QUANTIFYING NUTRIENT REMOVAL FROM GROUNDWATER SEEPAGE OUT OF A CONSTRUCTED WETLANDS RECEIVING WASTEWATER EFFLUENT

Jessica R Ackerman

75 Pages August 2011

Nutrient removal from wastewater effluent by groundwater processes is an unaccounted for sink. This study used ion analysis and numerical modeling to quantify nutrient removal from BNWRD constructed wetland seepage.

APPROVED:

Date	Eric W. Peterson, Chair
Date	Stephen J. Van der Hoven
Date	William L. Perry

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This study focused on the seepage coming from a constructed wetland receiving municipal wastewater effluent, and the groundwater processes that occurred to reduce the nutrients in the water. Concentrations of nitrate, ammonium, phosphate and chloride were used to determine the quantity of nutrients being removed/added from the seepage compared to the total amount removed/added by surface water processes. NO_3^--N concentrations in the surface water ranged 10.0-26.8 mg/L and ND-1.5 mg/L in groundwater. NH_4^+-N concentrations in the surface water ranged 0.05-2.3 mg/L and 0.004-4.5 mg/L in groundwater. Phosphate concentrations in the surface water ranged 0.1-3.2 mg/L and ND-0.4 mg/L in groundwater. Effluent-groundwater mixing calculations showed that a majority of the water sampled from the wells is effluent rich (50-100%), although 3 wells on the berm closest to the wetland are showing low effluent concentrations (<1-40%). Groundwater samples were analyzed and found to be either in iron or manganese reducing conditions. Preliminary data collected showed that there is a groundwater velocity of 3.6 m/day between the effluent and groundwater wells located between the wetland and stream. Using cross-sections constructed using boring logs, seismic data, a pumping test and geochemical data; a numerical model was constructed using MODFLOW and MODPATH to quantify the amount of water flowing through the wetland, the quantity of water seeping into the groundwater and the amount of nutrients being removed from the groundwater. MODFLOW simulations found that the seepage flux through the wetland was 3.0-10.6% of the surface water flux through the wetland. Nitrate and phosphate removal was determined to be significant in the groundwater – 1,940 g/day and 175 g/day respectively, but ammonium concentrations increased in the groundwater by 52.2 g/day. Dependent on surface water retention times in the wetland, nitrate removal ranged 4,750-16,800 g/day, ammonium removal ranged 10.5-37.1 g/day and phosphate removal ranged 500-1,800 g/day.

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JESSICA R ACKERMAN

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Fulfillment of the Requirements
for the Degree of

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I would first and foremost like to thank my committee chair, Dr. Stephan Van der Hoven, for his input and lab and field help. When I look back at what I knew when I first started this program and what I know now, I am so grateful for all the knowledge that you've imparted on me. Thank you so much for your help even after moving a couple thousand miles away! I would also like to thank my other committee members: Dr. Eric Peterson for his time and modeling help, and Dr. William Perry for his input and perspective. I am also thankful to the Illinois Groundwater Association for awarding me a student research grant which funded well and sampling supplies. Many graduate and undergraduate students were also helpful with field and lab help – I would especially like to thank Jonathan Love, Jarek Trela, David Hahn, Randi Liescheidt and Brianne Jacoby.

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J.R.A.

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CHAPTER I

INTRODUCTION

In recent years, wetlands have been recognized as natures' own filtration system for many different water quality issues. Wetlands provide water storage during wet periods and flood protection, water reserve during dry periods, retention of sediments and associated pollutants (deposition), retention of nutrients (adsorption, uptake, denitrification) and pollutants on the way to the river network, provision of habitat for fisheries, conservation of biological diversity, and provision of recreational areas (Hattermann et al., 2009).

Wastewater is nutrient rich when it is released back into lakes or streams, which can cause eutrophication and/or hypoxia – the most common impairment of surface waters in the United States (Ng et al. 2008 and Carpenter et al., 1998). Both point and non-point sources of nutrient-rich water are a problem for surface water systems. Wetland habitats can help in decreasing the nutrient richness of the wastewater through vegetation and algal uptake, adsorption, sedimentation, and denitrification. Plants require nutrients, like nitrate and phosphate, so they will readily take up the nutrients in the wetland if they require it. Phosphate from the wastewater will bind to soils through adsorption, although the process is not a permanent way of removing the nutrient (Fisher et al., 2001). Nitrate will go through denitrification where it is chemically changed to N_2 gas, which is essentially inert in the system. Denitrification will only happen in the system if it is in reducing conditions, where the oxygen has been consumed and nitrate is the next readily available electron acceptor.

The vast majority of research to date about constructed wetlands receiving wastewater effluent investigates nutrient cycling only in surface waters, and groundwater seepage into/out of the constructed wetlands has received far less attention. There are studies concerned with groundwater seepage, but not chemically – the studies are usually concerning water-table fluctuations or water mass balance equations (Rosenberry et al., 1997 and Hayashi et al., 1998). There is one study concerned with the chemical characteristics of groundwater seepage, but it is purely focused on the chloride cycle and not other processes that are of a concern for this study (Hayashi et al., 1998).

This investigation seeks to quantify the removal of nutrients from effluent that seeps out of the wetlands and flows along groundwater pathways towards Little Kickapoo Creek. The groundwater conditions are conducive for the adsorption of phosphorus and denitrification, and so this may be an unaccounted for sink of nutrients for constructed wetlands.

Nutrient Cycling

Phosphorus Cycling

The major processes in the phosphorous (P) cycle involve uptake of P in soil by plants, the recycling of P in the form of plant and animal residues, the biological turnover through mineralization-immobilization, adsorption to soil particles, fixation reactions at clay and oxide surfaces, and the solubilization and formation of mineral phosphates through chemical reactions and activities of microorganisms (Fig. 1) (Stevenson and Cole., 1999).

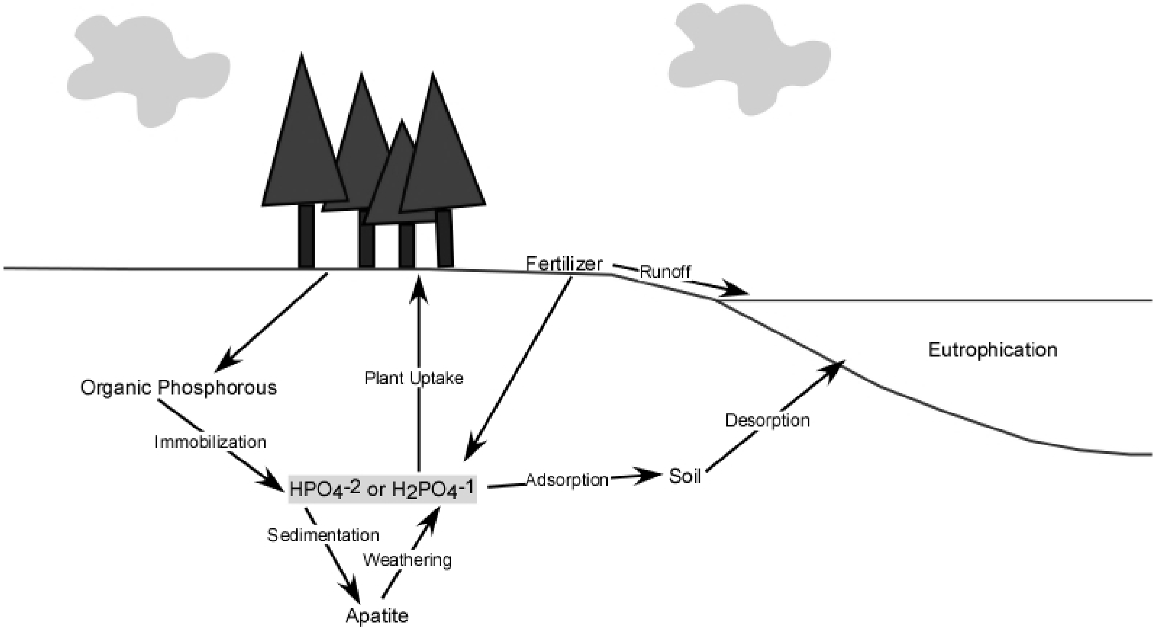

Fig. 1 Phosphorus cycle as it pertains to study site

The main process by which P leaves the unsaturated zone is by plant uptake during photosynthesis (Drever, 1988). Carbon and oxygen are not the only elements involved in photosynthesis. Plants also need nitrogen (N) and P compounds and other trace minerals. The chemical reaction for photosynthesis is (not mass balanced or product element balanced):

$$CO_2 + NO_3^- + HPO_4^{2-} + H_2O + H^+ + (\text{trace elements, energy}) = C_{organic} + O_2 \quad (1)$$

In natural areas, the P used by plants is returned to the soil by plant and animal residues in the form of urine, feces or dead plants and animals – and the amounts are equal (Stevenson et al., 1999). In reality, however, it is an open system due to human impact. Phosphorus can be added to the soil in forms of fertilizer, and if correct calculations are done, the plants should take up all the P. Phosphorus can leave the closed cycle through harvest, erosion and leaching due to field tile. Harvest will take most of the plant out of the soil, taking out approximately <5% of the P with it. Some of the plant is usually left in the soil in current agricultural process, so not all of the P is taken away at harvest (Stevenson et al., 1999). Other important aspects in the P cycle include the formation of P from the weathering of parent material. Some of the P found in soil is from apatite, a group of phosphate minerals consisting of a tricalcium phosphate having the empirical formula:

$$3[Ca_3(PO_4)_2]*CaX_2 \quad (2)$$

where the X can be either Cl^-, F^-, OH^-, or CO_3^{2-} making the chloro-, fluor-, hydroxy-, and carbonate-apatites (Stevenson et al., 1999). Apatite deposits are used today to make phosphate fertilizers. These deposits are formed by dissolved P entering the ocean that is consumed by ocean biota, and then released by the biota's dying bodies and fecal matter, which floats to the bottom compacting on each other until the deposit is formed.

Adsorption is an important aspect in the removal of P from the cycle. Phosphorus ions will adsorb to soil particles in varying quantities dependent on the particle composition. Experiments have shown that soils with high amounts of iron oxides present are successful at adsorbing P (Rhoton and Bigham, 2005). Ferrihydrite is the most common natural mineral found in soils that is accomplished at adsorbing P. However, the Rhoton and Bigham study showed that acidic soils containing ferrihydrtite will have the most success. Batch experiments using non-natural materials as adsorption materials are also being studied. Cucarella and Renman (2009) found that materials with the highest adsorption capacity included blast furnace ash, red mud (likely to be high in iron), fly ash, and crystalline slag.

The final aspect of the P cycle at the wetland is the P in microorganisms. The microorganisms in soil are usually bacteria and fungi and when P is discussed with microorganisms, it's talking about the microbial biomass actually made up of P. These microorganisms will compete with the plants to get the P in the soil. Stevenson et al. (1999) estimate that in soils with bacteria, about 1.5 to 2.5% of soil P is found in microbial biomass and in soils with fungi can reach up to 4.8% of soil P in the biomass. The P in the biomass is also available for plant uptake, once the bacteria or fungi dies and decays, releasing P back into the cycle.

In freshwater areas, on a global scale, there is about 90×10^9 kg of P (Stevenson et al., 1999). Most of this P is coming from soil, but P can also enter surface water due to human activity (wastewater would be an example). Phosphorus content in surface water is usually studied as either total P (TP) content or as a concentration of PO_4^{3-} - P (Terrio, 2006). The P cycle in surface water consists of the uptake of P by aquatic biological organisms, sediment deposition, sorption or desorption, and then either the remaining P would either flow out to the ocean or migrate into the groundwater (Blevins, 2004).

Phosphorus concentrations in surface water can vary depending on the amount of plants or microorganisms, the type of subsurface material, seasonal changes and the characteristics of the surrounding area. Generally, P concentrations should be low in areas with abundant plants and microorganisms. In the Illinois River Basin, this was found to be true. Studies found that at agricultural sites – the concentrations were the lowest (min 0.01 mg/L), and at urban sites – the concentrations were the highest (max 3.74 mg/L) (Terrio, 2006). Terrio also mentions that the type of materials the water is sitting on is important to how fast the P can leave through migration to the subsurface. Soils with high hydraulic conductivity, such as sandy soils, will readily transmit P to the subsurface, whereas soils with low hydraulic conductivity, such as clay-rich soils, will not. Seasonal changes also show varying P concentrations. During a study at Little Bean Marsh in Missouri, P concentrations seemed to increase during the spring and fall near the inlets of the marsh possibly correlating with major rain patterns (Blevins, 2004). One of the major influences on surface water P concentrations is the surrounding characteristic of the study areas. Agricultural areas dominate the Illinois River Basin, but also include urban and mixed land use areas. Other characteristics to consider in this area are livestock farms, because more P from animal waste will enter the watershed. Much attention should be given to the surrounding areas' characteristics, as P concentrations can vary accordingly.

Phosphorus in groundwater is usually a concern when drinking water wells are in the vicinity of a P plume. Phosphorus can leach into groundwater for a couple of reasons: over application of fertilizer could eventually migrate into the saturated zone, or septic system discharge. There is especially a problem with very porous unsaturated zones, like sand, that allow the P to filter down into the groundwater rather quickly (Joye et al., 2006).

The processes in groundwater with P include: sorption/desorption, ion exchange, oxidation/reductions and biologically mediated reactions (Senior and Cinotto, 2007).

Adsorption involves the bonding of P ions to solid surfaces. Oxidation/reduction reactions in groundwater involve a chemical reaction where one or more of the reactants changes valence states, or transfer their electrons from one chemical to another. Phosphorus itself is not the redox agent, NO_3^- is, which causes limitations on the reduction of P. Concentrations of HPO_4^{2-} in groundwater are related to reduction step and oxygen concentrations (Joye et al., 2006). Biologically mediated reactions deal with dissolved organic P (DOP) and microorganisms. The microorganisms will readily consume the DOP if the P concentrations are relatively low (related to natural conditions), but they may need to develop the new enzymes needed to digest the DOP during enzyme induction if large quantities of DOP are present (unnatural quantities).

Nitrogen Cycling

Nitrogen, unlike phosphorus, can exist in a variety of oxidized and reduced forms, which allow it to serve as either an electron donor or receiver in oxidation-reduction reactions important to nutrient cycling and biogeochemistry (Kalff, 2002). The processes in nitrogen cycling include nitrification, denitrification, and fixation. Nitrogen cycling is very important to the environment and in nutrient reduction in wetlands (Fig. 2). Denitrification is a process of great importance in wetlands for the removal of nitrate. Beneath the Bloomington Normal Wastewater Reclamation District (BNWRD) wetland it is likely that denitrification is happening because it is an anoxic groundwater environment and NO_3^- is serving as the terminal electron acceptor. The N cycle does not happen in isolation, though, it can also be linked with the sulfur cycle because NO_3^- can be denitrified when sulfur is oxidized. Also the N cycle and P cycle are linked because as

NO_3^- serves as an electron acceptor it can prevent the reduction and solubilization of iron phosphate complexes.

