. Collection of soil samples was done by G & R Remediation with the use of a direct-push Geoprobe r ig while und er t he s upervision o f U niversity o f C algary p ersonnel. S oil samples for the 2009 season were collected November 2. Samples were collected along a N-S transect (Figure 4.7). F or the 2010 s eason, soil samples were collected October 20 through t o O ctober 22 a nd w ere c ollected f ollowing a grid pa ttern. S ample de pths for both sampling p rograms ranged from 1.5 − 7 m. A ll core samples were placed in clear plastic tubing, sealed at both ends and transported back to the University of Calgary for analysis.

## 4.7 Laboratory Analysis

### 4.7.1 Water Samples

Prior t o a nalysis, w ater samples w ere f iltered us ing 0.45 um s yringe f ilters a nd placed i n 2 m L glass vi als ( supplied b y A gilent T echnologies, C anada). Analysis of DFBA and PFBA was accomplished via ion exclusion chromatography. A 25 uL aliquot of each sample as injected onto a Transgenomic ICSep ORH-801 column (6.5 x 300 mm) then separated by isocratic elution using 0.01N $H_2SO_4$ mobile phase, with a flow rate of

0.8 mL/min and column temperature of 45°C. A UV detection wavelength of 210 nm was used for both DFBA and PFBA. Prior to sample analysis, a calibration was completed using three concentration standards (predetermined based on expected measured concentrations). To ensure accuracy, the concentration of the analyzed sample had to be within the range of the concentration standards (i.e. if concentration of sample = 5 mg/L, then concentration standards would be 1, 5 and 10 mg/L). If the measured concentration was out of the calibrated range (e.g., if concentration of sample = 20 mg/L and concentration standards were 1, 5 and 10 mg/L), the sample was retested using a new set of concentration standards. The analytical error using this method has been calculated to be 5%.

*4.7.2 Soil Samples*

Soil samples were brought back to the University of Calgary soil laboratory, removed from their tubes, trimmed, separated into 10 cm sections and air dried. Once air dried, samples were crushed using a mortar and pestle and sieved using a 2 mm mesh following the procedure of Bowman (1984b). A 15 g sample of the sieved material was placed in a 50 mL Greiner polypropylene centrifuge tube along with 30 mL of deionized water. Samples were vigorously agitated, placed on a shaker table for 20 minutes and left to sit overnight. The following day, samples were suction filtered through Whatman 0.45 micron filter paper and the resulting filtrate was then sent to the lab for DFBA and PFBA analysis using the same procedure described in Section 4.7.1.

The resultant concentrations recovered by the soil extractions were then used to calculate the DFBA mass still residing within the soil. This calculated mass helped determine the vertical and lateral DFBA distribution in and around the plot. DFBA mass calculations were done using the 2:1 extracted concentration analyzed using high precision liquid chromatography. The following equation outlines how the total DFBA mass was determined

$$M_t = C_{2:1} \times 2 \times \rho_b \times 1000 \times d \times a \qquad (4.1)$$

where $M_t$ (mg) is total mass calculated for the depth interval corresponding to the representative surface area (area each borehole represents on the surface), $C_{2:1}$ (mg/L) is the 2:1 concentration result determined from the lab analysis, $\rho_b$ (g/cm$^3$) is the dry bulk density of the soil sample, $d$ (m) is the depth interval the soil sample represents and $a$ (m$^2$) is the surface area each specific borehole represents.

### 4.7.3 QA/QC

Throughout the duration of the field sampling programs, QA/QC samples were collected on a regular basis. Split samples were used to test for the precision of the tracer analysis, sample duplicates were used to test the sampling procedure/sampling bias, equipment/sample/trip blanks were used to ensure no sample cross contamination throughout the analysis and spiked samples were run through the lab to test the accuracy and precision of the lab equipment and sampling procedure. These procedures were performed for both the water and soil analysis. Results from the QA/QC sampling are found in Appendix D.

*4.7.4 Spiked Experimental Samples*

To be confident that the extraction procedure recovered 100% of the acid tracers, several spiked samples with known initial concentrations were analyzed. Soil was crushed and 50 g of sample was placed in 125 mL Nalgene bottles after which 40 mL of 100 mg/L DFBA solution was added. Once the samples were air dried, they were crushed again and processed following the same procedure as described above. Results showed that the tracer mass recovered from the extraction procedures was less than the initial applied tracer mass. Additional extractions were done using calcium chloride, methanol and sodium hexametaphosphate solution in place of deionized water to test whether they would improve the recovery of the DFBA soil extraction. Test results from the spiked samples showed that deionized water provided the highest recovery rate with an average of 67.5%. Results from this experiment can be found in Appendix B.

Results from the spike samples showed on average that 32.5% of the DFBA mass remains on the soil after the extraction procedure using deionized water (Appendix B). Using this information, a corrected tracer recovery was calculated by adding 32.5% to the lab analyzed 2:1 extract concentrations. The soil tracer extract values reported in the thesis represent the corrected values.

*4.7.5 Soil Batch Tests*

Soil batch tests were performed on four soils found at varying depths on the site. Although both PFBA and DFBA have generally been found to show limited retardation

or degradation (Bowman, 1984a; Bowman and Gibbens, 1992; Jaynes, 1994), the batch tests were performed to assess this for soils found on the experimental site. Soil samples were prepared in the same manner as the previous soil extractions (Sec. 4.7.2). Once the soils were crushed and sieved, 15 g of soil was placed in a 50 mL Greiner polypropylene centrifuge tube with 30 mL of DFBA or PFBA solution (ranging from 1 mg/L − 200 mg/L in concentration). The samples were vigorously agitated, placed on a shaker table for 20 minutes and let sit over night. The following day each sample was suction filtered through Whatman 0.45 micron filter paper and the resulting filtrate was analyzed. In total 102 samples were run and results can be found in Appendix B.

A second, small-scale experiment was created to test whether DFBA degraded over time as mentioned in Jaynes (1994). Two 50 g soil samples were ground and each placed in 1 L Nalgene bottles with 100 mL of 100 mg/L DFBA solution. The soil test solutions were placed in a refrigerator and samples were subsequently collected and analyzed for DFBA concentrations over a two month period. Water samples were taken from the prepared solutions without agitation, filtered through a 0.45 um filter and analysed using the method discussed in Section 4.7.1. Samples were collected in duplicate roughly every 15 days. Results indicated no measurable degradation occurred over the experiment and are shown in Appendix B. This is consistent with previous studies that have reported little to no mass loss of and DFBA over time in field soils (Bowman, 1984; Bowman and Gibbens, 1992).

**4.8 Hydraulic Parameters**

*4.8.1 Hydraulic Conductivity*

<u>4.8.1.1 Slug Testing</u>

Single well hydraulic conductivity testing was performed on all monitoring wells during the 2010 field season. Testing was done by either adding a slug of known volume, or by purging the well dry and monitoring the rate at which the water well recovered to its static level. Calculation and analysis of results was done using the Kansas Geological Survey Model (Wilkinson 2011) and are summarized in Table 4.1.

<u>4.8.1.2 Permeameter Testing</u>

A series of constant headwater, rising tailwater permeameter tests (Test Method C) (ASTM International, 2007) were performed using intact soil cores collected from the site to determine matrix hydraulic conductivity measurements. Intact soil cores (50.8 mm diameter by 100 mm nominal length) were prepared and placed into a rigid walled permeameter similar to the procedure used in Kodikara et al. (2002). A total of four cores for each of the glaciolacustrine and glacial till units were used to determine the matrix hydraulic conductivity of the soils. Prior to running the experiment, cores were inspected to ensure no fractures or roots were observed in the core. A constant hydraulic head was placed on the upstream end of the soil core and periodic measurements of the hydraulic head values on the rising, downstream end of the soil core were taken.

4.8.1.3 Tension Infiltrometer

Tension infiltrometer me asurements w ere p erformed to estimate th e s urface hydraulic c onductivity o f t he s oil a t va rious t imes t hroughout t he research pr oject. A series of t ension i nfiltrometer e xperiments w ere c onducted i n 2008 t o t est t he s urface hydraulic conductivities in and around Plot A. Results from the 2008 tests were combined with additional measurements taken during the 2010 season to determine a bulk hydraulic conductivity of t he t op s oil on s ite. T he f ive t ests pe rformed b etween A ugust a nd September of the 2010 s eason combined w ith 5 t ests used from the summer of the 2008 season provided a useful data set needed to calculated a representative top soil hydraulic conductivity value.

*4.8.2 Soil Water Characteristics*

Soil w ater r etention cu rves w ere es timated b y p erforming p ressure p late extractions on 5 soil cores collected from the top soil unit, and 2 soil cores taken from the glaciolacustrine unit i n 2010. E ach core w as first s aturated and pl aced in t he pr essure extraction ch amber. Water co ntents of t hese co res were m easured while ex posed t o pressures at 10 di fferent intervals ranging from 1 to 7500 mbar, and results were used to create s oil w ater ch aracteristic d rying cu rves. T he d etails o f t he t est p rocedure can b e found i n K lute (1986). No wetting cu rves were evaluated for the s oil co res. M easured soil w ater c ontent da ta from t he pr essure pl ate e xtractions w ere i nput i nto t he R ETC computer ( van G enuchten et a l., 1991) pr ogram and fitted t o t he va n G enuchten m odel parameters. T he R ETC an alysis results a re pr esented i n T able 4.2 f or each i ndividual soil. T hese h ydraulic p arameters w ere t hen u sed as i nput p arameters for t he f low an d

transport n umerical mo del.   Raw d ata f rom t he  pressure p late  extraction t ests an d t he

RETC fits can be found in Appendix G.
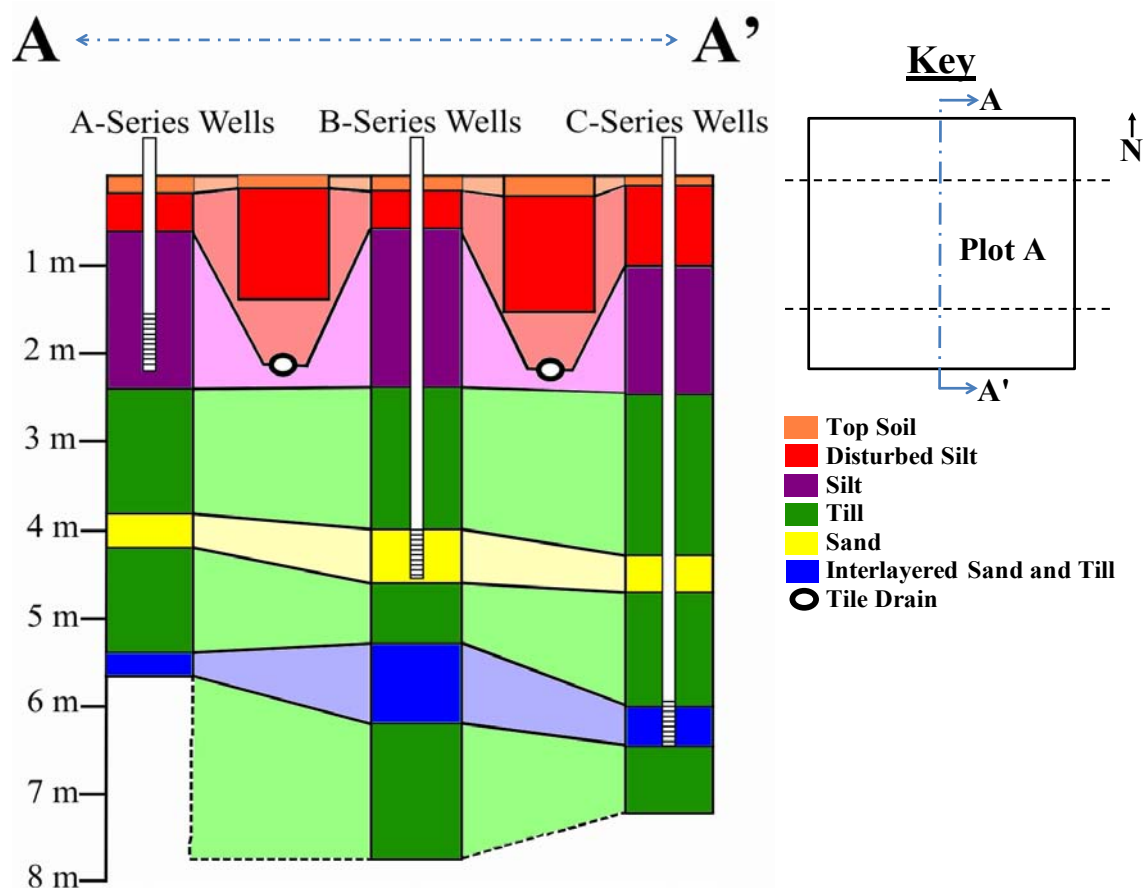
**Figure 4.1. Cross-section of sediment lithology beneath plot A. Cross-section stretches approximately 20 meters from north to south as shown in the key. Includes monitoring well and tile drain depths. Modified from Wilkinson (2011).**
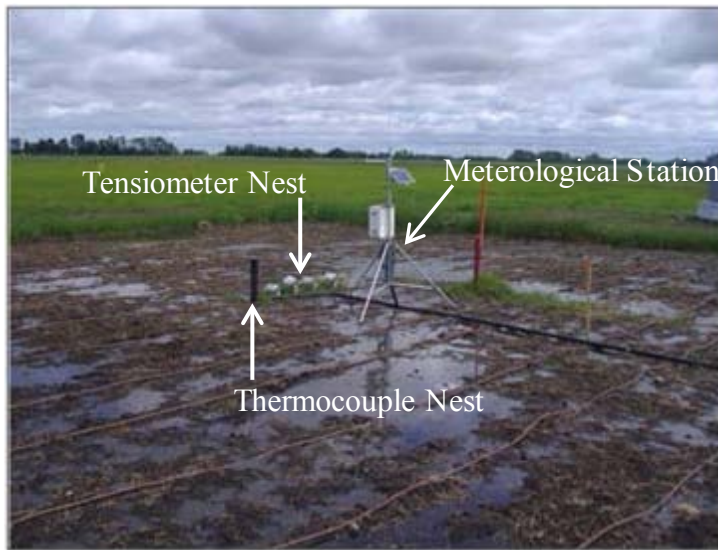
**Figure 4.2. Photo of Plot A in 2009 during irrigation. The location of the meterological along with tensiometer and thermocouple nests are indicated. Photo was taken prior to monitoring well installation.**
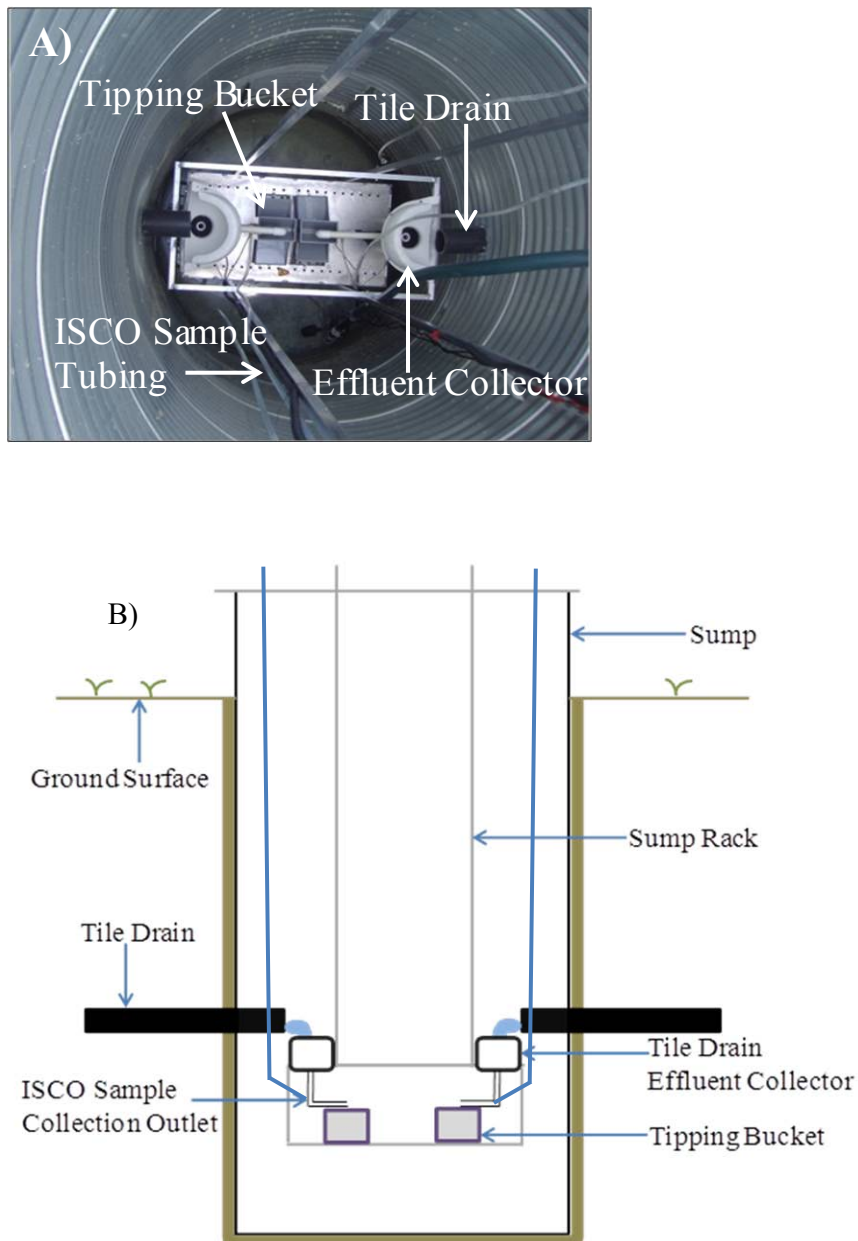
Figure 4.3. a)Photo of monitoring equipment located inside the sump. Photo includes both north and south tile drain outlets, tipping buckets and sample collection tubing. b) Cross-section of sump system with tile drain outlets, location of sample devices and location of ISCO sample collection outlets *Note, cross-section not to scale*.
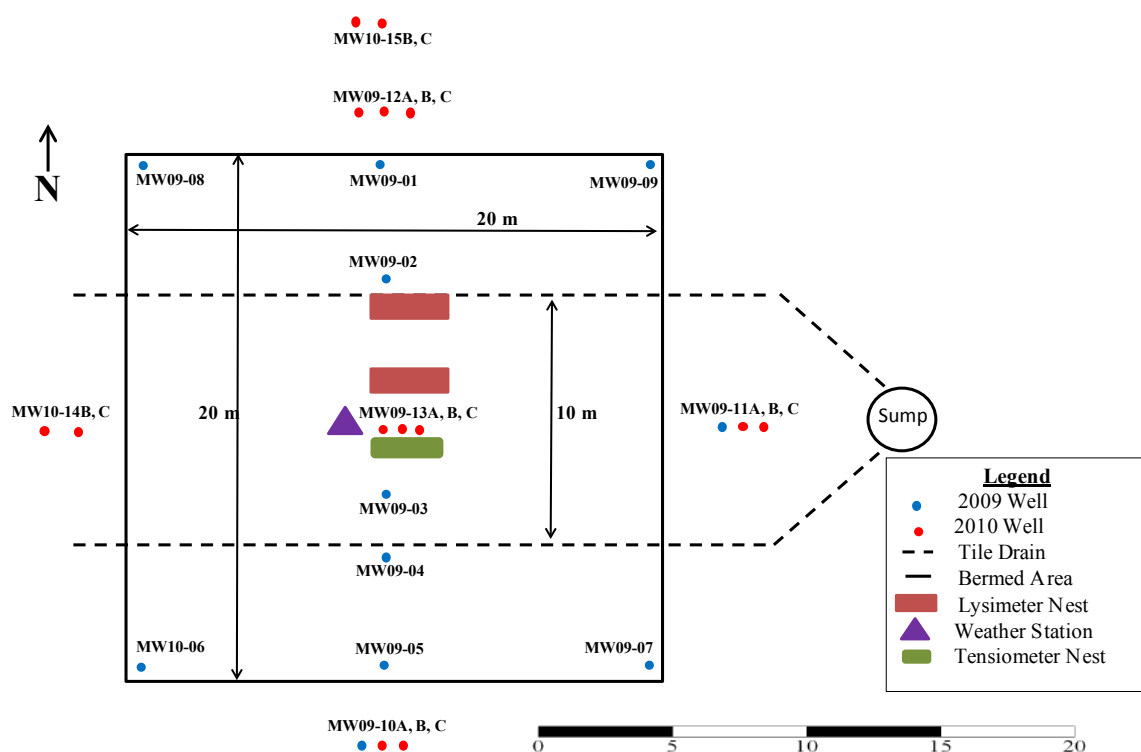
**Figure 4.4. Illustrated plan view map of Plot A at the end of the 2010 season. Legend indicates if monitoring well was installed in 2009 or 2010.**
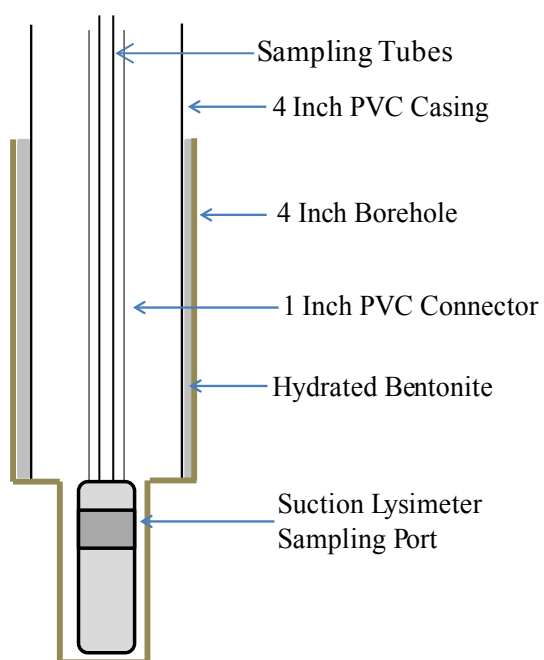
**Figure 4.5. Schematic of the suction lysimeter installation at depths below 30 cm. Note, not to scale.**
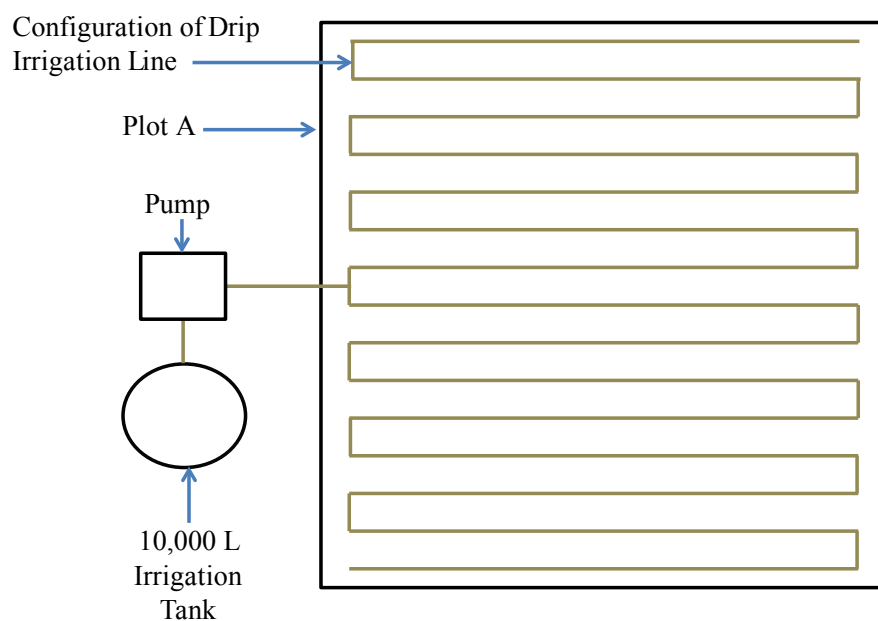


**Figure 4.6. Schematic of drip irrigation line configuration with tie-ins to the pump and irrigation tank.**
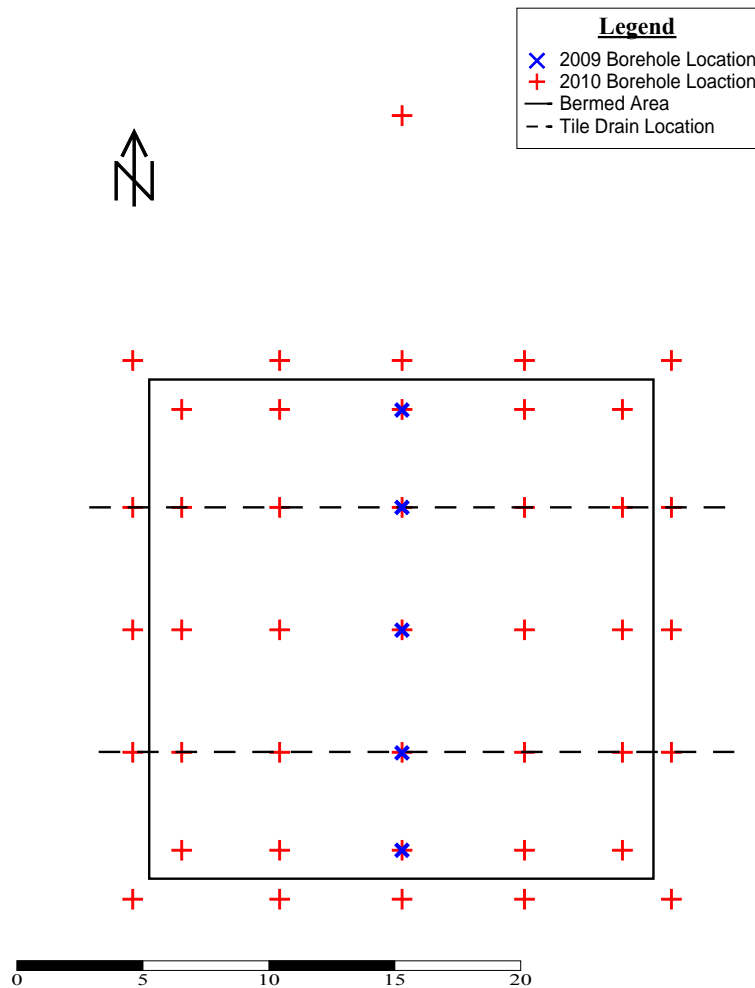
**Figure 4.7. Plan view map of sampling locations for the 2009 and 2010 DFBA soil sampling locations.**

**Table 4.1.  Geometric mean of hydraulic conductivities at three different depths calculated from single well rising head slug tests completed in 2010.**

| Series (Depth) | Number of Tests | Geometric Mean K (m/s) | Variance (m/s)$^2$ |
|---|---|---|---|
| A – 2.0 meters | 39 | 6.0E-08 | 9.30E-11 |
| B – 4.0 meters | 15 | 1.3E-06 | 1.00E-11 |
| C – 6.0 meters | 15 | 1.2E-07 | 1.40E-13 |

**Table 4.2.  Calculated van Genuchten (1980) parameters using the RETC software program.**

| Material | $\theta_r$ | $\theta_s$ | $\alpha$ (mm$^{-1}$) | n | l |
|---|---|---|---|---|---|
| Top Soil | 0 | 0.489 | 0.0016 | 1.091 | 0.5 |
| Glaciolacustrine Silt | 0 | 0.395 | 0.0045 | 1.083 | 0.5 |

**CHAPTER FIVE: DEVELOPMENT OF THE NUMERICAL MODEL**

The development of a numerical flow and transport model of the DFBA tracer experiment serves multiple purposes. Primarily, the model will help to better understand the processes influencing water flow and solute transport in a macroporous, tile-drained system. The flow and transport simulations will allow fluid and DFBA tracer mass balances to be calculated, which will help further define the role macropores play on the flow and transport in low permeability glacial soils. Model simulations will help quantify the flow dynamics of the preferential flow pathways as well as help conceptualize the effect the tile drains have on bulk (matrix and macropore) subsurface flow. The calibrated flow and transport model will then allow for future simulations pertaining to salt flushing, including estimation of remediation times and optimization of irrigation and drainage designs.

**5.1 Conceptual Model**

The conceptual model developed for the site involves several key hydrostratigraphic units. A cross-section below plot A (Figure 4.1) produced by Wilkinson (2011) illustrates these key units. In order for the tile drains to produce effluent the water table must be above the tile drains. Therefore, the assumption can be made that during periods of tile drain flow only the topsoil and glaciolacustrine unit will undergo variably saturated flow conditions, while saturated flow conditions will exist for all stratigraphic units below the tile drains. To accommodate variably saturated flow modeling, additional unsaturated flow parameters were needed for the glaciolacustrine

and top soil units. Additionally, a large zone of disturbed soil was created during the tile

drain installation directly over the north and south tile drains beneath Plot A that likely

altered the hydraulic parameters of the disturbed soil. This disturbed soil zone was not

simulated in the numerical model for simplicity.

## 5.2 Preferential Flow Models

Both glaciolacustrine and glacial till layers are known to have a large preferential

flow component due to fractures and root holes that have been observed during the

analysis of core extracted from the plots and from the results of the tracer tests. Previous

modeling of the Devon research site conducted by Smith (2008) suggested that

preferential flow is an influential process and must be accounted for in future model

simulations. Although macropores were not simulated in the modeling experiment

conducted by Smith (2008), macropores were observed during analysis of soil cores. In

order to properly simulate preferential flow and transport, it is important to capture the

relevant processes in the numerical model. Macropores can either be represented

numerically as discrete fractures or by the use of a dual-continuum formulation. As

mentioned earlier in Section 3.5 representing discrete fractures numerically generally

requires an extremely fine mesh, a large number of nodes and large amounts of data. The

dual continuum method represents the matrix and macropores as two separate but

overlapping domains. The matrix and macropore domains are connected with a coupling

term that allows for fluid and solute transfer to occur between domains. The dual

continuum method is generally more applicable to the field scale due to the smaller

number of nodes/elements required, and therefore will be used for simulating the Devon site.

## 5.3 Model Implementation

### 5.3.1 HYDRUS 2D

HYDRUS 2D is the dual permeability flow and transport modeling code that was selected for this study. The software program solves Richards' equation for flow and the advection-dispersion equation for transport under partially saturated conditions in both the matrix and macropore domains. The model contains two overlapping domains (matrix and macropore) each with individual van Genuchten soil hydraulic parameters ($n$, $\alpha$, $\theta_r$, $\theta_s$ and $K_{sat}$, $l$) to describe the unsaturated flow conditions and a coupling term to account for mass transfer between matrix and macropore domains (Simunek et al., 2003). As shown in Figure 3.1b, flow and transport occurs individually in each domain and exchange between the two domains is driven by hydraulic head differences for flow and a concentration gradient for solute transport. The model requires a large number of input parameters, many of which cannot be physically measured. Therefore, a lengthy literature review and calibration procedure was needed to choose physically reasonable variables. Future model development will require multiple geochemical simulations (cation exchange, variable hydraulic conductivity) to be completed and these can also be modeled using the HYDRUS 2D software.

*5.3.2 Governing Equations*

<u>5.3.2.1 Fluid Flow</u>

Equations 5.1 and 5.2 (Gardenas et al, 2006) are coupled Richards equations that describe unsaturated flow in the matrix (5.1) and macropore (5.2) domains. Variables containing the subscript $f$ denote macropore domain parameters, while the subscript $m$ denotes matrix domain.

$$\frac{\partial \theta_m(h_m)}{\partial t} = \frac{\partial}{\partial x_i}\left[K_m(h_m)\left\{K_{ij}^A \frac{\partial h_m}{\partial x_j} + K_{iz}^A\right\}\right] - S_m(h_m) + \frac{\Gamma_w}{1-\omega} \tag{5.1}$$

$$\frac{\partial \theta_f(h_f)}{\partial t} = \frac{\partial}{\partial x_i}\left[K_f(h_f)\left\{K_{ij}^A \frac{\partial h_f}{\partial x_j} + K_{iz}^A\right\}\right] - S_f(h_f) - \frac{\Gamma_w}{\omega} \tag{5.2}$$

Within both equations, $K_f$ and $K_m$ represent the unsaturated hydraulic conductivity of the pore system (L/T), $K_{ij}^A$ is the components of a dimensionless anisotropy tensor $K^A$ that when medium is isotropic reduces to unit matrix (Simunek et al., 2006), $\theta$ is the water content ($L^3/L^3$), $h$ is the pressure head (L), $S$ is a sink term (used to simulate water root uptake by plants) ($T^{-1}$), $\Gamma_w$ is the transfer rate of water between domains ($T^{-1}$) and $\omega$ is the ratio of the volume of macropores relative to the total soil system (unitless) (Gerke and van Genuchten, 1993a).

Mass exchange between the two domains is controlled by the $\Gamma_w$ (mass exchange) parameter. Expanding this parameter yields Equation (5.3), which shows that exchange between each domain is proportional to the difference between the macropore and matrix heads multiplied by the fluid mass exchange coefficient, $\alpha_w$ ($L^{-1}T^{-1}$).

$$\Gamma_w = \alpha_w(h_f - h_m) \quad (5.3)$$

The mass exchange coefficient $\alpha_w$ (L/T), expanded yields Equation (5.4)

$$\alpha_w = \frac{\beta}{a^2} K_{as}(h)\gamma_w \quad (5.4)$$

Where $a$ is the characteristic half width (L) of a matrix block, $\beta$ is a dimensionless geometry coefficient, $\gamma_w$ is a dimensionless scaling factor, and $K_{as}$ is the effective hydraulic conductivity of the interface between matrix and macropore domains (L/T) that expanded yields Equation 5.5

$$K_{as}(h) = 0.5\left[K_{as}(h_m) + K_{as}(h_f)\right] \quad (5.5)$$

where $h_m$ is the matrix pressure head at a corresponding node and $h_f$ is the macropore pressure head at the same node. A summary of the equations and physical description of each parameter are shown in Figure (5.1).

5.3.2.2 Solute Transport

Equations (5.6) and (5.7) (Gardenas et al, 2006) represent the modified advection-dispersion equations used to simulate solute transport in a variably saturated, dual permeability model. Coupling terms are used to simulate the transfer of solute mass between the matrix (subscript $m$) and macropore (subscript $f$) domains.

$$\frac{\partial \theta_m C_m}{\partial t} + \frac{\partial \rho S_m}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_m D_{ij}^m \frac{\partial C_m}{\partial x_i}\right) - \frac{\partial q_i^m C_m}{\partial x_i} - \phi_m - \frac{\Gamma_s}{1-\omega} \quad (5.6)$$

$$\frac{\partial \theta_f C_f}{\partial t} + \frac{\partial \rho S_f}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_f D_{ij}^f \frac{\partial C_f}{\partial x_i}\right) - \frac{\partial q_i^f C_f}{\partial x_i} - \phi_f - \frac{\Gamma_s}{\omega} \quad (5.7)$$

where $D$ is the dispersion tensor ($L^2/T$), $q$ is the Darcian flux (L/T), $\phi$ is the reaction parameter ($M/L^3T$) which accounts for the increase or decrease of a solute due to reaction (degradation, volatilization etc.), $\Gamma_s$ is the mass exchange parameter ($T^{-1}$) and $\omega$ is the volume of the fracture pore system as described above. The solute mass exchange parameter $\Gamma_s$ expanded (Equation 5.8) is,

$$\Gamma_s = \alpha_s (1-\omega_f)\theta_m (C_f - C_m) + \Gamma_w C^* \quad (5.8)$$

where $\alpha_s$ is a first-order solute mass transfer coefficient ($L^{-1}$), $C$ is the concentration in the respective pore system, and $C^*$ is equal to $C_f$ for $\Gamma_w > 0$ and $C_m$ for $\Gamma_w < 0$. This determines the advective solute transport direction (flowing from matrix into the macropores or vice versa). Expanding the $\alpha_s$ term yields Equation (5.9)

$$\alpha_s = \frac{\beta}{a^2} D_a \quad (5.9)$$

where $D_a$ is the effective dispersion coefficient ($L^2/T$), and $a$ and $\beta$ are defined previously. A summary of the equations and physical description of each solute parameter are shown in Figure (5.2).

*5.3.3 Equation Solutions*

The H YDRUS s oftware p ackage u ses t he G alerkin f inite el ement m ethod w ith linear basis functions to develop a solution for the flow equation (Simunek et al., 2006). An implicit finite difference scheme is used for time discretization (Simunek et al., 2006). To s olve t he t ransport e quation, t he C rank-Nicholson s cheme, w hich s ets t he t emporal weighting c oefficient t o 0.5, w as us ed f or t he t ime w eighting m ethod ( Simunek e t a l., 2006). T he G alerkin f inite e lement m ethod w ith a rtificial di spersion w as us ed f or t he spatial weighting scheme. A rtificial dispersion was used to decrease computational time by stabilizing the numerical solution and limiting the spatial oscillations within the results (Simunek et al., 2006).

**5.4 Model Domain and Material Distribution**

The m odel dom ain us ed i n t his s tudy i s a t wo-dimensional ( 2D) v ertical c ross section t aken along a 30 m l ong nor th – south t ransect c entered on pl ot A. T he s outh edge ends at MW09-10 and the north edge extends to MW09-12 (Figure 5.3) with each lateral bounda ry s ituated a t e xterior t ile dr ains. The dom ain r uns pe rpendicular t o t he north and south tile drains, with the drains running in and out of the model domain. The vertical depth of the domain extends down to the base of the first sand unit at 4.5 m. The center of the tile drains are located at horizontal distances of x = 10 and 20 m and a depth of 2.15 m be low g round s urface. It i s a cknowledged t hat t he i mplementation of a 2D model is not ideal for simulating a dynamic 3 dimensional (3D) system and may not fully capture t he s ystem f low be haviour ( e.g., pl ot e dge effects). H owever, due t o

computational a nd d ata limita tions, s implifying the mo del a s a 2 D c ross-section w as deemed necessary.

The depth of the lower boundary and the extent of the model domain were based on th e mo nitoring w ell c hemistry r esults f rom mo nitoring w ell s amples. E C measurements f rom w ater s amples co llected f rom t he C s eries m onitoring w ells w ere significantly lower than those from the A and B series wells. T his indicated decreased hydraulic connection between the B (4 m depth) and C series (6 m depth) sand intervals below the plot. Therefore, the lower boundary for the model domain was selected as the base of the B series sand unit.

Surface pondi ng i n P lot A r egularly oc curred dur ing t he i rrigation e vents a nd larger precipitation events. Numerically, HYDRUS assumes that all water applied to the soil surface in excess of the infiltration amount for a given time step is removed from the system vi a ov erland flow ( Simunek e t a l., 2006 ). In t his s tudy, pl ot A w as c arefully levelled and surrounded by compacted soil berms to restrict overland flow. Therefore, an artificial in filtration la yer w as c onstructed a bove th e to psoil in H YDRUS to a ct a s a temporary s torage unit for all ponded water. T he material properties o f this infiltration layer w ere s elected s uch t hat i t p ermitted r apid i nfiltration of w ater ( high K ), a nd ha d sufficient storage volume (high $\theta_s$) t o r etain a ny ponde d w ater f or e ventual i nfiltration into the soil.

