REACTIVE TRANSPORT MODELING OF NATURAL ATTENUATION IN

STORMWATER BIORETENTION CELLS AND UNDER LAND APPLICATION OF

WASTEWATER

A Thesis

by

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ABSTRACT

Natural attenuation is a cost effective method to treat wastewater applied into soil. The natural attenuation process includes diffusion, dispersion, microbial activity, oxidation, mineral precipitation, sorption, and ion exchange to mitigate hydrocarbon, nutrient, metals, and solids. Vegetation also plays an important role in reducing water volume, and removing nutrients and solutes from the contaminated soil. We used a reactive transport model MIN3P-THM to simulate the natural attenuation on stormwater runoff, and oil and gas produced wastewater.

In bioretention systems, the model results indicated that the bioretention systems were able to remove most of heavy metals, nitrate, and organic carbon through natural attenuation in the soil. Due to macropores and fast flow paths created by roots in vegetated cells, the water can carry ions flowing out of the system very quickly leading to a higher outflow rate and less removal efficiency than non-vegetated cells. The model also tested a range of possible design configurations to determine the optimal saturated zone thickness and outlet location for nitrate removal. In addition, different rainfall levels did influence the natural attenuation performance of bioretention cells under long time application. Due to less water and chemical input, climate patterns may lead to better removal of heavy metals.

For land application of Oil and Gas Exploration and Production wastewater, five scenarios were developed to study the impact of chloride, salts, and organic matters on natural attenuation. Water and salinity stress were considered in the model to deal with

high salinity wastewater in the root zone. For High-FDS and High-Cl treatments, long time application of high salinity wastewater did accumulate salts in the root zone and affect groundwater quality. Under the High-TOC treatment, TOC begins to build up in the root zone in concentrations up to 750 mg/L. More attention should be paid on long-term land application of high salinity wastewater; the application process may pollute groundwater and nearby rivers causing human health hazard. Plants would reduce water uptake to survive themselves when water and solute stress occurred under high salinity conditions.

DEDICATION

I would dedicate my thesis to my beloved parents, my husband, my grandmother, and my friends.

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I would first like to sincerely thank my advisor, Dr. Miller for her full support, expert guidance, patience, and encouragement during all my study and research. Her wisdom, enthusiasm, creativity impressed me. She helps me to have open ideas and to deal with problems using my own knowledge and creativity. I would also like to thank my committee members, Dr. Cahill, and Dr. Li, for their advices and guidance during the research.

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Finally, thanks to my dear mother and father for their support and to my husband for his encouragement and love. I would also thank my grandmother for her encouragement, who was unable to see me finish it.

NOMENCLATURE

BMPs	Best Management Practice
CTL	Control Treatment
EC	Electrical Conductivity
FDS	Fixed Dissolved Solid
HFDS	High FDS Treatment
HFDS-Cl	High Chloride Treatment
HSECL	Hydraulics, Sedimentation, and Erosion Control Laboratory
HTOC	High TOC Treatment
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LID	Low Impact Development
M-Cl	Moderate Chloride Treatment
MCLs	Maximum Contaminant Levels
NOAA	National Oceanic and Atmospheric Administration
NPDWR	National Primary Drinking Water Regulations
NSDWRs	National Secondary Drinking Water Regulations
OGEP	Oil and Gas Exploration and Production
PAR	Photosynthetically Active Radiation
TOC	Total Organic Carbon
TSS	Total Suspended Solids

TWDB	Texas Water Development Board
TxDOT	Texas Department of Transportation
USEPA	United State Environmental Protection Agency

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

This research focuses on natural attenuation process in soil. Natural attenuation is a cost effective method to treat wastewater applied to soil. USEPA defines natural attenuation as ''use of natural processes to contain the spread of the contamination from chemical spills and reduce the concentration and amount of pollutants at contaminated sites''(Mulligan and Yong 2004).

The natural attenuation process includes numerous physical, biological, and chemical methods to mitigate hydrocarbon, nutrient, metals, and solids. Diffusion, dispersion, microbial activity, oxidation, mineral precipitation, sorption, and ion exchange are all taken into account in this process. Numerous chemical species are included in the system. These species may interact, affecting each other's degradation and competing for surface areas (van Genuchten and Simunek 2004).

Natural attenuation processes can be divided into chemical and microbial-mediated reactions. For chemical reactions, they involve equilibrium and kinetic ones, both of which are important in the biogeochemical process. The equilibrium is a steady-state condition, during which the concentrations of reactants and products would not change with time. For equilibrium problems, each species should use an independent equation, which can be driven from chemical equilibrium relationships, material conservation, stoichiometry, electroneutrality. Furthermore, kinetic reaction is also

1

important, experiment conditions, temperature, and pressure can impact the rate of kinetic reactions.

In addition, sorption and ion exchange play an important role in attenuating metals. Different ions have different sorption rates, which also depend on ion exchange ability of the solid (Appelo and Postma 2005). For examples, heavy metals in the wastewater (Pb^{2+}, Cu^{2+}, Zn^{2+}) can be sorbed on the soil surface through cation exchange, replacing species with lower affinity (Na^+, Ca^{2+}, Mg^{2+}). pH value would also influence the sorption process, this value can reflect the change of ion strength which would influence the process of ion exchange in the system.

Microbes in subsurface can affect biogeochemical processes in the subsurface, inducing ions concentrations change in the soil solution. Organic matters, nutrients initially present in the soil affect the behaviors of microbial pollutions. (Hunter et al. 1998). For instance, in subsurface, the degradation of organic matters would release ions (such as Fe^{2+}, Mn^{2+}, Ca^{2+}), these ions can exchange with the ions on clay minerals. These reactions which may produce or consume acids (CO_3^{2-}, NH_4^+), would influence the pH environment in the subsurface (Hunter et al. 1998). Plants in the system will gain and lose carbon to and from the atmosphere through photosynthesis and respiration. The organic carbon will be then accumulated in the plants and microbes, and released upon their decay.

Processes such as nitrogen fixation, ammounification, nitrification, and denitrification also play a significant role. The nitrogen compounds can be converted into different formats, taken up by plants, leached to the groundwater, or released back

to the atmosphere. Carbon and nitrogen cycles are coupled together with cations through microbial reactions, sorption and ion exchange, i.e., microbes can consume organic carbon and nitrate, and release nitrogen gas through denitrification; iron and manganese reduction can decay hydrocarbons and release Fe^{2+}, Mn^{2+}, and CO_3^{2-} into the soil solution. Fe^{2+} and Mn^{2+} can then replace other ions on cation exchange sites and influence salinity levels in the pore water.

Vegetation also plays an important role in reducing water volume, and removing nutrients and solutes from the contaminated soil. Roots can uptake water depending on soil moisture, potential evapotranspiration, and root length density. Roots can also selectively uptake water and nutrients (Zn^{2+}, Fe^{2+}, NO_3^-, NH_4^+) for their growth, while excluding Cl^- and CO_3^{2-} (Gurska et al. 2009). In addition, water and solute stress conditions can occur when soil moisture is below the field capacity and/or electrical conductivity of soil (EC_e) increases to past a species specific threshold (EC_{stress}). The root can proportionately lower water uptake rates for their growth.

In order to investigate the influence of these biogeochemical processes on wastewater attenuation, we use different treatments to deal with stormwater runoff, and oil and gas wastewater in this paper.

For stormwater runoff, it contains large amount of water, and carries heavy metals, nitrogen compound, and organic matter which would cause flooding, contaminate surface water bodies. According to (USEPA 2013), several approaches have been applied to manage stormwater runoff: retention basin, combined sewer system, low impact development, and wet weather green infrastructure.

Retention basin is the first method for stormwater management which is still widely used in the United State. In this method, large ponds are used to retain stormwater, and remove suspended solids, metals, and trash. The disadvantage of this method is that this treatment cannot be conducted immediately at local place and occupy a lot of space.

Combined sewer system is another method to treat stormwater, stormwater associated with sanitary sewage would be conveyed to a wastewater treatment plant through a pipeline system. The limit of this system is the capacity of a combined sewer system. The system capacity would be exceeded during rainfall events, lead to the discharge of wastewater into rivers.

Unlike these traditional methods above, low impact development (LID) (USEPA 2000) and green infrastructure are natural treatments to deal with stormwater as close to its source as possible. They have minor influence on water resources and infrastructure, and apply both vegetation and soil to manage rainwater immediately.

Bioretention systems have been suggested as a Best Management Practice (BMPs) for stormwater runoff by the United State Environmental Protection Agency (USEPA) to mitigate pollutions from urban regions. They are normally located adjacent to parking lots, roofs, driveways, walkways, or lawns. The designed bioretention cells are applied to meet both hydrologic and water quality goals; they mitigate peak flow/total outflow amounts, and remove solids, nitrogen compound, phosphorus, metals, hydrocarbons, and oils. Native plantings, a mulch layer, and a temporary ponding area are included in bioretention cells. Bioretention soil and gravel beds are established above

4

underlying soil. The stormwater will be stored and delayed for a period of time in the bioretention soil, and be passively treated by a variety of biogeochemical reactions (such as plant water and solute uptake, infiltration, sorption, sedimentation, and biodegradation), and infiltrate in the subsurface or come out as outflow through the screened probe.

Oil and Gas Exploration and Production (OGEP) wastewater contains large amount of salts and organic compounds. Efficient and cost effective approaches are needed to remove pollutants in the wastewater and reuse the water to supplement fresh water resources. According to Ahmadun et al. (2009), current technologies available to treat this kind of wastewater can be divided into four types: physical, chemical, biological, and membrane treatments. Methods and costs of produced water disposal show that surface discharge, evaporation pits, and constructed wetlands have lower costs (Ahmadun et al. 2009).

A land application system is a natural treatment which distributes wastewater over the field site, and providing a beneficial reuse for it via irrigation. This method is considered as a more environmental friendly practice than other methods (such as pit disposal). This method has a series of benefits: it is cost effective, has no-sludge byproduct, has no discharge into surface waters, can be applied as irrigation water, and enhances groundwater recharge.

A reactive transport model MIN3P-THM is used in this paper to help better understand the complicated natural attenuation processes in soil. MIN3P-THM is used to construct different scenario simulations under two types of wastewater at both the field

5

and laboratory scales. This model is highly flexible, equilibrium, and kinetically controlled reactions, plant uptake of nutrient and solute can be all defined in a database.

In Chapter II, I focus on studying the performance of subsurface stormwater BMPs. This research presents natural attenuation of stormwater runoff in bioretention systems, trying to answer the following questions below: Do the bioretention systems positively remove heavy metals, nitrogen compound? What's the effect of vegetation on retaining water and removing pollutants? Is a permanent saturated zone essential to nitrate removal? What's the performance of bioretention systems under varying climatic conditions? In order to answer these questions, I apply the MIN3P-THM model to simulate the complicated biogeochemical processes in bioretention cells under stormwater application. The results indicate that bioretention cells have good performance in attenuating stormwater runoff. They also demonstrate the importance of vegetation, rainfall levels in removing pollutants; as well as the effect of a permanent saturated zone on nitrate removal.

Chapter III presents an engineering application of OGEP wastewater in Texas. The rapidly growing oil and gas development in Texas promotes applications of cost effective treatments for oil and gas produced wastewater. This work addresses a practical problem: land application of wastewater which contains large amount of salts and hydrocarbon. Does high salinity wastewater influence vegetations; will the wastewater induce water and solute stress of plants? Will this practice contaminate underlying groundwater (field site scale)? Will hydrocarbon and salts influence each other during the application? How do the hydrological and biogeochemical response to OGEP

wastewater under natural condition (container scale)? To answer these questions, I simulate changes in pore water chemical compositions through land application of high salinity OGEP wastewater at both the field and laboratory scales. This finding implies the importance of vegetation in attenuating high salinity wastewater.

CHAPTER II

REACTIVE TRANSPORT MODELING OF SUBSURFACE STORMWATER BMPS

Introduction

Urban stormwater runoff often carries pollutants, including nitrates, phosphates, heavy metals, and hydrocarbons (Moe et al. 1978; Wiland and Malina 1976). This runoff may lead to a range of water quality problems in surface water bodies. Bioretention systems are used to improve both quantity and quality of stormwater via retention of sediments as well as natural attenuation in the subsurface. These engineered systems are among a number of "Best Management Practices" (BMPs) that are increasingly being applied to reduce nonpoint source pollution from urban areas (USEPA 2000).

Bioretention cells are shallow, man-made depressions where stormwater is stored and delayed for a period of time (Dietz and Clausen 2005) and is passively treated by physical, chemical, and biological processes (Li et al. 2013) such as plant water and solute uptake, infiltration, sorption, sedimentation, and biodegradation (Davis et al. 2001; Hunt 2003). The designed bioretention cell is applied to meet both hydrologic and water quality goals: mitigate peak flow/total outflow amount, and solids, nitrogen, phosphorus, heavy metals, hydrocarbons, and oils. The bioretention system is considered to be among the most low-impact practices in urban water management and is very cost effective (Wossink and Hunt 2003). They are normally located adjacent to parking lots, roofs, driveways, walkways, or lawns; where runoff is generated in large quantities and

with poor water quality (USDOE 1993). The inflow into a system is the stormwater runoff from a nearby roadway or parking lot. Native plantings, a mulch layer, and a temporary ponding area, bioretention soil and gravel are essential in the bioretention cell. The inflow will be retained in the bioretention soil by a variety of biogeochemical reactions, and infiltrate in the subsurface or come out as outflow through the screened probe. Roots in the system can selectively uptake water and some ions (Zn^{2+}, Fe^{2+}, Cu^{2+}) for its growth, while exclude Cl^- and CO_3^{2-}.

The performance of bioretention cells has been tested at both the field and laboratory scales (Chen et al. 2013; Davis 2008; Hsieh et al. 2007; Hunt et al. 2011; Hunt et al. 2006; Kayhanian et al. 2007; Li et al. 2008; Li et al. 2013; Trowsdale and Simcock 2011). In their researches, sediments, zinc, lead are effectively removed by a stormwater bioretention system. For nitrate removal, it is hard to determine because its removal is limited by contact time under anoxic conditions. More and more research has been focused on the its removal (Chen et al. 2013; Davis et al. 2006; Li et al. 2012). Davis et al. (2006) indicated the importance of water retention and vegetation on nitrogen removal and Li et al. (2013) found that a permanent saturated zone can greatly enhance nitrate removal. A saturated zone is essential to provide the anoxic conditions required the conversion of nitrate g into nitrogen gas. Chen et al. (2013) focused on nitrifying and denitrifying bacteria quantification for the ammonia and nitrate removal under low infiltration conditions and long drainage times and found that saturation time, soil medium, and organic matters influenced denitrification rates.

At present, reactive transport models is relatively important in biogeochemistry modeling. This integrated approach is absolutely vital to improving the understanding of the Earth systems because of its combination of flow, nutrient transport, and biogeochemical processes (Steefel et al. 2005). This modeling method is useful for dealing with a variety of environmental problems, due to its ability to simulate different types of chemical and biological reactions (Langergraber and Simunek 2005). Prior applications include: natural attenuation of groundwater contamination (MacQuarrie et al. 2001; Mayer et al. 2001); rock weathering (Navarre-Sitchler et al. 2009); and CO_2 injection, sequestration and leakage (Gaus et al. 2005). In these models, transport (advection and dispersion of chemicals) and reactivity (chemical reactions) are interdependent and are simulated simultaneously and continuously (Van der Lee and Windt 2001).

This work uses MIN3P-THM to simulate variably saturated flow and biogeochemical processes that occur within two pilot-scale bioretention cells in Texas, with the goal of estimating their attenuation capacity for stormwater runoff contaminant. The specific objectives of this study were to:

1) Apply MIN3P-THM to simulate flow retention, and pollutant removals of the non-vegetated and vegetated bioretention cells, and to compare modeled results with measured ones;

2) Use MIN3P-THM to test possible design configurations in order to determine the optimal saturated zone thickness for better nitrate removal;

3) Simulate bioretention system performance under varying climatic conditions.

10

Materials and methods

Conceptual model

In order to simulate the natural attenuation process of stormwater runoff in the subsurface, a conceptual model was applied to depict key hydrological and biogeochemical processes under the subsurface.

A pilot-scale bioretention cell is constructed by Drs. Li and Chu at the Texas Department of Transportation (TxDOT/TTI) Hydraulics, Sedimentation, and Erosion Control Laboratory (HSECL) (Li et al. 2013). Synthetic stormwater runoff involving predetermined pollutants with target concentrations is applied into the system to study the effect of bioretention system on stormwater runoff. The runoff is determined from two Texas highways; the major chemicals focused in the model are nitrogen compounds, organic matter, and heavy metals (Cu^{2+}, Zn^{2+}, and Pb^{2+}).

Precipitation, irrigation water, and synthetic stormwater runoff were evenly applied on the soil surface as sources in the model, evapotranspiration occurs through a 0.3 m root zone as sink terms, and the water flowing in the bottom boundary condition is considered as free drainage. The 0.3m root zone is assumed to be representative of Bermuda grass (Li et al. 2013). Plant can selectively uptake essential nutrient for their growth while exclude Cl^-, CO_3^{2-}, and other ions, leading to increase in rejected ions in the pore water.

Figure 1 below shows the conceptual model of the bioretention cell. It can be divided into three zones based on its construction: compost sand, pea gravel, and gravel.

The zones were 0.6 m, 0.1 m, and 0.2 m thick, respectively. This figure illustrates the key biogeochemical reactions in a bioretention cell. Complexation, mineral dissolution-precipitation, soil gas exchange, oxidation-reduction reactions, sorption, and ion exchange between dissolved cations and those absorbed to mineral surface are included in the model.

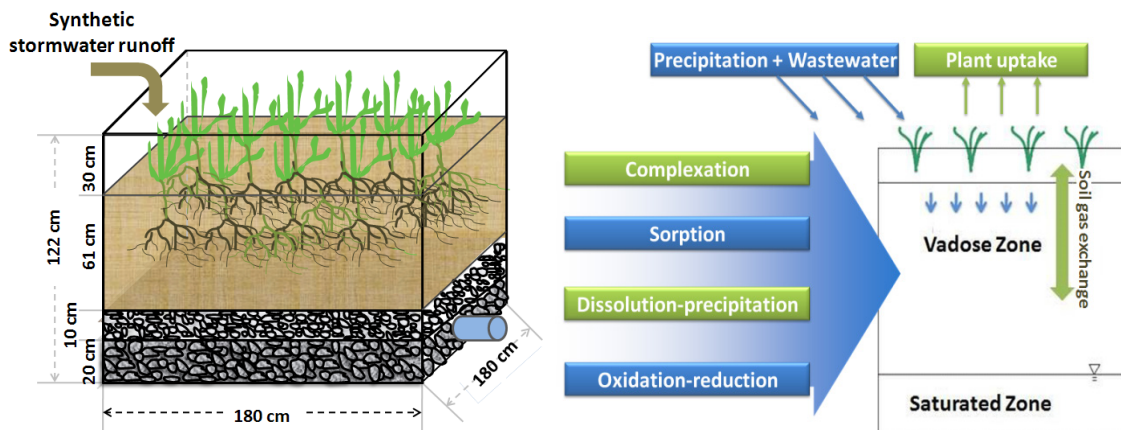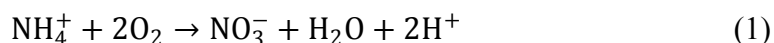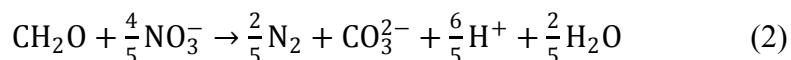**Figure 1.** Configuration of the bioretention cell.