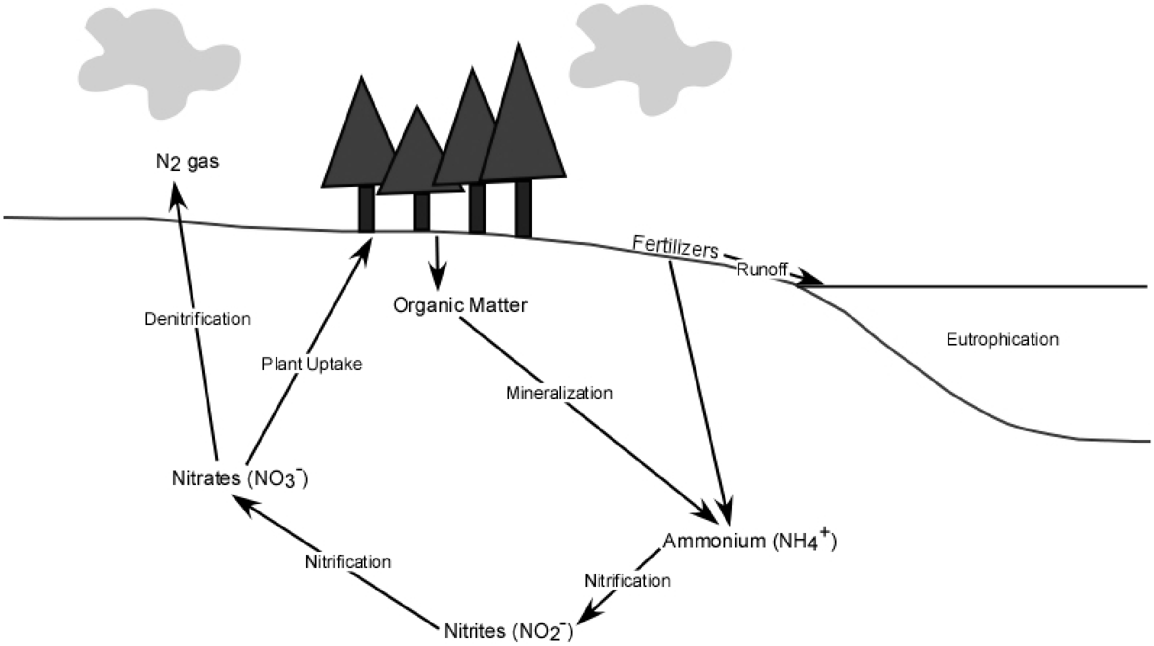

Fig. 2 Nitrogen cycle as it pertains to study site

Nitrification is the process of transforming NH_4^+ to NO_3^- through oxidation. The process is mediated biologically. Nitrification can be the pre-curser to denitrification because it creates the NO_3^- needed for the reaction. The nitrification equation looks as follows:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (3)$$

The main site for nitrification is at the interface of oxic or anoxic waters or sediments. Nitrification is an important process, but doesn't necessarily happen in wetlands receiving wastewater effluent as they are usually in anoxic conditions and the process requires oxygen to work. However, in the case of the BNWRD wetlands it is possible because the wetlands are shallow and have interaction with the atmosphere.

Denitrification is the process that takes the NO_3^- (or NO_2^- as an intermediate metabolite) from the nitrification process and first reduces it to nitrous oxides (NO or N_2O) and then to dinitrogen gas (N_2). This is a bacterially meditated process carried out by heterotrophic anaerobic bacteria and fungi at the oxic-anoxic interface. The bacteria use the N oxides as a terminal electron acceptor in the oxidation of organic matter. The general conditions required for denitrification to occur are:

1. Presence of bacteria possessing the metabolic capacity
2. Availability of suitable reductants such as organic C
3. Restriction of O_2 availability
4. Availability of N oxides (Follett, 2002)

Wastewater treatment plant managers know the close relationship between nitrification and denitrification and use that knowledge to remove N from the wastewater – like constructing wetlands as a final treatment to treated wastewater. There are two ways to determine the denitrification rate: a mass-balance approach or a steady-state mass-balance model – the former being labor-intensive but more process informational. Denitrification rates will increase as the water's residence time increases and water depth decreases. And most importantly, N_2 lost to the atmosphere is no longer available to plant and animal life, making wetlands a perfect place for wastewater treatment for nutrients.

Another process of the N cycle is fixation where atmospheric nitrogen (N_2) is reduced to NH_3, carried out by prokaryotic organisms like blue-green algae and heterocysts. Nitrogen fixation rate increases as the N:P ratio decreases, which is the case at the BNWRD wetland due to its eutrophic state. Fixation is happening at a slower rate at the BNWRD wetland compared to the high rates of denitrification. The organisms that complete N fixation are photosynthetic and need sunlight to reduce the N_2, which limits the activity to daytime hours and declines with depth. As with nitrification, fixation is not the main process happening at the BNWRD wetland due to large concentrations of NH_4^+ and NO_3^-, which the organisms prefer to N_2.

Nitrate is the primary form of N that seeps into the subsurface (Follett, 2001). It readily seeps into groundwater and is soluble at concentrations found in soil. The movement of NO_3^- through soil is done by convection, or mass-flow, along with the soil water. Seepage of NH_4^+ can also happen, but it usually readily adsorbed to soil.

Another process that is happening in the wetland (surface water) is the plant uptake of N in the form of NO_3^- or NH_4^-. Uptake is done through photosynthesis. Although plants will uptake NO_3^- they will more readily take up NH_4^+ because it is already in its reduced form. Plant uptake is really only a temporary fix of N, because as plants die and decompose they release the nutrients they used to photosynthesize and accumulate biomass back into the ecosystem.

Chloride as a Tracer

Chloride is a very important component to calculating residence times of water and the make-up of water resulting from the mixing of groundwater and surface water at the BNWRD constructed wetlands. Chloride is a good tracer to use because it is conservative, meaning that it is not readily used or gained in the environment by natural processes. Also, the mass balance equation for chloride is a good method to estimate groundwater recharge rate to aquifers (Hayashi et al., 1998). The main input of chloride into the BNWRD wetland system is the effluent, since it is used as a primary wastewater treatment. The effluent enters the wetland, some of it seeps into the subsurface and some exits the wetland through the outlet into Little Kickapoo Creek (LKC). The water that does seep into the subsurface can be collected through monitoring wells, and the knowledge of the groundwater chloride concentration up-gradient of the wetland can be used to calculate the amount of effluent water and groundwater that exists in the groundwater down-gradient from the wetland.

Study Area

The BNWRD facility is located in Randolph, IL south of Bloomington. The wetland is situated east of the facility and receives a fraction of the wastewater effluent, while a majority of the wastewater flows in a channel discharging directly into LKC (Fig. 3). The wetland sits above the water table on alluvium deposits, below which is glacial outwash deposited during the Wisconsinan Episode (Van der Hoven et al., 2008). The wetland was constructed by excavating the upper part of the alluvium, grading the area, and then using the alluvium to form the berm around the wetland. The geologic units underlying the site are the Cahokia Alluvium, the Henry Formation and the Wedron Formation. The Cahokia Alluvium was deposited on top of the outwash during the Holocene and is an unconfined aquifer with an approximate horizontal hydraulic conductivity (K) value of 1.0 x 10^{-3} cm/s and a vertical K value of 3.5 x 10^{-4} cm/s (Smith et al., 1997). The Henry Formation of outwash is also considered unconfined due to its interconnectedness with the surface because of macropores in the alluvium. The outwash has an approximate horizontal K value of 1.0 x 10^{-2} cm/s and a vertical K value of 1.0 x 10^{-4} cm/s. The Wedron Formation of till is considered unconfined and has an approximate horizontal K value of 1.0 X 10^{-6} cm/s and a vertical K value of 1.0 x 10^{-10} cm/s. The alluvium and outwash K values were measured in the field using an aquifer test and a double-ring infiltrometer, and the till K value is an approximation.

The BNWRD facility has constructed two wetlands to help reduce nutrients in the wastewater and provide wetland habitat (Fig. 3). Both wetlands sit upland from the creek. Some of the effluent seeps into the subsurface and will eventually end up in the creek along with regular groundwater flow (Labaugh et al., 1987). Geochemical conditions along the flow path can potentially remove nitrate and phosphate from the water. Surface water processes can also potentially remove nitrate and phosphate from the water – this is not the focus of this study, but is discussed in comparison to the amount of nutrients removed by seepage. Overall an understanding of the geochemical signature of the groundwater seepage from the wetland was obtained.

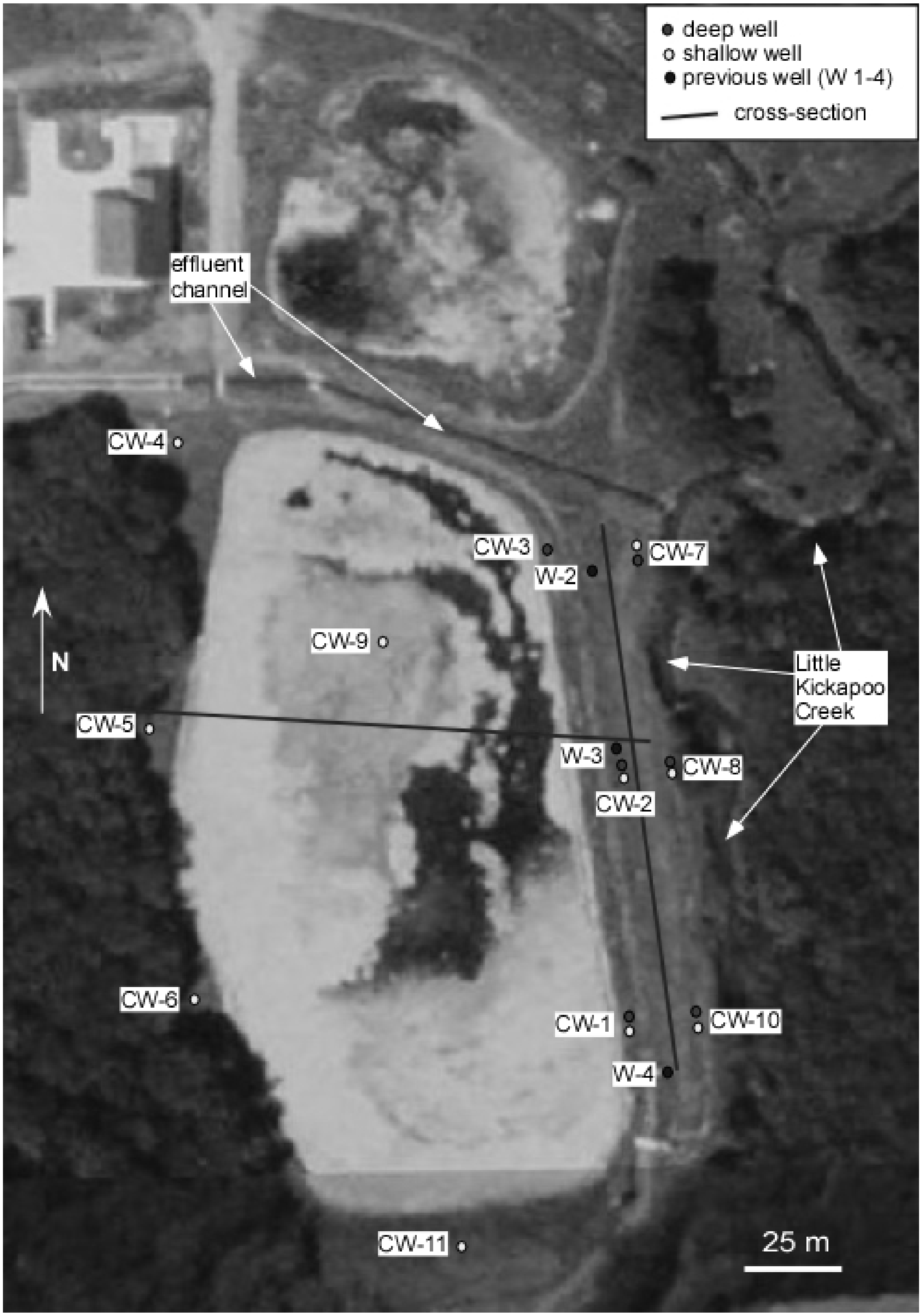

Fig. 3 BNWRD constructed wetlands with well locations

Sixteen wells were installed around the wetland to monitor groundwater chemistry, hydraulic heads and the movement of effluent through the subsurface (Table 1). Three of the wells are located upgradient of the wetland on the west side, one through an island in the wetland and the other 12 are located on the east and south side of the wetland – five on the bank adjacent to the wetland, six between those wells and the creek, and one on the south bank of the wetland. CW-1, 2, 7, 8, and 10 are nested with one deep well and one shallow well. CW-3, 4, 5, 6, 9 and 11 are all shallow wells (4 – 6 are the upland wells). Fig. 4 shows north-south and east-west geological cross-sections of the area.

Table 1 Summary of wells in study including top of casing elevation, surface elevation, approximate screened interval and location in study area

Well ID	TOC Elev. (m)	Surface Elev. (m)	Approx. Screened Interval (m bgs)	Location in Study Area
CW-1s	220.41	219.88	2.6-3.2	SE edge of wetland on berm
CW-1d	220.8	219.75	4.1-4.8	Nested with CW-1s
CW-2s	220.45	219.84	3.1-4.0	E of wetland on berm
CW-2d	221	219.76	7.9-9.4	Nested with CW-2s
CW-3	220.93	219.88	4.1-4.8	NE edge of wetland on berm
CW-4	221.69	220.95	0.9-2.4	NW edge of wetland, upgradient
CW-5	221.1	220.38	0.5-2.0	W of wetland, upgradient
CW-6	220.61	220.51	1.5-1.8	W of wetland, upgradient
CW-7s	219.91	219.04	2.8-3.7	E of wetland, near effluent
CW-7d	219.91	218.98	10.7-12.2	Nested with CW-7s
CW-8s	220.04	219.47	3.1-4.0	E of wetland, near creek
CW-8d	220.3	219.37	6.1-7.6	Nested with CW-8s
CW-9	220.68	219.84	2.3-2.9	On wetland island
CW-10s	n/a	n/a	2.7-3.6	E of wetland, near creek
CW-10d	n/a	n/a	5.5-6.4	Nested with CW-10s
CW-11	n/a	n/a	3.0-3.9	S of wetland on berm

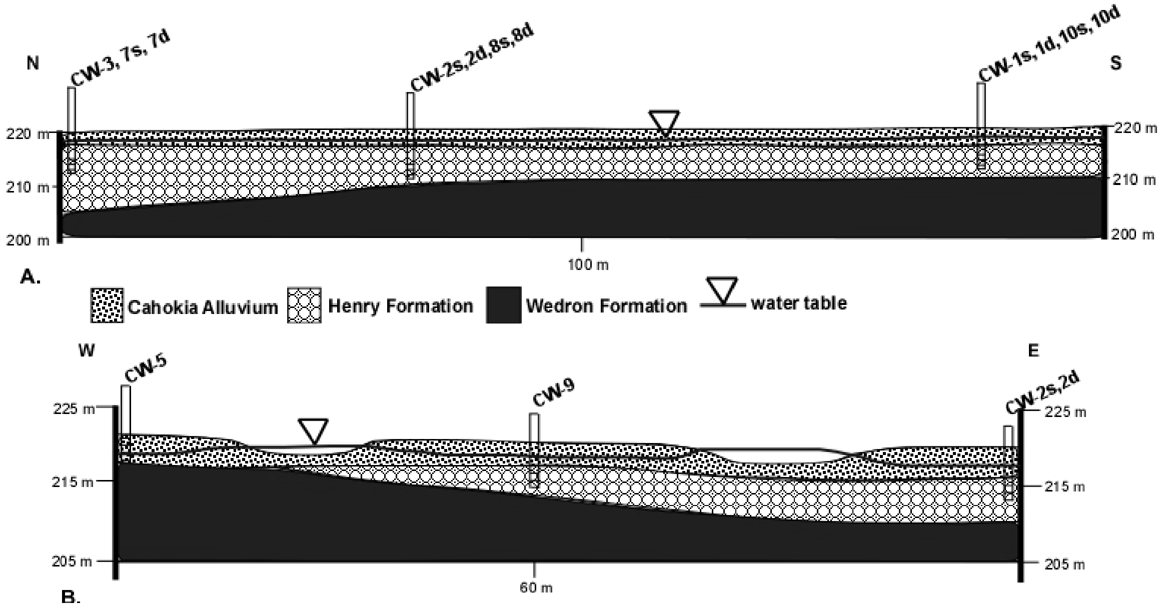

Fig. 4 A a) north-south and b) east-west geological cross-section showing well locations, ground surface elevation, water table elevation, alluvium-outwash boundary and outwash-till boundary

Statement of the Problem

Preliminary evidence from wells at this site show that nutrients in the effluent are seeping out of the wetlands, groundwater flow is rapid and nutrients are being reduced by groundwater processes. Given this, my research question was:

Does the groundwater seepage from a constructed wetland receiving wastewater effluent quantitatively show a significant (i.e. ≥10%) amount of removed nutrients?

