

USING THE O AND H STABLE ISOTOPES TO TRACK SOURCES  
OF WATER IN CONSTRUCTED WETLANDS

Randi M. Liescheidt

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May 2012

This study investigates the potential of using O and H isotopes of water to identify sources of water in a series of constructed wetlands in McLean County, IL.

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Agricultural drainage tiles transport excess water in the subsurface to the nearest water body. However, this process also flushes the fields of nitrogen and phosphorous fertilizers that have exceeded crop-uptake rates, affecting downstream water quality, and contributing to a seasonal zone of hypoxia (where dissolved oxygen concentrations are  $<2 \text{ mgL}^{-1}$ ) in the Gulf of Mexico. Installing constructed wetlands can remove/withhold a portion of these agricultural nutrients, via plant uptake and biogeochemical processes.

Groundwater is an essential part of wetland function and success; however, there is a need for reliable methods to demonstrate the effects. This study investigated the potential of O and H isotopes to track sources of water contributing to four different constructed wetlands (agricultural tile fed wetlands and a wetland that receives treated effluent) in McLean County, IL. Tile/effluent and groundwater were hypothesized to have different isotopic compositions since tile water should reflect precipitation (which varies seasonally from isotopic fractionation), while groundwater was expected to be a weighted annual average of precipitation. In this event, a mixing equation can be used to

determine the proportion that each end member (groundwater and tile/effluent water) contributes to the wetland water.

Tile water, shallow groundwater wells, and wetland surface water were sampled ~bi-monthly, from July 2010-June 2011 and analyzed for  $^{18}\text{O}/^{16}\text{O}$ ,  $^2\text{H}/^1\text{H}$ , major anions and  $\text{NH}_4^+$ . Plots of  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  indicated that end member calculations cannot be used for most of the sampling periods, since groundwater and tile water have very similar isotopic compositions, many of the wells experience seasonal variations in compositions, and the wetland cells can undergo evaporative enrichment of heavy isotopes in the dry, warmer months. However, in some events, isotopic results could be used to help delineate sources of water, confirm evaporation is occurring, and on one occasion, estimate which cells were receiving more groundwater input.

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OF WATER IN CONSTRUCTED WETLANDS

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## CHAPTER I

### INTRODUCTION

A conservative estimate of 1 million metric tons of nitrogen (N) is leached from the agricultural fields of the Midwest into the Mississippi River on a yearly basis (Kovacic et al., 2006), most of which is in nitrate ( $\text{NO}_3^-$ ) form (David et al., 1997). Since the 1950s, the use of N and phosphorous has far exceeded uptake rates (Mitsch and Day, 2006), tripling the nitrate flux from the Mississippi River to the Gulf of Mexico (Rabalais et al., 2002). The excess nutrients are rapidly transported via drainage tiles to the nearest water body source, affecting downstream water quality and vulnerable ecosystems. Surface water sources are impacted, as high levels of  $\text{NO}_3^-$ -N lead to excessive algae growth that consume the available oxygen, destroying natural habitats (Krause et al., 2009). Furthermore, these nutrient-rich waters cause eutrophication and contribute to a seasonal zone of hypoxia (a “dead zone,” where dissolved oxygen concentrations are  $<2 \text{ mgL}^{-1}$ ) in the Gulf of Mexico (Rabalais et al., 2002).

Although Illinois only occupies 3% of the Mississippi River watershed (Kovacic et al., 2006), the state is responsible for 15% of the total annual N load (David and Gentry, 2000). Reducing the use of  $\text{NO}_3^-$ -N released at the source would be the quickest solution. However, limiting fertilizer use could lead to reductions of crop yields, an important reason to initially investigate other methods of mitigation.

Constructed wetlands can be installed to help remove or withhold a portion of  $\text{NO}_3^-$ -N (as well as other nutrients) near the source via plant uptake and biogeochemical processes (Mitsch et al., 2001; Haberl et al., 2003). Tile water can be redirected to enter constructed wetland cells on the path to a stream or larger body of water, providing wetland plants and processes the time to uptake or transform some of the agricultural nutrients. It is estimated that  $\text{NO}_3^-$  concentrations from tile water can be reduced by averages as much as ~50% as the nutrient rich waters flow through the wetlands, primarily through denitrification (the microbial activated breakdown of nitrogen) (Xue et al., 1999; Chavan et al., 2008).

Since it is important to minimize the reduction of productive farmland, determining the area required to effectively remove nutrients is necessary. This is a vital step to demonstrate wetland manageability, in the hopes that private farmers will consider installing their own wetlands in the future.

To do so, many studies use mass balance calculations to estimate the percent concentration reductions of agricultural nutrients (Kovacic et al., 2006). Then, further estimates of the size requirement for wetlands to successfully “treat” the watershed by a goal percentage have been made. However, these studies commonly fail to incorporate the effects of groundwater, and hence dilution because  $\text{NO}_3^-$  concentrations are commonly low in groundwater due to geochemically reducing conditions that result in denitrification. Therefore, if groundwater is a source of water in a wetland, the mixing of nutrient rich tile water with less concentrated groundwater will dilute the nutrient concentrations. As a result, if groundwater interaction is abundant in a wetland, previous estimates of nutrient removal may be erroneous. Therefore, it is necessary to not only



consider, but attempt to quantify and estimate the volume of groundwater interacting within a constructed wetland. It is also important to understand the amount of groundwater interaction since groundwater can help maintain wet conditions in drier periods (when tiles stop flowing), buffer wetland water temperatures, and provide nutrients essential for biological activity.

However, groundwater flow and interaction with wetlands is poorly understood, and traditional methods of aquifer tests have not been successful at determining the importance of groundwater in wetland function (Hunt et al., 1999). As a result, there is need to investigate the use of non-traditional methods to define wetland hydrology. It is possible that the stable isotopes of water can help describe interactions and sources of water. In fact, isotopes have been used in the past to estimate the origins (Matheney and Gerla, 1996) and the extent of mixing of surface water and groundwater (Katz, 2010). This method can be applied if the local groundwater and surface water have different isotopic signatures.

This study focuses on using stable isotopes of water (oxygen and hydrogen) to estimate the fraction of groundwater, as opposed to tile water, that is contributing to the composition of a series of different constructed wetlands in central Illinois. When possible, results are used to help evaluate the interaction of groundwater with constructed wetlands, and may be of use in future estimations of nutrient removal and wetland size requirements.

## **Wetland hydrology**

A mere 4.5% of the pre-agricultural natural wetlands of Illinois exist today (Kovacic et al., 2006). Originally drained to increase agricultural land area, newly installed man-made versions of these natural filtrations systems can be used to mitigate agricultural chemical waste. These constructed wetlands are generally built by excavating soil to form basins. The removed soil is then deposited around the perimeter of the basin, forming berms. In many cases, tile drainage systems are rerouted so that water is intercepted by the constructed wetland before entering a larger body of water. Usually requiring a high water table near or at the ground surface in order to remain active year round (Cowardin et al., 1979), these wetlands are sustainable, have low operating costs and maintenance, and have proven to successfully treat domestic and industrial wastewater and a number of other contaminants as well (Haberl et al., 2003).

However, the poor understanding of groundwater interaction with constructed wetlands hinders the thorough conception and quantification of wetland processes (Hunt et al., 1999), water budget, and overall wetland restoration and construction design. For instance, the interaction of groundwater with a different chemistry than wetland surface water, may greatly affect the biogeochemical processes of a wetland (Howes et al., 1996). In addition, since groundwater affects pore-water chemistry and root zone temperature, the site specific hydrology of a wetland is a direct factor of what type of vegetation will flourish (Hunt et al., 1999). In fact, since groundwater discharge can vary within a single study area, Hunt et al. (1999) suggests that until hydrology is easier to characterize and understand, the use of costly wetland plants should be avoided.

Previous studies have also demonstrated that constructed wetlands are capable of altering the hydrology of an area. In a study conducted in Illinois (Hensel and Miller, 1991), a newly installed constructed wetland altered the groundwater table elevation in multiple well locations. This was an effect of variable recharge rates into the wetland (a factor of precipitation) and occasional seepage back into the groundwater system.

Kovacic et al. (2006) recommends that before large-scale created wetland projects are funded and constructed, critical questions regarding wetland function and design need to be addressed to ensure the success of wetlands. Therefore, even though the importance of incorporating groundwater into constructed wetland hydrology is acknowledged, there is a need for successful methods to demonstrate the possible physical and chemical effects (Hunt et al., 1999).

### **Use of isotopes**

Stable isotopes of water can provide insight to the hydrologic system of a constructed wetland by acting as a tracer. In fact, isotopes of water (O and H) are ideal tracers for hydrological studies since they are a part of the water molecule itself ( $\text{H}_2^{18}\text{O}$  and  $^1\text{H}^2\text{H}^{16}\text{O}$ ), and vary temporally and spatially (Gibson et al., 2005). This variation is caused by isotopic fractionation of water, which is the separation of isotopes by mass, due to a variance in reaction rates when water undergoes a phase change (Clark and Fritz, 1997).

When water evaporates from ocean waters (the source of most precipitation events), water molecules containing lighter isotopes ( $^1\text{H}$  and  $^{16}\text{O}$ ) are evaporated more easily and in more abundance, leaving an excess of the heavier isotopes ( $^2\text{H}$  and  $^{18}\text{O}$ ) behind (Clark and Fritz, 1997). Then, the water vapor that is isotopically lighter than the

ocean water left behind begins to migrate towards one of the poles. With a drop in temperature, resulting in condensation, heavier isotopes condense first and the leading precipitation event will be more enriched in  $^{18}\text{O}/^2\text{H}$  than  $^{16}\text{O}/^1\text{H}$ , while each subsequent rain event will be composed of smaller amounts of heavier isotopes. The further inland an air mass travels, the more isotopically depleted in heavy isotopes it becomes. This distillation process that occurs via natural air currents and precipitation events is called the Rayleigh fractionation.

The ratios of  $^{18}\text{O}/^2\text{H}$  and  $^{16}\text{O}/^1\text{H}$  are defined by their per mil (‰) variance from the VSMOW (Vienna Standard Mean Ocean Water), the average bulk isotopic composition of ocean water and the international standard where  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are considered equal to 0‰ (Clark and Fritz, 1997). The difference is represented by the  $\delta$  symbol, where:  $\delta^{18}\text{O}$  or  $\delta^2\text{H} = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000$  VSMOW, and  $R = ^{18}\text{O}/^{16}\text{O}$  or  $^2\text{H}/^1\text{H}$  ratio.

Reflections of the rainout process, colder climates are generally depleted in heavy isotopes (Clark and Fritz, 1997). Therefore, there is a trend of increasing depletion of  $\delta^{18}\text{O}$  isotopes with increases in latitudes, resulting in  $\delta^{18}\text{O}$  values that are negative compared to the standard.

The relationship of  $^{18}\text{O}$  and  $^2\text{H}$  of fresh waters correlate on a global scale (Clark and Fritz, 1997), represented by a global meteoric water line (GMWL), a linear relationship expressed by the equation:  $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ . More specific local isotopic ratios will usually plot linearly on a  $\delta^{18}\text{O}$  ‰ VSMOW vs.  $\delta^2\text{H}$  ‰ VSMOW graph as well. Local meteoric water lines (LMWLs) can be quite different than the GMWL, and a best-

fit line of amount-weighted monthly precipitation events can provide a trend that will reflect local details such as evaporation amounts and seasonal changes in origins of water vapor.

In Illinois, during the warmer seasons, precipitation originates from the tropical air masses of the Gulf of Mexico. This water is closer to the equator, and hence more isotopically enriched in the heavy isotopes. However, the opposite is true during the colder winter months as most precipitation events originate from the polar air masses that are depleted of heavy isotopes. In addition, evaporation during summer months may result in increases in  $^{18}\text{O}/^2\text{H}$  in surface water, since molecules with lighter isotopes evaporate easier and in more abundance (Clark and Fritz, 1997).

In general, the surface water isotopic signatures of a freshwater body will be a reflection of meteoric infiltration, evaporation, and contributions of groundwater, and therefore is subject to frequent change (Clark and Fritz, 1997). On the other hand, groundwater commonly represents close to a weighted average of annual recharge, meaning seasonal variations will be smoothed out by groundwater mixing along the flow-path. Therefore, ideally, surface water and groundwater will have different isotopic signatures.

As a result, looking at the stable isotopes of groundwater can help clarify wetland hydrogeology, including groundwater flow and sources. In the past, stable isotopes have been used to quantify groundwater inflow (Hunt et al., 1996) and to evaluate the residence time of groundwater (Soulsby et al., 2000) and the seasonal fluctuations of wetland water (Clay et al., 2004). Isotopes have also been used to determine different sources of groundwater entering a coastal wetland (Huddart et al., 1999).

Using isotopes of water can provide a representation of a groundwater system over a period of time, rather than a point in time. It is possible however, that the isotopic composition of groundwater may be biased due to seasonal differences in recharge rates. Regardless, there is still a strong probability that groundwater, which should be a weighted average of annual precipitation, will have a different isotopic signature than tile water that is quickly transported to the wetland after precipitation events. Even if the isotopic composition of a groundwater system is skewed toward spring or fall precipitation signatures (when recharge rates are generally highest), this precipitation tends to be isotopically intermediate compared to summer and winter precipitation, and hence will have a composition that is a close representation of the mean annual precipitation. As a result, it is expected that precipitation events (and therefore tile drainage) will have compositions that are different than the groundwater.

### **Research question**

The goals of this study were to investigate the potential of using O and H isotopes to track sources of water in constructed wetlands and to seek to determine the proportion that each source contributes to the wetland water. I hypothesized that the groundwater would have a significantly different isotopic composition compared to tile water, a requirement to utilize this method. In the event that this was true, then the following hypothesis would also be tested:

Isotopes of groundwater and tile water can be used to evaluate fractions of water in constructed wetlands from these two sources.

Illinois experiences seasonal variations in air mass temperature and origin, therefore precipitation events should vary isotopically throughout the year. The tile water

that enters the constructed wetlands should reflect these seasonal variations, whereas groundwater interacting with the wetlands should have isotopic signatures approximately equal to a weighted average of yearly precipitation.

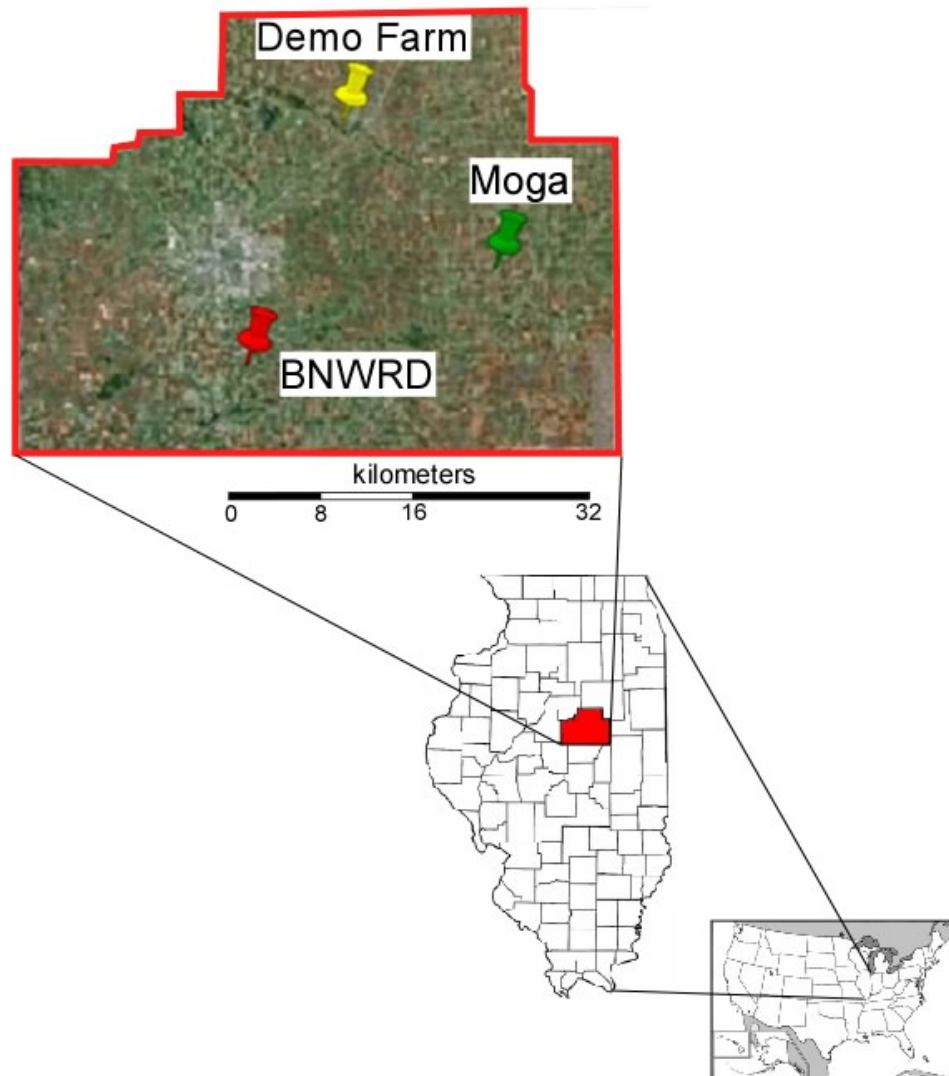
Samples of tile water entering the wetland and groundwater wells located up-gradient of the wetlands should have different isotopic signatures, and when displayed on an x-y scatter plot ( $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$ ) should have visibly different plot locations on the diagram. If so, the composition of the water leaving the wetland can be used to determine the relative contributions of each source to the wetland water.

This research will contribute to the understanding of wetland hydrology, which is directly related to wetland function and success. For instance, groundwater has a different ionic composition than surface water (Hunt et al., 1997), which can greatly influence nutrient removal processes. Therefore, understanding the interaction of groundwater in a wetland will help future studies involving plant communities and wetland nutrients as well. In addition, if groundwater contribution is significant, past estimates of  $\text{NO}_3^-$ -N removal efficiency of wetlands may have to be reevaluated in order to incorporate the effects of groundwater dilution, resulting in a more accurate estimate of the area of valuable farmland required to mitigate released  $\text{NO}_3^-$ .

### **Study area**

This study focuses on four different constructed wetlands in McLean County, IL (Fig. 1). These wetlands were installed by excavating soil to form basins, and then depositing the removed soil around the perimeter to form berms. Three of the five constructed wetlands, the Demonstration Farm and Moga, are tile fed wetlands. Agricultural drainage tile has been redirected to flow into the wetlands, the volume of

which is monitored constantly via weirs. The fourth wetland is down-gradient of the Bloomington-Normal Water Reclamation District (BNWRD) waste-water treatment plant. This wetland was constructed to help mitigate nitrate and phosphate levels in the portion of discharged effluent it receives.