Nitrogen and organic matter

Nitrogen, organic carbon, oxygen, and ions are coupled together in the system. These materials are affected by a range of redox reactions. These reactions can be divided into those occurring under aerobic (nitrification, respiration) and anoxic (denitrification, fermentation, iron reduction, and manganese reduction) conditions.

Nitrification:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \tag{1}$$

Denitrification:

$$CH_2O + \frac{4}{5}NO_3^- \rightarrow \frac{2}{5}N_2 + CO_3^{2-} + \frac{6}{5}H^+ + \frac{2}{5}H_2O \tag{2}$$

Fermentation:

$$CH_2O + \frac{1}{2}H_2O \rightarrow \frac{1}{2}CO_3^{2-} + \frac{1}{2}CH_4 + H^+ \tag{3}$$

Respiration:

$$CH_2O + O_2 \rightarrow CO_3^{2-} + 2H^+ \tag{4}$$

Iron reduction:

$$CH_2O + 4FeOOH + 6H^+ \rightarrow CO_3^{2-} + 4Fe^{2+} + 6H_2O \tag{5}$$

Manganese reduction:

$$CH_2O + 2MnO_2 + 2H^+ \rightarrow CO_3^{2-} + 2Mn^{2+} + 2H_2O \tag{6}$$
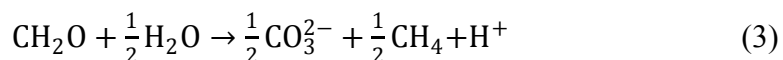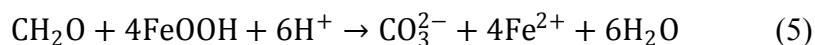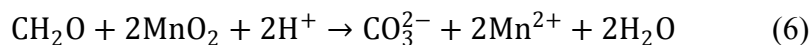
The equations above show how both nitrogen and carbon cycles are influenced

by redox processes of ammonium, iron, and manganese ions. The degradation of organic

substrate would release ions such as: CO_3^{2-}, NO_3^-, H^+, Fe^{2+}, Mn^{2+}, these ions can interact

with others through sorption, ion exchange processes and influence salinity in the soil

solution. These degradations reduces the possibility of extraction of external electron

acceptors, thus leading to utilization of electron acceptors by microbes (Baedecker and

Back 1979; Hunter et al. 1998). The release of H^+ from nitrification, respiration,

denitrification, and fermentation can also influence sorption process. Increase in pH

would promote the sorption process (Appelo and Postma 2005). Moreover, root can

uptake important nutrient from the byproducts of these processes (Fe^{2+}, NO_3^-, NH_4^+) and release CO_3^{2-} through respiration. The chemical constants (half-saturation, inhibition factors) for these oxidation-reduction processes can be found in Appendix B-Table 3.

Soil gas exchange

Four gases are considered in the model: carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), and methane (CH_4). For instance, the occurrence of oxygen is important in nitrate removal because it can promote nitrification and inhibit denitrification process. Under aerobic condition, nitrification process converts ammonia to nitrate, while anoxic condition would lead nitrate and nitrite to nitrogen gas. The fermentation process would convert organic carbon into methane and escape from the system. Moreover, the carbonate related reactions can produce CO_2 gas; this gas can affect the pH and alkalinity in the system, thus influencing the salinity in the soil solution.

Minerals

Several soil minerals are considered in the model based on soil type (compost sand): for instance, calcite ($CaCO_3$), manganese dioxide (MnO_2) and goethite ($FeOOH$) were considered to remove different pollutants in sand soil (Appelo and Postma 2005; Bajpai and Chaudhuri 1999; Cheng et al. 2004; Jalali and Rowell 2003). These minerals can lead to organic carbon degradation through iron and manganese reduction. Other minerals: gypsum ($CaSO_4 \cdot 2H_2O$), siderite ($FeCO_3$) and rhodochrosit ($MnCO_3$) can participate in dissolution-precipitation reactions. Their reaction products (Ca^{2+}, Fe^{2+},

14

Mn^{2+}) can influence soil salinity levels. In addition, the salinity can be coupled with carbon and nitrogen cycles (Equation 5 and 6), and participated in the redox reactions.

Numerical modeling

A numerical solution is needed to calculate the water and chemicals reaching the drainage pipe. The reactive transport model MIN3P-THM (Bea et al. 2012; Mayer et al. 2002) is used to simulate these processes.

The model uses a block-centered finite difference method and the global implicit solution approach (Nowack et al. 2006). New code was developed to represent ponding conditions within cells. This study considers five major categories of contaminants in stormwater: nitrogen, phosphorus, organic matter, salts, and heavy metals. Surface complexation, sorption, mineral precipitation and dissolution, organic matters oxidation-reductions are all considered. In addition, root water uptake is dependent on soil saturation, potential evapotranspiration, and root length density. Both passive and active root solute uptake is considered in the system for chemical removal. The rate of passive root solute uptake depends on the water availability and chemical concentrations in pore water, while active root solute uptake is calculated using the Michaelis-Menten formulation. Gas diffusion is modeled for the oxygen, carbon dioxide, methane, nitrogen, and hydrogen sulfide. Moreover, the effect of saturated zone depth on nitrogen removal is taken into account in the model.

The governing equation of variable saturated flow, used by the model (Mayer et al. 2002), is shown below:

$$S_a S_s \frac{\partial h}{\partial t} + n\frac{\partial S_a}{\partial t} - \nabla \times [k_{ra} K_s \nabla h] - W = 0 \qquad (7)$$

where *n* is the porosity [-]; *h* is the hydraulic head [m]; S_a is the water saturation

[m³/m³]; S_s is specific storage coefficient [m^{-1}]; k_{ra} is relative permeability of the medium

[-]; K_s is saturated hydraulic conductivity [ms^{-1}]; *W* is a source-sink term (including root

water uptake) [s^{-1}].

Three soil types are selected to represent the layers: compost sand, pea gravel,

and gravel. K_s values are selected basing on typical soil types: 3.3×10^{-5} m/s; 1.17×10^{-3}

m/s; and 8×10^{-3} m/s. Effective porosity of these layers are 0.4, 0.34, and 0.28

respectively (Todd and Mays 2005).

The reactive transport equation in the model is shown below (Mayer et al. 2002):

$$\frac{\partial}{\partial t}[S_a n T_j^a] + \frac{\partial}{\partial t}[S_g n T_j^g] + \nabla \times [q_a T_j^a] - \nabla \times [S_a n D_a \nabla T_j^a] - \nabla \times [S_g n D_g T_j^g] -$$

$$Q_j^{a,a} - Q_j^{a,s} - Q_j^{a,ext} - Q_j^{g,ext} = 0 \qquad (8)$$

where T_j^a is the total aqueous concentration of component *j* [mol/L]; T_j^g is the total

gaseous concentration of component *j* [mol/L]; $Q_j^{a,a}$ [mol/dm³] and $Q_j^{a,s}$ [mol/dm³] are

internal source/sink terms of intra-aqueous and dissolution-precipitation reactions; $Q_j^{a,ext}$

is external source/sink term of aqueous phase [mol/dm³]; $Q_j^{g,ext}$ is external source/sink

term of gaseous phase [mol/dm³]; S_g is the gas saturation [m³/m³].

Representing surface ponding

Ponding conditions may occur when the amount of water applied on the soil

surface exceeds the amount of infiltrating flow into soil, which primarily depends on the

soil properties. Ponding affects the system by controlling overall inflow rates, which are subject to the driving gradient at the surface (H_{i+1} -H_i) (Figure 2).
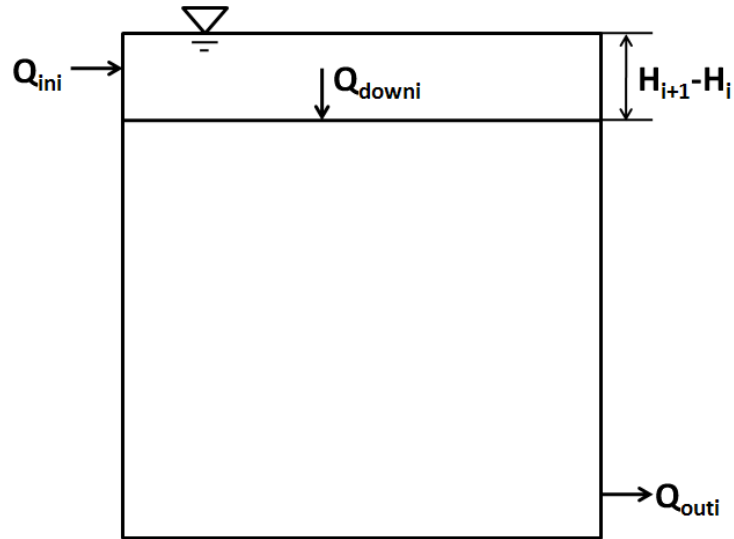
Figure 2. Conceptual model of ponding in a bioretention cell.

The equation below is used in the model to solve the ponding problem based on water balance:

$$H_{i+1} = \left(\frac{Q_{ini} - Q_{downi}}{A}\right) + H_i \tag{9}$$

where H_i is the hydraulic head in the system at time step i; Q_{ini} is the inflow in the system at time step i; and Q_{downi} is the infiltration into the system at time step i. We assumed that water inputs (natural precipitation and applied stormwater) were evenly distributed across on the soil surface, making head constant in the lateral direction.

Plant solute uptake

Vegetation is thought to play a relatively significant role in reducing peak flow volume, delaying outflow time and removing pollutants in bioretention systems. Root water uptake depends on soil moisture, potential evapotranspiration, root length density, and water stress function.

Moreover, root solute uptake is important in changing pore water concentration. Two types of root solute uptake are taken into account in the model: passive root solute uptake and active root solute uptake.

Passive plant solute uptake is calculated by the equation:

$$P_x(t, z) = R_x(t, z) \cdot C_x(t, z) \tag{10}$$

where $P_x(t,z)$ is the passive uptake rate of ion x at time t and depth z; $R_x(t,z)$ is the rate of root water uptake; $C_x(t,z)$ is the concentration of ion x. The equation above indicates that passive plant solute uptake depends on both the rate of root water uptake and ion concentrations.

Active plant solute uptake is calculated by a Michaelis-Menten kinetic equation:

$$A_x(t, z) = A_{x,max} \frac{C_x(t,z)}{K_m + C_x(t,z)} \tag{11}$$

where $A_x(t,z)$ is the active uptake rate of ion x at time t and depth z; $A_{x,max}$ is the maximum ion uptake rate; K_m is the concentration when the reaction rate is $0.5*A_{x,max}$; $C_x(t,z)$ is the concentration of ion x. As can be seen from the equation above, for active root solute uptake, different ions have different values of parameters ($A_{x,max}$, K_m) for

different plant species. The values of these parameters may be derived from literatures (Barber 1995; Goyal and Huffaker 1986; Miller et al. 2008; Rengel and Wheal 1997).

Description of bioretention cell

In a project funded by the Texas Department of Transportation (TxDOT), Drs. Li and Chu assessed the performance of bioretention boxes in treating synthetic stormwater runoff (Kim et al. 2012; Li et al. 2008; Li et al. 2011; Li et al. 2012; Li et al. 2013). Five bioretention boxes were constructed on April, 2008 at the Riverside Campus of Texas A&M University.

Each steel bioretention box was 1.8m long × 1.8m wide × 1.22m deep (Figure 1) and has three soil layers: compost sand, pea gravel, and gravel. The synthetic stormwater mimicked runoff from two Texas highways was applied to these bioretention boxes. Two kinds of bioretetention cells were used to demonstrate the effect of root on water retention and chemical removal: vegetated and non-vegetated cells.

Table 1 shows the initial chemical compositions of the soil medium, the synthetic stormwater runoff (Li et al. 2013), and initial condition of the model. The concentrations of compost sand were analyzed by the Soil, Water and Forage Testing Laboratory at Texas A&M University. The compost in the soil can provide nutrients that are essential for plant growth, which has a higher concentration of nitrogen, phosphorus, potassium, organic matter, and heavy metals than the soil without compost. These ions in the soil are essential nutrients for plant growth.

19

The initial condition of the model was established by applying rainfall water and irrigation water for one year to allow soil chemical concentrations to achieve equilibrium. The chemicals in tap water and rainfall water can alter the chemical concentrations of the soil. Compared with initial chemical composition of soil media and initial condition of the model, Pb^{2+} was accumulated on the soil media after long-term application of precipitation and irrigation water; while Cu^{2+}, Zn^{2+}, and other ions were released into the pore water. The difference between soil medium compositions and influent concentrations can affect influence the ions sorption direction. Taking into account of low concentrations influent (rainfall and tap water), high concentrations in the soil medium could lead to ions released into the pore water (Zn^{2+}, Cu^{2+}, PO_4^{3-}, NO_3^-, K^+, Ca^{2+}, Na^+, Fe^{2+}), while low concentrations in the soil medium could cause ions sorbed on the soil surface (Pb^{2+}).

This pilot-scale bioretention cells (3.34 m^2) was assumed to represent 1 percent of an actual drainage area (334 m^2). The application rate into this area was calculated from mean 3-hour designed stormwater in Brazos County with a runoff coefficient of 0.9 (Table 2).

Table 1. Chemical concentrations (mg/L) of key constituents in soil medium and stormwater runoff

Soil medium (Compost Sand)		Initial Condition in the model		Stormwater runoff	
Chemical	Concentration	Chemical	Concentration	Pollutant	Concentration
Cu^{2+}	1.16	Cu^{2+}	0.04	Cu^{2+}	0.02
Zn^{2+}	9.24	Zn^{2+}	0.07	Zn^{2+}	0.13
Pb^{2+}	0	Pb^{2+}	0.03	Pb^{2+}	0.08
PO_4^{3-}	191	PO_4^{3-}	23	NO_2-N	0.15
NO_3-N	14	NO_3-N	9.8	NO_3-N	0.15
K^+	190	K^+	32	NH_4-N	0.77
Ca^{2+}	4900	Ca^{2+}	230		
Na^+	147	Na^+	23		
Fe^{2+}	11.5	Fe^{2+}	7.6		
Organic Matter	2.90%	Organic Matter	3.20%	Organic-N	0.77

Table 2. Inflow rate

Time (hours)	Influent rate (m^3/hr)
0-1	0.59
1-2	2.36
2-3	0.45

The data of the chemical characteristics of soil and compost media, pollutant concentrations of systematic stormwater runoff were obtained from the technical report of Li et al. (2013).

Results and discussion

Model effluent with measured data

The simulations demonstrated the natural attenuation of water quantity. Peak flows were mitigated by both vegetated and non-vegetated cells, although those without vegetation showed dramatically more attenuation (Figure 3). In addition, non-vegetated cells had a longer detention time than the vegetated ones.
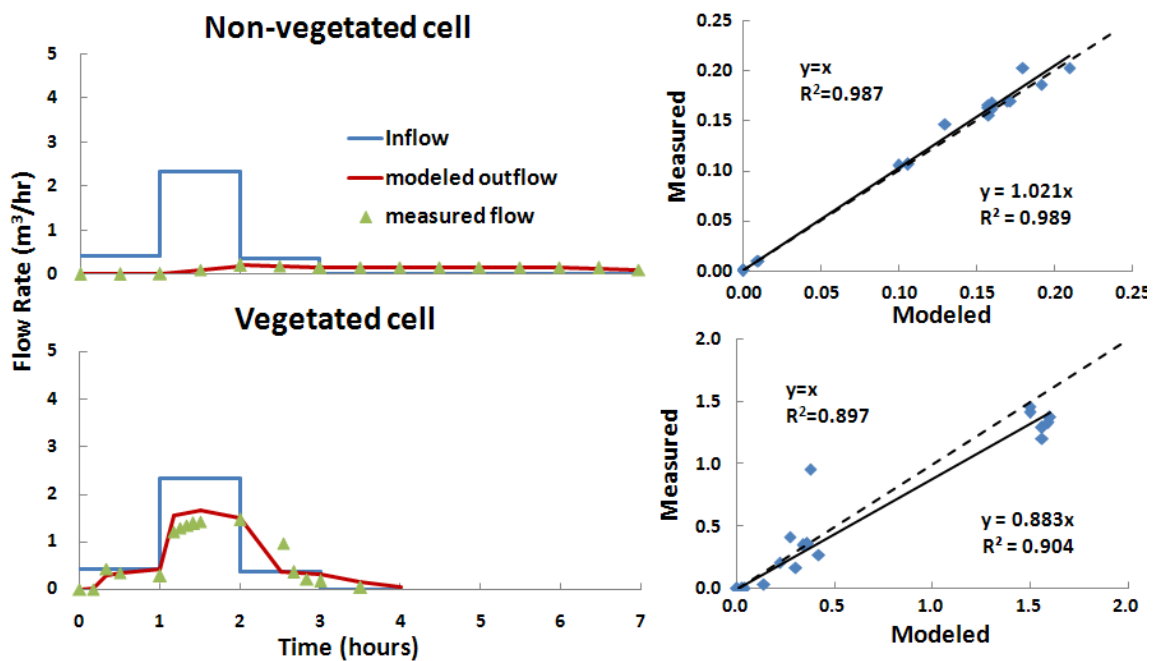

Figure 3. Inflow and outflow rate.

The measured influent and effluent hydrograph were derived from the technical report by Li et al. (2013). Figure 3 showed that the modeled outflow was very close to the measured one in both non-vegetated and vegetated cells. The r^2 was 0.99 and 0.90, respectively. For the non-vegetated cell, the peak of outflow was only 6 m^3/day; the peak of outflow reached 40 m^3/day and occurred much earlier than in non-vegetated cell.

The model results indicate the importance of ponding condition in a bioretention system. Compared with vegetated cells, the outflow rate of non-vegetated cell was much lower. Moreover, there was a much longer detention time of outflow in non-vegetated cell than the vegetated one. Ponding condition in non-vegetated cell can lower the inflow rate and amount applied into the soil. Before the ponding condition was considered in the model, the model results of outflow rates were always larger than the measured ones, and had shorter detention time. To solve this problem, a variable head boundary condition was added in the model. This boundary condition was based on water balance between total amount of water applied on the soil surface and actual amount of water infiltrated into the soil. The involvement of ponding condition in the model induced a good performance of simulating outflow rates.