The finite-element grid was constructed using the CAD MESHGEN program (Simunek et al., 2006) included in HYDRUS. A default global element size of 250 mm was used with grid refinements around the tile drains, material boundaries and near the top boundary that contained the atmospheric condition (Table 5.1). Finer node spacing (125 mm) was used for the upper materials (surface infiltration layer, topsoil) to limit the amount of numerical instability that occurs at infiltration boundaries. Due to the high flow velocities that occur around the tile drains, additional grid refinement was needed to stabilize the model solution. The grid was automatically generated using the MESHGEN program, which adheres to the rule that the ratio of element sizes between neighbouring elements should not exceed more than 1.5 (Simunek et al., 2006). This ensures that grid spacing changes occur gradually with no sharp element size boundaries. The final model domain consisted of 10,627 nodes, 20,704 2-D elements and 1094 1-D elements.

The model domain was subdivided into five distinct horizontal layers; surface infiltration layer, top soil, glaciolacustrine unit, glacial till unit and the B series sand unit (Figure 5.4). Material properties assigned to each layer were assumed to be homogenous and isotropic. Material boundaries and depths were set by averaging the contact depths between each layer found in soil cores taken across Plot A (Table 5.2).

## 5.5 Model Parameters

### 5.5.1 Hydraulic Parameters

The van Genuchten soil hydraulic parameters for the matrix were determined by importing pressure plate extraction data into the curve-fitting program RETC (van

Genuchten et al, 1991). Output values were then averaged and single $n_m$, $\alpha_m$, $\theta_{rm}$ and $\theta_{sm}$ values w ere u sed t o d escribe each o f t he t opsoil a nd g laciolacustrine uni ts. T he glaciolacustrine and glacial till ma trix h ydraulic c onductivity v alues were d etermined using the results of the constant headwater, rising tailwater tests (Sec 4.8.1.2).

The v an G enuchten ( VG) p arameters for t he macropore dom ain c annot be physically m easured i n t he s ame f ashion as t he m atrix p arameters. T herefore, V G macropore d omain p arameters n $_f$, $\alpha_f$, $\theta_{rf}$ and $\theta_{sf}$ were e stimated from li terature v alues (Simunek et al., 2003; Gerke and Kohne, 2004; Gardenas et al., 2006) while $K_{sf}$ was used as a c alibration pa rameter t o m atch t ile dr ain r esponses f or bot h f low a nd t racer concentrations. V alues acquired from the tension i nfiltrometer and slug tests were used as guidelines for bulk ( combined m atrix a nd m acropore) h ydraulic conductivity values. Due to the absence of macropores in the B series sand unit, VG matrix parameters were used for both the matrix and macropore domains. A lthough most macropores have been observed t o be ne ar ve rtical, w hich w ould i mply a c ertain d egree of a nisotropy, t he HYDRUS model currently does not include anisotropy in the macropore domain.

*5.5.2 Dual-Domain Fluid Transfer Parameters*

Transfer of fluid between the matrix and macropore domain is controlled by five specified p arameters; $\beta$, $\gamma_w$, $\omega$, $a$ and $K_{as}$. The p arameters $\beta$ and $\gamma_w$ were he ld c onstant during m odel d evelopment, w hile $\omega$, $a$ and $K_{as}$ were mo dified to o ptimize th e r esults during m odel c alibration. T able 5.3 s ummarizes t he va lue a nd s ource us ed f or e ach

variable in the base case simulation. The β parameter is used to represent the size and shape of matrix blocks (Gerke and van Genuchten, 1996) with β values of 3 used for rectangular slabs, 8 for solid cylinders and a value of 15 used to represent spheres. The input parameter $\gamma_w$ is described as a dimensionless scaling factor and a value of 0.4 was used based on the literature values found (Gerke and van Genuchten, 1993b). The parameter ω is used to represent the volume fraction of macropores found in a matrix block. The *a* parameter is used to describe the distance from the center of the matrix to the closest macropore and the $K_{as}$ parameter is used to describe the hydraulic conductivity of the matrix-macropore interface.

### 5.5.3 Solute Transport and Reaction Parameters

The solute mass transfer coefficient is a key factor that determines how much and how quickly the solute is transferred (Brusseasu and Rao, 1990), therefore the solute mass transfer coefficient ($\alpha_s$) was the primary calibration parameter used for the solute transport simulations. Calibrated values were compared with values reported in the literature, which ranged from 0.001 to 7.2 d$^{-1}$ (Gardenas et al., 2006; Gerke and Kohne, 2004; Lee et al., 2000).

The lateral and transverse dispersivities ($\alpha_L$ and $\alpha_T$) were set to 100 mm and 10 mm, respectively, which are within the range of values found in literature with comparable scales of observation (Gelhar et al., 1992). The molecular diffusion coefficient for DFBA set at 7.6 x 10$^{-10}$ m$^2$/s based on values found in literature (Bowman and Gibbens, 1992). Sorption was not used in the base case simulation but was tested

during the sensitivity analysis. The distribution coefficient, $K_d$ that was input into the model was calculated using the results from the laboratory batch tests (Appendix B). A linear isotherm was created that represented the maximum observed soil sorption. This isotherm was calculated using measured values of the highest sorption from all 4 soils at each concentration tested in all available lab data. A DFBA distribution coefficient of 0.0789 cm$^3$/g was used in the simulation sensitivity analysis to examine the affect retardation had on solute transport in our system.

## 5.5 Boundary and Initial Conditions - Fluid Flow

### 5.5.1 Boundary Conditions

5.5.1.1 Hydraulic Head Boundary Conditions

The boundary conditions used for the model are shown in Figure 5.3. Fixed head boundary conditions (1$^{st}$ type) were used to simulate the measured pressure head values from monitoring wells on the lateral boundaries of the model domain. Hydraulic head readings from MW09-10A and MW09-12A were used for the specified head boundary condition in the glaciolacustrine unit on the south and north edges of the domain, respectively (Figure 5.3). Likewise, the heads from wells MW10-11B and MW10-14B were used as boundary conditions for the B series sand unit in the south and north edges of the domain, respectively (Figure 5.3). Through development of the model complications arose due to the lack of water exiting the model from the lower sand boundaries. A large portion of this problem stems from attempting to model a 3D problem in 2D. The lower boundary condition heads were only allowing small amounts of lateral flow to pass through the model in the X direction, while realistically a large

amount of radial flow occurs both in the X and Y directions (in and out of the model domain). Therefore it was decided to use hydraulic heads taken from only MW10-14B for both sand boundary conditions, allowing for symmetrical radial flow to occur, thereby increasing the amount of water removed from the sand unit.

Theoretically, flow symmetries (mid-point between tile drains) should allow for no flow boundaries to be implemented between each tile drain because of groundwater flow divides. But a system failure occurring in mid-July 2010 caused the tile drain system across the entire site to stop draining water (while Plot A drains continued to function). This resulted in the water table surrounding Plot A to rise and there was a lateral influx of water to the plot during this period. Consequently, the rise in the site-wide water table during this time period was simulated using the specified head boundaries in the glaciolacustrine units rather than no flow boundaries to account for the lateral inflows.

A no flow boundary condition was used along the lateral boundary of the glacial till unit and at the base of the B series sand unit (Figure 5.3). A limited hydraulic connection is assumed between the B series sand unit and the C series sand unit, allowing for a no flow boundary condition at the base of the B series unit. Additionally, it was assumed there was a negligible amount of lateral flow through the till unit (relative to the sand units above and below the till) therefore a no flow boundary was used for the lateral boundaries of the glacial till unit.

5.5.1.2 Atmospheric Boundary Conditions

The irrigation plot area on the top boundary was simulated using an atmospheric boundary c ondition ( $2^{nd}$ – Type N eumann). The H YDRUS 2 D pr ogram s imulates atmospheric bounda ry c onditions b y requiring t he us er t o s pecify a p recipitation r ate (L/T) a nd a n e vaporation r ate ( L/T). E vaporation i s s ubtracted di rectly f rom t he precipitation in the numerical solution, which results in a fluid mass flux that is applied directly to the atmospheric boundary (Simunek et al, 2006). Transpiration was calculated separately from ev aporation u sing t he FAO P enman-Monteith dua l-crop co efficient (Allen et al., 1998) a nd was s imulated num erically us ing t he Feddes r oot w ater upt ake model i mplemented w ithin H YDRUS ( Simunek e t a l, 2006) . M aximum pot ential transpiration r ates were calculated on a da ily ba sis i n uni ts of m m/day. A r oot z one distribution profile was constructed with a maximum rooting depth of 1.0 m and a rooting depth intensity set to the upper top soil boundary. The root water uptake is simulated as a sink term in the solution. N umerically, two c onditions mu st b e met w ith r egard to the root water uptake in order to obtain a numerical solution. First, the absolute value of the flux must not exceed the infiltration or evaporation rate. Second, the pressure head at the soil surface must remain between the minimum pressure head value and zero (Simunek et al, 2006).

A $2^{nd}$ type, s pecified f lux bounda ry w as i mplemented on t op of t he r emaining model dom ain out side of pl ot A (i.e., on bot h s ides of t he a tmospheric bound ary condition as s hown i n Figure 5.3 ). T his bounda ry w as m eant t o s imulate pr ecipitation occurring out side of the irrigation plot. D aily rain ga uge m easurements t aken from the

nearby w eather s tation w ere u sed t o cal culate a d aily s pecified f lux. C alculated evaporation rates were subtracted directly from the measured precipitation similar to the atmospheric bounda ry c ondition. S ign c onvention di ctates w ater be ing a dded t o t he system is negative. Therefore, when precipitation > evaporation, all fluxes would carry a negative (-) sign. W hen precipitation < e vaporation, a ll fluxes c arry a pos itive (+) s ign indicating a mass flux out of the system or, evaporation from the soils. Transpiration was also implemented by the same procedure used in the atmospheric flux boundary.

5.5.1.3 Internal (Seepage Face) Boundary Conditions

To s imulate t he nor th a nd s outh t ile dr ains; a n i nternal c ircular ope ning w as constructed inside th e mo del d omain w ith th e d iameter e qual to th e tile d rain d iameter (200 mm). T he node s surrounding t his i nternal boundary w ere fixed as a s eepage face boundary c ondition t hat a llows w ater t o pa ss t hrough a nd b e r emoved from t he s ystem (Figure 5.3). The s eepage f ace b oundary i s n umerically r epresented b y as signing a 1 [st] type c ondition at each specified node to a va lue of h ( pressure h ead) = 0 ( atmospheric). When nodes surrounding the seepage face boundary are saturated (h > 0), water will flow across the internal boundary and be removed from the domain. When nodes surrounding the s eepage face boundary a re uns aturated (h < 0), the s eepage face bou ndary will t urn off, a nd no f low c onditions w ill oc cur be tween s eepage f ace node s a nd s urrounding nodes, thereby preventing flow from the seepage face back into the domain (Simunek et al, 2006).

*5.5.2 Initial Condition - Pressure Head*

The initial pressure head distribution (Figure 5.5) was calibrated by matching the simulated tile drain flux to the initial observed tile drain flux during the first 20 days of the 2010 field season. A hydrostatic pressure head distribution was first set by fixing the model's top and bottom pressure head values and applying a linear distribution between the two values. Specified precipitation fluxes were then applied to the top boundary over a 20 day period until the simulated tile drain fluxes matched the initial 2010 observed tile drain fluxes. Once the observed and simulated tile drain fluxes were equal, the domain pressure head distribution was imported into a new simulation as the initial pressure head distribution.

## 5.6 Boundary and Initial Conditions - Solute Transport

DFBA was applied on the surface of plot A in 2009 and subsequently infiltrated in the soil profile. In order to simulate the 2010 field season, the initial in-situ DFBA distribution was required. The DFBA concentration profiles from the soil core extractions at the end of the 2009 field season (Figure 6.3) were used to represent the initial solute distribution in the model (Figure 5.6). The lateral extent of the modeled DFBA distribution was limited to directly beneath the irrigation plot with no spreading beyond the vertical boundary of the irrigation plot. In the absence of measured data to indicate the lateral extent of the DFBA tracer, the bulk of the tracer mass was assumed to be retained within the plot due to the limited amount of lateral flow that occurs in the vadose zone. Requirements within the HYDRUS software made all non zero fluid flux boundary conditions to be specified as a 3rd – Type (Cauchy) boundary condition (Figure

5.7) f or t he s olute t ransport. The C auchy boundary c ondition is a mass co nservative boundary condition (Simunek et al., 2006) used for simulating mass flux in and out of the domain (i.e. mass leaving through tile drains or laterally out of domain). No DFBA mass entered t he dom ain dur ing 2010 be cause a ll w ater i nfiltrating ( irrigation a nd precipitation) was tracer free. Thus, only mass exiting the system through the tile drains and specified head conditions was considered.

## 5.7 Observation Nodes and Mesh Lines

Observation node s w ere i nserted i nto t he dom ain t o s imulate m onitoring w ells MW09-01, M W09-03, M W09-05, M W09-13A, M W09-13B a nd t he s outh l ysimeter sampling units at 0.15, 0.30, 0.60, 0.90 a nd 1.50 meters. Each node recorded the matrix and macropore pressure heads as well as the matrix and macropore DFBA concentrations at each time step. Observation node data was compared against the measured monitoring well hydraulic heads and lysimeter concentrations during model calibration.

Mesh l ines ar e a s eries o f co nnected elements i n t he m odel d omain used t o calculate fluid and solute fluxes passing through the constructed line. They were used to calculate the instantaneous and cumulative fluid and solute mass fluxes in both the matrix and m acropore dom ains throughout t he s imulation pe riod. M esh l ines w ere i nserted a t both t ile dr ains a nd e ach s pecified he ad bounda ry c ondition t o c alculate t he f luid a nd solute fluxes leaving or entering the domain.

**5.8 Mass Balance Error**

A mass balance error was calculated by comparing the total change in volume of the system through the simulation time against the measured cumulative fluxes (evaporation, irrigation, root uptake, tile drains etc.). A relative water balance error of 0.20% was calculated for the 138 day simulation period. The same procedure was used to determine the solute mass balance error by subtracting the initial and final solute volumes present in the domain, and comparing them against cumulative solute volumes measured exiting the system through the mesh lines. A relative error of 0.24% was calculated, indicating the model accurately accounted for all mass within the system throughout the simulation period.

## FLUID FLOW

| DOMAIN - MATRIX | DOMAIN - MACROPORE |
|---|---|
| Modified Richards' Eqn. | Modified Richards' Eqn. |
| $\dfrac{\partial \theta_m(h_m)}{\partial t} = \dfrac{\partial}{\partial x_i}\left[ K_m(h_m)\left\{ K_{ij}^A \dfrac{\partial h_m}{\partial x_j} + K_{iz}^A \right\}\right] - S_m(h_m) - \dfrac{\Gamma_w}{1-\omega}$ | $\dfrac{\partial \theta_f(h_f)}{\partial t} = \dfrac{\partial}{\partial x_i}\left[ K_f(h_f)\left\{ K_{ij}^A \dfrac{\partial h_f}{\partial x_j} + K_{iz}^A \right\}\right] - S_f(h_f) - \dfrac{\Gamma_w}{\omega}$ |

### MASS TRANSFER BETWEEN DOMAINS

$$\Gamma_w = \alpha_w(h_f - h_m) \qquad \alpha_w = \frac{\beta}{a^2} K_a(h)\gamma_w \qquad K_{as}(h) = 0.5\left[ K_a(h_m) + K_a(h_f)\right]$$

Where: ω = volume of fractures to total volume (macropore porosity)

β = geometry coefficient of matrix (3 = rectangular slabs, 8 = cylinders, 15 = spheres)

$a$ = Half width of matrix block (distance from center of matrix to matrix/macropore interface)

$\gamma_w$= dimensionless scaling factor

$K_{as}$= effective hydraulic conductivity of matrix/fracture domain interface

**Figure 5.1. Summary of fluid flow parameters. Flow in both the matrix and macropore domain using the Richards' equation and mass transfer between each domain and a short description of the variables used in the calculations.**

# SOLUTE TRANSPORT

| DOMAIN - MATRIX | DOMAIN - MACROPORE |
|---|---|
| Advection-Dispersion Eqn. | Advection-Dispersion Eqn. |
| $$\frac{\partial \theta_m C_m}{\partial t} + \frac{\partial \rho S_m}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_m D_{ij}^m \frac{\partial C_m}{\partial x_i}\right) - \frac{\partial q_i^m C_m}{\partial x_i} - \phi_m - \frac{\Gamma_s}{1-\omega}$$ | $$\frac{\partial \theta_f C_f}{\partial t} + \frac{\partial \rho S_f}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_f D_{ij}^f \frac{\partial C_f}{\partial x_i}\right) - \frac{\partial q_i^f C_f}{\partial x_i} - \phi_f - \frac{\Gamma_s}{\omega}$$ |

## MASS TRANSFER BETWEEN DOMAINS

$$\Gamma_s = \alpha_s (1-\omega_f)\theta_m (C_f - C_m) + \Gamma_w C^* \qquad \alpha_s = \frac{\beta}{a^2} D_a$$

Where: $\omega$ = volume of fractures to total volume (macropore porosity)

$\beta$ = geometry coefficient of matrix (3 = rectangular slabs, 8 = cylinders, 15 = spheres)

$\alpha_s$ = solute mass transfer rate that determines how quickly solute passes between the matrix and macropore domain ($L^{-1}$)

$a$ = Half width of matrix block (distance from center of matrix to matrix/macropore interface)

**Figure 5.2. Summary of solute transport parameters. Solute transport in both the matrix and macropore domain using the advection-dispersion equation and mass transfer between each domain and a short description of the variables used in the calculations.**
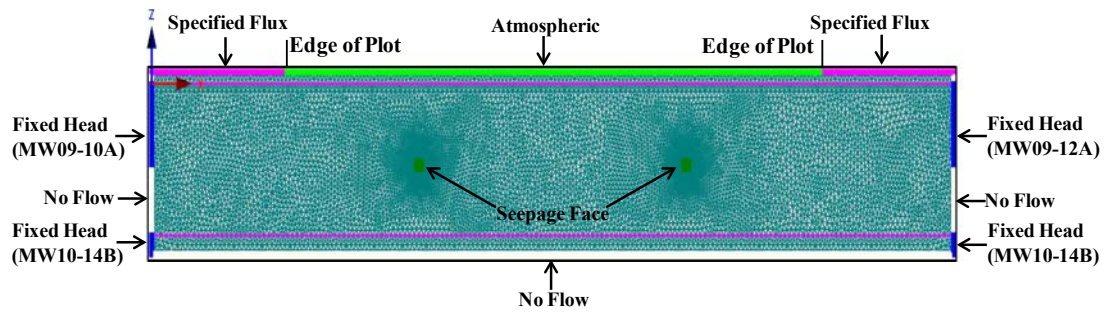
**Figure 5.3. Model domain and flow boundary conditions used for all simulations. Location of cross-section shown in key in Figure 5.1.**

**Table 5.1. Summary of node spacing refinements used while constructing the unstructured finite element grid.**

| Boundary | F-E Node Spacing (mm) |
|---|---|
| Top of Domain | 125 |
| Gravel - Topsoil | 150 |
| Topsoil - Glaciolacustrine | 175 |
| Glacial Till - Sand | 175 |
| Sand - Bottom of Boundary | 150 |
| Tile Drains | 21 |
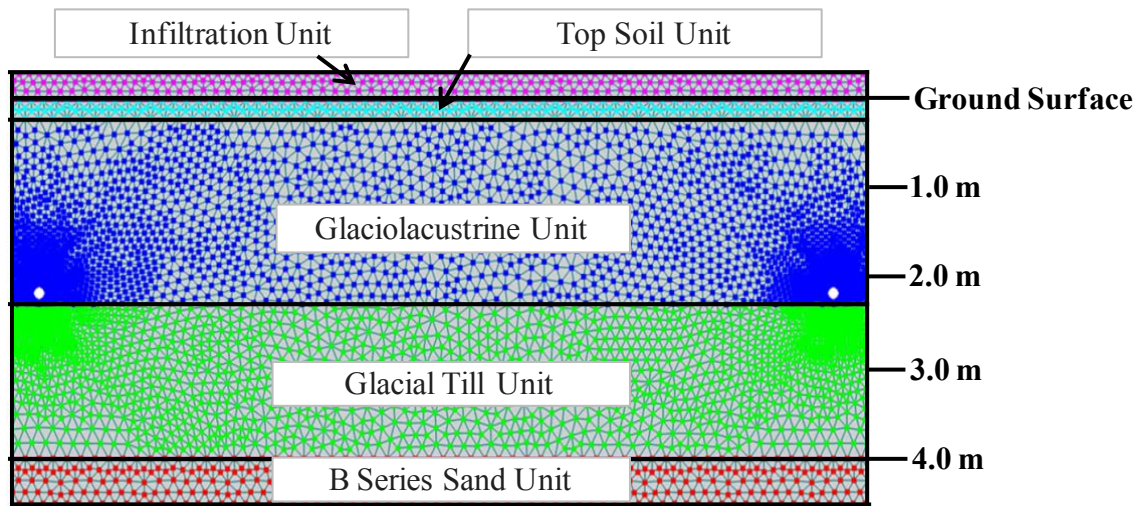
**Figure 5.4.  Material distribution used in simulations.**

**Table 5.2. Summary of depth material depth intervals used in numerical simulations**

| Material | Depth Interval (mm below ground) |
|---|---|
| Surface Infiltration Layer | +300 - 0 |
| Topsoil | 0 – 200 |
| Glaciolacustrine | 200 - 2400 |
| Glacial Till | 2400 - 4000 |
| B Series Fine – Medium Sand | 4000 - 4500 |

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**Table 5.3. Summary of dual-domain fluid mass transfer parameters used in the base case simulation.**

| Fluid Transfer Parameter | Value | Range of Literature Values | Calibration Parameter | Literature Sources |
|---|---|---|---|---|
| $\beta$ | 3 | 3-14 | No | Gerke and van Genuchten, 1993a; Simunek et al., 2003; Gerke and Kohne, 2004 |
| $\gamma$ | 0.4 | 0.4 | No | Gerke and van Genuchten, 1993b; Simunek et al., 2003 |
| $\omega$ | 0.0025 | 0.03-0.05 | Yes | Simunek et al., 2003; Gerke and Kohne, 2004; Gardenas et al., 2006 |
| $K_{as}$ (mm/day) | 0.01 | 0.01-.25 | Yes | Simunek et al., 2003; Gerke and Kohne, 2004; Gardenas et al, 2006 |
| $a$ (mm) | 5-25 | 10 | Yes | Simunek et al., 2003; Gerke and Kohne, 2004 |
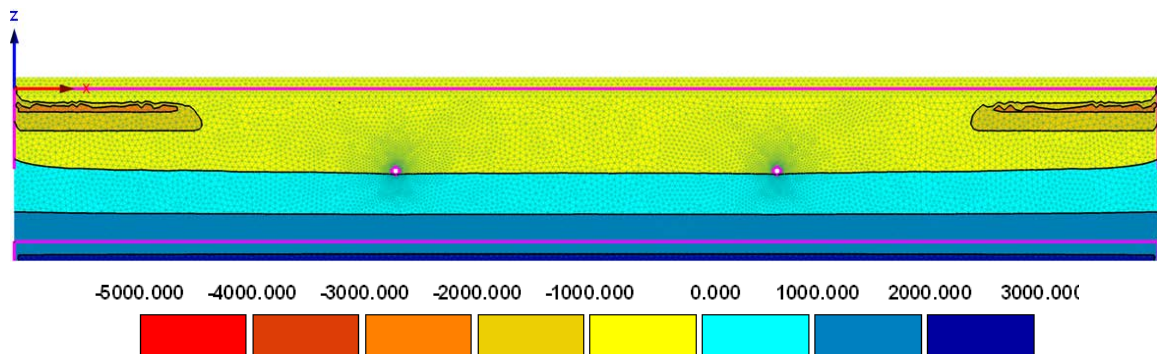


**Figure 5.5. Initial pressure head distribution for the 138 day simulation period. Blue colours indicate pressure head values greater than 0 (saturated). Yellow – red colours indicate pressure head values less than 0 (unsaturated).**
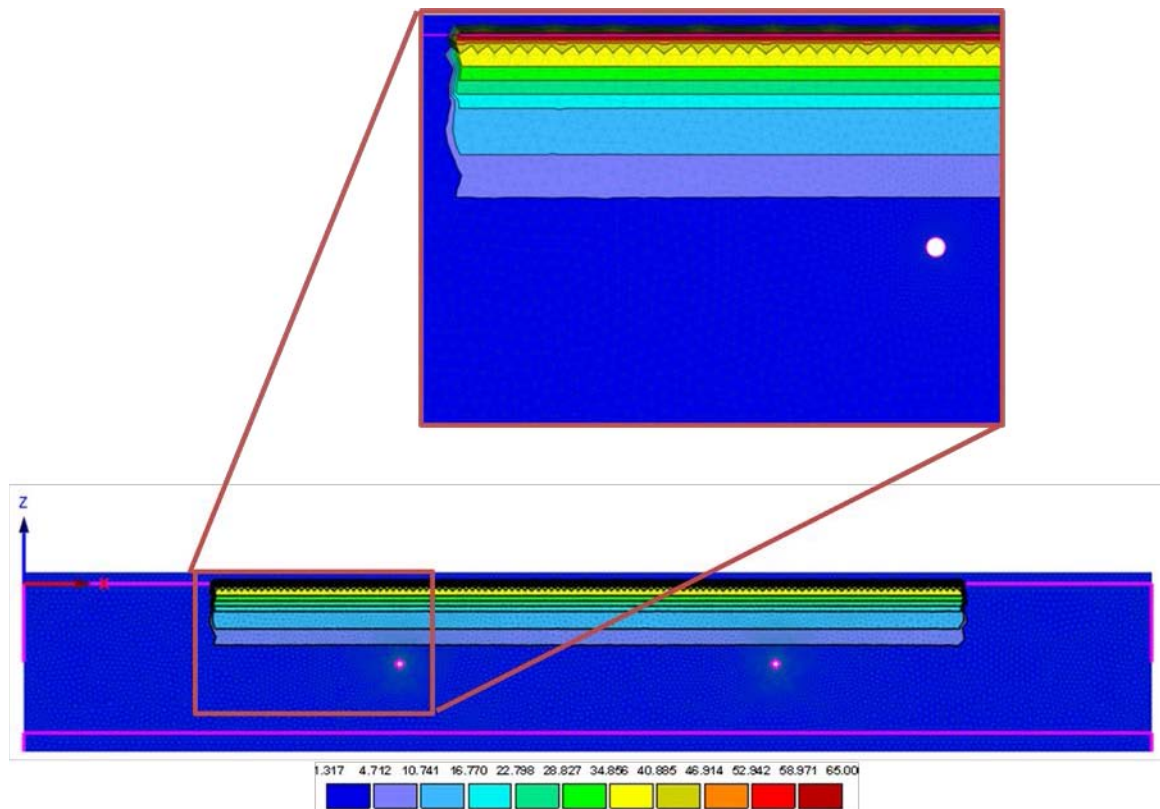
**Figure 5.6. Initial DFBA concentration distribution. Concentrations were set using results from the calculated pore water concentration extracted from the 2009 soil cores (Section 6.1.3.4).**
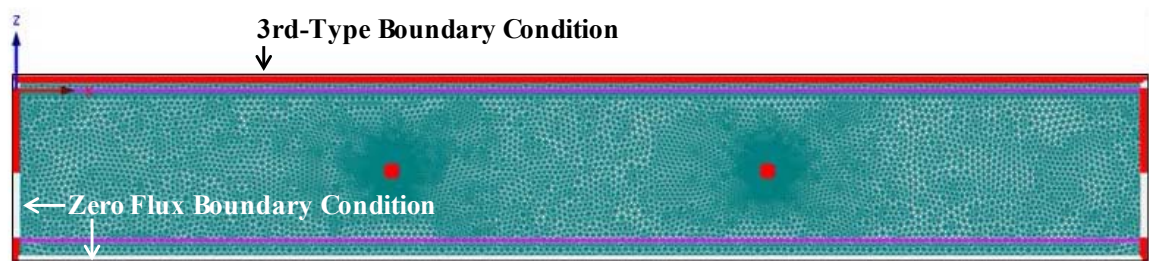


**Figure 5.7. Solute transport boundary condition used for all simulations.**

## CHAPTER 6: RESULTS AND DISCUSSION

### 6.1 2009 Field Results

*6.1.1 Soil Properties*

Soil properties of the four main soil materials are shown in Table 6.1. As described by the soil texture classes triangle (Haynes, 2005), the glaciolacustrine is classified as a silt, the glacial till as a loam and B series sand as a sand. The dry bulk density measurements show an increasing density with depth, indicating compaction is occurring with increasing depth. The cation exchange capacity (CEC) values calculated were compared to values found in Appelo and Postma (2005). The CEC of the glaciolacustrine unit fit within the range of a glauconite, illite and chlorite while the CEC of the glacial till fit within the range of a glauconite, kaolinite and chlorite.

*6.1.2 Tile Drain Flow Response*

Irrigation of plot A began on July 9 (day 190) and continued until October 1 (day 274) (Figure 6.1). Tile flow began in the south tile July 20 (day 201) while the north tile flow began July 27 (day 208) (Figure 6.1). The lag time from when irrigation was initiated to when tile effluent was produced was a result of the antecedent soil moisture conditions. Regionally the study site is centered in an arid region that was suffering from a severe soil moisture deficit (Alberta Agriculture, 2009), so prior to tile drain flow, soil had to become saturated and the water table needed to rise to the tile drain elevation. The lag time between north and south initial flow events was unexpected because theoretically north and south drains should behave in a similar fashion if situated in a homogenous material. This indicates that there are factors (soil heterogeneities) that act

as controls on the tile drain's ability to initiate and terminate flow. Once irrigation ended on October 1, the south tile flowed for 7 additional days while the north continued to flow for 16 days. The 2009 field season cumulative discharge from the south tile was 8.75 m$^3$ or 43.75 mm (half the area of plot A) while the north discharge was 5.46 m$^3$ or 27.3 mm. Cumulatively, the north and south drains captured the equivalent of 5.9% of the applied irrigation water volume.

The variability in tile drain flow rates and response to precipitation events illustrates that although both drains were installed at the same depth and only 10 m apart, soil heterogeneity had a large impact on drain flow. Although both the north and south tiles responded quickly to irrigation/precipitation events only after the soils became saturated and the water table was at the tile drain elevation, the peak flow rates of each tile were variable throughout the season. The south tile drain flow rate was consistently greater in the first half of 2009 (average south rate = 14 L/hr, average north rate = 5 L/hr), while the north tile drain reached a higher flow rate in the latter portion of 2009 (south rate = 8 L/hr, north rate = 12 L/hr) (Figure 6.1). The south drain discharged 3.29 m$^3$ more effluent than the north drain, even though the north drain flowed 2 days longer than the south drain. Analysis of core taken from the northern end of the experimental plot uncovered a 30 cm sand unit at approximately 1.5 m below ground surface that extended laterally north. This sand unit could act as a drain, transporting fresh irrigated water past the north tile drain and beyond the limits of the plot, thereby reducing the volume of water captured by the north tile.

A r ough calculation t o determine t he v olume o f w ater n eeded t o o vercome t he initial s oil mo isture d eficit a nd r aise th e w ater ta ble to th e level o f t he tile d rains suggested that theoretically, 18 m$^3$ of water was needed. In total, 63.6 m$^3$ of irrigation water w as applied b efore t he south dr ain be gan t o f low. It i s postulated then t hat t he additional applied irrigation (45.6 m$^3$) could have been lost to evapotranspiration, lateral losses beyond the plot or into the deeper B and C sand units.

*6.1.3 2009 DFBA Results*

6.1.3.1 Tile Drain Effluent

The DFBA tracer was applied on August 18, 2009 (day 230) and initial detection of DFBA in the tile drain effluent was observed 46.75 hours later in both north and south tile dr ains (Figure 6.1). T racer c oncentrations i n bot h nor th a nd s outh tiles f ollowed a similar upw ard t rend w ith f luctuations t hat a re t hought t o be a f unction of irrigation/precipitation events. The infiltration depth of the tracer during the 2009 season was n ot ex pected t o b e greater t han 1 m because a pplication of t he t racer o ccurred relatively late in the season and only 298 mm of water was able to be applied post DFBA application. Assuming uniform plug or piston-type flow, a quick calculation suggests the center o f DFBA mass would migrate to depths of up t o 0.75 m eters be low surface (298 mm of water applied divided by an average measured porosity of 0.40 e quals a depth of 0.745 meters). P eak DFBA c oncentrations of the north and s outh tiles were 5.23 m g/L ($C/C_0 = 6.04 \times 10^{-3}$) and 2.36 m g/L ($C/C_0 = 2.72 \times 10^{-3}$), respectively. Overall, 0.45% of the total tracer mass was captured in the tile drains during the 2009 irrigation season.

Due to the quick breakthrough of the tracers (46.75 hours) in the low permeability soils, it is evident that the primary mode of solute transport to the tile drains is through the macroporosity present on site. Furthermore, the low DFBA concentrations measured in the effluent combined with the low mass captured in the tile drains at the end of 2009 (0.45%) suggests the low permeability soils are retaining most of the DFBA. The quick breakthrough times measured in the tile drains support the findings of a similar studies conducted by Richard and Steenhuis (1988), Kung et al., (2000) and Zehe and Fluhler (2001). All studies mentioned measured breakthrough times to tile drains between 0.3 – 4.0 hours after tracer application and concluded the quick breakthrough times were likely caused by macropores acting as preferential flow pathways. The slower DFBA breakthrough time measured at the Devon research site could be caused by a lower matrix hydraulic conductivity or a smaller macropore density.

6.1.3.2 Monitoring Wells

Two sampling events occurred during the 2009 field season, one on August 28 (day 240) and the second on October 7 (day 280). All samples were taken from the A series wells completed at a depth of roughly 2 m because no B or C series wells were yet installed. The DFBA detections in the monitoring wells (Figure 6.2) were located primarily along the northern edge of the plot. Monitoring wells MW09-01, MW09-08, MW09-12A and MW09-09 all showed DFBA detections for both the August and October sampling events, while wells located in the southern portion of the plot (MW09-06, MW09-07) showed no DFBA detections. Monitoring well MW09-05 in the south-central region of the plot had a single detection during the August sampling event (0.17 mg/L)

but no DFBA was detected during the October sampling event. Concentrations of DFBA detected in the monitoring well samples averaged 0.74 mg/L while the maximum and minimum concentrations were 4.09 ($C/C_0 = 4.72\times10^{-3}$) and 0.11 mg/L ($C/C_0 = 1.27\times10^{-4}$) (excluding non-detects). The monitoring well detections support the observed DFBA breakthrough in the tile drains. The quick breakthrough of the DFBA to the monitoring wells indicates that macropores were allowing for rapid transport at depth, but the low concentrations suggest that the low permeability matrix is retaining the bulk of the DFBA mass in the upper portion of the soil profile.

There are a number of possible explanations for the spatial variability in DFBA concentrations measured in the monitoring wells. One possible reason is the non-uniform application of irrigation water as indicated by the consistent water ponding in the northern half of plot A. This could have caused a larger amount of DFBA to be applied in the northern half of the plot relative to the south, increasing the likelihood of monitoring well detections of DFBA in northern monitoring wells. Additionally, the ponding observed in the northern half of the plot could initiate an increased number of preferential flow pathways. Increasing the number of preferential flow pathways by increasing the irrigation intensity was observed by Gjettermann et al., (1997) and could explain the increased DFBA detections in the monitoring wells located in the northern half of Plot A.

Another interesting observation is DFBA detection measured outside of the plot in MW09-12A. The remaining monitoring wells located outside of the plot showed no

detections th roughout 2 009 s o it w as th ought th at little la teral tr ansport was o ccurring. The M W09-12A D FBA de tections c ould be e xplained b y t he p resence of a hi gher hydraulic c onductivity 3 0 c m t hick s and l ens l ocated approximately 1.5 m eters be low ground surface below MW09-01. If this sand lens were to extend laterally north, it would allow for preferential flow of DFBA to migrate in the direction of MW09-12A.

6.1.3.3 Tracer Degradation and Sorption Tests

Batch tests were performed to test the potential for sorption of DFBA and PFBA on soils from four depths at the site. Appendix B summarizes the results from the batch tests performed on each tracer. In general, the tracers were found to be conservative at both low (<15mg/L) and high (>15mg/L) concentrations. A linear isotherm was created for both PFBA and DFBA using the results from all four soil depths and the calculated distribution coefficients for each tracer represent the upper limit for sorption. A n upper limit for the distribution coefficient of 0.0789 $cm^3$/g and 0.0678 $cm^3$/g was calculated for DFBA and PFBA, respectively. Assuming a bulk density of 1.40 g/$cm^3$ and a porosity of 0.35, this equates to a retardation factor of 1.3 for both DFBA and PFBA. To determine if an y m easureable D FBA d egradation c ould be observed, a l aboratory e xperiment w as designed to test if DFBA degraded over time. As previously discussed in Section 4.7.5, no measurable DFBA mass loss was observed over the test period. Results are shown in Appendix B

6.1.3.4 Soil Extractions

Soil cores were taken at the end of the 2009 field season and analyzed at various depth intervals for DFBA. Results of the soil extractions for DFBA are shown in Figure 6.3. Cores were taken from a North-South transect through the center of the plot (Figure 4.8) and core depths ranged from 1.7 m (over tile) to 5.6 m. Calculated DFBA pore water extract concentrations in the top 10 cm of the soil profile ranged from 233 to 0 mg/L with higher concentrations of DFBA located in the southern portion of the plot. The site averaged depth profile (Figure 6.3) indicates 55% of the initial input DFBA mass lies in the top 10 cm of the profile and 83% of the initial mass lies in the top 20 cm. In total, 116% of the DFBA mass was accounted for in the soil extractions at the end of the 2009 field season (Table 6.2). The lack of overall movement of the tracer mass within the soil profile indicates a minimal amount of vertical advective transport occurs through the soil matrix. Vertical transport in the low permeability surface soils is mainly controlled by macroporosity (fractures, root holes) and is the primary cause of flow DFBA concentrations at depths of up to 5 meters. These results are similar to the findings of a study conducted by Chen et al., (1999) in that 40 days after a surface applied bromide application; the center of bromide mass resided in the top 26 cm of the soil profile, while bromide was detected at low concentrations in the deepest sample at 60 cm. These results suggest that preferential flow (macropores) were able to quickly transport solutes at low concentrations, deep into the soil profile while the majority of the mass remains close to the surface.

The s mall n umber o f soil s amples r esulted in  a r elatively la rge  amount o f uncertainty i n  the e xtraction r esults.  T his  may, i n pa rt, e xplain t he 116 % D FBA m ass recovery i n t he s oil ( Figure 6.3) .     Increasing t he s ample s ize t o acco unt f or heterogeneities within the soil could decrease the error of the total mass accounted for in the soil.  An additional source of error within this measurement is found in the extraction procedure used to remove DFBA from the soil.  As previously discussed in Section 4.7.4 the DFBA extraction technique for the soil samples was tested and showed that 32.5% of the DFBA r emained on t he s oil on a verage.   Although, t he r eported r esults ha ve be en corrected t o a ccount f or t his unr ecovered t racer m ass, t here i s l ikely t o be  va riability between samples.  Fine-tuning the soil extraction process used for the DFBA would also decrease the uncertainty within the measurement.

