

COUPLED BIOGEOCHEMICAL CYCLES IN RIPARIAN ZONES
WITH CONTRASTING HYDROGEOMORPHIC CHARACTERISTICS
IN THE US MIDWEST

Xiaoqiang Liu

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Philippe G. Vidon, Ph.D., Chair

Pierre-Andre Jacinthe, Ph.D.

Master's Thesis
Committee

Meghna Babbar-Sebens, Ph.D.

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ABSTRACT

Xiaoqiang Liu

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Numerous studies have investigated the fate of pollutants in riparian buffers, but few studies have focused on the control of multiple contaminants simultaneously in riparian zones. To better understand what drives the biogeochemical cycles of multiple contaminants in riparian zones, a 19-month study was conducted in riparian buffers across a range of hydrogeomorphic (HGM) settings in the White River watershed in Indiana. Three research sites [Leary Webber Ditch (LWD), Scott Starling (SS) and White River (WR)] with contrasting hydro-geomorphology were selected. We monitored groundwater table depth, oxidation reduction potential (ORP), dissolved oxygen (DO), dissolved organic carbon (DOC), NO_3^- , NH_4^+ , soluble reactive phosphorus (SRP), SO_4^{2-} , total Hg and methylmercury (MeHg). Our results revealed that differences in HGM conditions translated into distinctive site hydrology, but significant differences in site hydrology did not lead to different biogeochemical conditions. Nitrate reduction and sulfate re-oxidation were likely associated with major hydrological events, while sulfate reduction, ammonia and methylmercury production were likely associated with seasonal changes in biogeochemical conditions. Results also suggest that the LWD site was a small sink for nitrate but a source for sulfate and MeHg, the SS site was a small sink for MeHg but had little effect on NO_3^- , SO_4^{2-} and SRP, and the WR was an intermediate to a large sink for nitrate, an intermediate sink for SRP, and a small source for MeHg. Land use and point source appears to have played an important role in regulating solute concentrations (NO_3^- , SRP and THg). Thermodynamic theories probably oversimplify the

complex patterns of solute dynamics which, at the sites monitored in the present study, were more strongly impacted by HGM settings, land use, and proximity to a point source.

Philippe G Vidon, Ph.D., Chair

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LIST OF ABBREVIATIONS

HGM	Hydrogeomorphic
LWD	Leary Webber Ditch
SS	Scott Starling
WR	White River
ORP	Oxidation reduction potential
DO	Dissolved oxygen
DOC	Dissolved organic carbon
NO_3^-	Nitrate
NH_4^+	Ammonium
SO_4^{2-}	Sulfate
Cl^-	Chloride
THg	Total Mercury
MeHg	Methyl-mercury

INTRODUCTION

Intensification in agricultural production, industrial activities and urban development has greatly amplified anthropogenic influences on both quantity and quality of freshwater resources - an utmost essential resource. Excessive nutrients and toxic contaminants are major threats to water quality, ecosystem health and human health. In the context of this thesis, contaminant is defined as chemical elements or molecules that are harmful to the quality of water, and have the potential of producing undesirable ecological outcomes. In this study, we focused on four contaminants found in groundwater and surface water: Nitrate (NO_3^-), Phosphorus (P), Sulfate (SO_4^{2-}) and Methyl-mercury (MeHg).

Nitrate (NO_3^-) is one of the best-known freshwater contaminants, and has been implicated as the key nutrient causing eutrophication in oceans and estuaries (Kirchmann et al., 2002). With regard to human health, drinking water containing more than 10 mg N- NO_3^- /L is unfit for consumption as it could cause cyanosis in infants less than six months (Fan and Steinberg, 1996). Phosphorus (P) is a key limiting nutrient of terrestrial and aquatic ecosystems productivity (Wassen et al., 2005), and increased P availability has resulted in numerous documented cases of eutrophication. The United States Environmental Protection Agency has identified P pollution as the greatest impediment to achieve the water quality goals stated in the Clean Water Act (Gentry et al., 2007). Although sulfate doesn't pose a direct threat to human health, US-EPA has established a Secondary Maximum Contaminant Level of 250 mg/L for sulfate. Methyl-mercury (Me-Hg) is a neurotoxic metal, and represents a serious concern to human health due to its bio-accumulation throughout the aquatic food chain (Boening, 2000).