The unexpected increase in flow in the vegetated cells was likely due to preferential flow through cracks and macropores created by plant roots in the soil. This finding is significant for both flow and chemical transport; preferential flow can lead to both higher water flow and leaching chemicals from the bioretention system.

Gas diffusion

Gas diffusion acts an essential role in flow and contaminants transport. For instance, the occurrence of oxygen gas in the soil can create an aerobic condition, promoting nitrification, respiration, and methane oxidation. Figure 4 showed the occurrence of O_2, N_2 and CO_2 in the bioretention cell. Compared with CO_2, N_2 and O_2 occupy large volume of gas in the soil.

The results indicated that the active soil layer (root zone: soil depth between 0.0 m to 0.6 m) is significant to gas diffusion. The gases in the top layer can interact with those in the atmosphere. For instance, the occurrence of oxygen gas in the soil can create aerobic conditions, thus promoting nitrification, respiration, and methane oxidation and inhibiting anoxic processes. In addition, the plants can uptake water and more gas is filled into the soil volume. The gas volumes decrease with the soil depth, especially those near the saturated zone. Low gas concentrations occurred near the saturated zone, which would create anoxic conditions, promoting fermentation, denitrification, reduction of manganese, sulfate, and iron.
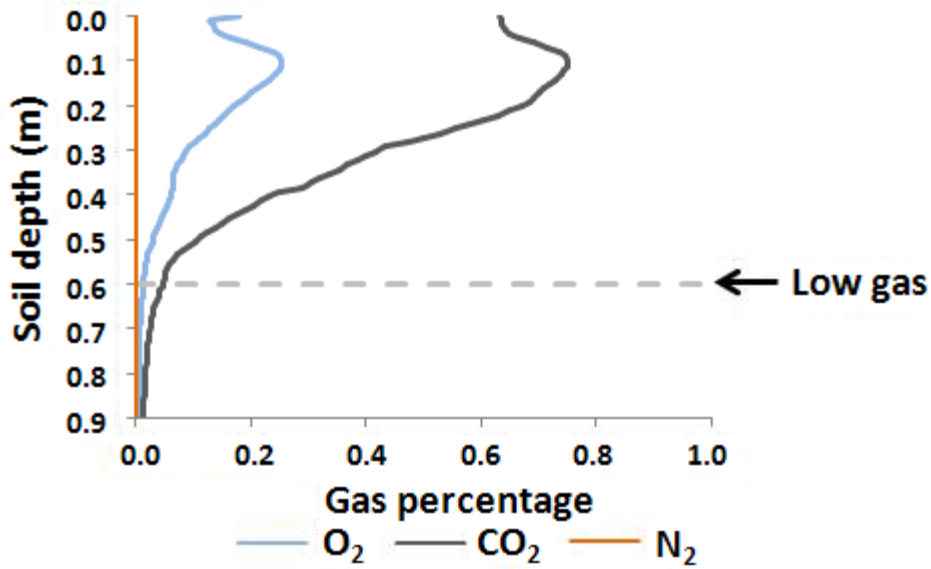
Figure 4. Gases present in the soil.

Heavy metals removal

For heavy metals removal, the effluent concentration of Zn^{2+}, Cu^{2+}, and Pb^{2+} varied in both non-vegetated and vegetated cells (Figure 5). The model can reproduce trends in effluent concentrations in both non-vegetated and vegetated cells. Based on removal efficiency, Zn^{2+} and Pb^{2+} in both non-vegetated and vegetated boxes were effectively removed; Cu^{2+} was partially attenuated by the non-vegetated cell, but leached from the system in the vegetated cell (Figure 6).

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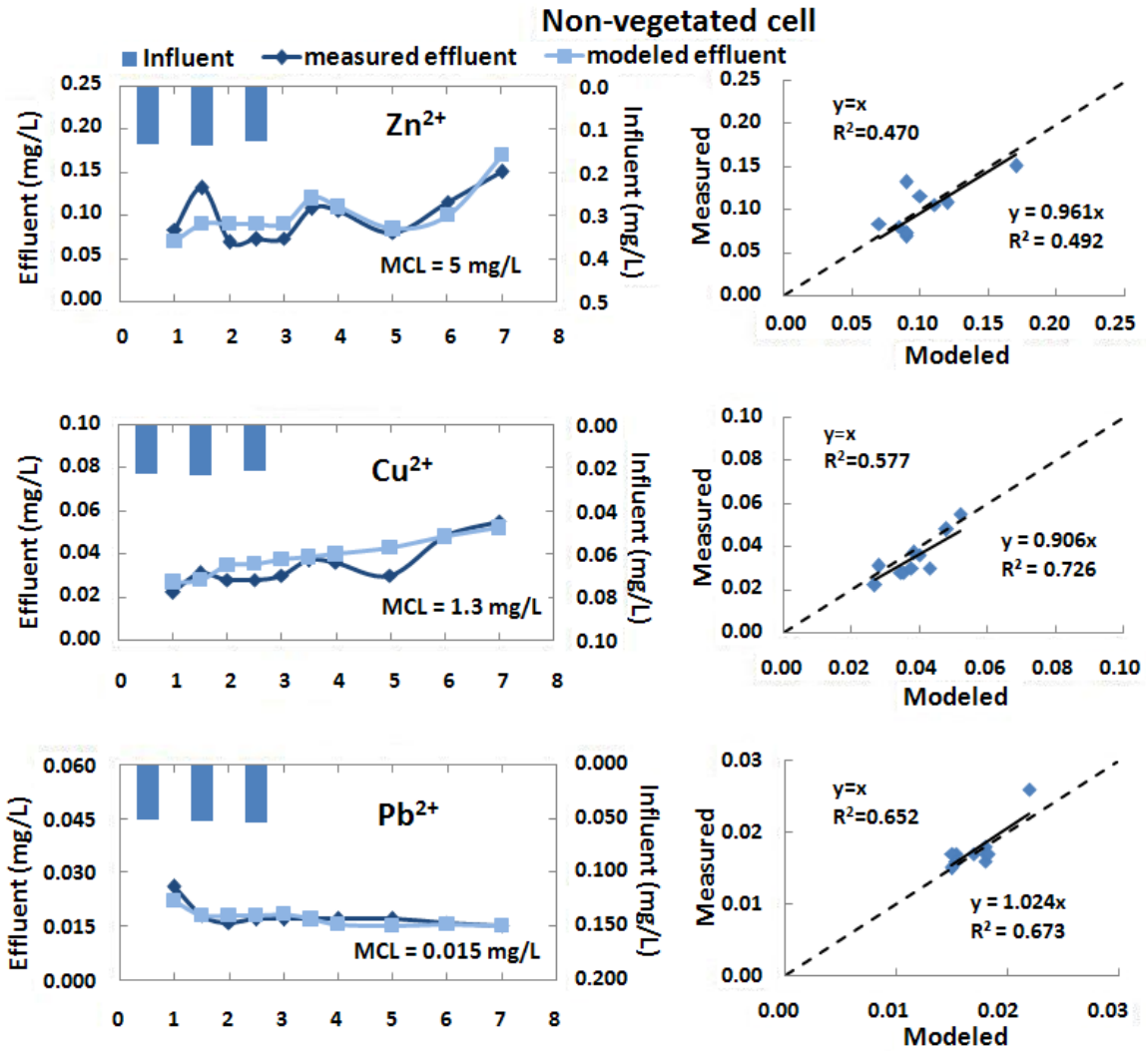
Non-vegetated cell

(a) Non-vegetated cell

Figure 5. Influent and effluent concentration (measured with modeled data).
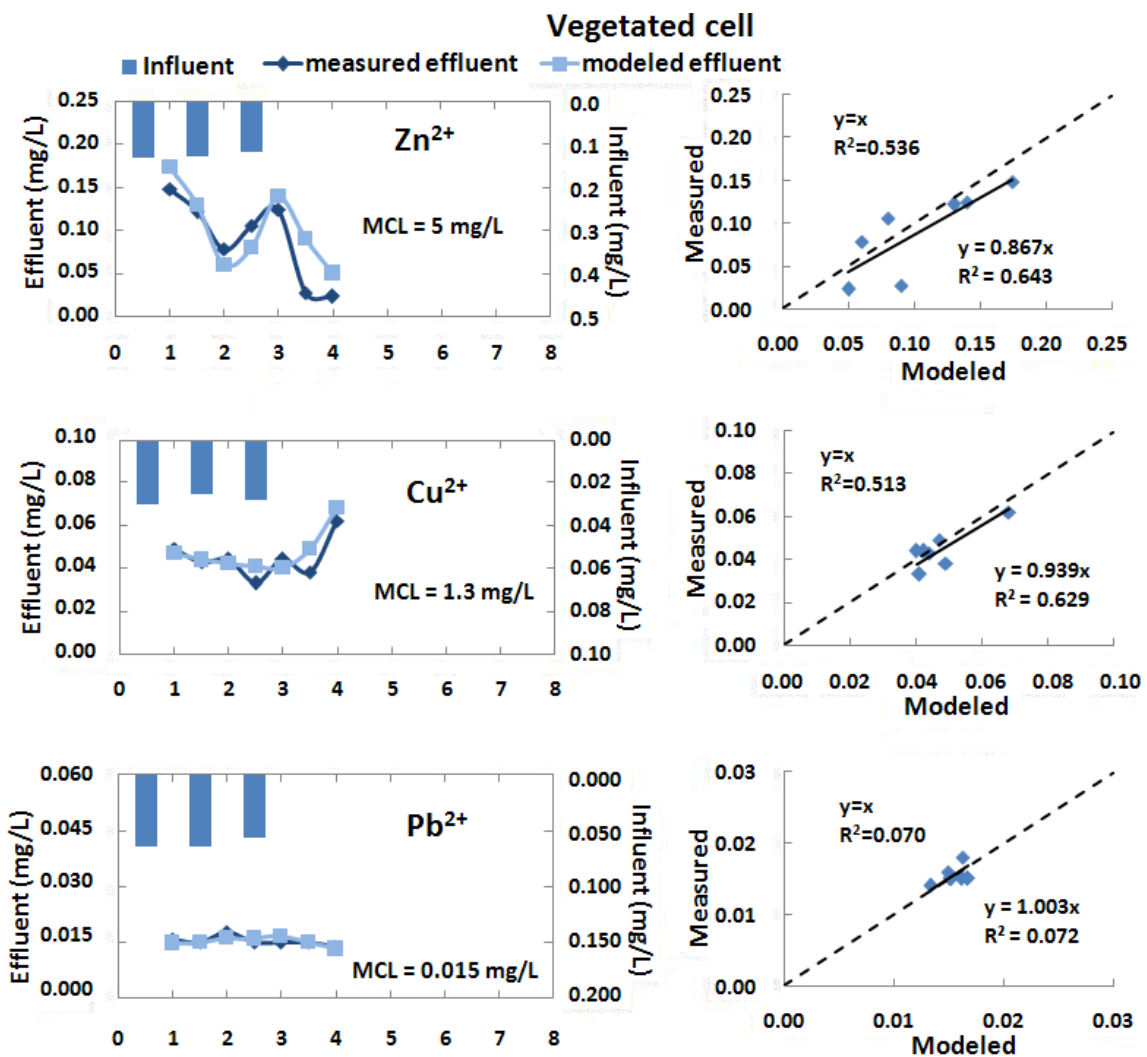
(b) Vegetated cell

Figure 5. Continued.

Two stochastic parameters: r^2 and p values were used to compare modeled data with measured ones. For the non-vegetated one, the r^2 (measured versus modeled data) ranged from 0.47-0.65 with 1:1 slope; for the vegetated one, the r^2 ranges from 0.070-0.536 with 1:1 slope. In addition, p values was calculated to determine the relation between measured and modeled data, when the p values were less than 0.05, then the correlation between these data are significant. For non-vegetated cell, p value ranged from 0.002 to 0.0148; for vegetated ones, p value ranged from 0.0258 to 0.27. Lower p values in non-vegetated cells showed a better performance in simulating chemical changes in non-vegetated bioretention cells. Due to a longer retention time of water and chemicals in the non-vegetated cell, more data points were measured leading to a higher r^2 for the non-vegetated one. In addition, the r^2 for Pb^{2+} in the vegetated cell was only 0.070 because of the low effluent concentration: a very small change would cause a very large bias in the r^2.

According to National Primary Drinking Water Regulations (NPDWR 2013) and National Secondary Drinking Water Regulations (NSDWRs 2013), MCLs (Maximum Contaminant Levels) for Cu^{2+}, Pb^{2+}, and Zn^{2+} are 1.3mg/L, 0.015 mg/L, and 5 mg/L respectively. The results showed that the effluent concentration of Zn^{2+} and Cu^{2+} were substantially below MCLs. However, the effluent concentration of Pb^{2+} was very close to MCLs.

Moreover, the removal efficiency in the non-vegetated cell ranged from 45 to 91%, while the efficiency in the vegetated one ranged from -17 to 75%. More outflow in

the vegetated cell flushed more chemical mass out of the system, leading to a better removal performance in the non-vegetated cell than the vegetated one.

Due to macropores and fast flow paths created by roots in vegetated cells, the water can carry ions flowing out of the system very quickly, leading to a less conspicuous retardation process in these ones (Figure 6 b).

Figure 7 shows the chemical composition throughout the bioretention soils during the application of stormwater runoff. The vegetated cell has higher concentrations of ions in pore water and on sorption sites than the non-vegetated one. Due to plant water uptake, the plant can uptake water and leave undesirable ions in the soil, leading to increase in concentrations of certain ionic species (e.g., Na^+, Cl^-).

In addition, the initial concentrations of Zn^{2+}, Cu^{2+} and Pb^{2+} in the solid and influent concentration would also affect the direction of sorption process. Sorption processes were taken into account for Cu^{2+}, Zn^{2+}, and Pb^{2+}; different ions have different sorption rates and ion exchange ability of the solid (Appelo and Postma 2005). Pb^{2+} has stronger attraction ability than Zn^{2+} and Cu^{2+}. As mentioned in Li et al. (2013)'s report, "Under a low influent concentration condition, the mass of pollutant leached out of the pilot boxes could be higher than the mass removed by the boxes." The model results indicated that during the application of stormwater runoff, the concentration of Pb^{2+} and Zn^{2+} were increasing in the soil while the concentration of Cu^{2+} was decreasing. Pb^{2+} and Zn^{2+} were accumulated in the soil while and Cu^{2+} was released into the pore water.

29
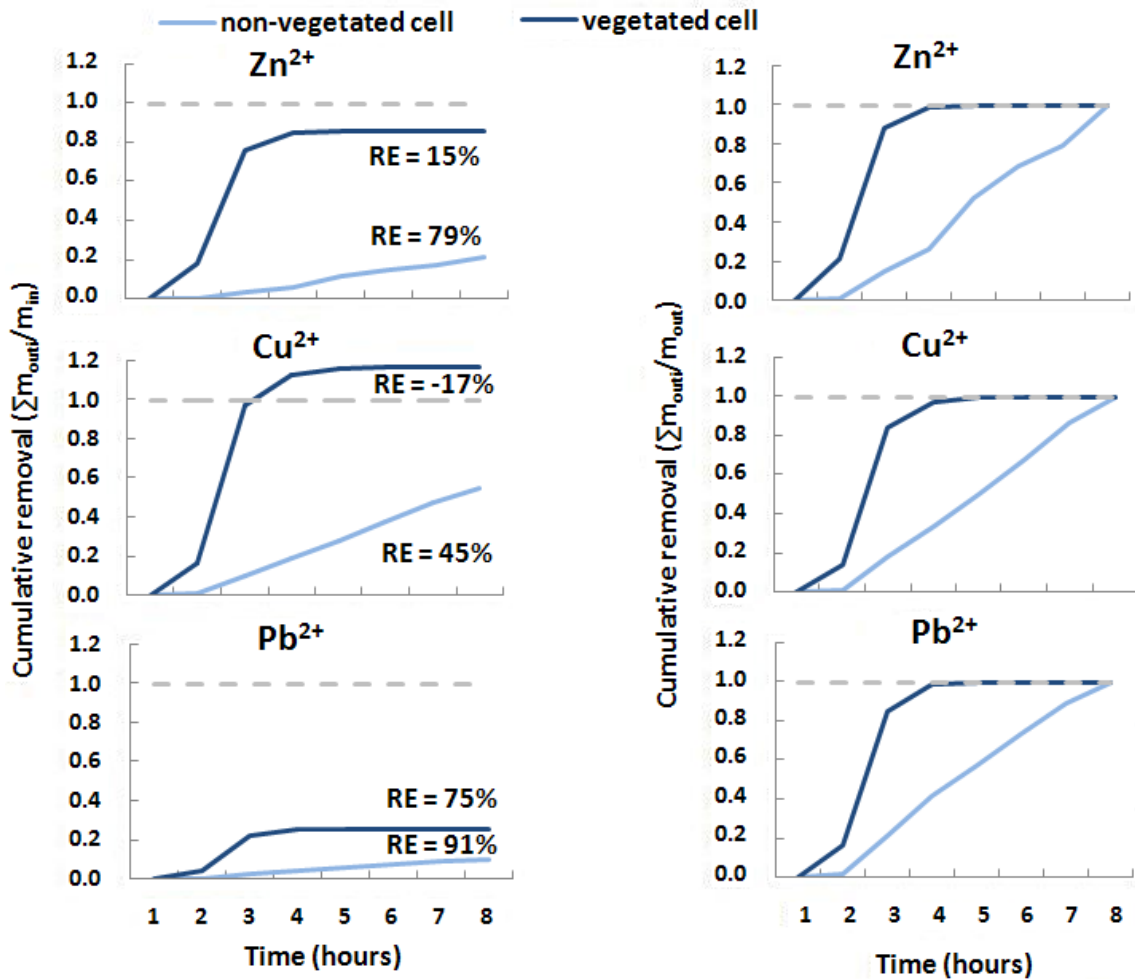
(a) Cumulative removal　　　　　　　(b) Cumulative mass

m_{outi} is effluent mass (mg) at each hour i, i from 1 to 8;

m_{in} is total influent mass (mg);

m_{out} is total effluent mass (mg);

RE is removal efficiency.

Figure 6. Relative mass of heavy metals from modeled data.

When the ion concentrations of soil medium were higher than influent, the ion would be released into soil solution, and vice versa. For instance, at the first hour, the initial condition of Pb^{2+} (0.03 mg/L) and Zn^{2+} (0.07 mg/L) in the soil are lower than the influent concentration of Pb^{2+} (0.08 mg/L) and Zn^{2+} (0.13 mg/L) (Table 1), Pb^{2+} and Zn^{2+} in the soil have capacity to be sorbed on the soil surface, leading to the accumulation of Pb^{2+} and Zn^{2+} in the soil (Figure 7). For Zn^{2+}, after one hour application, large amount of Zn^{2+} was sorbed on to the soil, leading to the soil composition of Zn^{2+} higher than the influent concentration, the direction of sorption converted (Zn^{2+} began to release into the soil solution at the second hour). However, after one hour releasing into the water, the soil composition of Zn^{2+} became lower than the influent concentration, the direction changed again at the third hour (Zn^{2+} was sorbed on to the soil again).