## 6.2 2010 Field Results

### 6.2.1 Tile Drain Flow Response

The 2010 f low results (Figure 6.4) yielded s ignificantly different results than the 2009 season as both north and south tiles were flowing prior to irrigation.  A verage flow rates and cumulative discharge volumes were higher for both the north and south tiles in 2010.  O ne e vent t hat ha d a  m ajor i nfluence on t ile dr ain be haviour w as a  l arge precipitation event that occurred on J uly 13 (day 194), which applied 51.7 mm of water over a 24 hour p eriod.  The s outh t ile ha d a pe ak di scharge r ate of 203  L/h, 3.4 t imes greater t han t he nor th t ile ( 62  L/hr) du ring t he J uly 1 3 rainfall ev ent.  T he c umulative discharge i n 2010 w as  78.5 m $^3$  from t he s outh t ile a nd 60.1  m $^3$  from th e n orth tile .  Altogether, t he t iles c aptured t he e quivalent o f 51 %   of  t he a pplied w ater vol ume

(including irrigation and precipitation). The tile drains in 2010 were able to capture a total volume of 9.7 times more water than in 2009.

Both north and south tile drains responded very similar (almost identical) to all irrigation and precipitation events in 2010, with the notable exception of the large July 13 rainfall event. One observation made during the 2010 season was the plateau reached by the north tile's discharge during the July 13 event. The north tile was not able to flow beyond 62 L/hr which differed from the south's response during the same period. One hypothesis for this behaviour is that the sand lens (previously discussed in Sec 6.1.2) located in the northern half of the plot could function as a lateral drain when exposed to saturated conditions. This sand lens could limit the volume of water available to be captured by the north tile drain by transporting any excess water laterally away.

One of the key reasons for the difference between the 2009 and 2010 seasons was the lack of soil moisture present at the start of the 2009 field season that severely hindered tile drain effluent production. The winter leading into 2009 saw a "below average" to "very low" snowpack in the Devon research site region as defined by Alberta Agriculture (Alberta Agriculture, 2009), which amplified the drought conditions experienced in the region. The large amount of winter precipitation prior to the 2010 field season (approximately 90 mm more than the previous year) helped replenish the soil moisture deficit, increasing the water table elevation and resulting in earlier tile drain production. Continual precipitation and irrigation throughout the summer helped maintain wet conditions on site, allowing for a more consistent tile drain flow.

*6.2.2 Hydraulic Response in Monitoring Wells*

Only the 2010 hydraulic head data will be discussed due to the limited number of large irrigation events and the limited number of monitoring wells present in 2009. Results presented in Wilkinson (2011) show that the hydraulic response to precipitation and irrigation events in each set of wells (A,B,C series) provide an understanding of how each unit is connected hydraulically and how each response is influenced by the lithology that the well is completed in.

It is assumed that the A series wells have a strong hydraulic connection to the ground surface because of the quick response to irrigation and precipitation events. The degree of hydraulic connection is also supported by the rapid detection of DFBA in monitoring well samples (Sec 6.1.3.2). Monitoring wells completed next to tile drains (MW09-04, MW09-03 and MW09-12A) showed little hydraulic response during minor irrigation and precipitation events (less than 25 mm). This is likely because the tile drains regulated the hydraulic head in these monitoring wells dampening the hydraulic response. The hydraulic response of the B and C series monitoring wells was similar to the A series wells when irrigation events occurred, but the magnitude of the responses was lower. This suggests that although both B and C series wells are influenced by irrigation events, their connection to the glaciolacustrine unit is buffered by the glacial till layer.

The seasonal hydraulic gradient between the A-B and B-C series wells indicated that localized flow is mostly in a vertically downward direction. One exception to this was the upward hydraulic gradients observed at the beginning of July that lasted roughly two weeks, likely caused by an increase in evapotranspiration. The large volume of water applied during the July 13 rain event then caused a reversal in vertical flow gradients between the A and B series lithological units. Immediately after the large rainfall event the hydraulic gradients reversed, showing a downward groundwater flow direction. Roughly one week after the large rain event, the vertical gradient reversed again, moving water from the B series sand unit upwards. As discussed in Wilkinson (2011), this is likely due to the over-pressurization of the B series sand unit relative to the glaciolacustrine unit.

Advective transport of tracer will follow this gradient and flow in the direction of the groundwater. For a large portion of the season, this would be towards the C series sand unit. Low concentrations of DFBA have been found in monitoring wells samples taken from the C series sand (Sec 6.2.3.2 and Appendix A) which lends support to the idea that measureable flow exists between the major lithological units on site. The fact that solutes are able to be transported to the deeper sand layers is troublesome in terms of salt remediation due to the higher hydraulic conductivities these sands exhibit. Once DFBA and salts are transported to these lower sand units, increased lateral flow will likely occur, carrying the salts and DFBA beyond the limits of the tile drains.

*6.2.3 2010 DFBA Results*

6.2.3.1 Tile Drain Effluent Concentrations

The 2010 DFBA tracer results (Figure 6.4) showed a more dynamic response to irrigation and precipitation events than the 2009 DFBA results (Figure 6.1). The tiles were able to capture 6.6% of the initial applied mass, representing 13 times more mass than the 2009 results. The south tile captured 64% more mass than the north tile through 2010 because it typically had higher DFBA concentrations and higher flow volumes than the north tile. One reason for the difference in DFBA mass captured between the north and south tile drain is due to the July 13, 51.7 mm precipitation event in which the south tile captured nearly twice as much DFBA mass as the north tile. Peak DFBA concentrations for the north and south tiles were 3.44 mg/L and 4.97 mg/L, respectively.

One observation of the 2010 tile effluent DFBA concentrations was the concentration response in both north and south tiles to the large July 13 precipitation event. The traditional response of tile DFBA concentrations early in the season was to increase simultaneously with increased tile flows, whereas the large flow increase during the July 13 flow event caused a sharp decrease in DFBA concentrations. This sharp decrease could be caused by the large influx of fresh water. The excess loading of fresh water on the surface allowed the macropores to continually transmit water to the tile drains, flushing the macropores clean of most of the DFBA. Only DFBA stored in the matrix was available for transport to the tile drains once the initial macropore flush occurred. Supplying the macropores with DFBA would then be dependent on the delivery of DFBA from the matrix into the macropore domain, occurring via diffusion

and advection. During the July 13 rainfall event, the solute transfer rate occurring from the matrix into the macropores was not able to replenish the macropores with DFBA quickly enough to maintain a steady concentration. All DFBA that was transferred into the macropore continually got flushed due to the fresh water influx, resulting in a concentration drop measured in both the north and south tile drains. This observation is important in that future irrigation planning should try to avoid such occurrences. A decrease in solute concentration in the tile drains would likely be observed when a volume of water is applied to the surface that exceeds a specific "threshold" volume. This is due to the limiting rate at which solutes can move from the matrix domain into the macropores. A rough estimate from the 2010 data indicates that when a water depth of over 40 mm is applied to the surface the resulting tile drain flux will be greater than 35 L/hr. Analysis of the tile data shows that once the tile drains (north and south) exceed a discharge of 35 L/hr, the DFBA effluent concentrations drop as shown in the 2010 DFBA tile drain data. An irrigation management plan should be developed that would take into consideration this matrix-macropore transfer rate and base the irrigation volume/frequency applied on maximizing the mass of solute flushed per unit volume of irrigation water.

Another interesting observation is the switch of the north and south effluent DFBA concentrations between the 2009 and 2010 seasons. During the 2009 season, north tile DFBA concentrations were consistently higher than the south, but the 2010 data shows the south tile consistently had higher concentrations than the north. Currently no working hypothesis has been formed to explain why the switch occurred.

6.2.3.2 Monitoring Well Detections

Monitoring w ell s ampling oc curred f ive t imes dur ing t he 2010 s eason a t approximately 30 day intervals from June through to October (Appendix A). Figures 6.5, 6.6 a nd 6.7 s how t he m onitoring w ell D FBA c oncentrations dur ing t he f ive s ampling events i n t he A , B and C s eries w ells, r espectively. T he s patial di stribution of D FBA detections t hat oc curred dur ing t he 2009 m onitoring w ell s ampling i s r epeated i n t he 2010 samples. MW09-01, MW09-12A, MW09-09 and MW09-08 near the northern edge of the plot all show consistent DFBA detections throughout the 2010 season (Figure 6.5). Additionally, deeper wells in the northern portion of the plot (MW10-12B & C, MW10-15B & C) showed DFBA tracer detections, although at lower concentrations (Figure 6.7 and 6.8). A greater pr oportion of A s eries w ells s howed D FBA de tections i n t he 2010 season ( 11 of 12) when compared t o the 2009 s eason ( 4 of 12). S everal of t he A series wells lo cated i n t he s outhern ha lf of t he pl ot ( MW09-06, M W09-04, M W09-03) ha ve consistent D FBA de tections t hroughout t he 2010 s eason w hich di ffers f rom 2009. T he increase in A series DFBA detections suggest that the DFBA mass is migrating vertically down t he s oil pr ofile t hroughout t he i rrigation pl ot.

During t he 2010 s eason, no upw ard o r dow nward concentration t rends w ere observed i n a ny o f t he A, B or C s eries m onitoring w ells. T he l ack of de crease or increase i n D FBA concentrations m akes i t di fficult t o s peculate on t he l ocation of t he DFBA cen ter o f m ass. D FBA de tections i n bot h B a nd C s and uni ts i ndicate t hat transport (most likely via macropores) is occurring across the glacial till units overlying

both t he B and C s and units. T he B a nd C s eries m onitoring w ell d etections l ocated outside of the plot suggest that increased lateral flow occurs in the deeper B and C series sand uni ts r elative t o t he uppe r glacial uni ts. N o obvi ous s patial c orrelation e xists between DFBA detections in the monitoring wells and the tile drains.

6.2.3.3 Suction Lysimeter Concentrations

Two nests of suction l ysimeters were installed at the beginning o f the 20 10 field season, one in the c enter of the pl ot (South) between tile dr ains and the other a bove the north tile drain (North) (Figure 4.4). Similar to the monitoring wells, the lysimeters were sampled five times throughout the season at approximately 30 day intervals from June to October. B oth no rth a nd s outh l ysimeters ne sts s how c oncentrations decreasing with time be tween t he J une and O ctober s ampling e vents ( Figure 6.8) , s uggesting ve rtical migration of D FBA t racer i s oc curring. P eak c oncentrations i n t he s outh l ysimeter ne st reached 30.4 m g/L while the north nest reached a peak concentration of 18.5 m g/L, both occurring at a depth of 30 cm during the June sampling event. The measured decrease in DFBA concentrations in both north and south lysimeters suggest that matrix flushing is occurring and that DFBA mass is being transported vertically downwards.

One of the noticeable changes that occur during the 2010 season is the increasing DFBA c oncentration w ith time in th e th ree lo wer s ampling lo cations paired w ith th e decreasing D FBA c oncentration i n t he uppe r t wo s ampling l ocations i n t he nor th lysimeter nest. T his s uggests t hat f lushing i s oc curring i n t he t op 30 c m of t he s oil profile, while DFBA is migrating deeper into the soil. This is also observed in the south

lysimeter n est, b ut n ot t o t he s ame d egree. D ecreases i n D FBA co ncentrations ar e measured in th e to p th ree l ysimeters, p aired w ith s light in creases in th e b ottom tw o lysimeters. T he di fferences i n D FBA flushing between t he no rth a nd s outh l ysimeter nests c ould b e c aused b y the p roximity to th e tile d rains. T he n orth l ysimeter n est is located di rectly above t he nor th t ile dr ain, w hich s hould c ause e nhanced fluid dr ainage and an increase in solute movement. The tile drain could enhance drainage by creating a lower w ater t able w hich i ncreases t he u nsaturated z one d irectly above t he d rain. T his unsaturated zone could enhance the solute transport relative to areas with a higher water table. The south nest, which is situated in the center of the plot and away from the tile drains, should experience less drainage due to the lack of tile drain influence.

Uncertainty arises w hen i nterpreting t he l ysimeter d ata d ue t o t he v ertical separation b etween s ampling poi nts. T he five s ampling poi nts c over 1. 5 m eters d epth, translating into a relatively coarse depth profile. It is difficult to determine whether the center of m ass actually m oves f urther dow n t he s oil c olumn due t o the a bsence o f intermediate sample locations between 30 and 60 cm depth.

6.2.3.4 Soil Extraction

A total of 42 boreholes with depths ranging between 1.5 and 6 m were drilled in a grid pattern across the plot at the end of the 2010 field season to aid in characterizing the DFBA tracer distribution (Figure 6.9). A total of 394 samples were analyzed. The results from the soil extractions showed that 55% of the mass measured in the cores was situated in the top 75 cm of the soil profile (Figure 6.3). In total, 32% of the applied DFBA mass

was accounted for in the soil extractions. Samples taken to a depth of 1.5 m outside the plot (Figure 4.7) all showed non-detectable levels of DFBA indicating that little lateral transport is occurring in the upper 1.5 m. In total, 16 of the 26 profiles show a similar distribution with the center of mass residing between 25 and 75 cm below ground surface (Figure 6.9 and Appendix C). The fact that the DFBA depth profiles show similar distributions between boreholes is somewhat surprising given the high level of lithological heterogeneity observed. Results from the 2010 DFBA soil extraction support previous observations that advection within the low permeability soil matrix is quite slow and accounts for a small amount of DFBA transport.

Four of the five soil cores located on the northern edge of the plot (boreholes 64-67) show non-detections for in samples located above 1 m. This indicates that solutes are being transported quickly enough that nearly all DFBA has been transported beyond 1 m depth. This supports the quick breakthrough of DFBA in the monitoring wells located in the northern edge of the plot. This quick breakthrough and enhanced solute transport can be caused by an increased macropore density relative to other sections in the plot, or increased macropore flow due to surface ponding as previously discussed in Sec 6.1.2.

A similar pattern is observed in the southern edge of the plot with 3 sample locations (62, 68 and 69) showing a comparable depth distribution. It would be expected that increased DFBA monitoring well detections would be measured in samples taken from the wells located in the southern half of the plot, but that did not occur. Boreholes located above the tile drains all produced similar depth distributions with the center of

mass lying between 0.5-0.7 meters below ground surface. In total, it appears that the top 50 c m of s oil a re be ing f lushed of D FBA in 14 of the 26 bor ehole l ocations. Additionally, it appears that boreholes located above the south tile drain are experiencing greater f lushing c ompared t o t he bor ehole l ocated a bove t he nor th t ile due t o t heir decrease in DFBA in the top 50 cm. B oreholes located in between the north and south tile drains appear to be experiencing the least amount of DFBA flushing which supports the l ysimeter r esults ( Sec 6.2.3.3) i n that l ocations a bove t he t ile dr ains a re be ing m ore efficiently flushed, relative to locations in between the tile drains. Although results from all soil core samples showed an increase in DFBA infiltration compared to the 2009 s oil extraction results, and showed an overall mass reduction of DFBA indicating that matrix flushing is occurring, these spatial concentration differences could be due to the varying initial distribution of DFBA. Unfortunately no initial DFBA concentration distribution was m easured di rectly after application, s o no certain c onclusions c an b e m ade on t he spatial differences in DFBA flushing. Literature searches have been unable to find any studies that have tracked solute movement in tile drained, macroporous soils over a two year time period, making it difficult to compare the results found.

Although a l arge portion of t he 1.5 m DFBA de pth pr ofiles ha d non-detectable DFBA f or m any o f t he d eepest s amples ( 80-90 c m), ni ne of t he b oreholes ha d a continuous detection of DFBA extending to the deepest sample available. This indicates that some of the DFBA mass could have been left unaccounted for below the maximum sampling depths. Because a small portion of the boreholes (4 of the 42) extended beyond

1.5 m depth and DFBA has been recovered in cores as deep as 5 meters, a degree of uncertainty arises on where the DFBA mass is residing below 1.5 meters.

6.2.3.5 DFBA Mass Balance

The total DFBA mass accounted for at the end of the 2010 season was 38% of the initial applied mass (Table 6.3). The tile drains were able to capture 6.5% of the initial applied mass during the 2010 season, giving a total tile drain capture of 7.0% of the initial mass over the two seasons. Extractions of DFBA from the soil cores accounted for 32% of the total mass remaining in the soil. Of the mass that remained in the soil profile at the end of 2009, 73% of that mass was removed by the end of the 2010 field season. One possible mechanism that could account for the loss of DFBA is transport into the lower sand units, presumably along macropores. This is indicated by DFBA detections in the monitoring well samples collected in both B and C sand units. Due to the lateral hydraulic gradients and increased hydraulic conductivity values measured in the B and C unit sands, the mobility of the DFBA would increase in the sand units and potentially be transported down gradient away from the site. The possibility for DFBA degradation has been tested (Sec 4.7.5) and has shown that no measureable degradation occurs.

*6.2.4 PFBA Injection Results*

Two PFBA injections occurred over a two day period between July 20 and 21, 2010. The first injection occurred above the north tile at a depth of 1.72 m and breakthrough was monitored at the tile drain sump. Initial breakthrough of PFBA took

place 13 hour s a fter i njection, w ith t he pe ak concentration a rriving 32.2 hr s a fter application (Figure 6.10). A pproximately 75% o f the total P FBA mass w as c aptured in the north tile drain over a 58 day period. The breakthrough curve characteristics suggest two di fferent m echanisms c ould i nfluence the P FBA t ransport t o t he t ile dr ain. Macropores a re m ost l ikely r esponsible f or t he qui ck i nitial br eakthrough a nd concentration pe ak, w hile t he s ustained P FBA c oncentration a fter t he r ecession of t he peak i s a ttributed t o s lower di ffusive t ransport f rom the m atrix i nto the m acropores followed by rapid transport to the drain. This second "matrix diffusion" mechanism was first not ed b y Foster (1975) a nd h as be en s hown t o e ffectively reduce t he rate of migration of solutes through macropores (Maloszewski and Zuber, 1993; Shapiro 2001).

The s econd P FBA i njection oc curred i n M W09-13A on J uly 21. T he i ntent of this injection was to examine how hydraulically connected the upper glaciolacustrine unit is t o the l ower B s eries s and uni t. R outine s amples w ere collected ev ery 6 h rs f rom MW09-13B and analyzed for PFBA. N o detection of PFBA oc curred within the 72 day sampling program. A lthough the absence of PFBA in MW09-13B samples suggests that a limite d h ydraulic c onnection e xists b etween e ach u nit, a s imple explanation is th at PFBA detection in MW09-13B was unlikely from the onset of the experiment due to the low probability that the injected PFBA would be captured by MW09-13B. Therefore, no conclusions can be made from the results of the second PFBA injection.

**6.3 Model Calibration and Sensitivity Analysis**

*6.3.1 Calibration*

<u>6.3.1.1 Flow Parameters</u>

Calibration of the flow and transport model was done primarily by comparing observed and simulated water and DFBA tile drain fluxes. Additionally, matching observed hydraulic heads in monitoring wells (MW09-01, MW09-03, MW09-05, MW09-13A and MW09-13B) helped calibrate the flow and transport model. Water tile drain fluxes and hydraulic head measurements were calibrated by modifying the hydraulic parameters of each soil layer within the model (top soil, glaciolacustrine, glacial till, B series sand). Calibration of the upper infiltration unit was not required because it only served to limit the amount of water lost to runoff.

Initially, van Genuchten matrix parameters were taken from the measured values obtained from the pressure plate extraction and further adjusted when needed. Calibration of each parameter was done systematically by changing a specific variable (ex. $K_{sf}$) for an individual material and documenting the results. The main variables used to calibrate the model were the macropore hydraulic conductivity variable ($K_{sf}$), macropore volume ($\omega$) and matrix block half width (*a*). The results showed that the model was highly sensitive to changes in these variables. Table 6.4 provides a summary of the affect each of the main calibration variables had on the tile drain flow in the numerical simulations. Initial values for the calibrated variables were set using literature values used in similar modeling exercises (Simunek et al., 2003; Gerke and Kohne, 2004; Gardenas et al, 2006). All remaining hydraulic parameters ($\gamma$, $\beta$, $\theta_{rf}$, $\theta_{sf}$ and

*l*) w ere s et u sing l iterature s ources. T he m odel's s ensitivity t o t hese p arameters w as minimal and it was determined they would be omitted from the calibration procedure.

6.3.1.2 Transport Parameters

The main solute transport calibration parameter was the mass transfer coefficient ($\alpha_s$) between the matrix and fracture domain. This parameter characterizes the exchange of solutes between the matrix and macropore domains. Calibration of $\alpha_s$ was done step-wise s imilar to th at o f th e p revious c alibration o f the h ydraulic f low p arameters. Calibration w as a chieved b y m atching t he obs erved D FBA c oncentrations i n t he s outh tile dr ain m easured i n 2 010. A ba se va lue o f 0 .05 w as us ed (HYDRUS de fault) a nd several s imulations w ere r un w ith d ecreased or i ncreased v alues. The c alibration procedure w as completed b y matching t he hi gh and l ow obs erved D FBA c oncentration peaks with the simulated peaks.

*6.3.2 Sensitivity Analysis*

Sensitivity a nalysis o f th e mo del p arameters w as d one s imultaneously with th e calibration procedure. This was primarily completed by evaluating the goodness of fit of the s imulated tile d rain flow r esults a nd DFBA tile d rain c oncentration r esults to th e measured d ata. Q uantitative ev aluation w as conducted b y calculating t he r oot m ean square e rror ( RMSE) ( Equation 6.1) be tween s imulated, $x_s$, and observed r esults, $x_o$, as follows:

$$RMSE = \sqrt{\frac{1}{n}\sum(x_m - x_s)^2} \qquad (6.1)$$

where $n$ is the number of data points. This allowed all model simulation results to be compared against each other in a consistent manner. A large number of simulations were conducted in a systematic fashion by varying one parameter at a time and evaluating the quality of the simulation results using the RMSE and visual observations of the goodness of each fit. Although the RMSE method provides a quantitative measure for comparing simulations, it can occasionally be misleading. Therefore, the ability of the model to match the timing and magnitude of fluctuations in tile drain flow and tile effluent concentrations was also used to evaluate the simulation results.

As part of the calibration process, a set of parameters that was determined to be the "best fit" to both observed tile drain flow and tile drain effluent DFBA concentrations was arrived at. This set of parameters will be referred to as the base case and are summarized in Table 6.5. Note that the RMSE results for all sensitivity analysis runs have been normalized by dividing the simulated RMSE values for any given run by the base case RMSE values. The sensitivity analysis focused primarily on the hydraulic parameters in the glaciolacustrine unit because they tended to have the largest influence on the flow system response. The parameters tested were $n_m$, $\alpha_m$, $K_{sf}$, $K_{as}$, $a$, $\omega$ and $\alpha_s$. The changes in normalized RMSE for selected sensitivity runs are presented in Table 6.6 and the corresponding influence on tile drain flow and concentration response is given in Figures 6.11 and 6.12. The parameters that caused the largest change in the RMSE

results were the *a* (matrix block half width) and ω (macropore volume) variables for both simulated tile drain flow and solute transport and $\alpha_s$ for solute transport (Table 6.6). Changes in $K_{sa}$, $\alpha_m$, $n_m$ and $K_{sf}$ had a relatively small (up to 12%) influence on calculated RMSE values but impacted the timing and shape of the tile flow peaks in comparison to the observed data (Figure 6.11).

## 6.4 Simulated Flow Results

### *6.4.1 Tile Drain Discharge*

Flow was simulated by modeling a 138 day period spanning from May 29, 2010 (day 149) until October 13, 2010 (day 286). Only flow from the south tile was simulated as it offered the greatest magnitude of change between high and low flows. The model results showed that the dual-permeability method accurately captured the timing of peak flows during the simulation period, but overestimated tile drainage during the simulation period (Figure 6.13). The July 13 (day 194) rainfall peak was the only event in which the model underestimated flows. Additionally, results from the flow simulations showed that macropores accounted for 99% of the cumulative tile drain flow. Overall, the model overestimated flow by 50% with the tiles capturing 80% of the irrigation water volume applied to plot A (irrigation + precipitation without subtracting evapotranspiration) compared to the actual measured amount of 51%. In order to successfully simulate the cumulative flow volumes the macropore contribution must be reduced. Reducing the amount of flow contributed by the macropores by decreasing $K_{sf}$ and ω values (see Figure 6.11, $K_{sf}$ value of 5000 mm/day) allowed the correct cumulative flow volumes to

be simulated, but the timing of the tile drain response to irrigation/precipitation events was adversely affected (Figure 6.11).

One possible reason for the overestimation in tile drain flow is an inaccurate flux boundary condition used for the top of the model. Underestimating the evapotranspiration component of the flux will lead to an overestimation of infiltration, which would increase the amount of water in the domain. The model's overestimation of tile drain flow could also be due in part to the lack of drainage from the base sand unit (B series sand). Flow within this unit is limited by the fact that it can only enter or exit at the lateral edges of the model domain (1D), whereas realistically flow in the lower sand unit could move radially (2D) or vertically down into the underlying till unit. As discussed in a similar modeling exercise completed by Gardenas et al. (2006), the dual permeability approach does an excellent job at matching peak drain response, but overestimates the total drain flow due to a lack of drain bypass into the deeper units.

Another explanation for the overestimation in the simulated drain flow is the absence of vertical anisotropy due to computational limitations. Soil fractures and root holes at the site have been observed to be near vertical, which is expected to give rise to increased permeability in the vertical direction relative to the lateral directions. This anisotropy in the macropore domain currently cannot be simulated with HYDRUS. Furthermore, representing a heterogeneous, 3 dimensional system with a 2 dimensional, homogenous model will create difficulties when attempting to match observed field data with the simulation results. The lack of vertical anisotropy may mean that vertical and

horizontal flow components in the macropores are not being accurately represented. If vertical anisotropy were implemented in the model, it would increase the magnitude of flow occurring vertically, while decreasing the lateral flow component. Reducing the amount of lateral flow in the macropore domain should decrease the effective capture zone of the tile drains, resulting in an increase in the amount of flow bypassing the tile drains and decreasing the total volume captured by the drains. Further work is needed to characterize the measurable vertical anisotropy in soil cores from the site. Additionally, incorporating vertical anisotropy in both matrix and macropore domains in the numerical model should produce more realistic results. Currently, no substantial amount of research has been done in the scientific community on characterizing vertical anisotropy in macroporous soils and this is an area that could benefit from additional research.

*6.4.2 Hydraulic Head Response*

The simulated hydraulic heads were similar to the observed hydraulic heads in the response to irrigation events throughout the simulation period, but were consistently underestimated relative to the observed heads (Figure 6.14). This underestimation could also be attributed to the lack of vertical anisotropy in the simulations. Decreasing the amount of lateral flow occurring in the domain would reduce the overall amount of drainage occurring, resulting in an increase in hydraulic heads throughout the domain.

Temporally, the simulation did an adequate job at matching changing hydraulic heads with time (Figure 6.15). Simulated hydraulic heads for selected monitoring wells were able to capture some of the time varying fluctuations. All simulated monitoring

wells respond similarly to the large July 13 precipitation event, but differ in how they respond before and after. The simulated response of monitoring wells located on the north and south edge of Plot A (MW09-01 and MW09-05) were able to match the observed response with better accuracy than wells located in the center of the plot (MW09-13A). Results from monitoring well MW09-03, which is located close to the south tile drain, appear to be the least accurate as they are underestimated by approximately 0.5 meters throughout the entire simulation period.

The primary reason why the fixed head boundary conditions were used instead of a no flow symmetry boundary (Figure 5.3) was due to the lateral influx of water observed when the water table surrounding the plot increased in July and August of 2010. Although the total volume of water entering the domain was minimal, the model was able to successfully capture the influx of water along the boundaries on both the north and south sides. The overall impact this influx had on the simulated results is minimal as less than 0.01% of water entered the domain from these hydraulic boundaries. It would be recommended for future simulations to simulate this boundary as a no flow boundary, which would significantly reduce computational time.

### 6.4.4 Simulated Fluid Mass Balance

Results from the simulated fluid mass balance show that 64% of the applied water volume equivalent exits the domain via the tile drains during the simulation period. The B series sand unit accounts for less than 1% of the flow exiting the system. Flow into and out of the domain through the glaciolacustrine head boundaries accounted for a very

small percentage of water flow (less than 0.01%). Transpiration accounted for 22% and evaporation accounted for 12% of water exiting the system. One possible factor contributing to the overestimation of the tile drain discharge could be the absence of vertical anisotropy in the domain. By implementing vertical anisotropy in future simulations, it is expected that tile drain discharge will decrease, while increasing the bypass to the lower sand unit.

## 6.5 Simulated DFBA Transport

### 6.5.1 Tile Drain Effluent Concentrations

The results of DFBA transport simulations are presented in Figure 6.16. The early time response of the simulated DFBA tracer is similar in both magnitude and timing to the observed south tile concentrations. As previously mentioned in Section 6.3.1.2, the simulated results track the observed data closely up until the July 13 rain event, when the simulated results begin to deviate considerably from the observed data. The simulated base case results show that 28% of the initial 2010 DFBA mass is removed during the 2010 field season, with 98% of that mass removed via the north and south tile drains. Macropores accounted for 99% of the DFBA transport to the drains, which is consistent with the simulated flow results. Field measurements show that of the initial DFBA mass in 2010, 31% remained at the end of 2010 (69% removed), indicating the model underestimates the total mass removal that occurred in 2010.

The large discrepancy between the observed versus simulated DFBA mass removal could be due to a number of factors. First, the model does not accurately

simulate the lateral migration of the tracer beyond the plot as observed in the monitoring well DFBA detections in 2009 and 2010. Second, transport of DFBA into the lower sand units and beyond is not able to take place due to the presence of a no flow boundary at the base of the simulated B series sand unit. The current no flow boundary condition is not allowing DFBA to infiltrate deeper, which could account for a portion of the discrepancy in tracer mass.

Although 98% of the tracer transport occurs via the macropores, the model results show that flushing of the matrix domain is occurring. This is important in terms of salt removal as the salt mass resides primarily in the soil matrix. Simulation results show that the main mechanism of advective solute transport is through the macropores, but flushing of the matrix is occurring due to the transfer of solute from the matrix to the macropores. The transfer of solutes from the matrix to the macropores is sustaining transport in the macropore domain, allowing the macropores to continually be supplied with salt or tracer

One challenge that regularly occurred during model calibration was attempting to fit the peak responses of the tile drain DFBA concentrations in both the early time (prior to 50 simulation days) and the late time responses (after 50 days) while simultaneously calibrating for fluid flow. As shown in Figure 6.12, manipulating the solute mass transfer coefficient ($\alpha_s$) allows for either early or late time simulated DFBA tile drain data to be matched to the observed DFBA tile drain data. Figure 6.12 illustrates that when using a $\omega$ value of 0.025 the simulation can successfully match the peak response of the DFBA in early and late time. But as shown in Figure 6.11, using the same $\omega$ value of 0.025, tile

drain f lows a re va stly overestimated t hroughout t he e ntire s imulation pe riod. This required a compromise on both ends to adequately fit the fluid flow and DFBA simulated data to the observed.

The d ifficulty e xperienced in s uccessfully f itting th e s imulated d ata to th e observed tile DFBA concentration data could be caused by the numerical representation of how the solute mass is initially distributed in the model. When the solute is partitioned into the matrix domain, the concentration is assumed to be distributed equally throughout the node (Figure 6.17a). T his approach doe s n ot a ccount f or t he va riable c oncentration distribution w ithin th e s oil ma trix th at w ould o ccur a s a r esult o f th e variable time allowed f or t he s olute t o m igrate o r di ffuse i nto t he m atrix ( Figure 6. 17b). M ultiple studies ha ve s hown t hat t he s olute c oncentration i s not e qually di stributed t hrough t he matrix-macropore r egion ( van G enuchten e t a l., 1984; A llaire-Leung e t a l, 2000) . A major factor controlling the matrix solute distribution is the length of time the solute has had t o m igrate or di ffuse i nto the ma trix b lock. A l onger e xposure time w ill a llow the solute to migrate d eeper in to th e ma trix, w hile a s horter e xposure time will r esult in a shallow solute distribution, close to the matrix-macropore interface (van Genuchten et al., 1984). T he short residence time of the DFBA tracer in this study translates into a solute distribution th at r esides c lose to th e matrix-macropore i nterface ( Figure 6.17b) . T he numerical r epresentation of t he s olute di stribution i n t he m odel doe s not a ccurately describe the processes occurring on site.

Another i ssue t hat m ust be t aken i nto a ccount i s t he e rrors t hat a rise w hen constructing an initial solute distribution from a limited number of core samples (Figure 4.8). T he l imited da ta s et t hat w as us ed t o c onstruct t he initial s olute d istribution contained a l arge u ncertainty b ecause o nly f ive b orehole l ocations w ere av ailable t o represent the DFBA depth distribution over the entire experimental plot. The alternative to using the 2009 D FBA core data would have been to use the north and south suction lysimeter r esults. T his was n ot co nsidered b ecause t here w ere ev en f ewer l ysimeter locations available (only two locations with five sampling depths at each).

*6.5.2 Lysimeter Concentrations*

Observation nodes were inserted into the model domain at the same locations and depths as t he l ysimeters i n t he s outh n est. The s imulated a nd obs erved c oncentration profiles in the lysimeters are shown in Figure 6.18. C omparisons between the observed and s imulated r esults in dicate th at t he m odel i s cap turing t he d ecrease o f D FBA m ass through the 2010 season, but is unable to simulate the observed change in vertical DFBA distribution for each simulated sampling event. The simulated results show the center of mass moving vertically down the soil profile through the field season. This is not shown in the observed lysimeter results as the center of mass remains situated at 30 cm depth and doe s not a ppear t o migrate dow nward. D iscrepancies be tween t he s imulated a nd observed r esults s uggest th e mo del is o verestimating th e d egree o f tr acer mo vement through the soil profile. The results from the simulated lysimeters suggest that too much vertical t ransport i s o ccurring i n t he m odel. T his i s s hown b y t he l arge i ncrease ( 3.2 mg/L) in DFBA concentrations in the simulated 1.5 m lysimeter that was not measured in

the field. Although the field lysimeter does show a slight increase (0.72 mg/L) in DFBA concentration, the simulations overestimate the DFBA increase at depths of 1.5 m.

The simulated lysimeter results also did not properly capture the low tracer concentrations present below 90 cm, which were observed in the south lysimeter. This problem is likely due to the initial vertical DFBA distribution used in the model. The initial depth distribution for the transport simulation was determined using the 2009 DFBA soil extraction results (Figure 6.3) and not the June 2010 lysimeter results. The 2009 DFBA soil extraction results represent a site wide average concentration depth distribution with a small sample size, and thus a relatively large degree of uncertainty.

*6.5.3 Simulated Tracer Migration*

The evolutions of DFBA concentrations through the simulation in the matrix and macropore domains are shown in Figures 6.19 and 6.20. The matrix domain DFBA concentration distribution (Figure 6.19) shows a slow vertical migration through the soil profile and a decrease in DFBA concentrations throughout the simulation period. Throughout the simulation time, the matrix appears to be losing DFBA mass and the center of DFBA mass is migrating deeper below the ground surface. The DFBA migration through the matrix domain shows similar results to the DFBA soil core depth distribution (Appendix C) in that the center of mass remains above the tile drains, primarily in the top 1 m of the simulated domain.

The m igration of t he m acropore D FBA ( Figure 6.20) i nitially s tarts w ith z ero mass a t th e in itial c ondition, b ut a s th e s imulation p rogresses th e D FBA ma ss f rom matrix transfers into the macropore domain and remains throughout the simulation. The DFBA concentrations in the macropores were consistently lower compared to the matrix DFBA c oncentrations t hroughout t he s imulation, but t he m acropore D FBA w as a ble t o infiltrate to greater depths, particularly e arly i n t he s imulation pe riod ( prior t o da y 80). The m odel doe s a poo r j ob a t s imulating DFBA m igration i nto t he l ower s and l ayer, likely due to the no flow boundary located at the base of the sand. Data from the B series monitoring wells have shown that measurable quantities of DFBA have been transported to this lower sand unit. Much of the DFBA mass loss occurring in the field is believed to be a r esult of D FBA b ypassing t he t ile dr ains, a nd i nfiltrating de eper i nto l ower uni ts. Currently, t his i s not being captured in th e s imulations a nd is lik ely a f actor th at is causing the underestimation in the simulated DFBA flushing to the lower units.

Both ma trix a nd ma cropore d omains s howed little la teral mi gration b eyond th e extent of P lot A . T his s upports t he id ea th at little la teral tr acer o r s alt mig ration is occurring on s ite, and that solute transport above the tile drains is a vertically dominated process. The capture zone of the tile drains appears to be larger than previously assumed and i s l ikely du e t o t he f act t hat ve rtical a nisotropy of t he m acropore dom ain i s no t included i n t he m odel. A s maller t ile dr ain c apture z one is e xpected t o transport l arger amounts of tracer and salt past the tile drains, mo ving the tracer and salt deeper into the lower uni ts. C urrent field obs ervations de tected DFBA in both the B a nd C s eries s and units but no measurable amounts of DFBA were present in the s imulated B series sand.

Introducing vertical anisotropy in the model is expected to increase tile drain bypass in the simulations, thereby increasing DFBA concentrations in the lower sand unit and better replicating field observations. Furthermore, both tile drains exhibit an "upwelling" effect that forces water from the sand layer directly below each drain vertically upward into the drain, similar to that observed by Van Schaik and Milne (1961). This increases the capture zone of the tile drain which subjects larger areas of soil to drainage, increasing the efficiency of each drain. This allows for salts and tracer that may have originally passed in between a set of drains to be "recaptured" in the future. The implications of the simulated upwelling are an increased flow discharge, as water would be pulled from above and below the drains. The simulated upwelling could be a contributor to the overestimation in tile flow. This would be similar for solutes, as any DFBA residing below the drains would be transported to the drains. Whether this is upwelling is real or an artifact of the simulation is currently unknown.