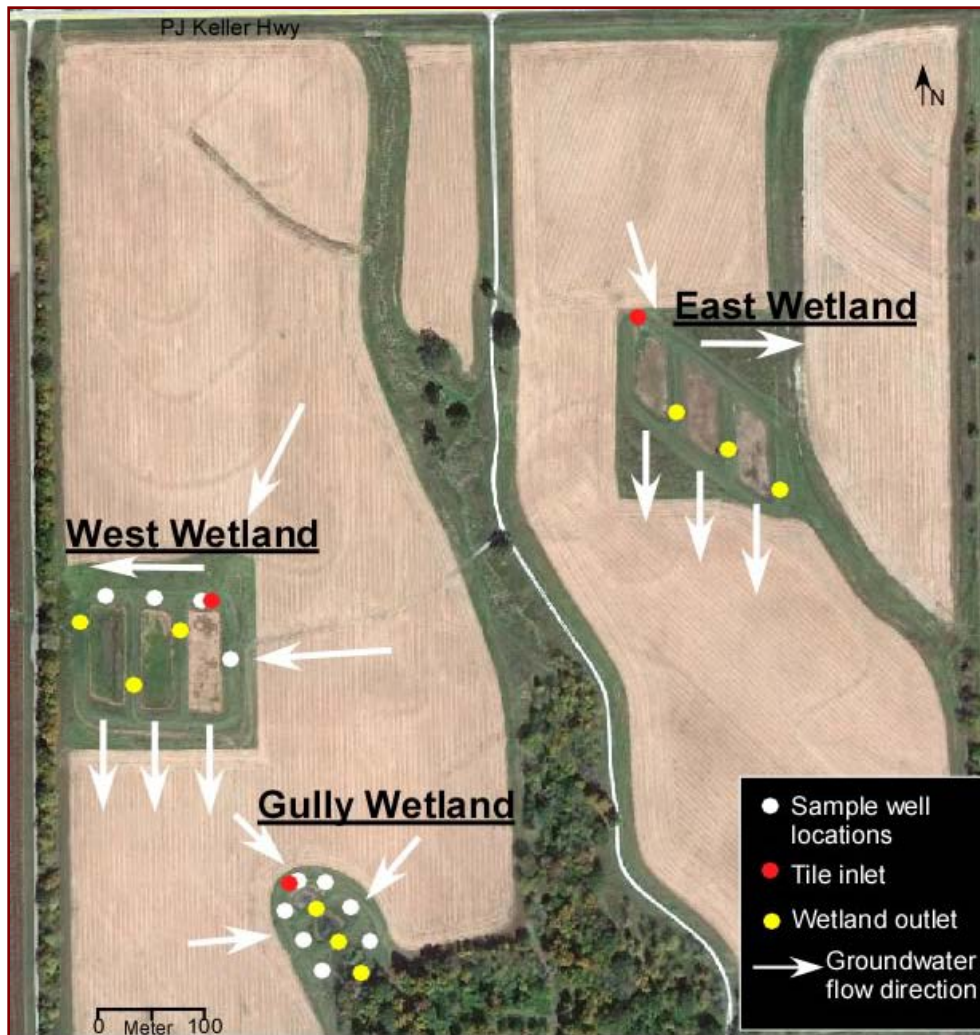


**Fig. 1** Locations of the study sites in McLean County, IL. The Demonstration Farm and Moga wetlands are fed agricultural tile drainage, while BNWRD receives a portion of the treated effluent from a waste water treatment plant



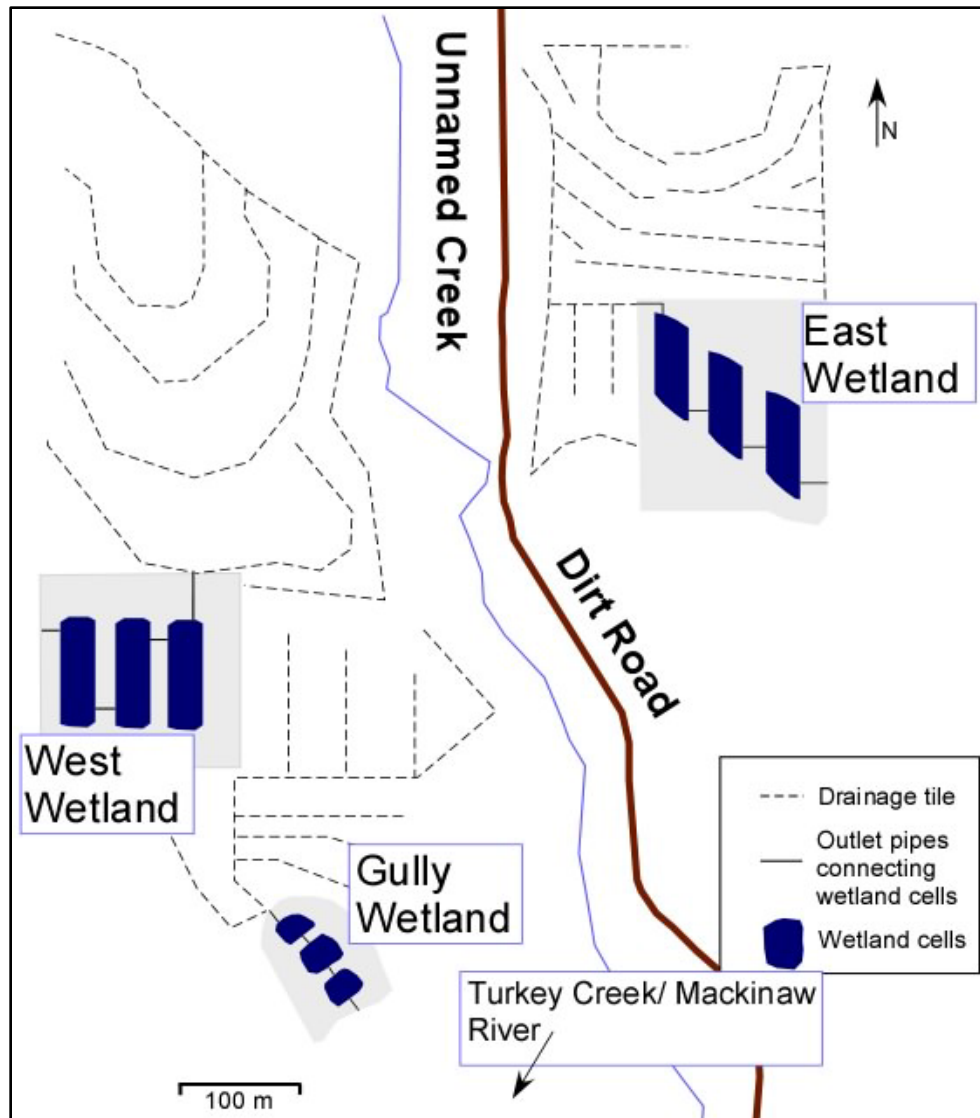
### *The Demonstration Farm*

The first study area is a demonstration farm in Lexington, Illinois. Located approximately one mile west of the I-55 Lexington Exit (178) and directly South of PJ Keller Highway, there are a series of three constructed wetlands located on the Franklin family's 250 acre farm (Fig. 2). These wetlands were completed in fall 2005 and, in conjunction with The Nature Conservancy, conservation farming techniques and nutrient removal efforts (constructed wetlands, grass waterways, and native plant restoration) are implemented in an attempt to study their potential of nutrient removal from agricultural tile drainage. The wetlands are located on the El Paso Moraine of the Wedron Group, a glacial diamicton, deposited during the Wisconsinan Glacial Episode (20,000-10,000 years ago).



**Fig. 2** Aerial view of the wetlands, well locations, and groundwater flow directions at the Demonstration Farm

Each set of wetlands were designed to evaluate the minimum area required per area of watershed to successfully remove nutrients (in particular nitrate) from agricultural fertilizer application. Drainage tile water has been redirected to feed into the wetlands (Fig. 3). The three experimental wetlands: Gully, East, and West, are each composed of three wetland cells that represent 3, 6, and 9% of the draining area of each wetland series.



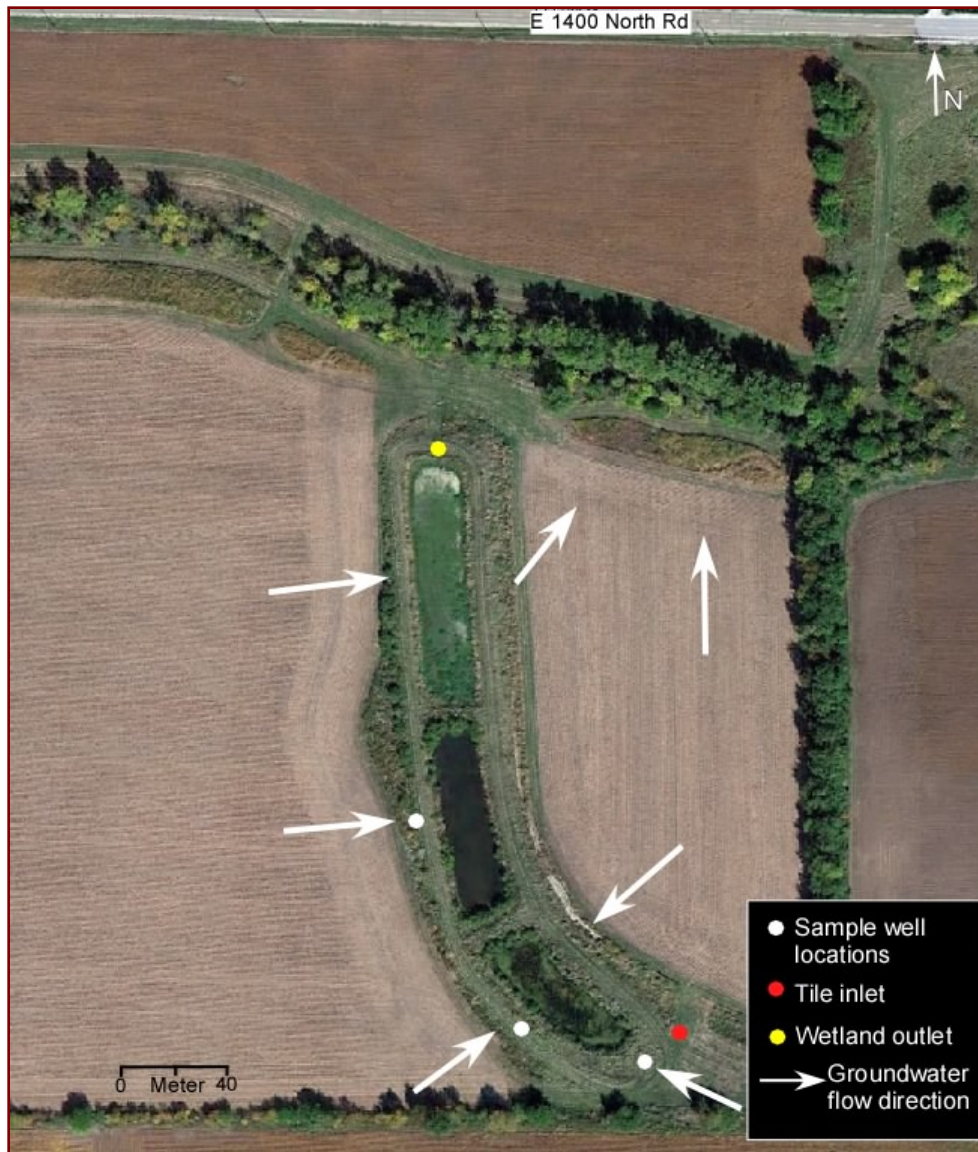
**Fig. 3** Overview of the Demonstration Farm showing the tile routing into the West, Gully, and East wetlands

The inflow and outflow of each wetland cell are monitored by weirs and pressure transducers. ISCO portable samplers collect samples for nutrients on a flow weighted basis, and are used to determine the reduction of  $\text{NO}_3^-$  in water leaving the wetlands verses entering. However, water retention times and methods of nutrient removal are not included in these data.

### *Moga Wetlands*

The Moga wetlands (Fig. 4) are also a project overseen by The Nature Conservancy. Located south of County Rd 1400 N (IL 9E) and between County Rd 3300 and 3400 E in eastern McLean County, near Colfax, Illinois, the wetland is composed of three cells. Each cell occupies approximately 0.7 acres, and is an average of 0.5 to 0.8 m deep. The deepest part of the cells is on the downstream end. It is estimated that tile drainage from approximately 200 acres of farmland enters the wetlands via a 38 cm diameter inlet pipe. Quaternary maps indicate that the wetlands reside on glacial diamicton of the Wedron Group, deposited during the Wisconsin Glaciation (Warner, 1998).

The cells of this wetland were constructed by digging a 3.0-3.6 m trench and packing it with clay. The berms were then built on top of the trench. This process was utilized to reduce seepage under the berms. There are three wells at the wetland. The two southern most cells appear to remain wet year round. As a result, groundwater wells were installed around these two cells.

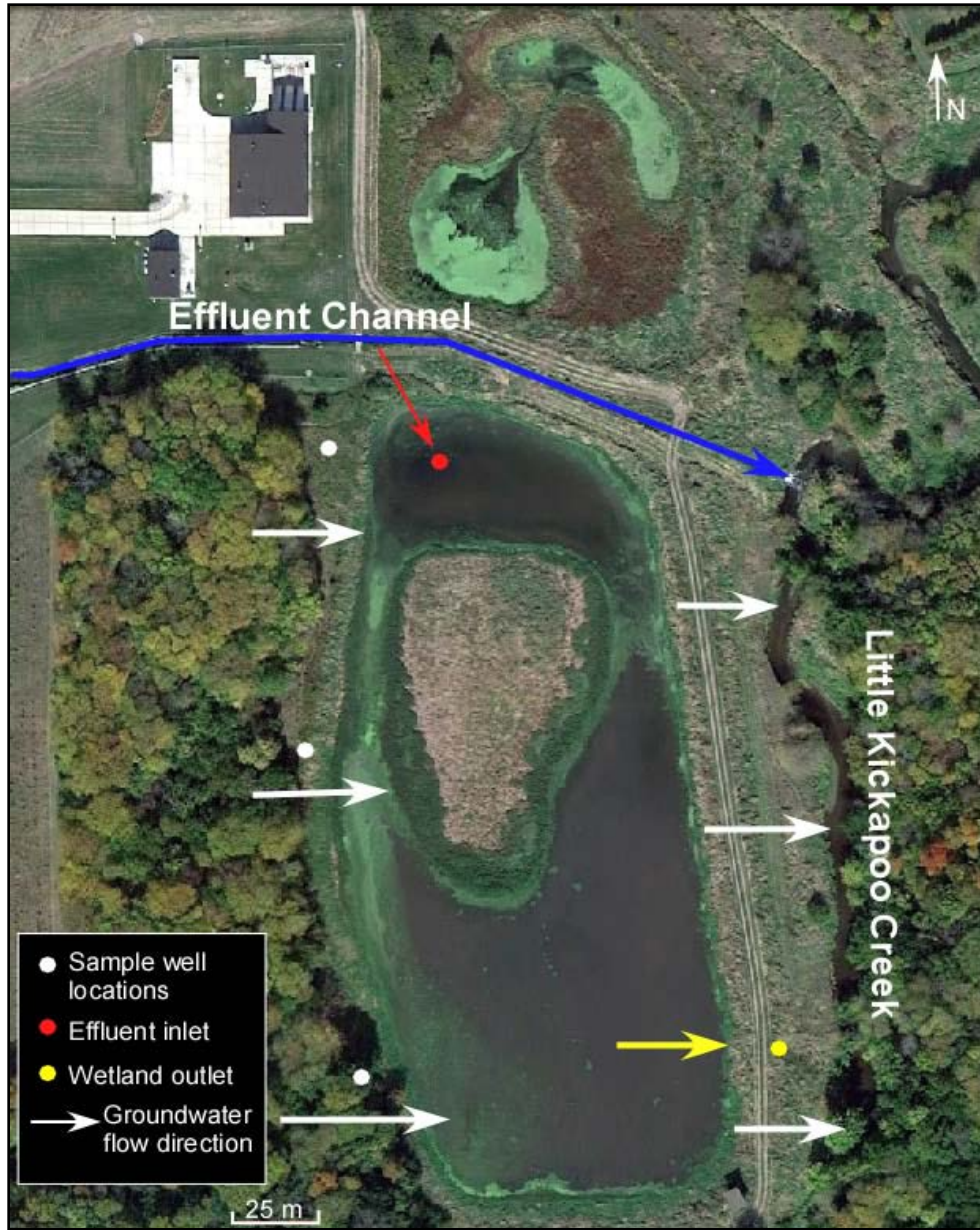


**Fig. 4** Aerial view of Moga wetland, where the inlet enters Cell 1 (southern-most cell) and exits Cell 3 (northern-most cell) via the outlet

### *BNWRD Wetlands*

The final set of constructed wetlands is located in Randolph, Illinois, just south of E 700 North Rd. These two wetlands were constructed at the Bloomington-Normal Wastewater Reclamation District (BNWRD) municipal waste water treatment plant.

Treated effluent is discharged east of the plant, most of which is directed into Little Kickapoo Creek. However, some of the effluent flows into the wetlands (Fig.5). The wetland resides on fine-grained Cahokia Alluvium deposited on coarse-grained Pleistocene glacial outwash (Henry Formation) of the Wisconsinan Glaciation. There are currently a series of 11 wells in and around the wetland that are used to monitor the groundwater chemistry and effluent nutrient removal.



**Fig. 5** Aerial view of the BNWRD wetland

CHAPTER II  
USING THE O AND H STABLE ISOTOPES TO TRACK SOURCES  
OF WATER IN CONSTRUCTED WETLANDS

**Abstract**

Key Words: stable isotopes, oxygen isotopes, hydrogen isotopes, constructed wetland, wetland, ground water, source of water

This study investigated the potential of O and H isotopes to track sources of water contributing to four different constructed wetlands (agricultural tile fed wetlands and a wetland that receives treated effluent) in McLean County, IL. Tile/effluent and groundwater were hypothesized to have different isotopic compositions since tile water should reflect precipitation (which varies seasonally due to isotopic fractionation), while groundwater was expected to be a weighted annual average of precipitation. In this event, a mixing equation can be used to determine the proportion that each end member (groundwater and tile/effluent) contributes to the wetland water. To test the hypothesis, tile water, shallow groundwater wells, and wetland surface water were sampled approximately once every two months, from July 2010-June 2011 and analyzed for  $^{18}\text{O}/^{16}\text{O}$ ,  $^2\text{H}/^1\text{H}$ , major anions and  $\text{NH}_4^+$ . Plots of  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  indicated that end member calculations cannot be used for most of the sampling periods, since groundwater and tile water have very similar isotopic compositions, many of the wells experience seasonal



variations in compositions, and the wetland cells can undergo evaporative enrichment of heavy isotopes in the dry, warmer months. However, isotopic results could be used to help delineate sources of water (ex. West wetland data indicated primary input from WMW-1, which was confirmed by the groundwater contour map), confirming evaporation is occurring (and as early as March 2011 at Gully) and that groundwater input is not abundant enough to completely eliminate this effect, but that slight dilution effects (Gully Cells 2 and 3 in October 2010) can be used to determine which cells are receiving more groundwater input.

### **Introduction**

Illinois only occupies 3% of the Mississippi River watershed (Kovacic et al., 2006), yet it is estimated that the state is responsible for 15% of the total annual nitrogen (N) load (David and Gentry, 2000). Since the 1950s, the use of N and phosphorus has far exceeded crop uptake rates (Mitsch and Day, 2006), tripling the nitrate flux from the Mississippi River to the Gulf of Mexico (Rabalais et al., 2002). These excess nutrients are quickly transported via drainage tiles to nearest water bodies, affecting downstream water quality and vulnerable ecosystems. In addition, these nutrient-rich surface waters cause eutrophication and a seasonal zone of hypoxia (a “dead zone,” where dissolved oxygen concentrations are  $<2\text{mgL}^{-1}$ ) in the Gulf of Mexico (Rabalais et al., 2002).

Constructed wetlands can be used to help remove and/or withhold some of the  $\text{NO}_3^-$ -N (as well as other nutrients) near the source (Mitsch et al., 2001). Constructed wetlands act as holding cells for tile water that is commonly redirected to enter the wetland on the path to a larger water body, providing wetland plants and biogeochemical

processes (primarily denitrification: the microbial activated breakdown of N) the time to utilize or transform agricultural nutrients from tile water, reducing  $\text{NO}_3^-$  concentrations by as much as nearly 50% (Xue et al., 1999; Chaven et al., 2008). Determining the minimum size requirement of a wetland (which occupies valuable farmland) to effectively remove nutrients requires an understanding of groundwater interaction.

In the past, estimated percent concentration reductions of agricultural nutrients, derived from traditional mass balance calculations (Kovacic et al., 2006) have been used to estimate a size requirement for wetlands to successfully “treat” the watershed by a certain goal percentage. However, these studies often do not incorporate the effects of groundwater, and hence dilution. Groundwater typically has less  $\text{NO}_3^-$  concentrations than tile water due to geochemically reducing conditions that result in denitrification. As a result, if groundwater interaction is abundant in a wetland, previous estimates of nutrient removal may be inaccurate.