Compared with Zn^{2+} and Pb^{2+} concentration in the synthetic runoff (0.13 mg/L and 0.08 mg/L), Cu^{2+} concentration was much lower (0.02 mg/L). Cu^{2+} was released into the soil solution during the applications while Pb^{2+} and Zn^{2+} were sorbed through cation exchange with other ions (Na^{2+}, Ca^{2+}, Mg^{2+}, etc).
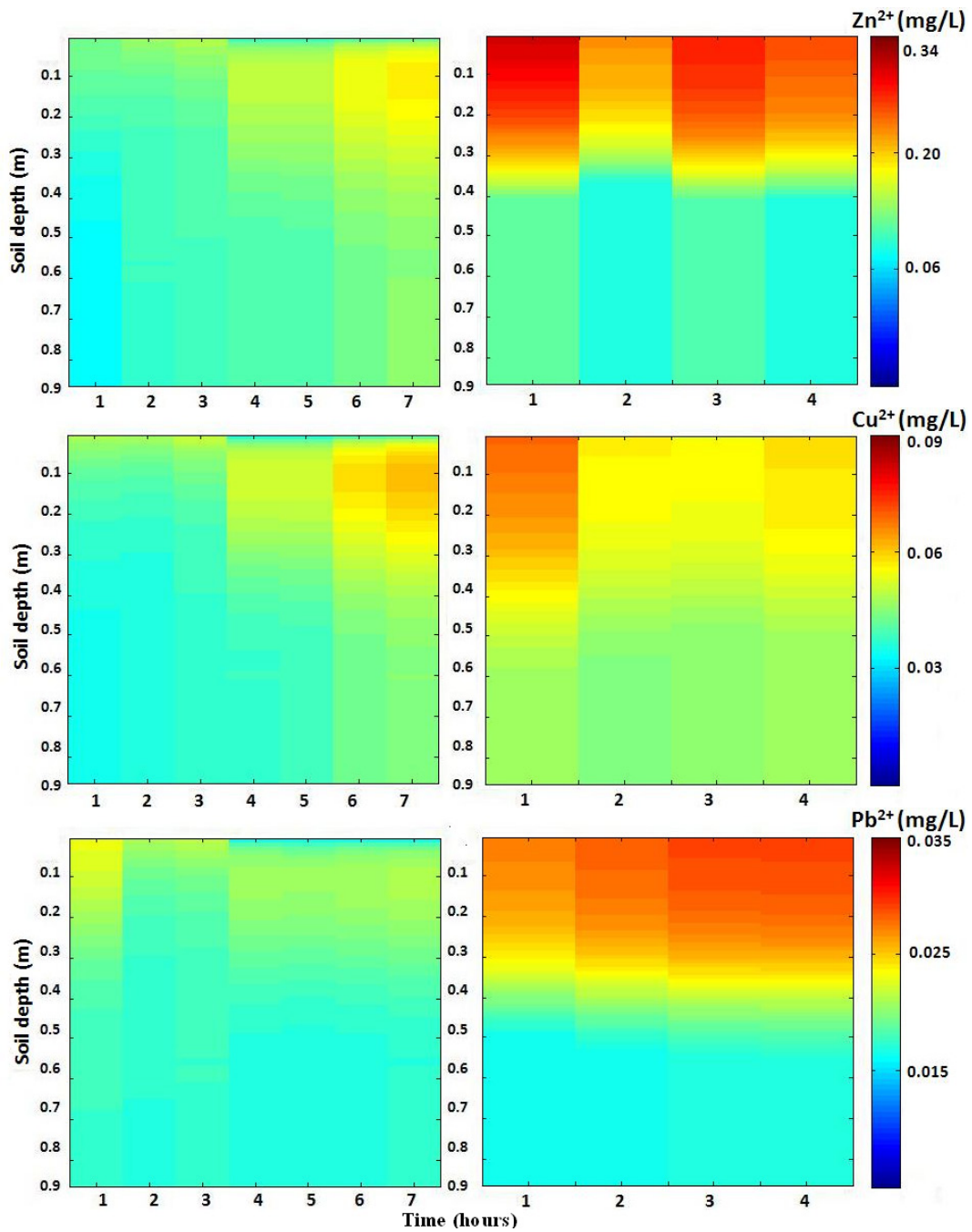
(a) non-vegetated cell   **(b) vegetated cell**

Figure 7. Chemical composition of Zn^{2+}, Cu^{2+}, and Pb^{2+} through soil columns.

Nitrogen removal - thickness of saturated zone determination

Oxygen plays an important role in nitrogen system by promoting nitrification and inhibiting denitrification; under aerobic conditions ammonium converts into nitrite and then nitrate via oxidation by nitrifying bacteria, while under anoxic conditions, nitrate would convert into nitrogen gas. A permanent water saturated zone is essential to provide an anoxic condition for promoting denitrification process, leading to better nitrate removal performance (Figure 8). As can be seen from Figure 4, gas concentrations decreased with soil depth, and high oxygen gas concentration occurred in the vadose zone, promoting nitrification process. Oxygen gas can be consumed through nitrification, and increase nitrate concentration in the pore water. Little oxygen occurred near the saturated zone, which creates anoxic condition. Nitrogen gas created by denitrification process can escape from the soil system though gas diffusion thus decreasing nitrate concentration in the soil.

The cell without saturated zone had the highest nitrate effluent (0.28 mg/L) because of nitrification process. For those cells with saturated zone, the nitrate concentration largely decreased (the concentration ranged from 0.003 to 0.008 mg/L). The nitrate effluent concentration decreases with the saturated thickness increase; however, when the thickness increase to a threshold, the nitrate effluent concentration may increase. Too little oxygen in the soil would affect other oxidation reactions, leading to less removal of NH_4^+, and CH_4. According to the result, a ratio of 2:1 between unsaturated and saturated zone had the best performance in nitrate removal.

33
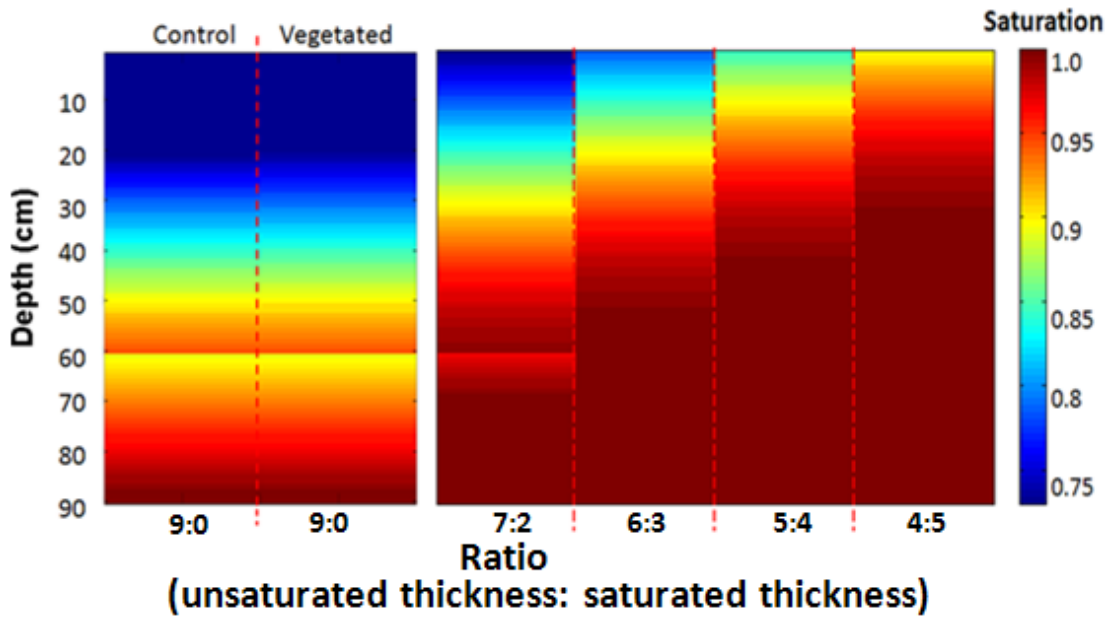
(a) Saturation in the soil
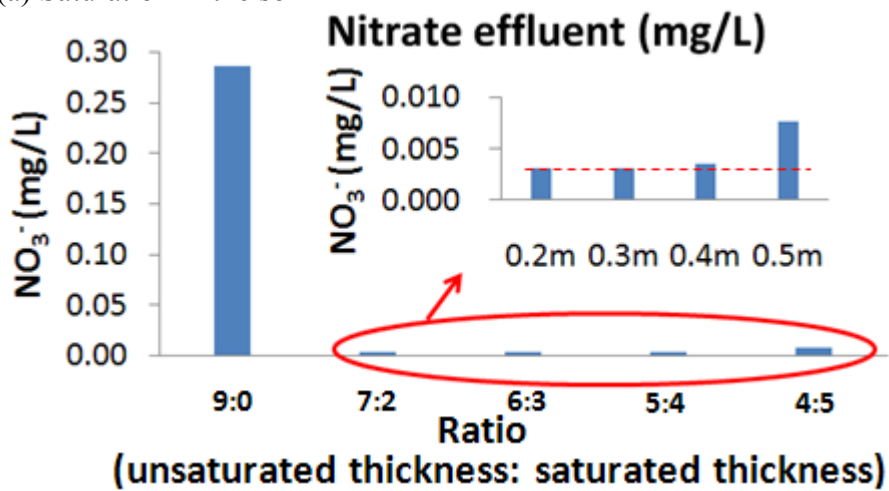
(b) Nitrate effluent concentration

Figure 8. Nitrate removal performance.

Simulated bioretention performance under varying climatic conditions

As shown above, the MIN3P-THM was applied in simulating changes in effluent from the bioretention system. Thus, three scenarios were developed to demonstrate the effect of different rainfall patterns on the performance of heavy metal removal: dry conditions (Year 2003-2004), wet conditions (Year 2010-2011), and medium wet conditions (Year 2009-2010). These years were selected from 15 years (from Year 1999 to 2013) hourly precipitation in College Station (NOAA 2013). A one-year period simulation was conducted for each scenario to compare the removal performance among Cu^{2+}, Zn^{2+}, and Pb^{2+}.

The model results of removal efficiency indicated that rainfall levels did influence the heavy metal removal (Figure 9). Simulated bioretention cells performed better under drier conditions than wetter conditions; all the ions had higher removal efficiencies. In addition, only Cu^{2+} leached from the bioretention cells in wetter conditions, while other ions were removed from the cells in both wet and dry conditions. This phenomenon can be explained as less water and chemical input into the model in a drier condition. The bioretention system had enough capacity to eliminate the heavy metals though a range of biogeochemical reactions.

Sorption process contributed to heavy metals removal in the bioretention cells. In each scenario, Pb^{2+} was the most effectively removed ion while Cu^{2+} was the least removed, suggesting that most of heavy metal effluent concentrations are contributable to sorption process, and ion exchange, since they would affect chemical transport in the soil (Appelo and Postma 2005). In each scenario, the sorption processes were different

35

among these three ions. A negative sorption rate indicated the ion was released from the soil while a positive sorption rate means the ion was sorbed on the soil. Cu^{2+} and Zn^{2+} always had a more frequently negative sorption rate while Pb^{2+} had a more frequently positive sorption rate, that means much more Cu^{2+} and Zn^{2+} were released into the solution while Pb^{2+} was sorbed on the soil. The difference between the initial chemical concentrations in the soil and the influent concentration would also affect the direction of sorption and ion exchange process. With respect to concentration values in Table 1, Zn^{2+} and Cu^{2+} had a higher concentration in the soil than in the influent, while Pb^{2+} was higher in the influent. The soil has less capacity to sorb Zn^{2+} and Cu^{2+} than to sorb Pb^{2+}, thus leading to a negative sorption rate for Zn^{2+} and Cu^{2+} (release) while a positive sorption rate for Pb^{2+} (sorption). The cation exchange with other ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, etc) also released Zn^{2+} and Cu^{2+} into the solution.

Meanwhile, pH was another important factor that would influence the sorption process. The sorption rate would increase with pH increase (Appelo and Postma, 2005). The pH can reflect the change of ion strength which would influence the process of ion exchange in the system.

Root solute uptake also plays an important role in Zn^{2+} removal. The grass actively uptake Zn^{2+}, NH_4^+, Ca^{2+}, K^+, Mg^{2+}, NO_3^-, SO_4^{2-} as essential plant nutrient for its growth in growing seasons, and released Cl^- and CO_2, which became CO_3^{2-}. Their uptake rates vary based on ion concentrations in the soil solution. The active plant uptake can remove much of Zn^{2+} from the system leading to an effective removal of Zn^{2+}.
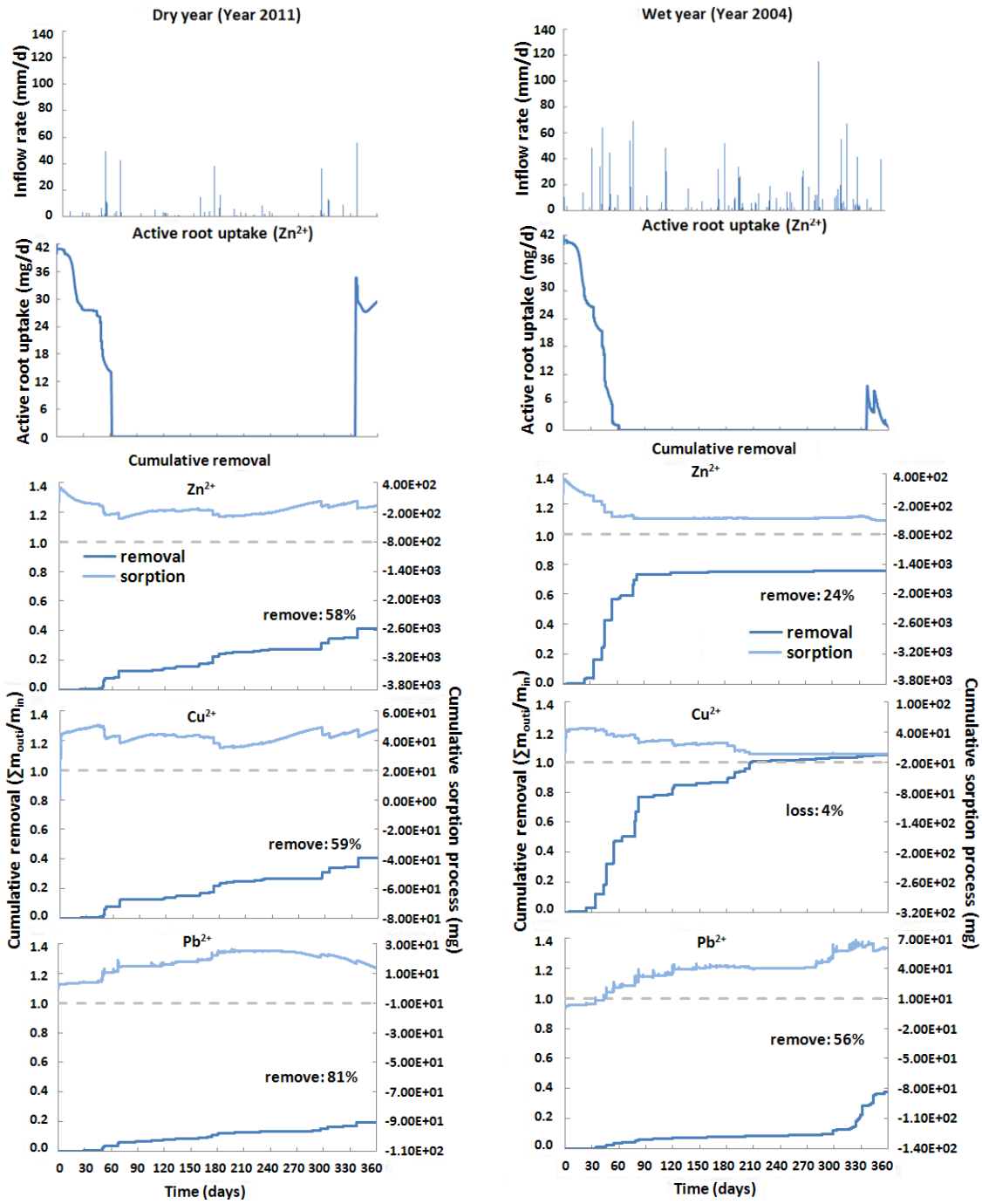
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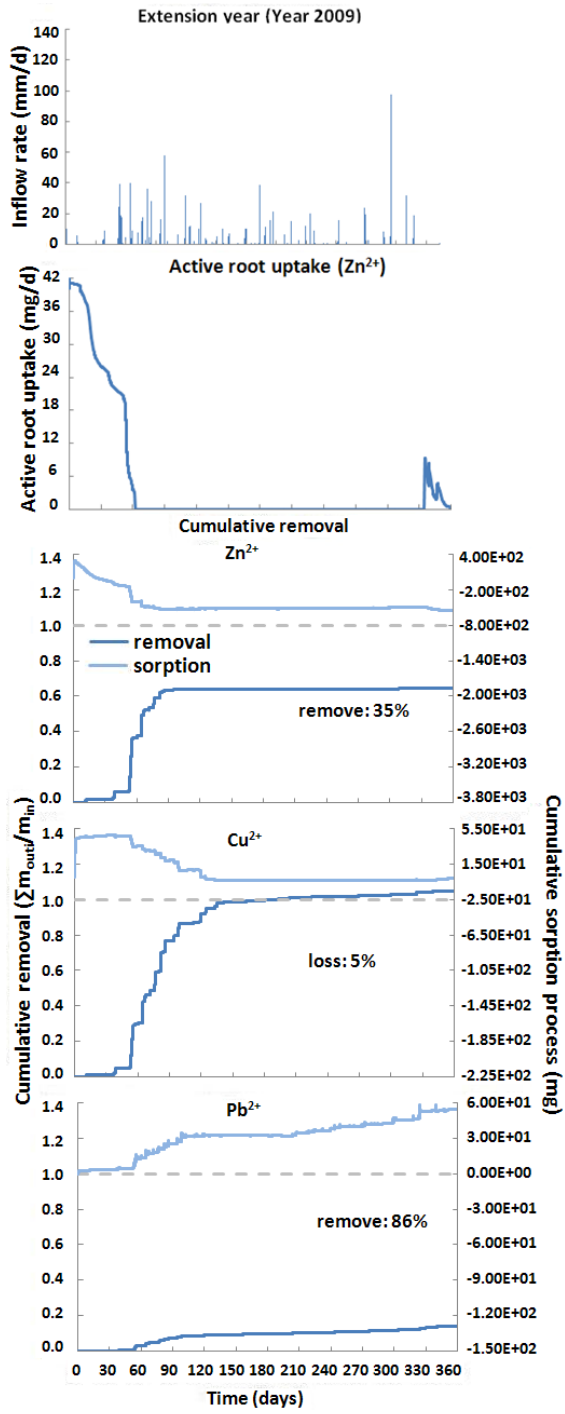**Figure 9.** Simulations under varying climatic conditions.