**Table 6.1.  Properties of soils on site**

| Material | Particle Size Analysis (% Composition) | | | | Dry Bulk Density $(g/cm^3)$ | Porosity | CEC (meq/kg) |
|---|---|---|---|---|---|---|---|
| | clay | Silt | Fine Sand | Medium Sand | | | |
| Top Soil | N/A | N/A | N/A | N/A | 1.05 | 0.475 | N/A |
| Glaciolacustrine | 15 | 83 | 2 | - | 1.545 | 0.417 | 219.66 |
| Glacial Till | 11 | 34 | 40 | 15 | 1.735 | 0.345 | 112.43 |
| B Series Sand | - | 17 | 75 | 8 | N/A | N/A | N/A |
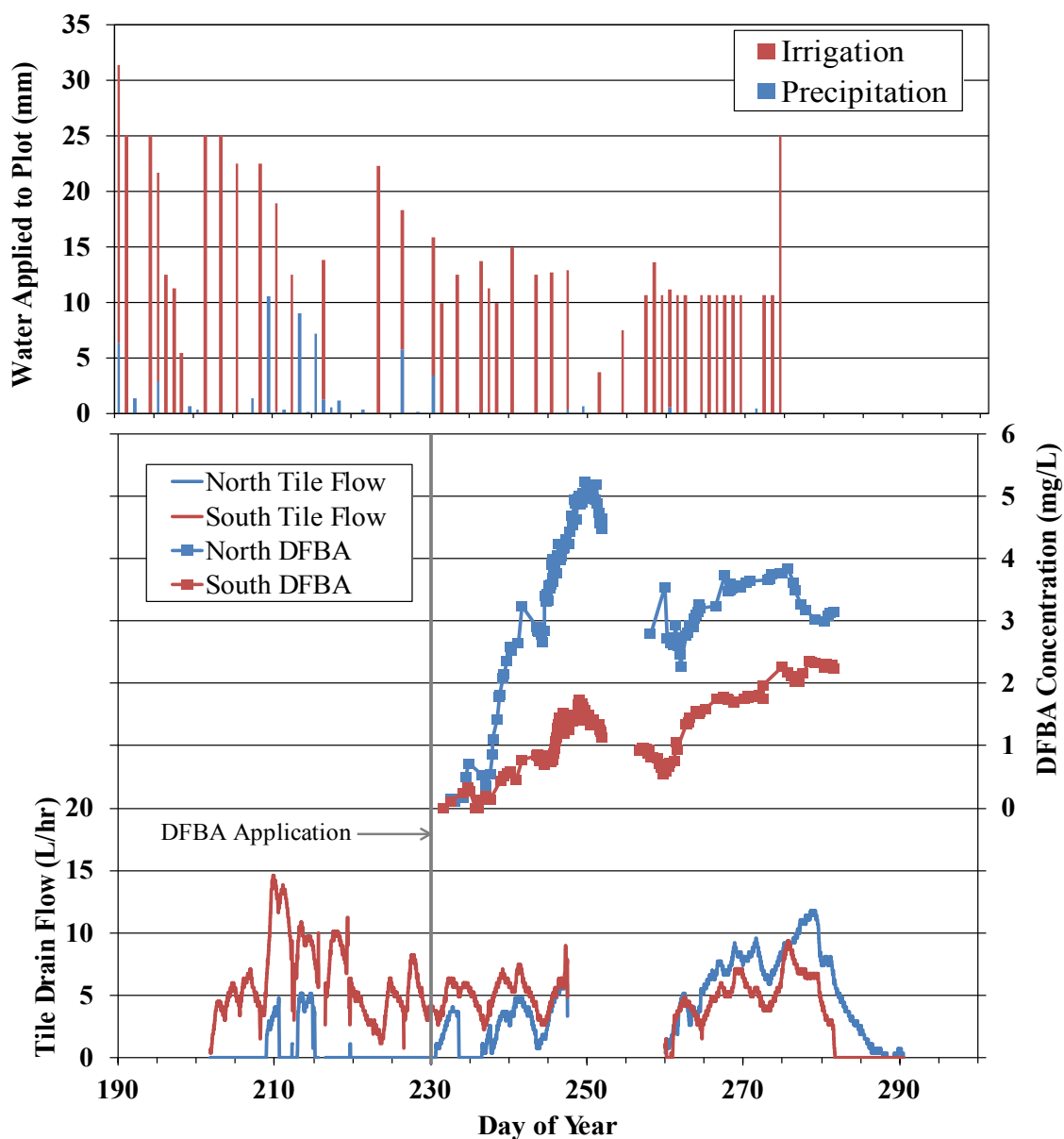
**Figure 6.1.  Applied irrigation/precipitation (mm), measured tile drain flow (L/hr) and DFBA concentration in water samples recovered from the north and south tile drains in 2009.  DFBA surface application occurred August 18 (day 230).**
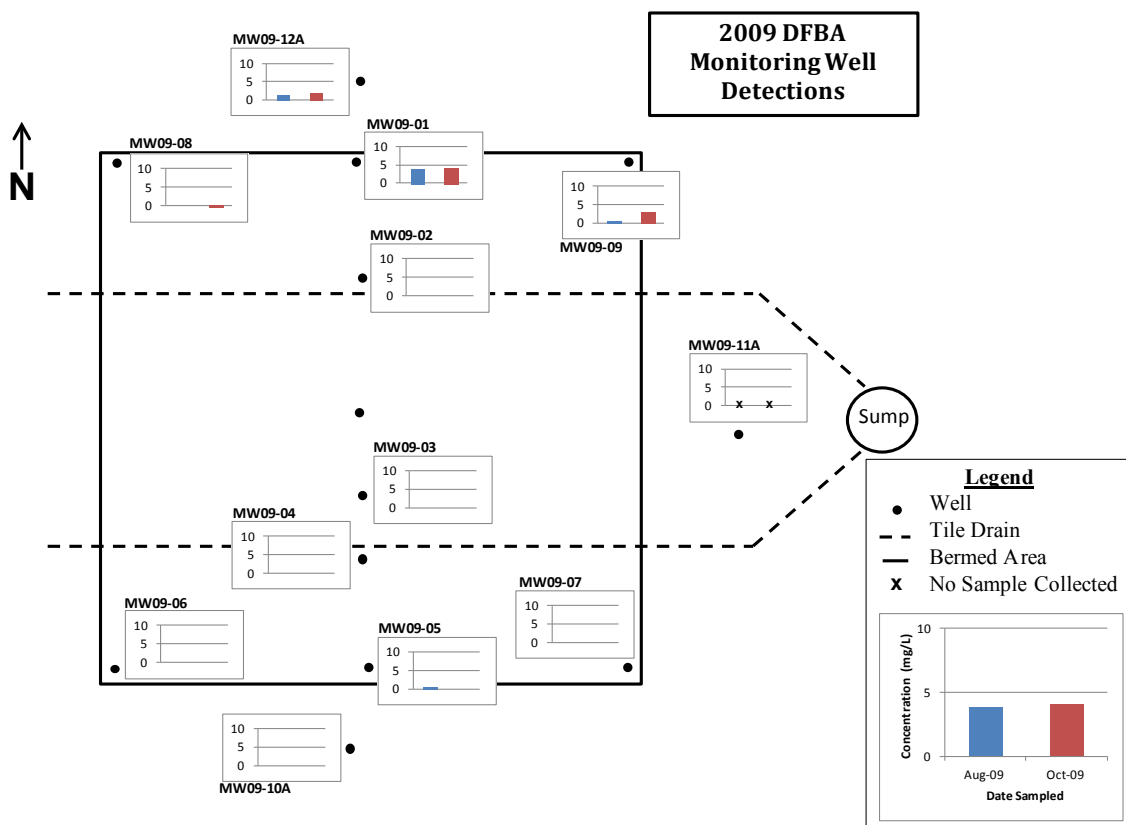
**Figure 6.2. Plan view map of monitoring well DFBA concentrations in 2009.**
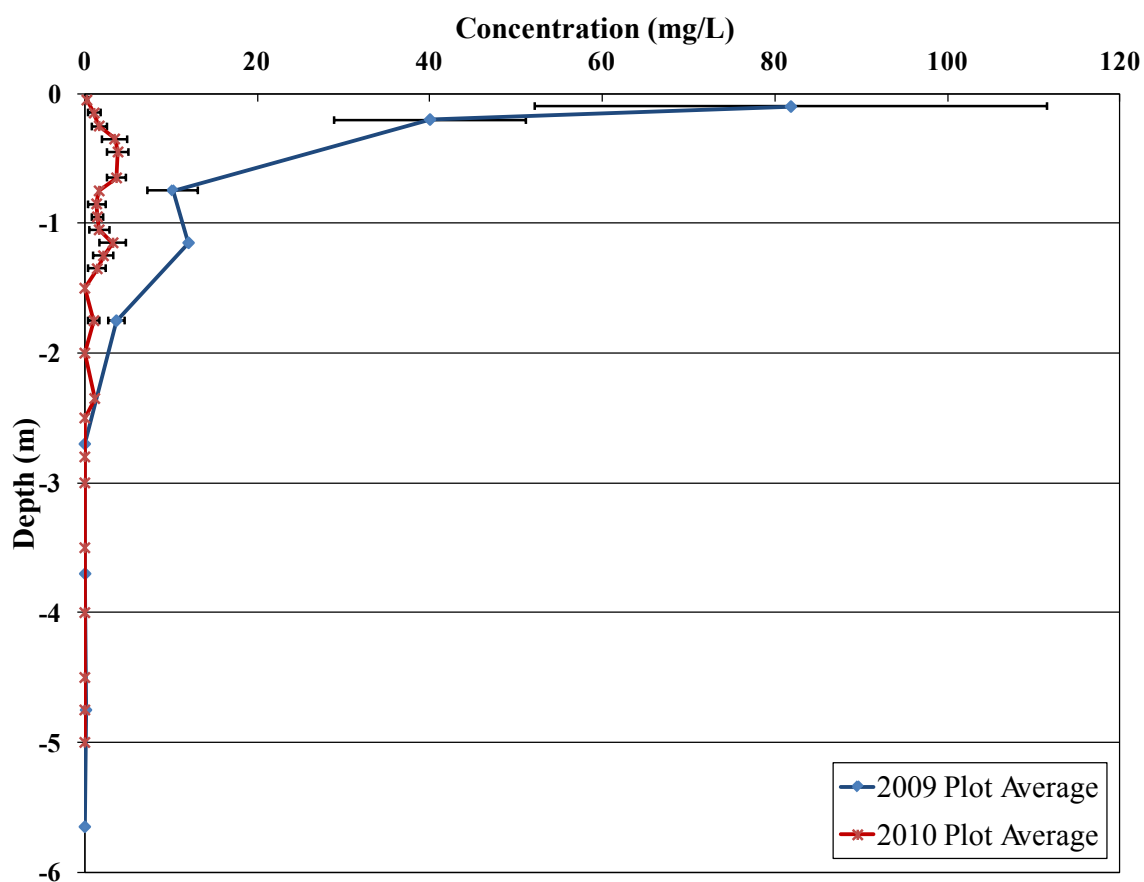
**Figure 6.3. Depth profile of average DFBA soil pore water extract concentrations in Plot A. Data are derived from 2:1 soil extracts collected in 2009 (blue) and 2010 (red). Error bars represent the standard error calculated from the sample population.**

**Table 6.2.  Summary of DFBA mass recovery at the end of the 2009 season.  Soil corrected values indicate the total DFBA mass accounted for after a correction had been applied based on the DFBA soil extraction method (Section  4.5.2.2).**

| | 2009 Mass Recovered (g) | $M/M_o$ (%) |
|---|---|---|
| **South Tile** | 7.01 | 0.16 |
| **North Tile** | 14.9 | 0.33 |
| **Combined** | 21.9 | 0.49 |
| **Soil Extraction (Corrected)** | 5230 | 116.13 |
| **Total** | 5250 | 116.62 |
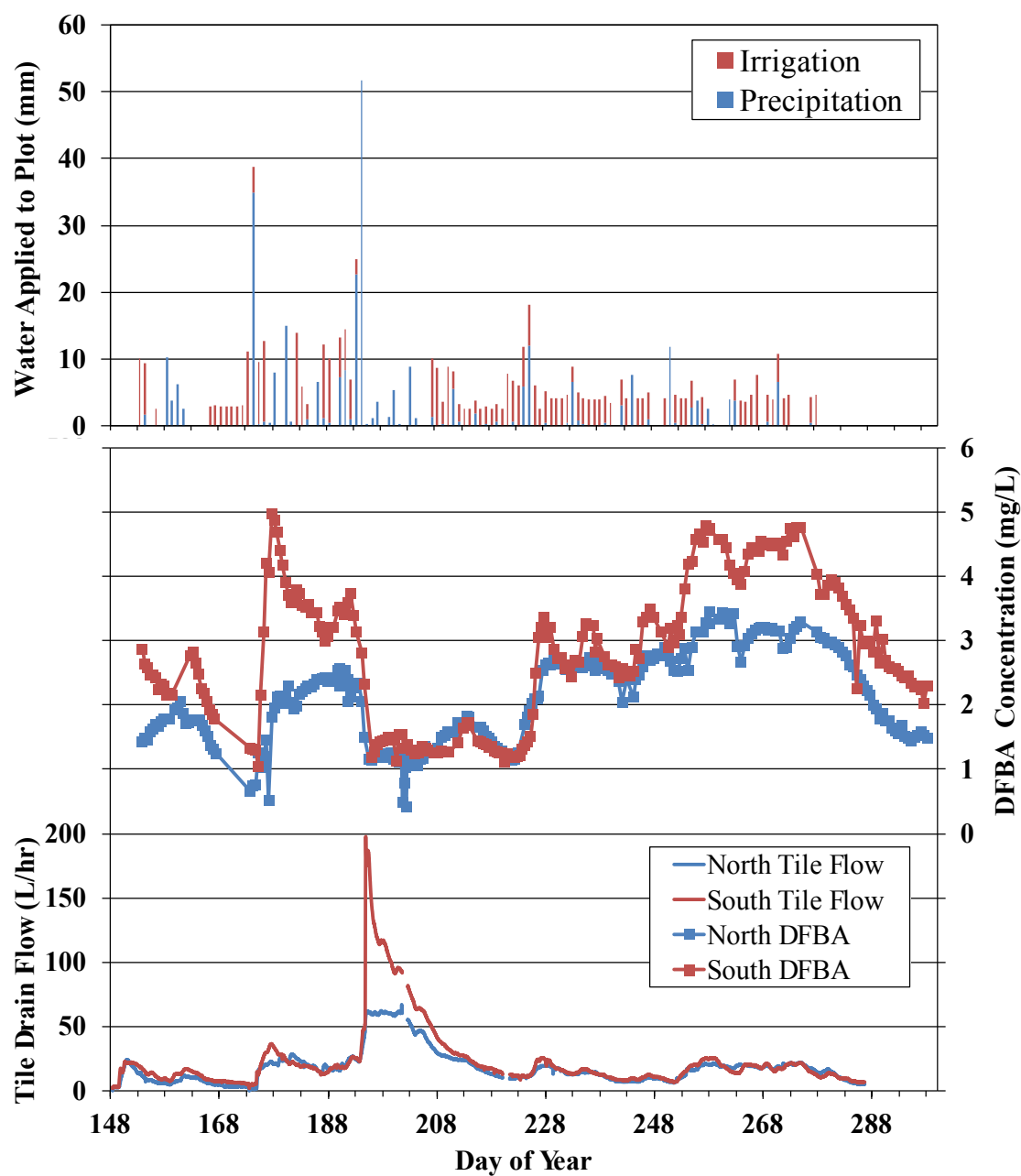
**Figure 6.4. Applied irrigation/precipitation (mm), measured tile drain flow (L/hr) and DFBA concentration in water samples recovered from the north and south tile drains in 2010.**
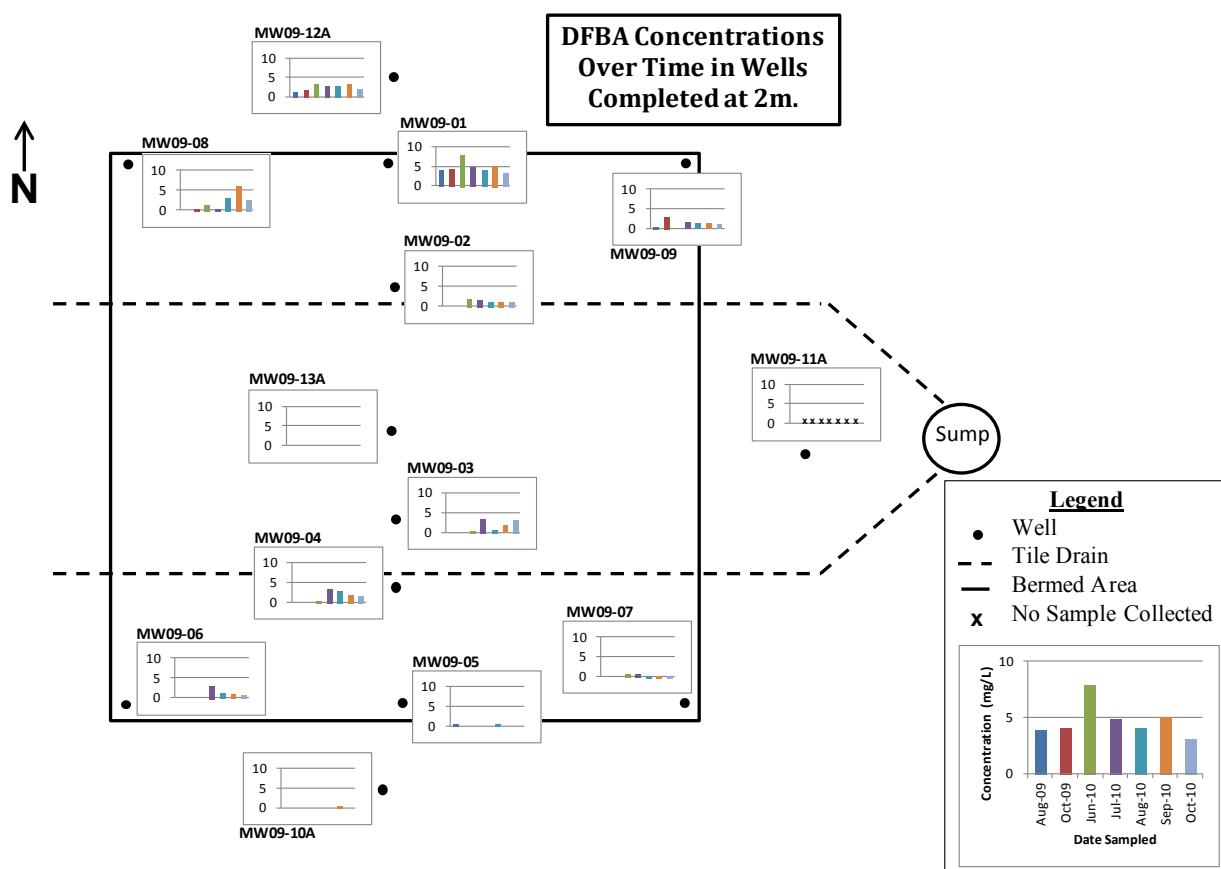
**Figure 6.5. Plan view map of DFBA detections in A series monitoring wells during 2009 and 2010.**
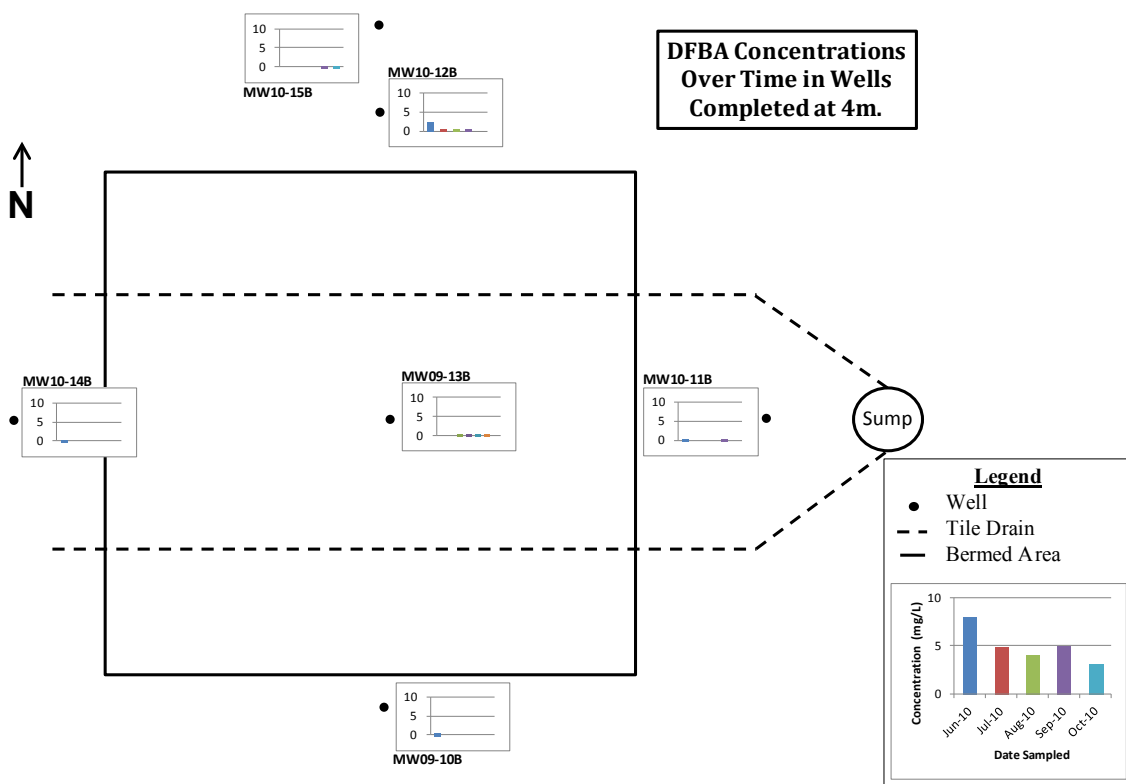
**Figure 6.6. Plan view map of DFBA detections in B series monitoring wells in 2010.**
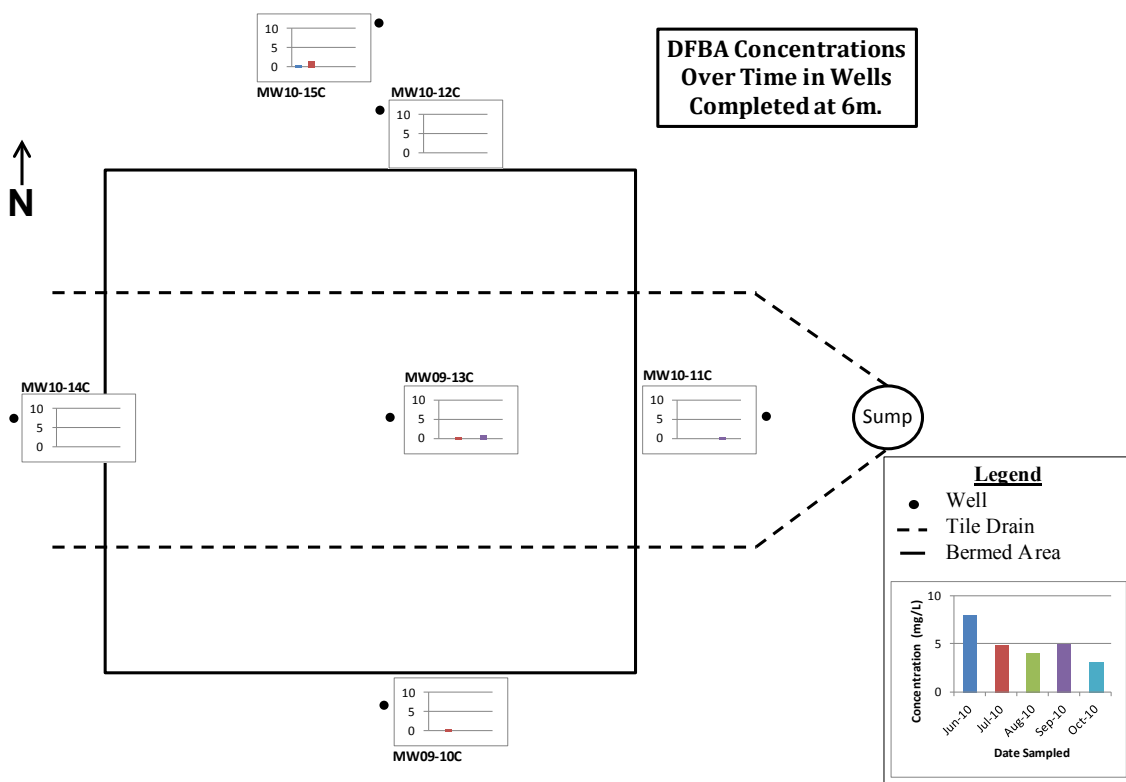
**Figure 6.7.  Plan view map of DFBA detections in C series monitoring wells in 2010.**
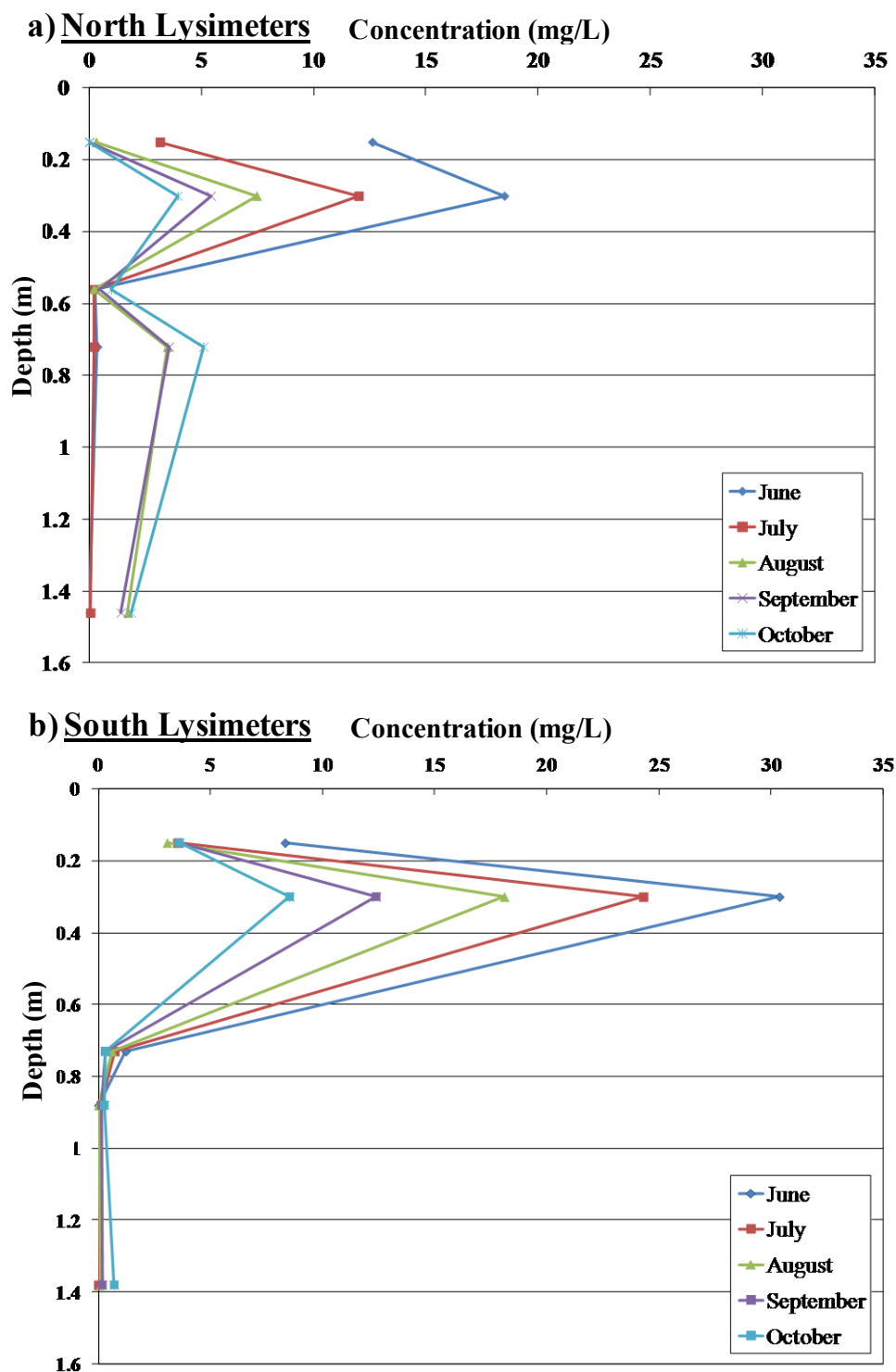
Figure 6.8. North (a) and south (b) lysimeter DFBA depth profiles from June 2010 to October, 2010. The north nest lies above the north tile drain and the south nest lies in the center of the plot, between the tile drains.

**Figure 6.9. Plan view map showing DFBA depth distribution of 2010 soil extractions. Boreholes outside of plot are not included due to non-detects. Extracted DFBA concentration and sampling depth shown in legend unless otherwise indicated on specific borehole.**
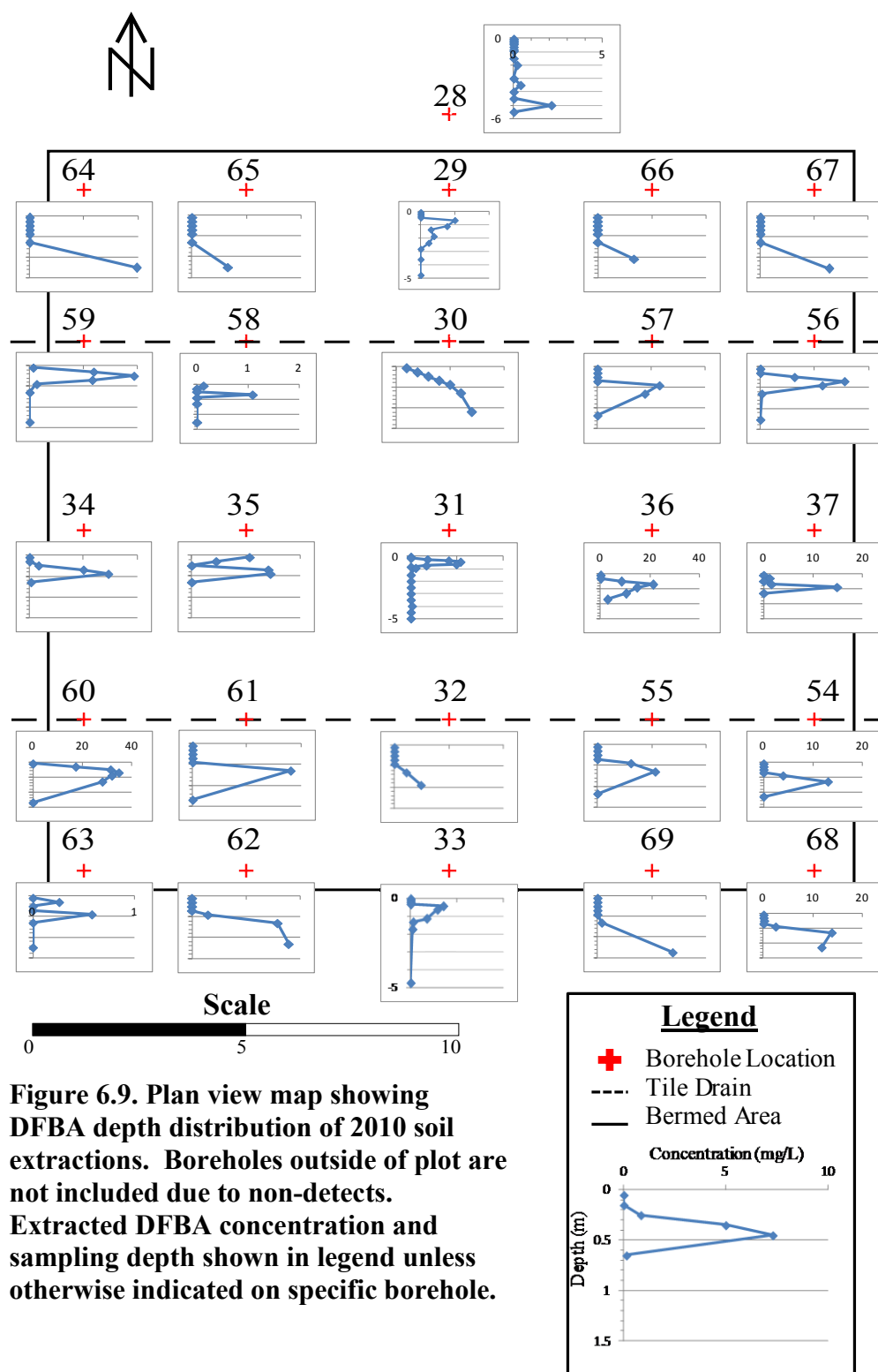
**Table 6.3. Summary of DFBA mass recovery at the end of the 2010 season compared against the total mass applied ($M_o$) at the beginning of the 2009 season. Soil extraction numbers have been corrected based on the DFBA soil extraction method (Section 4.5.2.2)**

|  | 2010 Mass recovered (g) | $M/M_o$ |
|---|---|---|
| South Tile | 180 | 4.00 |
| North Tile | 116 | 2.58 |
| Combined Tile Flow | 296 | 6.58 |
| Soil Extraction (Corrected) | 1430 | 31.76 |
| Total | 1730 | 38.34 |
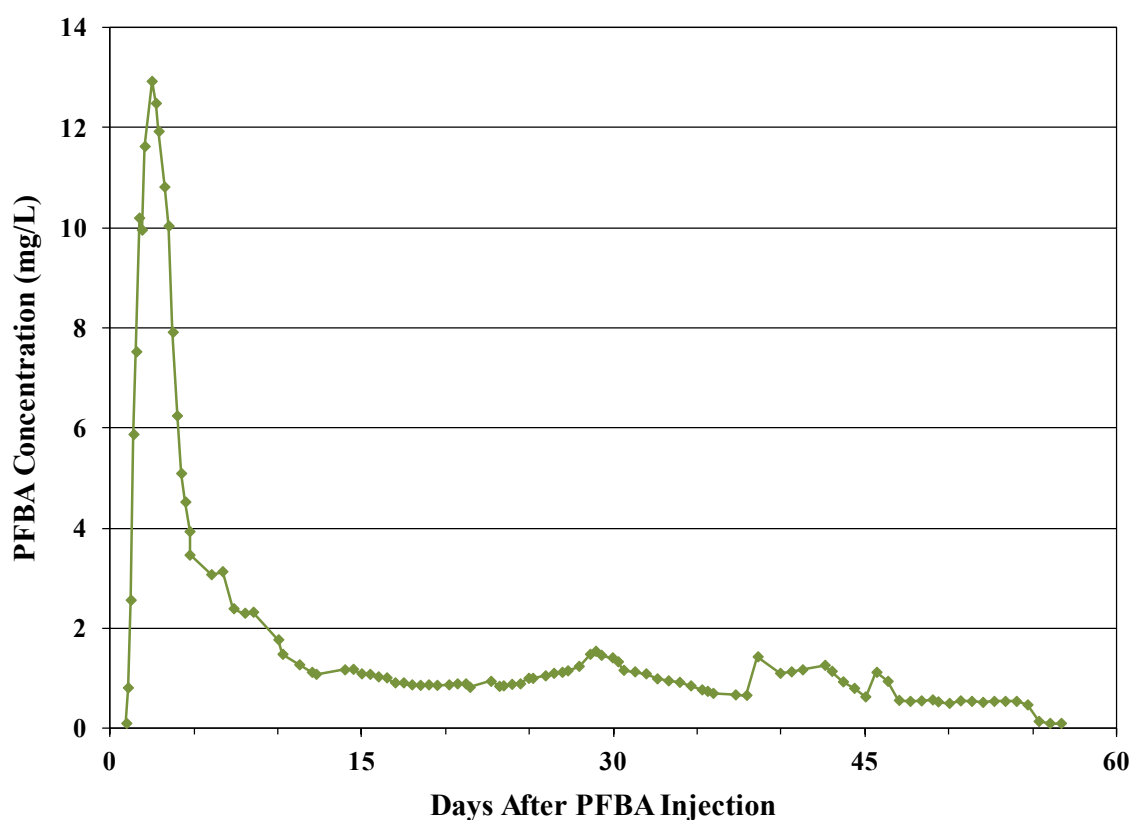


**Figure 6.10. Monitored breakthrough of PFBA in North tile during the 2010 season.**

**Table 6.4.  Summary of the reported literature values of the main calibration variables $K_{sf}$, $\omega$ and $a$ as well as their effect on the simulated tile drain flow.**

| Calibrated Parameter | Literature Value | Simulated Tile Drain Response to Changing Parameter | Literature Sources |
|---|---|---|---|
| $K_{sf}$ (mm/day) | 3300 - 22288 | Magnitude of peak flow and responsiveness to precip/irrigation events largely determined by $K_{sf}$. Matching magnitude and timing of flow events was done by changing this value for the glaciolacustrine and top soil unit. | Simunek et al., 2003; Gerke and Kohne, 2004; Gardenas et al., 2006 |
| $\omega$ | 0.03 - 0.05 | Literature values increased the tile drain flow higher than observed values. Decreasing the value too low resulted in a tile drain response unable to capture precip/irrigation events. | Simunek et al., 2003; Gerke and Kohne, 2004; Gardenas et al., 2006 |
| $a$ (mm) | 10 | Controlled the rate and sensitivity of the macropore influence in tile drain response. Decreasing the value increased the tile drain sensitivity to precip/irrigation events. Increasing the value slowed the transfer rate of fluid moving from the matrix domain into the macropores. | Simunek et al., 2003; Gerke and Kohne, 2004 |

**Table 6.5. Parameters used in base case simulation for matrix, macropore, fluid mass transfer and solute mass transfer.**

| Material | Matrix Hydraulic Parameters | | | | | |
|---|---|---|---|---|---|---|
| | $\theta_r$ | $\theta_s$ | $\alpha_m$ (mm$^{-1}$) | $n_m$ | $K_{sat}$ (mm/d) | $l$ |
| Top Soil | 0.0001 | 0.39 | 0.001 | 1.48 | 120 | 0.5 |
| Glaciolacustrine silt | 0.0001 | 0.38 | 0.002 | 1.23 | 0.5 | 0.5 |
| Glacial Till | 0.07 | 0.36 | 0.0005 | 1.09 | 0.5 | 0.5 |
| B Series Fine - Medium Sand | 0.045 | 0.43 | 0.0145 | 2.68 | 125 | 0.5 |
| Infiltration Unit | 0 | 0.8 | 0.01 | 2 | 7000 | 0.5 |

| Material | Macropore Hydraulic Parameters | | | | | |
|---|---|---|---|---|---|---|
| | $\theta_{rf}$ | $\theta_{sf}$ | $\alpha_f$ (mm$^{-1}$) | $n_f$ | $K_{sf}$ (mm/d) | $l$ |
| Top Soil | 0 | 0.8 | 0.01 | 2 | 35000 | 0.5 |
| Glaciolacustrine silt | 0 | 0.8 | 0.01 | 2 | 35000 | 0.5 |
| Glacial Till | 0 | 0.8 | 0.01 | 2 | 35000 | 0.5 |
| B Series Fine - Medium Sand | 0.045 | 0.43 | 0.0145 | 2.68 | 125 | 0.5 |
| Infiltration Unit | 0 | 0.8 | 0.01 | 2 | 7000 | 0.5 |

| Material | Fluid Mass Transfer Parameters | | | | | Solute Mass Transfer Parameter |
|---|---|---|---|---|---|---|
| | $\omega$ | $\beta$ | $\gamma$ | $a$ (mm) | $K_{as}$ (mm/d) | $\alpha_s$ (d$^{-1}$) |
| Top Soil | 0.0025 | 3 | 0.4 | 7 | 0.01 | 0.25 |
| Glaciolacustrine silt | 0.0025 | 3 | 0.4 | 5 | 0.01 | 0.25 |
| Glacial Till | 0.0025 | 3 | 0.4 | 25 | 0.01 | 0.25 |
| B Series Fine - Medium Sand | 0.0025 | 3 | 0.4 | 5 | 0.01 | 0.25 |
| Infiltration Unit | 0.0025 | 3 | 0.4 | 7 | 0.01 | 0.25 |

**Table 6.6. Results of sensitivity analysis normalized against base case simulation. Values less than 1 indicate the simulation results fit closer to observed data than base case results.**

| Parameter Tested | Normalized RMSE of Simulated Tile Drain Flow | Normalized RMSE of Simulated Tile Drain Effluent DFBA |
|---|---|---|
| $\alpha_m = .0005$ | 1.12 | 1.05 |
| $\alpha_m = .006$ | 1.13 | 0.98 |
| n = 1.13 | 1.03 | 1.00 |
| n = 1.35 | 1.02 | 1.05 |
| $K_{sa} = .05$ | 1.01 | 0.97 |
| $K_{sa} = .005$ | 1.13 | 1.06 |
| $\omega = .00075$ | 1.26 | 1.27 |
| $\omega = .025$ | 4.50 | 1.21 |
| $K_{sf} = 5000$ | 1.37 | 0.96 |
| $K_{sf} = 50000$ | 1.03 | 1.01 |
| a = 2.5 | 1.20 | 1.52 |
| a = 15 | 1.38 | 2.08 |
| $\alpha_s = 1$ | N/A | 1.14 |
| $\alpha_s = .01$ | N/A | 1.69 |
| $\alpha_s = .1$ | N/A | 1.49 |
| $\alpha_s = 0.05$ | N/A | 1.02 |
| Retardation ($K_d = 0.0789$) | N/A | 1.07 |
| **Base case** | **1** | **1** |
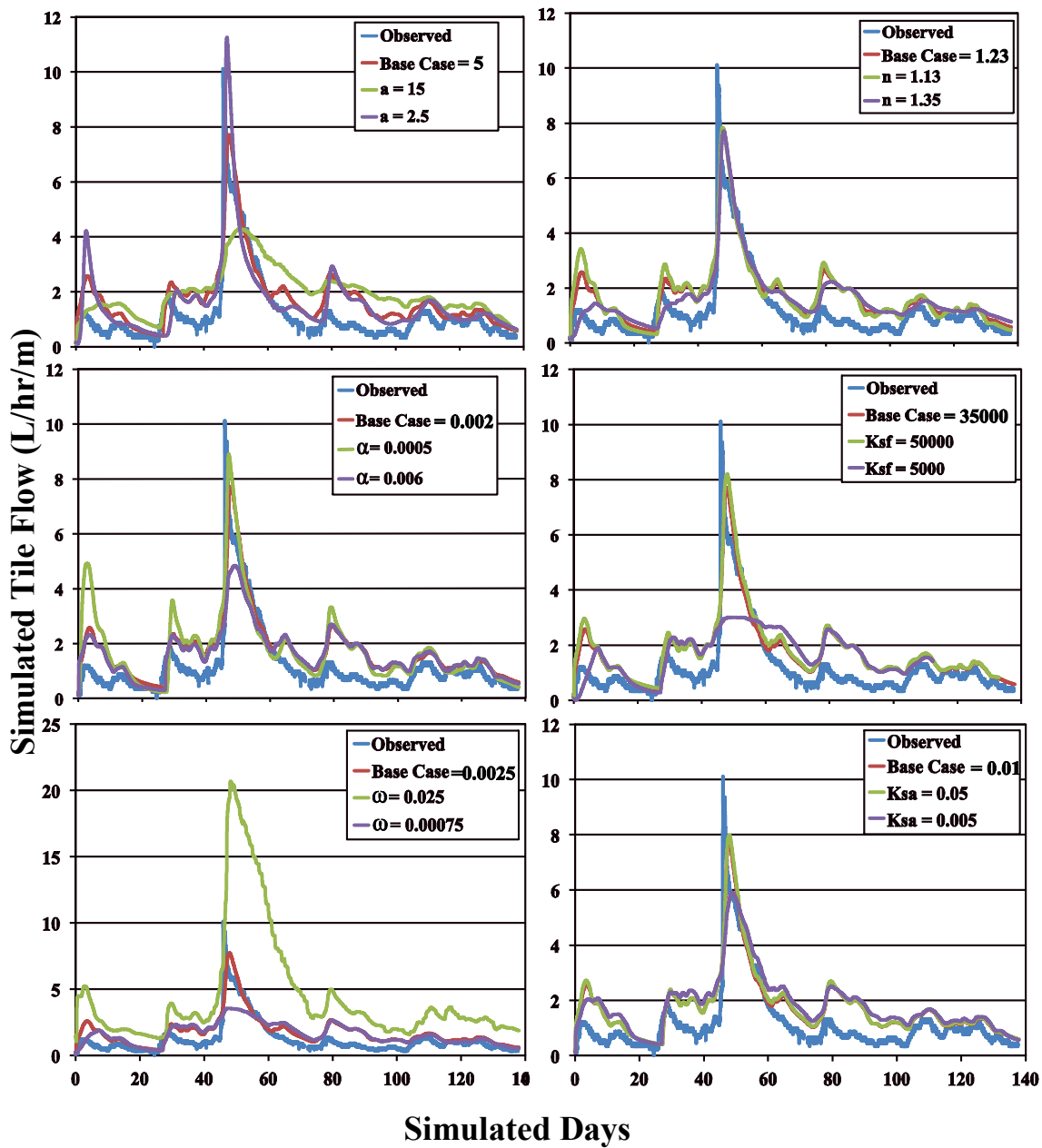
**Figure 6.11.** Sensitivity of simulated tile drain flow when specific glaciolacustrine hydraulic parameters were changed. Variables tested were $a$, $n_m$, $\alpha_m$, $K_{sf}$, $\omega$, $K_{sa}$. Results are shown with the base case simulation results and the observed 2010 south tile drain flow. Note the different scale used for the $\omega$ simulations.