With this question in mind and also from evidence seen in preliminary data, the hypothesis that this research tested was:

> *Groundwater seepage from the wetland will show significant (i.e. ≥10%) amounts of removed nitrogen and phosphorus in comparison to the total flux of nitrogen and phosphorus through the wetlands.*

Through denitrification, sorption and uptake processes both NO_3^- and dissolved phosphorus concentrations in the groundwater samples will be quantitatively less than in the wastewater effluent. There is a significant amount of seepage through the wetland due to high hydraulic conductivity seen in the fast movement of nutrient-rich water from the wetland to the first piezometers (monitoring wells) on the east bank. Natural chloride concentration for groundwater at the site is about 15 mg/L, so concentrations that are higher than that show that chloride from the seepage is reaching those wells. The proximity of LKC to the downgradient wells is unlikely to affect the groundwater chloride concentration because the stream is gaining.

Another factor possibly affecting groundwater N and P concentrations is plant and algae uptake. During the growing season (March – September) the area around the wetland gets very lush with grassy plants and the wetland itself holds large amounts of algae on its surface. So, the thought is that some N and P is being sequestered before it is seeps or flows out.

CHAPTER II

QUANTIFYING NUTRIENT REMOVAL FROM GROUNDWATER SEEPAGE OUT OF A CONSTRUCTED WETLANDS RECEIVING WASTEWATER EFFLUENT

Introduction

Wetlands are recognized as natures' own filtration system for many different water quality issues. Constructed wetlands are currently being used to provide water storage during wet periods and flood protection, water reserve during dry periods, retention of sediments and associated pollutants (deposition), retention of nutrients (adsorption, uptake, denitrification) and pollutants on the way to the river network, provision of habitat for fisheries, conservation of biological diversity, and provision of recreational areas (Hattermann et al., 2009). The focus of this study was constructed wetlands for use as final treatment at city wastewater treatment facilities. Wastewater is nutrient rich when it is released back into lakes or streams, which can cause eutrophication and/or hypoxia – the most common impairment of surface waters in the United States (Ng et al., 2008 and Carpenter et al., 1998). Wetland habitats can help in decreasing the nutrient richness of the wastewater through vegetation and algal uptake, adsorption, sedimentation, and denitrification.

Groundwater and surface water interaction is an important component to understanding how constructed wetlands will affect hydrology and solute transport of an area (Hensel et al., 1991). Wetlands can affect water table configurations, causing water table mounds or troughs (Rosenberry et al., 1996). Infiltration of wetland waters is also dependent on what geologic materials are below the water (Hayashi et al., 1998; Rains, 2011) and what sort of inputs or outputs there are to the system (Choi et al., 2000; Min et al., 2010). Most constructed wetlands significantly recharge groundwater compared to groundwater discharge into wetlands plus precipitation (Choi et al., 2000; Min et al., 2010; Rains, 2011).

This investigation seeks to quantify the removal of nutrients from effluent that seeps out of the wetlands and flows along groundwater pathways towards the adjacent creek. The groundwater conditions are conducive for the adsorption of phosphorus and denitrification, and so this may be an unaccounted for sink of nutrients for constructed wetlands. The hypothesis that this research tested was:

> *Groundwater seepage from the wetland will result in significant (i.e. ≥10%) removal of nitrogen and phosphorus in comparison to removal by surface processes in the wetlands.*

Data gathered when the facility first started discharging to the wetlands showed that chloride-rich water is impacting the groundwater (Fig. 10). There is a significant amount of seepage through the wetland due to high hydraulic conductivity seen in the fast movement of nutrient-rich water from the wetland to the first monitoring wells on the east bank. Natural chloride concentrations for groundwater is about 15 mg/L, so higher concentrations showed that chloride from the seepage is reaching those wells (Fig. 10). Through denitrification, sorption and uptake processes both NO_3^- and dissolved phosphorus concentrations in the groundwater samples will be quantitatively less than in the wastewater effluent. Analyzed groundwater samples showed that water is in iron or manganese reducing conditions – an indication that denitrification is occurring.

Study Site

The Bloomington Normal Wastewater Reclamation District (BNWRD) facility is located in Randolph, IL south of Bloomington. The wetland is situated east of the facility and receives a fraction of its wastewater effluent, while a majority of the wastewater flows in a channel discharging directly into Little Kickapoo Creek (LKC) (Fig. 5). The wetland sits on alluvium deposits, below which is glacial outwash deposited during the Wisconsinan Episode (Van der Hoven et al., 2008). The wetland was constructed by excavating the upper part of the alluvium, grading the area, and then using the alluvium to form the berm around the wetland.

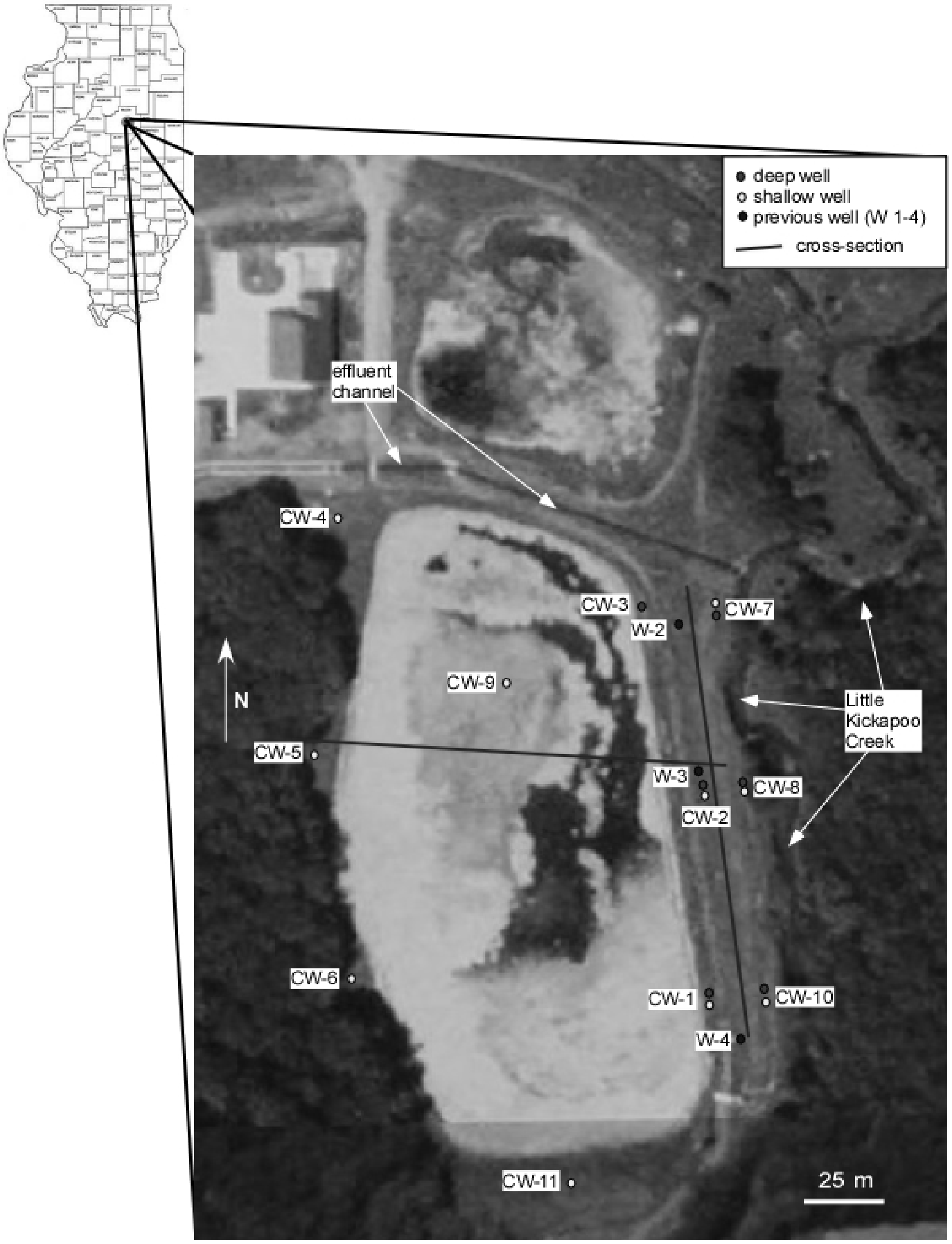

Fig. 5 BNWRD constructed wetlands with well locations and general location in Illinois

The BNWRD facility has constructed two wetlands to help reduce nutrients in the wastewater and provide wetland habitat (Fig. 5). Both wetlands sit upland from the creek.

Some of the effluent seeps into the subsurface and will eventually end up in the creek along with regular groundwater flow (Labaugh et al., 1987). Geochemical conditions along the flow path can potentially remove nitrate and phosphate from the water. Surface water processes can also potentially remove nitrate and phosphate from the water – this is not the focus of this study, but is discussed in comparison to the amount of nutrients removed by seepage.

Geology

LKC flows in an ancient stream valley first created by glacial melt water. Most of the area has a relative low slope due to the glaciers flattening the landscape. East of LKC there is an increase in land surface elevation and also further west of BNWRD there is a slight increase in the land surface elevation, determining the edges of the stream valley.

The geologic units underlying the site are the Cahokia Alluvium, the Henry Formation and the Wedron Formation. Cross-sections were created using soil boring data and a seismic refraction survey (Fig. 6). The soil in the study area is approximately a meter thick and is part of the alluvium unit. Cut banks of LKC show about ¾ of a meter of dark organic soil full of macropores followed by about a foot of a transition between the organic soil and the fine grained clay of the alluvium beneath.

The Cahokia alluvium has an average thickness of 3 m, and consists of fine grained high plasticity clayey silt with organic material with areas of mottling (orange colored and well oxidized) about a meter below ground surface. The unit is dark brown to black in color. Macropores created in alluvium by rotting plant roots, worm holes and animal burrows makes the alluvium more porous. The lateral extent is as wide as the stream valley (seen throughout wetland soil borings). There is a transition area between the alluvium and glacial outwash made up of clayey coarse sand. The unit is thinner towards the west and east edges of the valley.

Below the alluvium, the glacial outwash of the Henry Formation varies in thickness from 4 m to 12 m. Subangular poorly sorted gravel dominates the unit with areas of better sorted subrounded gravel and sand grains. The color varies, but a majority of the gravel is light to dark gray. There are also areas of gravel fining upwards toward the alluvium. Alluvium “lenses” occur in areas approximately 75 m west of LKC, and till lenses are seen within approximately 5 m of LKC. Sand lenses are also visible in soil borings – 5 meters thick in some areas. The transition area between the outwash and till is made up of sorted sand and gravel. The outwash appears to pinch at the edge of the valley but there is a lack of data to show where it actually pinches out.

The glacial till of the Wedron Formation is at least 70 m thick with sand and gravel lenses throughout of approximate thicknesses of 1m. The till is gray colored and is dense high plasticity lean clay and consists of approximately 5% subangular gravel. The Wedron is a regional unit found throughout Central Illinois.

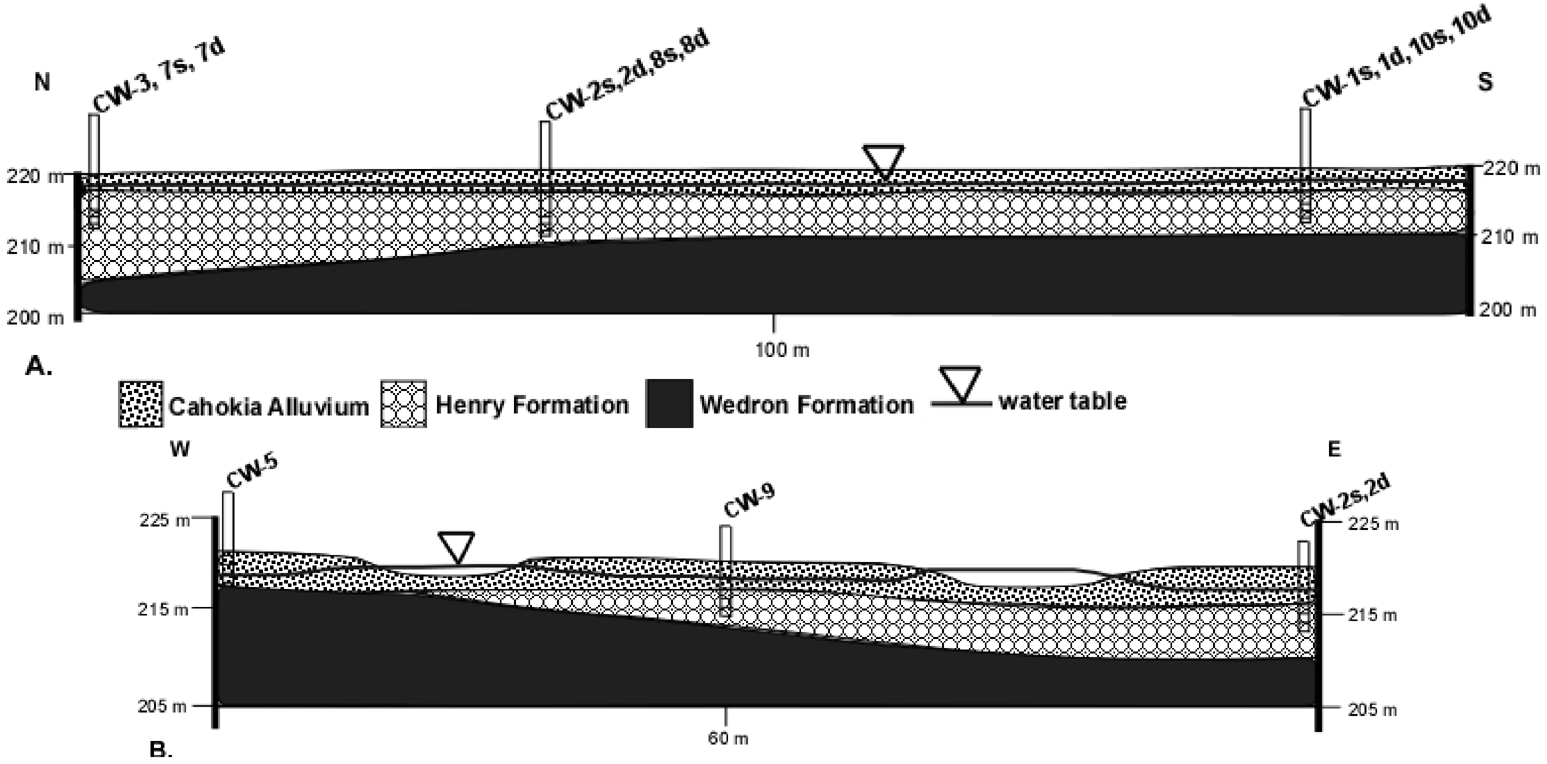

Fig. 6 A a) north-south and b) east-west geological cross-section showing well locations, ground surface elevation, water table elevation, alluvium-outwash boundary and outwash-till boundary

A seismic refraction survey was also completed at BNWRD to better define geologic boundaries and create model layers. Seven transects were completed around three sides of the wetland and two on the island in the wetland (one N-S and one W-E). The sides of the wetland that were surveyed was the north (2 transects), the east (2 transects) and the south (1 transect). The main goal of the refraction survey was to make a till surface for the area. Data points were retrieved from the survey along with boring log data were included in Surfer surfaces that were imported into Groundwater Vista 5 to create the MODFLOW domain.