Figure 9. Continued.

Conclusions

Urban stormwater runoff carries a variety of pollutants, which may lead to water quality problems. Bioretention cell can be treated as an important method in mitigating environmental problems of urban stormwater runoff. It can mitigate water quantity and quality through soil retention, root uptake, ion exchange, sorption, and a range of biochemical reactions.

Numerical modeling MIN3P-THM showed that the bioretention systems were able to remove heavy metals, nitrate, and organic carbon through natural attenuation in the soil. The model can catch the trend of outflow rate and pollutant concentrations in both vegetated and non-vegetated systems.

Cation exchange is responsible for the change of salinity, while media minerals (calcite, gypsum, siderite and rhodochrosite) influence the concentration of iron, calcite, and manganese through dissolution-precipitation reactions. The difference between the initial soil chemical concentrations and the influent concentration would affect the direction of sorption and cation exchange process. Compared with Zn^{2+} and Pb^{2+}, Cu^{2+} had a lower concentration in the influent, which led to negative removal efficiency. In addition, low soil concentration of Pb^{2+} allowed the soil to have large capacity to sorb Pb^{2+} from synthetic runoff. However, the effluent concentration of Pb^{2+} was very close to MCLs, much more attenuation should be paid to Pb^{2+} avoiding human health hazard.

Nitrogen compounds and organic carbon were coupled together through nitrification, denitrification, other redox reactions with ammonium, iron, and manganese

ions, and plant solute uptake. These reactions can decay hydrocarbons and release salts (NO_3^-, CO_3^{2-}, Fe^{2+}, Mn^{2+}) into the pore water. These salts can influence salinity levels through interacting with other ions by sorption and ion exchange processes. Nitrogen compounds were removed through nitrification and denitrification processes. The carbonate related reactions can produce CO_2 gas; this gas can affect the pH and alkalinity in the system, thus influencing the salinity in the soil solution. Plant can release carboxylic acid into the soil through respiration process.

The root zone had a significant role in mitigating both water and pollutants in the bioretention cells. Due to macropores and fast flow paths created by roots in vegetated cells, the water can carry ions flowing out of the system very quickly leading to a higher outflow rate and less removal efficiency than non-vegetated cells.

In addition, plant can selectively uptake essential nutrient for their growth (Zn^{2+}, Mg^{2+}, K^+, Ca^{2+}, NO_3^-, NH_4^+) while excluding Cl^-, CO_3^{2-}, and other ions. The active solute uptake rates vary based on ion concentrations in the soil solution. The uptake will lead to increase in rejected ions in the pore water.

A saturated zone is demonstrated as an important part in nitrate removal. The saturated zone provides an anoxic condition to promote denitrification process thus convert nitrate into nitrogen gas. A range of possible design configurations have been tested to determine the optimal saturated zone thickness and outlet location for nitrate removal by using the model.

Moreover, scenario developments showed that different rainfall levels did influence the natural attenuation performance of bioretention cells. Due to less water and

chemical input, drier conditions may have a better performance in heavy metal removal than wetter conditions. In addition, only Cu^{2+} leached from the bioretention cells in wetter conditions, while other ions were removed from the cells in both wet and dry conditions. The bioretention system had enough capacity to eliminate the heavy metals though a range of biogeochemical reactions. Soil concentration, sorption process, pH, and active plant solute uptake can all affect heavy metals removal.

These results indicate that a clear understanding of the site-specific properties of stormwater runoff (types and quantity of pollutants), soil characteristics, and plant properties (macropores, fast flow paths) is important in constructing a successful bioretention system. In future work, available laboratory data should be used to test and calibrate the model.

CHAPTER III

LAND APPLICATION OF HIGH SALINITY OGEP WASTEWATER

Introduction

The rapidly growing oil and gas development in Texas promotes applications of cost effective treatments for oil and gas produced wastewater. Land application is treated as an effective alternative to manage industrial and municipal wastewater (Corwin and Bradford 2008; Lu et al. 2012; USEPA 2002; Veil 2002). This approach is suggested as a successful way to treat sewage sludge and petroleum industry wastes (Aroca et al. 1982). A land application system is a natural treatment which distributes wastewater over the field site, and reclaims wastewater by soil and vegetation (USEPA 1974). The natural attenuation process in a land application system includes numerous physical, biological, and chemical methods to mitigate hydrocarbon, nutrient, metals, and solids. Diffusion, dispersion, microbial activity, oxidation, mineral precipitation, sorption, and ion exchange are all taken into account in this process. There are a series of benefits of this system: cost effective, no-sludge byproduct, no discharge into waters, can be applied as irrigation water (Cortland 2013). This method is treated as a more cost effective and more environmentally friendly practice than other methods (such as pit disposal).

OGEP wastewater contains large amount of salts, heavy metals, and hydrocarbons (Utvik 1999). This kind of wastewater may influence plant growth, following with groundwater contamination. The wastewater may also have naturally

occurring radioactive material, while drilling fluids or mud may also contain a variety of chemical additives to enhance their performance (USDOE 2012). A maximum contaminant concentration should be determined before land application (Harrison et al. 1999). According to Environmental Protection Agency (USEPA) regulations of United States, the daily maximum limit discharge offshore for oil and grease wastewater is 42 mg/L and the limit of monthly discharge is 29 mg/L (Ahmadun et al. 2009).

Many studies have focused on attenuating salts and hydrocarbons in OGEP wastewater (Ahmadun et al. 2009; Cakmakce et al. 2008; Tellez et al. 2002). As summarized by Ahmadun et al. (2009), physical, chemical, biological, and membrane treatments are used currently to treat this kind of wastewater. For instance, Cakmakce et al. (2008) used membrane method to desalinate oil produced wastewater. Tellez et al. (2002) applied an activated sludge system to remove hydrocarbons.

Fixed Dissolved Solid (FDS), and Total Organic Carbon (TOC) are the major concerns in the OGEP wastewater (Stephenson 1992). FDS, as a secondary drinking water contaminant, is an index of salinity level in the water, it includes Ca^{2+}, Na^+, Mg^{2+}, K^+, Al^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, HCO_3^-. High salinity level in the soil may alter essential biodegradation processes by inhibiting microbial degradation of organic matters (Lee and Liu 2006; Rietz and Haynes 2003) and lowering plant water uptake rates (Hoffman et al. 1983; Katerji et al. 2000; Maas and Hoffman 1977). The attenuation of dissolved solids in soils is much more complicated than that of organic carbon. Cations (Ca^{2+}, Fe^{2+}, Mg^{2+}, Na^+, K^+, Mn^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}) can interact with other ions through sorption, mineral precipitation, and

cation exchange. In addition, Cl⁻, a conservative species in the dissolved solids, can induce FDS concentration increasing because of its inability to attenuate in the soil solution through plant uptake and biotransformation.

To simulate the complicated natural attenuation process and to determine the negative impact of OGEP wastewater application on vegetation and soil, a reactive transport model is used. Because of its combination of flow, nutrient transport, and biogeochemical processes, this integrated approach is absolutely important to improving the understanding of the Earth systems (Steefel et al. 2005). The process is complex because of natural variations in soil and water chemistry and heterogeneity of subsurface materials (Donado et al. 2009). Due to its ability to simulate a range of biogeochemical reactions (Langergraber and Simunek 2005), this method can be useful for addressing an array of environmental problems: natural attenuation of groundwater contamination (MacQuarrie et al. 2001; Mayer et al. 2001); simulating land application of food-processing wastewater (Miller et al. 2008); rock weathering (Navarre-Sitchler et al. 2009); and CO_2 injection, sequestration and leakage (Gaus et al. 2005).

At present, numerous computer codes are available for simulating reactive transport processes. (Carrayrou et al. 2010) compared a number of reactive transport models, including MIN3P, GDAE1D, Hoffmann et al., SPECY, HYTEC. The results demonstrated that these models had the ability to provide accurate data; and gave users confidence to apply reactive transport model in addressing environmental problems.

The reactive transport code MIN3P-THM is chosen in this paper to simulate pore water composition changes in the subsurface under applications of different levels of

OGEP wastewater. MIN3P-THM is a finite difference reactive transport model which can be used in a variably saturated medium across one to three dimensions. Various types of reactions are involved in the framework, such as oxidation-reduction, ion exchange, aqueous complexation, hydrolysis, dissolution, precipitation and others. This model is highly flexible, equilibrium, and kinetically controlled reactions, plant uptake of nutrient and solute can be all defined in a database.

A theoretical application of four wastewaters over a ten-year period was simulated at a field site scale, and a simulation of wastewaters application for two months was conducted at a pilot scale. These simulations were used to demonstrate the effect of chloride, FDS, and TOC on natural attenuation in the soil. The objectives of this study were to determine the respective below through modeling work:

1) Study the effect of high salinity OGEP wastewater on vegetation (field scale);

2) Estimate the influence of OGEP wastewater on groundwater (field scale);

3) Study the interactions between hydrocarbon and salts (field scale);

4) Investigate the ecohydrological responses to OGEP wastewater under natural application (pilot scale).

Materials and methods

Conceptual model

The reactive transport model MIN3P-THM was used to simulate natural attenuations of FDS and TOC in the soil at field site scale and laboratory scale. First, the

hydrogeology and several representative wastewater concentrations of a well-documented field site were simulated using the existing reactive transport model MIN3P-THM. Then a laboratory column study was conducted using the actual application of a representative wastewater.

A conceptual model was developed to depict the natural attenuation process of the high salinity wastewater with their accumulation in the root zone and reaching to the water table (Figure 10). OGEP wastewater was applied onto the soil surface. Before the applied water reaches to the water table, sorption, ion exchange between dissolved cations and those absorbed to mineral surface, mineral dissolution-precipitation, oxidation-reduction, and soil gas exchange would occur in the variable saturated soil. Meanwhile, plant water uptake and crop nutrient uptake take place in the root zone for plant growth which would remove essential nutrients (K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, NH_4^+, NO_3^-) from the system.
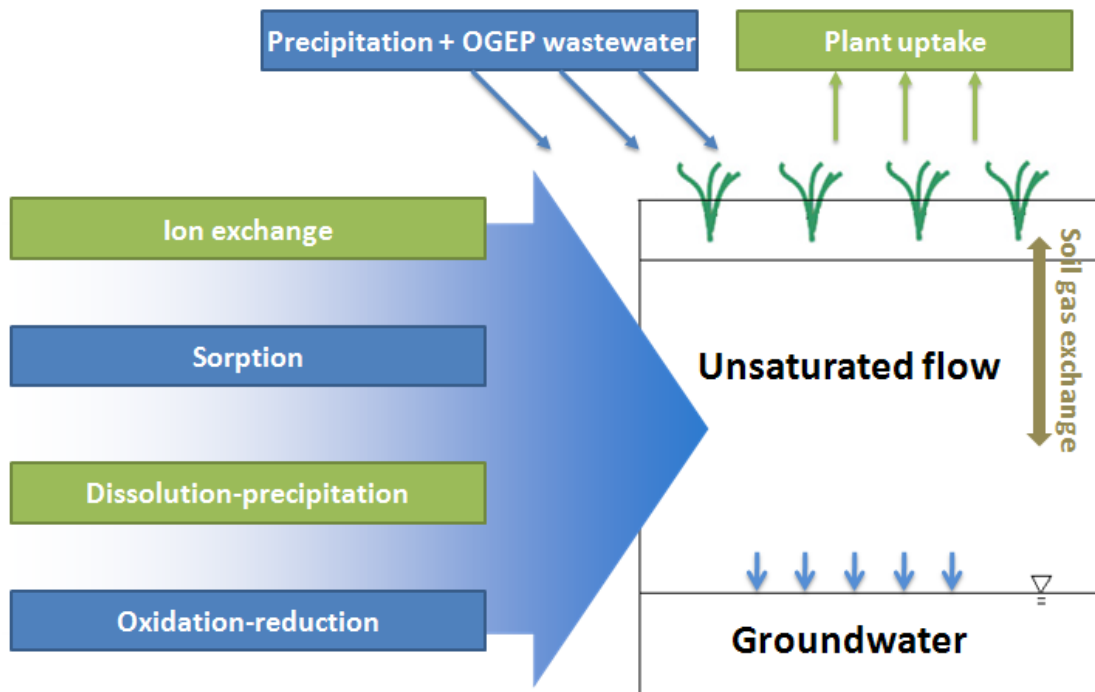
Figure 10. Conceptual model of land application.

TAMU hydrogeology field site

A well-documented field site was simulated to test the performance of reactive transport model (Chakka and Munster 1997; Chakka and Munster 1997; Chakka and Munster 1997; Munster et al. 1996). The Texas A&M University Hydrogeology Site was selected (Figure 11); it overlies the Brazos River alluvial aquifer and the eastern extent of the Eagle Ford Oil Shale Play, and is located adjacent to the Brazos River. The soil type of this site is primarily clay and silt clay, which limits its capacity of infiltration. The soil, which had been previously cropped, is currently fallow and being allowed to return to its prior state.
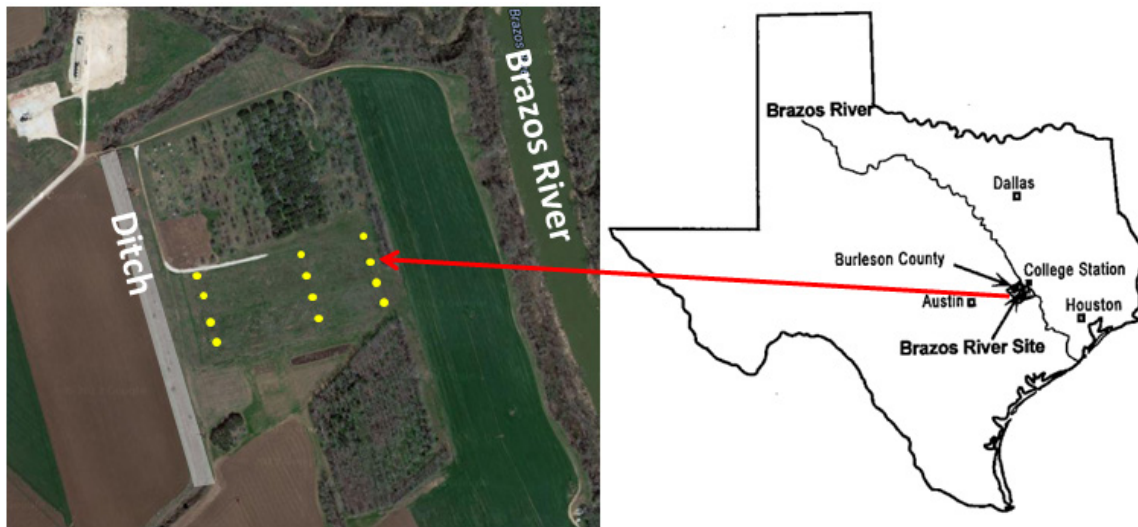
Figure 11. Field site description.

Floodplain and terrace deposits exist in this area. Recharge in this site is primarily precipitation or from surface water during flooding. Evapotranspiration, pumping wells, and base flows are the principal discharges in this area. The first layer of the site is Ships clay, the depth ranges from 9.1 m (near the Brazos River) to 6.1 m (near the ditch). A sand layer lies below the clay layer; it coarsens downward from fine sand near the top to coarse sand with cobbles below. Under this layer is a confining layer of shale. In addition, of the expansive nature of the surface layer of clay creates macropores in the unsaturated zone, potentially leading to preferential flow (Munster et al. 1996).

The top boundary conditions, at the soil surface, were based on existing climate data. Precipitation data was obtained from the National Climatic Data Center of National Oceanic and Atmospheric Administration (NOAA) (NOAA 2013). Monthly ET data was downloaded from the Texas Water Development Board's database (TWDB 2012). A constant head boundary condition was set at 8.8 m below the soil surface, representing the water table based on normal year. Two soil types were used in the model: a clay layer with 6.7 m depth and a gravel layer with 2 m depth. A root zone was assumed with 1.2 m depth to stand for grass.

Since preferential flow was found at this field site by Chakka and Munster (1997), effective hydraulic conductivity was applied here to represent the hydrogeological characteristic of the soil with preferential flow. The hydraulic conductivity of these two soil layers in the model were 3.25×10^{-6} m/s, and 4.63×10^{-4} m/s respectively.

The model was initialized by applying local irrigation water in a realistic, seasonal pattern until the soil moisture and pore water chemical concentrations reached equilibrium. The chemical concentration of irrigation water in this site can be derived from (Chakka and Munster 1997; Chakka and Munster 1997; Chakka and Munster 1997; Munster et al. 1996) since some pesticide transport models have been done in this site before. The groundwater drilled from local site was used as irrigation water. The concentration of FDS in the groundwater is 694 mg/L. After the initial condition was established, a ten-year simulation was conducted from year 2001 to 2010 to depict the fate of FDS and TOC in the soil.

49

Water stress was taken into account in the model for plant water uptake depending on soil moisture (the stress occurs when the soil moisture is below the field capacity of clay and root water uptake would cease when the water content is lower than the wilting point of clay). Since high salinity wastewater was applied in the system, salinity stress was also considered based on the electrical conductivity in the soil (Figure 12). Irrigation water was added in the simulations to keep crops healthy based on soil salinity (the salinity stress occurs when the electrical conductivity of soil (EC_e) increases to EC_{stress}).
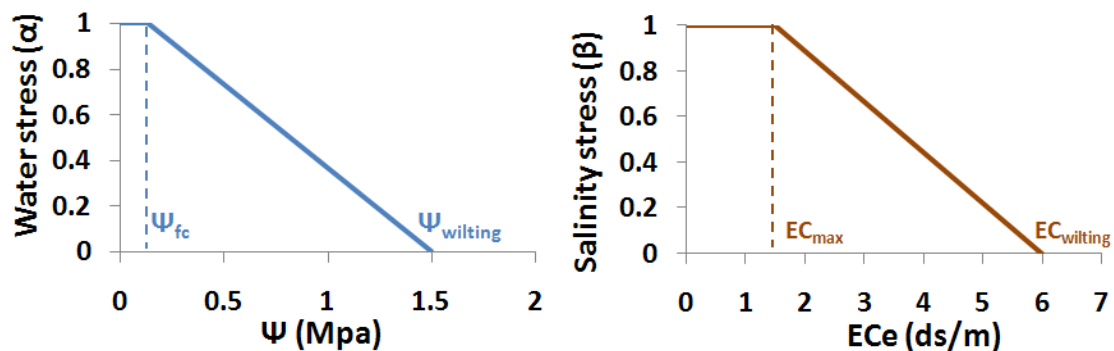

Figure 12. Water and solute stress factor.

Scenario development

Five treatments were conducted in this study: Control, High – FDS, High – Chloride, Medium – Chloride, and High – TOC treatments. The major contaminants of concern in the model are FDS, chloride, and TOC. Since ions in FDS can interact with

others through ion exchange, sorption, and mineral dissolution-precipitation, attenuation of FDS is complicated. The baselines were set up depending on separating the effect of chloride, other dissolved solid, and hydrocarbon on FDS attenuation:

- Control Treatment (CTL): Typical irrigation water for Brazos County (Munster et al. 1996).