Groundwater interactions with constructed wetlands can help maintain wet conditions in drier periods (when tiles stop flowing), buffer wetland temperatures, provide nutrients essential for biological activity, and determine what type of vegetation will flourish (Hunt et al., 1999), adding to the importance of understanding the groundwater dynamics. In fact, Kovacic et al., (2006) recommends that before large-scale created wetland projects are funded and constructed, critical questions regarding wetland function and design need to be addressed to assure their success.

Stable isotopes of water (O and H) have the potential of serving as tracers to quantify interactions and sources of water entering constructed wetlands. Isotopes of water are ideal tracers for hydrological studies since they are part of the water molecule

itself ( $\text{H}_2^{18}\text{O}$  and  $^1\text{H}^2\text{H}^{16}\text{O}$ ) and vary temporally and spatially (Gibson et al., 2005). As a result of these variations, stable isotopes of water have been used to estimate the origins (Matheney and Gerla, 1996), to calculate residence times (Soulsby et al., 2000), to determine seasonal variations of wetlands (Clay et al., 2004), and to define the extent of mixing of surface water and groundwater (Katz, 2010).

Based on the framework of isotopes, the wetland surface water in this study was predicted to be a reflection of meteoric infiltration, evaporation, groundwater and tile water, and therefore subject to frequent change (Clark and Fritz, 1997). It was also expected that the groundwater and tile water have significantly different isotopic compositions, since the composition of precipitation is dependent on the origin of the air mass, while groundwater is a weighted average of annual precipitation events (Clark and Fritz, 1997). If true, the composition of the water leaving the wetland could be used to determine the relative contributions of each source (tile vs. groundwater) to the wetland water. If groundwater interaction proves to be abundant, past estimates of wetland  $\text{NO}_3^-$ -N removal efficiency may require reevaluation to incorporate the effects of groundwater dilution.

This study focused on using the stable O and H isotopes of water to estimate the fraction of groundwater, as opposed to tile water, that is contributing to four different constructed wetlands in McLean County, Illinois. The use of isotopes in describing hydrological conditions was explored as a substitute of extensive and/or expensive sampling and analyses. The overall objectives of this study were: (1) to attempt to use the O and H isotopes to determine the hydrology of four constructed wetlands, (2) to compare the O and H isotopic signatures of the wetlands, and (3) in the circumstance that

the isotopic composition of groundwater, tile water (or effluent) and wetland waters were significantly different, use end-member calculations to estimate the proportion contribution to wetland water, with the equation:

$$\delta_{\text{wetland water}} = x \cdot \delta_{\text{ground water}} + (1-x) \cdot \delta_{\text{tile water}}$$

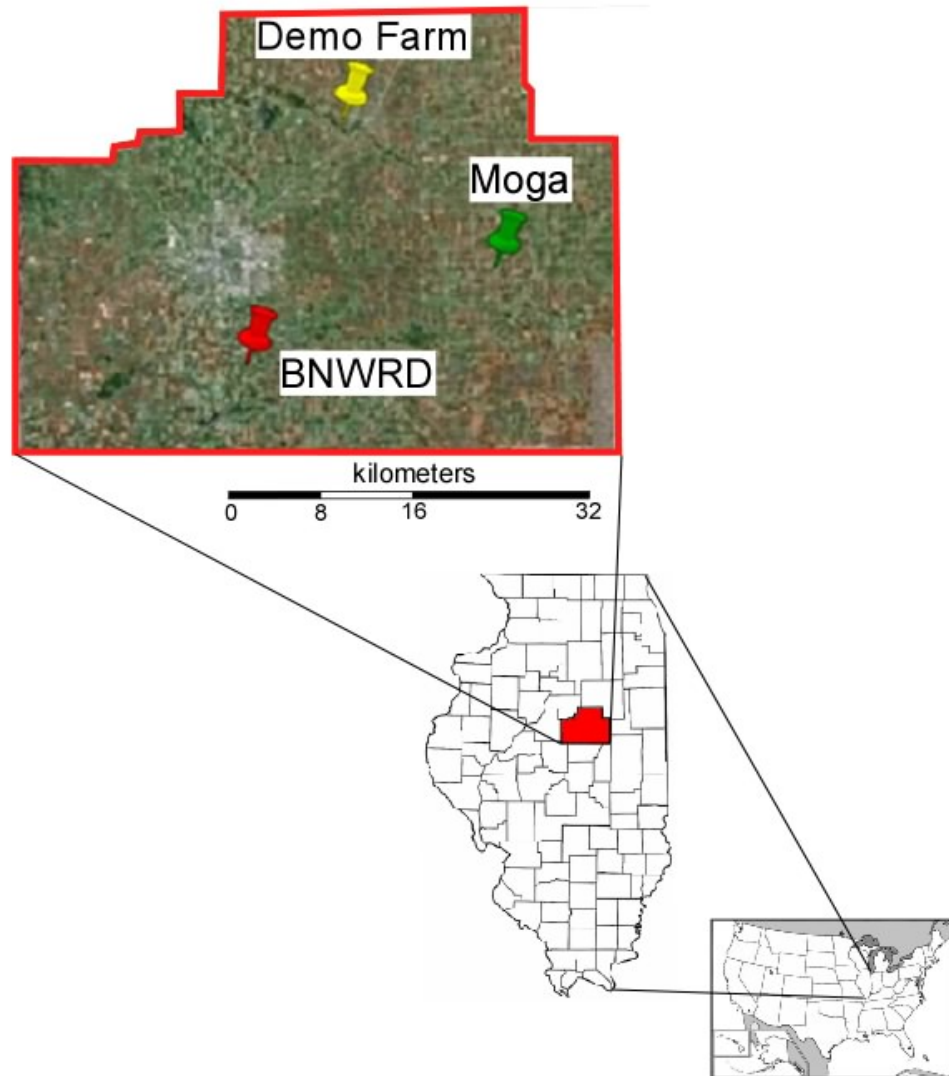
The proportion variable in the equation is represented by “x,” and  $\delta$  is the isotopic composition. The objectives were reached by coupling anion geochemistry of the waters ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ -N, and  $SO_4^{2-}$ ) and  $NH_4^+$ , with stable isotopes (O and H).

This research will contribute to the understanding of wetland hydrology, which is directly related to wetland function and success. For instance, groundwater has a different ionic composition than surface water (Hunt et al., 1997), which can greatly influence nutrient removal processes. Therefore, understanding the interaction of groundwater in a wetland will help future studies involving plant communities and wetland nutrients. In addition, the results of this study may be of future use to help calculate a more accurate estimate of the area of valuable farmland required to mitigate released  $NO_3^-$ .

### **Site descriptions**

This study focuses on four different constructed wetlands in McLean County, IL (Fig. 6). These wetlands were installed by excavating soil to form basins, and then depositing the removed soil around the perimeter to form berms. Three of the five constructed wetlands, the Demonstration Farm and Moga, are tile fed wetlands. Agricultural drainage tile has been redirected to flow into the wetlands, the volume of which is monitored constantly via weirs. The fourth wetland is down-gradient of the Bloomington-Normal Water Reclamation District (BNWRD) waste-water treatment

plant. This wetland was constructed to help mitigate nitrate and phosphate levels in the portion of discharged effluent it receives.



**Fig. 6** Locations of the study wetlands in McLean County, IL

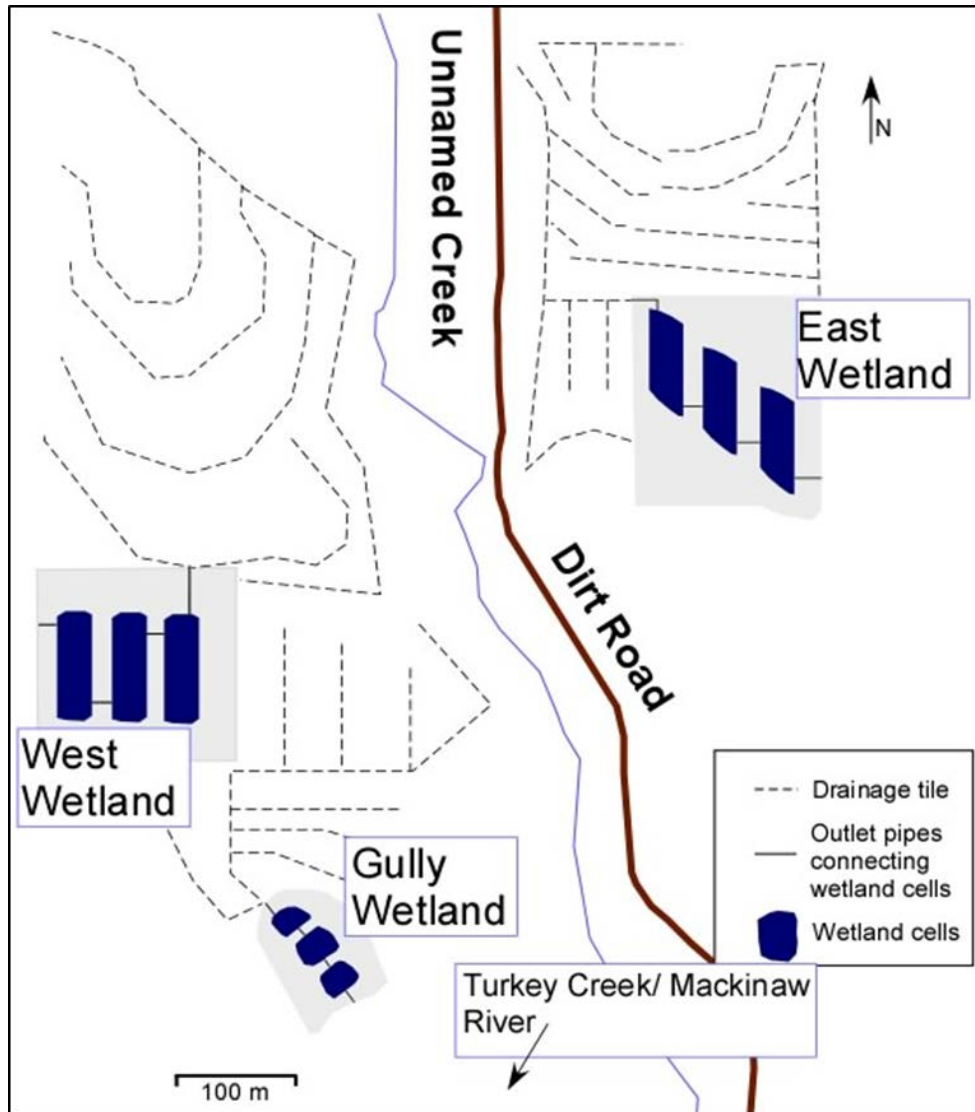
***The Demonstration Farm***

The first series of wetlands (Gully and West Wetlands) are part of a 250 acre demonstration farm, where in conjunction with The Nature Conservancy, the Franklin

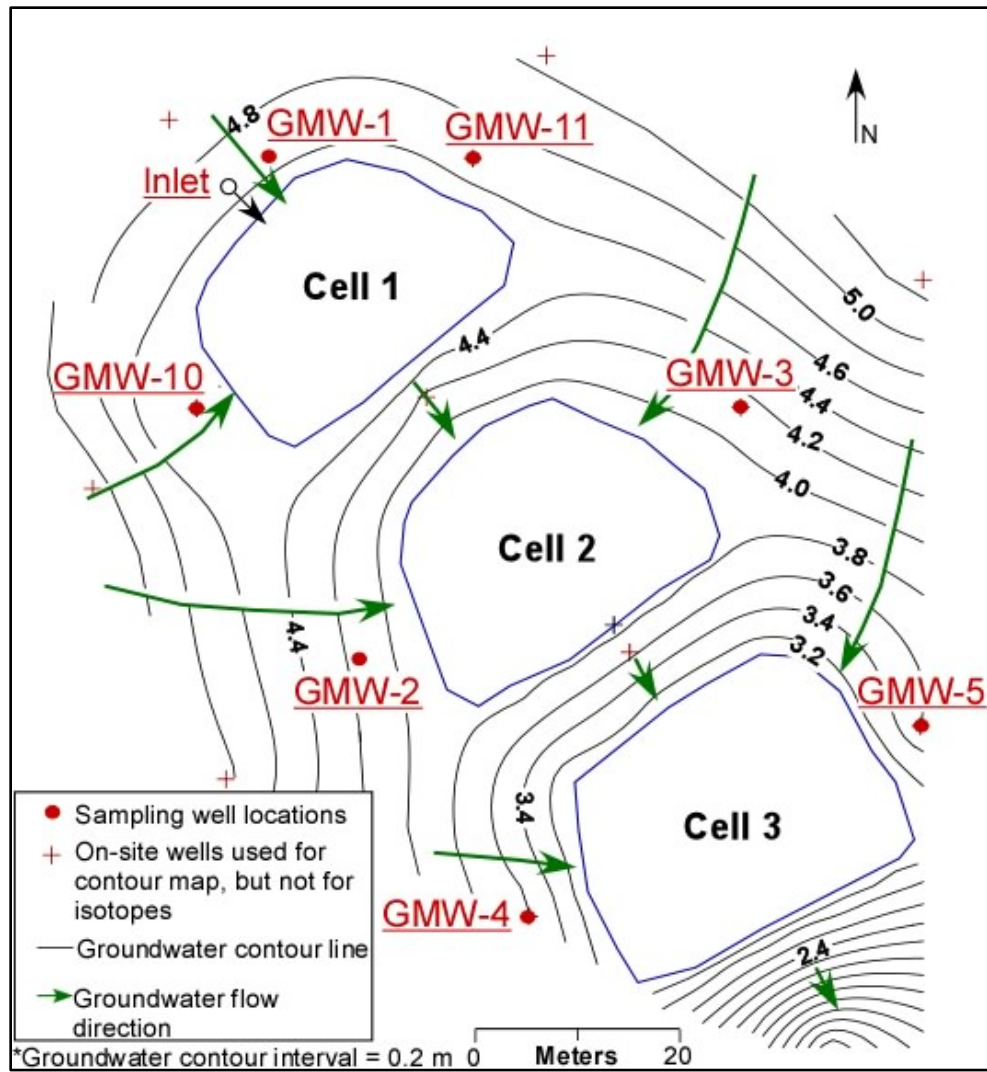
Family practices conservation farming and agricultural nutrient removal techniques using constructed wetlands, grass waterways and native plant restoration. Located on the El Paso Glacial Moraine of the Wedron Group, a glacial diamicton, deposited during the Wisconsin Glacial Episode, agricultural drainage tiles from corn and soy bean fields were rerouted to flow directly into the wetlands, the volume of which is monitored continuously via weirs.

Each set of wetlands was designed to evaluate the minimum area required per area of watershed to successfully remove nutrients (in particular  $\text{NO}_3^-$ ) from agricultural field fertilizer use. There are three experimental wetlands, each being composed of three cells that represent 3, 6, and 9% of the surface area draining into each wetland series (Fig. 7): Gully (Fig. 8), West (Fig. 9), and East (not used in this study) on site.

Gully wetland has 14 water-table monitoring wells located up-gradient of the wetland cells and in the berms between cells (seven of which were sampled for this study and shown on Fig. 8). At West wetland, there is a water-table well located to the north, south, east and west of each cell.

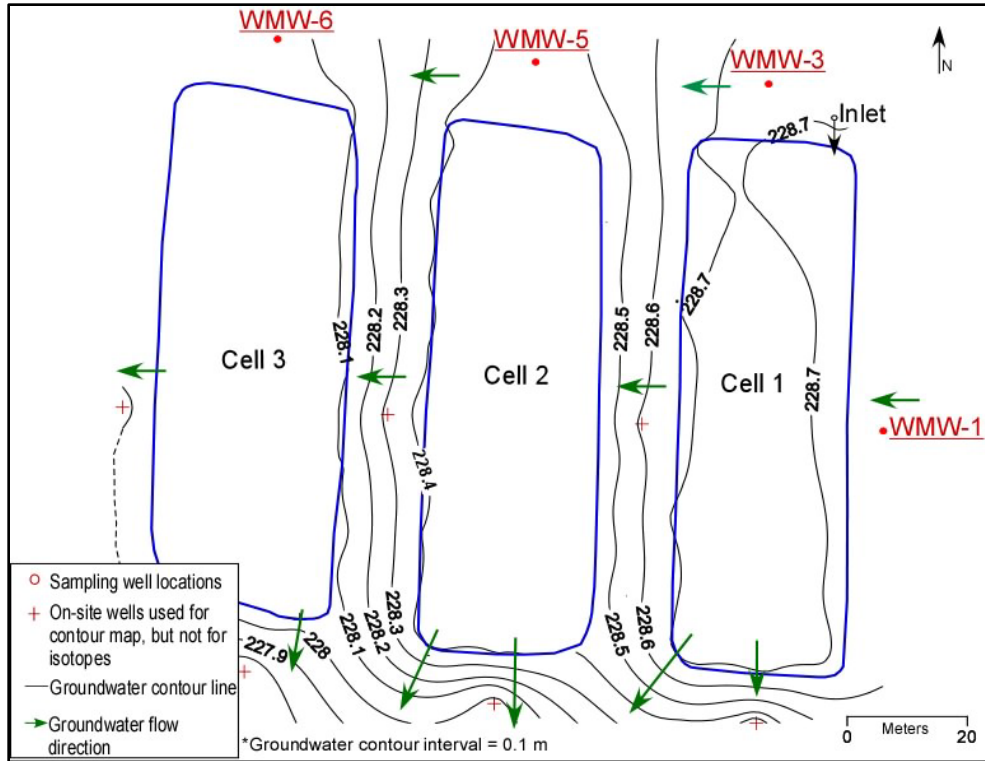


**Fig. 7** Overview of the Demonstration Farm study site



**Fig. 8** Water table contour map of Gully wetland (located at the Demonstration Farm). The map indicates that groundwater is entering the wetland cells from all up-gradient directions, and discharging to the south of the wetland cells



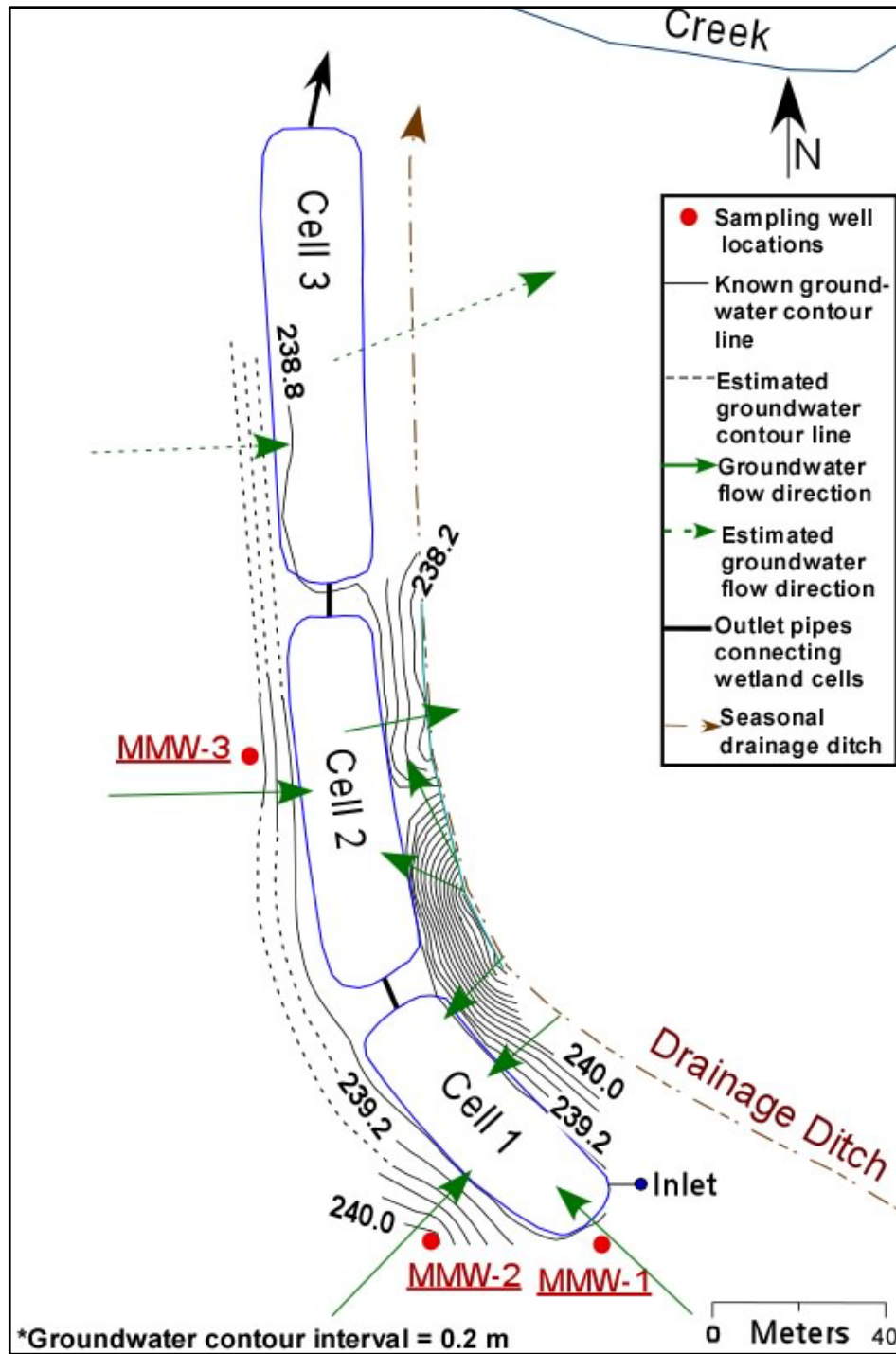


**Fig. 9** Groundwater contour map of West Wetland based on June 2011 water levels. Results demonstrate that the wetland cells only receive groundwater from the east, and waters continue to flow to the east and/or south of the wetland

### *Moga Wetlands*

The Moga wetland (Fig. 10) is also a project overseen by The Nature Conservancy. Located south of County Rd 1400 N (IL 9E) and between County Rd 3300 and 3400 E, near Colfax, Illinois, the wetland is composed of three cells, each occupying approximately 0.7 acres. It is estimated that tile drainage from approximately 200 acres of farmland enters the wetlands via a 38 cm diameter inlet pipe. Quaternary maps indicate that the wetland resides on glacial diamicton of the Wedron Group, deposited during the Wisconsin Glaciation (Warner, 1998). The two southern most cells (Cell 2

and 3) appear to remain wet year round. As a result, groundwater wells were installed around these two cells.