Hydrogeology

The general groundwater flow in the study area is thought to seep from the wetland, vertically through the alluvium and then horizontally through the outwash (both shallow and deeper flow paths) towards LKC where the stream gains the groundwater – this can be seen in a water table contour map (Fig. 7). There is also a groundwater flow path starting west of the wetland and moving under the wetland towards LKC.

The Cahokia Alluvium was deposited on top of the outwash during the Holocene and is an unconfined aquifer. A double-ring infiltrometer test was conducted at the surface in undisturbed alluvium, and yielded an approximate vertical K value of 3.5×10^{-4} cm/s. A horizontal hydraulic conductivity (K) value of 1.0×10^{-3} cm/s was an estimation. The Henry Formation of outwash is also considered unconfined due to its interconnectedness with the surface because of macropores in the alluvium, and a direct connection through the bed of the stream. An aquifer test conducted in the outwash near the wetland yielded approximate horizontal K value of 1.0×10^{-2} cm/s and a vertical K value of 1.0 x 10^{-4} cm/s. The Wedron Formation is considered confined and has an estimated horizontal K value of 1.0 X 10^{-6} cm/s and a vertical K value of 1.0 x 10^{-10} cm/s.

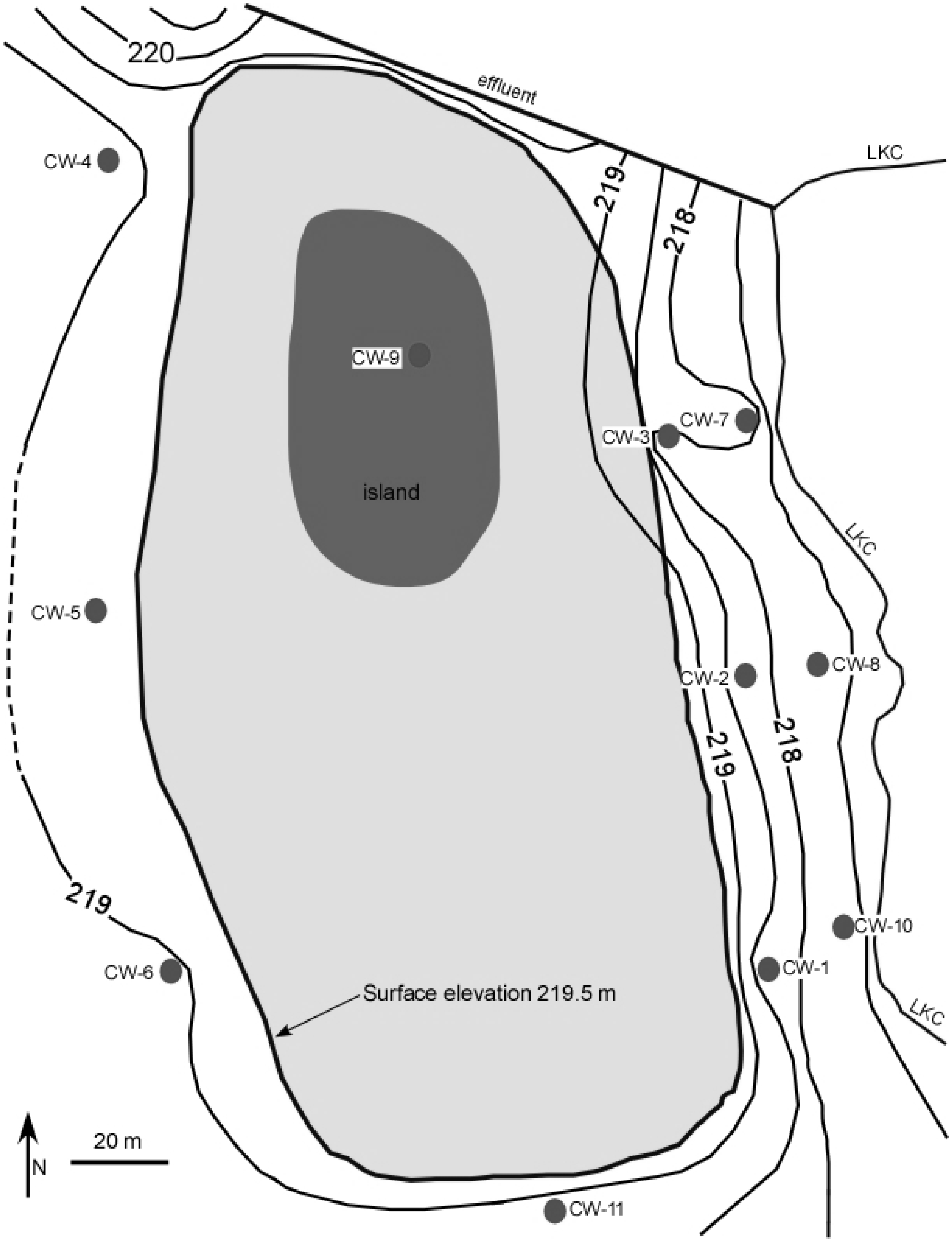

Fig. 7 Water table contour map of BNWRD study site – constructed using hydraulic head measurements from October 2010

Horizontal and vertical gradients at BNWRD were calculated using hydraulic head measurements and well logs. Vertical gradients between nested wells CW-2, 7, 8, and 10 range from 0.0 – 0.02 over the course of a year. All of the vertical gradients are in the upwards direction, except for CW-2 measurements taken in June 2010. It is likely that the vertical gradient is mostly upward due to the nested wells proximity to LKC. Horizontal gradient in the area ranges from 0.02 – 0.04 between wells screened in the outwash on the east side of the wetland. The direction of the horizontal gradient is west to east or from the wetlands towards the creek.

Methods

Well installation at the site was completed using either hand augers or a Geoprobe Direct Push drilling rig. Wells were constructed using metal or plastic casings and screens varied in length from 0.3 to 1.5 m. Well diameters ranged from 2 to 7.6 cm. Wells CW-1s, 4, 5, 6 and 9 were constructed using the hand auger. Wells CW-4, 5, 6 on the west side of the wetland were hand augered about a foot below the water table in the Cahokia alluvium. These wells were used to gain an understanding of what the groundwater chemistry was like before it was impacted by the effluent seepage. Coarse sand was packed around the screen. CW-1s and 9 are drive-point wells and were installed by hand augering to the top of the outwash unit and then driven into the outwash with a slide hammer so that the length of the screen was in the outwash. All other wells were installed using the Geoprobe Direct Push and were installed in the glacial outwash. Coarse sand was packed around the screens of these wells also, and the remainder of the soil boring hole was filled in with bentonite. These wells were also developed using a surge block and peristaltic pump to run water through the well until it looked relatively clear. For contouring and modeling purposes, the wetland perimeter, Little Kickapoo Creek, the effluent channel and the well locations were surveyed using a local coordinate system.

The wells east of the wetland were regularly sampled between September 2009 and September 2010 – every other week for anions, every month for NH_4^+ and DRP (dissolved reactive phosphorus) and every six months for cations, HCO_3^-, temperature, pH and conductivity. Wells were first purged until a stable conductivity was reached. Samples were collected in a sealed plastic container using a peristaltic pump and then immediately preserved in a cooler with an ice pack. Anion samples were kept in the refrigerator; HCO_3^- samples were titrated on the day the samples were collected; cation samples were filtered, acidified with HNO_3^- and stored in the refrigerator; and NH_4^+ and DRP samples were filtered and then frozen. The wells on the west side of the wetland were also sampled, as part of the every six months round of sampling.

Anions, including NO_3^--N, were analyzed on an ion chromatograph. The cations, except K, were analyzed by inductively coupled plasma (ICP) emission spectrometry. Potassium (K) was analyzed on atomic adsorption spectrometry (AA). Ammonium (NH_4^+) and DRP were analyzed with UV spectrometry.

Modeling

After collecting geologic, hydrogeologic and geochemical data, MODFLOW and MODPATH models were constructed using Groundwater Vistas 5. First a conceptual model was developed for the study area (Fig. 8). Conceptually, the wetland water seeps vertically through the alluvium and then horizontally through the glacial outwash towards LKC where the stream gains the groundwater. Both shallow and deeper flow paths through the glacial outwash are seen by elevated chloride concentrations in most wells. The domain of the model included the alluvium and outwash aquifer, the wetland, the effluent channel and LKC. The west boundary was where the outwash unit pinched out, the north boundary was the effluent channel, the east boundary was LKC and the south boundary was an arbitrary distance away from the wetland (50 m). A cell size of 1 m by 1 m by 1 m was used to represent the study area – the entire area was represented as 200 m by 300 m. The model was in 10 layers – 2 for the alluvium and 8 for the outwash – and the wetland itself was seen as a constant recharge or water “mound”. Hydraulic conductivity values mentioned in the Hydrogeology section were used in the model and hydraulic head values measured in the monitoring wells were used as calibration points for the model.

Groundwater Vista 5 was used to construct a simple model of the study area to perform MODFLOW and MODPATH simulations. The MODLFOW simulation was made under the assumption that groundwater flow is in steady state and that the aquifers are homogeneous and isotropic. After importing the geologic surfaces from Surfer 8 into Groundwater Vista 5, the following boundary conditions were put into place:

- The top boundary (ground surface) of the model acts as a Neumann recharge boundary, incorporating a fraction of annual precipitation.
- The bottom boundary is a no-flow boundary due to the change in hydraulic conductivity between the outwash and till.

- The west boundary will act as no-flow boundary where the outwash pinches out at the edge of the stream valley and is replaced with till.
- The east boundary is at LKC and acts as a constant head boundary.
- The north boundary is the effluent channel that runs from the wastewater treatment plant to LKC and acts as a constant head boundary.
- The south boundary is an arbitrary distance south of the wetland (50 m) and acts as a constant head boundary.
- The wetland itself acts as a constant head boundary.

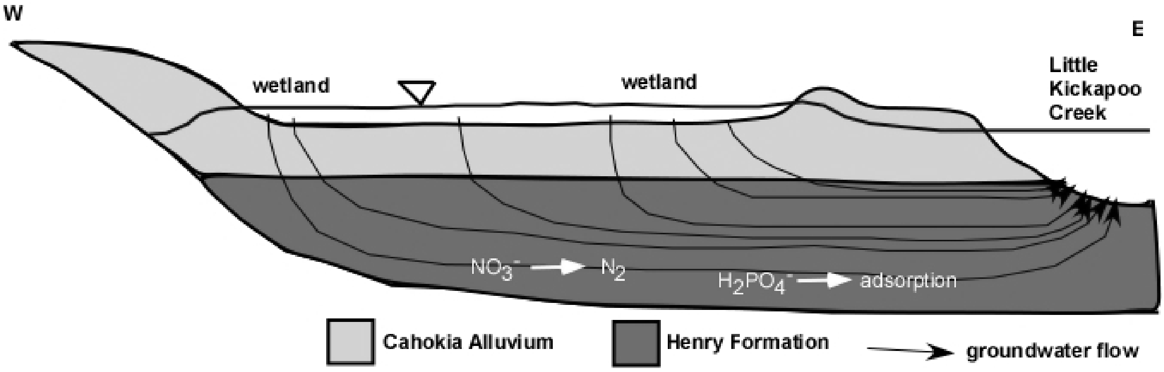

Fig. 8 Conceptual model of groundwater flow at study site. Flow is thought to be mostly vertical through alluvium and then horizontal through outwash towards LKC

To calibrate the model, targets were inserted using the wells installed at the wetland and their hydraulic head measurements from October 2010. Once the model was constructed, MODFLOW runs were performed to attain the best-fit model with respect to the target wells (Fig. 9). Variables were changed one-by-one until the least absolute residual mean was reached for all of the target wells (and specifically the wells on the east side of the wetlands in which up-to-date survey information was available). Once one of the variables reached “best-fit” than the next variable was varied to again reach the least absolute residual mean for the model. For this study, first the hydraulic conductivities of the alluvium and outwash were varied, and then the recharge was varied. The topography of the surfaces were also changed slightly to better represent the study site – the cells next to the cells with the LKC constant head boundary were increased to show the approximately 2 meter drop into the creek, and the area where the outwash pinches out was also adjusted. The values on the constant head boundaries were not varied. In the process of trying to find the best-fit model, specified flux boundaries were used instead of constant head boundaries for the wetland and the effluent channel, but it was found that these boundaries did not help lower the absolute residual mean of the model.

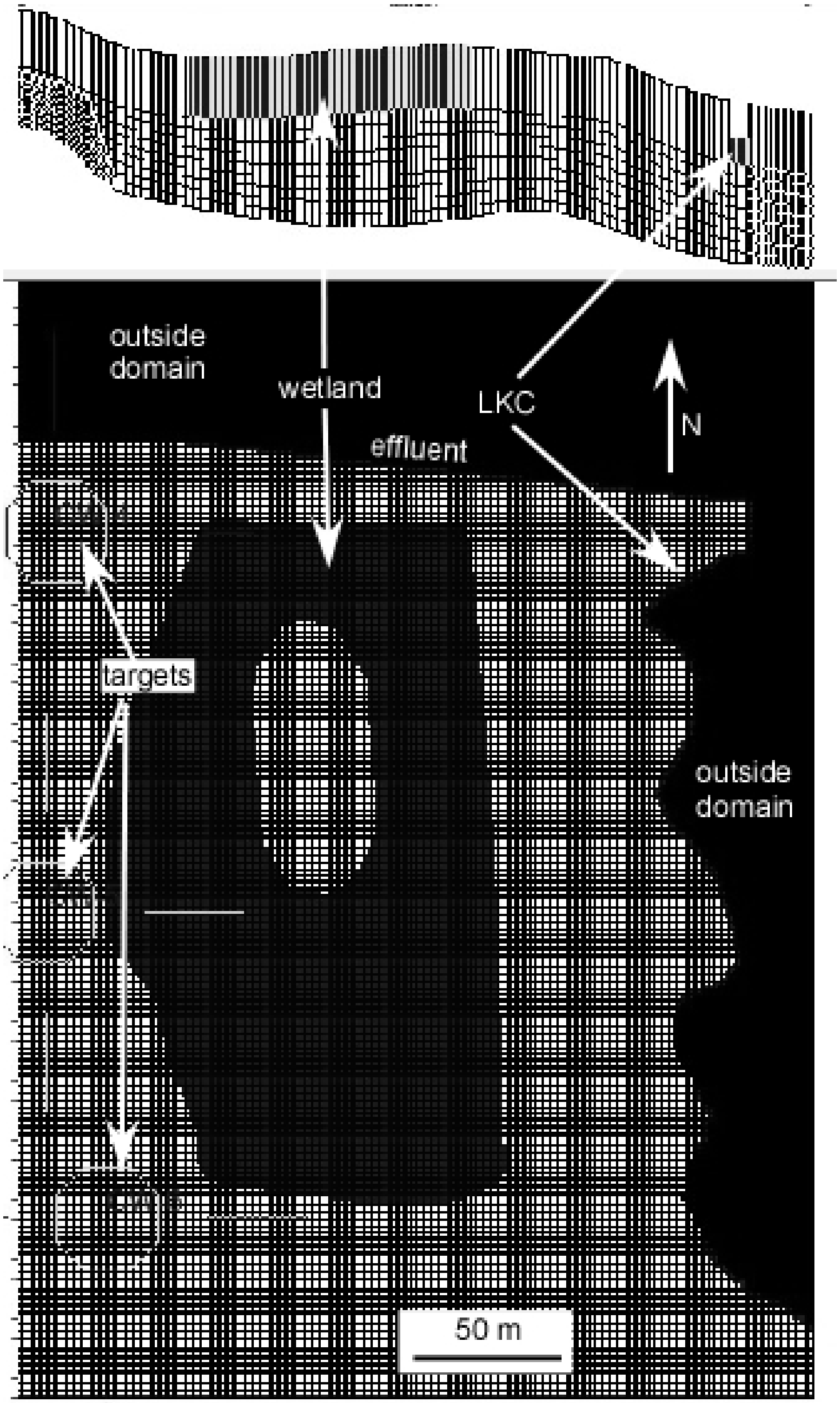

Fig. 9 Constructed model in Groundwater Vista 5 including plan view (below) and cross-section (above) on layer 1

The best-fit MODPATH simulation was found by calibrating to the known travel time from preliminary data of when the wastewater treatment plant first went online in 2005 (Fig. 8). Porosity and hydraulic conductivity values were varied to accomplish the best-fit model. The porosity used for the alluvium layers was 0.25 and the porosity used for the outwash layers was 0.35.