- High FDS Treatment (HFDS): An OGEP wastewater with a moderate TOC concentration, a control level chloride concentration, and a high non‐chloride FDS profile.

- High Chloride Treatment (HFDS‐Cl): An OGEP wastewater with a moderate TOC concentration, a non‐chloride FDS profile matching the control, and a chloride concentration of 3000 mg/L, the limit for land application set by the Railroad Commission of Texas (RRC 2009; RRC 2010).

- Moderate Chloride Treatment (M‐Cl): An OGEP wastewater with a moderate TOC concentration, a non‐chloride FDS profile matching the control, and a 250 mg/L chloride concentration, the secondary maximum contaminant limit set by the (USEPA 2002).

- High TOC Treatment (HTOC): An OGEP wastewater with control levels of chloride and FDS and a high TOC concentration.

The ion concentrations for precipitation, irrigation water, and applied wastewater scenarios were shown in Appendix B-Table 3.

Laboratory scale

After the existing model was adapted to simulate the well-documented field site, an actual application of representative OGEP wastewaters was conducted using laboratory soil macrocosms, monitoring the hydrological and biogeochemical variables for a two-month application period. Five $32 \times 32 \times 50$ cm glass aquariums were filled with 4 cm of gravel followed by 40 cm of topsoil and topped with local Bermudagrass turf (Figure 13).

An outlet was drilled into the bottom and fitted with flexible tubing to allow for drainage of the effluent into a glass collection bottle. For each column, four Phillips T8, 32 watt Daylight Deluxe fluorescent lights were placed 30 cm overhead and timed to simulate a summer diurnal light cycle. The photosynthetically active radiation (PAR) of the lights and albedo of grass were applied to determine net energy available for photosynthesis. This net energy was used to calculate potential evapotranspiration through Penman-Monteith equation (Appendix B- Table 2).

An individual irrigation system, consisting of perforated plastic pipeline located right above the grass, allowed irrigation water and OGEP wastewater to drip onto the grass and soil at a controlled rate. Capacitance type soil sensors (5TE, Decagon Devices) were placed at depths of 5 cm and 26 cm below the surface of the soil. Suction lysimeters (UMS) were installed at 12 cm and 39 cm below the soil surface to extract pore water samples. During the experiment, soil moisture, electrical conductivity, and soil temperature were measured every five minutes using the 5TE probes (Appendix A-

Figure 2). Relative humidity and air temperature above the containers were monitored and used to calculate potential evapotranspiration from the grass.

At the beginning of the experiment, the columns were irrigated with tap water for a period of 49 days, in order to make sure that the grass established roots and the soil moisture within the columns equilibrated. Application of actual OGEP wastewater began after this initial irrigation period. The actual OGEP wastewater was available from a nearby disposal facility managed by Advance Hydrocarbon, and thirty gallons were obtained directly from an arriving tanker.
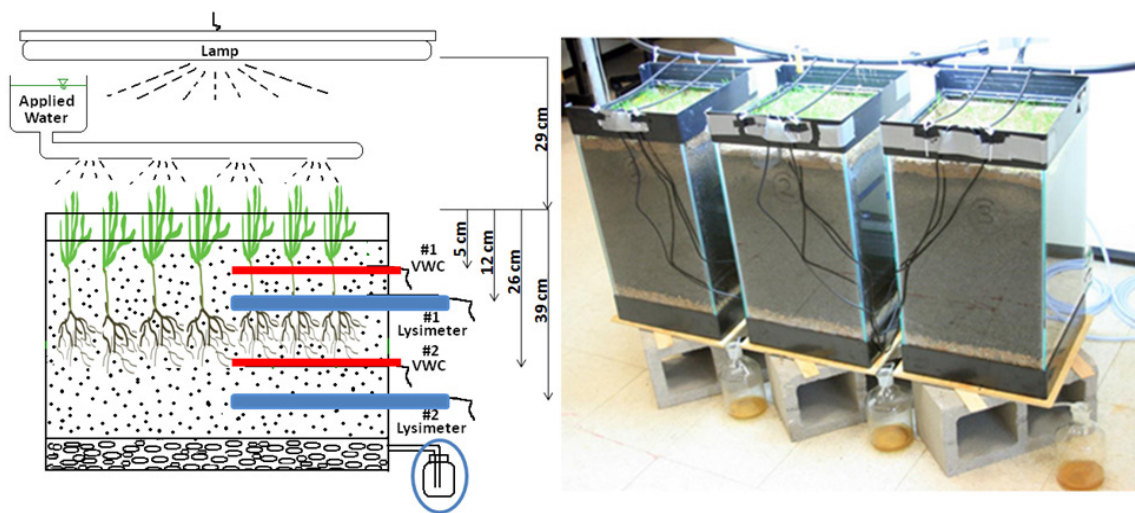

Figure 13. Configuration of the containers.

After an initial chemical analysis of the wastewater, the wastewater was diluted into four different levels (High, Medium-High, Medium-Low, and Low), with the highest wastewater concentration being based on the legal limit of chloride for land application in Texas. These columns were irrigated once per week for eight weeks (Appendix A-Figure 2); on average, applications totaled were 14.7 mm over 57 minutes.

Four kinds of water samples were collected prior to the beginning of first application, during, and after each of the eight applications. These samples were from different locations of the containers: applied wastewater collected at the point of application (influent); pore water extracted at a 15 cm depth; pore water extracted at a 40 cm depth; and effluent water exiting the column at the bottom outlet.

Numerical model

Governing equation

The reactive transport model MIN3P-THM was used to describe the natural attenuation process of OGEP wastewater in the subsurface. This model uses a block-centered finite difference equation and a global implicit solution solver (Nowack et al. 2006). The model is highly flexible, not requiring external code generation by users; energy balance, plant uptake of nutrients and solute, equilibrium, and kinetically controlled reactions are all taken into account (Bea et al. 2012; Mayer et al. 2002; Mayer and MacQuarrie 2010). There are two governing equations in the model to control both water and chemicals in the system.

The Richard's equation to simulate variable saturated flow (Mayer et al. 2002) is given below:

$$S_a S_s \frac{\partial h}{\partial t} + n \frac{\partial S_a}{\partial t} - \nabla \times [k_{ra} K_s \nabla h] - W = 0 \qquad (12)$$

where n is the porosity [-]; h is the hydraulic head [m]; S_a is the saturation of the aqueous phase [m^3/m^3]; S_s is specific storage coefficient [m^{-1}]; k_{ra} is the relative permeability of the medium [-]; K_s is saturated hydraulic conductivity [ms^{-1}]; W is a source-sink term (including root water uptake) [s^{-1}].

The reactive transport equation is shown below (Mayer et al. 2002):

$$\frac{\partial}{\partial t}\left[S_a n T_j^a\right] + \frac{\partial}{\partial t}\left[S_g n T_j^g\right] + \nabla \times \left[q_a T_j^a\right] - \nabla \times \left[S_a n D_a \nabla T_j^a\right] - \nabla \times \left[S_g n D_g T_j^g\right] -$$

$$Q_j^{a,a} - Q_j^{a,s} - Q_j^{a,ext} - Q_j^{g,ext} = 0 \qquad (13)$$

where T_j^a is the total aqueous concentration of component j [mol/L]; T_j^g is the total gaseous concentration of component j [mol/L]; $Q_j^{a,a}$ [mol/dm^3] and $Q_j^{a,s}$ [mol/dm^3] are internal source/sink terms of intra-aqueous and dissolution-precipitation reactions; $Q_j^{a,ext}$ is external source/sink term of aqueous phase [mol/dm^3]; $Q_j^{g,ext}$ is external source/sink term of gaseous phase [mol/dm^3]; S_g is the saturation of the gaseous phase [m^3/m^3].

Redox reactions

Nitrogen, organic carbon, oxygen, and dissolved species are taken into account in the model. Nitrogen cycle, carbon cycle and salts are coupled together in the system (Table 3). These reactions can be separated into two conditions: aerobic (nitrification, respiration) and anoxic (denitrification, fermentation, iron reduction, and manganese

reduction). The half-saturation and inhibition constants values of these redox reactions can be found in Appendix B – Table 1.

These reactions can decay hydrocarbons and release salts (NO_3^-, CO_3^{2-}, Fe^{2+}, Mn^{2+}) into the soil solution. These salts can influence FDS concentration through interacting with other ions by sorption and ion exchange processes. For instance, if Mg^{2+} replace Fe^{2+}, Mn^{2+} through cation exchange, the Fe^{2+} and Mn^{2+} concentration in pore water would increase while the Mg^{2+} concentration would decrease, thus the FDS concentration would increase, since the atomic mass of Fe^{2+} and Mn^{2+} are larger than that of Mg^{2+}. The release of H^+ from nitrification, respiration, denitrification, and fermentation can also influence sorption process. Increase in pH would promote the sorption process (Appelo and Postma 2005).

In addition, the occurrence of oxygen can promote nitrification and inhibit denitrification process. For nitrogen compound, nitrification process converts ammonia to nitrate under aerobic conditions; while under anoxic conditions, denitrification will lead to the conversion of nitrate to nitrogen gas.

Table 3. Key redox reactions for nitrogen, hydrocarbons and ions

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Aerobic reactions (in the unsaturated zone)

Nitrification: $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$

Respiration: $CH_2O + O_2 \rightarrow CO_3^{2-} + 2H^+$
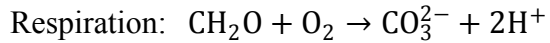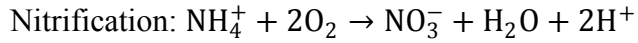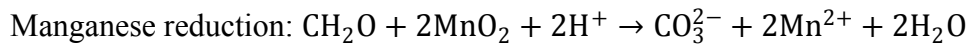
Anoxic reactions (near the water table)

Denitrification: $CH_2O + \frac{4}{5}NO_3^- \rightarrow \frac{2}{5}N_2 + CO_3^{2-} + \frac{6}{5}H^+ + \frac{2}{5}H_2O$

Fermentation: $CH_2O + \frac{1}{2}H_2O \rightarrow \frac{1}{2}CO_3^{2-} + \frac{1}{2}CH_4 + H^+$

Iron reduction: $CH_2O + 4FeOOH + 6H^+ \rightarrow CO_3^{2-} + 4Fe^{2+} + 6H_2O$

Manganese reduction: $CH_2O + 2MnO_2 + 2H^+ \rightarrow CO_3^{2-} + 2Mn^{2+} + 2H_2O$
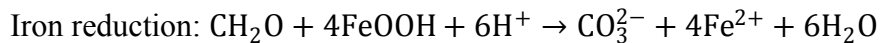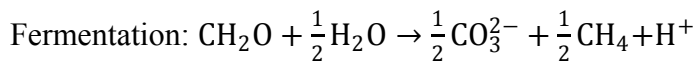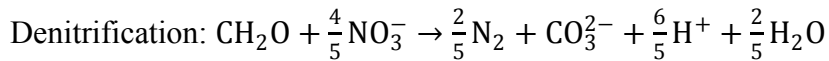
Water and salinity stress

Water stress was taken into account in the model for plant water uptake depending on soil moisture (the stress occurs and root water uptake would cease when the water content is lower than the wilting point of clay).

Water and solute stress factors were taken into account to proportionately decreased evapotranspiration rate to survive the plant when soil moisture is below the field capacity of clay; and/or electrical conductivity of soil (EC_e) increases to EC_{stress}.

Both soil moisture deficit and salinity excess were included in the equation:

$$ET_{actual}\ (t) = ET_0(t) \times k_c(t) \times \alpha\big(\theta(t)\big) \times \beta\big(EC_e(t)\big) \qquad (15)$$

where $ET_0(t)$ is total ET for the crop at time t [L/T]; $k_c(t)$ is crop function at time t [-];

$\alpha(\theta(t))$ is water stress factor which relates to water potential at time t [-]; $\beta(EC_e(t))$ is

salinity stress factor which relates to electrical conductivity in the soil at time t [-].

Crop nutrient uptake depends on concentration, and time

Vegetation also plays an important role in changing pore water concentrations.

The plant can uptake important nutrient from the byproducts of these processes (Zn^{2+},

Ca^{2+}, Mg^{2+}, K^+, NO_3^-, NH_4^+) and release CO_3^{2-} into the soil solution through respiration.

Crop nutrient uptake is calculated by the Michaelis-Menten kinetic equation:

$$A_x(t,z) = A_{x,max} \frac{C_x(t,z)}{K_m + C_x(t,z)} \tag{14}$$

where $A_x(t,z)$ is the nutrient uptake rate of ion x at time t, and depth z; $A_{x,max}$ is the

maximum ion uptake rate; K_m is the ion concentration when the reaction rate is

$0.5*A_{x,max}$; $C_x(t,z)$ is the concentration of ion x.

Results and discussion

Field scale modeling

Ten years application of the representative OGEP wastewater at the field site was

simulated. The model results showed that long-term application of OGEP wastewater

(especially those with high salinity levels) can influence plant growth and pollute

groundwater after several years. The use of this practice should be paid more attention to avoid contaminating groundwater and nearby surface water bodies.

Gas diffusion plays an important role in flow, chemicals transport, and FDS attenuation. Figure 14 showed the occurrence of O_2, N_2 and CO_2 in the soil. These gases can transport in the system by gas diffusion. Compared with CO_2, N_2 and O_2 occupy large volume of gas in the soil.

The results indicated that the active soil layer (root zone) is significant to gas diffusion. The gases in the top layer can interact with those in the atmosphere. For instance, the occurrence of oxygen gas in the soil can create aerobic conditions, thus promoting nitrification, respiration, and methane oxidation. In addition, the plants can uptake water and more gas is filled into the soil volume. The gas volumes decrease with the soil depth, especially those near the water table. Low gas concentration occurred near the saturated zone, which would create anoxic conditions, promoting fermentation, denitrification, reduction of manganese, sulfate, and iron.
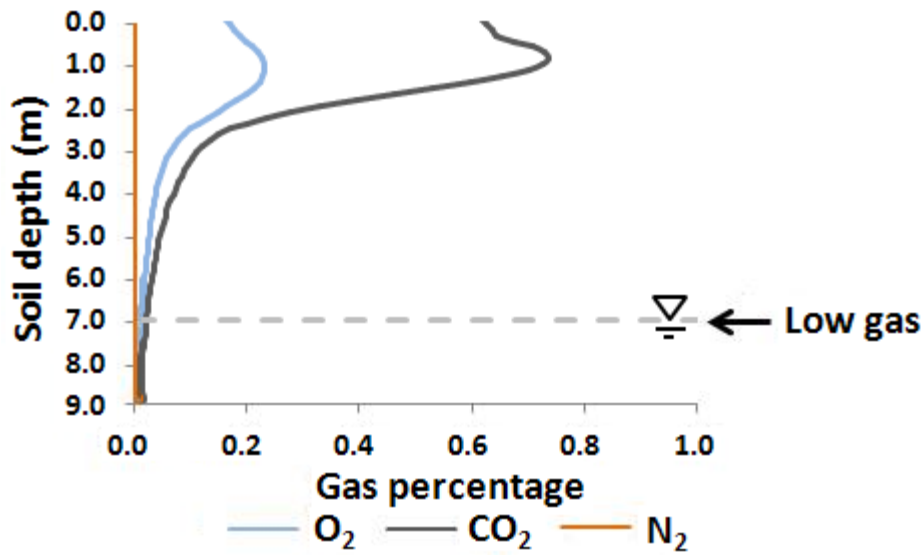
Figure 14. Gases presented in the soil.

Figure 15 showed the change of FDS concentration throughout the soil zone during ten years period under four different treatments. In the figures, the area above dashed line represents the root zone and the bottom of the figures stands for the water table. After a large rainfall event (more than 20 mm/d), large amount of salts were flushed into the soil. Both Figure 15 and 16 showed that salts began to build up in the root zone during extended wastewater application. In addition, TOCs are accumulated in the root zone throughout the ten application of High TOC and reached to groundwater after 6 years of application (Figure 16 and 17).

In the HFDS and HFDS-Cl treatments, FDS concentrations in the root zone reach upwards of 1500 mg/L, while in the other treatments, FDS concentrations stay under 600 mg/L for the duration of the application. Water and salinity stress occur when the water

content is lower than field capacity of clay (0.45) and/or electrical conductivity of the pore water is higher than EC_{stress} (1.5 ds/m) or FDS concentration in soil solution is 1000 mg/L, the plant would linearly decrease their evapotranspiration rate for their growth based on water ($\alpha(\theta(t))$) and salinity stress factors ($\beta(EC_e(t))$). For HFDS and HFDS-Cl treatments, EC_e levels in the root zone did exceed the threshold (1000 mg/L) induce solute stress in the vegetation, which would inhibit plant water uptake and ultimately growth.