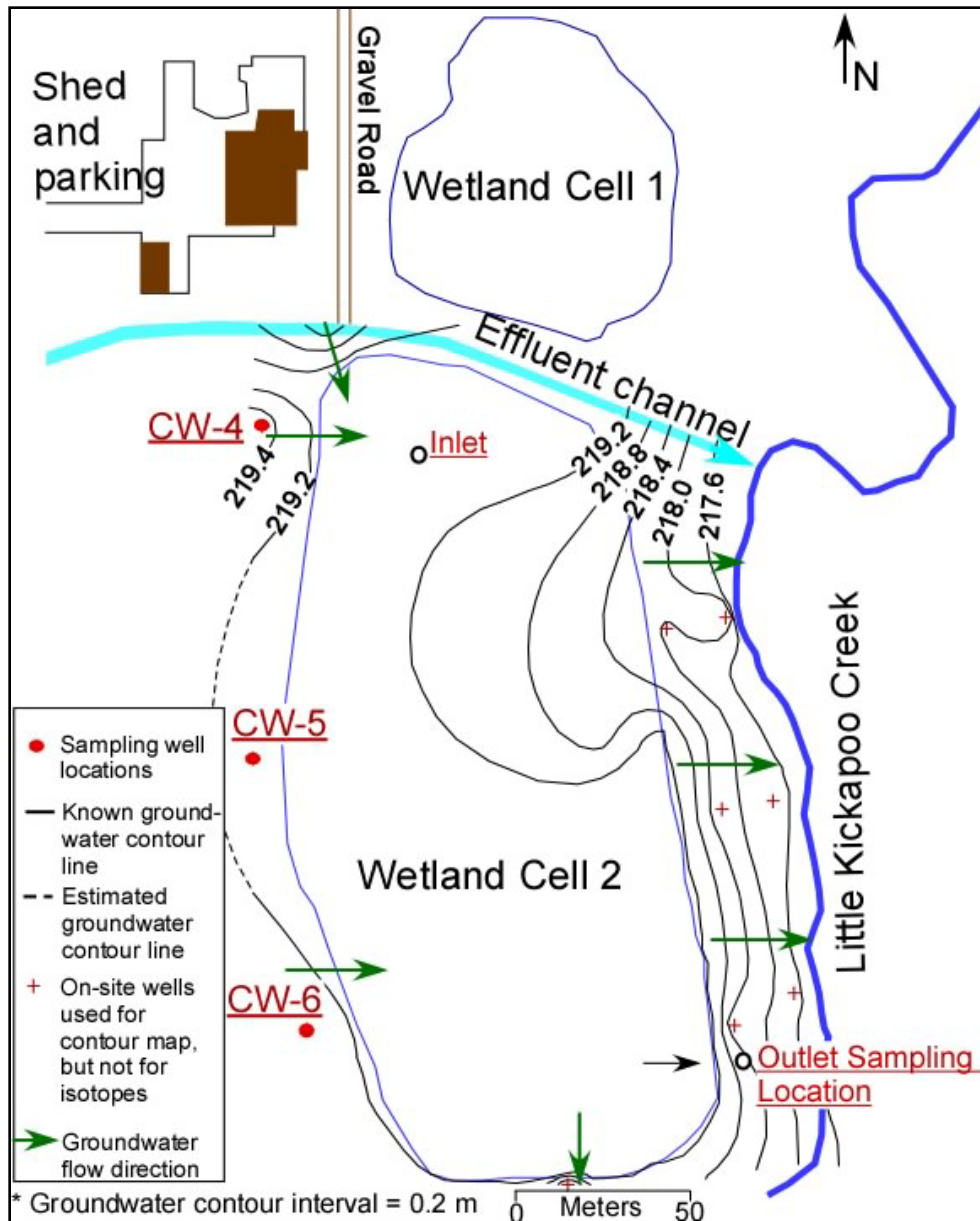


**Fig. 10** Overview of Moga wetland. The wetland was surveyed during wet, spring conditions when Cell1 and Cell 2 were receiving water from the east (from the drainage ditch). When the ditch is dry (much of the year), the cells would likely only receive groundwater from the east and the south (based on land surface topography and estimated flow towards the creek)

### ***BNWRD Wetlands***

The final set of constructed wetlands is located in Randolph, Illinois, just south of E 700 North Rd. These two wetlands were installed at the Bloomington-Normal Wastewater Reclamation District (BNWRD) municipal waste water treatment plant to help reduce nitrate and phosphate levels as a portion of the effluent is discharged into the wetland. Treated effluent is discharged east of the plant, most of which is directed into the Little Kickapoo Creek. However, some of the effluent flows into the wetlands (Fig. 11), which reside on fine-grained Cahokia Alluvium deposited on coarse-grained Pleistocene glacial outwash (Henry Formation) of the Wisconsinan Glaciation.

There are sixteen wells located around the wetland. The wells, with screens located at the water table, used in this study (CW-4, 5 and 6) are located up-gradient of the main wetland cell (Cell 2: this study did not include Cell 1). The effluent inlet and the wetland outlet are both subsurface pipes. The outlet pipe can be sampled via a trap-door, but there is no instrumentation to measure flow and monitor chemistry.



**Fig. 11** Overview of BNWRD wetland. The wells used in the study were previously installed to monitor the groundwater chemistry and effluent nutrient removal

## Methods

### *Sample/data collection*

Water samples of shallow groundwater monitoring wells, wetland surface water, and tile or effluent water were collected from July 2010–June 2011 from wetland that had

wells installed at the time. Samples were collected approximately every two months, in order to represent all seasons and potential variations in isotopic signatures.

Wells had previously been installed at BNWRD and Gully wetlands, Moga wetland wells were installed in October 2010, and West wetland wells were installed in March 2011. These wells have 2.5 cm diameters, 1.5 m screen lengths, and were hand augured to a depth of 0.3 to 0.6 m below the water table at the study sites. A minimum of three up-gradient (according to land surface topography) wells were installed at each site.

During sampling, groundwater wells were purged until pH and conductivity stabilized before samples were taken by peristaltic pump into 250-500 ml plastic bottles. The bottles were filled completely and tightly capped to avoid evaporation. Samples were then promptly preserved on ice until refrigeration. Slug tests were completed manually with water level readers and a 127 cm<sup>3</sup> slug.

### *Analyses*

Samples for stable isotope analyses were filtered (0.45 µm) in the lab and stored in 60 ml glass bottles with PTFE-faced silicone septum caps or in 60 ml plastic vials with small caps and necks, filled completely, and sealed with paraffin wax to avoid evaporation. The stable isotope ratios <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>H were measured at California State University East Bay by a Los Gatos Research Liquid Water Isotope Analyzer spectrometer with a precision of 0.2 ‰ and 0.6 ‰ respectively. Isotopic compositions were reported as a per mil (‰) deviation from the international V-SMOW (Vienna Standard Mean Ocean Water) standard using the delta (δ) notation (Clark and Fritz, 1997).

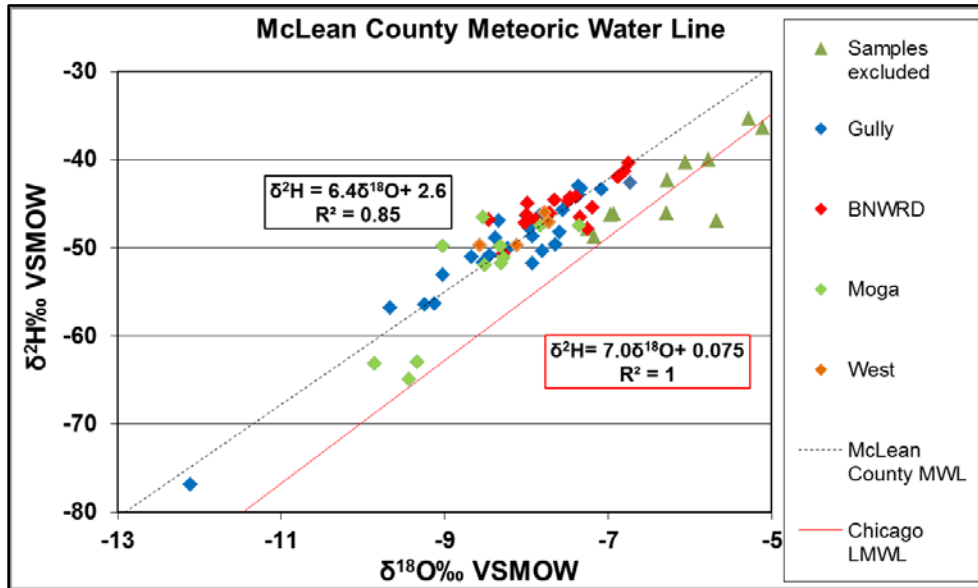
Although the isotopic composition of global precipitation varies temporally and spatially, the relationship of  $^{18}\text{O}$  and  $^2\text{H}$  of fresh waters correlate on a global scale (Clark and Fritz, 1997), resulting in a global meteoric water line (GMWL) with the linear relationship of  $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ . More specific local isotopic ratios will also usually plot linearly on a  $\delta^{18}\text{O} \text{‰ VSMOW}$  vs.  $\delta^2\text{H} \text{‰ VSMOW}$  graph. LMWLs can be quite different than the GMWL, and a best fit line of amount-weighted monthly precipitation events can provide a trend that will reflect details such as evaporation and seasonal changes in origins of water vapor. The IAEA precipitation data for Chicago, IL, the closest city with a long term record, was used as a closer representation of regional conditions as compared to the GMWL. The Chicago LMWL was plotted on  $\delta^{18}\text{O} \text{‰ VSMOW}$  vs.  $\delta^2\text{H} \text{‰ VSMOW}$  graphs along with the data, and best-fit lines through the data were used to estimate the LMWL.

The concentrations of the common anions were measured using ion chromatography at Illinois State University.  $\text{NH}_4^+$  samples were measured in Illinois State University's Biology Department with UV spectrometry. The Hvorslev method was used to calculate hydraulic conductivity from the slug test results, and Darcy's Law was used to calculate groundwater flow into the wetlands.

## **Results**

When the isotopic results of the groundwater and tile water samples (Appendix A) are plotted the waters plot with a best-fit line of  $\delta^2\text{H} = 6.4\delta^{18}\text{O} + 2.6$  (Fig. 12). However, wells that were notably enriched in heavy isotopes from evaporation were excluded from the best fit line, since they were not representative of meteoric precipitation. This

McLean county (or site-specific) line has a lower slope, and is isotopically depleted when compared with the Chicago LMWL ( $\delta^2\text{H} = 7.0\delta^{18}\text{O} + 0.075$ ).



**Fig. 12**  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  plot of groundwater and tile/effluent water of the study sites, compared with the LMWL of Chicago, IL

However, this McLean MWL is weighted towards the BNWRD and Gully wetlands where the majority of samples were collected (given that these sites had pre-existing wells, allowing sampling to begin in July 2010), and winter and spring 2011 precipitation (when Moga and West wetlands started to be sampled as well).

### ***Gully Wetland***

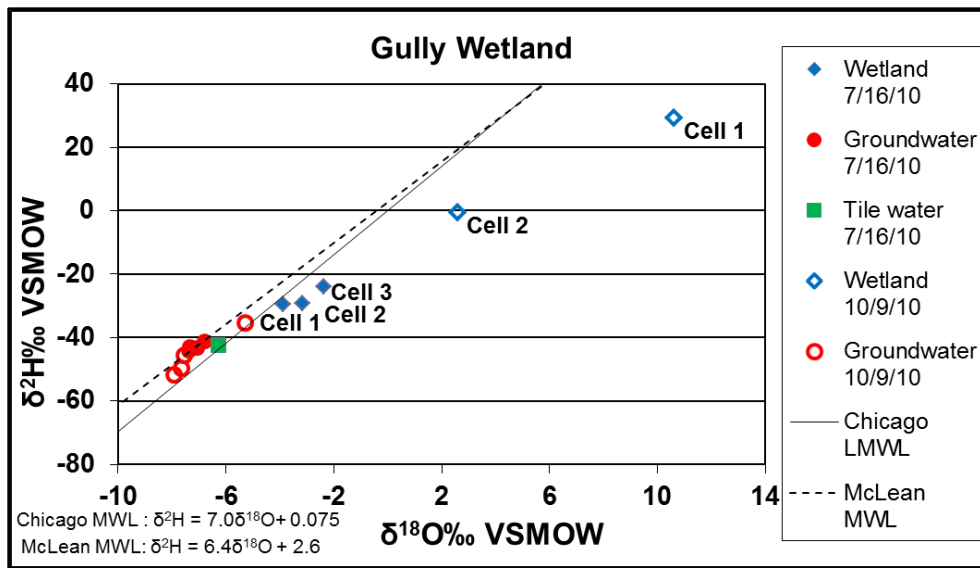
Isotopic signatures of samples gathered in July 2010 plot to the right of the groundwater trend line, indicating that evaporative enrichment in heavy isotopes of wetland cell water was occurring (Fig. 13).

By October 2011, the cells at Gully wetland were nearly dry. The tile had stopped flowing, and Cell 1 had the least amount of water, even though it was the last to receive



tile water. The isotopic signatures exhibit this continued evaporation for Gully (Fig. 13) since July 2010, resulting in positive  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  compositions compared to the international standard (VSMOW). The groundwater composition remained relatively constant between the sampling periods, with the tile water in July being very similar in composition to the groundwater.

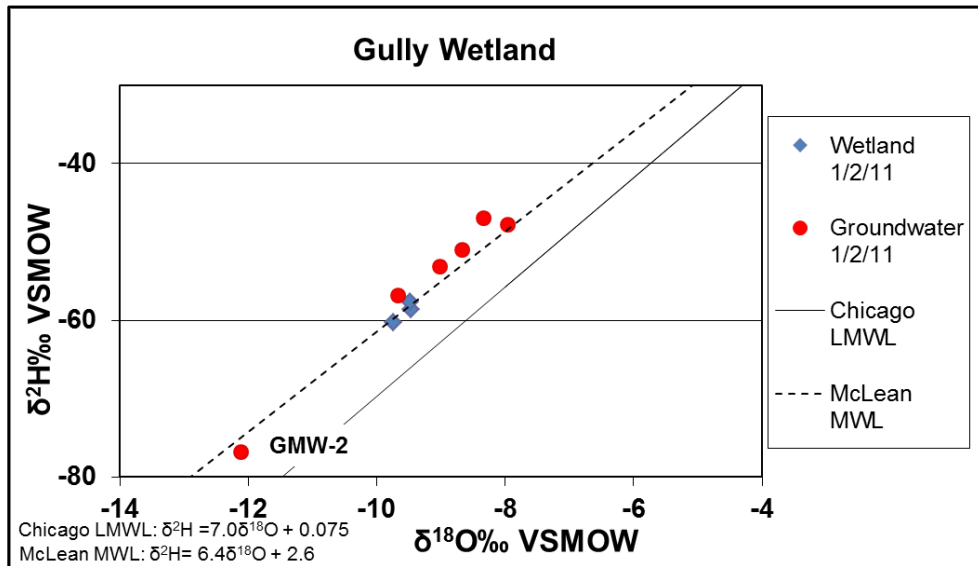
Results of manual slug tests estimate the hydraulic conductivity (K) to be  $1 \times 10^{-3}$  cm/sec. This value is estimated based on an arithmetic mean of the K values obtained from eight slug tests (a rising and a falling head test in wells: GMW-1, GMW-3, GMW-4 and GMW-5).



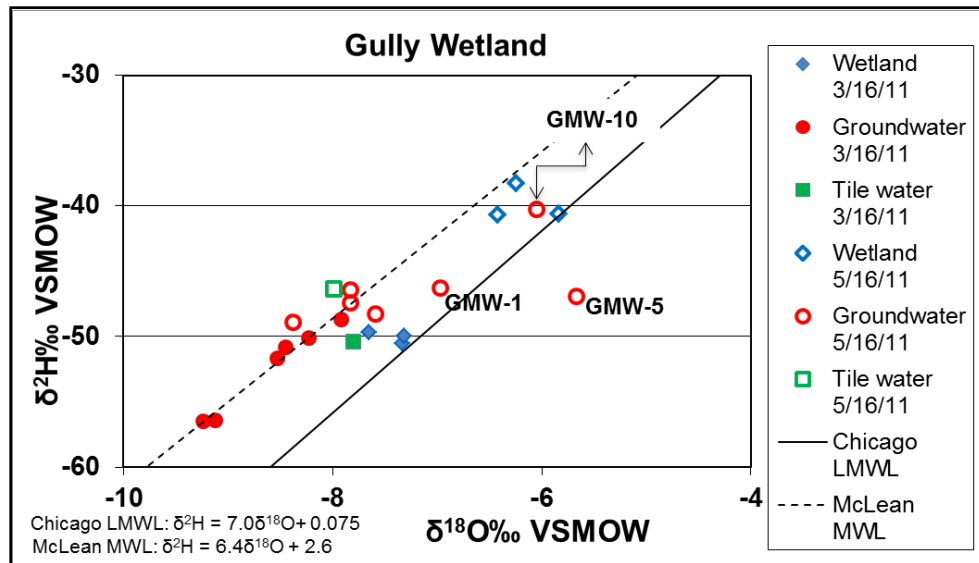
**Fig. 13** Isotopic composition of Gully wetland for both July and October 2010. There were minimal changes in groundwater composition between sampling periods, but evaporative enrichment continued into October. Cell 3 data were not available for October, but Cell 1 experienced the most evaporative enrichment

In January, 2011, the tile was not flowing, and the wetland water and groundwater samples had similar isotopic compositions (Fig. 14), with the exception of outlier well

GMW-2, which had a more negative composition compared to the other samples. An evaporative enrichment signal was present again in tile and wetland water samples in March 2011 (Fig. 15) and in wetland water samples in May 2011. In addition, the compositions of the different water types overlapped in locations on the plot in May 2011, and groundwater wells GMW-1, GMW-5, and GMW-10 had also experienced evaporative enrichment.