Results

Chemical Results

The first data that were gathered at the site were in 2005, when the wastewater treatment plant first went on line. Preliminary findings (Fig. 10) show how the groundwater in shallow wells W-2 through W-4 (shown on Fig. 5) went from natural chloride concentrations in area groundwater (10-15 mg/L) to effluent chloride concentrations (100-170 mg/L). The average linear groundwater velocity from these data was calculated to be about 3.6 m/day.

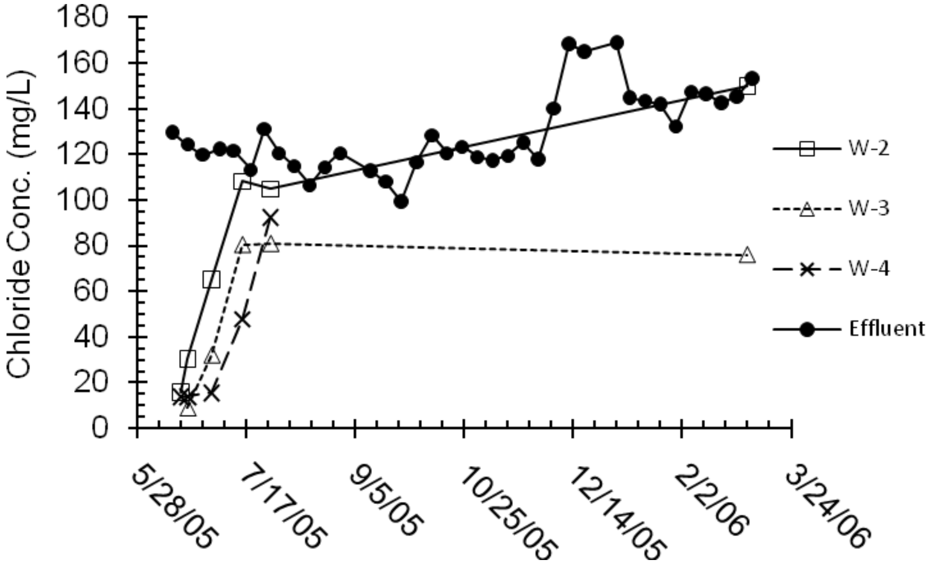

Fig. 10 Chloride concentrations in wells W-2 through W-4 compared to chloride concentrations in the effluent

Major ion analysis indicates that bicarbonate (HCO_3^-), calcium (Ca^{+2}), iron (Fe^{+2}), manganese (Mn^{+2}), and silicon (Si^{+4}) concentrations are relatively higher in the groundwater compared to the surface water. Fluoride (F^-) and bromide (Br^-) are relatively the same in both the groundwater and the surface water (Fig. 11). Sodium (Na^+) and potassium (K^+) are relatively higher in surface water compared to the groundwater. Chloride concentrations continued to remain elevated in the effluent, outlet and wells east of the wetland (Fig. 12). Effluent and outlet chloride concentrations peak in March 2010, likely due to melting snow washing road salt in the effluent entering the BNWRD plant.

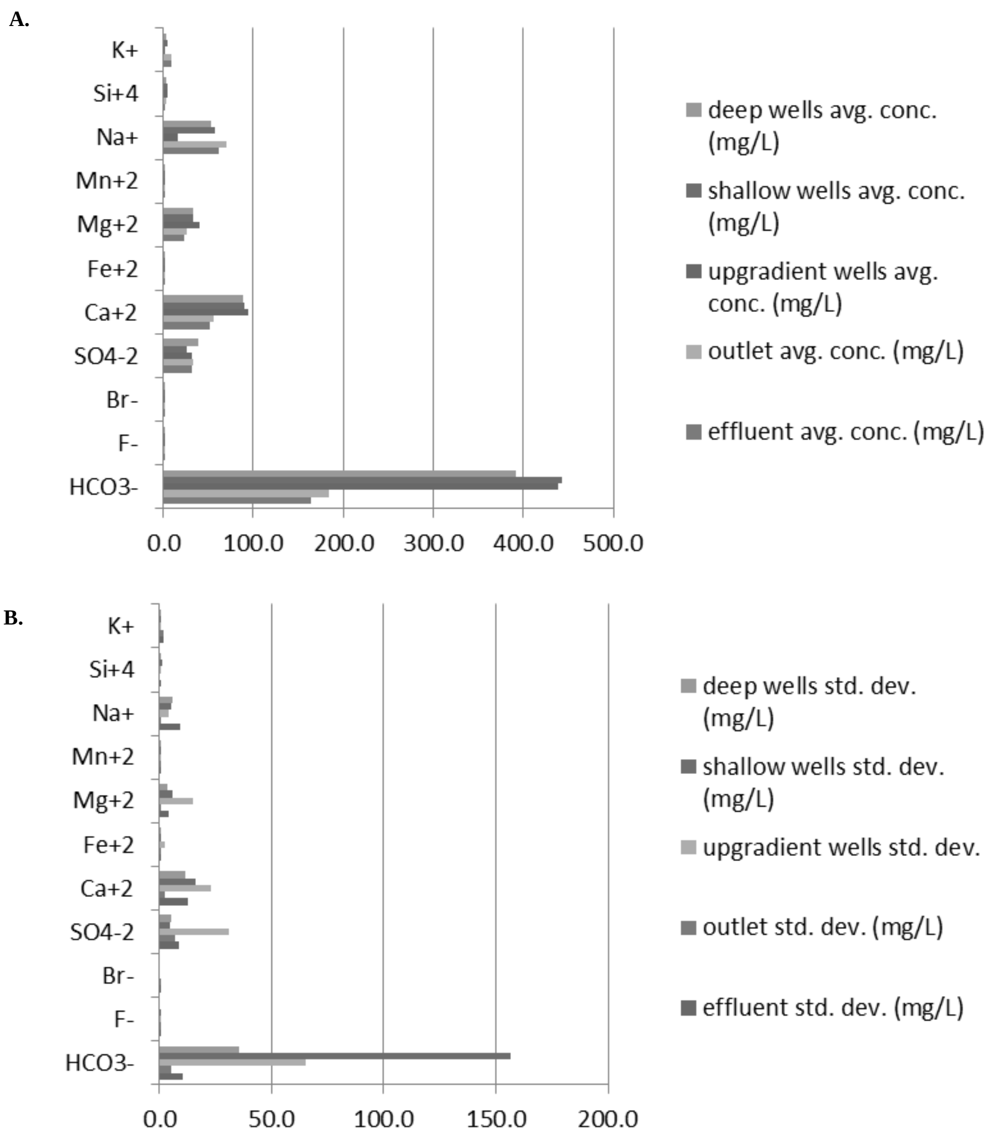

Fig. 11 Summary of ion analysis for effluent, outlet, upgradient wells, shallow wells and deep wells (excluding nutrients and Cl^-) – a) average concentration and b) concentration standard deviations

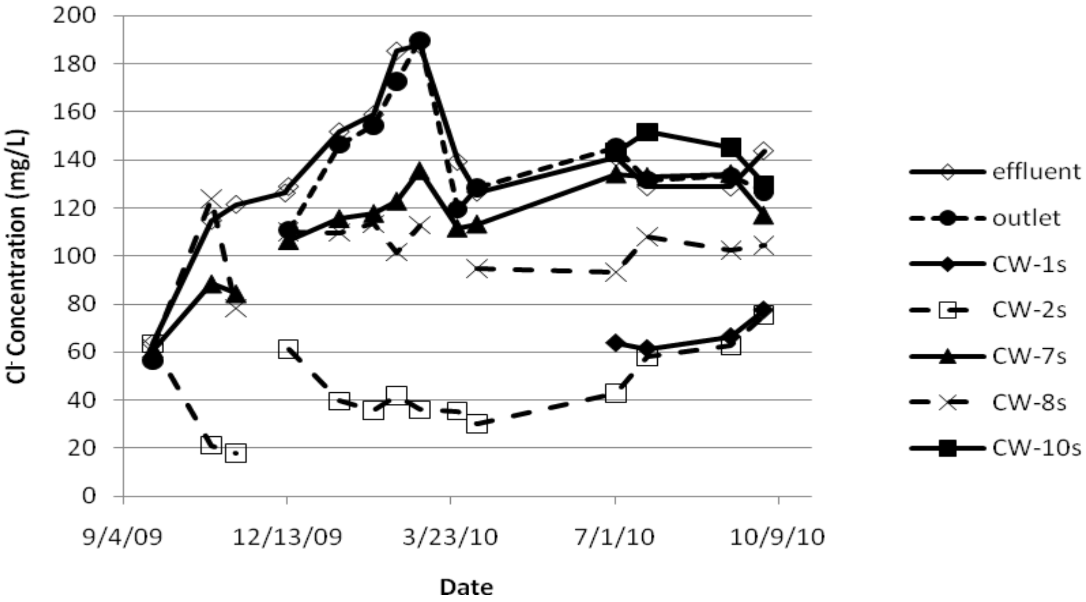

Fig. 12 Chloride concentrations in effluent, outlet and shallow wells

The water was also sampled for nitrate, dissolved reactive phosphorus (DRP) and ammonium from September 2009 – September 2010 (effluent, outlet and shallow wells shown in Figs. 13-15). Nitrogen as nitrate ranged from ND-1.4 mg/L in deep wells. DRP ranged from ND-0.06 mg/L in deep wells. Nitrogen as ammonium ranged from 0.04-4.5 mg/L in deep wells.

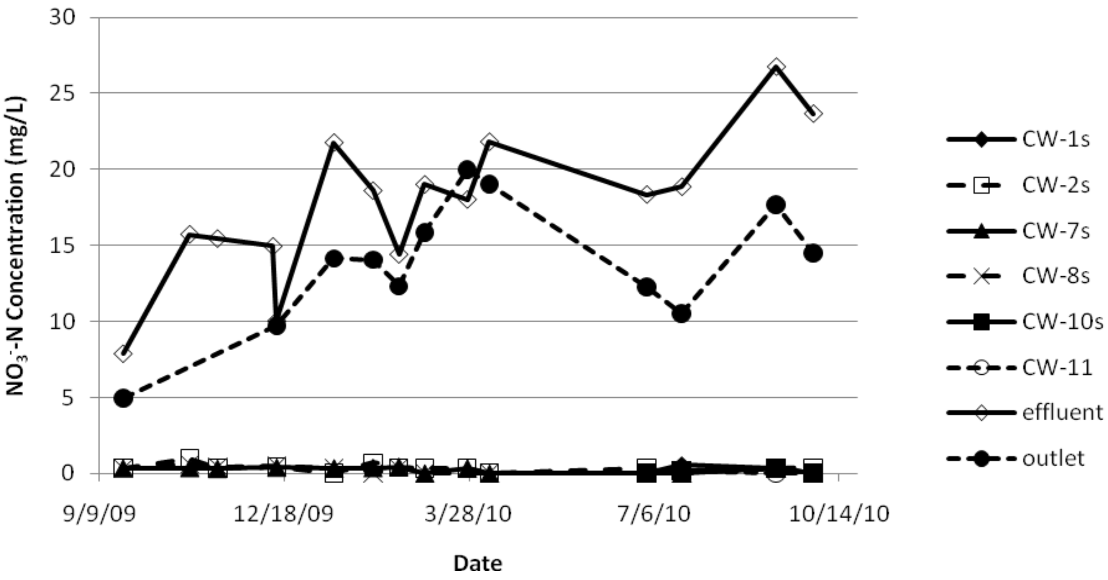

Fig. 13 N as nitrate concentrations in shallow well water samples compared to N as nitrate concentrations in the effluent and outlet

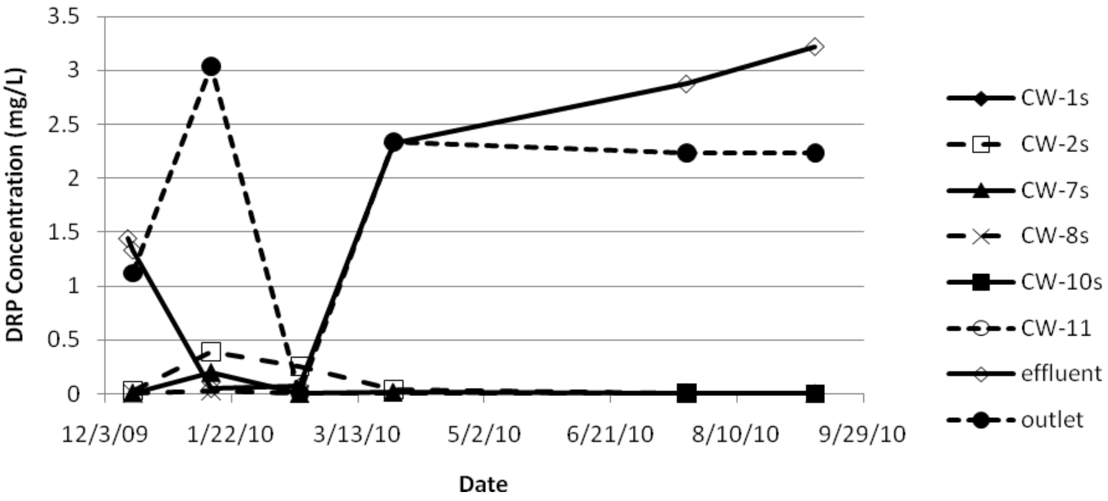

Fig. 14 DRP concentrations in shallow well water samples compared to DRP concentrations in the effluent and outlet

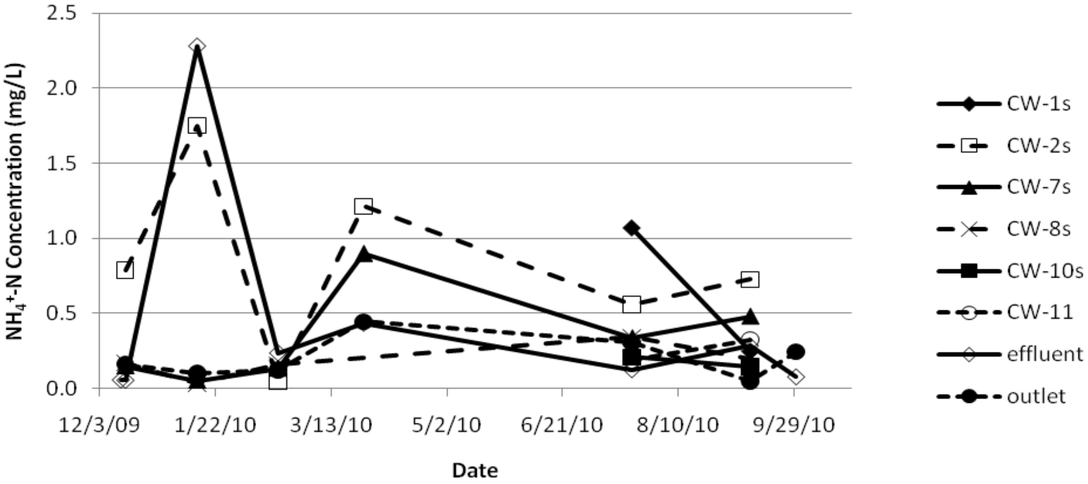

Fig. 15 N as ammonium concentrations in shallow well water samples compared to N as ammonium concentrations in the effluent and outlet

Modeling Results

Approximately 45 model runs were completed using MODFLOW to find the values of the above stated variables of the model that gave the least absolute residual mean of hydraulic head in target wells. For the purposes of this model the absolute residual mean was only calculated for wells on the east side of the wetland that had survey data associated with it. Table 2 shows the criteria for the best-fit model found for the situation, with an absolute residual mean of 0.26 m. Fig. 16 shows the results of the best-fit model run with hydraulic head contours – a modeled water table contour map was constructed by subtracting/adding hydraulic head residuals from actual hydraulic head values, for easy comparison between actual hydraulic head (Fig. 7) and modeled head (Fig. 16).