In addition to the individual impact of each contaminant, interactions among contaminants might lead to additional indirect impacts on water quality. Sulfate reducing bacteria is an important mediator of mercury methylation in lacustrine sediments

(Gilmour et al., 1992). However, excess SO_4^{2-} may limit methylation if increased sulfide production results in reduced availability of Hg through formation of charged complexes (Benoit et al., 1999). Several studies (Hedin et al., 1998; Van Der Welle et al., 2006) have reported on the interactions between the N and S cycles. Positive correlations between groundwater NO_3^- and SO_4^{2-} have been reported, probably indicating evolution of these species under oxic conditions (Hedin et al., 1998). It should also be noted that desiccation and oxidation of S-rich sediments can lead to acidification and mobilization of toxic metals (Smolders et al., 2006), ultimately limiting nitrification. Sulfide (S^{2-}) production under reducing conditions can induce iron deficiency and can be toxic to some microorganisms. In addition, because of the competition between PO_4^{3-} and S^{2-} for binding sites with iron, elevated sulfide production can increase P availability and eutrophication without external P input (Van Der Welle et al., 2006).

In light of the negative impacts of these contaminants (N, P, Hg) on water quality and the complex interactions among them, a better understanding temporal and spatial patterns of biogeochemical cycles of those contaminants across ecosystems, will provide a better strategy for nutrient management at landscape scale. Riparian zones are the most obvious and important control points along paths of nutrient flux from terrestrial to aquatic ecosystems (Lowrance 1984; Hill, 1996; Hedin et al., 1998; Vidon and Hill, 2004a, b). Riparian zones are interfaces between terrestrial and aquatic systems, with unusually high potential for biogeochemical transformations, preventing the direct discharge of various contaminants from terrestrial ecosystems into water bodies (Hill, 1996). Over the past several decades, studies have shown that riparian zones serve as critical control points that regulate nutrient transport from agricultural land to aquatic systems. Riparian vegetation, especially dense grassy areas, favors sediment trapping as well as the adsorption and degradation of pesticides in overland flow (Benoit et al., 1999, 2000; McKergrow et al., 2003). Across Europe, Canada and

United States, many riparian zones have been investigated for their high N removal efficiency (60-90%). It is also worth noting that some riparian zones have limited N removal capacity and can even become a source of NO_3^- to adjacent streams.

Riparian zones contribute to water quality maintenance (Hill, 1996). However, variability in soil moisture, redox potential, bioavailable carbon content, chemistry of upland aquifer, and temperature could affect the fate and transport of solutes through riparian zones (Korom, 1992; Hedin et al., 1998; Hill et al., 2004; Vidon and Hill, 2004a). In particular, subtle changes in biogeochemical conditions of riparian ecosystems have important implications for the speciation and availability of N (Gold et al., 1998; Jacinthe et al., 1998), P (Reddy and De-laune, 2008), mercury (Hg) (Mitchell et al., 2008), sulfur (S) (Devito and Hill, 1997; Eimers et al., 2004), and organic matter (OM) (Jacinthe et al., 2003; Gurwick et al., 2008).