**Fig. 14** Isotope results for January 2011 at Gully Wetland. The groundwater is more enriched in heavy isotopes than the wetland, with the exception of well GMW-2



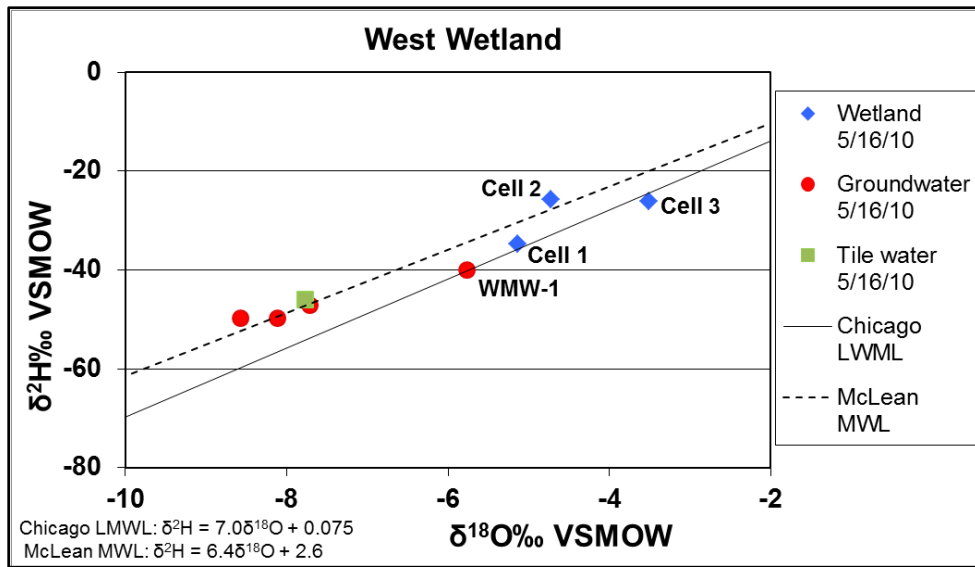
**Fig. 15** Evaporative enrichment occurring at Gully wetland in March 2011. This evaporation is preferential enrichment of O isotopes compared to H. The wells that were notably enriched in heavy isotopes from evaporation (GMW-1, 5, and 10) were not included in the estimated McLean MWL

### *West Wetland*

Based on the groundwater contour map (Fig.8), West wetland only receives tile water (when flowing) and groundwater from the east (from the direction of WMW-1), with an estimated K of  $9 \times 10^{-3}$  cm/sec. This value was calculated by the arithmetic mean of two slug test results (a rising head test of WMW-1 and a falling head test of WMW-6). The wetland cell water then discharges to the south and the east. This wetland is dry throughout much of the year.

At the time of sampling (May 2011), the water level was low enough that the cell outlets were not flowing (cells were cut off from each other). The well located east of the wetland (WMW-1) had a different isotopic composition and a notably higher CI concentration (Appendix B) compared to the northern wells. The isotopic results (Fig. 16)

also reveal that the compositions of the wetland cells were most similar to WMW-1 than the other wells, with a slight evaporative enrichment signal. Cell 1 was the least enriched in heavy isotopes and Cell 2 was slightly more enriched, followed by Cell 3 (the strongest evaporative signal).



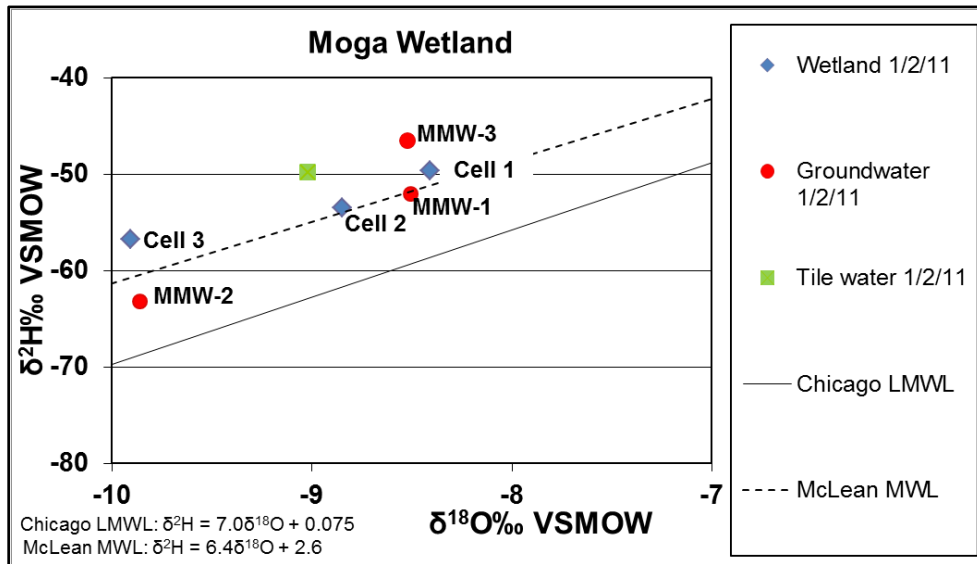
**Fig. 16** Isotopic composition plot of the West Wetland results of May 2011. Well WMW-1 is most similar to the wetland water, while the tile water is most similar to the wells located to the north of the wetland cells

### *Moga Wetlands*

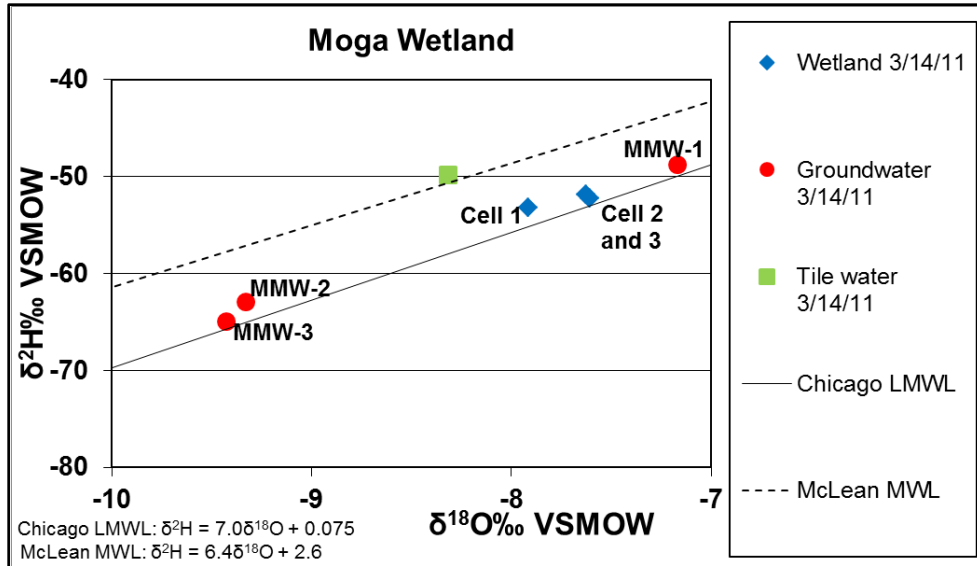
By January 2011, groundwater wells at Moga had been installed, allowing the wetland to be sampled. A plot of the January sample results revealed that the tile water, surface water, and groundwater all had similar compositions (Fig. 17). For each subsequent sampling period (March and June 2011), the waters at Moga did not have a defined isotopic signature (Fig. 18 and 19). In January 2011, well MMW-2 was more depleted in heavy isotopes than MMW-1 and 3, while MMW-1 groundwater was more enriched than the other two wells in March and June 2011. However, MMW-2 and 3

were located in standing water during the March and June sampling periods. Residing in a small depression, these wells may not have been representative of the groundwater at the site, due to increased infiltration rates as water seeped into the ground.

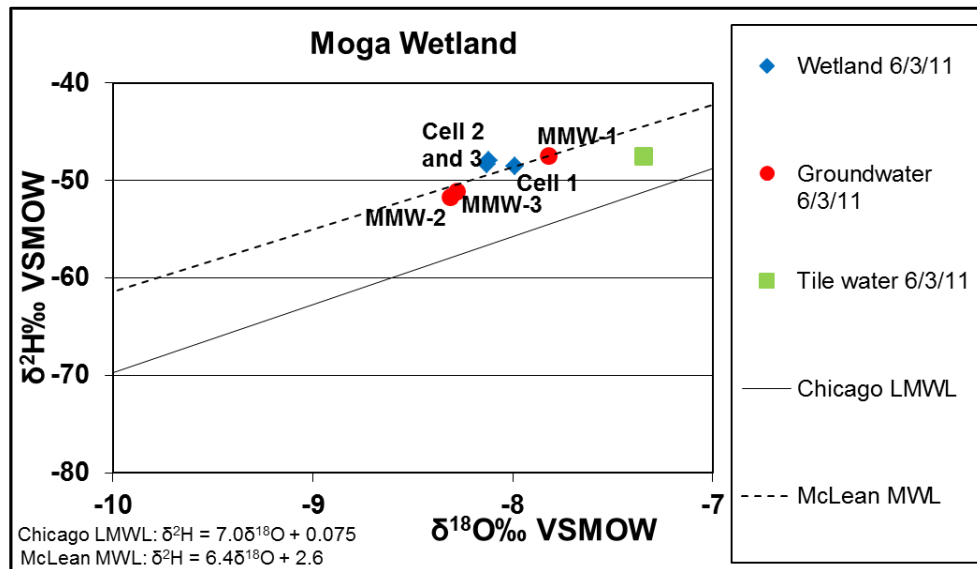
Slug tests results estimated K values to be  $2 \times 10^{-3}$  cm/sec. A rising and a falling slug tests was conducted in wells MMW-1 and MMW-3. The estimated K value is the arithmetic average of the four slug tests results.



**Fig.17** Isotopic composition plot of Moga wetland results for January 2011. The groundwater did not have a defined isotopic signature



**Fig. 18** Isotopic composition plot of Moga wetland results for March 2011. The groundwater did not have a defined isotopic signature



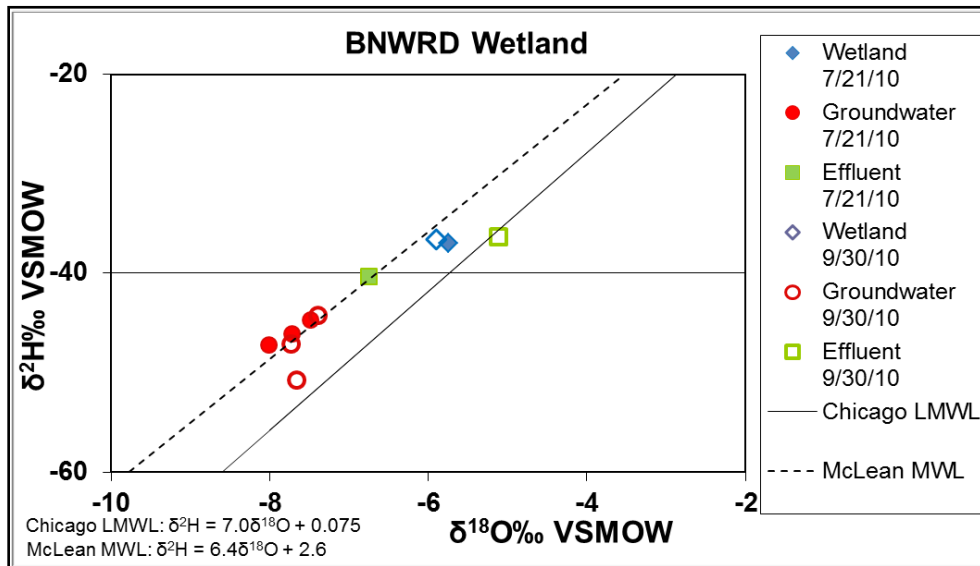
**Fig. 19** Isotopic composition plot of Moga wetland results for June 2011. The groundwater did not have a defined isotopic signature

***BNWRD Wetland***

The isotopic signature of BNWRD wetland in July 2010 plots slightly to the right of the groundwater trend line, indicating that evaporative enrichment in heavy isotopes of

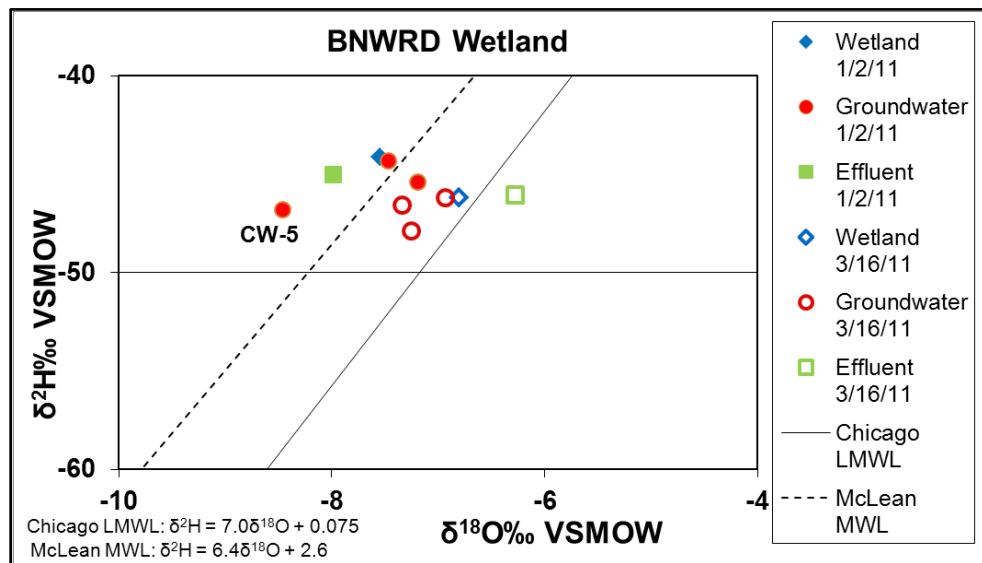
the wetland cell water might have been occurring (Fig. 20). However, the three water types (groundwater, tile/effluent and wetland water) were different isotopically at BNWRD. By September 2010, the evaporative signal was no longer present in the wetland water, and instead, the effluent was more enriched in heavy isotopes than the wetland, and the wetland water composition fell between the groundwater and effluent compositions. The groundwater composition had remained fairly consistent between the sampling periods.

The groundwater has an estimated K of  $9 \times 10^{-4}$  cm/sec. This value is the arithmetic mean of K values calculated from the results of four slug tests (a rising head and falling head test in wells CW-4 and CW-5).



**Fig. 20** Isotopic composition plot for samples from BNWRD wetland in July and September 2010. The outlet water composition is more enriched in heavy isotopes than the groundwater and effluent, the result of evaporation. In September, end-members (groundwater and effluent) and the outlet had different isotopic signatures, and the composition of the wetland water fell between the two end-members

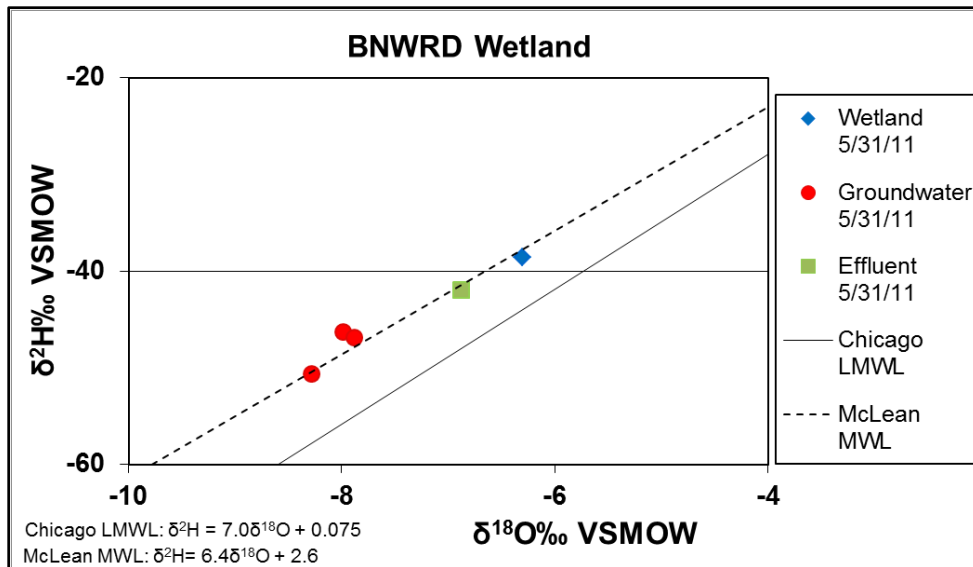
By January, 2011 (Fig. 21) the wetland and effluent isotopic compositions both plotted in between the groundwater signatures. Ignoring the outlier well (CW-5), and considering that the groundwater at BNWRD has similar concentrations in the remaining sampling months, if an average well composition is used. By March 2011 (Fig. 21) the effluent was more enriched in heavy isotopes than the wetland and the groundwater, and the composition of the wetland water fell between the groundwater and effluent signatures (the two end-members).



**Fig. 21** Isotopic composition plot of BNWRD waters in January and March 2011. The water compositions are overlapping in January, but the wetland water does fall between the effluent and the groundwater (when using an average value of groundwater composition) in March

In May 2011 (Fig. 22) the wetland water was more enriched in heavy isotopes than the effluent and groundwater. The compositions of the waters were very similar to the compositions of July 2010, especially the tile and groundwater compositions.