Table 2 Model construction criteria and best-fit values for variables of MODFLOW simulation

Variable	Best-fit value	Variable	Best-fit value
# of rows	300	S head (m)	217.22
# of columns	200	wetland elevation (m)	219.83
uniform X spacing	1	alluvium K_x (m/day)	0.00864
uniform Y spacing	1	alluvium K_y (m/day)	0.00864
# of layers	10	alluvium K_z (m/day)	0.00864
recharge (m/day)	0.000261	outwash K_x (m/day)	10
effluent head start (m)	220.72	outwash K_y (m/day)	10
effluent head end (m)	219.01	outwash K_z (m/day)	10
LKC head start (m)	217.35	Absolute Residual Mean (m)	0.26
LKC head end (m)	217.21		

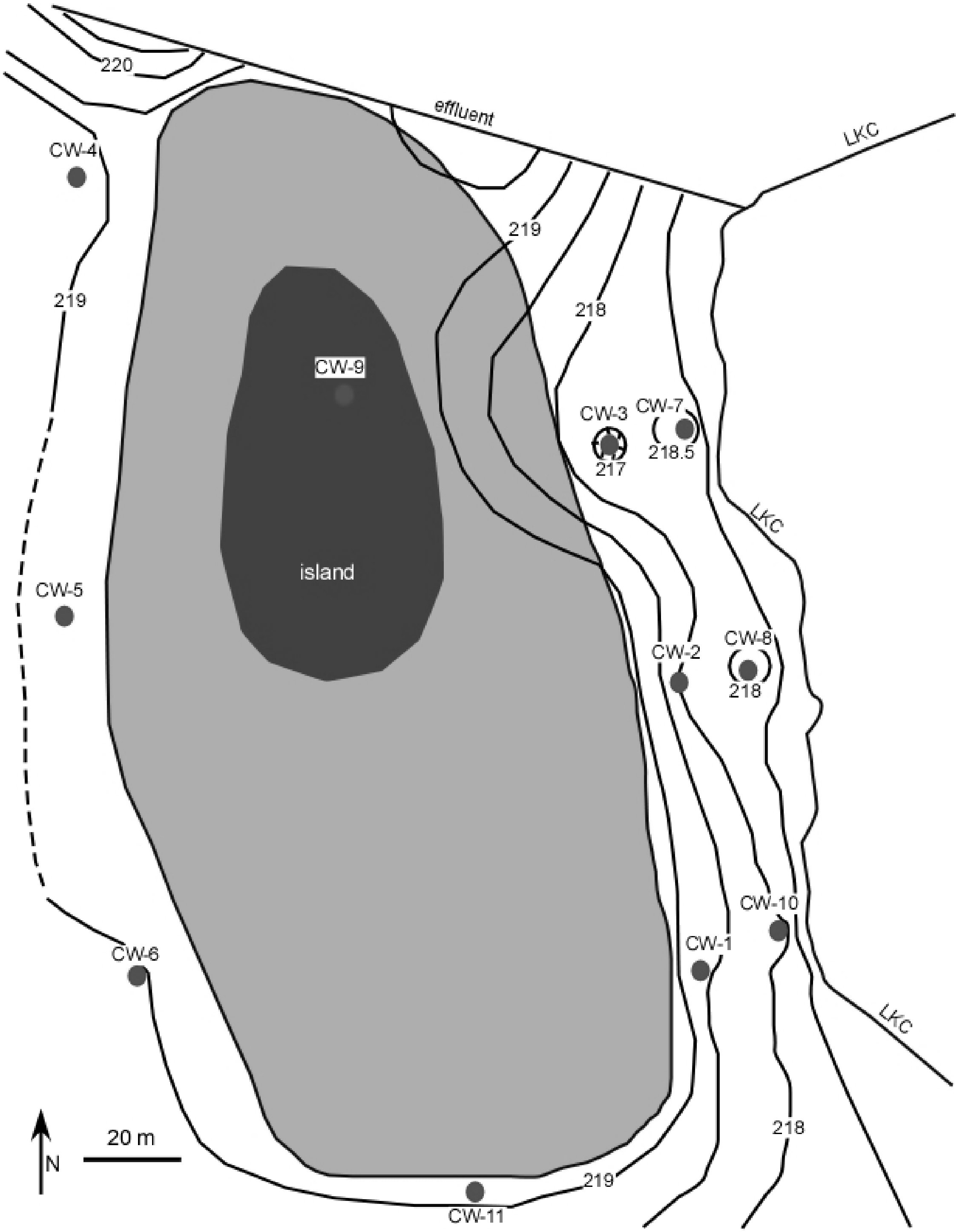

Fig. 16 Modeled hydraulic head – constructed by subtracting/adding residual values from actual hydraulic head values

Particle velocities from MODPATH simulations were similar to average linear velocity calculated from the data on Fig. 10. From that data it was determined that the length of time it took for wetland water to reach the old well W-2 was approximately 26 days. The range of travel times for the best-fit MODPATH simulation was 20-30 days. Decreasing the alluvium K an order of magnitude, from 0.00864 m/day to 0.000864 m/day, resulted in a better fit to observed average linear velocity. The difference in best-fit values for alluvium K between MODFLOW and MODPATH may be due to the fact that the MODPATH simulations are calibrated to a single well. While the MODFLOW simulations were calibrated to nine wells simultaneously.

The groundwater flow path simulated by MODPATH is somewhat different than what was found when contouring modeled head value – flow is heading in a SE direction toward LKC or the constant head boundary at the S end of the model (Fig. 17). MODPATH also showed deeper flow paths penetrating to the bottom of the model.

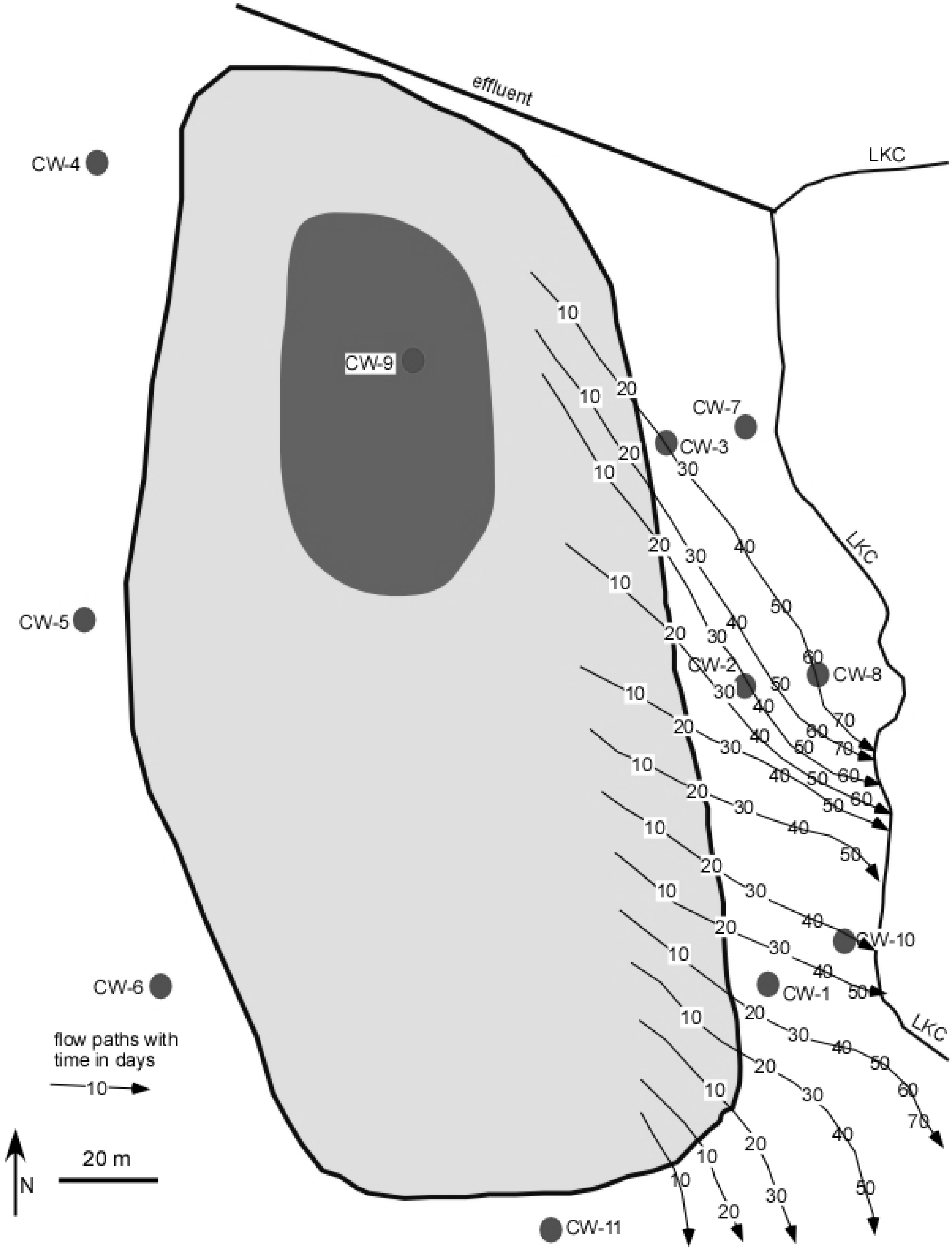

Fig. 17 MODPATH simulated particle flow

A seepage of 111 m^3/day out of the wetland was also calculated by determining the flux across the wetland constant head cells in the MODFLOW simulation. For comparison, a 2008 study at BNWRD was conducted using estimated measurements (“Report on a study of BNWRD SEWWTP wetland outlets”, 2008). Flow rates at the wetland were calculated by multiplying the acreage of the wetland (6 acres) by volume with a 1 foot average depth (650,000 gal). The estimated flow rate through the wetland varied from 1052 to 3706 m^3/day for 7 day and 2 day retention times, respectively. Therefore, the seepage out of the wetland represents between 3 and 11% of the flow rate through the wetland.

When comparing hydraulic head between the actual and modeled contour maps (Figs. 7 and 17) the contours look very similar. The only differences are the increase in head values at some wells on the east side. The groundwater flow path was the same – flowing either east into LKC, southeast (SE) towards the outlet location or south (S) toward CW-11.

Discussion

Nutrient removal from wetland seepage is a sink at the BNWRD constructed wetlands. It is important to know how much water is actually seeping from a constructed wetland in an effort to understand the impact the groundwater processes can have on nutrient reduction. Hayashi et al. (1998) concluded that in natural prairie wetlands without an outlet, it’s common for a majority of wetland water to become seepage – approximately 75% – but that it also changes seasonally. In a constructed wetlands study where there was surface water flow through, Choi et al. (2000) found that 31% of wetland water was recharging the groundwater and that surface water inputs greatly influenced the amount of seepage. This study found that BNWRD wetland water seepage is 3.0-10.6% - less than what was found in other studies. However, wetland water flow through rates were estimated due to flow meters not being present on wetland inlet or outlets – which, in turn, caused seepage percentages to also be theoretical in part. Retention of surface water in constructed wetlands also has an effect on seepage and nutrient reduction. Min et al.'s (2010) study of natural subtropical depressional wetlands showed that the longer that water is retained in a wetland the more water seeps into the subsurface.

The main goal of this study was to quantify the nutrient removal in the groundwater that was receiving wastewater effluent, and to determine if that amount was actually significant compared to removal by surface processes in the wetland. Because of the elevated chloride concentrations in wells, it is evident that the effluent is impacting the groundwater east of the wetland at BNWRD. Groundwater chloride concentrations increased from groundwater to effluent values, or at least increased above natural groundwater chloride concentrations (Fig. 10). The effluent-groundwater mixing calculation used to determine the effluent to groundwater ratio in well water east of the wetland was:

$$\%\ effluent\ in\ well\ water\ = \frac{Cl^{-}\ conc.in\ well\ water - groundwater\ Cl^{-}\ endmember}{effluent\ Cl^{-}\ endmember - groundwater\ Cl^{-} endmember} * 100$$

(4)

The calculations showed that a majority of the water sampled from the wells is effluent rich (50-100%), although 3 wells on the berm close to the wetland (CW-1s, 1d, and 2s) showed low effluent concentrations (<1-40%). Elevated chloride concentrations present in deeper wells below the berm are also an indication of the deeper flow paths occurring at the wetland. Samples collected on September 22, 2009 were run through the Jurgens et al. (2009) redox calculator, which assigned a general redox category and redox process. The redox state of most wells was Fe, Mn, or SO_4^- reducing conditions. Reducing conditions in the groundwater are conducive to denitrification.

The modeling process proved to be successful at recreating the groundwater flow at the BNWRD wetland and finding the wetland seepage flux value. Although a lower absolute residual mean could not be accomplished, the results were still satisfactory in understanding how the groundwater flows in the area and how the effluent water affects the area. CW-3 and CW-7d consistently had the highest residuals in all simulations. In a majority of the simulations CW-3 had the highest residual. The residuals for CW-7d are higher than CW-3 when the alluvium K values were changed or when the wetland had a specified flux boundary. When considering model sensitivity overall, the variable that had the most impact was the horizontal or vertical outwash K values.

It is known that a tile drain is in the vicinity of the CW-3 and CW-7d which is likely to be causing the problem with the model residuals for these two wells. The modeled hydraulic head contour map (Fig. 16) shows a bulge into the wetland adjacent to CW-3 and CW-7 – another sign that the tile drain is running near these wells. It’s likely that too much water is being simulated in the wells because they are so close to this tile drain. An effort was made as the wetland was being constructed to tear up any remaining tile drains from the area, but it is also possible that other tile drains still exist at the study site, which could be affecting the overall absolute residual mean of the model. The three wells with the low effluent concentrations (CW-1s, CW-1d and CW-2s) could also be affected by tile drainage in the area.

Using the chemistry data and flux data the equation:

nutrient loss = (seepage flux out) x (nutrient concentration decrease) (5)

was used to calculate nutrient loss compared to effluent nutrient concentrations (Table 3). Nitrate and phosphate concentrations in the groundwater were considerably lower compared to surface water concentrations Ammonium concentrations were generally low, but were higher in the groundwater.

Table 3 Nutrient loss from groundwater and surface water, calculated for nitrate, ammonium and DRP

	NO_3^--N	NH_4^+-N	DRP
Groundwater			
seepage flux out (L/day)	111000	111000	111000
avg. concentration change (mg/L)	-17.51	0.47	-1.58
mass loss/gain (g/day)	-1943.61	52.17	-175.38
Surface Water (2-day retention)			
flux of water (L/day)	3706300	3706300	3706300
avg. concentration change (mg/L)	-4.52	-0.01	-0.48
mass loss/gain (g/day)	-16,752.48	-37.06	-1,779.02
Surface Water (7-day retention)			
flux of water (L/day)	1051900	1051900	1051900
avg. concentration change (mg/L)	-4.52	-0.01	-0.48
mass loss/gain (g/day)	-4754.59	-10.52	-504.91

Groundwater

Nitrate concentrations in groundwater east of the wetland were lower compared to effluent and outlet nitrate concentrations – an indication that denitrification is occurring in the groundwater. There was a decrease in nitrate between the effluent and outlet and the majority of the nitrate was removed in groundwater (Fig. 13). The average rate of loss of nitrate due to groundwater processes was 1,940 g/day. The nitrate concentrations in the groundwater were 73-100% lower compared to effluent concentrations taken on the same day.