Importantly, N, P, S and MeHg transformations are all subject to changes in soil redox conditions and the availability of electron donors and acceptors. For instance, NO_3^- will be first species to undergo reduction following depletion of oxygen in soil pore. Nitrate reduction is favored in the presence of electron donors, such as, dissolved organic matter (DOC). Phosphorous mobilization and immobilization in riparian areas is a function of the interactions of P sources, transport pathways and biogeochemical transformations. Riparian soils may be P sources to streams when soils are anoxic or when mineral dissolution leads to P release (Baldwin and Mitchell, 2000). Sulfate reduction can be significant in anoxic soils and during periods when water table is low (Eimer et al., 2004). The production of methylmercury is facilitated under well reduced soil condition and in the presence of adequate amounts of sulfate and organic matter (St. Louis et al., 1996). The sequence of reactions described above (e.g. denitrification vs iron reduction vs. sulfate reduction vs. methanogenesis) occurred on the basis of energy production from a thermodynamic perspective (Korom 1992).

Hedin et al. (1998) found that biogeochemical processes at stream-soil interface are predictable outcomes of microbial communities and supplies of electron donors and acceptors, and proposed that the processes are strongly associated with subsurface hydrologic paths (Hedin et al., 1998). In another study, Vidon and Hill (2004c) found that the organized patterns of electron donors and acceptors in 8 riparian zones in Ontario (Canada) further supported such an analysis, but these authors (Vidon and Hill, 2004c) also pointed out that biogeochemical processes are affected by hydrologic flow path, residence time, N input from upland, and available carbon distribution in the subsurface. There is much evidence in literature that riparian HGM and hydrology affect biogeochemical condition in groundwater and the fate of redox sensitive contaminants (N, S, P and MeHg) in the subsurface (Hill, 2000; Hefting et al., 2003; Vidon et al., 2010, Burns et al., 2012). The success of linking landscape characteristics and site hydrology to N removal, have shown that landscape variables, such as topography, soil and surficial geology, regulate hydrologic flow paths and NO_3^- removal in riparian zones which is subject to soil reducing condition and available electron donors (Hill, 1996; Hedin et al., 1998; Gold et al., 2001; Burt et al., 2002; Vidon and Hill, 2004b, c; Vidon and Hill, 2006). As aforementioned, the transformations of SRP, SO_4^{2-} and methyl mercury are also linked to soil redox condition and subject to thermodynamic constraints similar to NO_3^- . Therefore, landscape variables controlling nitrate removal likely control the removal of other contaminants. Based on these considerations, we hypothesized that hydro-geomorphic (HGM) characteristics, site hydrology and soil redox condition can be used to generalize riparian zone functions with respect to biogeochemical cycles of N, S, P, and Hg. The objectives of this study were to: 1) evaluate to what extent HGM and major events affect water table fluctuations, and biogeochemical conditions control the dynamics of N, S, P and MeHg in riparian groundwater, and 2) compare the dynamics of these contaminants in morphologically-distinct riparian buffers.

LITERATURE REVIEW

Biogeochemical cycles of contaminants from thermodynamic perspective

Coupled biogeochemical cycles are ultimately driven by the flow of electrons in redox reactions, and from a micro-scale perspective, the biogeochemical functions of riparian zones are predictable and the outcomes of interactions between microbial communities and supplies of electron donors and electron acceptors (Hedin et al., 1998). Analysis of these interactions can improve our mechanistic understanding of denitrification and other important biogeochemical processes in riparian zones. The sequence of the reactions (denitrification, iron reduction, sulfate reduction, and methanogenesis) is determined by their thermodynamic energy production (Morel and Hering, 1993), proceeding in the direction leading to progressively lower redox potentials. The redox potentials corresponding to specific electron acceptor are: 0.816 Volt (V) for oxygen, 0.421 V for nitrate, -0.182 V for Fe^{3+} , -0.215V for sulfate and -0.244 V for CO_2 , respectively (Stevenson, 1986).