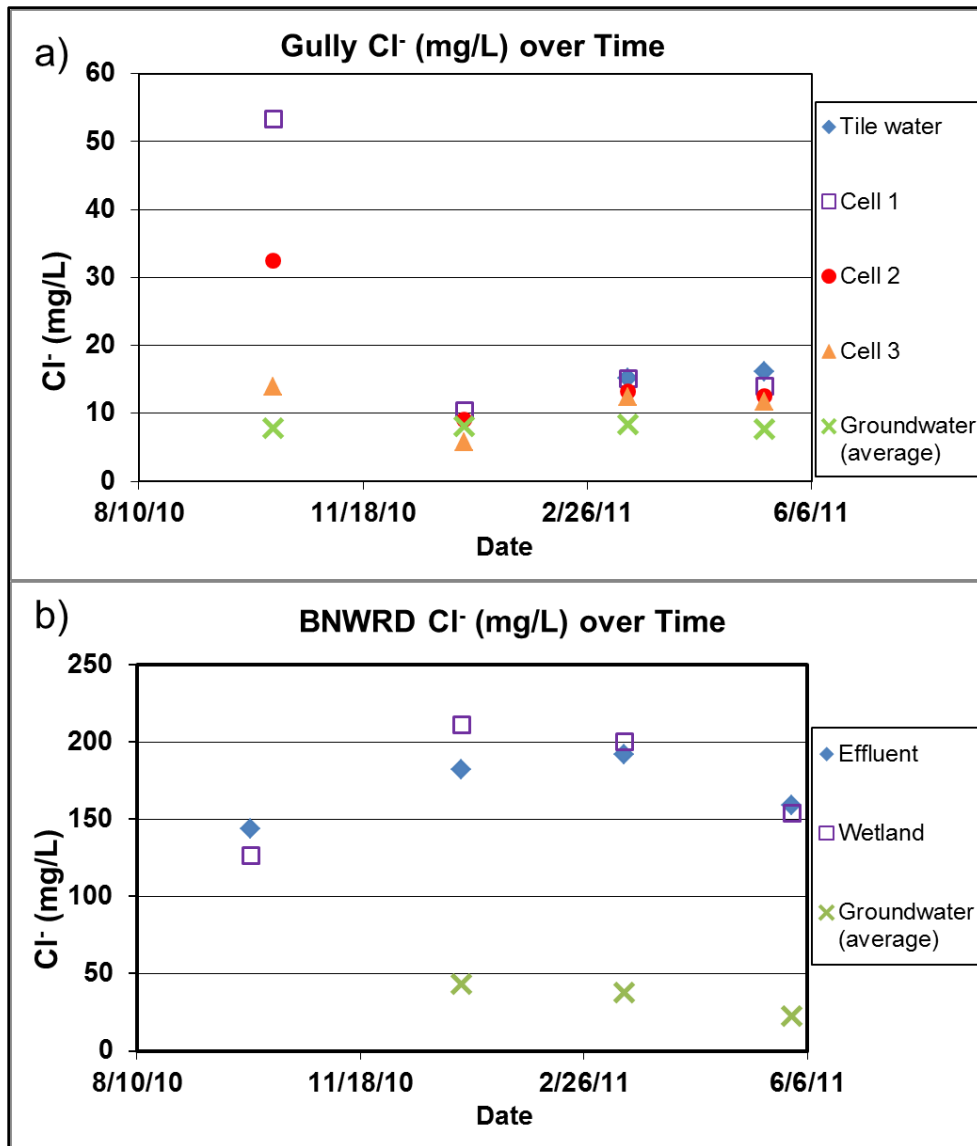




**Fig. 22** Isotopic composition plot of BNWRD in May 2011. The wetland water is more enriched in heavy isotopes than the two end-members (wetland and effluent water), a possible signature of evaporation

### *Chloride and NO<sub>3</sub><sup>-</sup>*

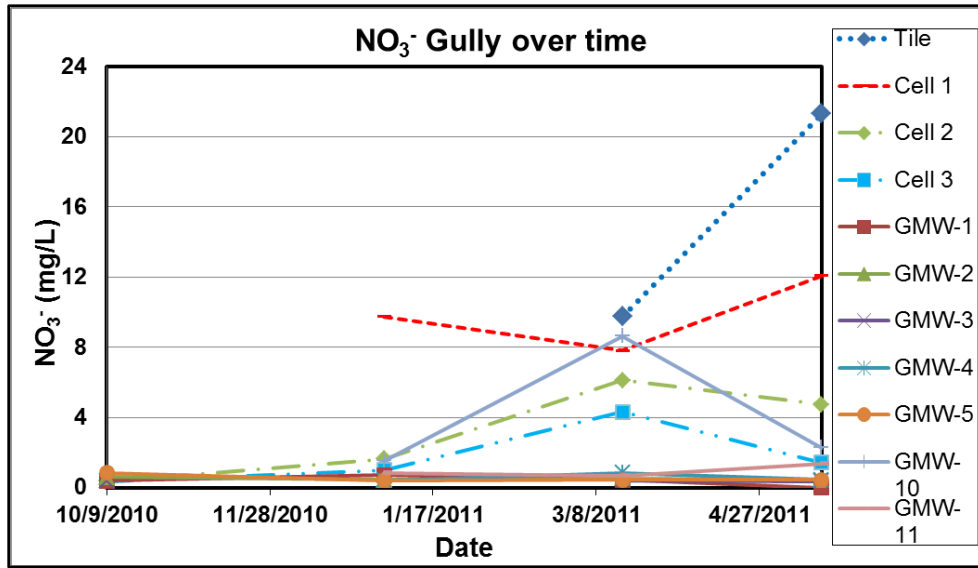
The major anion and NH<sub>4</sub><sup>+</sup> analyses (Appendix B) were completed to determine if there were any patterns or if they could be used to support isotopic results. Chloride (Cl<sup>-</sup>) concentrations over time could be used as a natural tracer. At Gully wetland, wetland cells reached maximum Cl<sup>-</sup> concentrations (Fig. 23) during the October 2010 sampling period, with Gully Cell 1 having the highest Cl<sup>-</sup> concentration. However, at BNWRD, Cl<sup>-</sup> concentrations peaked in the winter months instead.



**Fig. 23** a) Graph of Gully Cl<sup>-</sup> concentrations over time, showing that Cl<sup>-</sup> concentrations in the wetland water were much higher in the dry, warm fall month of October 2010, with Gully Cell 1 having experienced the most evaporative enrichment, while at BNWRD (b), Cl<sup>-</sup> concentrations peak in the winter months, while at Gully

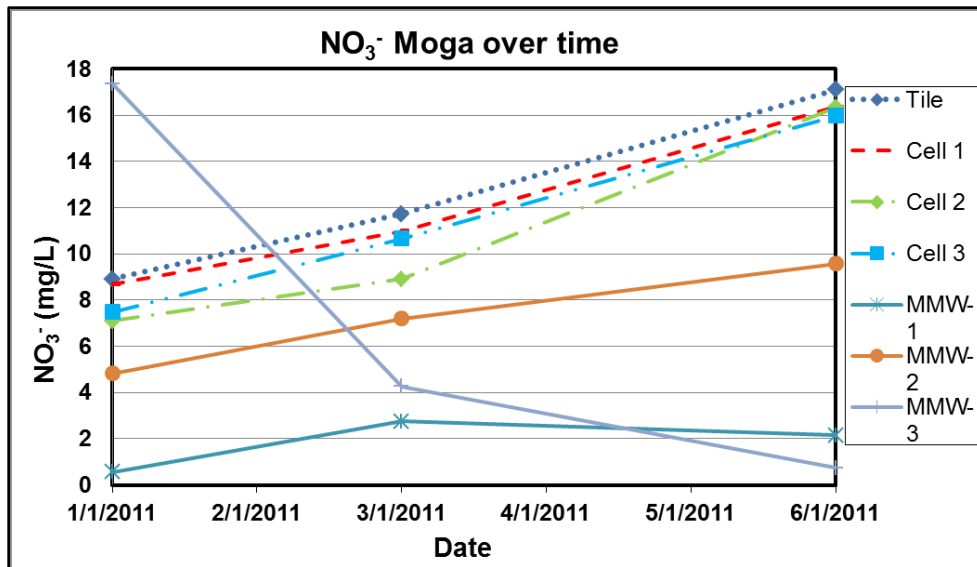
NO<sub>3</sub><sup>-</sup> data over the course of the study was plotted to help evaluate the NO<sub>3</sub><sup>-</sup> removal efficiency of the wetlands. At Gully (Fig. 24), NO<sub>3</sub><sup>-</sup> levels of the wetland cells were at concentrations as low as the groundwater in October 2010. In January 2011, Cell

1 had higher concentrations, while concentrations of cells 2 and 3 remained similar to groundwater. In the spring months, the tile has the highest  $\text{NO}_3^-$  concentrations, followed by Cell 1 (which tile flows directly into), Cell 2, and Cell 3. However, in March 2011 well GMW-10 had a concentration higher than Cell 1.

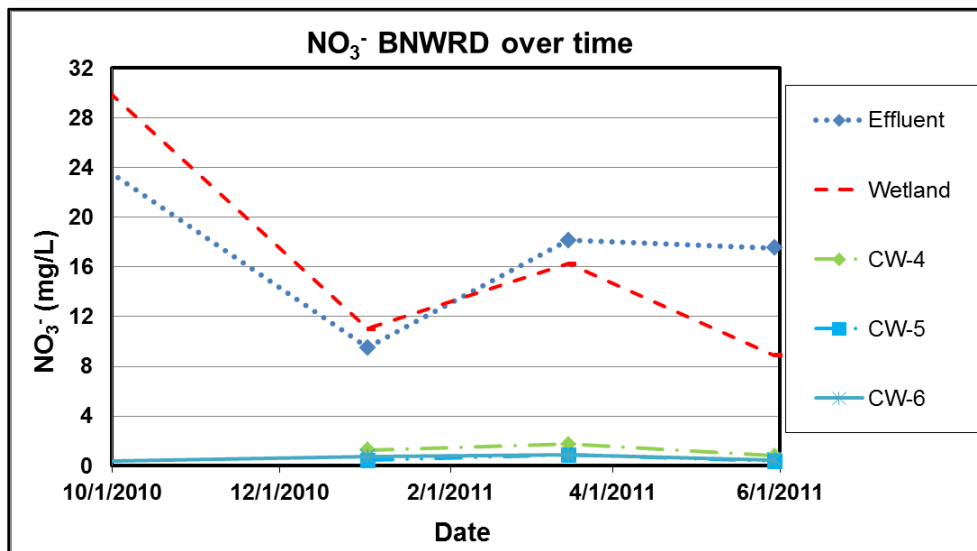


**Fig. 24** Plot of  $\text{NO}_3^-$  over time for Gully Wetland. Groundwater had low concentrations, with the exception of GMW-10 in March 2011. Ignoring GMW-10, tile water had the highest concentrations (when flowing), followed by Cell 1, 2, and then 3.

At Moga, MMW-3 had the highest  $\text{NO}_3^-$  concentration out of the waters in January 2011 (Fig. 25). In the remaining months, tile had the highest concentrations, the cells all had similar concentrations (slightly less than the tile), and groundwater had the lowest concentrations. However, Cell 2 did have lowest  $\text{NO}_3^-$  concentration of the cells in January and March 2011.



**Fig. 25** Plot of NO<sub>3</sub><sup>-</sup> over time for Moga Wetland. Groundwater had low concentrations, with the exception of MMW-3 in January 2011. Ignoring MMW-3, tile water had the highest concentrations (when flowing), followed by Cell 1. Cell 2 had the lowest concentration of the surface waters in January and March 2011



**Fig. 26** Plot of NO<sub>3</sub><sup>-</sup> over time at BNWRD Wetland. Groundwater has low NO<sub>3</sub><sup>-</sup> concentrations throughout the sampling period; wetland water has the highest concentrations in the fall and winter months, and effluent had the highest concentrations in the spring and early summer months

At West wetland, during the May 2011 sampling period, the tile water was  $\text{NO}_3^-$  rich (39.5 mg/L), wetland Cell 1 had less  $\text{NO}_3^-$  (18.9 mg/L), and Cells 2 (0.45 mg/L) and 3 (0.38 mg/L) had significantly less.

The remaining anions and  $\text{NH}_4^+$  data were analyzed for potential trends, but did not prove to be of use to help support the results of the study.

## **Discussion**

### *Isotopic differences between water types*

In the absence of evaporative enrichment, in some months, the three different waters (cell water, groundwater and effluent/tile water) were too similar and even overlapped when displayed on a  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  plot. This was the case for each sampling period at Moga wetland, ruling out the use of end member calculations to determine the contribution of groundwater versus tile water at the wetland. In addition, the difference between MMW-1 and MMW-2 plus MMW-3 in the spring season indicated that the groundwater to the south of the wetland (in the same direction of the tile flow) was different than to the west during these snow melt/heavy precipitation months (when wells 2 and 3 were located in standing water). Waters were also too similar in January 2011 at BNWRD, and May 2011 at Gully.

### *Isotopic composition of the waters over time*

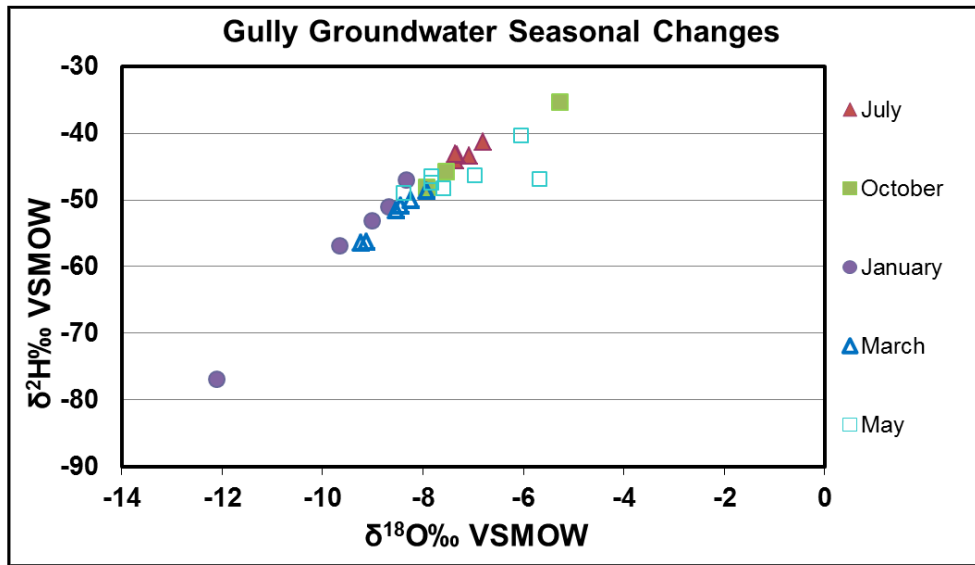
The waters at the study sites were isotopically enriched compared to Chicago (since the local line plots above the Chicago line), which was expected since Chicago is further north, receives more snow, and receives some precipitation from evaporation of

Lake Michigan waters. The waters also fell parallel to the Chicago LMWL, confirming that the tile water and groundwater were entirely meteoric in origin.

Overall, the composition of the groundwater samples did not remain consistent (Table 1). In fact, individual wells at the sites fluctuated in isotopic compositions seasonally by as much as 33.5  $\delta^2\text{H}$  and 5.0  $\delta^{18}\text{O}$  (GMW-2) over the course of the study. Instead, the groundwater composition at Gully wetland followed a seasonal trend of being more enriched in heavy isotopes in the warmer months, and less enriched in colder temperatures (Fig. 27).

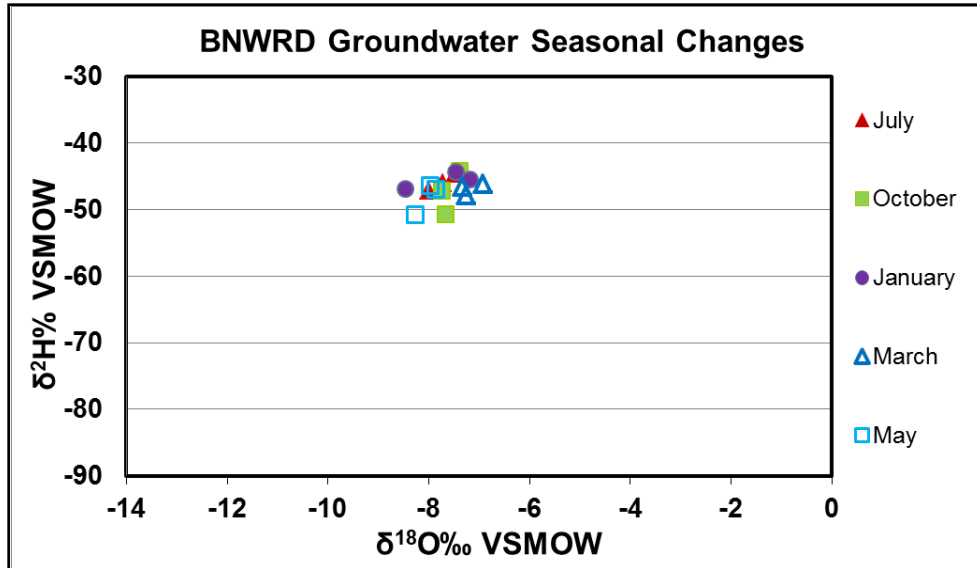
**Table 1** Minimum and maximum groundwater isotopic composition values for each wetland over the course of the study.

Range of Groundwater Sample Compositions				
	$\delta^2\text{H}\text{‰}$ VSMOW ( $\pm 0.6$ )		$\delta^{18}\text{O}\text{‰}$ VSMOW ( $\pm 0.2$ )	
Wetland	Max.	Min.	Max.	Min.
Gully	-35.3	-76.9	-5.3	-12.1
BNWRD	-42.7	-50.6	-6.7	-8.5
Moga	-46.5	-64.9	-7.2	-9.9

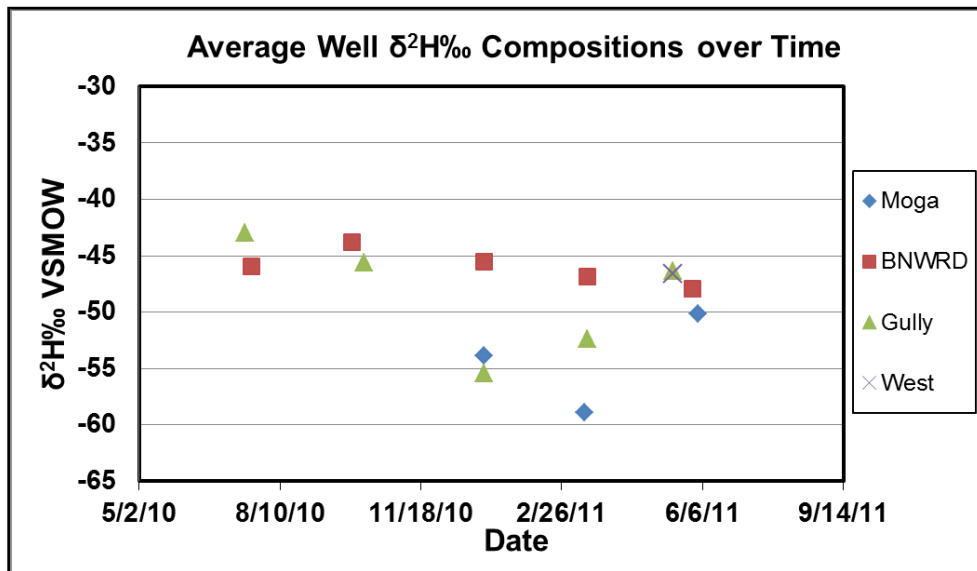


**Fig. 27** The isotopic compositions of groundwater samples over time at Gully Wetland were more depleted in heavy isotopes in the colder months, and more enriched in heavy isotopes in the warmer, more evaporative months

Groundwater at BNWRD was less affected by seasonal variations in groundwater composition (Fig. 28), but did experience fluctuations. Comparing the average well compositions for each wetland over time (Fig. 29), BNWRD well water experienced the least changes, only slightly peaking in composition during the warm, fall months. The largest variation in composition at Gully and Moga wetland took place in the winter and early spring months, as the compositions become more depleted in heavy isotopes.



**Fig. 28** Groundwater isotopic composition over time at BNWRD Wetland experienced less variations in composition seasonally, compared to Gully Wetland (Fig. 22)



**Fig. 29** Average well compositions over time at BNWRD remain fairly consistent, whereas Gully and Moga groundwater are more depleted in heavy isotopes in the winter and early spring months

Regardless, groundwater δ<sup>2</sup>H values have a minimum standard deviation of 1.3‰ (BNWRD well CW-6), and can vary in composition as much, or even more than, tile



water (Table 2). Since the wells are screened at the water table, the wells must not be deep enough for the water to be a weighted average of yearly precipitation, meaning the composition is not completely smoothed out by mixing along the groundwater flow path. These variations in groundwater compositions could also hint at the fact that the drainage tiles have altered the hydrogeology (especially at Gully). The groundwater at Gully may be more heavily affected by recent precipitation events because water infiltrates the groundwater in more abundance and with more ease than at BNWRD (in the absence of tiles).