**Figure 6.12. Sensitivity of simulated south tile drain effluent DFBA concentration to specific glaciolacustrine hydraulic parameters. Variables tested were *a*, $n_m$, $\alpha_m$, $K_{sf}$, $\omega$, $K_{sa}$ and the solute mass transfer coefficient $\alpha_s$. All scenario results are shown with the base case simulation and the observed 2010 south DFBA effluent concentration.**
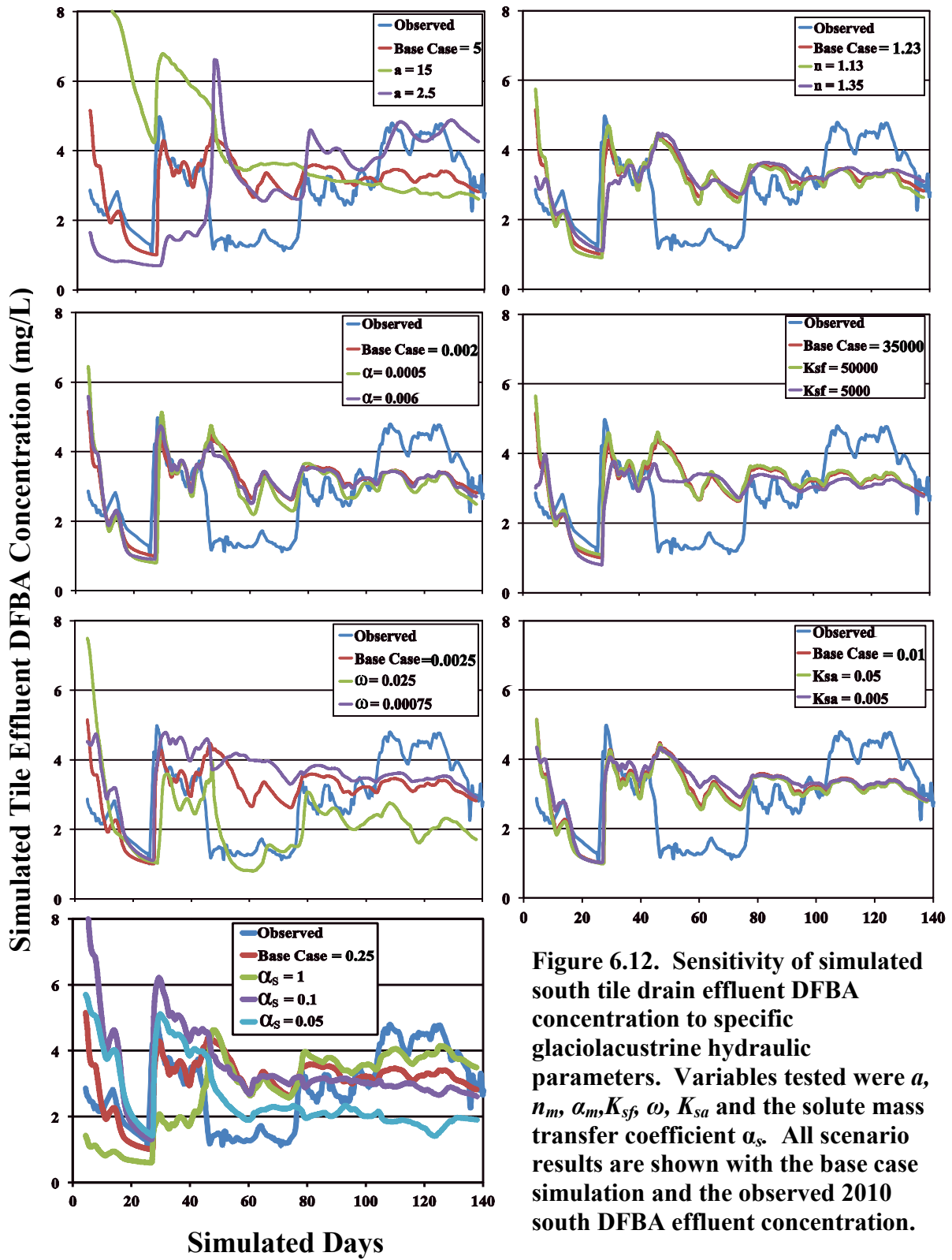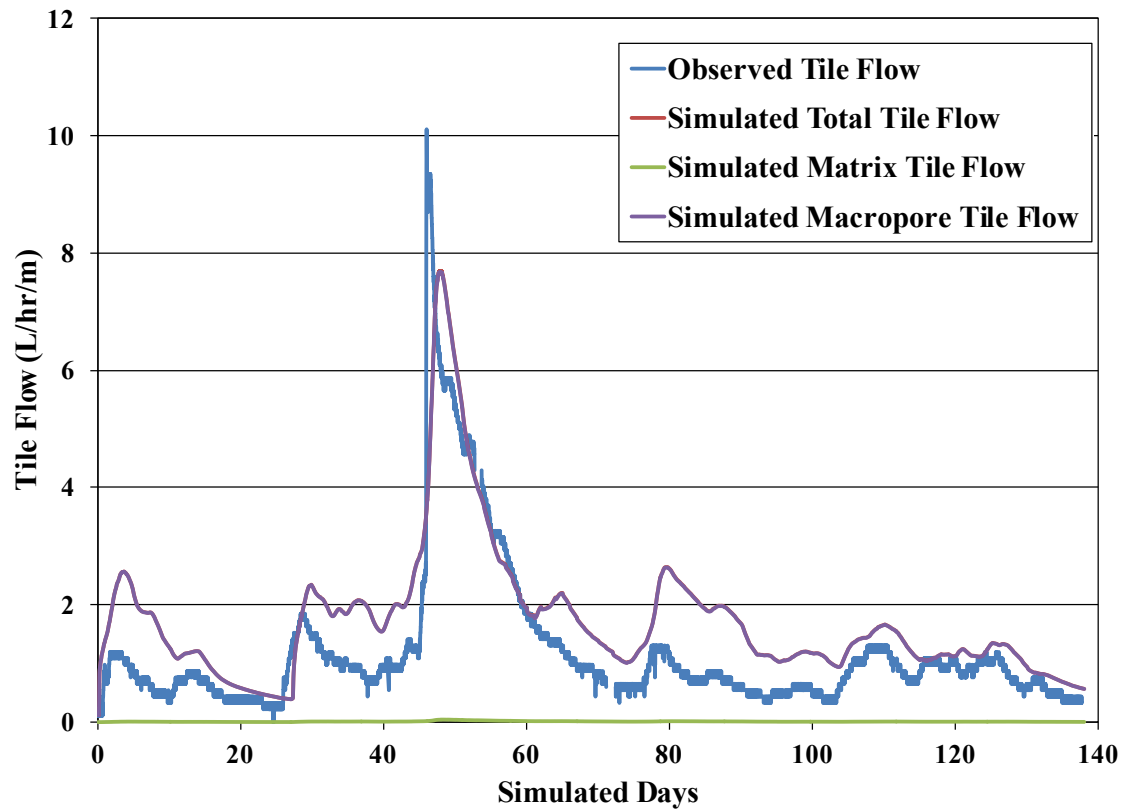
**Figure 6.13. Results of base case 2010 simulation of south drain tile flow. Flow measured in tile drain is separated into matrix, macropore and combined flow components all of which are compared to the observed 2010 south tile drain flow.**
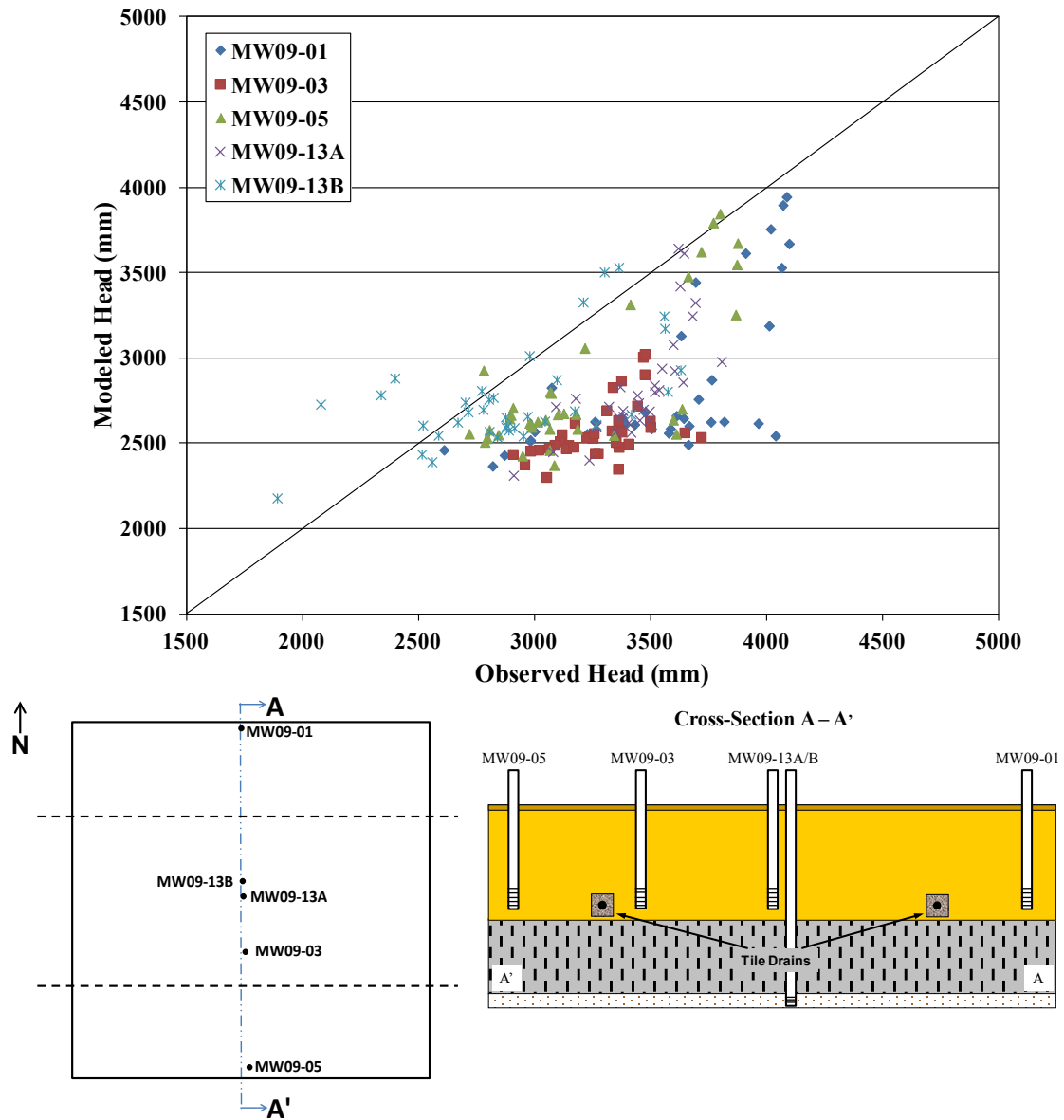
**Figure 6.14.  Comparison of observed and simulated hydraulic heads selected monitoring wells at 37 different times throughout the simulation period.  Locations of wells are indicated in the map and cross-section shown below.**
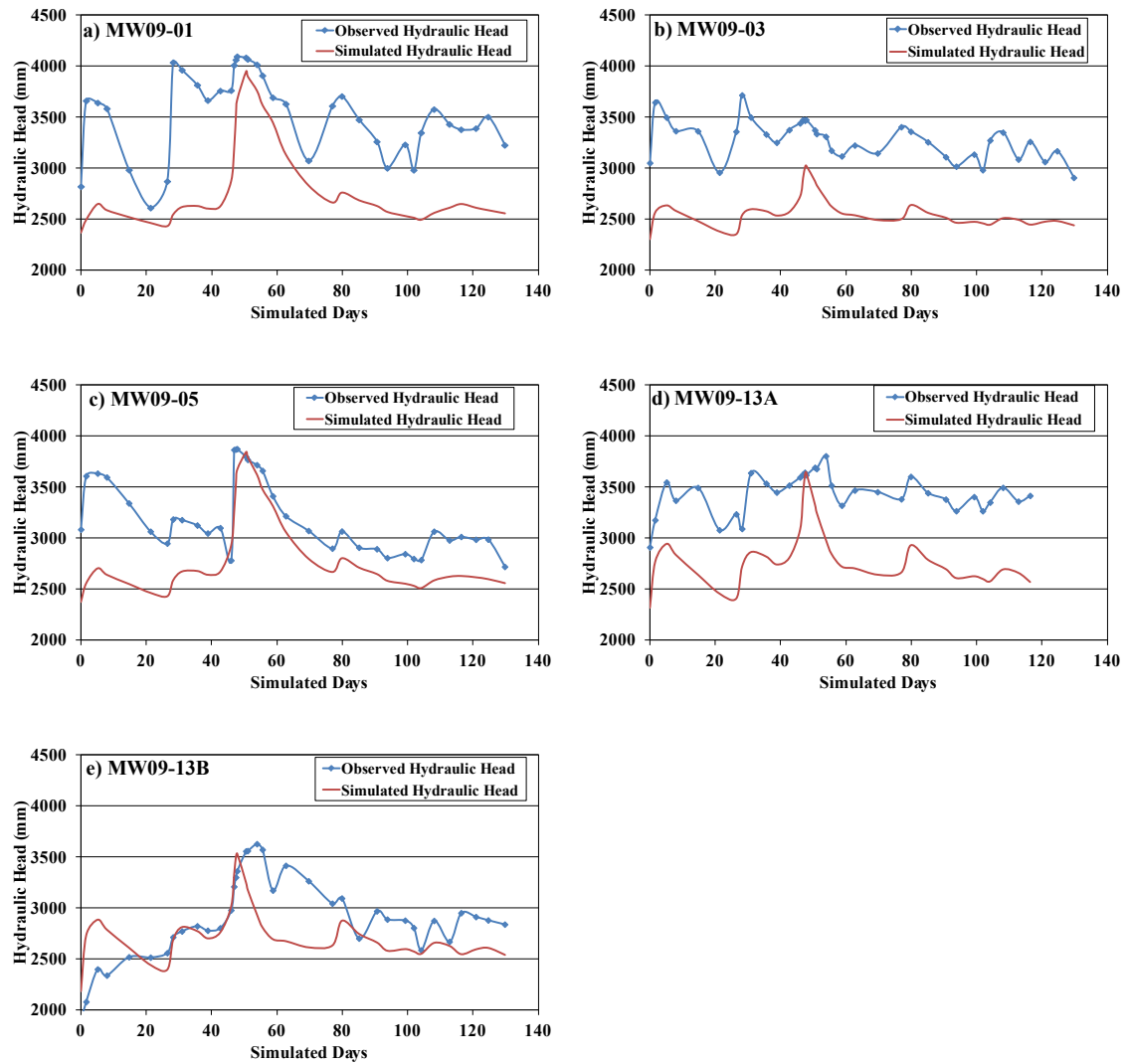
**Figure 6.15. Comparison of simulated and observed hydraulic heads measured throughout the simulation period of 2010. Monitoring wells compared are MW09-01 (a), MW09-03 (b), MW09-05 (c), MW09-13A (d) and MW09-13B (e).**
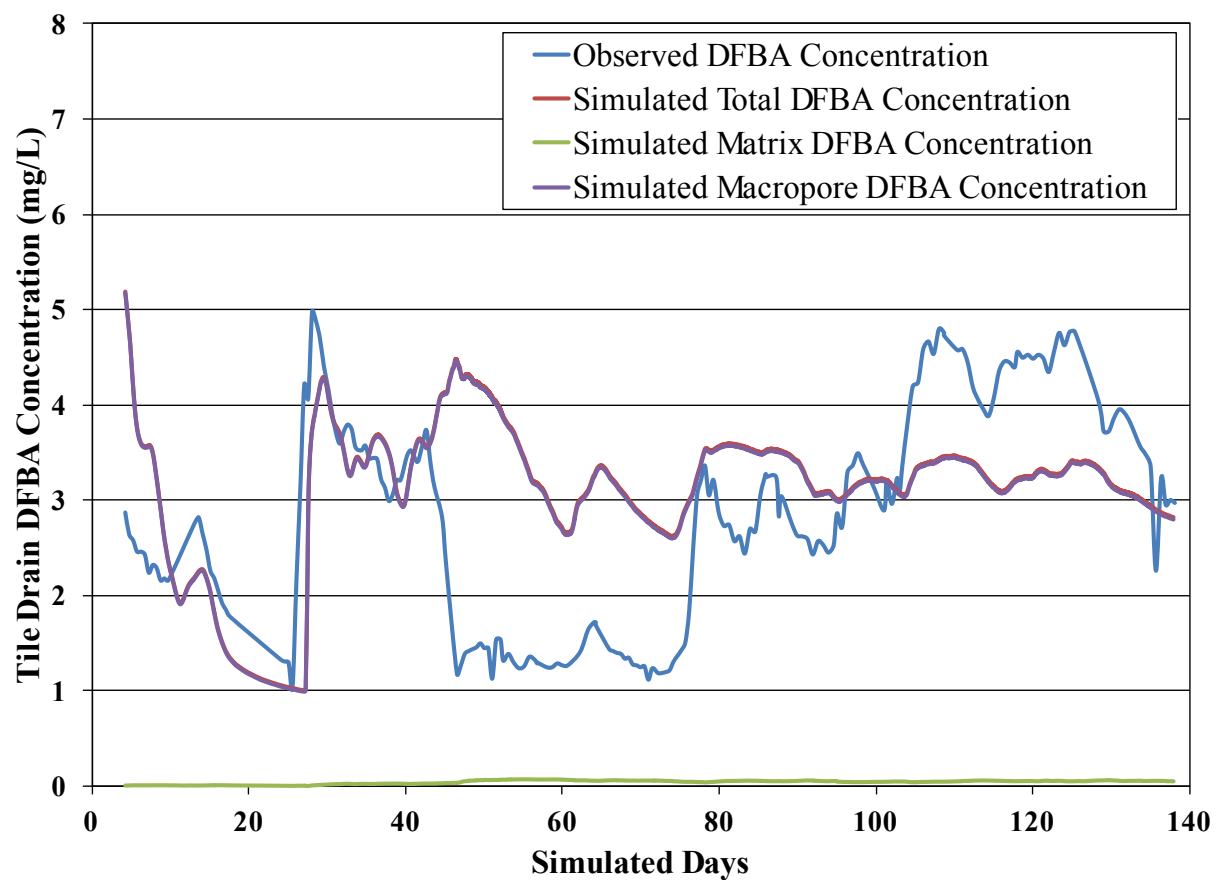
**Figure 6.16. Results of base case simulation of the 2010 south drain effluent DFBA concentration. DFBA transport into tile drain is separated into matrix, macropore and combined flow components all of which are compared to the observed 2010 south effluent DFBA measured concentration.**
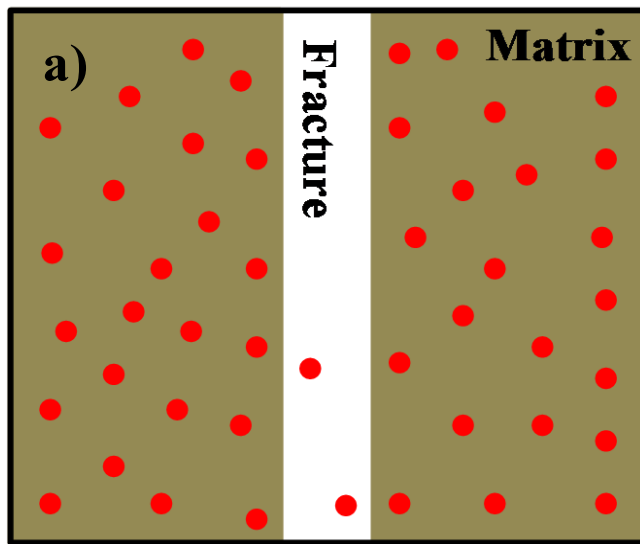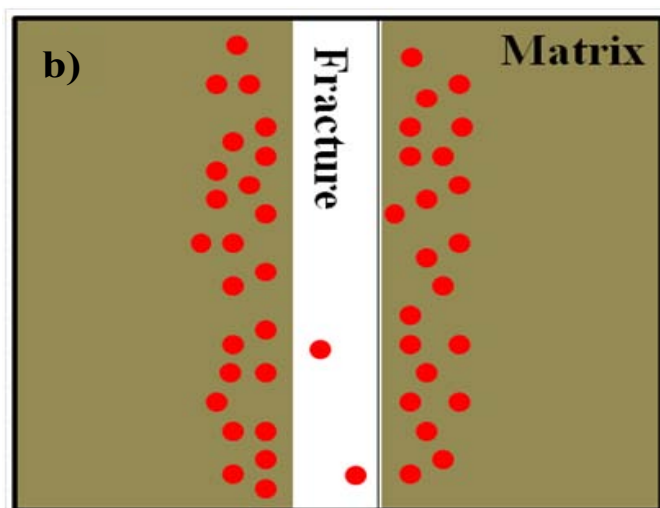
**Figure 6.17.  Schematic diagram comparing how DFBA tracer mass is spatially distributed in (a) the numerical model versus (b) the field at the start of the 2010 season.**

Figure 6.18. Results from the simulated lysimeters (a) simulated in the base case scenario shown with the observed lysimeters (b).

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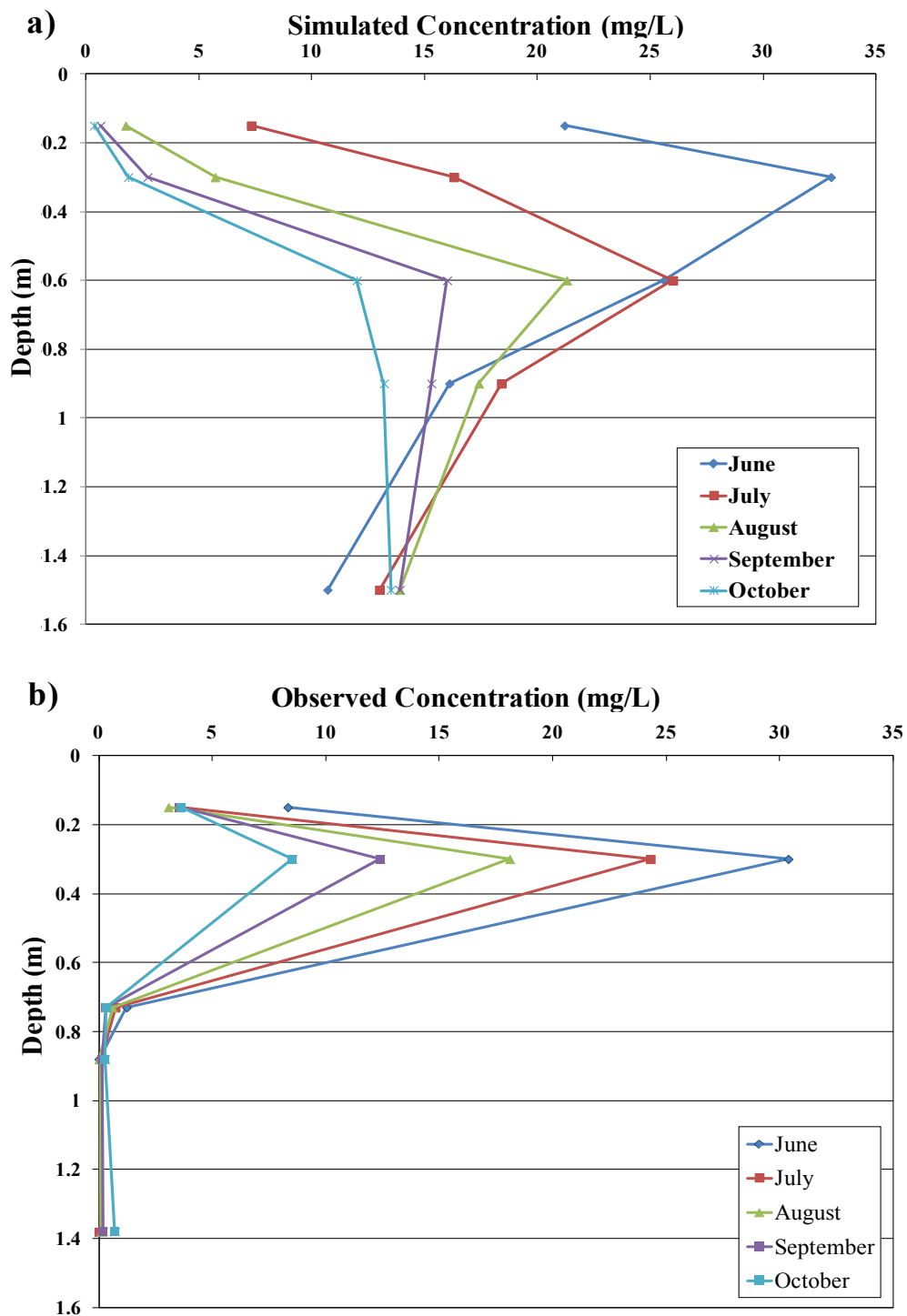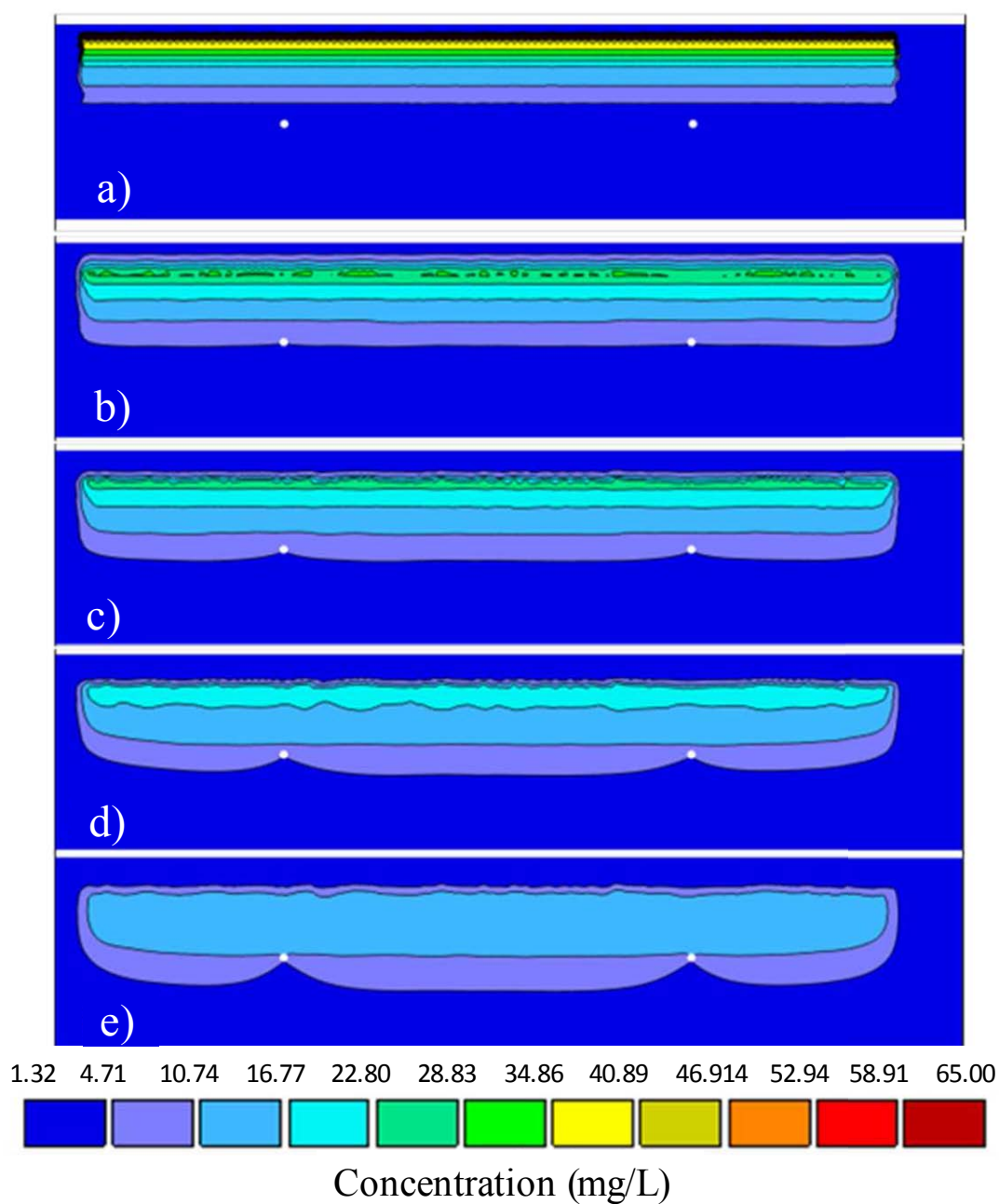


**Figure 6.19.  Time lapse of simulated DFBA concentrations in the matrix domain at (a) t=0 days, (b) t=36 days, (c) t=51 days, (d) t=80 days, (e) t =138 days.**
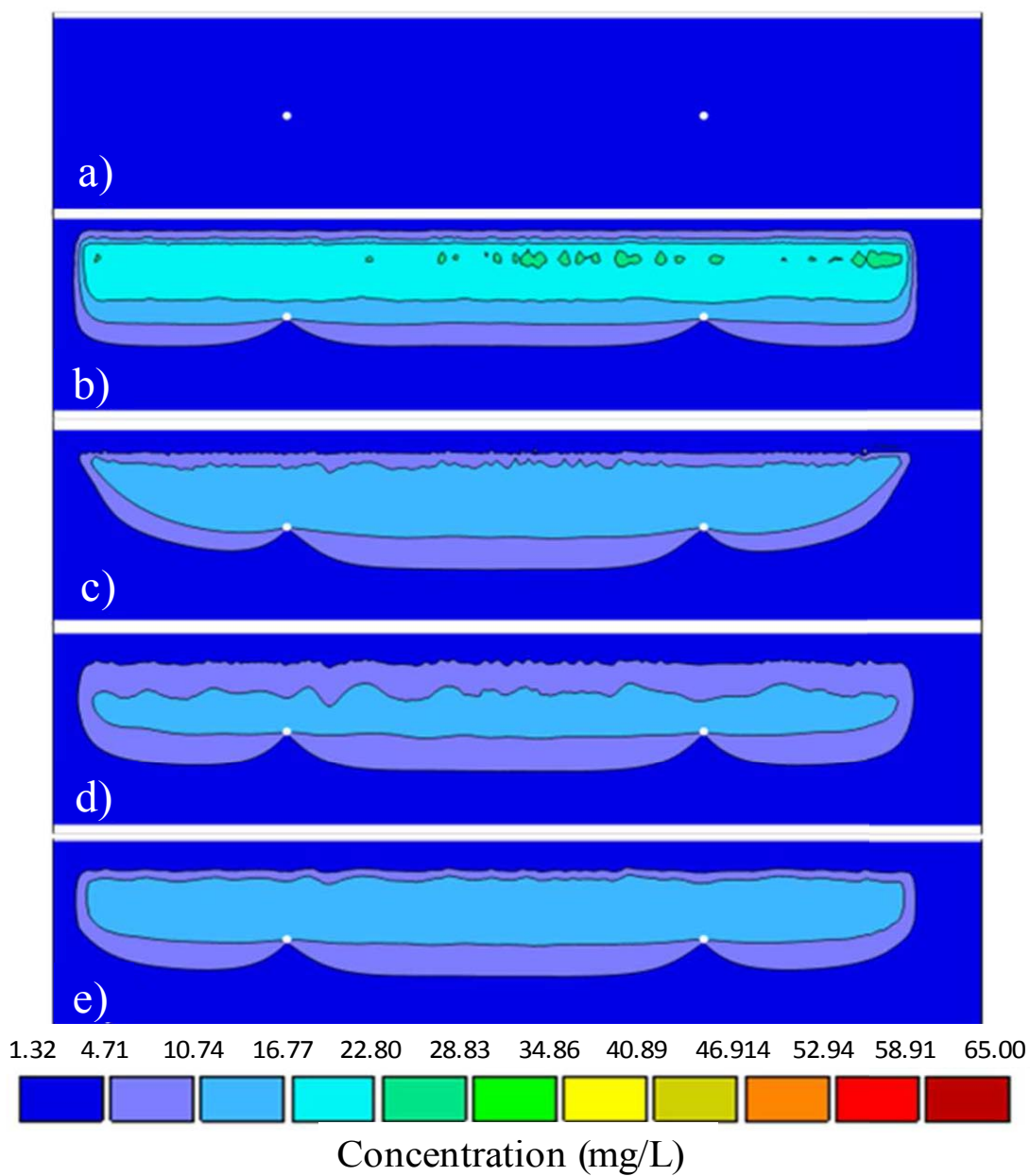
Figure 6.20. Time lapse of simulated DFBA concentration in the macropore domain at (a) t=0 days, (b) t=36 days, (c) t=51 days, (d) t=80 days, (e) t =138 days.

**CHAPTER SEVEN: CONCLUSIONS AND FUTURE WORK**

**7.1 Conclusions**

Results f rom b oth th e tile d rain m onitoring a nd t racer e xperiments showed macropores w ere influential in both fluid flow and solute transport in low permeability soils. T he quick DFBA (46.75 hrs) and PFBA (13 hrs) tile drain breakthrough and the rapid r esponse of t he t ile dr ains t o i rrigation/precipitation e vents in dicated th at macropores w ere c ontrolling how w ater and solutes w ere transported t o subsurface t ile drains. T he l arge m acropore i nfluence w as a lso i llustrated b y t he qui ck de tection o f DFBA in monitoring well samples and the results from the numerical simulations showed that 99% of t he f luid f low a nd s olute t ransport oc curred i n t he m acropores. T he significance o f h aving a la rge ma cropore in fluence in a r emediation s ite is th at limited volume w ater pa sses t hrough t he m atrix, hi ndering th e s alt f lushing c apabilities. T he macropores a re able t o transmit l arge por tions of t he w ater t o t he dr ains, w hile onl y exposing a small percentage of the matrix to fresh water.

Although m acropores a re r esponsible f or a lmost a ll s olute t ransport to the tile drains, matrix flushing appears to be occurring. This is shown by the reduction of DFBA concentrations observed in the suction lysimeters and by the reduction of mass in the soil core e xtractions a t t he end of t he 2010 s eason. R esults f rom t he s oil de gradation experiments have shown that no m easurable amount of DFBA degradation has occurred, therefore, i t c an b e c oncluded t hat removal of DFBA ha s oc curred vi a m ass t ransfer between the matrix and the macropores and subsequent transport deeper in the soil profile (i.e., to the tile d rains or deeper s and units). R esults from the numerical model further

support the hypothesis that matrix flushing has occurred with simulated DFBA mass loss observed in the matrix domain and in the simulated lysimeters. Understanding the solute mass transfer process that occurs between the matrix and macropore domains and determining the rate at which solute migrates from the matrix into the macropores will allow for a quicker, more efficient remediation of in situ salt. Determining the optimal irrigation rates for maximizing salt removal will help accelerate the remediation process and limit the amount of water required for irrigation and disposal.