Ultimately the biogeochemical fates of contaminants are driven by microbial activity, and microbial metabolism is controlled by available electron acceptors and donors, and the amount of energy generated for growth and maintenance through coupled redox reactions (Zehnder and Stumm, 1988; Morel and Hering, 1993). Based on the free energy generated by redox reactions, we could theoretically predict both the temporal and spatial patterns of microbial reactions in riparian zones (Stumm and Morgan, 1981). Such thermodynamically-based predictions depend on the assumption that, in a given environment, the metabolic reaction that yields most energy will dominate over any competing reactions (Zehnder and Stumm, 1988; Morel and Hering, 1993). From a thermodynamic perspective, the sequence - soil respiration, denitrification, iron reduction, sulfate reduction and methanogenesis - should take place in the order of energy production, and these reactions should be mutually exclusive in theory. However,

we need to accept this assumption with caution for two reasons. First, when the energy yields are close and one microbial community have high affinity to electron donors or much lower concentrations comparing to its competitor. Secondly, the thermodynamic perspective does not take into account localized reducing conditions that may be present. Jacinthe et al. (1998) reported the presence of anoxic patches within otherwise oxic environment in the subsurface of riparian zones.

The redox environment of riparian soils exists in a dynamic equilibrium maintained by the availability of oxygen as determined by soil pore space volume occupied by water, and oxygen level of incoming water. A large gradient of redox potential may develop in sediments over a depth as short as 2 mm (Howeler and Bouldin, 1971). Due to the fluctuations of the water table, the position of individual redox reaction may shift in the soil profile (Schlesinger, 1991). From high to low oxygen availability, a series of redox reactions occur. Ammonia and ammonium ions are transformed (nitrified) into NO_3^- by microbes under aerobic soil conditions, and soil respiration produces CO_2 . After oxygen is depleted by aerobic respiration, the redox potential falls to below 0.421 V, and NO_3^- becomes the electron acceptor and the denitrification process begins (Schlesinger, 1991). Several studies have indicated that reduced conditions, where DO concentration are <2-3 mg/L and redox potentials of between +200 and -300 mV, are necessary for denitrification to occur (Gillham and Cherry 1978; Lensi and Chalamet 1982; Cey et al., 1999). Shallow groundwater flows near the root zone, where more organic matter is available for bacteria consumption, leading to increased denitrification (Lowrance et al., 1997; Dosskey, 2001). N_2O and N_2 are produced in the process depending on the soil anaerobic condition and available electron donors.

P solubility varies with redox condition. Under aerobic conditions, PO_4^{3-} interacts with cations (e.g., Fe^{3+} and Ca^{2+}) to form relatively insoluble precipitates, leading therefore to decreased availability of P (Wetzel, 2001). The classical model first

proposed by Mortimer (1941) also pointed out that PO_4^{3-} is rendered insoluble through either strong sorption onto iron oxyhydroxide (FeOOH) or through formation of FePO_4 precipitates under aerobic conditions. However, under reduced conditions (Eh of about 200 mV), Fe^{3+} is reduced to the more soluble Fe^{2+} , leading to the dissolution of FeOOHPO_4 , and thus the release of PO_4^{3-} and Fe^{2+} . Iron reduction can occur when Eh is below -200 mV (Jordan et al., 1993). In a sandy riparian zone, Carlyle and Hill (2001) measured low soluble reactive phosphorus concentrations (<2 ug/L) and low ferrous iron (Fe^{2+}) concentrations (<0.2 mg/L) when dissolved oxygen (DO) concentrations (>3 mg/L) were high. In contrast, in a buried channel where more reduced conditions prevailed (DO<3 mg/L), high concentrations of soluble reactive phosphorus (50-950 ug/L), and ferrous iron (Fe^{2+}) (>1 mg/L) were recorded.

Sulfate acts as an electron acceptor after the depletion of oxygen, nitrate and iron. Because the free energy generated by sulfate reduction and methanogenesis do not differ significantly, it would be reasonable to assume the co-occurrence of the two processes in most natural settings (Hedin et al., 1998). When redox potential drops to <-244 mV, methanogenic bacteria can only use certain organic substrates for acetate splitting. However, because sulfate-reducing bacteria are more effective competitors for acetate, they tend to out-compete methanogens (Schonheit et al., 1982). Consequently, there is little or no overlap between sulfate reduction zone and methanogenesis zone in sediments (Schlesinger, 1991). Under highly reduced conditions, a riparian zone or wetland can serve as a sink for CO_2 and a source of CH_4 (Mistch and Gosselink, 2000). Mercury biomethylation is the transformation of inorganic mercury (Hg (II)) to CH_3Hg^+ , which is mainly carried out by sulfate-reducing bacteria that live in anoxic (low dissolved oxygen) environment (USGS, 2010).