Ammonium was being produced in the subsurface, except for one exception in January when the effluent ammonium concentration was greater than groundwater concentrations (Fig. 15). Production of ammonium in the subsurface could occur by the mineralization of organic matter or infiltration of fertilizer impacted water (Fig. 2). The average groundwater concentration of ammonium was 0.5 mg/L and the average rate of ammonium gained due to groundwater processes was 52.2 g/day.

A decrease of phosphate (analyzed as DRP), was also occurring in the subsurface possibly due to adsorption sites being available in the soil, alluvium or outwash (Fig. 14). The average rate of DRP loss due to groundwater processes was 175 g/day. DRP loss did not occur in January or February samples. The DRP concentrations were decreased by an average of 99% in groundwater compared to effluent concentrations of samples taken on the same day (excluding January and February samples).

Surface Water

Surface water processes in the wetland were on average removing 4,750-16,800 g/day of nitrate, 10.5-37.1 g/day of ammonium, and 500-1,800 g/day of DRP. Overall, the removal of nitrate, ammonium and DRP was occurring in the surface water processes of the wetland. Nitrate reduction through the wetland ranged 0-44% when comparing effluent to outlet samples taken on the same day. Ammonium reduction through the wetland ranged 0-96% when comparing effluent to outlet samples taken on the same day. DRP reduction through the wetland ranged 0-100% when comparing effluent to outlet samples taken on the same day.

Conclusions

Geochemically, effluent water was impacting groundwater at the study site – seen as chloride-rich groundwater east of the wetland. Groundwater chloride concentrations increased 85% on average compared to natural groundwater chloride concentrations seen upgradient of the wetland. Groundwater at the site is under iron or manganese reducing conditions. MODFLOW simulations generated a wetland seepage flux of 111 m^3/day.

Nitrate and DRP reduction due to groundwater processes are significant at this site. Nitrate was well reduced by 17.51 mg/L or 1,940 g/day, on average, and 1.58 mg/L or 175 g/day of phosphate (analyzed as DRP) was also lost on average. Ammonium concentrations increased in the subsurface (0.47 mg/L or 52.2 g/day on average), but were reduced in the wetland. Phosphate amounts decreased in the wetland (0.48 mg/L or 500-1,800 g/day) and ammonium also (0.01 mg/L or 10.5-37.1 g/day). Groundwater nitrate removal ranged between 10-41% and groundwater phosphate removal ranged between 10-35%.

Although wetland water flow rates were estimated, it can be seen that the retention time of wetland water can impact the nutrient reduction in the wetland itself – five days cause a large difference in the amount of nutrients that can be reduced (Table 3). Shorter retention times allow more water flow through and thus higher nutrient reduction. Mass flux of nutrients is consistently larger through the wetland compared to groundwater processes. However, the concentration of nitrate and phosphate is more reduced than in the surface water (per L of water). Groundwater processes should be considered in an effort to really maximize the efficiency of a constructed wetland for wastewater treatment.

CHAPTER III
CONCLUSIONS

Nutrient reduction from wetland seepage is an often overlooked pathway in constructed wetlands used for wastewater treatment. It is important to know how much water is actually seeping from a constructed wetland in an effort to understand the impact the groundwater processes can have on nutrient reduction. Hayashi et al. (1998) discovered that in natural prairie wetlands without an outlet, it’s common for a majority of wetland water to recharge groundwater – approximately 75% – but that it also changes seasonally. In a constructed wetlands study where there was an inlet and outlet, it was found that 31% of wetland water was recharging the groundwater and that surface water inputs greatly influenced the amount of seepage (Choi et al., 2000). This study found that BNWRD wetland water seepage is 3.0-10.6%. However, wetland water flow through rates were calculated theoretically due to flow meters not being present on wetland inlet or outlets – which, in turn, caused seepage percentages to also be theoretical.

The retention time of wetland water can impact the nutrient reduction in the wetland itself (Table 3). Shorter retention times allow more water flow through and thus higher nutrient reduction. Min et al.’s (2010) study of natural subtropical depressional wetlands showed that the longer that water is retained in a wetland the more water seeps into the groundwater. If the amount of water flowing through the wetland could be monitored and correlated with seepage amounts, this may be seen at the BNWRD site also.

Nitrate and DRP reduction due to groundwater processes are significant at this site. Nitrate was well reduced by 17.51 mg/L or 1,940 g/day, on average, and 1.58 mg/L or 175 g/day of phosphate (analyzed as DRP) was also lost on average. Ammonium concentrations increased in the subsurface (0.47 mg/L or 52.2 g/day on average), but were reduced in the wetland. Phosphate amounts decreased in the wetland (0.48 mg/L or 500-1,800 g/day) and ammonium also (0.01 mg/L or 10.5-37.1 g/day). The wetland encounters large amounts of water every day compared to the amount of water that seeps into the subsurface, but what is important is what has the greater impact – groundwater processes or surface water processes.

Although wetland water flow rates were estimated, it can be seen that the retention time of wetland water can impact the nutrient reduction in the wetland itself – five days cause a large difference in the amount of nutrients that can be reduced (Table 3). Shorter retention times allow more water flow through and thus higher nutrient reduction. Mass flux of nutrients is consistently larger through the wetland compared to groundwater processes. However, the concentration of nitrate and phosphate is more reduced than in the surface water (per L of water). Groundwater processes should be considered in an effort to really maximize the efficiency of a constructed wetland for wastewater treatment.

Future Work

This study's findings were helpful in understanding the overall impact that groundwater processes have on water affected by wastewater effluent. To better define the conclusions made with this study, a flow meter needs to be installed in the effluent inlet and at the wetland outlet to better approximate the actual amount of water entering and leaving the wetland. Quantifying the amount of water in the wetland would allow a better calculation of the nutrient reduction in the wetland itself and how it compares to the nutrient reduction capabilities of the groundwater processes. Also, to better qualify the groundwater flow path at the wetland, a well could be installed just south of the wetland outlet, across the path from the bird observation building on the SE edge of the wetland (Fig. 5). This well could give chemical and head data that could better qualify the SE groundwater flow that was seen in both the modeled head contour map and actual head contour map. Surveying with a local coordinate system would need to be completed again for modeling purposes also.

At one point in the study a conductivity logger was installed in CW-2s in hopes that a lag time could be quantified between when a certain chloride concentration of effluent water left the plant and the same water reached CW-2s. After analyzing the data, however, no lag time could be quantified. It was thought that this could be due to the fact that the water collected from CW-2s was majority groundwater and not effluent. No further investigation was done in a different well. Quantifying the actual lag time, however, would allow more accurate calculations of nutrient reduction – the effluent water that left the plant could be compared to the same effluent water however many days later in the wells when it has been mixed with groundwater.

A model with a larger study area could also be completed to quantify groundwater flow paths under the effluent channel from the smaller wetland just north of the large wetland of this study. Incorporating both wetlands in the study could also better quantify the overall nutrient reduction capabilities of the entire BNWRD wetland site.

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APPENDIX A

ION ANALYSIS OF GROUNDWATER SAMPLES

		9/22/09	*10/28/09*	*11/12/09*	*12/14/09*	*1/14/10*	*2/4/10*	*2/18/10*	*3/4/10*	*3/27/10*	*4/8/10*	*7/2/10*	*7/21/10*	*9/10/10*	*9/30/10*
CW-1s	HCO_3^- (mg/L)												358.68		
	F^- (mg/L)											0.97	1.25	1.22	0.43
	Cl^- (mg/L)											63.69	61.38	66.29	77.42
	Br^- (mg/L)											0.06	0.38	0.20	0.18
	NO_3^--N (mg/L)											ND	0.55	0.35	ND
	SO_4^{2-} (mg/L)											30.69	28.10	4.44	2.89
CW-2s	HCO_3^- (mg/L)	749.08											753.96		
	F^- (mg/L)	0.19	0.21	0.97	0.21	1.46	0.24	0.20	0.14	0.11	0.06	0.23	0.20	0.22	0.22
	Cl^- (mg/L)	63.41	21.15	17.96	61.25	39.57	35.71	41.81	36.11	35.45	30.30	42.94	58.18	62.54	75.47
	Br^- (mg/L)	0.34	0.15	0.11	0.38	ND	0.34	0.35	0.37	0.33	0.27	0.26	0.45	0.44	0.81
	NO_3^--N (mg/L)	0.36	0.98	0.35	0.44	ND	0.70	0.38	0.33	0.33	ND	0.37	0.19	0.32	0.38
	SO_4^{2-} (mg/L)	21.38	25.32	15.28	24.58	11.06	24.41	19.45	22.22	22.53	24.27	22.23	20.50	16.72	7.52
CW-7s	HCO_3^- (mg/L)	488.00											453.84		
	F^- (mg/L)	0.30	0.29	0.31	0.32	0.26	0.17	0.30	0.29	0.20	0.20	0.36	0.38	0.57	0.42
	Cl^- (mg/L)	60.73	88.41	84.35	106.38	115.50	117.63	122.73	135.35	111.55	113.24	133.94	132.93	134.10	116.91
	Br^- (mg/L)	0.18	0.21	0.15	0.27	0.28	0.28	0.26	0.31	0.17	0.20	0.32	0.53	0.31	0.50
	NO_3^--N (mg/L)	0.35	0.37	0.31	0.39	0.34	0.37	0.44	ND	0.34	ND	ND	ND	0.33	ND
	SO_4^{2-} (mg/L)	15.42	30.28	28.95	33.71	1.11	32.86	40.72	46.72	40.00	43.46	10.49	10.40	28.26	27.46
CW-8s	HCO_3^- (mg/L)	585.60											529.48		
	F^- (mg/L)	0.18	0.26	0.22	0.23	0.16	0.29	0.21	0.15		0.08	1.73	0.25	0.24	0.25
	Cl^- (mg/L)	61.62	123.63	78.29	109.89	109.74	113.40	101.57	112.74		94.80	93.11	107.93	102.32	104.40
	Br^- (mg/L)	0.19	0.25	0.15	0.27	0.29	0.27	0.27	0.38		0.25	0.26	0.39	0.27	0.43
	NO_3^--N (mg/L)	0.34	0.62	0.44	0.48	0.33	ND	0.38	ND		ND	ND	ND	0.31	ND
	SO_4^{2-} (mg/L)	25.09	28.83	17.70	36.21	0.69	34.77	38.09	41.09		38.34	6.35	4.20	35.42	38.29

		7/2/10	*7/21/10*	*9/10/10*	*9/30/10*
CW-9	HCO_3^- (mg/L)		234.24		
	F^- (mg/L)		0.76	0.55	0.67
	Cl^- (mg/L)		104.47	103.49	110.77
	Br^- (mg/L)		0.26	0.19	0.39
	NO_3^--N (mg/L)		0.17	ND	0.40
	SO_4^{2-} (mg/L)		31.03	30.37	35.57
CW-10s	HCO_3^- (mg/L)		358.68		
	F^- (mg/L)	0.45	0.44	0.45	0.44
	Cl^- (mg/L)	143.23	151.56	145.26	129.62
	Br^- (mg/L)	0.27	0.38	0.28	0.53
	NO_3^--N (mg/L)	ND	0.21	0.31	ND
	SO_4^{2-} (mg/L)	33.56	30.99	43.44	37.80
CW-11	HCO_3^- (mg/L)		412.36		
	F^- (mg/L)	0.28	0.30	0.32	0.35
	Cl^- (mg/L)	126.11	n.a.	133.25	134.43
	Br^- (mg/L)	0.19	0.29	0.30	0.50
	NO_3^--N (mg/L)	ND	0.16	ND	ND
	SO_4^{2-} (mg/L)	13.28	10.97	31.88	28.38

		9/22/09	*7/21/10*			*9/22/09*	*7/21/10*
CW-1s	Ca^{+2} (mg/L)		68.30	**CW-9**	Ca^{+2} (mg/L)		43.74
	Fe^{+2} (mg/L)		0.10		Fe^{+2} (mg/L)		0.03
	Mg^{+2} (mg/L)		29.69		Mg^{+2} (mg/L)		21.23
	Mn^{+2} (mg/L)		1.82		Mn^{+2} (mg/L)		0.24
	Na^{+} (mg/L)		37.53		Na^{+} (mg/L)		66.13
	Si (mg/L)		4.96		Si (mg/L)		3.50
	K^{+} (mg/L)		2.50		K^{+} (mg/L)		8.70
CW-2s	Ca^{+2} (mg/L)	95.91	146.60	**CW-10s**	Ca^{+2} (mg/L)		93.48
	Fe^{+2} (mg/L)	1.54	3.99		Fe^{+2} (mg/L)		0.24
	Mg^{+2} (mg/L)	33.49	51.33		Mg^{+2} (mg/L)		32.41
	Mn^{+2} (mg/L)	2.488	3.57		Mn^{+2} (mg/L)		0.96
	Na^{+} (mg/L)	27.33	37.96		Na^{+} (mg/L)		63.56
	Si (mg/L)	5.07	8.33		Si (mg/L)		3.70
	K^{+} (mg/L)	4.55	7.00		K^{+} (mg/L)		4.10
CW-7s	Ca^{+2} (mg/L)	87.63	103.20	**CW-11**	Ca^{+2} (mg/L)		91.39
	Fe^{+2} (mg/L)	0.25	0.06		Fe^{+2} (mg/L)		0.15
	Mg^{+2} (mg/L)	31.55	36.58		Mg^{+2} (mg/L)		34.51
	Mn^{+2} (mg/L)	0.86	0.89		Mn^{+2} (mg/L)		0.82
	Na^{+} (mg/L)	57.82	73.34		Na^{+} (mg/L)		67.23
	Si (mg/L)	4.76	5.25		Si (mg/L)		5.04
	K^{+} (mg/L)	3.31	3.90		K^{+} (mg/L)		1.20
CW-8s	Ca^{+2} (mg/L)		118.00				
	Fe^{+2} (mg/L)		0.01				
	Mg^{+2} (mg/L)		40.46				
	Mn^{+2} (mg/L)	0.00	1.09				
	Na^{+} (mg/L)		57.51				
	Si (mg/L)	0.54	4.14				
	K^{+} (mg/L)	1.14	4.00				

		9/22/09	*3/4/10*	*3/27/10*	*4/8/10*	*7/2/10*	*7/21/10*	*9/10/10*	*9/30/10*
CW-1d	HCO_3^- (mg/L)	346.48					392.84		
	F^- (mg/L)	0.31	0.24	0.18	0.15	0.31	0.33	0.32	0.34
	Cl^- (mg/L)	63.30	40.81	39.50	37.51	52.84	53.99	76.26	67.56
	Br^- (mg/L)	0.14	0.15	0.11	0.15	0.04	0.16	0.21	0.29
	NO_3^--N (mg/L)	1.61	0.42	0.45	0.34	0.65	0.21	0.32	0.70
	SO_4^{2-} (mg/L)	27.40	17.96	39.14	12.16	26.88	29.67	48.21	49.91
CW-2d	HCO_3^- (mg/L)	402.60					395.28		
	F^- (mg/L)	0.26	0.36	0.29	0.24	0.41	0.40	0.44	0.41
	Cl^- (mg/L)	75.95	130.12	121.14	112.94	145.74	140.50	133.54	123.39
	Br^- (mg/L)	0.18	0.33	0.22	0.24	0.29	0.37	0.27	0.49
	NO_3^--N (mg/L)	0.34	0.37	0.48	0.36	ND	0.16	0.31	ND
	SO_4^{2-} (mg/L)	22.81	34.68	34.72	35.02	25.52	20.93	35.26	41.07
CW-3	HCO_3^- (mg/L)	387.96					407.48		
	F^- (mg/L)	0.39		0.28	0.28	0.48	0.47	0.51	0.50
	Cl^- (mg/L)	91.03		82.38	133.53	135.82	140.08	131.45	122.41
	Br^- (mg/L)	0.19		0.17	0.17	0.28	0.27	0.32	0.52
	NO_3^--N (mg/L)	2.16		1.46	1.32	0.37	ND	0.34	ND
	SO_4^{2-} (mg/L)	29.59		48.47	44.65	17.94	14.02	26.00	24.03
CW-7d	HCO_3^- (mg/L)	375.76					405.04		
	F^- (mg/L)	0.23	0.20		0.12		0.28	0.25	0.31
	Cl^- (mg/L)	87.29	122.99		94.38		120.03	122.66	104.32
	Br^- (mg/L)	0.20	0.34		0.17		0.51	0.26	0.41
	NO_3^--N (mg/L)	0.42	1.35		1.08		ND	ND	0.38
	SO_4^{2-} (mg/L)	37.64	30.50		33.01		21.05	58.79	57.66
CW-8d	HCO_3^- (mg/L)	448.96					444.08		
	F^- (mg/L)	0.17	0.24	0.17	0.16	0.30	0.31	0.29	0.32
	Cl^- (mg/L)	80.78	120.74	107.63	103.03	113.59	121.39	119.21	115.79
	Br^- (mg/L)	0.21	0.33	0.19	0.28	0.51	0.43	0.24	0.57
	NO_3^--N (mg/L)	0.35	0.41	0.42	ND	ND	ND	ND	ND
	SO_4^{2-} (mg/L)	17.95	48.20	52.55	55.52	15.66	28.17	40.92	44.20
CW-10d	HCO_3^- (mg/L)						351.36		
	F^- (mg/L)					0.49	0.44	0.39	0.39
	Cl^- (mg/L)					139.28	139.55	125.35	119.56
	Br^- (mg/L)					0.26	0.33	0.28	0.44
	NO_3^--N (mg/L)					ND	0.17	ND	ND
	SO_4^{2-} (mg/L)					46.65	51.12	56.46	47.98