Numerically, the model does a successful job at simulating the breakthrough and the dynamic response of the tile drain flow, but cumulatively overestimates the total drain discharge by 50 %. Additionally, the model consistently underestimates observed hydraulic heads, which could be caused by not incorporating vertical anisotropy in the matrix and macropore domains. The DFBA transport simulations do not accurately capture most of the observed tile drain DFBA concentration response. The model is able to simulate the early time tile drain DFBA response (before 40 days), but struggles to match the observed data for the remainder of the simulation. The solute mass transfer term in the model does not appear to accurately represent the physical processes occurring. Furthermore, the model underestimates the transport of DFBA beyond the tile drains and into the lower sand unit. Additional model refinement is needed in order to accurately capture the transport of DFBA and salt to the lower sand unit.

**7.2 Future Work**

Continual monitoring (soil geochemistry, near surface geophysics) of the field site is needed until soil conditions meet Alberta Environment remediation guidelines. Furthermore, developing a strategy targeted at reducing the volume of water and time needed to remediate a site would help this remediation technique to be used in similar sites in the future. More advanced modeling of the site will also requires the use of vertical anisotropy as well as geochemical modeling to describe how the major ion chemistry influences solute transport and the hydraulic parameters of the soils. As previously mentioned in Sec 3.1, hydraulic conductivities of soil can vary when exposed to changing levels of sodium. Removing salts will alter the geochemistry of the soil, changing the hydraulic parameters. This should be accounted for in future simulations. Additionally, accurately deriving the van Genuchten macropore properties by running small scale laboratory experiments on soil core would help constrain the simulated macropore properties used in the model. This could help reduce the model uncertainty and provide more accurate results.

In conjunction with this project, large amounts of chloride data have been collected during the monitoring program. Although the chloride flushing analysis lies outside this project's scope of work, much of the model construction and calibration has created a foundation for future model runs to be completed. The chloride has a much different initial distribution than the benzoic acid tracers and together with the observed tile concentration data will be used to further improve the flow and transport model, particularly calibration of the solute mass exchange parameters. The revised model will

allow for estimations of salt remediation times under various conditions. Additional forward model runs with differing tile drain spacing and alternative flushing methods (continual irrigation vs infrequent irrigation pulses) will help in designing more efficient remediation strategies for future salt contaminated sites. Construction of a site wide 3-dimensional model would be beneficial to develop a stronger understanding of the salt migration and to determine if any further remediation methods are needed (additional soil removal from site).

Finally, additional long-term studies investigating the influence macropores have on solute transport are needed to better understand how solute transfer processes may vary with time. Most research programs are only aimed at looking at the initial breakthrough and migration of solutes, lasting no more than four months. By increasing the length of time monitoring the migration of the solute, a stronger understanding can be developed on how solute mass transfer processes evolve. Developing a stronger understanding of matrix-macropore mass transfer processes would help create more robust dual domain models.

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# APPENDIX A: TRACER DATA

## 2009 North and south tile drain DFBA concentrations

| North Tile | | South Tile | |
|---|---|---|---|
| Date | Concentration (mg/L) | Date | Concentration (mg/L) |
| 8/19/09 14:00 | 0.00 | 8/19/09 14:00 | 0.00 |
| 8/20/09 14:00 | 0.15 | 8/20/09 14:00 | 0.11 |
| 8/21/09 2:00 | 0.15 | 8/22/09 2:00 | 0.24 |
| 8/21/09 2:00 | 0.11 | 8/22/09 17:00 | 0.33 |
| 8/22/09 2:00 | 0.16 | 8/22/09 23:00 | 0.27 |
| 8/22/09 11:00 | 0.49 | 8/23/09 17:00 | 0.00 |
| 8/22/09 20:00 | 0.71 | 8/24/09 2:00 | 0.00 |
| 8/24/09 14:00 | 0.53 | 8/24/09 5:00 | 0.14 |
| 8/25/09 2:00 | 0.36 | 8/25/09 2:00 | 0.20 |
| 8/25/09 14:00 | 0.54 | 8/25/09 14:00 | 0.13 |
| 8/25/09 20:00 | 0.86 | 8/27/09 0:00 | 0.443 |
| 8/25/09 23:00 | 1.10 | 8/27/09 9:00 | 0.51 |
| 8/26/09 12:00 | 1.42 | 8/27/09 21:00 | 0.56 |
| 8/26/09 18:00 | 1.79 | 8/28/09 3:00 | 0.58 |
| 8/26/09 21:00 | 1.81 | 8/28/09 21:00 | 0.45 |
| 8/27/09 6:00 | 2.09 | 8/29/09 16:00 | 0.77 |
| 8/27/09 9:00 | 2.14 | 8/31/09 14:30 | 0.84 |
| 8/27/09 18:00 | 2.36 | 8/31/09 17:30 | 0.85 |
| 8/28/09 3:00 | 2.58 | 8/31/09 20:30 | 0.82 |
| 8/28/09 6:00 | 2.53 | 8/31/09 23:30 | 0.75 |
| 8/29/09 4:00 | 2.65 | 9/1/09 2:30 | 0.76 |
| 8/29/09 16:00 | 3.23 | 9/1/09 5:30 | 0.76 |
| 8/31/09 14:30 | 2.90 | 9/1/09 8:30 | 0.84 |
| 8/31/09 17:30 | 2.85 | 9/1/09 11:30 | 0.69 |
| 8/31/09 20:30 | 2.82 | 9/1/09 17:30 | 0.81 |
| 8/31/09 23:30 | 2.89 | 9/1/09 20:30 | 0.79 |
| 9/1/09 2:30 | 2.78 | 9/1/09 23:30 | 0.78 |
| 9/1/09 5:30 | 2.66 | 9/2/09 2:30 | 0.76 |
| 9/1/09 8:30 | 2.84 | 9/2/09 5:30 | 0.77 |
| 9/1/09 11:30 | 2.85 | 9/2/09 8:30 | 0.75 |
| 9/1/09 14:30 | 3.40 | 9/2/09 11:30 | 0.80 |
| 9/1/09 17:30 | 3.32 | 9/2/09 14:00 | 0.83 |
| 9/1/09 20:30 | 3.44 | 9/2/09 14:00 | 0.78 |
| 9/1/09 23:30 | 3.32 | 9/2/09 14:30 | 0.78 |

| | | | |
|---|---|---|---|
| 9/2/09 2:30 | 3.57 | 9/2/09 17:00 | 0.87 |
| 9/2/09 5:30 | 3.52 | 9/2/09 20:00 | 0.96 |
| 9/2/09 8:30 | 3.59 | 9/2/09 23:00 | 1.07 |
| 9/2/09 11:30 | 3.91 | 9/3/09 2:00 | 1.13 |
| 9/2/09 14:00 | 3.63 | 9/3/09 5:00 | 1.28 |
| 9/2/09 14:00 | 3.69 | 9/3/09 8:00 | 1.34 |
| 9/2/09 14:30 | 3.99 | 9/3/09 11:00 | 1.45 |
| 9/2/09 17:00 | 3.76 | 9/3/09 14:00 | 1.35 |
| 9/2/09 20:00 | 3.90 | 9/3/09 17:00 | 1.38 |
| 9/2/09 23:00 | 3.99 | 9/3/09 20:00 | 1.36 |
| 9/3/09 2:00 | 3.77 | 9/3/09 23:00 | 1.52 |
| 9/3/09 5:00 | 4.05 | 9/4/09 2:00 | 1.20 |
| 9/3/09 8:00 | 4.24 | 9/4/09 2:00 | 1.30 |
| 9/3/09 14:00 | 3.98 | 9/4/09 5:00 | 1.25 |
| 9/3/09 17:00 | 4.04 | 9/4/09 8:00 | 1.31 |
| 9/3/09 20:00 | 4.24 | 9/4/09 16:00 | 1.26 |
| 9/3/09 23:00 | 4.16 | 9/4/09 20:00 | 1.41 |
| 9/4/09 2:00 | 4.17 | 9/5/09 0:00 | 1.39 |
| 9/4/09 2:00 | 4.19 | 9/5/09 4:00 | 1.39 |
| 9/4/09 5:00 | 4.23 | 9/5/09 8:00 | 1.5 |
| 9/4/09 8:00 | 4.31 | 9/5/09 12:00 | 1.47 |
| 9/4/09 16:00 | 4.23 | 9/5/09 16:00 | 1.41 |
| 9/4/09 20:00 | 4.43 | 9/5/09 20:00 | 1.66 |
| 9/5/09 0:00 | 4.69 | 9/6/09 0:00 | 1.74 |
| 9/5/09 4:00 | 4.54 | 9/6/09 4:00 | 1.58 |
| 9/5/09 8:00 | 4.95 | 9/6/09 8:00 | 1.67 |
| 9/5/09 12:00 | 4.88 | 9/6/09 12:00 | 1.62 |
| 9/5/09 16:00 | 4.62 | 9/6/09 16:00 | 1.57 |
| 9/5/09 20:00 | 4.96 | 9/6/09 20:00 | 1.41 |
| 9/6/09 0:00 | 5.01 | 9/7/09 0:00 | 1.46 |
| 9/6/09 4:00 | 4.87 | 9/7/09 4:00 | 1.49 |
| 9/6/09 8:00 | 4.90 | 9/7/09 8:00 | 1.4 |
| 9/6/09 12:00 | 5.05 | 9/7/09 12:00 | 1.33 |
| 9/6/09 16:00 | 5.23 | 9/7/09 16:00 | 1.36 |
| 9/6/09 20:00 | 5.03 | 9/7/09 20:00 | 1.42 |
| 9/7/09 0:00 | 5.09 | 9/8/09 0:00 | 1.35 |
| 9/7/09 4:00 | 4.99 | 9/8/09 4:00 | 1.35 |
| 9/7/09 12:00 | 5.01 | 9/8/09 8:00 | 1.33 |
| 9/7/09 16:00 | 5.05 | 9/8/09 12:00 | 1.35 |
| 9/7/09 20:00 | 4.96 | 9/8/09 15:00 | 1.25 |

| | | | | |
|---|---|---|---|---|
| 9/8/09 0:00 | 4.94 | | 9/8/09 18:00 | 1.22 |
| 9/8/09 4:00 | 5.18 | | 9/8/09 21:00 | 1.13 |
| 9/8/09 8:00 | 4.89 | | 9/9/09 0:00 | 1.16 |
| 9/8/09 12:00 | 4.74 | | 9/9/09 6:00 | 1.16 |
| 9/8/09 15:00 | 4.62 | | 9/9/09 9:00 | 1.09 |
| 9/8/09 15:00 | 4.56 | | 9/9/09 15:00 | 1.18 |
| 9/8/09 18:00 | 4.64 | | 9/9/09 18:00 | 1.12 |
| 9/8/09 21:00 | 4.64 | | 9/9/09 21:00 | 1.08 |
| 9/8/09 21:00 | 4.47 | | 9/10/09 0:00 | 1.11 |
| 9/15/09 2:00 | 2.79 | | 9/12/09 16:00 | 0.88 |
| 9/17/09 0:15 | 3.54 | | 9/12/09 19:00 | 1.00 |
| 9/17/09 6:15 | 2.72 | | 9/12/09 22:00 | 0.94 |
| 9/17/09 18:15 | 2.65 | | 9/13/09 1:00 | 0.95 |
| 9/17/09 21:15 | 2.69 | | 9/13/09 16:00 | 0.95 |
| 9/18/09 0:15 | 2.62 | | 9/13/09 16:00 | 0.92 |
| 9/18/09 3:15 | 2.73 | | 9/13/09 19:00 | 0.93 |
| 9/18/09 6:15 | 2.93 | | 9/14/09 1:00 | 0.97 |
| 9/18/09 12:15 | 2.73 | | 9/14/09 4:00 | 0.96 |
| 9/18/09 15:00 | 2.60 | | 9/14/09 13:00 | 0.95 |
| 9/18/09 21:00 | 2.46 | | 9/14/09 20:00 | 0.88 |
| 9/19/09 0:00 | 2.26 | | 9/14/09 23:00 | 0.93 |
| 9/19/09 15:00 | 2.77 | | 9/15/09 5:00 | 0.81 |
| 9/19/09 21:00 | 2.81 | | 9/15/09 11:00 | 0.81 |
| 9/20/09 3:00 | 2.94 | | 9/16/09 0:15 | 0.80 |
| 9/20/09 15:00 | 2.91 | | 9/16/09 6:15 | 0.71 |
| 9/20/09 18:00 | 3.04 | | 9/16/09 12:15 | 0.65 |
| 9/21/09 0:00 | 3.10 | | 9/16/09 18:15 | 0.54 |
| 9/21/09 6:00 | 3.15 | | 9/17/09 3:15 | 0.59 |
| 9/21/09 9:00 | 3.26 | | 9/17/09 12:15 | 0.67 |
| 9/21/09 12:00 | 3.21 | | 9/17/09 15:15 | 0.73 |
| 9/23/09 11:00 | 3.24 | | 9/18/09 3:15 | 0.75 |
| 9/24/09 15:00 | 3.74 | | 9/18/09 9:15 | 1.05 |
| 9/25/09 3:00 | 3.48 | | 9/18/09 12:15 | 0.93 |
| 9/25/09 7:00 | 3.60 | | 9/19/09 15:00 | 1.34 |
| 9/25/09 7:00 | 3.50 | | 9/19/09 18:00 | 1.34 |
| 9/25/09 14:00 | 3.53 | | 9/20/09 0:00 | 1.37 |
| 9/25/09 14:00 | 3.55 | | 9/20/09 3:00 | 1.45 |
| 9/26/09 8:00 | 3.57 | | 9/21/09 0:00 | 1.56 |
| 9/26/09 8:00 | 3.57 | | 9/21/09 9:00 | 1.51 |
| 9/26/09 14:00 | 3.54 | | 9/21/09 12:00 | 1.54 |

| | | | | |
|---|---|---|---|---|
| 9/27/09 8:00 | 3.61 | | 9/22/09 3:00 | 1.58 |
| 9/27/09 20:00 | 3.64 | | 9/23/09 15:00 | 1.75 |
| 9/30/09 2:00 | 3.66 | | 9/24/09 11:00 | 1.79 |
| 9/30/09 8:00 | 3.68 | | 9/24/09 23:00 | 1.76 |
| 9/30/09 14:00 | 3.75 | | 9/25/09 3:00 | 1.74 |
| 10/1/09 16:00 | 3.77 | | 9/25/09 20:00 | 1.69 |
| 10/1/09 22:00 | 3.76 | | 9/25/09 20:00 | 1.71 |
| 10/2/09 16:00 | 3.84 | | 9/27/09 2:00 | 1.75 |
| 10/3/09 10:00 | 3.62 | | 9/27/09 14:00 | 1.77 |
| 10/3/09 16:00 | 3.50 | | 9/27/09 14:00 | 1.80 |
| 10/4/09 10:00 | 3.27 | | 9/28/09 2:00 | 1.79 |
| 10/4/09 22:00 | 3.18 | | 9/29/09 2:00 | 1.81 |
| 10/6/09 4:00 | 3.03 | | 9/29/09 14:00 | 1.76 |
| 10/7/09 10:00 | 3.00 | | 9/29/09 14:00 | 1.97 |
| 10/7/09 21:00 | 3.09 | | 10/1/09 22:00 | 2.26 |
| 10/8/09 3:00 | 3.13 | | 10/2/09 16:00 | 2.18 |
| 10/8/09 15:00 | 3.15 | | 10/3/09 4:00 | 2.11 |
| | | | 10/3/09 16:00 | 2.02 |
| | | | 10/4/09 4:00 | 2.03 |
| | | | 10/4/09 16:00 | 2.16 |
| | | | 10/5/09 10:00 | 2.36 |
| | | | 10/5/09 16:00 | 2.34 |
| | | | 10/6/09 4:00 | 2.33 |
| | | | 10/7/09 10:00 | 2.25 |
| | | | 10/7/09 15:00 | 2.31 |
| | | | 10/8/09 9:00 | 2.29 |
| | | | 10/8/09 15:00 | 2.24 |

**2010 North and south tile drain DFBA concentrations**

| North Tile | | South Tile | |
|---|---|---|---|
| Date | Concentration (mg/L) | Date | Concentration (mg/L) |
| 6/2/10 19:30 | 1.43 | 6/2/10 19:30 | 2.87 |
| 6/3/10 7:30 | 1.48 | 6/3/10 7:30 | 2.64 |
| 6/3/10 19:30 | 1.45 | 6/3/10 19:30 | 2.58 |
| 6/4/10 7:30 | 1.59 | 6/4/10 7:30 | 2.46 |
| 6/4/10 19:30 | 1.63 | 6/4/10 19:30 | 2.46 |
| 6/5/10 7:30 | 1.70 | 6/5/10 7:30 | 2.43 |
| 6/5/10 19:30 | 1.67 | 6/5/10 19:30 | 2.24 |
| 6/6/10 7:30 | 1.74 | 6/6/10 7:30 | 2.32 |
| 6/6/10 19:30 | 1.79 | 6/6/10 19:30 | 2.29 |
| 6/7/10 7:30 | 1.78 | 6/7/10 7:30 | 2.16 |
| 6/7/10 19:30 | 1.78 | 6/7/10 19:30 | 2.18 |
| 6/8/10 19:30 | 1.93 | 6/8/10 7:30 | 2.16 |
| 6/9/10 7:30 | 1.95 | 6/11/10 16:00 | 2.76 |
| 6/9/10 19:30 | 2.05 | 6/12/10 4:00 | 2.82 |
| 6/10/10 7:30 | 1.87 | 6/12/10 16:00 | 2.65 |
| 6/10/10 19:30 | 1.71 | 6/13/10 4:00 | 2.48 |
| 6/11/10 7:30 | 1.73 | 6/13/10 16:00 | 2.26 |
| 6/11/10 22:00 | 1.77 | 6/14/10 4:00 | 2.18 |
| 6/12/10 10:00 | 1.76 | 6/14/10 16:00 | 2.05 |
| 6/12/10 22:00 | 1.77 | 6/15/10 4:00 | 1.92 |
| 6/13/10 10:00 | 1.77 | 6/15/10 16:00 | 1.85 |
| 6/13/10 22:00 | 1.69 | 6/16/10 4:00 | 1.78 |
| 6/14/10 10:00 | 1.60 | 6/22/10 15:20 | 1.33 |
| 6/14/10 22:00 | 1.51 | 6/23/10 3:20 | 1.31 |
| 6/15/10 10:00 | 1.37 | 6/23/10 15:20 | 1.30 |
| 6/15/10 22:00 | 1.31 | 6/24/10 3:20 | 1.04 |
| 6/16/10 10:00 | 1.24 | 6/24/10 15:20 | 2.16 |
| 6/22/10 15:20 | 0.66 | 6/25/10 3:20 | 3.13 |
| 6/23/10 3:20 | 0.75 | 6/25/10 15:20 | 4.21 |
| 6/23/10 15:20 | 0.76 | 6/26/10 3:20 | 4.06 |
| 6/24/10 3:20 | 1.25 | 6/26/10 15:20 | 4.97 |
| 6/24/10 15:20 | 1.03 | 6/27/10 3:20 | 4.87 |
| 6/25/10 3:20 | 1.20 | 6/27/10 15:20 | 4.69 |
| 6/25/10 15:20 | 1.45 | 6/28/10 3:20 | 4.40 |
| 6/26/10 3:20 | 0.51 | 6/28/10 16:30 | 4.17 |

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|---|---|---|---|
| 6/26/10 15:20 | 1.81 | 6/29/10 4:30 | 3.91 |
| 6/27/10 3:20 | 1.96 | 6/29/10 16:30 | 3.70 |
| 6/27/10 15:20 | 2.13 | 6/30/10 4:30 | 3.59 |
| 6/28/10 3:20 | 2.14 | 6/30/10 16:30 | 3.72 |
| 6/28/10 16:30 | 2.02 | 7/1/10 4:30 | 3.79 |
| 6/29/10 4:30 | 2.13 | 7/1/10 16:30 | 3.74 |
| 6/29/10 16:30 | 2.29 | 7/2/10 4:30 | 3.55 |
| 6/30/10 4:30 | 2.04 | 7/2/10 22:10 | 3.52 |
| 6/30/10 16:30 | 1.94 | 7/3/10 10:10 | 3.57 |
| 7/1/10 4:30 | 1.98 | 7/3/10 22:10 | 3.44 |
| 7/1/10 16:30 | 2.17 | 7/4/10 10:10 | 3.44 |
| 7/2/10 4:30 | 2.21 | 7/4/10 22:10 | 3.43 |
| 7/2/10 22:10 | 2.26 | 7/5/10 10:10 | 3.22 |
| 7/3/10 4:10 | 2.29 | 7/5/10 22:10 | 3.13 |
| 7/3/10 22:10 | 2.28 | 7/6/10 10:10 | 2.99 |
| 7/4/10 10:10 | 2.33 | 7/6/10 22:10 | 3.06 |
| 7/4/10 22:10 | 2.40 | 7/7/10 10:10 | 3.21 |
| 7/5/10 10:10 | 2.39 | 7/7/10 22:10 | 3.21 |
| 7/5/10 22:10 | 2.41 | 7/8/10 17:30 | 3.46 |
| 7/6/10 10:10 | 2.42 | 7/9/10 5:30 | 3.52 |
| 7/6/10 22:10 | 2.37 | 7/9/10 23:30 | 3.40 |
| 7/7/10 10:10 | 2.43 | 7/10/10 5:30 | 3.42 |
| 7/7/10 22:10 | 2.41 | 7/10/10 17:30 | 3.59 |
| 7/8/10 17:30 | 2.36 | 7/11/10 5:30 | 3.73 |
| 7/8/10 17:30 | 2.54 | 7/11/10 17:30 | 3.39 |
| 7/9/10 5:30 | 2.30 | 7/12/10 5:30 | 3.14 |
| 7/9/10 5:30 | 2.57 | 7/13/10 5:30 | 2.81 |
| 7/9/10 23:30 | 2.53 | 7/13/10 17:30 | 2.32 |
| 7/10/10 5:30 | 2.54 | 7/15/10 2:30 | 1.18 |
| 7/10/10 17:30 | 2.06 | 7/15/10 14:30 | 1.27 |
| 7/10/10 17:30 | 2.39 | 7/16/10 2:30 | 1.39 |
| 7/11/10 5:30 | 2.12 | 7/16/10 14:30 | 1.42 |
| 7/11/10 5:30 | 2.25 | 7/17/10 2:30 | 1.44 |
| 7/11/10 17:30 | 2.27 | 7/17/10 14:30 | 1.46 |
| 7/12/10 5:30 | 2.29 | 7/18/10 2:30 | 1.50 |
| 7/12/10 17:30 | 2.34 | 7/18/10 14:30 | 1.45 |
| 7/13/10 5:30 | 2.05 | 7/19/10 2:30 | 1.45 |
| 7/13/10 17:30 | 1.50 | 7/19/10 14:30 | 1.13 |
| 7/14/10 14:30 | 1.15 | 7/20/10 2:30 | 1.54 |
| 7/15/10 2:30 | 1.14 | 7/20/10 16:00 | 1.54 |

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|---|---|---|---|---|
| 7/15/10 14:30 | 1.19 | | 7/21/10 0:00 | 1.32 |
| 7/16/10 2:30 | 1.20 | | 7/21/10 16:00 | 1.39 |
| 7/16/10 14:30 | 1.24 | | 7/22/10 8:00 | 1.30 |
| 7/17/10 2:30 | 1.19 | | 7/23/10 0:00 | 1.24 |
| 7/17/10 14:30 | 1.23 | | 7/23/10 16:00 | 1.26 |
| 7/18/10 2:30 | 1.20 | | 7/24/10 8:00 | 1.36 |
| 7/18/10 14:30 | 1.25 | | 7/25/10 0:00 | 1.33 |
| 7/19/10 2:30 | 1.15 | | 7/25/10 8:00 | 1.29 |
| 7/19/10 14:30 | 1.18 | | 7/25/10 8:00 | 1.30 |
| 7/20/10 2:30 | 1.12 | | 7/26/10 13:30 | 1.25 |
| 7/20/10 13:00 | 1.22 | | 7/27/10 5:30 | 1.25 |
| 7/20/10 17:00 | 0.49 | | 7/27/10 21:30 | 1.29 |
| 7/20/10 21:00 | 1.22 | | 7/28/10 13:30 | 1.27 |
| 7/21/10 2:00 | 1.19 | | 7/29/10 5:30 | 1.27 |
| 7/21/10 4:00 | 0.78 | | 7/30/10 19:30 | 1.41 |
| 7/21/10 6:00 | 1.03 | | 7/31/10 19:30 | 1.64 |
| 7/21/10 8:00 | 1.21 | | 8/1/10 13:30 | 1.72 |
| 7/21/10 10:00 | 0.42 | | 8/1/10 19:30 | 1.72 |
| 7/21/10 12:00 | 1.20 | | 8/1/10 19:30 | 1.69 |
| 7/21/10 14:18 | 1.06 | | 8/3/10 12:30 | 1.44 |
| 7/21/10 18:18 | 1.13 | | 8/4/10 0:30 | 1.42 |
| 7/21/10 22:18 | 1.20 | | 8/4/10 12:30 | 1.40 |
| 7/22/10 2:18 | 1.22 | | 8/5/10 0:30 | 1.39 |
| 7/22/10 6:18 | 1.20 | | 8/5/10 12:30 | 1.34 |
| 7/22/10 10:18 | 1.23 | | 8/6/10 0:30 | 1.35 |
| 7/22/10 14:18 | 1.24 | | 8/6/10 12:30 | 1.28 |
| 7/23/10 0:18 | 1.24 | | 8/7/10 0:30 | 1.27 |
| 7/23/10 6:18 | 1.16 | | 8/7/10 12:30 | 1.25 |
| 7/23/10 10:18 | 1.06 | | 8/8/10 0:30 | 1.26 |
| 7/23/10 18:30 | 1.16 | | 8/8/10 12:30 | 1.12 |
| 7/24/10 0:30 | 1.16 | | 8/9/10 0:30 | 1.24 |
| 7/24/10 6:30 | 1.17 | | 8/9/10 17:30 | 1.19 |
| 7/24/10 12:30 | 1.17 | | 8/10/10 5:30 | 1.19 |
| 7/24/10 18:30 | 1.35 | | 8/10/10 17:30 | 1.20 |
| 7/25/10 0:30 | 1.26 | | 8/11/10 5:30 | 1.22 |
| 7/25/10 6:30 | 1.30 | | 8/11/10 17:30 | 1.31 |
| 7/25/10 6:30 | 1.29 | | 8/12/10 5:30 | 1.37 |
| 7/26/10 13:30 | 1.29 | | 8/12/10 17:30 | 1.43 |
| 7/27/10 5:30 | 1.33 | | 8/13/10 5:30 | 1.51 |
| 7/27/10 21:30 | 1.50 | | 8/13/10 17:30 | 1.85 |

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|---|---|---|---|---|
| 7/28/10 13:30 | 1.53 | | 8/14/10 5:30 | 2.50 |
| 7/29/10 1:30 | 1.59 | | 8/14/10 17:30 | 3.05 |
| 7/30/10 13:30 | 1.57 | | 8/15/10 5:30 | 3.21 |
| 7/30/10 19:30 | 1.73 | | 8/15/10 17:30 | 3.36 |
| 7/31/10 19:30 | 1.72 | | 8/16/10 5:30 | 3.05 |
| 8/1/10 13:30 | 1.82 | | 8/16/10 19:30 | 3.21 |
| 8/1/10 19:30 | 1.81 | | 8/17/10 11:30 | 2.87 |
| 8/3/10 12:30 | 1.66 | | 8/18/10 3:30 | 2.73 |
| 8/4/10 0:30 | 1.65 | | 8/18/10 19:30 | 2.74 |
| 8/4/10 12:30 | 1.60 | | 8/19/10 11:30 | 2.57 |
| 8/5/10 0:30 | 1.51 | | 8/20/10 3:30 | 2.62 |
| 8/5/10 12:30 | 1.48 | | 8/20/10 19:30 | 2.44 |
| 8/6/10 0:30 | 1.43 | | 8/21/10 11:30 | 2.70 |
| 8/6/10 12:30 | 1.36 | | 8/22/10 3:30 | 2.67 |
| 8/7/10 0:30 | 1.33 | | 8/22/10 19:30 | 3.06 |
| 8/7/10 12:30 | 1.28 | | 8/23/10 11:30 | 3.27 |
| 8/8/10 0:30 | 1.28 | | 8/23/10 11:30 | 3.24 |
| 8/8/10 12:30 | 1.21 | | 8/24/10 19:30 | 3.24 |
| 8/9/10 0:30 | 1.22 | | 8/25/10 3:30 | 2.83 |
| 8/9/10 17:30 | 1.14 | | 8/25/10 11:30 | 3.04 |
| 8/10/10 5:30 | 1.16 | | 8/26/10 19:30 | 2.75 |
| 8/10/10 17:30 | 1.22 | | 8/27/10 11:30 | 2.63 |
| 8/10/10 23:30 | 1.26 | | 8/28/10 3:30 | 2.62 |
| 8/12/10 5:30 | 1.70 | | 8/28/10 19:30 | 2.59 |
| 8/12/10 17:30 | 1.81 | | 8/29/10 11:30 | 2.43 |
| 8/12/10 23:30 | 1.91 | | 8/30/10 3:30 | 2.57 |
| 8/13/10 11:30 | 2.02 | | 8/30/10 19:30 | 2.53 |
| 8/13/10 23:30 | 2.10 | | 8/31/10 11:30 | 2.45 |
| 8/14/10 11:30 | 2.10 | | 9/1/10 3:30 | 2.53 |
| 8/14/10 17:30 | 2.14 | | 9/1/10 13:30 | 2.86 |
| 8/15/10 11:30 | 2.54 | | 9/2/10 5:30 | 2.72 |
| 8/15/10 23:30 | 2.63 | | 9/2/10 21:30 | 3.29 |
| 8/16/10 11:30 | 2.65 | | 9/3/10 13:30 | 3.36 |
| 8/16/10 19:30 | 2.62 | | 9/4/10 5:30 | 3.49 |
| 8/17/10 11:30 | 2.69 | | 9/4/10 21:30 | 3.37 |
| 8/18/10 3:30 | 2.69 | | 9/6/10 5:30 | 3.14 |
| 8/18/10 11:30 | 2.65 | | 9/7/10 13:30 | 2.89 |
| 8/18/10 19:30 | 2.64 | | 9/7/10 21:30 | 3.19 |
| 8/19/10 11:30 | 2.57 | | 9/8/10 13:30 | 2.96 |
| 8/19/10 19:30 | 2.55 | | 9/9/10 5:30 | 3.23 |

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|---|---|---|---|---|
| 8/20/10 3:30 | 2.57 | | 9/9/10 13:30 | 3.09 |
| 8/20/10 19:30 | 2.60 | | 9/9/10 21:30 | 3.36 |
| 8/21/10 11:30 | 2.59 | | 9/10/10 13:30 | 3.81 |
| 8/22/10 3:30 | 2.58 | | 9/11/10 5:30 | 4.19 |
| 8/22/10 19:30 | 2.58 | | 9/11/10 21:30 | 4.23 |
| 8/23/10 11:30 | 2.61 | | 9/12/10 13:30 | 4.58 |
| 8/24/10 3:30 | 2.74 | | 9/13/10 5:30 | 4.66 |
| 8/24/10 19:30 | 2.69 | | 9/13/10 21:30 | 4.53 |
| 8/25/10 3:30 | 2.54 | | 9/14/10 13:30 | 4.79 |
| 8/25/10 11:30 | 2.67 | | 9/15/10 5:30 | 4.75 |
| 8/26/10 19:30 | 2.56 | | 9/15/10 5:30 | 4.72 |
| 8/27/10 11:30 | 2.54 | | 9/16/10 21:30 | 4.57 |
| 8/28/10 3:30 | 2.48 | | 9/17/10 13:30 | 4.58 |
| 8/29/10 11:30 | 2.36 | | 9/18/10 5:30 | 4.44 |
| 8/30/10 3:30 | 2.04 | | 9/18/10 21:30 | 4.18 |
| 8/30/10 19:30 | 2.41 | | 9/19/10 13:30 | 4.05 |
| 9/1/10 3:30 | 2.12 | | 9/20/10 5:30 | 3.95 |
| 9/1/10 13:30 | 2.40 | | 9/20/10 21:30 | 3.88 |
| 9/2/10 5:30 | 2.46 | | 9/21/10 13:30 | 4.07 |
| 9/2/10 21:30 | 2.59 | | 9/22/10 5:30 | 4.35 |
| 9/3/10 13:30 | 2.76 | | 9/22/10 21:30 | 4.45 |
| 9/4/10 5:30 | 2.69 | | 9/23/10 13:30 | 4.44 |
| 9/4/10 21:30 | 2.72 | | 9/24/10 5:30 | 4.39 |
| 9/5/10 13:30 | 2.79 | | 9/24/10 13:30 | 4.55 |
| 9/6/10 5:30 | 2.77 | | 9/25/10 5:30 | 4.49 |
| 9/6/10 21:30 | 2.90 | | 9/25/10 21:30 | 4.52 |
| 9/7/10 13:30 | 2.79 | | 9/26/10 13:30 | 4.48 |
| 9/7/10 21:30 | 2.68 | | 9/27/10 5:30 | 4.52 |
| 9/8/10 13:30 | 2.54 | | 9/27/10 21:30 | 4.48 |
| 9/9/10 5:30 | 2.52 | | 9/28/10 13:30 | 4.34 |
| 9/9/10 21:30 | 2.72 | | 9/29/10 5:30 | 4.55 |
| 9/10/10 13:30 | 2.88 | | 9/29/10 21:30 | 4.75 |
| 9/11/10 5:30 | 2.54 | | 9/30/10 13:30 | 4.62 |
| 9/11/10 21:30 | 2.90 | | 10/1/10 5:30 | 4.76 |
| 9/12/10 13:30 | 3.13 | | 10/1/10 21:30 | 4.76 |
| 9/13/10 5:30 | 3.14 | | 10/4/10 21:30 | 4.04 |
| 9/13/10 21:30 | 3.13 | | 10/5/10 13:30 | 3.72 |
| 9/14/10 13:30 | 3.28 | | 10/6/10 5:30 | 3.72 |
| 9/15/10 5:30 | 3.45 | | 10/6/10 21:30 | 3.86 |
| 9/15/10 5:30 | 3.26 | | 10/7/10 13:30 | 3.95 |

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|---|---|---|---|---|
| 9/16/10 21:30 | 3.34 | | 10/8/10 5:30 | 3.91 |
| 9/17/10 13:30 | 3.44 | | 10/8/10 21:30 | 3.82 |
| 9/18/10 5:30 | 3.38 | | 10/9/10 13:30 | 3.69 |
| 9/18/10 21:30 | 3.27 | | 10/10/10 5:30 | 3.56 |
| 9/19/10 13:30 | 3.42 | | 10/10/10 21:30 | 3.48 |
| 9/20/10 5:30 | 2.91 | | 10/11/10 13:30 | 3.35 |
| 9/20/10 21:30 | 2.67 | | 10/12/10 5:30 | 2.26 |
| 9/21/10 13:30 | 2.92 | | 10/12/10 21:30 | 3.23 |
| 9/22/10 5:30 | 3.03 | | 10/13/10 11:30 | 2.95 |
| 9/22/10 21:30 | 3.11 | | 10/14/10 1:30 | 3.0 |
| 9/23/10 13:30 | 3.17 | | 10/14/10 15:30 | 2.97 |
| 9/24/10 5:30 | 3.20 | | 10/15/10 5:30 | 2.82 |
| 9/24/10 13:30 | 3.21 | | 10/15/10 19:30 | 3.31 |
| 9/25/10 5:30 | 3.21 | | 10/16/10 9:30 | 2.65 |
| 9/25/10 21:30 | 3.16 | | 10/16/10 23:30 | 3.02 |
| 9/26/10 13:30 | 3.19 | | 10/17/10 13:30 | 2.70 |
| 9/27/10 5:30 | 3.15 | | 10/18/10 3:30 | 2.60 |
| 9/27/10 21:30 | 3.15 | | 10/18/10 17:30 | 2.57 |
| 9/28/10 13:30 | 2.88 | | 10/19/10 7:30 | 2.57 |
| 9/29/10 5:30 | 2.90 | | 10/19/10 21:30 | 2.53 |
| 9/29/10 21:30 | 3.04 | | 10/20/10 11:30 | 2.45 |
| 9/30/10 13:30 | 3.18 | | 10/21/10 1:30 | 2.42 |
| 10/1/10 5:30 | 3.22 | | 10/21/10 15:30 | 2.45 |
| 10/1/10 21:30 | 3.28 | | 10/22/10 5:30 | 2.34 |
| 10/1/10 21:30 | 3.30 | | 10/22/10 19:30 | 2.28 |
| 10/4/10 21:30 | 3.14 | | 10/23/10 9:30 | 2.29 |
| 10/5/10 13:30 | 3.05 | | 10/23/10 23:30 | 2.24 |
| 10/6/10 5:30 | 3.04 | | 10/24/10 13:30 | 2.03 |
| 10/6/10 21:30 | 2.96 | | 10/25/10 3:30 | 2.29 |
| 10/7/10 13:30 | 2.98 | | | |
| 10/8/10 5:30 | 2.93 | | | |
| 10/8/10 21:30 | 2.90 | | | |
| 10/9/10 13:30 | 2.82 | | | |
| 10/10/10 5:30 | 2.77 | | | |
| 10/10/10 21:30 | 2.63 | | | |
| 10/11/10 13:30 | 2.59 | | | |
| 10/12/10 5:30 | 2.47 | | | |
| 10/12/10 21:30 | 2.40 | | | |
| 10/13/10 11:30 | 2.30 | | | |
| 10/14/10 1:30 | 2.23 | | | |

| | |
|---|---|
| 10/14/10 15:30 | 2.15 |
| 10/15/10 5:30 | 1.99 |
| 10/15/10 19:30 | 1.94 |
| 10/16/10 9:30 | 1.79 |
| 10/16/10 23:30 | 1.87 |
| 10/17/10 13:30 | 1.75 |
| 10/18/10 3:30 | 1.75 |
| 10/18/10 17:30 | 1.64 |
| 10/19/10 7:30 | 1.60 |
| 10/19/10 21:30 | 1.56 |
| 10/20/10 11:30 | 1.69 |
| 10/21/10 1:30 | 1.51 |
| 10/21/10 15:30 | 1.48 |
| 10/22/10 5:30 | 1.44 |
| 10/22/10 19:30 | 1.50 |
| 10/23/10 9:30 | 1.53 |
| 10/23/10 23:30 | 1.58 |
| 10/24/10 13:30 | 1.53 |
| 10/25/10 3:30 | 1.49 |