In addition to the availability of electron acceptors, anaerobic reactions are tightly regulated by the availability of dissolved organic carbon (DOC) which is the dominant

electron donor in soils. DOC includes the water soluble and leachable fraction of the soil organic matter; in general, the concentration of DOC is higher in surface soil horizons and decreases with depth (McDowell and Wood, 1984). Since reduced soil conditions generally facilitate the accumulation of organic matter, it follows that wetlands and periodically-flooded riparian soils are areas with high DOC concentration. The co-occurrence of the high organic matter content and reducing conditions in riparian soils can significantly impact N, P, S and Hg fate and GHG production/consumption in riparian systems. Riparian ecosystems are characterized by seasonally variable water tables which, through periodic contact with the more biologically active upper soil layers, could influence C supply to microbial communities in the subsurface.

Organic carbon (OC) contributes to the formation of organo-mineral complexes that control the transport and solubility of heavy metals in soil and aquatic systems (Rencz et al., 2003). In particular, the behavior of mercury in the environment is impacted by this mechanism due to the strong affinity of Hg for organic matter in soils, surface waters, peats and sediments. A study found that lake water pH and dissolved organic carbon (DOC) were the variables most strongly correlated with mercury in lake waters and yellow perch (Rencz et al., 2003). In terrestrial ecosystems, another study found that significant positive relationships exist between Hg and DOC in both throughfall (36–57% of the variation) and stemflow waters (55–88% of the variation), and Hg complexation by DOC appears to be related to the contact time between precipitation and carbon sources (Kolka et al., 1999). In addition to the strong correlation between OC and Hg, interactions among sulfate, MeHg, P and sulfate have been reported in the literature. These relationships will be introduced in a latter section.

Overall, wet and anaerobic soil conditions, as often observed in riparian systems, are favorable for denitrification and removal of NO_3^- , but P and methyl-Hg could be released in solution under these same conditions; large amounts of GHG (especially

N₂O and CH₄) could also be produced (Jacinthe and Lal, 2004; Mitchell et al., 2008; Hoffman et al., 2009; Vidon et al., 2010). Therefore, it raises the question as to what extent are we improving water quality in relation to nitrate, pesticide and sediments at the expense of water quality, with respect to P and Hg or air quality, when we use riparian zones as our best management practice (Allan et al., 2008; Vidon et al., 2010). It is thus of great significance to understand the interactions of multiple contaminants when riparian functions are examined at the landscape scale.

Landscape and climate controls on hydrology and biogeochemical cycles

From a macro-scale perspective, the biogeochemical functions of a riparian zone reflect the interactions among climate and landscape characteristics (surficial geology, topography, soil lithology, vegetation and land use) at a specific site. The biogeochemistry and functions of riparian zones are closely linked to the reactions occurring in the surrounding terrestrial environment by the movement of surface runoff and groundwater (Likens and Bormann, 1974). The combined effects of climate and landscape characteristics create identifiable characteristics such as water table variations (high and low) and water flow paths (shallow subsurface flow, deep ground water flow, seeps, overland flow or macro-pore flow) that ultimately control redox conditions and the intensity of biogeochemical transformations in riparian zones.