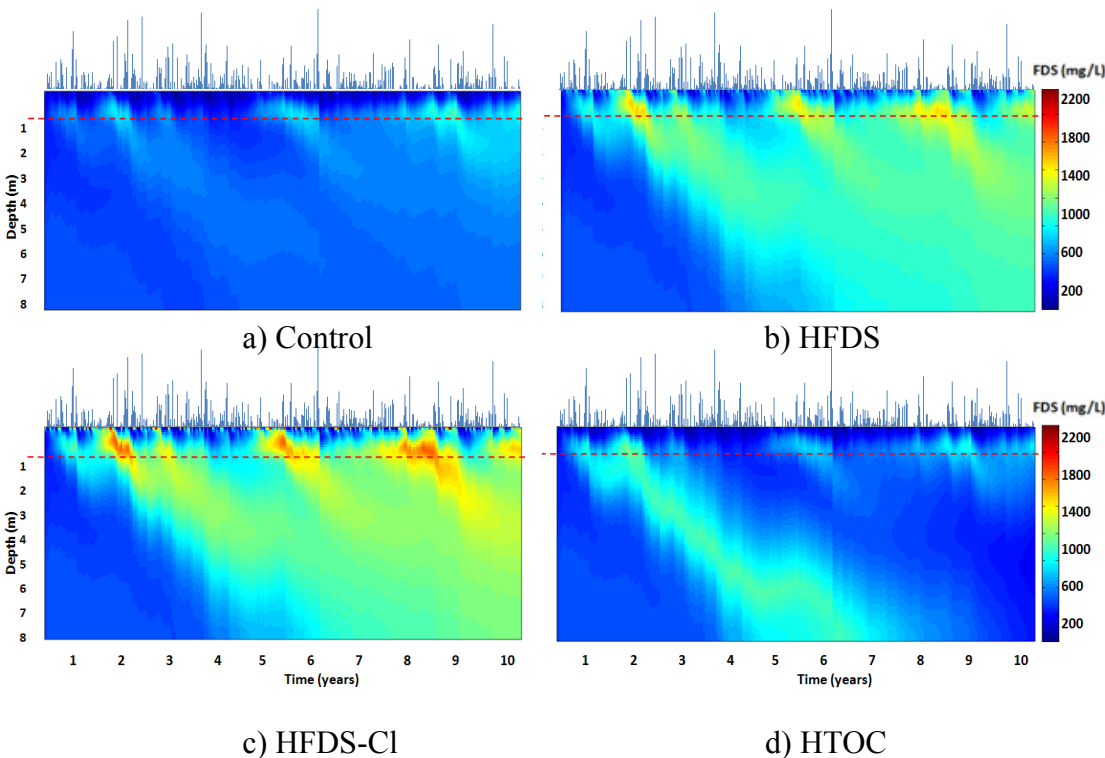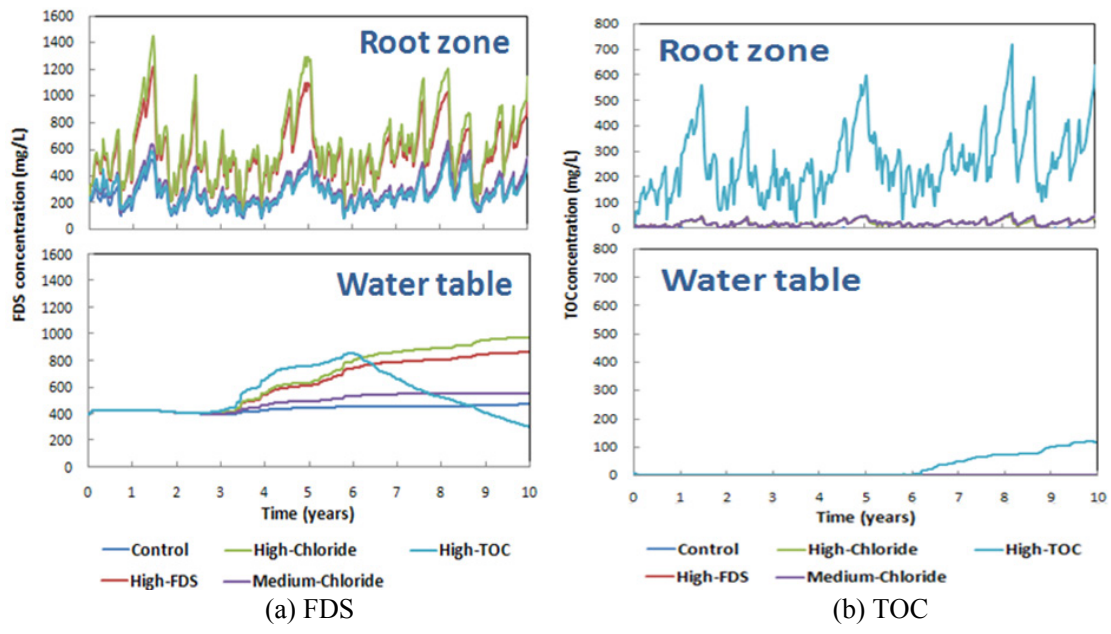**Figure 15.** Soil profile of FDS in 10 years.

Figure 16. Modeled fixed dissolved solids (FDS) concentrations.
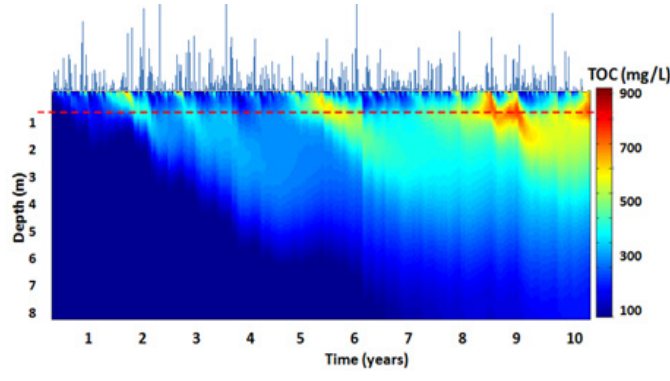
Figure 17. Soil profile of TOC in 10 years (H-FDS treatment).

The simulations suggest that root zone salinity increases after application and that dissolved salts eventually reach the underlying groundwater. Under these

62

treatments, salt begins leaching to the water table after 3 years of application, inducing concentrations up to 1000 mg/L after 6 years. Due to the flow direction in the groundwater, the high salinity groundwater may later migrate to the Brazos River. Moreover, high chloride levels in the wastewater (HFDS-Cl) resulted in higher concentrations in root zone and water table, as unlike other FDS constituents, Cl^- is a conservative species which cannot be removed by the natural treatment processes. The high Cl^- concentration would lead to high FDS concentration without attenuation.

Meanwhile, wastewater with high organic carbon levels (HTOC) caused an initial increase in FDS to the water table, due to the microbial conversion of nutrients initially present in the subsurface (Figure 13 and 14), its production of carbon dioxide, and the subsequent increase in carbonate species. Once these initial nutrients are exhausted, FDS concentrations in the HTOC treatment return to levels below 400 mg/L, but TOC begins to build up in the root zone and leach to the water table, in concentrations up to 750 mg/L and 120 mg/L, respectively.

Removal efficiency of salinity and organic matter

Removal efficiencies of Cl^-, FDS, TOC, and NO_3^- after 10 years' application vary widely based on the characteristics of wastewater applied (Table 4). The model results indicated that conservative species (Cl^-) suggested minor impact on the application of wastewater due to differing hydrology. The removal efficiency of Cl^- ranges from 26% to 34%, which shows little difference between these four treatments.

Table 4. Effects of salinity and organic matter complex

	Treatment	TOC	FDS	Cl$^-$	NO$_3^-$
Removal Efficiency (%)	**Control**	92	-18	34	12
	High Cl	70	2.3	33	-20
	High FDS	62	3.2	26	-6.6
	High TOC	44	-41	30	22

Positive removal efficiency of FDS (2.3% and 3.2%) can be found in HFDS and HFDS-Cl treatments indicates that high salinity levels in these two treatments induce the salts begin to precipitate slightly. The high concentration of Ca^{2+} would contribute to the positive removal in HFDS treatment. Since Ca^{2+} has stronger attraction than Mg^{2+}, Mn^{2+}, Fe^{2+}, K^+, NH_4^+, Na^+, inhibit salt removal. Ions which have lighter atomic mass (Mg^{2+}, K^+, Na^+, NH_4^+) than Ca^{2+} can be replaced by Ca^{2+} on the cation exchange site, and the total FDS mass will decrease. For HFDS-Cl treatment, large amount of Cl$^-$ (which is difficult to be sorbed) released into the soil solution and induced increasing of the total FDS concentration.

In addition, the negative efficiency of FDS (-18% and -41%) in CTL and HTOC treatments indicated that increasing CO_3^{2-} levels contributed to the increase of FDS concentration. The CO_3^{2-} cannot be sorbed on the soil surface easily, thus would release into the soil solution and contribute to the total FDS increase.

For TOC removal, the lowest removal efficiency occurs in HTOC treatment (44%). When the applied level of TOC is too high (in HTOC treatment), the organic removal capacity is exhausted, leading to much lower removal efficiency than other treatments.

Additionally, the removal efficiency of NO_3^- in different treatments shows negative removal efficiency (-20% and -6.6%) only in both HFDS and HFDS-Cl treatment. The negative value illustrated that less nitrate would be removed when the FDS level is very high. This result suggests that high FDS concentrations suppress nitrogen removal.

Removal efficiency of heavy metals

Table 5 shows the removal efficiency of heavy metals after 10 years of application depending on ion exchange, sorption, and mineral precipitation processes. Different cations have different removal ability based on their ability adsorbing on the soil surface. Among these heavy metals, Pb^{2+} and Ba^{2+} experience the most attenuation, with 85% and 63% removal efficiencies for the HFDS treatment. However, the other heavy metals (Zn^{2+}, Cu^{2+}, Pb^{2+}, and Fe^{2+}) are leached from the soil.

Table 5. Removal efficiency of heavy metals

	Treatment	Zn^{2+}	Cu^{2+}	Pb^{2+}	Fe^{2+}	Mn^{2+}	Ba^{2+}
Removal Efficiency (%)	**Control**	-22	-20	53	-9.3	15	-20
	High Cl	-81	-87	53	-49	-54	63
	High FDS	-41	-46	85	29	-180	57
	High TOC	-51	-60	52	-35	-62	63

Mn^{2+} in HFDS treatment was the least removal in this table. As we discussed above, large occurrence of Ca^{2+} in HFDS treatment would replace Mn^{2+} on the cation exchange site since Ca^{2+} has a stronger attraction than Mn^{2+}, thus large amount of Mn^{2+} will release into the solution.

Removal of barium under the HFDS treatment can be explained by the barium-sodium adsorption process; this case has a higher sodium level than the others allowing for more barium to be exchanged for sodium on sorption sites. In addition, when the soil exhausts its capacity to absorb ions on the surface, less Zn^{2+}, Cu^{2+}, Pb^{2+}, and Mn^{2+} can be removed through ion exchange, leading to leaching.

Pilot scale - container study

Based on pre-processing data (soil texture analysis, and water retention curve), a model of the containers was established. The simulated soil moisture data was compared with the measured data from Decagon 5TE soil moisture sensors to check the capability

of the model. The soil moisture results compared poorly; the r^2 ranged from 0.052 to 0.617 in shallow soil while r^2 ranged from 0.029 to 0.590 in deep soil (Figure 18). This figure showed modeled and measured data of soil moisture in both shallow and deep zones (under Control, High, MedHigh, MedLow, and Low treatments).

The comparison shows that soil moisture in shallow zones always have a more damped response to water application than the deeper ones. Preferential flow is likely the cause; macropores created by roots and wires of sensors induce preferential flow in the soil, especially in the shallow zone where large amount of roots exist. The much more flat trend in shallow root zone than in deep ones showed that water applied into the soil would flow very quickly through the fast flow paths to the bottom without retaining in the shallow ones.

To address this problem, a dual-porosity module for depicting the preferential flow was added into the model (Gerke and Genuchten 1993). However, the model still cannot match the measured data very well. The reason may be large amount of root in shallow zone. These roots may influence the measurement of soil moisture sensors.

In addition, the big mismatch often occurs before the application of wastewater (0-50 days). We can assume that the roots are growing during this time period, that is why the soil moistures here are always higher than the ones after wastewater application (50-80 days).
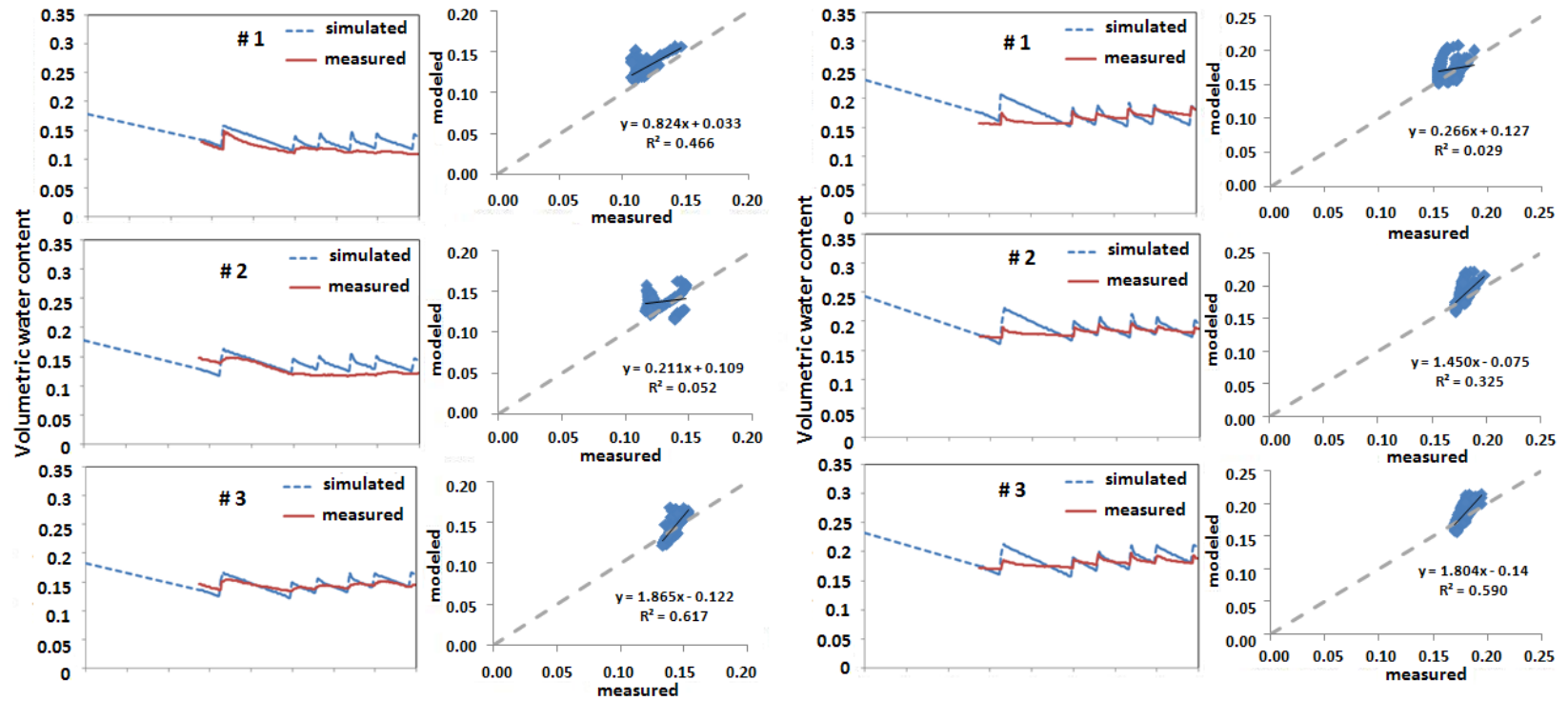
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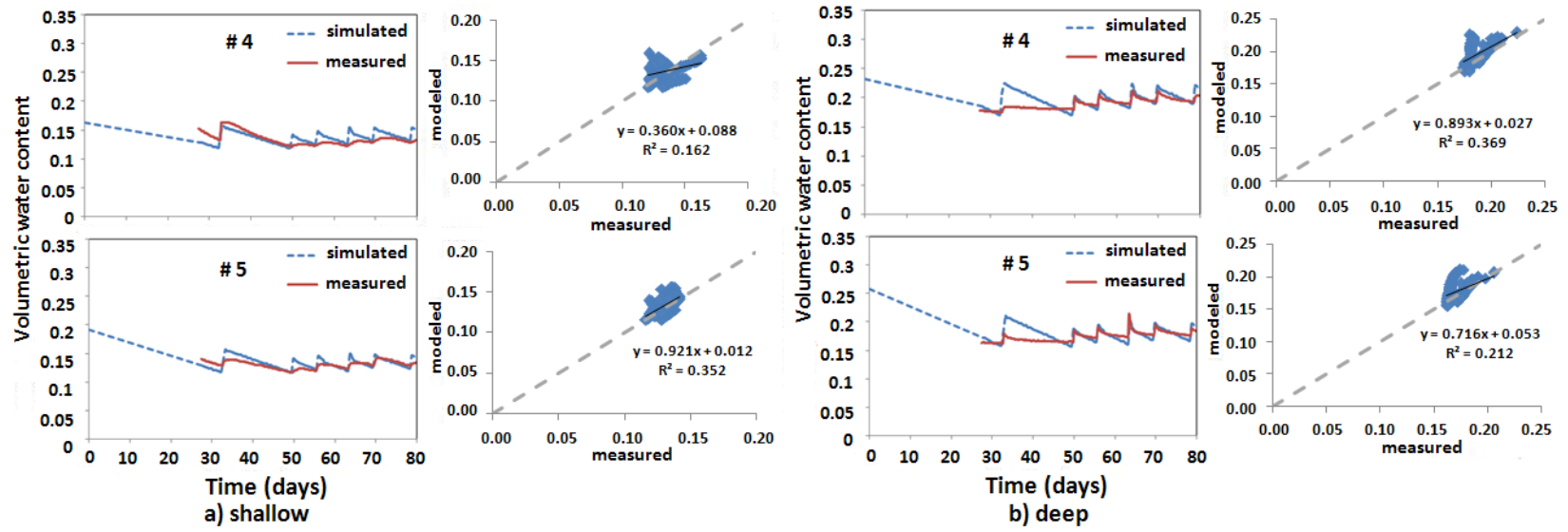**Figure 18.** Soil moisture in different depths (measured vs. modeled).

Figure 18. Continued.

69

Conclusions

Land application is treated as an effective and natural system to manage industrial and municipal wastewater. To determine the effect of salts, and hydrocarbons on the whole system, MIN3P-THM is used to simulate chemical composition changes after land application of OGEP wastewater at both field site and lab containers.

Long-term application of OGEP wastewater (especially those with high salinity levels) can influence plant growth and pollute groundwater after several years. Use of this practice should be paid more attention to avoid contaminating groundwater and nearby rivers. The results demonstrated that long time application of high salinity wastewater (both Chloride-included High FDS and non-Chloride High FDS) would accumulate salts in the root zone and affect groundwater quality. Solute stress plays an important role in High FDS condition: when the FDS concentration in the soil reaches a threshold value. In the root zone, high FDS levels in applied OGEP wastewater inhibit root uptake of water and contaminants. Due to the microbial conversion of nutrients initially present in the subsurface TOC has a negative effect on FDS concentration: for HTOC treatment, due to the microbial conversion of nutrients initially present in the subsurface, its production of carbon dioxide, and the subsequent increase in carbonate species. Once these initial nutrients are exhausted, FDS concentrations in the HTOC treatment will decrease. Although Cl^- is a conservative species which may have little impact on natural attenuation, the high Cl^- concentration will increase the total FDS concentration. For heavy metals, land application is efficient at removing Pb^{2+} and Ba^{2+}

from the system while the other metals (Zn^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}) may not be removed or may be leached from the existing soil.

The challenge for the model in simulating soil moisture in pilot scale is the preferential flow. Although a dual-porosity module was added into the model to describe the preferential flow, the model cannot catch the trend of soil moisture very accurately; especially those in the shallow zone where root density is high and where roots may create macropores leading to preferential flow. The large amount of roots may influence the performance of soil moisture sensors. Moreover, if we can better understand the root growth process during the applications, and develop an entirely plant growth mode in the model in the future, the model would match measured data better.

CHAPTER IV

SUMMARY

The soil plays an important role in attenuating municipal and industrial wastewater. The natural attenuation process includes physical, biological, and chemical treatment to mitigate hydrocarbon, nutrient, metals, and solids through the effect of soil and vegetation. Diffusion, dispersion, microbial activity, oxidation, mineral precipitation, sorption, ion exchange, and plant uptake are all taken into account in these processes. This thesis aimed to use the reactive transport model MIN3P-THM to better understand the complicated natural attenuation process in the subsurface.