**2010 North tile drain PFBA concentrations**

| Date | Concentration (mg/L) |
|---|---|
| 7/21/10 6:00 | 0.10 |
| 7/21/10 8:00 | 0.81 |
| 7/21/10 10:00 | 2.56 |
| 7/21/10 12:00 | 5.87 |
| 7/21/10 14:18 | 7.52 |
| 7/21/10 18:18 | 10.19 |
| 7/21/10 22:18 | 9.95 |
| 7/22/10 2:18 | 11.62 |
| 7/22/10 6:18 | 12.92 |
| 7/22/10 10:18 | 12.48 |
| 7/22/10 14:18 | 11.92 |
| 7/23/10 0:18 | 10.81 |
| 7/23/10 6:18 | 10.03 |
| 7/23/10 10:18 | 7.91 |
| 7/23/10 18:30 | 6.24 |
| 7/24/10 0:30 | 5.09 |
| 7/24/10 6:30 | 4.52 |
| 7/24/10 12:30 | 3.93 |
| 7/24/10 18:30 | 3.46 |
| 7/25/10 0:30 | 3.07 |
| 7/25/10 6:30 | 3.13 |
| 7/25/10 6:30 | 2.39 |
| 7/26/10 13:30 | 2.30 |
| 7/27/10 5:30 | 2.32 |
| 7/27/10 21:30 | 1.77 |
| 7/28/10 13:30 | 1.48 |
| 7/29/10 1:30 | 1.27 |
| 7/30/10 13:30 | 1.12 |
| 7/30/10 19:30 | 1.08 |
| 7/31/10 19:30 | 1.17 |
| 8/1/10 13:30 | 1.18 |
| 8/1/10 19:30 | 1.09 |
| 8/3/10 12:30 | 1.08 |
| 8/4/10 0:30 | 1.03 |
| 8/4/10 12:30 | 1.01 |
| 8/5/10 0:30 | 0.91 |

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|---|---|
| 8/5/10 12:30 | 0.91 |
| 8/6/10 0:30 | 0.87 |
| 8/6/10 12:30 | 0.86 |
| 8/7/10 0:30 | 0.87 |
| 8/7/10 12:30 | 0.86 |
| 8/8/10 0:30 | 0.87 |
| 8/8/10 12:30 | 0.89 |
| 8/9/10 0:30 | 0.89 |
| 8/9/10 17:30 | 0.82 |
| 8/10/10 5:30 | 0.94 |
| 8/10/10 17:30 | 0.84 |
| 8/10/10 23:30 | 0.85 |
| 8/12/10 5:30 | 0.88 |
| 8/12/10 17:30 | 0.89 |
| 8/12/10 23:30 | 1.00 |
| 8/13/10 11:30 | 1.00 |
| 8/13/10 23:30 | 1.05 |
| 8/14/10 11:30 | 1.10 |
| 8/14/10 17:30 | 1.12 |
| 8/15/10 11:30 | 1.15 |
| 8/15/10 23:30 | 1.24 |
| 8/16/10 11:30 | 1.48 |
| 8/16/10 19:30 | 1.54 |
| 8/17/10 11:30 | 1.46 |
| 8/18/10 3:30 | 1.41 |
| 8/18/10 11:30 | 1.33 |
| 8/18/10 19:30 | 1.16 |
| 8/19/10 11:30 | 1.13 |
| 8/19/10 19:30 | 1.09 |
| 8/20/10 3:30 | 0.99 |
| 8/20/10 19:30 | 0.95 |
| 8/21/10 11:30 | 0.92 |
| 8/22/10 3:30 | 0.85 |
| 8/22/10 19:30 | 0.77 |
| 8/23/10 11:30 | 0.74 |
| 8/24/10 3:30 | 0.70 |
| 8/24/10 19:30 | 0.67 |
| 8/25/10 3:30 | 0.66 |
| 8/25/10 11:30 | 1.43 |
| 8/26/10 19:30 | 1.10 |

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|---|---|
| 8/27/10 11:30 | 1.13 |
| 8/28/10 3:30 | 1.17 |
| 8/29/10 11:30 | 1.26 |
| 8/30/10 3:30 | 1.14 |
| 8/30/10 19:30 | 0.93 |
| 9/1/10 3:30 | 0.80 |
| 9/1/10 13:30 | 0.63 |
| 9/2/10 5:30 | 1.12 |
| 9/2/10 21:30 | 0.94 |
| 9/3/10 13:30 | 0.56 |
| 9/4/10 5:30 | 0.54 |
| 9/4/10 21:30 | 0.55 |
| 9/5/10 13:30 | 0.57 |
| 9/6/10 5:30 | 0.53 |
| 9/6/10 21:30 | 0.50 |
| 9/7/10 13:30 | 0.55 |
| 9/7/10 21:30 | 0.54 |
| 9/8/10 13:30 | 0.52 |
| 9/9/10 5:30 | 0.54 |
| 9/9/10 21:30 | 0.54 |
| 9/10/10 13:30 | 0.54 |
| 9/11/10 5:30 | 0.47 |
| 9/11/10 21:30 | 0.14 |
| 9/12/10 13:30 | 0.10 |
| 9/13/10 5:30 | 0.10 |
| 9/13/10 21:30 | 0.06 |
| 9/14/10 13:30 | 0.10 |
| 9/15/10 5:30 | 0.10 |

**2009 irrigation and precipitation rates**

| 2009 Irrigation and Precipitation Events | | |
|---|---|---|
| Date | Irrigation (mm) | Precipitation (mm) |
| 7/9/2009 | 25 | 6.4 |
| 7/10/2009 | 25 | 0 |
| 7/11/2009 | 0 | 1.4 |
| 7/12/2009 | 0 | 0 |
| 7/13/2009 | 25 | 0 |
| 7/14/2009 | 18.75 | 2.9 |
| 7/15/2009 | 12.5 | 0 |
| 7/16/2009 | 11.25 | 0 |
| 7/17/2009 | 5.5 | 0 |
| 7/18/2009 | 0 | 0.7 |
| 7/19/2009 | 0 | 0.4 |
| 7/20/2009 | 25 | 0 |
| 7/21/2009 | 0 | 0 |
| 7/22/2009 | 25 | 0 |
| 7/23/2009 | 0 | 0 |
| 7/24/2009 | 22.5 | 0 |
| 7/25/2009 | 0 | 0 |
| 7/26/2009 | 0 | 1.4 |
| 7/27/2009 | 22.5 | 0 |
| 7/28/2009 | 0 | 10.6 |
| 7/29/2009 | 18.75 | 0.2 |
| 7/30/2009 | 0 | 0.4 |
| 7/31/2009 | 12.5 | 0 |
| 8/1/2009 | 0 | 9 |
| 8/2/2009 | 0 | 0.2 |
| 8/3/2009 | 0 | 7.2 |
| 8/4/2009 | 12.5 | 1.3 |
| 8/5/2009 | 0 | 0.6 |
| 8/6/2009 | 0 | 1.2 |
| 8/7/2009 | 0 | 0 |
| 8/8/2009 | 0 | 0 |
| 8/9/2009 | 0 | 0.4 |
| 8/10/2009 | 0 | 0 |
| 8/11/2009 | 22.25 | 0 |
| 8/12/2009 | 0 | 0 |

| | | |
|---|---|---|
| 8/13/2009 | 0 | 0 |
| 8/14/2009 | 12.5 | 5.8 |
| 8/15/2009 | 0 | 0 |
| 8/16/2009 | 0 | 0.2 |
| 8/17/2009 | 0 | 0 |
| 8/18/2009 | 12.5 | 3.4 |
| 8/19/2009 | 10 | 0 |
| 8/20/2009 | 0 | 0 |
| 8/21/2009 | 12.5 | 0 |
| 8/22/2009 | 0 | 0 |
| 8/23/2009 | 0 | 0 |
| 8/24/2009 | 13.75 | 0 |
| 8/25/2009 | 11.25 | 0 |
| 8/26/2009 | 10 | 0 |
| 8/27/2009 | 0 | 0 |
| 8/28/2009 | 15 | 0 |
| 8/29/2009 | 0 | 0 |
| 8/30/2009 | 0 | 0 |
| 8/31/2009 | 12.5 | 0 |
| 9/1/2009 | 0 | 0 |
| 9/2/2009 | 12.75 | 0 |
| 9/3/2009 | 0 | 0 |
| 9/4/2009 | 12.5 | 0.4 |
| 9/5/2009 | 0 | 0 |
| 9/6/2009 | 0 | 0.7 |
| 9/7/2009 | 0 | 0 |
| 9/8/2009 | 3.75 | 0 |
| 9/9/2009 | 0 | 0 |
| 9/10/2009 | 0 | 0 |
| 9/11/2009 | 7.5 | 0 |
| 9/12/2009 | 0 | 0 |
| 9/13/2009 | 0 | 0 |
| 9/14/2009 | 10.625 | 0 |
| 9/15/2009 | 13.625 | 0 |
| 9/16/2009 | 10.625 | 0 |
| 9/17/2009 | 10.625 | 0.6 |
| 9/18/2009 | 10.625 | 0 |
| 9/19/2009 | 10.625 | 0 |
| 9/20/2009 | 0 | 0 |
| 9/21/2009 | 10.625 | 0 |

| 9/22/2009 | 10.625 | 0 |
|-----------|--------|-----|
| 9/23/2009 | 10.625 | 0 |
| 9/24/2009 | 10.625 | 0 |
| 9/25/2009 | 10.625 | 0 |
| 9/26/2009 | 10.625 | 0 |
| 9/27/2009 | 0 | 0 |
| 9/28/2009 | 0 | 0.5 |
| 9/29/2009 | 10.625 | 0 |
| 9/30/2009 | 10.625 | 0 |
| 10/1/2009 | 25 | 0 |
| 10/2/2009 | 0 | 0 |

**2010 irrigation and precipitation rates**

| 2010 Irrigation and Precipitation Events | | |
|---|---|---|
| Date | Irrigation (mm) | Precipitation (mm) |
| 6/2/2010 13:40 | 10.08 | 0.00 |
| 6/3/2010 11:20 | 7.62 | 1.70 |
| 6/4/2010 11:20 | 0.00 | 0.00 |
| 6/5/2010 18:00 | 2.49 | 0.00 |
| 6/6/2010 18:00 | 0.00 | 0.00 |
| 6/7/2010 18:00 | 0.00 | 10.20 |
| 6/8/2010 18:00 | 0.00 | 3.80 |
| 6/9/2010 18:00 | 0.00 | 6.20 |
| 6/10/2010 18:00 | 0.00 | 2.60 |
| 6/11/2010 18:00 | 0.00 | 0.00 |
| 6/12/2010 18:00 | 0.00 | 0.00 |
| 6/13/2010 18:00 | 0.00 | 0.00 |
| 6/14/2010 18:00 | 0.00 | 0.00 |
| 6/15/2010 18:00 | 2.99 | 0.00 |
| 6/16/2010 18:00 | 3.02 | 0.00 |
| 6/17/2010 18:00 | 2.99 | 0.00 |
| 6/18/2010 18:00 | 2.98 | 0.00 |
| 6/19/2010 18:00 | 2.95 | 0.00 |
| 6/20/2010 18:00 | 2.98 | 0.00 |
| 6/21/2010 18:00 | 3.03 | 0.00 |
| 6/22/2010 18:00 | 11.18 | 0.00 |
| 6/23/2010 18:00 | 3.80 | 34.90 |
| 6/24/2010 18:00 | 9.30 | 0.20 |
| 6/25/2010 18:00 | 11.99 | 0.70 |
| 6/26/2010 18:00 | 0.00 | 0.40 |
| 6/27/2010 18:00 | 0.00 | 8.00 |
| 6/28/2010 18:00 | 0.00 | 0.00 |
| 6/29/2010 18:00 | 0.00 | 14.90 |
| 6/30/2010 18:00 | 0.00 | 0.60 |
| 7/1/2010 17:19 | 13.87 | 0.00 |
| 7/2/2010 18:00 | 5.87 | 0.00 |
| 7/3/2010 18:00 | 2.34 | 1.00 |
| 7/4/2010 18:00 | 0.00 | 0.00 |
| 7/5/2010 18:00 | 0.00 | 6.50 |
| 7/6/2010 18:00 | 11.05 | 1.20 |

| | | |
|---|---|---|
| 7/7/2010 18:00 | 9.71 | 0.40 |
| 7/8/2010 18:00 | 0.00 | 0.00 |
| 7/9/2010 18:00 | 6.03 | 7.20 |
| 7/10/2010 18:00 | 5.99 | 8.40 |
| 7/11/2010 18:00 | 6.00 | 1.00 |
| 7/12/2010 18:00 | 2.35 | 22.60 |
| 7/13/2010 18:00 | 0.00 | 51.70 |
| 7/14/2010 18:00 | 0.00 | 0.20 |
| 7/15/2010 18:00 | 0.00 | 1.20 |
| 7/16/2010 18:00 | 0.00 | 3.60 |
| 7/17/2010 18:00 | 0.00 | 0.00 |
| 7/18/2010 18:00 | 0.00 | 1.40 |
| 7/19/2010 18:00 | 0.00 | 5.30 |
| 7/20/2010 18:00 | 0.00 | 0.20 |
| 7/21/2010 18:00 | 0.00 | 0.00 |
| 7/22/2010 18:00 | 0.00 | 8.90 |
| 7/23/2010 18:00 | 0.00 | 1.10 |
| 7/24/2010 18:00 | 0.00 | 0.00 |
| 7/25/2010 18:00 | 0.00 | 0.00 |
| 7/26/2010 18:00 | 8.75 | 1.40 |
| 7/27/2010 18:00 | 8.68 | 0.00 |
| 7/28/2010 18:00 | 3.40 | 0.20 |
| 7/29/2010 18:00 | 8.80 | 0.00 |
| 7/30/2010 18:00 | 2.61 | 5.60 |
| 7/31/2010 18:00 | 2.62 | 0.60 |
| 8/1/2010 18:00 | 2.56 | 0.00 |
| 8/2/2010 18:00 | 2.58 | 0.00 |
| 8/3/2010 18:00 | 1.99 | 1.80 |
| 8/4/2010 18:00 | 2.62 | 0.00 |
| 8/5/2010 18:00 | 2.66 | 0.20 |
| 8/6/2010 18:00 | 2.59 | 0.00 |
| 8/7/2010 18:00 | 2.59 | 0.60 |
| 8/8/2010 18:00 | 2.59 | 0.00 |
| 8/9/2010 18:00 | 7.88 | 0.00 |
| 8/10/2010 18:00 | 6.11 | 0.70 |
| 8/11/2010 18:00 | 6.07 | 0.00 |
| 8/12/2010 18:00 | 5.93 | 5.90 |
| 8/13/2010 18:00 | 6.06 | 12.00 |
| 8/14/2010 18:00 | 6.08 | 0.00 |
| 8/15/2010 18:00 | 2.57 | 0.00 |

| | | |
|---|---|---|
| 8/16/2010 18:00 | 4.79 | 0.40 |
| 8/17/2010 18:00 | 4.09 | 0.00 |
| 8/18/2010 18:00 | 4.08 | 0.00 |
| 8/19/2010 18:00 | 4.06 | 0.00 |
| 8/20/2010 18:00 | 4.08 | 0.50 |
| 8/21/2010 18:00 | 2.33 | 6.60 |
| 8/22/2010 18:00 | 4.12 | 0.80 |
| 8/23/2010 18:00 | 3.93 | 0.20 |
| 8/24/2010 18:00 | 4.00 | 0.00 |
| 8/25/2010 18:00 | 3.99 | 0.00 |
| 8/26/2010 18:00 | 3.98 | 0.00 |
| 8/27/2010 18:00 | 4.10 | 0.40 |
| 8/28/2010 18:00 | 3.46 | 0.00 |
| 8/29/2010 18:00 | 0.00 | 0.00 |
| 8/30/2010 18:00 | 3.93 | 3.00 |
| 8/31/2010 18:00 | 4.10 | 0.00 |
| 9/1/2010 18:00 | 0.00 | 7.60 |
| 9/2/2010 18:00 | 4.13 | 0.00 |
| 9/3/2010 18:00 | 4.08 | 0.00 |
| 9/4/2010 18:00 | 4.12 | 0.90 |
| 9/5/2010 18:00 | 0.00 | 0.00 |
| 9/6/2010 18:00 | 0.00 | 0.00 |
| 9/7/2010 18:00 | 4.17 | 0.00 |
| 9/8/2010 18:00 | 0.00 | 11.80 |
| 9/9/2010 18:00 | 4.13 | 0.50 |
| 9/10/2010 18:00 | 4.15 | 0.00 |
| 9/11/2010 18:00 | 4.17 | 0.00 |
| 9/12/2010 18:00 | 3.99 | 2.70 |
| 9/13/2010 18:00 | 0.00 | 3.70 |
| 9/14/2010 18:00 | 4.18 | 0.20 |
| 9/15/2010 18:00 | 0.00 | 2.60 |
| 9/16/2010 18:00 | 0.00 | 0.20 |
| 9/17/2010 18:00 | 0.00 | 0.00 |
| 9/18/2010 18:00 | 0.00 | 0.00 |
| 9/19/2010 18:00 | 0.00 | 4.00 |
| 9/20/2010 18:00 | 3.15 | 3.70 |
| 9/21/2010 18:00 | 3.70 | 0.00 |
| 9/22/2010 18:00 | 3.65 | 0.00 |
| 9/23/2010 18:00 | 4.66 | 0.00 |
| 9/24/2010 18:00 | 7.64 | 0.00 |

| | | |
|---|---|---|
| 9/25/2010 18:00 | 0.00 | 0.00 |
| 9/26/2010 18:00 | 4.02 | 0.60 |
| 9/27/2010 18:00 | 4.03 | 0.00 |
| 9/28/2010 18:00 | 4.10 | 6.60 |
| 9/29/2010 18:00 | 4.08 | 0.00 |
| 9/30/2010 18:00 | 4.68 | 0.00 |
| 10/1/2010 18:00 | 0.00 | 0.00 |
| 10/2/2010 18:00 | 0.00 | 0.00 |
| 10/3/2010 18:00 | 0.00 | 0.00 |
| 10/4/2010 18:00 | 3.93 | 0.40 |
| 10/5/2010 18:00 | 4.61 | 0.00 |

**Completed list of monitoring well benzoic acid concentrations during the 2009 and 2010 sampling seasons**

| | Sampling Date and Concentration (mg/L) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Well | Aug 2009 DFBA | Oct 2009 DFBA | Jun 2010 DFBA | Jul 2010 DFBA | Aug 2010 DFBA | Aug 2010 PFBA | Sep 2010 DFBA | Sep 2010 PFBA | Oct 2010 DFBA | Oct 2010 PFBA |
| MW09-01 | 3.86 | 4.09 | 7.94 | 4.89 | 4.02 | 1.12 | 5.01 | 0 | 3.1 | 0 |
| MW09-02 | 0 | 0 | 1.75 | 1.68 | 0.96 | 2.24 | 1.18 | 0 | 1.18 | 0 |
| MW09-03 | 0 | 0 | 0.14 | 3.37 | 0.58 | 0 | 1.72 | 0 | 3.19 | 0 |
| MW09-04 | 0 | 0 | 0.3 | 3.38 | 2.73 | 0 | 1.74 | 0 | 1.71 | 0 |
| MW09-05 | 0.14 | 0 | 0 | 0 | 0.03 | 0 | 0 | 0 | 0 | 0 |
| MW09-06 | N/A | N/A | 0 | 3.13 | 1.03 | 0 | 0.81 | 0 | 0.63 | 0 |
| MW09-07 | 0 | 0 | 0.47 | 0.37 | 0.19 | 0 | 0.11 | 0 | 0.14 | 0 |
| MW09-08 | 0 | 0.14 | 1.41 | 0.23 | 3.04 | 0 | 6.21 | 0 | 2.45 | 0 |
| MW09-09 | 0.11 | 2.75 | 0 | 1.51 | 1.28 | 0 | 1.13 | 0 | 0.96 | 0 |
| MW09-10A | N/A | N/A | 0 | 0 | 0 | 0 | 0.01 | 0 | 0 | 0 |
| MW09-10B | N/A | N/A | 0.39 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MW09-10C | N/A | N/A | 0 | 0.04 | 0 | 0 | 0 | 0 | 0 | 0 |
| MW09-11A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| MW10-11B | N/A | N/A | 0.12 | 0 | 0 | 0 | 0.01 | 0 | 0 | 0 |
| MW10-11C | N/A | N/A | 0 | 0 | 0 | 0 | 0.08 | 0 | 0 | 0 |
| MW09-12A | 1.24 | 1.75 | 3.19 | 2.56 | 2.58 | 0 | 3.3 | 0 | 2.02 | 0 |
| MW10-12B | N/A | N/A | 2.26 | 0.21 | 0.07 | 0 | 0.17 | 0 | 0 | 0 |
| MW10-12C | N/A | N/A | 0 | 0 | 0 | 0.02 | 0 | 0 | 0 | 0 |
| MW09-13A | N/A | N/A | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

| MW09-13B | N/A | N/A | 0.09 | 0.02 | 0.11 | 0 | 0.1 | 0 | 0 | 0 |
|----------|-----|-----|------|------|------|-----|------|-----|------|------|
| MW09-13C | N/A | N/A | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0.04 |
| MW10-14B | N/A | N/A | 0.06 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MW10-14C | N/A | N/A | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MW10-15B | N/A | N/A | 0 | 0 | 0 | 0 | 0.01 | 0 | 0.05 | 0 |
| MW10-15C | N/A | N/A | 0.21 | 1.41 | 0 | 0 | 0 | 0 | 0 | 0 |

**2010 Lysimeter Results - Results from the north and south lysimeter sampling nests**

|  | | Concentrations (mg/L) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | | June | July | | August | | September | | | October | |
|  | Sampling Depth (m) | Original | Original | Split | Original | Split | Overnight | 1 hour Original | 1 hour Duplicate | Overnight | 1 hour Original |
| **North** | 0.15 | 12.61 | 3.15 | N/A | 0.3 | N/A | 0 | 0.02 | 0.05 | 0 | 0.01 |
|  | 0.3 | 18.5 | 12.16 | 11.85 | 7.46 | N/A | 5.42 | 4.08 | 2.25 | 3.94 | 3.55 |
|  | 0.56 | 0.24 | 0.21 | N/A | 0.2 | 0.56 | 0.45 | 0.28 | 0.14 | 0.97 | 0.55 |
|  | 0.72 | 0.36 | 0.21 | N/A | 3.48 | N/A | 3.55 | 2.51 | N/A | 5.08 | 3.33 |
|  | 1.46 | 0.02 | 0.04 | 0.06 | 1.72 | 1.72 | 1.41 | N/A | N/A | 1.86 | 0 |

|  | | Concentrations (mg/L) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | | June | July | | August | | September | | | October | |
|  | Sampling Depth (m) | Original | Original | Split | Original | Split | Overnight | 1 hour Original | 1 hour Duplicate | Overnight | 1 hour Original |
| **South** | 0.15 | 8.32 | 3.53 | N/A | 3.06 | N/A | 3.59 | 2.28 | 1.81 | 3.61 | 0 |
|  | 0.3 | 30.37 | 24.3 | N/A | 18.18 | 18.01 | 12.39 | 13.19 | 8.48 | 8.53 | 9.52 |
|  | 0.73 | 1.22 | 0.72 | N/A | 0.59 | N/A | 0.31 | 0.31 | N/A | 0.33 | 0 |
|  | 0.88 | 0 | 0.12 | N/A | 0 | 0 | 0.15 | 0.1 | N/A | 0.27 | 0.33 |
|  | 1.38 | 0 | 0 | 0 | 0.1 | N/A | 0.18 | N/A | N/A | 0.71 | 0.72 |

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# APPENDIX B: SOIL BATCH TESTS

## DFBA Soil Degradation Test

| Soil Degradation Set 1 | |
|---|---|
| Date | Concentration (mg/L) |
| 5/18/2011 | 101.64 |
| 6/2/2011 | 102.02 |
| 6/27/2011 | 101.48 |

| Soil Degradation Set 2 | |
|---|---|
| Date | Concentration (mg/L) |
| 5/18/2011 | 101.81 |
| 6/2/2011 | 101.53 |
| 6/27/2011 | 101.23 |
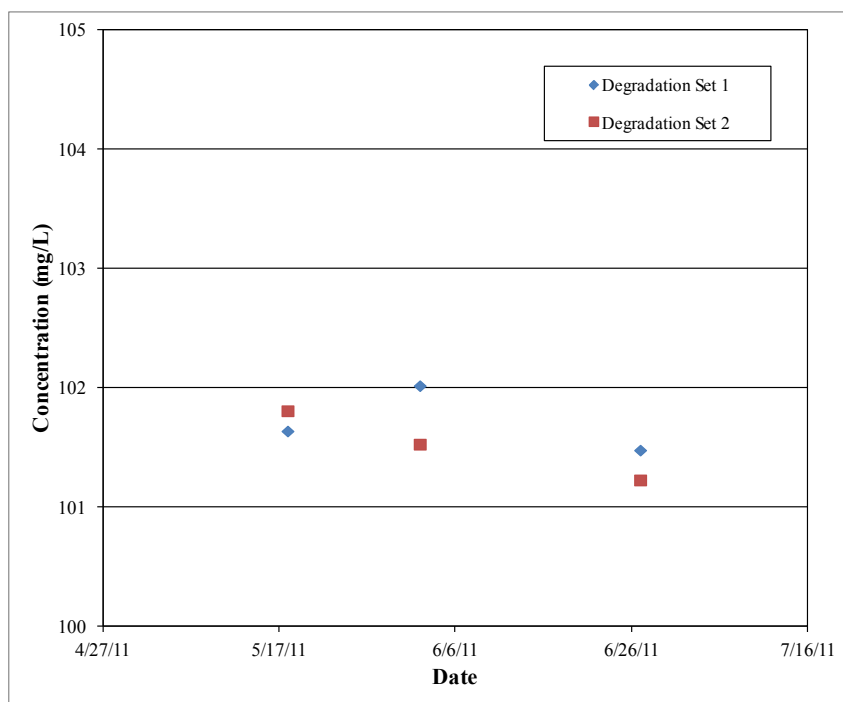
**Summary of DFBA Soil Extraction Results**

| Extraction Method | Percent Recovered |
|---|---|
| $H_2O$ | 69.5 |
| $H_2O$ | 40.3 |
| $H_2O$ | 66.1 |
| $H_2O$ | 85.1 |
| $H_2O$ | 81.0 |
| $H_2O$ | 59.2 |
| $H_2O$ | 61.5 |
| $H_2O$ | 75.9 |
| $H_2O$ | 55.3 |
| $H_2O$ | 55.3 |
| $H_2O$ | 84.3 |
| $H_2O$ | 76.7 |
| **Average** | **67.5** |

| Extraction Method | Percent Recovered |
|---|---|
| Methanol | 41.1 |
| Methanol | 32.1 |
| Methanol | 58.6 |
| Methanol | 46.2 |
| Methanol | 46.5 |
| **Average** | **44.9** |

| Extraction Method | Percent Recovered |
|---|---|
| CaCl | 43.3 |
| CaCl | 41.5 |
| CaCl | 65.0 |
| CaCl | 59.3 |
| CaCl | 53.3 |
| CaCl | 39.3 |
| CaCl | 49.3 |
| CaCl | 45.5 |
| CaCl | 46.5 |
| **Average** | **49.2** |

| Extraction Method | Percent Recovered |
|---|---|
| Sonication | 42.4 |
| Sonication | 50.5 |
| Sonication | 0.0 |
| Sonication | 56.9 |
| **Average** | **37.5** |

**Raw data of batch test trials.  In total 4 soil depths were tested over 7 different concentrations.**

| Depth | Applied Concentration (mg/L) | | Measured Concentration (mg/L) (Ceq) | | | | Average Measured Concentration (mg/L) | | q (g/g) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DFBA | PFBA | DFBA Sample 1 | DFBA Sample 2 | PFBA Sample 1 | PFBA Sample 2 | DFBA | PFBA | DFBA Sample 1 | DFBA Sample 2 | PFBA Sample 1 | PFBA Sample 2 |
| | 0.97 | 0.68 | 1.00 | 1.01 | 0.79 | 0.75 | 1.01 | 0.77 | -6.00E-08 | -8.00E-08 | -2.20E-07 | -1.40E-07 |
| | 4.86 | 3.68 | 4.79 | 4.85 | 3.51 | 4.23 | 4.82 | 3.87 | 1.40E-07 | 2.00E-08 | 3.40E-07 | -1.10E-06 |
| | 9.54 | 7.50 | 9.79 | 10.46 | 8.22 | 7.88 | 10.13 | 8.05 | -5.00E-07 | -1.84E-06 | -1.44E-06 | -7.60E-07 |
| 2.1-2.4m | 14.30 | 10.25 | 15.49 | 19.05 | 10.97 | 11.85 | 17.27 | 11.41 | -2.38E-06 | -9.50E-06 | -1.44E-06 | -3.20E-06 |
| | 48.75 | 45.95 | 50.53 | 50.42 | 46.75 | N/A | 50.48 | 46.75 | -3.56E-06 | -3.34E-06 | -1.60E-06 | N/A |
| | 105.21 | 91.87 | 101.72 | 102.55 | 90.94 | 99.37 | 102.14 | 95.16 | 6.98E-06 | 5.32E-06 | 1.86E-06 | -1.50E-05 |
| | 191.25 | 195.79 | 191.91 | 185.34 | 192.38 | 195.29 | 188.63 | 193.84 | -1.32E-06 | 1.18E-05 | 6.82E-06 | 1.00E-06 |
| | 0.97 | 0.68 | 0.98 | 0.96 | 0.69 | 0.65 | 0.97 | 0.67 | -2.00E-08 | 2.00E-08 | -2.00E-08 | 6.00E-08 |
| | 4.86 | 3.68 | 4.98 | 4.82 | 4.17 | 5.48 | 4.90 | 4.83 | -2.40E-07 | 8.00E-08 | -9.80E-07 | -3.60E-06 |
| | 9.54 | 7.50 | 10.11 | 10.39 | 6.72 | 6.56 | 10.25 | 6.64 | -1.14E-06 | -1.70E-06 | 1.56E-06 | 1.88E-06 |
| 1.7-1.9m | 14.30 | 10.25 | 16.95 | 17.49 | 9.37 | 9.04 | 17.22 | 9.21 | -5.30E-06 | -6.38E-06 | 1.76E-06 | 2.42E-06 |
| | 48.75 | 45.95 | 49.15 | 51.03 | 43.86 | 43.70 | 50.09 | 43.78 | -8.00E-07 | -4.56E-06 | 4.18E-06 | 4.50E-06 |
| | 105.21 | 91.87 | 99.09 | 119.13 | 89.19 | 92.48 | 109.11 | 90.84 | 1.22E-05 | -2.78E-05 | 5.36E-06 | -1.22E-06 |
| | 191.25 | 195.79 | 215.59 | 205.42 | 191.50 | 198.39 | 210.51 | 194.95 | -4.87E-05 | -2.83E-05 | 8.58E-06 | -5.20E-06 |

| Depth | Applied Concentration (mg/L) | | Measured Concentration (mg/L) (Ceq) | | | | Average Measured Concentration (mg/L) | | q (g/g) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DFBA | PFBA | DFBA Sample 1 | DFBA Sample 2 | PFBA Sample 1 | PFBA Sample 2 | DFBA | PFBA | DFBA Sample 1 | DFBA Sample 2 | PFBA Sample 1 | PFBA Sample 2 |
| 0.3-0.4m | 0.97 | 0.68 | 0.98 | 0.99 | 0.53 | N/A | 0.99 | 0.53 | -2.00E-08 | -4.00E-08 | 3.00E-07 | N/A |
| | 4.86 | 3.68 | 4.99 | 5.19 | 3.64 | N/A | 5.09 | 3.64 | -2.60E-07 | -6.60E-07 | 8.00E-08 | N/A |
| | 9.54 | 7.50 | 10.09 | 10.25 | 7.09 | 6.96 | 10.17 | 7.03 | -1.10E-06 | -1.42E-06 | 8.20E-07 | 1.08E-06 |
| | 14.30 | 10.25 | 16.90 | 16.49 | 9.37 | 9.67 | 16.70 | 9.52 | -5.20E-06 | -4.38E-06 | 1.76E-06 | 1.16E-06 |
| | 48.75 | 45.95 | 50.14 | N/A | 41.63 | N/A | 50.14 | 41.63 | -2.78E-06 | N/A | 8.64E-06 | N/A |
| | 105.21 | 91.87 | 111.30 | N/A | 94.17 | N/A | 111.30 | 94.17 | -1.22E-05 | N/A | -4.60E-06 | N/A |
| | 191.25 | 195.79 | 200.89 | N/A | 188.62 | N/A | 200.89 | 188.62 | -1.93E-05 | N/A | 1.43E-05 | N/A |
| 0.6-0.9m | 0.97 | 0.68 | 0.84 | 0.84 | 0.94 | 0.87 | 0.84 | 0.91 | 2.60E-07 | 2.60E-07 | -5.20E-07 | -3.80E-07 |
| | 4.86 | 3.68 | 5.00 | 4.91 | 4.75 | 4.58 | 4.96 | 4.67 | -2.80E-07 | -1.00E-07 | -2.14E-06 | -1.80E-06 |
| | 9.54 | 7.50 | 9.78 | 11.17 | 8.96 | 8.98 | 10.48 | 8.97 | -4.80E-07 | -3.26E-06 | -2.92E-06 | -2.96E-06 |
| | 14.30 | 10.25 | 15.05 | 15.35 | 11.01 | 14.94 | 15.20 | 12.98 | -1.50E-06 | -2.10E-06 | -1.52E-06 | -9.38E-06 |
| | 48.75 | 45.95 | 52.10 | 51.25 | 48.51 | 45.46 | 51.68 | 46.99 | -6.70E-06 | -5.00E-06 | -5.12E-06 | 9.80E-07 |
| | 105.21 | 91.87 | 112.57 | 106.92 | 98.06 | 94.42 | 109.75 | 96.24 | -1.47E-05 | -3.42E-06 | -1.24E-05 | -5.10E-06 |
| | 191.25 | 195.79 | 191.75 | 203.11 | 197.93 | N/A | 197.43 | 197.93 | -1.00E-06 | -2.37E-05 | -4.28E-06 | N/A |

**Summary statistics of applied vs recovered concentrations over all soil depths.**

| Applied Concentrations (mg/L) | | Average Recovered Concentrations (mg/L) | | Total Number of Samples | | Standard Deviation of Recovered Concentration (mg/L) | | Standard Error of Concentration (mg/L) | | Average 'q' Value (g/g) | | Standard Deviation of 'q' (g/g) | | Standard Error of 'q' (g/g) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DFBA | PFBA | DFBA | PFBA | DFBA | PFBA | DFBA | PFBA | DFBA | PFBA | DFBA | PFBA | DFBA | PFBA | DFBA | PFBA |
| 0.97 | 0.68 | 0.95 | 0.74 | 8 | 7 | 0.065 | 0.12 | 0.022 | 0.048 | 4E-08 | -1E-07 | 1.3E-07 | 2.55E-07 | 4.6E-08 | 9.65E-08 |
| 4.86 | 3.68 | 4.94 | 4.33 | 8 | 7 | 0.120 | 0.62 | 0.042 | 0.23 | -1.6E-07 | -1E-06 | 2.41E-07 | 1.25E-06 | 8.52E-08 | 4.73E-07 |
| 9.54 | 7.5 | 10.25 | 7.67 | 8 | 8 | 0.416 | 0.91 | 0.14 | 0.32 | -1.4E-06 | -3E-07 | 8.33E-07 | 1.83E-06 | 2.94E-07 | 6.47E-07 |
| 14.3 | 10.25 | 16.59 | 10.77 | 8 | 8 | 1.23 | 1.82 | 0.43 | 0.64 | -4.6E-06 | -1E-06 | 2.47E-06 | 3.66E-06 | 8.74E-07 | 1.29E-06 |
| 48.75 | 45.95 | 50.66 | 44.98 | 7 | 6 | 0.86 | 2.23 | 0.32 | 0.91 | -3.8E-06 | 1.9E-06 | 1.72E-06 | 4.47E-06 | 6.51E-07 | 1.82E-06 |
| 105.21 | 91.87 | 107.61 | 94.09 | 7 | 7 | 6.59 | 3.38 | 2.49 | 1.29 | -4.8E-06 | -4E-06 | 1.32E-05 | 6.77E-06 | 4.98E-06 | 2.56E-06 |
| 191.25 | 195.79 | 199.14 | 194.02 | 7 | 6 | 9.45 | 3.51 | 3.57 | 1.43 | -1.6E-05 | 3.5E-06 | 1.89E-05 | 7.03E-06 | 7.15E-06 | 2.87E-06 |

**Calculated "Worst Case" Linear Isotherm for both DFBA and PFBA**

| DFBA "Worst Case" Linear Isotherm | | | PFBA "Worst Case" Linear Isotherm | | | Calculated "Worst Case" distribution coefficient (Kd) Value ($cm^3$/g) | |
|---|---|---|---|---|---|---|---|
| Recovered Concentration (mg/L) | Converted Concentration ($g/cm^3$) | Calculated 'q' (g/g) | Recovered Concentration (mg/L) | Converted Concentration ($g/cm^3$) | Calculated 'q' (g/g) | | |
| 0.84 | 8.40E-07 | 2.60E-07 | 0.53 | 5.30E-07 | 3.00E-07 | DFBA | PFBA |
| 4.79 | 4.79E-06 | 1.40E-07 | 3.51 | 3.51E-06 | 3.40E-07 | 0.0789 | 0.0678 |
| 9.78 | 9.78E-06 | -4.80E-07 | 6.56 | 6.56E-06 | 1.88E-06 | | |
| 15.05 | 1.51E-05 | -1.50E-06 | 9.04 | 9.04E-06 | 2.42E-06 | | |
| 49.15 | 4.92E-05 | -8.00E-07 | 41.63 | 4.16E-05 | 8.64E-06 | | |
| 99.09 | 9.91E-05 | 1.22E-05 | 89.19 | 8.92E-05 | 5.36E-06 | | |
| 185.34 | 1.85E-04 | 1.18E-05 | 188.62 | 1.89E-04 | 1.43E-05 | | |

**Calculated isotherms for both DFBA and PFBA**
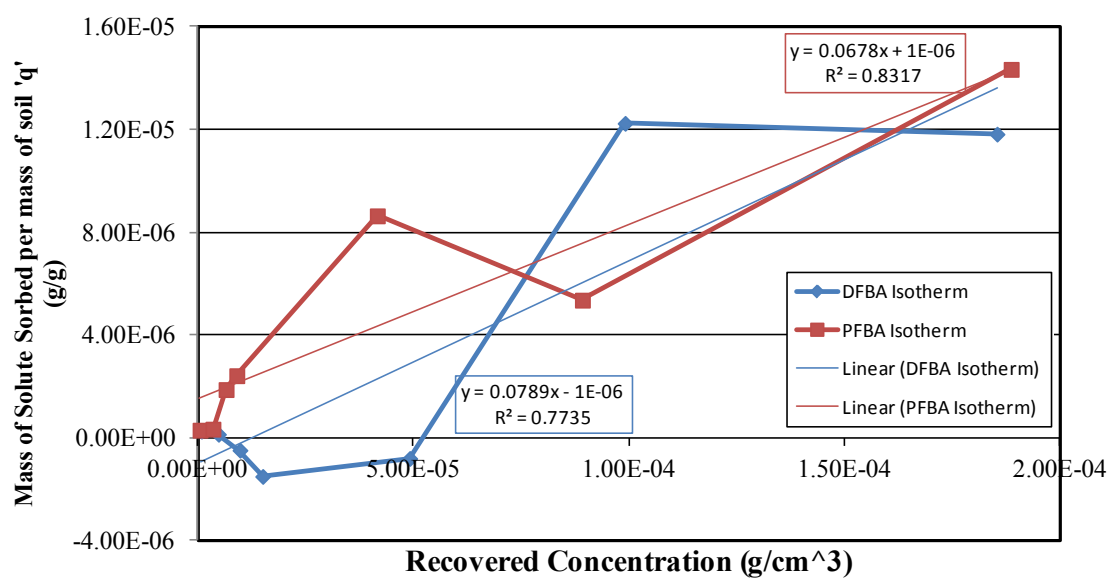
**APPENDIX C: FIELD SOIL EXTRACTIONS**