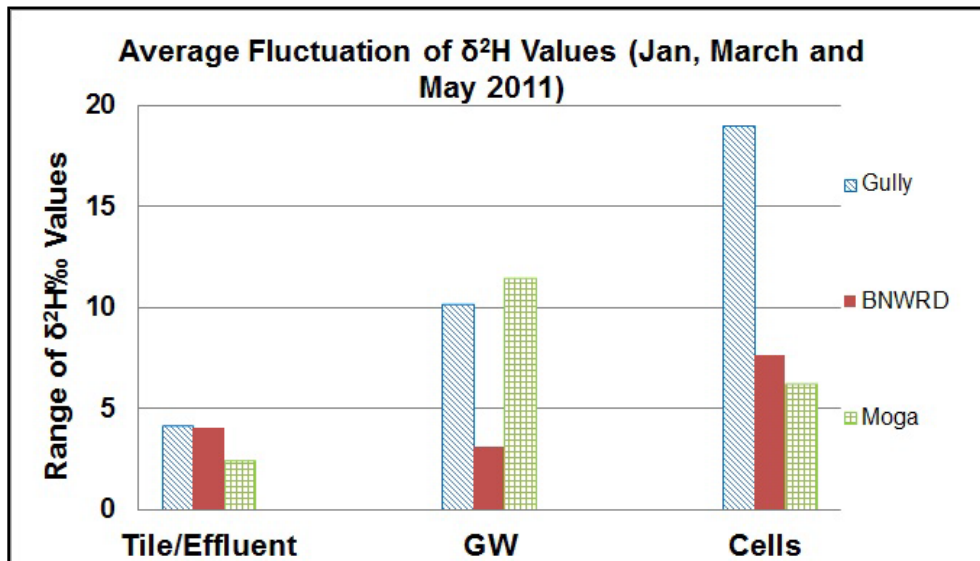
**Table 2.** Means, medians, and standard deviations of the samples, showing that majority of the wells were not consistent in isotopic composition throughout the sampling periods

$\delta^2\text{H}\text{‰}$ VSMOW			
Moga	mean	median	standard deviation
<b>Tile</b>	<b>-49.0</b>	<b>-49.8</b>	<b>1.4</b>
<b>MMW-1</b>	<b>-49.4</b>	<b>-48.8</b>	<b>2.3</b>
<b>MMW-2</b>	<b>-59.3</b>	<b>-62.9</b>	<b>6.5</b>
<b>MMW-3</b>	<b>-54.2</b>	<b>-51.2</b>	<b>9.6</b>
<b>Cell 1</b>	<b>-50.5</b>	<b>-49.6</b>	<b>2.4</b>
<b>Cell 2</b>	<b>-51.2</b>	<b>-51.8</b>	<b>2.6</b>
<b>Cell 3</b>	<b>-52.3</b>	<b>-52.2</b>	<b>4.4</b>
<b>BNWRD</b>			
<b>CW-4</b>	<b>-46.2</b>	<b>-45.4</b>	<b>2.6</b>
<b>CW-5</b>	<b>-45.9</b>	<b>-46.2</b>	<b>2.0</b>
<b>CW-6</b>	<b>-45.9</b>	<b>-46.6</b>	<b>1.3</b>
<b>Effluent</b>	<b>-41.9</b>	<b>-42.0</b>	<b>3.9</b>
<b>Outlet</b>	<b>-40.5</b>	<b>-38.5</b>	<b>4.4</b>
<b>Gully</b>			
<b>Tile</b>	<b>-46.4</b>	<b>-46.3</b>	<b>4.0</b>
<b>GMW-1</b>	<b>-45.2</b>	<b>-46.3</b>	<b>7.8</b>
<b>GMW-2</b>	<b>-53.5</b>	<b>-47.0</b>	<b>15.7</b>
<b>GMW-3</b>	<b>-49.6</b>	<b>-51.6</b>	<b>3.8</b>
<b>GMW-4</b>	<b>-47.3</b>	<b>-47.6</b>	<b>3.3</b>
<b>GMW-5</b>	<b>-50.6</b>	<b>-49.6</b>	<b>6.0</b>
<b>GMW-10</b>	<b>-46.1</b>	<b>-47.8</b>	<b>5.1</b>
<b>GMW-11</b>	<b>-49.9</b>	<b>-49.9</b>	<b>1.4</b>
<b>Cell 1</b>	<b>-30.0</b>	<b>-40.6</b>	<b>34.9</b>
<b>Cell 2</b>	<b>-36.1</b>	<b>-40.7</b>	<b>23.0</b>
<b>Cell 3</b>	<b>-42.4</b>	<b>-44.0</b>	<b>14.6</b>

At BNWRD, the wetland and wells are located at the bottom of a hill and likely interact with deeper, more mixed groundwater, whereas Gully wetland gets mostly shallow discharge (which is more of a function of seasonal variations in precipitation)

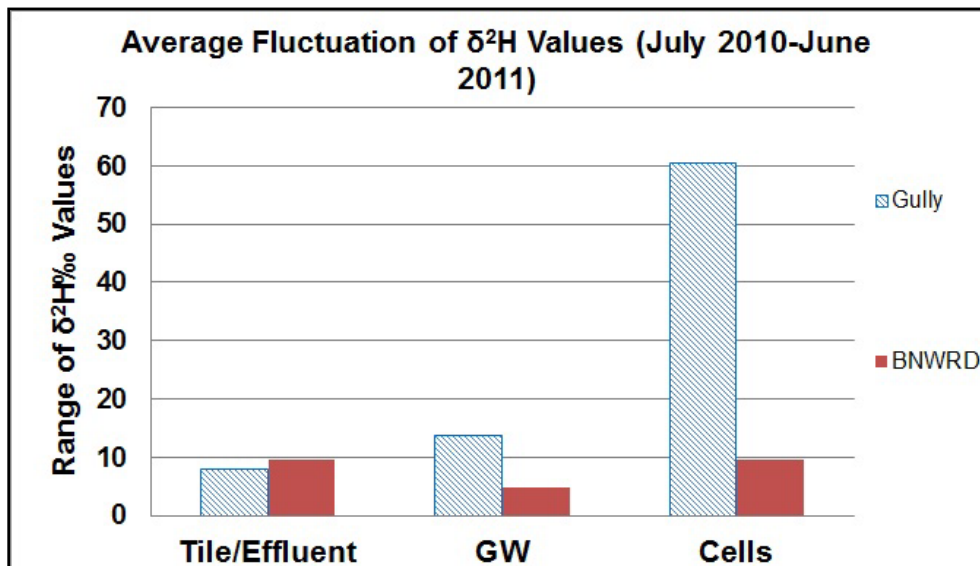
and Moga MMW-2 and MMW-3 were potential areas of recharge (residing in standing water in March and May 2011). This combination of well location and the lack of drainage tile at BNWRD are the most likely reason that BNWRD groundwater was the most consistent water type between the three main wetlands.

When comparing the waters of only January, March, and May 2011 (when Moga, BNWRD, and Gully were all sampled), the most consistent water type was the Moga tile water, while Gully wetland cell compositions varied the most out of all the waters (Fig. 30). However, the tile water at Moga would be expected to vary more if all seasons were included, since the results are biased because the wetland was not sampled during the dry, evaporative months of July and October, resulting in less evaporation and variation in the composition of precipitation as well.



**Fig.30**  $\delta^2\text{H}$  values over the sampling months of January, March and May 2011 show that Gully Cell 1 composition experienced the most changes in isotopic composition, followed by the groundwater samples at Moga and Gully waters. Tile water was the most consistent in isotopic composition at Moga and BNWRD

However, the results are similar over the course of the entire year of sampling (Fig. 31), with Gully wetland cells having experienced the most fluctuations in isotopic composition (a combination of the evaporation and variations in groundwater and tile water input), and the tile water/effluent remaining fairly constant. This yearly account also confirms that the groundwater at BNWRD was the most consistent water type in this study.

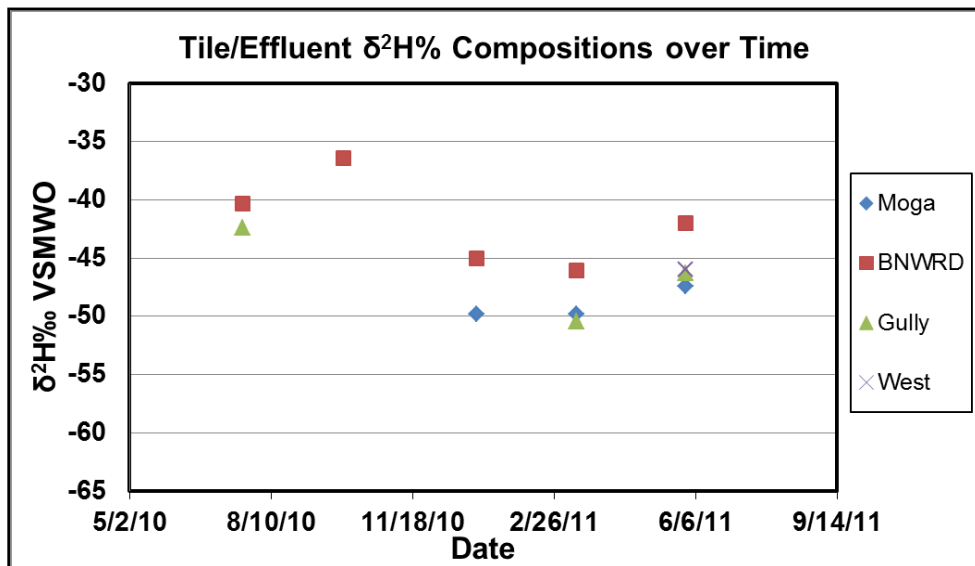


**Fig. 31** Figure showing the extent that the waters at Gully and BNWRD changed over the course of the entire sampling period. Gully wetland cells experienced the most variation in  $\delta^2\text{H}$  composition (largely a factor of evaporation), and BNWRD groundwater was the most consistent in isotopic composition among the water types and between the three sites

The tile water was the most similar water type between the wetlands, while the surface water was the most variable. This was expected since the wetlands are all within 20 kilometers from each other, meaning that precipitation would have similar compositions. However, the effluent at BNWRD was not as comparable as the agricultural tile waters, because these waters are more than just direct precipitation

infiltration, and are a combination of lake water (Bloomington’s water supply) and the Mahomet aquifer (Normal’s supply).

A plot of tile/effluent water over time though, does demonstrates that even though the tile and effluent water was the most similar water type between the wetlands, the effluent at BNWRD was isotopically enriched compared to the agricultural tile waters (Fig. 32).



**Fig. 32** The effluent compositions over time at BNWRD are different than the agricultural wetlands

***Evaporation***

The evident evaporation in July 2010 (BNWRD and Gully), October 2010 (Gully), March 2011 (Gully) and May 2011 (West and possibly BNWRD) was not expected to rule out end-member calculation use, since the wetland cells have fairly small surface areas and low residence times when the tile/effluent is flowing (which it was in July 2010, March 2011, and May 2011 in the wetlands with the evaporative signatures).

In October 2010, the positive  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values at Gully confirmed that evaporation was the main means of water loss, and that groundwater input was not supplying the cells with enough water in the absence of tile flow. It was during this time that the impact of the groundwater was the most obvious compared to the other sampling months. When the tile stops flowing, it is expected that Cell 1 would have the most water (and therefore have isotopic compositions that were less impacted by evaporation) out of the three cells, since it is the last to be cut off from the water source. However, the isotopic signatures of the wetland cells (Fig. 13), as well as  $\text{Cl}^-$  concentrations in the water samples over time (Fig. 23) show that Cells 2 and 3 were less impacted by evaporation. This means that they had to have been receiving more groundwater. In particular, Cell 3 was receiving the most groundwater at that time since it had the least evaporative enrichment in heavy isotopes and the lowest  $\text{Cl}^-$  concentration out of the three cells. This matches visual field observations of wetland water levels during the sampling time.

During the drier months, the agricultural wetland cells would be more prone to evaporative enrichment than BNWRD. When the tile stops flowing, the groundwater interaction is not plentiful enough to keep the outlets flowing between cells, increasing the residence time of the wetland cell water. At BNWRD, where the effluent acts as a steady water source to the wetland, along with groundwater input, the wetland outlet continues to flow resulting in less variations in residence time than the agricultural wetlands. Therefore, by October 2010, the evaporative enrichment was no longer evident in the wetland water. Instead, the effluent appeared to have an evaporative signature. This was most likely due to a lag time of the waste-water treatment plant receiving water from

summer rains, and lake water (Lake Bloomington and Lake Evergreen, where Bloomington, IL gets its city water) that had experienced evaporative enrichment in heavy isotopes as the source in the dry, summer months.

***End member calculations***

End member calculations could often not be used to determine reliable proportions of water contributions to the wetlands due to either: a large evaporation signal resulting in wetland waters that had more positive isotopic signatures than either end member (a factor that was not predicted as part of the hypothesis of this study), the different waters did not have unique signatures, or there was an absence of tile flow completely (Table 3).

**Table 3** Table displaying the sample months at each wetland where end member calculations could be used, or the reason why end member calculations could not be used

	<b>Reason why, and sampling dates when end-member calculations could not be used</b>			<b>Potential to be used in end member calculations</b>
	Not enough difference between the three water types	No tile flow	Enrichment in heavy isotopes from evaporation of wetland water, resulting in value more positive than end members	
<b>Gully</b>	May 2011	Oct. 2010 Jan. 2011	July 2010 Oct. 2010 March 2011	
<b>BNWRD</b>	Jan. 2011?		July 2010 May 2011	Sept. 2010 March 2011 Jan. 2011?
<b>Moga</b>	Jan. 2011 March 2011 June 2011			
<b>West</b>			May 2011	

The only months that met the requirements of using end-member calculations were September 2010 and March 2011 at BNWRD wetland. These were the only occurrences where the wetland composition fell between the effluent and the groundwater (end-members) and the three water types plotted in different locations, meeting the assumptions of the mixing equation. In September (Fig. 20), when focusing on the  $\delta^{18}\text{O}$  calculations combined with the  $\text{Cl}^-$  data for the anion analyses, an estimate could be made that the wetland water at BNWRD was approximately 70-90% effluent water at that time. However, when considering the overall values of the effluent and the wetland (especially  $\delta^2\text{H}$  values), the effluent and the wetland had similar compositions.

**Table 4** Isotopic composition values from September 30, 2010 at BNWRD, used in end member calculations to estimate the fractions that effluent and groundwater were contributing to the wetland water.

	<b>GW (average)</b>	<b>Wetland</b>	<b>Effluent</b>	<b>X= fraction of GW</b>	<b>(1-x) = Fraction of effluent water</b>
<b><math>\delta^2\text{H}</math></b>	-47.4	-36.6	-36.4	0.02	0.98
<b><math>\delta^{18}\text{O}</math></b>	-7.6	-5.9	-5.1	0.32	0.68
<b><math>\text{Cl}^-</math></b>	17.55	126.88	143.79	0.13	0.87

Although the calculated error for the fraction of effluent entering the wetland based on the standard deviation of well averages ( $+0.01$  or  $-0.00$   $\delta^2\text{H}$  and  $\pm 0.02$   $\delta^{18}\text{O}$ ) is minimal, when considering the potential analytical error ( $\pm 0.6\text{‰}$   $^2\text{H}/^1\text{H}$  and  $\pm 0.2\text{‰}$   $^{18}\text{O}/^{16}\text{O}$ ) it is possible that the effluent may even have more  $\delta^2\text{H}$  than the outlet, ruling out the use of the calculations. However, this does likely mean that the wetland was nearly



100% effluent at this time, and that  $\delta^{18}\text{O}$  values underestimated the fraction of wetland water that was effluent.

In March 2011 (Fig. 21), when using the average composition of the wells, the difference between the waters was enough to plug into the end member calculations. However, there was even less of a difference in composition between the three water types than in September.

The results for March 2011 were significantly different when  $\delta^2\text{H}$  values were used in the mixing equation versus  $\delta^{18}\text{O}$  (Table 5). Since the  $\delta^2\text{H}$  values were nearly identical when factoring in analytical error, the  $\delta^{18}\text{O}$  values were considered first, indicating that the groundwater was the primary supplier of water to the wetland in March (58%). However, there was more  $\text{Cl}^-$  in the wetland than in the effluent at this time, eliminating the use of  $\text{Cl}^-$  to support the mixing equation results.

**Table 5.** Isotopic composition values from March, 2011 at BNWRD, used in end member calculations to estimate the fractions that effluent and groundwater were contributing to the wetland water at that time. Chloride concentrations could not be used to support the fractions, since the outlet (the mixture) had higher chloride values than the two end-members (effluent and groundwater)

	<b>GW (average)</b>	<b>Wetland</b>	<b>Effluent</b>	<b>x = fraction of GW</b>	<b>(1-x) = fraction of effluent water</b>
$\delta^2\text{H}$	-46.9	-46.2	-46.1	0.20	0.80
$\delta^{18}\text{O}$	-7.2	-6.8	-6.3	0.58	0.42
$\text{Cl}^-$	37.90	200.53	191.81	n/a	n/a

The potential error based on using well averages was calculated to be +0.68 or -0.10  $\delta^2\text{H}$  and +0.19 and -0.11  $\delta^{18}\text{O}$ . However, groundwater, effluent and outlet waters have very similar  $\delta^2\text{H}$  values. This fact, along with the calculated error, would mean that the  $\delta^{18}\text{O}$  values had more merit, and that groundwater was supplying the wetland with approximately half of its volume. However, the  $\text{Cl}^-$  concentration in the wetland was a direct result of the high  $\text{Cl}^-$  concentrations in the effluent, meaning that the wetland was again, mostly entirely effluent (a fact not revealed by the end member calculations).

Although in January 2011, the outlier well CW-5 resulted in an overlapping of the three different water types, in the other sampling months, the groundwaters all plotted with very similar isotopic compositions. Therefore, by ignoring CW-5 and using only CW-4 and CW-6 isotopic compositions as the average groundwater signature, end-member calculations can be used for  $\delta^{18}\text{O}$  values (Table 6).  $\delta^2\text{H}$  values cannot be used in the equation, however, since the wetland water is more negative in composition than either end-member.  $\text{Cl}^-$  concentrations also could not be used in the equation, since the wetland higher concentrations than the end-members.

**Table 6** Isotopic composition values from January, 2011 at BNWRD, used in end member calculations to estimate the fractions that effluent and groundwater were contributing to the wetland water at that time.  $\delta^2\text{H}$  and  $\text{Cl}^-$  concentrations could not be used to support the fractions, since the outlet (the mixture) values did not fall between the two end-members (effluent and groundwater)

	<b>GW (average)</b>	<b>Wetland</b>	<b>Effluent</b>	<b>x = fraction of GW</b>	<b>(1-x) = fraction of effluent water</b>
<b><math>\delta^2\text{H}</math></b>	-44.9	-44.1	-45.0	n/a	n/a
<b><math>\delta^{18}\text{O}</math></b>	-7.3	-7.5	-8.0	0.67	0.33
<b><math>\text{Cl}^-</math></b>	54.33	211.46	182.17	n/a	n/a

$\delta^{18}\text{O}$  values indicate that the wetland was composed of mostly groundwater (67%). The potential error based on using well averages was calculated to be +0.13 or - 0.23  $\delta^{18}\text{O}$ . This error potential, along with the analytical error, would mean that the  $\delta^{18}\text{O}$  values of groundwater and wetland water could have nearly identical values. In addition, the  $\text{Cl}^-$  concentrations in the groundwater were higher during this sampling period. However, the concentrations in the wetland are higher than the effluent, indicating that although groundwater input into the wetland may have been more abundant, effluent was, again, likely the main contributing source of water to the wetland.

***Calculated groundwater flow into the wetlands***

The hydraulic conductivity values for the wetlands were used in Darcy's Law to calculate estimates of groundwater flow discharge into cell 1 of the wetlands (Table 6). Minimum discharge ( $Q_1$ ) was calculated by using only the lateral input flow, moderate

discharge ( $Q_2$ ) was calculated by using the vertical input flow, while maximum discharge ( $Q_3$ ) was calculated as the sum of lateral and vertical discharge ( $Q_1 + Q_2$ ).

**Table 7.** Calculated flow into Cell 1 of the wetlands, demonstrating that groundwater input (especially into BNWRD) is fairly small

Wetland	K (m/sec)	Min. Q ( $Q_1$ ) (m <sup>3</sup> /day)	Mod. Q ( $Q_2$ ) (m <sup>3</sup> /day)	Max Q ( $Q_3 = Q_1 + Q_2$ ) (m <sup>3</sup> /day)	Estimated total m <sup>3</sup> of wetland cell	Possible max % of total wetland volume groundwater contributes per day
Gully	1.E-05	2	27	29	296	9
West	9.E-05	3	56	59	1303	4
BNWRD	9.E-06	2	119	121	962	1
Moga	2.E-05	3	55	57	19410	6

This data can be used to confirm that the wetland water at BNWRD was nearly 100% effluent. Although the potential maximum Q at BNWRD is the highest among the study wetlands, groundwater input (2-121 m<sup>3</sup>/day) is small compared to the large volume of the wetland.

However, it is important to consider that the estimates of groundwater contribution are directly related to the estimated K values. K values obtained from the manual slug tests at the sites only represent a small area surrounding the wells. Therefore, these Q estimates are calculated under the assumption that the K values are representative of all groundwater entering the wetland, an accuracy limitation for the calculations.