We applied both municipal (stormwater runoff) and industrial wastewater (oil and gas produced wastewater) to test the effect of soil on natural attenuation. For stormwater runoff, bioretention system is treated as the most low-impact practice in stormwater BMPs. The system can mitigate peak flow and retain water for a long time. The soil would also attenuate heavy metals, nitrogen compound, and organic carbon though sorption, cation exchange, respiration, fermentation, nitrification, denitrification and root nutrient uptake.

For oil and gas wastewater, land application is used as a cost effective and more environmentally friendly to treat OGEP wastewater. High salinity wastewater was treated naturally through active solute uptake, hydrocarbon reduction, cation exchange, and sorption process.

These two treatments were used to test the performance of the MIN3P-THM model. The reactive transport model MIN3P-THM helped a lot to understand the fate and transport of stormwater and OGEP wastewater in the soil. The model simulated the complicated hydrological and biogeochemical processes in subsurface soils. Surface complexation, sorption, dissolution-precipitation, equilibrium oxidation-reduction, and intra-aqueous kinetic reactions are all taken into account in the model.

Firstly, I worked on studying the performance of bioretention systems in a pilot scale. In bioretention systems, the model can catch the trend of outflow rate and pollutant concentrations in both vegetated and non-vegetated systems. The model also tested a range of possible design configurations to determine the optimal saturated zone thickness and outlet location for nitrate removal. The results indicated that the bioretention systems were able to remove most of heavy metals, nitrate, and organic carbon through natural attenuation in the soil.

Vegetation had a significant role in mitigating both water and pollutants in the bioretention cells. Due to macropores and fast flow paths created by roots in vegetated cells, the water can carry ions flowing out of the system very quickly leading to a higher outflow rate and less removal efficiency than non-vegetated cells. In addition, plant can selectively uptake essential nutrient for their growth while exclude Cl^-, CO_3^{2-}, and other ions, leading to increase in rejected ions in the pore water.

A saturated zone is demonstrated as an important part in nitrate removal. A bioretention cell with a saturated zone can largely remove nitrate. The saturated zone

73

provides an anoxic condition to promote denitrification and inhibit nitrification thus convert nitrate into nitrogen gas.

In addition, different rainfall levels did influence the natural attenuation performance of bioretention cells under long time application. Due to less water and chemical input, drier conditions may have a better performance in heavy metal removal than wetter conditions; all the ions had higher removal efficiencies.

Then, I provided an example of land application of Oil and Gas Exploration and Production wastewater. Land application is treated as a popular alternative to address OGEP wastewater. Biogeochemical reactions within the subsurface serve to naturally attenuate hydrocarbons, nutrients, and solids present in the wastewater. Under land application systems, the model can simulate the hydrogeology of a well-documented field site, and replicate biogeochemical response under applications of high salinity wastewater for a long simulation period. We studied the impact of hydrocarbon and salts on the plant and groundwater quality.

This case study was conducted at both the field site and laboratory scales. In field site, a ten years simulation was done to study the effect of salinity, hydrocarbon on the root zone, and the underlying groundwater. Long time application of high salinity wastewater did accumulate salts in the root zone and affect groundwater quality. We need to pay more attention on long-term land application of high salinity wastewater; the application process may pollute groundwater and nearby rivers and cause human health hazard. Plants would reduce evapotranspiration to survive themselves when water and solute stress occurred under high salinity conditions. In addition, organic carbon has a

negative effect on salinity. Due to microbial activities, high organic carbon levels caused an initial increase in salinity to the water table, and produced carbon dioxide and carbonate species. Once these initial nutrients were exhausted, salinity would drop to control level and organic carbon accumulated in the root zone and reached to the water table.

Due to many factors, land application in lab scale does not give a very good result. The model cannot catch the trend of soil moisture very accurately, especially those in the shallow zone where large amount of root existed (the roots can create macropores and lead to preferential flow). In addition, an entirely plant growth pattern is needed to represent the actual ecohydrology process in the soil.

Overall, this study highlights the importance of reactive transport model in depicting biogeochemical processes in the soil system. Natural attenuation in soil is an effective approach to treat municipal and industrial wastewater. In addition, the model could be very useful in helping us understand biogeochemical processes in both engineered and natural systems in future.

This research work suggests several specific problems which can be considered for future studies:

- How the reactive transport model can be more representative of the real world to address much more environment problems?
- Can we have a better way to address preferential flow problem?
- Can we add a new plant growth pattern in the model?
- Can we consider microbial growth and decay in the model?

- How to deal with negative removal of metals in bioretention systems?

- Can we control soil concentration and influent concentration to positively remove metals? (The difference between the initial soil chemical concentrations and the influent concentration would affect the direction of sorption and cation exchange process).

- How to establish a better land application system in the pilot scale?

- How can we have a better understanding of the entirely plant growth process?

- Do we need other equipments, and more perspectives to consider the container?

- Would a longer experimental period have a better performance in obtaining credible data?

Answering these problems will require the understanding of complicated, integrated natural attenuation subsurface systems which is fundamental to biogeochemistry.

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APPENDIX A

Figure 1. Precipitation and evapotranspiration data (field site study)
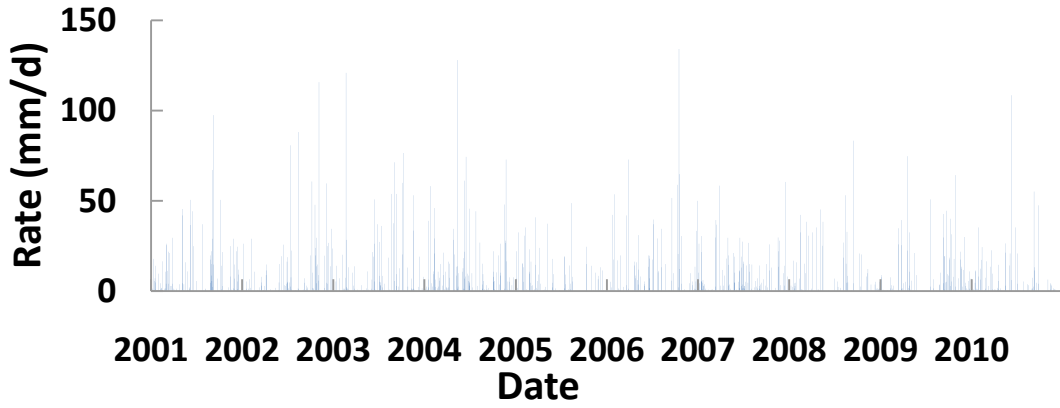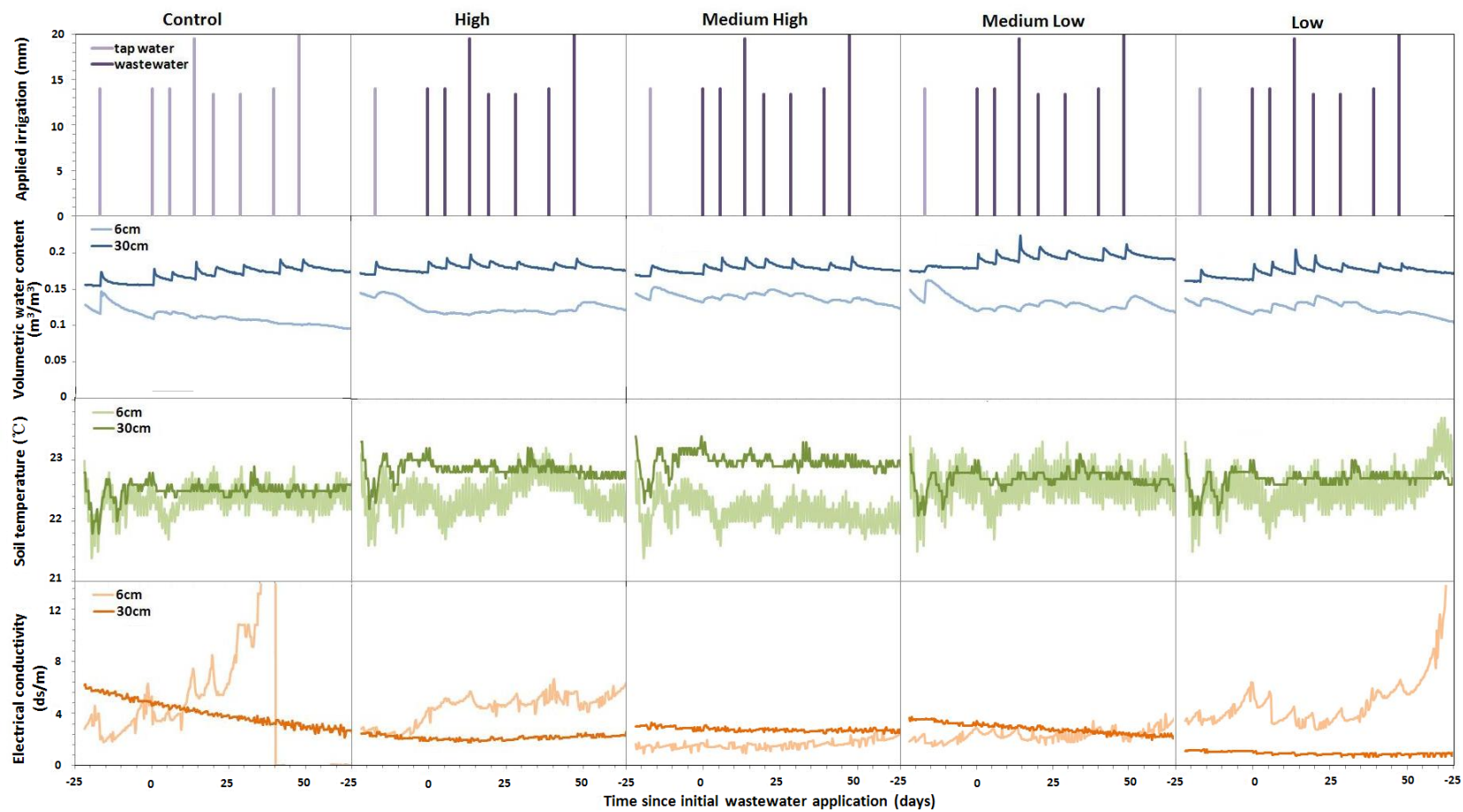

a.   Precipitation (NOAA, 2013)
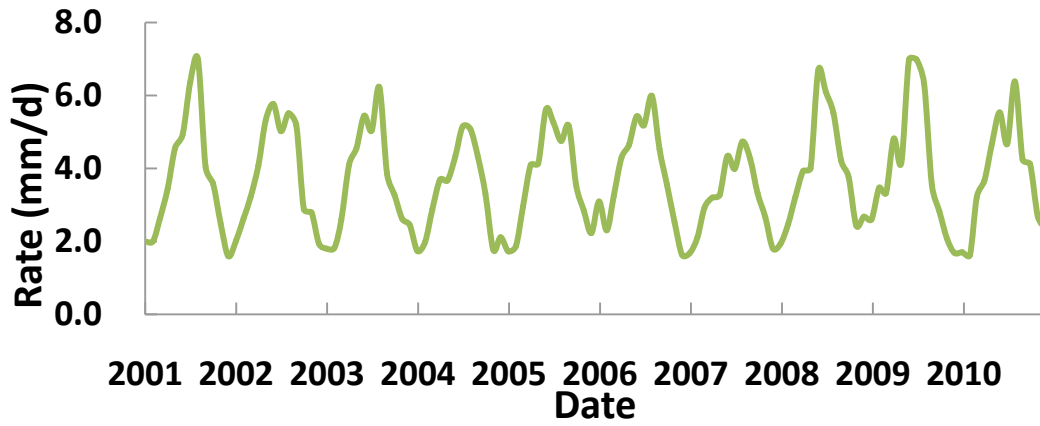
b.   Evapotranspiration (TWDB, 2012)

Figure 2. Values measured during container studies, with FDS ranging from 5374 mg/L (High) to 413 mg/L (Control).

Table 1. The half-saturation and inhibition constants values of those aerobic and anoxic reactions

Unit: mol/L

Reactions		Half-saturation constants		Inhibition constants	
		K_{CH2O}	K	$K_{inhibit,o2}$	$K_{inhibit,no3}$
Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	na	$K_{O2}=1.7\times10^{-5}$	na	na
			$K_{NH4}=1.9\times10^{-4}$		
Respiration	$CH_2O + O_2 \rightarrow CO_3^{2-} + 2H^+$	1.9×10^{-4}	$K_{O2}=4.7\times10^{-6}$	na	na
Methane oxidation	$CH_4 + 2O_2 \rightarrow CO_3^{2-} + 2H^+ + H_2O$	na	$K_{CH4}=1.0\times10^{-5}$	na	na
			$K_{O2}=1\times10^{-6}$		
Denitrification	$CH_2O + 4/5NO_3^- \rightarrow 2/5N_2 + CO_3^{2-} + 6/5H^+ + 2/5H_2O$	1.6×10^{-4}	$K_{NO3}=3\times10^{-5}$	6.3×10^{-6}	
Fermentation	$CH_2O + 1/2H_2O \rightarrow 1/2CO_3^{2-} + 1/2CH_4 + H^+$	1.0×10^{-3}	na	1×10^{-5}	1.6×10^{-5}
Sulfate reduction	$CH_2O + 1/2SO_4^{2-} \rightarrow CO_3^{2-} + 1/2HS^- + 3/2H^+$	1.1×10^{-4}	$K_{SO4}=1.6\times10^{-3}$	1×10^{-5}	1.6×10^{-5}

Sources of the reactions constants values: original MIN3P database; MINTEQ/WATEQ databases; Mayer et al. (2001); Macquarrie et al. (2001); Miller et al., (2008).

Table 2. Selection of potential evapotranspiration data for laboratory scale study

Date Time	time	Ta	RH	e_a^* (hPa)	e_a (hPa)	Δ (hPaK^{-1})	u(m/s)	Q_{ne} (W/ m^2)	pET (mm/day)
2013-6-5 11:30	11:30	23.3	0.6377	28.8497	18.397	1.7384	0	271.15	6.9
2013-6-5 11:35	11:35	23.31	0.6368	28.8663	18.382	1.7393	0	271.15	6.9
2013-6-5 11:40	11:40	23.21	0.6371	28.7003	18.285	1.7305	0	271.15	6.89
2013-6-5 11:45	11:45	23.22	0.6367	28.7169	18.284	1.7314	0	271.15	6.89
2013-6-5 11:50	11:50	23.22	0.6369	28.7169	18.29	1.7314	0	271.15	6.89
2013-6-5 11:55	11:55	23.24	0.6366	28.7501	18.302	1.7331	0	271.15	6.89
2013-6-5 12:00	12:00	23.24	0.6368	28.7501	18.308	1.7331	0	271.15	6.89
2013-6-5 12:05	12:05	216	0.6372	28.6173	18.235	1.7261	0	271.15	6.89
2013-6-5 12:10	12:10	21	0.6385	28.5178	18.209	1.7208	0	271.15	6.88
2013-6-5 12:15	12:15	23.08	0.6388	28.4846	18.196	1.719	0	271.15	6.88
2013-6-5 12:20	12:20	23.09	0.6392	28.5012	18.218	1.7199	0	271.15	6.88
2013-6-5 12:25	12:25	23.04	0.6391	28.4182	18.162	1.7155	0	271.15	6.87
2013-6-5 12:30	12:30	21	0.6392	28.5178	18.229	1.7208	0	271.15	6.88
2013-6-5 12:35	12:35	23.23	0.637	28.7335	18.303	1.7322	0	271.15	6.89
2013-6-5 12:40	12:40	23.31	0.637	28.8663	18.388	1.7393	0	271.15	6.9
2013-6-5 12:45	12:45	23.28	0.637	28.8165	18.356	1.7366	0	271.15	6.9
2013-6-5 12:50	12:50	23.32	0.6366	28.8829	18.387	1.7402	0	271.15	6.9
2013-6-5 12:55	12:55	23.39	0.6369	28.999	18.47	1.7463	0	271.15	6.91
2013-6-5 13:00	13:00	23.3	0.6374	28.8497	18.389	1.7384	0	271.15	6.9
2013-6-5 13:05	13:05	23.22	0.6382	28.7169	18.327	1.7314	0	271.15	6.89
2013-6-5 13:10	13:10	23.22	0.6385	28.7169	18.336	1.7314	0	271.15	6.89
2013-6-5 13:15	13:15	23.21	0.638	28.7003	18.311	1.7305	0	271.15	6.89

Table 2. Continued.

Date Time	time	Ta	RH	e_a^* (hPa)	e_a (hPa)	Δ (hPaK^{-1})	u(m/s)	Q_{ne} (W/ m^2)	pET (mm/day)
2013-6-5 13:20	13:20	218	0.6385	28.6505	18.293	1.7278	0	271.15	6.89
2013-6-5 13:25	13:25	23.24	0.6381	28.7501	18.345	1.7331	0	271.15	6.89
2013-6-5 13:30	13:30	23.27	0.6377	28.7999	18.366	1.7358	0	271.15	6.9
2013-6-5 13:35	13:35	23.32	0.6372	28.8829	18.404	1.7402	0	271.15	6.9
2013-6-5 13:40	13:40	23.42	0.6371	29.0488	18.507	1.749	0	271.15	6.91
2013-6-5 13:45	13:45	23.47	0.6368	29.1318	18.551	1.7534	0	271.15	6.92

91

Table 3. Modeled chemical concentrations for precipitation, irrigation water (A - Control), and applied wastewater scenarios

(B-E)

Unit: (mg/L)

Component	Precipitation	Control[b]	High-FDS[c]	High-Chloride	Medium-Chloride	High-TOC
FDS	11.76[a]	694[e]	3622	3622	872	694
nutrients						
Calcium	0.18	147	841	147	147	147
Magnesium	0.04	41	235	41	41	41
Potassium	0.47	3.5	20	3.5	3.5	3.5
Nitrate	99	40	14	40	40	40
Ammonium	1.82	0.3	1.72	0.3	0.3	0.3
Phosphorous	0	0.02	0.11	0.02	0.02	0.02
Zinc	0	0.023	0.13	0.023	0.023	0.023
Heavy metals						
Copper	0	0.004	0.023	0.004	0.004	0.004
Lead	0	0.005	20[f]	0.005	0.005	0.005
Iron	0	0.63	3.62	0.63	0.63	0.63
Manganese	0	0.37	12	0.37	0.37	0.37
Others						
Sodium	0.13	66	378	66	66	66
Aluminum	0	0.074	0.42	0.074	0.074	0.074
Carbonate	5.48	300	1716	300	300	300

Table 3. Continued.

Component	Precipitation	Control[b]	High-FDS[c]	High-Chloride	Medium-Chloride	High-TOC
Sulfate	0.13	61	349	61	61	61
Chloride	0.52	42	42	3000[d]	250[e]	42
TOC	0.57	26	250[c]	250[c]	250[c]	3000[c]
Barium	0	0.12	56[f]	56[f]	56[f]	56[f]

a. TWDB (2005)

b. Munster et al. (1996)

c. Assumed.

d. USEPA (2002), the secondary maximum contaminant limit

e. RRC (2010)

f. Coker and Olumagin (1995)