		9/22/09	*7/21/10*			*9/22/09*	*7/21/10*
CW-1d	Ca^{+2} (mg/L)	72.73	84.51	**CW-7d**	Ca^{+2} (mg/L)	65.68	91.95
	Fe^{+2} (mg/L)	0.08	0.02		Fe^{+2} (mg/L)	2.23	0.03
	Mg^{+2} (mg/L)	29.67	35.44		Mg^{+2} (mg/L)	30.43	38.97
	Mn^{+2} (mg/L)	0.08	0.13		Mn^{+2} (mg/L)	0.10	0.13
	Na^{+} (mg/L)	35.00	37.05		Na^{+} (mg/L)	41.27	48.80
	Si (mg/L)	4.10	4.74		Si (mg/L)	4.13	5.35
	K^{+} (mg/L)	2.07	1.10		K^{+} (mg/L)	3.20	2.70
CW-2d	Ca^{+2} (mg/L)	100.10	94.54	**CW-8d**	Ca^{+2} (mg/L)	72.38	114.70
	Fe^{+2} (mg/L)	0.72	0.24		Fe^{+2} (mg/L)	0.50	0.02
	Mg^{+2} (mg/L)	36.14	34.71		Mg^{+2} (mg/L)	26.00	39.36
	Mn^{+2} (mg/L)	0.99	0.87		Mn^{+2} (mg/L)	0.28	0.39
	Na^{+} (mg/L)	68.99	75.67		Na^{+} (mg/L)	36.73	58.11
	Si (mg/L)	3.63	3.62		Si (mg/L)	2.79	4.28
	K^{+} (mg/L)	2.50			K^{+} (mg/L)	2.21	4.60
CW-3	Ca^{+2} (mg/L)	93.59	86.63	**CW-10d**	Ca^{+2} (mg/L)		97.81
	Fe^{+2} (mg/L)	0.09	0.02		Fe^{+2} (mg/L)		0.03
	Mg^{+2} (mg/L)	33.96	32.49		Mg^{+2} (mg/L)		33.51
	Mn^{+2} (mg/L)	1.01	1.06		Mn^{+2} (mg/L)		0.57
	Na^{+} (mg/L)	73.24	74.18		Na^{+} (mg/L)		67.63
	Si (mg/L)	5.50	5.10		Si (mg/L)		3.51
	K^{+} (mg/L)	5.09	6.90		K^{+} (mg/L)		3.40

	Anions	*9/22/09*	*7/21/10*	**Cations**	*9/22/09*	*7/21/10*
CW-4	HCO_3^- (mg/L)		475.80	Ca^{+2} (mg/L)	49.69	133.30
	F^- (mg/L)	0.23	0.23	Fe^{+2} (mg/L)	5.18	0.01
	Cl^- (mg/L)	45.43	21.21	Mg^{+2} (mg/L)	17.83	55.97
	Br^- (mg/L)	0.23	ND	Mn^{+2} (mg/L)	1.82	0.06
	NO_3^--N (mg/L)	0.38	0.20	Na^+ (mg/L)	29.59	11.96
	SO_4^{2-} (mg/L)	14.16	85.26	Si (mg/L)	4.11	4.56
				K^+ (mg/L)	0.43	1.30
CW-5	HCO_3^- (mg/L)	473.36	514.84	Ca^{+2} (mg/L)	137.80	100.40
	F^- (mg/L)	0.21	0.34	Fe^{+2} (mg/L)	0.04	0.01
	Cl^- (mg/L)	44.40	17.18	Mg^{+2} (mg/L)	55.92	47.75
	Br^- (mg/L)	0.17	ND	Mn^{+2} (mg/L)	0.14	0.42
	NO_3^--N (mg/L)	0.45	0.20	Na^+ (mg/L)	21.86	12.61
	SO_4^{2-} (mg/L)	43.07	17.24	Si (mg/L)	6.62	6.20
				K^+ (mg/L)	1.91	1.10
CW-6	HCO_3^- (mg/L)		363.56	Ca^{+2} (mg/L)		73.25
	F^- (mg/L)		0.31	Fe^{+2} (mg/L)		0.09
	Cl^- (mg/L)		15.03	Mg^{+2} (mg/L)		32.32
	Br^- (mg/L)		0.15	Mn^{+2} (mg/L)		0.98
	NO_3^--N (mg/L)		0.39	Na^+ (mg/L)		9.70
	SO_4^{2-} (mg/L)		13.07	Si (mg/L)		5.17
				K^+ (mg/L)		1.10

APPENDIX B

ION ANALYSIS OF SURFACE WATER SAMPLES

Anions		HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^--N (mg/L)	SO_4^{-2} (mg/L)
effluent	*9/22/09*	156.16	0.74	63.52	0.13	7.86	20.98
	10/28/09		0.52	114.75	0.15	15.73	45.30
	11/12/09		0.58	121.47	ND	15.45	22.45
	12/12/09		0.57	126.22	0.16	14.94	16.89
	12/14/09		0.55	128.91	0.13	10.02	18.54
	1/14/10		0.64	151.79	0.16	21.77	33.69
	2/4/10		0.67	158.91	0.17	18.61	40.20
	2/18/10		0.70	185.40	0.24	14.40	40.31
	3/4/10		0.58	188.07	0.22	19.02	35.02
	3/27/10		0.48	139.33	0.14	18.02	29.71
	4/8/10		0.49	126.51	0.18	21.83	34.05
	7/2/10		0.77	141.23	0.46	18.35	41.99
	7/21/10	170.80	0.84	128.79	0.21	18.86	40.94
	9/10/10		0.90	128.66	0.23	26.77	29.66
	9/30/10		0.81	143.79	0.43	23.68	30.08

	Cations	*9/22/09*	*7/21/10*
effluent	Ca^{+2} (mg/L)	41.95	60.32
	Fe^{+2} (mg/L)	0.02	0.04
	Mg^{+2} (mg/L)	20.88	26.61
	Mn^{+2} (mg/L)	0.02	0.01
	Na^+ (mg/L)	54.78	68.15
	Si (mg/L)	2.19	2.91
	K^+ (mg/L)	7.78	10.40

Anions		HCO_3^- (mg/L)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^--N (mg/L)	SO_4^{-2} (mg/L)
outlet	*9/22/09*	180.56	0.80	56.33	0.12	4.93	19.45
	10/28/09						
	11/12/09						
	12/12/09						
	12/14/09		0.50	110.76	0.17	9.74	18.89
	1/14/10		0.60	146.32	0.14	14.14	32.05
	2/4/10		0.66	154.21	0.18	14.04	37.87
	2/18/10		0.69	172.59	0.24	12.32	39.81
	3/4/10		0.56	189.68	0.23	15.83	34.87
	3/27/10		0.48	119.35	0.14	19.98	32.29
	4/8/10		0.48	128.35	0.20	19.04	34.99
	7/2/10		0.74	145.13	0.51	12.25	41.27
	7/21/10	187.88	0.84	131.59	0.29	10.53	39.64
	9/10/10		0.87	133.20	0.23	17.66	35.61
	9/30/10		0.86	126.88	0.43	14.49	33.31

	Cations	*9/22/09*	*7/21/10*
outlet	Ca^{+2} (mg/L)	54.78	58.36
	Fe^{+2} (mg/L)	0.05	0.05
	Mg^{+2} (mg/L)	26.80	25.96
	Mn^{+2} (mg/L)	0.02	0.03
	Na^+ (mg/L)	69.52	69.42
	Si (mg/L)	2.64	2.64
	K^+ (mg/L)	7.61	10.00

APPENDIX C

DEPTH TO WATER MEASUREMENTS FOR GROUNDWATER WELLS

	10/7/09			**6/3/10**			**10/21/10**	
Well	*TOC elev. (m)*	*DTW (m)*	*groundwater elev. (m)*	*TOC elev. (m)*	*DTW (m)*	*groundwater elev. (m)*	*DTW (m)*	*groundwater elev. (m)*
CW-1s				220.41	2.55	217.98	2.61	217.39
CW-1d	220.86	3.28	217.58	220.86	3.09	217.96	2.58	217.42
CW-2s	220.43	2.82	217.61	220.43	2.62	218.00	2.56	217.44
CW-2d	221.03	3.45	217.58	221.03	3.24	217.99	2.56	217.44
CW-3	220.98	3.39	217.59	220.98	3.11	217.94	2.68	217.32
CW-4	221.13	1.68	219.45	221.69	2.05	218.69	1.62	218.38
CW-5	220.21	1.14	219.07	221.1	1.48	219.24	1.63	218.37
CW-6	220.58	1.55	219.03	220.61	1.21	218.89		
CW-7s	219.91	2.48	217.43	219.91	2.27	218.60	1.89	218.11
CW-7d	219.96	2.48	217.48	219.96	2.25	218.68	1.85	218.15
CW-8s	220.04	2.54	217.50	220.04	2.36	218.21	2.25	217.75
CW-8d	220.34	2.79	217.55	220.34	2.58	218.36	2.19	217.81
CW-9				218.92	1.92	218.92	1.08	218.92
CW-10s							2.11	217.89
CW-10d							2.11	217.89
CW-11							2.78	217.22

APPENDIX D

2005 PRELIMINARY DATA

Ion		HCO_3^-	F^-	Cl^-	PO_4^{-3}	NO_3-N	SO_4^{-2}	Ca^{+2}	K^+	Mg^{+2}	Na^+	Fe^{+2}	Mn^{+2}	NH_4^+	Si
Sample	**Date**	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
W-1	6/17/05	478.6	0.2	13.7	0.0	0.0	46.3	146.1	N/A	59.9	11.1	0.1	0.6	0.0	4.0
W-2	6/17/05	461.1	0.1	15.6	0.0	0.3	40.1	101.2	N/A	35.2	9.3	0.0	0.3	N/A	4.4
W-4	6/17/05	619.8	0.1	13.7	0.0	2.0	37.4	131.4	N/A	48.2	9.1	0.0	1.4	N/A	4.6
W-1	6/20/05	N/A	0.2	14.3	0.0	0.0	45.7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
W-2	6/20/05	N/A	0.3	30.3	0.0	1.8	42.7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
W-3	6/20/05	N/A	0.3	9.0	0.0	0.6	43.4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
W-4	6/20/05	N/A	0.2	13.9	0.0	4.3	33.5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
W-1	7/1/05	N/A	0.2	19.8	0.0	0.0	51.0	132.1	N/A	53.5	5.2	0.1	0.6	N/A	3.9
W-2	7/1/05	N/A	0.2	65.3	0.0	0.2	50.7	121.3	N/A	40.4	7.5	0.0	0.1	N/A	4.6
W-3	7/1/05	N/A	0.2	32.2	0.0	1.1	41.1	147.2	N/A	60.0	7.5	0.2	0.6	N/A	4.5
W-4	7/1/05	N/A	0.1	15.5	0.0	3.8	27.1	118.7	N/A	45.7	5.2	0.1	1.0	N/A	4.6
W-1	7/15/05	741.8	0.1	26.9	0.0	0.1	56.1	159.4	N/A	62.3	9.0	0.1	0.8	N/A	4.7
W-2	7/15/05	407.5	0.1	108.2	0.0	1.5	61.6	129.3	N/A	42.2	16.4	0.1	0.3	N/A	4.4
W-3	7/15/05	558.8	0.2	80.3	0.0	2.7	43.8	139.7	N/A	53.5	9.5	0.8	0.4	N/A	4.5
W-4	7/15/05	536.8	0.2	47.9	0.0	2.4	30.3	131.1	N/A	46.9	6.7	0.0	1.3	N/A	4.7
W-1	7/28/05	719.8	0.2	21.7	0.0	0.0	58.4	156.4	N/A	58.8	7.3	0.0	0.7	0.3	4.5
W-2	7/28/05	366.0	0.5	104.8	0.0	3.7	57.7	117.0	N/A	36.8	23.8	0.0	0.5	0.7	3.8
W-3	7/28/05	505.1	0.3	80.8	0.0	1.8	42.2	140.2	N/A	51.1	10.2	0.0	0.3	0.8	4.5
W-4	7/28/05	449.0	0.3	92.4	0.0	0.6	35.6	133.1	N/A	44.9	8.1	0.0	1.3	0.1	5.0
W-1	3/4/06	N/A	0.2	38.5	0.0	0.0	44.3	N/A	N/A	N/A	N/A	N/A	N/A	0.1	N/A
W-2	3/4/06	N/A	0.2	149.8	0.0	5.8	72.1	N/A	N/A	N/A	N/A	N/A	N/A	0.0	N/A
W-3	3/4/06	N/A	0.1	76.0	0.0	0.0	14.8	N/A	N/A	N/A	N/A	N/A	N/A	0.1	N/A

Effluent	*Cl^- (mg/L)*	*NO_3-N (mg/L)*		*Cl^- (mg/L)*	*NO_3-N (mg/L)*
6/13/05	129.7	23.5	11/7/05	117.4	20.5
6/20/05	124.2	19.6	11/14/05	119.4	22.1
6/27/05	119.8	23.1	11/21/05	125.1	22.3
7/5/05	122.3	18.6	11/28/05	118.0	25.7
7/11/05	121.6	18.3	12/5/05	140.1	20.9
7/19/05	113.2	21.2	12/12/05	168.4	25.6
7/25/05	131.0	25.2	12/19/05	165.0	25.8
8/1/05	120.4	16.0	1/3/06	169.0	19.6
8/8/05	114.7	16.7	1/9/06	144.9	22.1
8/15/05	106.5	14.8	1/16/06	143.4	14.7
8/22/05	114.4	14.5	1/23/06	142.0	19.2
8/29/05	120.6	19.2	1/30/06	132.1	14.7
9/12/05	112.9	22.3	2/6/06	147.5	19.2
9/19/05	108.0	18.6	2/13/06	146.4	18.6
9/26/05	99.5	18.6	2/20/06	142.5	22.4
10/3/05	116.7	20.5	2/27/06	145.4	22.0
10/10/05	128.4	18.6	3/6/06	153.2	20.7
10/17/05	120.6	22.7	3/13/06	142.8	17.6
10/24/05	123.3	24.0	3/20/06	141.5	18.0
10/31/05	118.8	23.1	3/27/06	157.8	20.3