***West wetland implications***

Although there are only data for May 2011 at the West wetland, the isotopic signatures of the wetland cells do help confirm the groundwater contour maps and the

interaction of groundwater with the wetland. The wells located north of the site all plotted in the same location as the tile inlet isotopic signature; whereas the water from the east of the wetland (WMW-1) was distinct both in isotopic and  $\text{Cl}^-$  concentrations. The wells to the north were all very similar to the tile water, likely because they are on the same path of the tile water pipes that drain the field north of the wetland. However, West Cell 1 was most like WMW-1 in composition and was the least enriched in heavy isotopes because the evaporative signal has been diluted by groundwater and most recent input of tile, helping to confirm the groundwater flow direction.

#### *Chloride and $\text{NH}_4^+$*

Overall  $\text{Cl}^-$  data proved to be the most helpful anion, as a natural tracer, to support evaporative patterns. Since the concentrations should increase, with increased evaporation in surface waters,  $\text{Cl}^-$  concentrations helped support evaporation and groundwater input at Gully and West wetlands. However, at BNWRD,  $\text{Cl}^-$  concentrations peaked in the winter months instead. The effluent at BNWRD is already  $\text{Cl}^-$  rich, from anthropologic additives and road salt from snow melt runoff into the waste water entering the BNWRD plant, a reason why  $\text{Cl}^-$  concentrations peak in winter and early spring months, rather than the evaporative summer months, like at Gully wetland. This surge of  $\text{Cl}^-$  that accumulates into the wetland at BNWRD, results in  $\text{Cl}^-$  concentrations that are higher than the effluent and the groundwater (the two end-members) during the winter and early spring months, ruling out the potential of  $\text{Cl}^-$  to help support isotope end-member calculations during these months.

Overall,  $\text{NO}_3^-$  data plotted overtime could be used to evaluate the efficiency of  $\text{NO}_3^-$  removal at the wetlands. In general, during the warmer months, with plant cover and temperatures that promotes biogeochemical processes, concentrations of  $\text{NO}_3^-$  in the wetland cells is much less than the concentrations of the tile water entering the wetland. Gully wetland appears to be the most efficient wetland at removing  $\text{NO}_3^-$ . In the absence of tile flow in fall and winter 2010, the  $\text{NO}_3^-$  composition of the wetland cells was very similar to groundwater (which is consistently low). During the warm, dry, evaporative fall months, the increased groundwater input (which would help dilute  $\text{NO}_3^-$  concentrations in the wetland water), along with evapotranspiration and biogeochemical processes, had successful mitigated the high concentrations from tile input in the recent months. Then, in March and May 2011, when tile was flowing again, in general, the concentrations of  $\text{NO}_3^-$  decreased from Cell 1 to Cell 3, meaning that the longer the residence time of the wetland water, the more successful the wetland processes are at removing/withholding the  $\text{NO}_3^-$ .

Moga wetland appeared to be less efficient than Gully at  $\text{NO}_3^-$  removal.  $\text{NO}_3^-$  concentrations of wetland surface water were similar to tile concentrations. In addition, concentrations did not always decrease from Cell 1 to Cell 3. Instead, Cell 2 had the lowest surface water composition in both January 2011 and March 2011. This could possible mean that it was receiving the most groundwater input during this time (diluting the concentrations).

At BNWRD, wetland  $\text{NO}_3^-$  removal is the most apparent in the spring and early summer months. This is when the plant uptake would be the greatest. In the fall and early

winter months, in the absence of plant cover to utilize the excess nutrients, the wetland water actually had higher concentrations than the effluent.

Although the lack of data for West wetland meant that the efficiency of  $\text{NO}_3^-$  removal overtime could not be gauged, in May 2011 Cell 1 had much less  $\text{NO}_3^-$  than the tile water, and Cells 2 and 3 were progressively more depleted in  $\text{NO}_3^-$  concentrations. This insinuates that West wetland is capable of successfully removing  $\text{NO}_3^-$  as well.

### **Conclusions**

The shallow groundwaters of the study sites do not have a constant isotopic signature that is an average of yearly precipitation events, but rather reflect seasonal changes in isotopic composition due to temperature, origin of the precipitation air mass, and evaporation. The groundwater at BNWRD varies in composition the least (likely due to well locations and lack of tile) and Gully varies the most. Regardless, even at BNWRD, the groundwater is not consistent in composition. This is likely because the groundwater samples (taken from the water table) are too shallow to be a well-mixed average of annual recharge. Furthermore, at the agricultural wetlands, since tile water is essentially just shallow water, there were generally minimal difference in isotopic compositions between tile and groundwater.

In the end, end-member calculations commonly could not be used due to either: a large evaporation signal resulting in wetland waters that had more positive isotopic signatures than either end member (a factor that was not predicted as part of the hypothesis of this study), the different waters did not have unique signatures, or there was an absence of tile flow completely. Overall, the end member equation is functional in

September 2010, January 2011 (using selective well averages), and March 2011 at BNWRD. This is a combination of the fact that the groundwater remained more consistent in signature than the other wetlands, and that the effluent composition is affected by more than just recent precipitation (giving it a slightly different composition than the groundwater on these occasions). Although the accuracy of the results was affected by analytical error and the fact that well averages were used in the calculations, the end-member calculations (supported by Cl<sup>-</sup> concentrations and groundwater discharge estimates) could be used to determine that the wetland was mostly effluent.

Although end member calculations could not be used for the agricultural wetlands,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  could still help describe the hydrologic processes of the constructed wetlands in the study area by: delineating sources of water (ex. West wetland data indicated primary input from WMW-1, which was confirmed by the groundwater contour map), confirming evaporation was occurring (and as early as March 2011 at Gully) and that groundwater input was not abundant enough to completely eliminate this effect, but that slight dilution effects (Gully Cells 2 and 3 in October 2010) can be used to determine which cells are receiving more groundwater input.

In the future, similar studies on constructed wetlands that are known to receive more groundwater input or receive waste water (where the composition is notably different than the groundwater) could be conducted to determine if this method could produce reliable results. Furthermore, based on the results of west wetland (how it receives very little groundwater interaction: a reason that it is dry most of the year) it could be beneficial to install initial groundwater monitoring wells to confirm groundwater flow in an area before installing a constructed wetland.



### CHAPTER III

#### SUMMARY OF CONCLUSIONS

The O and H stable isotopes of water can provide insight into constructed wetland hydrology. The fact that some of the constructed wetlands used in this study were undergoing evaporative enrichment of heavy isotopes at a quicker pace than groundwater could supply water to dilute the signature was determined by isotopic compositions of the wetland water versus the tile water and the groundwater. Furthermore, the patterns of isotopic composition change in the wetland cells at Gully wetland over time, showed that Cells 2 and 3 were receiving more groundwater input than Cell 1 during the warm, dry fall months (the reason that Cell 1 was visibly losing volume at a pace quicker than Cells 2 and 3, regardless of the fact that it was the last cell to be cut off from the tile water source). Stable isotopes also could be used to confirm the groundwater flow path into the West wetland as well.

The variations in the isotopic composition of the groundwater over time were not expected. The fact that the groundwater is influenced by fluctuations in the composition of precipitation, as well as evaporation, suggests that the sampled groundwater was too shallow to be a well-mixed average of yearly recharge. In addition, the variations of groundwater composition among wells at individual study sites (even among those along

the same flow path) suggests that there is a variation of recharge rates and/or mixing of different waters, within these small study areas.

Overall, the main flaw in this study was that groundwater and tile water were too similar. Both are reflections of seasonal precipitation. In order for this method to work, the two end members had to be unique, and since tile water is essentially shallow groundwater, the two were too similar. It was only at BNWRD wetland that values could even be inserted into the mixing equation since the effluent is more than just recent precipitation, and therefore is more likely to be different than groundwater in isotopic composition. However, the differences were still marginal, and only when backed up by Cl data and estimates of groundwater discharge could it be determined that wetland was nearly entirely composed of effluent.

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APPENDIX A

O AND H ISOTOPE RESULTS

		$\delta^2\text{H}$					
<b>Moga</b>		9/30/10	1/2/11	3/14/11	6/3/11	Range	
Tile			-49.8	-49.8	-47.5	2.3	
MMW-1			-52.0	-48.8	-47.5	4.5	
MMW-2			-63.2	-62.9	-51.8	11.4	
MMW-3			-46.5	-64.9	-51.2	18.4	
Cell 1			-49.6	-53.2	-48.6	4.7	
Cell 2			-53.4	-51.8	-48.4	5.1	
Cell 3			-56.7	-52.2	-48.0	8.7	
<b>BNWRD</b>							
	7/21/10	9/30/10	1/2/11	3/16/11	5/30/11	Range	
CW-4	-44.7	-44.2	-45.4	-46.2	-50.6	6.4	
CW-5	-46.1	-42.7	-46.8	-47.9	-46.2	5.2	
CW-6	-47.2	-44.6	-44.3	-46.6	-46.8	2.9	
Effluent	-40.4	-36.4	-45.0	-46.1	-42.0	9.7	
Outlet	-37.0	-36.6	-44.1	-46.2	-38.5	9.6	
<b>Gully</b>							
	7/16/10	10/9/10	1/2/11	3/16/11	5/16/11	Range	
Tile	-42.36	no flow		-50.42	-46.32	8.06	
GMW-1	-41.31	-35.34	-46.97	-56.38	-46.25	21.04	
GMW-2	-43.35	-45.72	-76.87		-48.23	33.52	
GMW-3	-44.03	-51.77	-53.11	-51.64	-47.39	9.09	
GMW-4	-43.25		-50.99	-48.70	-46.40	7.73	
GMW-5	-43.05	-49.64	-56.86	-56.45	-46.91	13.81	
GMW-10			-47.80	-50.12	-40.27	9.85	
GMW-11				-50.83	-48.91	1.92	
Cell 1	-29.57	29.34	-58.59	-50.50	-40.59	79.84	
Cell 2	-29.32	-0.46	-60.23	-49.97	-40.68	59.76	
Cell 3	-23.96		-57.62	-49.67	-38.29	33.66	
<b>West</b>							
					5/16/11		
WMW-1					-40.1		
WMW-3					-49.7		
WMW-5					-47.1		
WMW-6					-49.8		
Cell 1					-34.8		
Cell 2					-25.8		
Cell 3					-26.0		
Tile					-46.0		

$\delta^{18}\text{O}$						
<b>Moga</b>		<b>9/30/10</b>	<b>1/2/11</b>	<b>3/14/11</b>	<b>6/3/11</b>	<b>Range</b>
Tile			-9.0	-8.3	-7.4	1.7
MMW-1			-8.5	-7.2	-7.8	1.3
MMW-2			-9.9	-9.3	-8.3	1.5
MMW-3			-8.5	-9.4	-8.3	1.2
Cell 1			-8.4	-7.9	-8.0	0.5
Cell 2			-8.8	-7.6	-8.1	1.2
Cell 3			-9.9	-7.6	-8.1	2.3
<b>BNWRD</b>						
	<b>7/21/10</b>	<b>9/30/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/30/11</b>	<b>Range</b>
CW-4	-7.5	-7.4	-7.2	-6.9	-8.3	1.4
CW-5	-7.7	-6.7	-8.5	-7.3	-8.0	1.7
CW-6	-8.0	-7.7	-7.5	-7.3	-7.9	0.7
Effluent	-6.8	-5.1	-8.0	-6.3	-6.9	2.9
Outlet	-5.8	-5.9	-7.5	-6.8	-6.3	1.8
<b>Gully</b>						
	<b>7/16/10</b>	<b>10/9/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/16/11</b>	<b>Range</b>
Tile	-6.27	no flow		-7.80	-7.99	1.72
GMW-1	-6.80	-5.28	-8.34	-9.12	-6.97	3.84
GMW-2	-7.08	-7.55	-12.11		-7.59	5.04
GMW-3	-7.36	-7.93	-9.02	-8.53	-7.83	1.66
GMW-4	-7.33		-8.67	-7.92	-7.83	1.35
GMW-5	-7.36	-7.64	-9.66	-9.24	-5.67	3.99
GMW-10			-7.96	-8.23	-6.05	2.18
GMW-11				-8.45	-8.38	0.07
Cell 1	-3.88	10.60	-9.46	-7.33	-5.84	17.93
Cell 2	-3.18	2.58	-9.75	-7.32	-6.42	12.32
Cell 3	-2.37		-9.48	-7.65	-6.24	7.11
<b>West</b>						
					<b>5/16/11</b>	
WMW-1					-5.8	
WMW-3					-8.6	
WMW-5					-7.7	
WMW-6					-8.1	
Cell 1					-5.1	
Cell 2					-4.7	
Cell 3					-3.5	
Tile					-7.8	



APPENDIX B

ANION AND NH4+ ANALYSES

Name	mg/L F <sup>-</sup>				mg/L Cl <sup>-</sup>				mg/L Br <sup>-</sup>			
	9/30/10	1/2/11	3/14/11	6/3/11	9/30/10	1/2/11	3/14/11	6/3/11	9/30/10	1/2/11	3/14/11	6/3/11
<b>Moga</b>												
Tile		0.31	0.14	0.15		14.49	13.63	13.33		n.a.	n.a.	n.a.
MMW-1		0.35	0.13	0.13		19.47	11.80	13.92		n.a.	0.06	n.a.
MMW-2		0.28	0.11	0.12		15.94	15.74	14.20		n.a.	0.05	n.a.
MMW-3		0.44	0.16	0.14		20.86	16.90	13.24		n.a.	0.07	0.123
Cell 1		0.30	0.11	0.15		14.92	13.08	13.39		n.a.	n.a.	n.a.
Cell 2		0.32	0.16	0.15		13.47	14.26	13.22		n.a.	0.11	n.a.
Cell 3		0.34	0.13	0.15		13.70	13.73	13.36		n.a.	n.a.	n.a.
<b>BNWRD</b>												
CW-4	just installed	0.29	0.12	1.34		87.34	69.64	34.18		0.25	0.23	n.a.
CW-5	just installed	0.40	0.25	0.27		21.68	23.75	16.25		0.13	0.14	n.a.
CW-6	0.25	0.40	0.23	0.19	17.55	21.32	20.29	17.33	0.13	n.a.	n.a.	n.a.
Effluent	0.81	1.29	0.41	0.65	143.79	182.17	191.81	159.18	0.43	n.a.	0.33	0.35
Outlet	0.86	1.24	0.41	0.62	126.88	211.46	200.53	154.25	0.43	n.a.	0.26	0.35
<b>Gully</b>												
Tile	not flowing		0.16	0.23			15.20	16.11			n.a.	0.20
GMW-1	0.21	0.33	0.14	0.15	9.82	5.74	5.29	4.98	0.32	0.15	0.06	n.a.
GMW-2	0.24	0.48	0.24	0.19	7.23	5.93	8.14	5.67	0.13	n.a.	0.06	n.a.
GMW-3	0.22	0.28	0.16	0.19	5.96	6.77	5.32	4.89	0.10	n.a.	n.a.	n.a.
GMW-4		0.34	0.26	0.25		8.28	12.10	10.15		n.a.	0.16	n.a.
GMW-5	0.43	0.38	0.24	0.19	8.50	18.17	6.75	4.72	n.a.	n.a.	0.06	n.a.
GMW-10		0.33	0.16	0.20		6.04	13.88	13.40		0.15	0.08	n.a.
GMW-11		0.31	0.13	0.13		5.87	7.26	10.45		n.a.	0.06	n.a.
Cell 1	1.40	0.39	0.27	0.19	53.35	10.41	15.16	14.07	2.08	0.16	0.26	n.a.
Cell 2	0.33	0.33	0.13	n.a.	32.48	9.10	13.22	12.59	0.72	0.23	0.15	n.a.
Cell 3	0.294	0.287	0.176	0.157	13.89	5.74	12.46	11.65	0.40	0.18	0.11	n.a.
<b>West</b>				5/16/11				5/16/11				5/16/11
WMW-1				0.24				16.74				1.87
WMW-3				0.20				9.29				n.a.
WMW-5				0.22				2.32				n.a.
WMW-6				0.15				5.77				0.17
Cell 1				0.34				18.95				2.71
Cell 2				0.23				12.32				2.86
Cell 3				0.18				9.76				1.06
Tile				0.29				26.77				n.a.

Name	mg/L NO <sub>3</sub> <sup>-</sup> -N				mg/L SO <sub>4</sub> <sup>2-</sup>				mg/L NH <sub>4</sub> <sup>+</sup>			
	9/30/10	1/2/11	3/14/11	6/3/11	9/30/10	1/2/11	3/14/11	6/3/11	9/30/10	1/2/11	3/14/11	6/3/11
<b>Moga</b>												
Tile		8.90	11.73	17.11		19.09	17.39	14.48		0.12	0.08	0.04
MMW-1		0.56	2.75	2.16		15.09	20.25	20.70		0.04	0.08	0.05
MMW-2		4.82	7.19	9.57		n.a.	14.97	14.92		0.02	0.07	0.05
MMW-3		17.36	4.25	0.73		73.29	28.91	22.45		0.05	0.11	0.07
Cell 1		8.70	10.98	16.36		n.a.	17.94	14.44		0.08	0.10	0.20
Cell 2		7.11	8.91	16.33		n.a.	24.66	14.36		0.27	0.09	0.07
Cell 3		7.49	10.66	15.98		n.a.	18.08	14.32		0.37	0.10	0.06
<b>BNWRD</b>	<b>9/30/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/30/11</b>	<b>9/30/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/30/11</b>	<b>9/30/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/31/11</b>
CW-4		1.29	1.76	0.80		n.a.	180.16	97.37		0.03	0.07	0.06
CW-5		0.43	0.89	0.38		n.a.	192.23	75.01		0.03	0.03	0.07
CW-6	0.42	0.74	0.89	0.47	24.74	n.a.	46.13	37.08	0.15	0.03	0.10	0.07
Effluent	23.68	9.53	18.14	17.54	30.08	n.a.	77.33	51.85	0.08	0.04	0.11	0.11
Outlet	30.08	11.04	16.27	8.91	33.31	60.14	81.86	52.10	0.24	0.49	0.11	0.33
<b>Gully</b>	<b>10/9/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/16/11</b>	<b>10/9/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/16/11</b>	<b>10/9/10</b>	<b>1/2/11</b>	<b>3/16/11</b>	<b>5/16/11</b>
Tile			9.76	21.30			201.39	56.61			0.10	0.06
GMW-1	0.39	0.71	0.43	n.a.	32.55	22.08	25.26	27.80	0.11	0.21	0.11	0.10
GMW-2	0.60	0.46	0.53	0.44	30.18	10.32	28.04	29.58	0.10	0.06	0.11	0.05
GMW-3	0.39	n.a.	0.43	0.38	18.44	7.67	15.62	15.30	0.08	0.03	0.08	0.03
GMW-4		0.43	0.85	0.43		27.05	185.26	77.34		0.07	0.11	0.07
GMW-5	0.84	0.41	0.45	0.45	47.26	46.95	36.29	54.25	0.05	0.07	0.11	0.05
GMW-10		1.54	8.63	2.27		n.a.	45.92	59.57		0.08	0.09	0.06
GMW-11		0.85	0.67	1.38		n.a.	14.41	13.30		0.03	0.41	0.05
Cell 1	n.a.	9.76	7.81	12.09	165.54	44.92	86.98	56.78	4.05	0.78	0.06	0.08
Cell 2	0.37	1.63	6.12	4.75	39.11	n.a.	140.05	69.19	0.43	0.69	0.07	0.07
Cell 3	0.37	1.00	4.31	1.43	25.70	37.12	45.91	61.49	0.04	0.54	0.10	0.05
<b>West</b>				<b>5/16/11</b>				<b>5/16/11</b>				<b>5/16/11</b>
WMW-1				3.62				91.98				0.08
WMW-3				2.17				144.85				0.09
WMW-5				0.63				26.24				0.04
WMW-6				n.a.				72.24				0.05
Cell 1				18.90				77.50				0.04
Cell 2				0.45				72.26				0.06
Cell 3				0.38				65.56				0.06
Tile				39.54				159.59				0.08