**Summary statistics and concentrations of 2009 DFBA soil extractions**

| Core Sample Depth (m) | Borehole Location and Porewater Concentration | | | | | |
|---|---|---|---|---|---|---|
| | 1 - North Edge Plot A (mg/L) | 1- Duplicate (mg/L) | 2 - Above North Tile (mg/L) | 2- Duplicate (mg/L) | 3 - Center of Plot (mg/L) | 3- Duplicate (mg/L) |
| -0.1 | 0 | 0 | 9.84 | N/A | 110.21 | 107.72 |
| -0.2 | 0.36 | 0 | 45.13 | 46.29 | 12.57 | 13.33 |
| -0.75 | 11.64 | N/A | 20.70 | 20.19 | 0 | 0 |
| -1.15 | N/A | N/A | N/A | N/A | N/A | N/A |
| -1.75 | 4.45 | 6.91 | N/A | N/A | N/A | N/A |
| -2.7 | 0 | 0 | N/A | N/A | N/A | N/A |
| -3.7 | 0 | N/A | N/A | N/A | 0 | 0.13 |
| -4.75 | 0 | N/A | N/A | N/A | 0.40 | N/A |
| -5.65 | 0 | 0 | N/A | N/A | 0 | N/A |

| Core Sample Depth (m) | Borehole Location and Porewater Concentration | | | |
|---|---|---|---|---|
| | 4 - Above South Tile (mg/L) | 4- Duplicate (mg/L) | 5 - Southern Edge Plot A (mg/L) | 5- Duplicate (mg/L) |
| -0.1 | 15.88 | N/A | 233.07 | 178.03 |
| -0.2 | 44.0774 | 34.86 | 102.01 | 101.52 |
| -0.75 | 13.9085 | 14.02 | 1.0859 | N/A |
| -1.15 | 12.029 | N/A | N/A | N/A |
| -1.75 | 3.04 | 3.90 | 0.01 | N/A |
| -2.7 | N/A | N/A | 0 | N/A |
| -3.7 | N/A | N/A | N/A | N/A |
| -4.75 | N/A | N/A | 0.01 | N/A |
| -5.65 | N/A | N/A | 0.01 | N/A |

| Core Sample Depth (m) | Average (mg/L) | Max (mg/L) | Min (mg/L) | Standard Deviation (mg/L) | Standard Error (mg/L) |
|---|---|---|---|---|---|
| -0.1 | 81.84 | 233.07 | 0.00 | 84.06 | 29.72 |
| -0.2 | 40.01 | 102.01 | 0.00 | 35.18 | 11.12 |
| -0.75 | 10.19 | 20.70 | 0.00 | 8.15 | 2.88 |
| -1.15 | 12.03 | 12.03 | 12.03 | 0.00 | 0.00 |
| -1.75 | 3.66 | 6.91 | 0.01 | 2.23 | 1.00 |
| -2.7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -3.7 | 0.04 | 0.13 | 0.00 | 0.06 | 0.03 |
| -4.75 | 0.14 | 0.40 | 0.00 | 0.19 | 0.11 |
| -5.65 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |

**Summary statistics of 2010 DFBA soil extraction results and porewater concentrations at each borehole**

| Depth of Core Sample (m) | N | Average (mg/L) | Maximum (mg/L) | Minimum (mg/L) | Standard Deviation (mg/L) | Standard Error (mg/L) |
|---|---|---|---|---|---|---|
| -0.05 | 30 | 0.22 | 5.32 | 0.00 | 0.96 | 0.17 |
| -0.15 | 28 | 1.01 | 17.29 | 0.00 | 3.34 | 0.63 |
| -0.25 | 37 | 1.58 | 31.38 | 0.00 | 5.39 | 0.89 |
| -0.35 | 29 | 3.22 | 34.71 | 0.00 | 7.35 | 1.37 |
| -0.45 | 31 | 3.61 | 31.89 | 0.00 | 6.47 | 1.16 |
| -0.65 | 31 | 3.45 | 28.05 | 0.00 | 6.04 | 1.09 |
| -0.75 | 2 | 0.83 | 1.67 | 0.00 | 0.83 | 0.59 |
| -0.85 | 3 | 0.92 | 2.75 | 0.00 | 1.30 | 0.75 |
| -0.95 | 3 | 0.98 | 2.43 | 0.00 | 1.05 | 0.60 |
| -1.05 | 2 | 1.67 | 3.33 | 0.00 | 1.67 | 1.18 |
| -1.15 | 8 | 3.27 | 11.72 | 0.00 | 4.31 | 1.52 |
| -1.25 | 9 | 2.16 | 9.86 | 0.00 | 3.43 | 1.14 |
| -1.35 | 6 | 1.44 | 6.92 | 0.00 | 2.50 | 1.02 |
| -1.5 | 3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -1.75 | 2 | 1.06 | 1.92 | 0.19 | 0.86 | 0.61 |
| -2 | 3 | 0.06 | 0.19 | 0.00 | 0.09 | 0.05 |
| -2.35 | 1 | 1.15 | 1.15 | 1.15 | N/A | N/A |
| -2.5 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -2.8 | 1 | 0.00 | 0.00 | 0.00 | N/A | N/A |
| -3 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -3.5 | 3 | 0.13 | 0.38 | 0.00 | 0.18 | 0.10 |
| -4 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -4.5 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -4.75 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -5 | 2 | 1.06 | 2.11 | 0.00 | 1.06 | 0.75 |

| Core Sample Depth (m) | Borehole Location and Porewater Concentration | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 |
| -0.05 | 0 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 5.32 | 0.00 | 0.00 |
| -0.15 | 0 | 0 | 0.00 | 0.45 | 0.00 | 0.00 | 0.00 | 0.00 | 2.24 | 0.00 | 1.15 |
| -0.25 | 0 | 0 | 0.00 | 2.37 | 1.79 | 0.00 | 0.00 | 0.83 | 0.00 | 8.39 | 0.00 |
| -0.35 | 0 | 0 | 0.00 | 5.19 | 4.10 | 0.00 | 0.00 | 5.00 | 7.04 | 21.20 | 1.54 |
| -0.45 | 0 | 0 | 0.00 | 0.96 | 5.38 | 0.00 | 3.52 | 7.30 | 7.24 | 14.67 | 14.79 |
| -0.65 | 0 | 0 | 5.00 | 0.00 | 4.93 | 1.09 | 2.88 | 0.13 | 0.00 | 10.25 | 0.00 |
| -0.75 | 0 | | | | 1.67 | | | | | | |
| -0.85 | | 0 | | | 0.00 | | | | | 2.75 | |
| -0.95 | | 0 | | | 0.51 | 2.43 | | | | | |
| -1.05 | | | | 0.00 | | | | | | | |
| -1.15 | | | 3.84 | | | | 1.73 | | | | |
| -1.25 | | | | | | | | | | | |
| -1.35 | | | 1.47 | | | | 0.26 | | | | |
| -1.5 | 0 | 0 | | | 0.00 | | | | | | |
| -1.75 | | | 1.92 | | | | 0.19 | | | | |
| -2 | 0 | 0.19 | | | 0.00 | | | | | | |
| -2.35 | | | 1.15 | | | | | | | | |
| -2.5 | 0 | | | | 0.00 | | | | | | |
| -2.8 | | | 0.00 | | | | | | | | |
| -3 | | 0 | | | 0.00 | | | | | | |
| -3.5 | | 0.38 | 0.00 | | 0.00 | | | | | | |
| -4 | | 0 | | | 0.00 | | | | | | |
| -4.5 | | 0 | | | 0.00 | | | | | | |
| -4.75 | | | 0.00 | | | | 0.00 | | | | |
| -5 | | 2.11 | | | 0.00 | | | | | | |

| Core Sample Depth (m) | Borehole Location and Porewater Concentration | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 |
| -0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.13 | 0.32 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 5.89 | 17.29 | 0.00 | 0.00 | 0.26 | 0.00 |
| -0.25 | 0.00 | 0.00 | 3.14 | 0.00 | 0.00 | 9.61 | 31.38 | 0.00 | 0.00 | 0.00 | 0.00 |
| -0.35 | 0.00 | 0.00 | 7.75 | 0.00 | 1.09 | 5.76 | 34.71 | 0.00 | 0.00 | 0.00 | 0.00 |
| -0.45 | 3.91 | 3.07 | 5.70 | 5.70 | 0.00 | 0.64 | 31.89 | 0.00 | 1.47 | 0.58 | 0.00 |
| -0.65 | 13.00 | 5.32 | 0.13 | 4.35 | 0.00 | 0.00 | 28.05 | 9.03 | 7.88 | 0.00 | 0.00 |
| -0.75 | | | | | | | | | | | |
| -0.85 | | | | | | | | | | | |
| -0.95 | | | | | | | | | | | |
| -1.05 | | | | | | | | | | | |
| -1.15 | 0.00 | 0.00 | | 0.00 | | | | | 8.90 | | |
| -1.25 | | | 0.00 | | 0.00 | | | | | 0.00 | 9.86 |
| -1.35 | | | | | | 0.00 | 0.00 | 0.00 | | | |
| -1.5 | | | | | | | | | | | |
| -1.75 | | | | | | | | | | | |
| -2 | | | | | | | | | | | |
| -2.35 | | | | | | | | | | | |
| -2.5 | | | | | | | | | | | |
| -2.8 | | | | | | | | | | | |
| -3 | | | | | | | | | | | |
| -3.5 | | | | | | | | | | | |
| -4 | | | | | | | | | | | |
| -4.5 | | | | | | | | | | | |
| -4.75 | | | | | | | | | | | |
| -5 | | | | | | | | | | | |

| Core Sample Depth (m) | Borehole Location and Porewater Concentration | | | | |
|---|---|---|---|---|---|
| | 65 | 66 | 67 | 68 | 69 |
| -0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -0.25 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 |
| -0.35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| -0.45 | 0.00 | 0.00 | 0.00 | 2.43 | 0.00 |
| -0.65 | 0.00 | 0.00 | 0.00 | 13.77 | 0.38 |
| -0.75 | | | | | |
| -0.85 | | | | | |
| -0.95 | | | | | |
| -1.05 | | 3.33 | | | |
| -1.15 | | | | 11.72 | |
| -1.25 | 3.27 | | 6.34 | | |
| -1.35 | | | | | 6.92 |
| -1.5 | | | | | |
| -1.75 | | | | | |
| -2 | | | | | |
| -2.35 | | | | | |
| -2.5 | | | | | |
| -2.8 | | | | | |
| -3 | | | | | |
| -3.5 | | | | | |
| -4 | | | | | |
| -4.5 | | | | | |
| -4.75 | | | | | |
| -5 | | | | | |

**APPENDIX D: QA/QC**

**Complete List of 2009 and 2010 QA/QC samples analyzed**

| 2010 Soil Extraction Duplicates | |
|---|---|
| Primary Sample Concentration (mg/L) | Duplicate Sample Concentration (mg/L) |
| 0.21 | 0.00 |
| 0.41 | 0.15 |
| 8.59 | 6.53 |
| 0.00 | 0.00 |
| 0.64 | 0.45 |
| 1.27 | 1.41 |
| 0.80 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.76 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.82 | 0.61 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |
| 0.17 | 0.00 |
| 0.00 | 0.00 |
| 1.06 | 0.92 |
| 0.00 | 0.00 |
| 0.00 | 0.00 |

| 2010 Monitoring Well Equipment Blanks | |
|---|---|
| Date | Concentration (mg/L) |
| 7/8/10 0:00 | 0 |
| 7/8/10 0:00 | 0 |
| 10/4/10 0:00 | 0 |
| 10/4/10 0:00 | 0 |
| 10/4/10 0:00 | 0 |

| 2009-2010 Tile and Monitoring Well Duplicate/Split | | |
|---|---|---|
| Date | Primary Sample Concentration (mg/L) | Duplicate or Split Sample Concentration (mg/L) |
| 9/3/09 20:00 | 4.32 | 4.24 |
| 9/3/09 23:00 | 4.08 | 4.16 |
| 9/4/09 2:00 | 1.40 | 1.30 |
| 9/5/09 12:00 | 4.50 | 4.88 |
| 9/8/09 15:00 | 1.08 | 1.25 |
| 9/21/09 0:00 | 3.10 | 3.06 |
| 9/21/09 9:00 | 3.26 | 3.44 |
| 9/27/09 2:00 | 1.75 | 1.77 |
| 10/3/09 16:00 | 3.50 | 3.41 |
| 10/6/09 4:00 | 2.33 | 2.30 |
| 10/6/09 4:00 | 3.03 | 3.17 |
| 6/27/10 3:20 | 2.03 | 1.96 |
| 6/28/10 16:30 | 4.17 | 4.17 |
| 6/29/10 16:30 | 2.19 | 2.29 |
| 7/2/10 4:30 | 3.55 | 3.55 |
| 7/9/10 0:00 | 5.01 | 5.04 |
| 7/9/10 0:00 | 1.13 | 1.09 |
| 7/9/10 0:00 | 2.42 | 2.48 |
| 7/9/10 0:00 | 0.06 | 0.00 |
| 7/10/10 17:30 | 3.59 | 3.10 |
| 7/13/10 17:30 | 1.50 | 1.32 |
| 7/25/10 6:30 | 1.30 | 1.29 |
| 7/25/10 6:30 | 2.30 | 2.32 |
| 7/25/10 8:00 | 1.29 | 1.30 |
| 7/26/10 6:00 | 0.08 | 0.06 |
| 8/1/10 19:30 | 1.72 | 1.69 |
| 8/3/10 0:00 | 473.62 | 475.20 |
| 8/3/10 8:30 | 0.12 | 0.12 |
| 8/7/10 0:00 | 12.16 | 11.85 |
| 8/7/10 0:00 | 0.04 | 0.06 |
| 8/7/10 0:00 | 0.00 | 0.00 |
| 8/7/10 0:00 | 3.38 | 1.97 |
| 8/7/10 0:00 | 0.02 | 0.00 |
| 8/7/10 0:00 | 0.00 | 0.00 |

| | | |
|---|---|---|
| 8/7/10 0:00 | 1.54 | 1.47 |
| 8/10/10 0:00 | 1.28 | 1.23 |
| 8/10/10 0:00 | 1.72 | 1.72 |
| 8/10/10 0:00 | 0.58 | 0.59 |
| 8/10/10 0:00 | 18.18 | 18.01 |
| 8/13/10 23:30 | 2.08 | 2.10 |
| 8/14/10 17:30 | 3.06 | 3.05 |
| 8/17/10 10:30 | 0.15 | 0.13 |
| 8/19/10 19:30 | 2.57 | 2.55 |
| 8/23/10 11:30 | 3.27 | 3.24 |
| 8/24/10 2:30 | 0.11 | 0.01 |
| 9/1/10 2:30 | 0.11 | 0.13 |
| 9/8/10 13:30 | 2.54 | 2.09 |
| 9/8/10 13:30 | 0.47 | 0.37 |
| 9/8/10 13:30 | 2.96 | 2.59 |
| 9/15/10 5:30 | 4.75 | 4.72 |
| 9/15/10 5:30 | 3.45 | 3.26 |
| 9/21/10 13:30 | 4.07 | 4.01 |
| 10/1/10 21:30 | 3.28 | 3.30 |
| 10/2/10 2:30 | 0.00 | 0.00 |
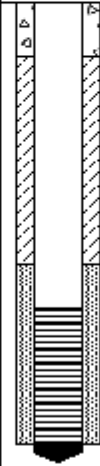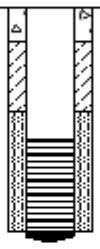
**APPENDIX E: BOREHOLE LOGS**

| PROJECT: | Devon Salt Research | | MW09-01/C0X-01 | |
|---|---|---|---|---|
| BORING LOCATION: | Devon site, North edge of plot A | | GROUND SURFACE ELEVATION AND DATUM: 725.051 m.a.s.l. | |
| DRILLING CONTRACTOR: | Envirocore | | DATE STARTED: 22-Aug-08 | DATE FINISHED: 22-Aug-08 |
| DRILLING METHOD: | Direct Push Macropore 38mm (1.5 in) | | BH DEPTH (m): 6.65 | Well Stick Up (m): 0.387 |
| DRILLING EQUIPMENT: | Geoprobe 6610 Track Unit | | Well hole Diameter (inch): 2 | Well Diameter (inch): 1 |
| SAMPLING METHOD: | Coring with PVC liner | | LOGGED BY: M. Callaghan | |
| Easting: 314648.96 | Northing: 5907209.362 | | Well Installation: U of C | REG. NO. |

| DEPTH (meter) | SAMPLES | | | | DESCRIPTION NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.051 m.a.s.l. | | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|---|
| | Sample No. | Sample | Blows/ Foot | OVM Reading | | | |

Lithology descriptions (by depth):

- Topsoil - Loose, black to brown, dry to wet
- Glaciolacustrine Silty Loam (Disturbed)- Dense, black to brown, moist to wet, massive, roots
- Glaciolacustrine Silty Loam (Undisturbed)- Dense, yellow to brown, moist to wet, locally thinly bedded, roots to till contact
- Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel
- Sand- Loose to dense, yellow to brown, fine to medium grained sand, moist to wet
- Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel, fractures visible through entirety section, interlayered sands from 4.9-5.1 m
- Sand- Loose to dense, yellow to brown, fine to medium grained sand, moist to wet

Well Construction Details and/or Drilling Remarks:
- Backfill, 0-0.3m
- Bentonite, 0.3-1.63m
- Sandpack, 1.613-2 m
- Screen, 1.75-2 m

University of Calgary - Imperial Oil Limited — 04-05-50-26W4M

| PROJECT: | Devon Salt Research | | | | | MW09-02/C0X-02 | |
|---|---|---|---|---|---|---|---|

**BORING LOCATION:** Devon site, North of the center of plot A

**GROUND SURFACE ELEVATION AND DATUM:** 725.086

**DRILLING CONTRACTOR:** Envirocore

**DATE STARTED:** 22-Aug-08  **DATE FINISHED:** 22-Aug-08

**DRILLING METHOD:** Direct Push Macropore 38mm (1.5 in)

**BH Depth (m):** 2.4  **Well Stick Up (m):** 0.5

**DRILLING EQUIPMENT:** Geoprobe 6610 Track Unit

**Well hole diameter (inch):** 2  **Well Diameter (inch):** 1

**SAMPLING METHOD:** Coring with PVC liner

**LOGGED BY:** M. Callaghan

**Easting:** 314648.32  **Northing:** 5907202.387

**Well Installation:** U of C  **REG. NO.**

| DEPTH (meter) | SAMPLES | | | | DESCRIPTION — NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.086 m.a.s.l. | | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|---|
| | Sample No. | Sample | Blows/Foot | OVM Reading | | | |

Topsoil- Loose, black to brown, dry to wet

Glaciolacustrine Silty Loam (Disturbed)- Dense, black to brown, moist to wet, massive, roots observed to 0.7 m

Backfill, 0-0.3 m

Bentonite, 0.3-1.23 m

Sandpack, 1.23-2.4 m

Screen, 1.48-2.4 m

University of Calgary - Imperial Oil Limited

04-05-50-26W4M

| PROJECT: | Devon Salt Research | | MW09-04/C0X-04 |
|---|---|---|---|

| BORING LOCATION: | Devon site, South of central plot A |
|---|---|

**GROUND SURFACE ELEVATION AND DATUM:** 725.161 m.a.s.l.

| DRILLING CONTRACTOR: | Envirocore |
|---|---|

DATE STARTED: 8-Aug-08  DATE FINISHED: 8-Aug-08

| DRILLING METHOD: | Direct Push Macropore 38mm (1.5 in) |
|---|---|

BH DEPTH (m): 2.46   Well Stick Up (m): 0.5

| DRILLING EQUIPMENT: | Geoprobe 6610 Track Unit |
|---|---|

Well hole Diameter (inch): 2   Well Diameter (inch): 1

| SAMPLING METHOD: | Coring with PVC liner |
|---|---|

LOGGED BY: M. Callaghan

| Easting: | 314648.26 | Northing: 5907193.786 |
|---|---|---|

Well Installation: U of C   REG. NO.

### SAMPLES / DESCRIPTION

| DEPTH (meter) | Sample No. | Sample | Blows/Foot | OVM Reading | DESCRIPTION — NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.161 m.a.s.l. | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|
| 0 | | | | | Topsoil- Loose, black to brown, dry to wet | |
| | | | | | Glaciolacustrine Silty Loam (Disturbed)- Dense, black to brown, moist to wet, massive, roots | |
| 1 | | | | | | Bentonite, 0.3-1.46 m |
| 2 | | | | | | Sandpack, 1.46-2.46 m |
| | | | | | | Screen, 1.71-2.46 m |
| 3 | | | | | | |

| University of Calgary - Imperial Oil Limited | | 04-05-50-26W4M | |
|---|---|---|---|

| PROJECT: | Devon Salt Research | MW09-05/C0X-05 |
|---|---|---|
| BORING LOCATION: | Devon site, South edge of plot A | GROUND SURFACE ELEVATION AND DATUM: 725.259 m.a.s.l. |
| DRILLING CONTRACTOR: | Envirocore | DATE STARTED: 22-Aug-08   DATE FINISHED:22-Aug-08 |
| DRILLING METHOD: | Direct Push Macropore 38mm (1.5 in) | BH DEPTH (m): 1.98   Well Stick Up (m): 0.5 |
| DRILLING EQUIPMENT: | Geoprobe 6610 Track Unit | Well hole diameter (inch): 2   Well Diameter (inch): 1 |
| SAMPLING METHOD: | Coring with PVC liner | LOGGED BY: M. Callaghan |
| Easting: 314648.269 | Northing: 5907189.181 | Well Installation: U of C   REG. NO. |
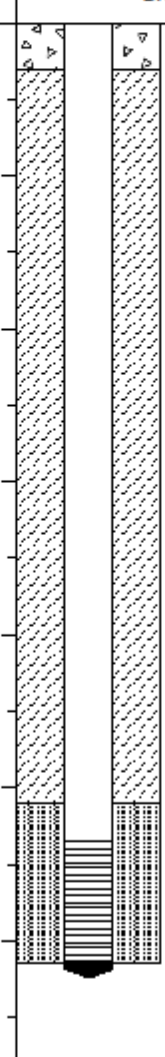
**DESCRIPTION** — NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.259 m.a.s.l.

**WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS**

- Topsoil- Loose, black to brown, dry to wet
- Glaciolacustrine Silty Loam (Disturbed)- Dense, black to brown, moist to wet, massive, roots
- Glaciolacustrine Silty Loam (Undisturbed)- Dense, yellow to brown, moist to wet, locally thinly bedded, roots to till contact, dark grey laminations and brittle fracture at 1.5-2.1 m
- Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel, trace sand laminations at 2.45 m, oxidized fracture between 3.04-4.5 m
- Sand- Loose to dense, yellow to brown, fine to medium grained sand, moist to wet
- Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel
- Missing
- Sand- Loose to dense, yellow to brown, fine to medium grained sand, moist to wet
- Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel, sand mixed in at 6.34 to 6.45 m

Bentonite, 0.3-0.93
Sandpack, 0.93-1.98 m
Screen, 1.18-1.98 m

University of Calgary - Imperial Oil Limited    04-05-50-26W4M

| PROJECT: | Devon Salt Research | | MW09-11B | |
|---|---|---|---|---|

| BORING LOCATION: | Devon site, East of plot A |
|---|---|

**GROUND SURFACE ELEVATION AND DATUM:** 725.094 m.a.s.l.

| DRILLING CONTRACTOR: | Envirocore |
|---|---|

| DATE STARTED: | Nov-09 | DATE FINISHED: Nov-09 |
|---|---|---|

| DRILLING METHOD: | Solid Stem Auger 6 in |
|---|---|

| BH DEPTH (m): | 4.44 | Well Stick Up (m): | 0.78 |
|---|---|---|---|

| DRILLING EQUIPMENT: | Diedrich D-50 Track Unit |
|---|---|

| Well hole Diameter (inch): 6 | Well Diameter (m): | 2 |
|---|---|---|

| SAMPLING METHOD: | None |
|---|---|

| LOGGED BY: | N/A |
|---|---|

| Easting: | 314665.403 | Northing: | 5907195.819 |
|---|---|---|---|

| Well Installation: | Envirocore | REG. NO. |
|---|---|---|

| DEPTH (meter) | SAMPLES | | | | DESCRIPTION NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.094 m.a.s.l. | | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|---|
| | Sample No. | Sample | Blows/ Foot | OVM Reading | | | |

No corresponding borehole log for this well location

Backfill, 0-0.3m

Bentonite, 0.3-3.835 m

Sandpack, 3.835-4.4 m

Screen, 4.1-4.4 m

| University of Calgary - Imperial Oil Limited | 04-05-50-26W4M | |
|---|---|---|

| PROJECT: | | | | Devon Salt Research | | | MW09-11C | | |
|---|---|---|---|---|---|---|---|---|---|

**BORING LOCATION:** Devon site, East of plot A

**GROUND SURFACE ELEVATION AND DATUM:** 725.096 m.a.s.l.

**DRILLING CONTRACTOR:** Envirocore

**DATE STARTED:** 14-Aug-09  **DATE FINISHED:** 14-Aug-09

**DRILLING METHOD:** Solid Stem Auger 6 in

**BH DEPTH (m):** 6.41  **Well Stick Up (m):** 0.767

**DRILLING EQUIPMENT:** Diedrich D-50 Track Unit

**Well hole Diameter (inch):** 6  **Well Diameter (m):** 2

**SAMPLING METHOD:** None

**LOGGED BY:** N/A

**Easting:** 314664.381  **Northing:** 5907195.669

**Well Installation:** Envirocore  **REG. NO.**

| DEPTH (meter) | SAMPLES | | | | DESCRIPTION NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.096 m.a.s.l. | | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|---|
| | Sample No. | Sample | Blows/Foot | OVM Reading | | | |

No corresponding borehole log for this location

Back fill, 0-0.3 m

Bentonite, 0.3-5.8 m

Sandpack, 5.8-6.4 m

Screen, 6.1-6.4 m

University of Calgary - Imperial Oil Limited

04-05-50-26W4M

| PROJECT: | | | | | Devon Salt Research | | MW09-13A/C0X-03 | |
|---|---|---|---|---|---|---|---|---|

**PROJECT:** Devon Salt Research — **MW09-13A/C0X-03**

**BORING LOCATION:** Devon site, Center of plot A

**GROUND SURFACE ELEVATION AND DATUM:** 725.104 m.a.s.l.

**DRILLING CONTRACTOR:** Envirocore

**DATE STARTED:** 22-Aug-08  **DATE FINISHED:** 22-Aug-08

**DRILLING METHOD:** Direct Push Macropore 38mm (1.5 in)

**BH DEPTH (m):** 2.05  **Well Stick Up (m):** 0.5

**DRILLING EQUIPMENT:** Geoprobe 6610 Track Unit

**Well hole Diameter (inch):** 2  **Well Diameter (inch):** 1

**SAMPLING METHOD:** Coring with PVC liner

**LOGGED BY:** M. Callaghan

**Easting:** 314647.894  **Northing:** 5907198.559  **Well Installation:** U of C  **REG. NO.**

**SAMPLES** — DEPTH (meter), Sample No., Sample, Blows/Foot, OVM Reading

**DESCRIPTION** — NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. — Surface Elevation: 725.104 m.a.s.l.

**WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS**

Topsoil- Loose, black to brown, dry to wet

Glaciolacustrine Silty Loam (Disturbed)- Dense, black to brown, moist to wet, massive, roots

Glaciolacustrine Silty Loam (Undisturbed)- Dense, yellow to brown, moist to wet, locally thinly bedded, roots to till contact, grey clay laminations at 2 m

Bentonite, 0.3-1.5 m

Sandpack, 1.5-2.03 m

Screen, 1.75-2.03 m

University of Calgary - Imperial Oil Limited — 04-05-50-26W4M

| PROJECT: | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Devon Salt Research** | | | | | **MW09-13B/C0X-03** | | |

| BORING LOCATION: Devon site, Center of plot A | GROUND SURFACE ELEVATION AND DATUM: 725.59 m.a.s.l. | |
|---|---|---|
| DRILLING CONTRACTOR: Envirocore | DATE STARTED: Nov-09 | DATE FINISHED: Nov-09 |
| DRILLING METHOD: Solid Stem Auger 6 in | BH DEPTH (m): 4.52 | Well Stick Up (m): 0.5 |
| DRILLING EQUIPMENT: Diedrich D-50 Track Unit | Well hole Diameter (inch): 6 | Well Diameter (inch): 1 |
| SAMPLING METHOD: None | LOGGED BY: M. Callaghan | |
| Easting: 314648.663 | Northing: 5907198.583 | Well Installation: Envirocore | REG. NO. |

**DESCRIPTION**
NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs.
Surface Elevation: 725.59 m.a.s.l.

| SAMPLES | | | | | DESCRIPTION | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|
| DEPTH (meter) | Sample No. | Sample | Blows/Foot | OVM Reading | | |

Topsoil- Loose, black to brown, dry to wet

Glaciolacustrine Silty Loam (Disturbed)- Dense, black to brown, moist to wet, massive, roots

Glaciolacustrine Silty Loam (Undisturbed)- Dense, yellow to brown, moist to wet, locally thinly bedded, roots to till contact, grey clay laminations at 2 m

Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel, trace coarse sand

Sand- Loose to dense, yellow to brown, fine to medium grained sand, moist to wet

Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel, sand lens at 5.13-5.16 m

Bentonite, 0.3-3.9 m

Sandpack, 3.9-4.52 m

Screen, 4.15-4.52 m

University of Calgary - Imperial Oil Limited

04-05-50-26W4M

| PROJECT: | Devon Salt Research | | | MW09-13C/C0X-03 | |
|---|---|---|---|---|---|

| BORING LOCATION: Devon Site, Center of plot A | GROUND SURFACE ELEVATION AND DATUM: 724.864 m.a.s.l. | |
|---|---|---|

| DRILLING CONTRACTOR: Envirocore | DATE STARTED: Nov-09 | DATE FINISHED: Nov-09 |
|---|---|---|

| DRILLING METHOD: Solid Stem Auger 6 in | BH DEPTH (m): 6.14 | Well Stick Up (m): 0.5 |
|---|---|---|

| DRILLING EQUIPMENT: Diedrich D-50 Track Unit | Well hole Diameter (inch): 6 | Well Diameter (m): 1 |
|---|---|---|

| SAMPLING METHOD: None | LOGGED BY: M. Callaghan | |
|---|---|---|

| Easting: 314649.415 | Northing: 5907198.57 | Well Installation: Envirocore | REG. NO. |
|---|---|---|---|

| DEPTH (meter) | SAMPLES | | | | DESCRIPTION — NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 724.864 m.a.s.l. | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|
| | Sample No. | Sample | Blows/ Foot | OVM Reading | | |

Description column (top to bottom):

- Topsoil- Loose, black to brown, dry to wet
- Glaciolacustrine Silty Loam (Disturbed)- Dense, black to brown, moist to wet, massive, roots
- Glaciolacustrine Silty Loam (Undisturbed)- Dense, yellow to brown, moist to wet, locally thinly bedded, roots to till contact, grey clay laminations at 2 m
- Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel, trace coarse sand
- Sand- Loose to dense, yellow to brown, fine to medium grained sand, moist to wet
- Glacial Till- Dense to very dense, grey to brown, moist, locally thinly bedded sand, local oxidization, trace fine gravel, sand lens at 5.13-5.16 m

Well construction remarks:

- Bentonite, 0.3-5.1 m
- Sandpack, 5.1-6.14 m
- Screen, 5.35-6.14 m

| University of Calgary - Imperial Oil Limited | 04-05-50-26W4M | |
|---|---|---|

| PROJECT: | Devon Salt Research | | | | | | | MW09-14B | | |
|---|---|---|---|---|---|---|---|---|---|---|

| BORING LOCATION: | Devon site, West of plot A | GROUND SURFACE ELEVATION AND DATUM: 725.198 m.a.s.l. |
|---|---|---|

| DRILLING CONTRACTOR: | Envirocore | DATE STARTED: Nov-09 | DATE FINISHED: Nov-09 |
|---|---|---|---|

| DRILLING METHOD: | Solid Stem Auger 6 in | BH DEPTH (m): 4.66 | Well Stick Up (m): 0.88 |
|---|---|---|---|

| DRILLING EQUIPMENT: | Diedrich D-50 Track Unit | Well hole diameter (inch): 6 | Well Diameter (m): 2 |
|---|---|---|---|

| SAMPLING METHOD: | None | LOGGED BY: N/A | |
|---|---|---|---|

| Easting: 314634.05 | Northing: 5907197.04 | Well Installation: Envirocore | REG. NO. |
|---|---|---|---|

| DEPTH (meter) | SAMPLES | | | | DESCRIPTION NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.198 m.a.s.l. | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|
| | Sample No. | Sample | Blows/Foot | OVM Reading | | |

No corresponding borehole log for this location

Back fill, 0-0.3 m

Bentonite, 0.3-4.16 m

Sandpack, 4.16-4.66 m

Screen, 4.3-4.66 m

| University of Calgary - Imperial Oil Limited | 04-05-50-26W4M | |
|---|---|---|

| PROJECT: | | | | Devon Salt Research | | MW09-14C | | |
|---|---|---|---|---|---|---|---|---|

| BORING LOCATION: | Devon site, West of plot A |
|---|---|

**GROUND SURFACE ELEVATION AND DATUM:** 725.169 m.a.s.l.

| DRILLING CONTRACTOR: | Envirocore |
|---|---|

| DATE STARTED: Nov-09 | DATE FINISHED: Nov-09 |
|---|---|

| Drilling Method: | Solid Stem Auger 6 in |
|---|---|

| TOTAL DEPTH (m): 6.63 | Well Stick Up (m): 0.883 |
|---|---|

| DRILLING EQUIPMENT: | Diedrich D-50 Track Unit |
|---|---|

| Well hole Diameter (inch): 6 | Well Diameter (m): 2 |
|---|---|

| SAMPLING METHOD: | None |
|---|---|

**LOGGED BY:** N/A

| Easting: 314635.01 | Northing: 5907197.016 |
|---|---|

| Well Installation: Envirocore | REG. NO. |
|---|---|

| DEPTH (meter) | SAMPLES | | | | DESCRIPTION NAME (USCS): Density, Color, Classification, Moisture, Sed. Structure, Weathering, Secondary Grain, Local Obs. Surface Elevation: 725.169 m.a.s.l. | | WELL CONSTRUCTION DETAILS AND/OR DRILLING REMARKS |
|---|---|---|---|---|---|---|---|
| | Sample No. | Sample | Blows/ Foot | OVM Reading | | | |

No corresponding borehole log for this location

Back fill, 0-0.3 m

Bentonite, 0.3-5.9 m

Sandpack, 5.9-6.63 m

Screen, 6.3-6.6 m

| University of Calgary - Imperial Oil Limited | 04-05-50-26W4M | |
|---|---|---|

**APPENDIX F: HYDRUS INPUTS**

Only available electronically

## APPENDIX G: SOIL DATA

| C10-01 0-5 cm | |
|---|---|
| Nominal Pressure (mbar) | Water Content (v/v) |
| 0 | 0.482 |
| 2.49 | 0.476 |
| 10 | 0.472 |
| 30 | 0.469 |
| 63 | 0.454 |
| 125 | 0.436 |
| 250 | 0.422 |
| 500 | 0.406 |
| 1000 | 0.377 |
| 3000 | 0.338 |
| 6000 | 0.291 |

| C10-02 0-5 cm | |
|---|---|
| Nominal Pressure (mbar) | Water Content (v/v) |
| 0 | 0.484 |
| 2.49 | 0.477 |
| 10 | 0.471 |
| 30 | 0.466 |
| 63 | 0.455 |
| 125 | 0.447 |
| 250 | 0.440 |
| 500 | 0.429 |
| 1000 | 0.411 |
| 3000 | 0.408 |
| 6000 | 0.370 |

| C10-03 0-5 cm | |
|---|---|
| Nominal Pressure (mbar) | Water Content (v/v) |
| 0 | 0.482 |
| 2.49 | 0.469 |
| 10 | 0.465 |
| 30 | 0.462 |
| 63 | 0.445 |
| 125 | 0.428 |
| 250 | 0.411 |
| 500 | 0.389 |
| 1000 | 0.362 |
| 3000 | 0.346 |
| 6000 | 0.305 |

| C10-04 0-5 cm | |
|---|---|
| Nominal Pressure (mbar) | Water Content (v/v) |
| 0 | 0.506 |
| 2.49 | 0.494 |
| 10 | 0.489 |
| 30 | 0.487 |
| 63 | 0.470 |
| 125 | 0.448 |
| 250 | 0.427 |
| 500 | 0.407 |
| 1000 | 0.377 |
| 3000 | 0.355 |
| 6000 | 0.304 |

| C10-05 0-5 cm | |
|---|---|
| Nominal Pressure (mbar) | Water Content (v/v) |
| 0 | 0.520 |
| 2.49 | 0.511 |
| 10 | 0.505 |
| 30 | 0.501 |
| 63 | 0.482 |
| 125 | 0.456 |
| 250 | 0.439 |
| 500 | 0.420 |
| 1000 | 0.384 |
| 3000 | 0.364 |
| 6000 | 0.311 |

| C08-03 0.6-0.7 cm | |
|---|---|
| Nominal Pressure (mbar) | Water Content (v/v) |
| 0 | 0.541 |
| 1.21 | 0.481 |
| 30 | 0.457 |
| 60 | 0.436 |
| 120 | 0.429 |
| 250 | 0.419 |
| 500 | 0.409 |
| 1000 | 0.387 |
| 2040 | 0.364 |
| 4000 | 0.343 |
| 7500 | 0.323 |

| C08-10 0.6-0.7 cm | |
|---|---|
| Nominal Pressure (mbar) | Water Content (v/v) |
| 0 | 0.583 |
| 1.21 | 0.544 |
| 10 | 0.545 |
| 30 | 0.513 |
| 60 | 0.500 |
| 120 | 0.486 |
| 250 | 0.467 |
| 500 | 0.441 |
| 1000 | 0.417 |
| 2040 | 0.391 |

**Van Genuchten parameters calculated using the RETC fitting program**

| Top Soil Unit | RETC Calculated Values | | | |
|---|---|---|---|---|
| Test | $\theta_r$ | $\theta_s$ | $\alpha$ (mm$^{-1}$) | n |
| C10-01 0-5 cm | 0 | 0.4757 | 0.00068 | 1.12 |
| C10-02 0-5 cm | 0 | 0.4791 | 0.00277 | 1.04 |
| C10-03 0-5 cm | 0 | 0.4749 | 0.00177 | 1.08 |
| C10-04 0-5 cm | 0 | 0.499 | 0.00144 | 1.1 |
| C10-05 0-5 cm | 0 | 0.5148 | 0.00159 | 1.1 |

| Glaciolacustrine Unit | RETC Calculated Values | | | |
|---|---|---|---|---|
| Test | $\theta_r$ | $\theta_s$ | $\alpha$ (mm$^{-1}$) | n |
| C08-03 0.6-0.7 | 0 | 0.429 | 0.00663 | 1.06 |
| C08-10 0.6-0.7 | 0 | 0.03947 | 0.01519 | 1.08 |