Regional climate and hydrological regime add strong temporal components into riparian biogeochemical functions as well. In regions where soil does not freeze during the winter months, like in Western Europe, most nitrate leaching occurs at the same time as the maximum amount of precipitation, from December to March. In regions where the soil freezes during the winter and where snow accumulation is observed (Northern United States, Canada, Northern Europe), the low flow period generally occurs in winter and summer; the high flow period occurs in spring when snow melts, and sometime in the fall if precipitation is significant. Winter soil freezing events and their duration, are the

determining factors of the lag of nutrient transport in temperate climates. The timing, intensity and the amount of solute entering riparian zones vary seasonally. During the spring thaw, extensive amounts of water flow through riparian systems, and this is the time of the year when runoff and solute loads entering riparian systems are generally the largest (Vidon et al., 2009). During the summer, the amount of water and the nitrate load entering the riparian zone are generally low. Cold temperature during snowmelt may reduce soil biological activity in surface riparian soils, while higher rates of biological activity may occur in summer when solute fluxes are lower. For example, THg concentrations is commonly associated with periods of high stream flow, while MeHg concentration often decreases during high flow periods such as snowmelt due to low sediment methylation rates at low temperature (Shanley et al., 2008).

Hydrologic flow paths have profound impact on solutes dynamics in riparian zones. Hedin et al. (1998) reported that high rate of biogeochemical activities occurred at the interface between shallow subsurface flow with high levels of electron donors (DOC, CH₄ and NH₄⁺) and deep subsurface flow with high levels of electron acceptors (NO₃⁻, N₂O and SO₄²⁻). The water table fluctuates seasonally in riparian zones with wet-dry events, which plays a dominant role in determining the amount of oxygen available in soils. On the other hand, high flow events during wet periods are also associated with hot-moment phenomena which largely determine the capacity of riparian zones as contaminant sources or sinks. For example, a general tendency for Hg concentrations to increase during storm flow has been found in several studies (Allan and Heyes, 1998; Shanley et al., 2008). Elevated DOC concentrations are commonly associated with storm flow and snowmelt events (Boyer et al., 1997; Inamdar et al., 2006; Sebestyen et al., 2009). Overland flows during wet periods are the primary vector for P transport in agricultural settings (Peterjohn and Correl, 1984; Royer et al., 2006) and in many arid and semiarid environments (Jacobs et al., 2007).

The hydrogeomorphic features of riparian zones along a river channel can vary greatly in slope, topography (concave, convex or flat), geological setting (till, outwash, alluvial) (Gold et al., 2001; Kellogg et al., 2005), soil texture (coarse or fine) and vegetation (grass, forest). These attributes form various combinations to determine groundwater flow from uplands to water bodies, and to a large extent control the interactions of riparian soils with nutrients transported across the riparian zone (Jacinthe et al., 1998; Devito et al., 2000; Hill, 2000; Burt et al., 2002; Kellogg et al., 2005). For riparian zones residing in lowland floodplains in the UK, kinematic wave processes dominate water flow from stream into adjacent riparian zones and temporarily block water flow from hillside toward stream (Jung et al., 2004).

Slope gradient between riparian zone and adjacent upland field is an approximate predictor of the hydraulic gradient driving the fluxes on contaminants entering a riparian zone (Vidon and Hill, 2006), but there is a risk to overestimate hydraulic gradient by slope gradient in riparian sites with thick permeable upland sediments (for example >6 m). Moderate to steep slopes of upland-riparian interface are likely to produce greater inputs than gentle slopes with similar depths of permeable sediments (Vidon and Hill, 2004b). When the average slope gradient across the riparian zone is larger than 5%, ground water almost always flows in the direction of the steepest topographical gradient (Vidon and Hill, 2006).

Several studies showed that topography plays an important role in riparian biogeochemical functions with regard to nutrient retention (Clément et al., 2002; Sabater et al., 2003; Vidon and Hill, 2004b). A concave profile at field perimeter favors the interactions between subsurface water and the surface soil horizons (0-50 cm) where denitrification and plant uptake are likely to occur. In contrast, convex topography at upland-riparian margin favors deeper groundwater flows, so that the groundwater may

bypass the biogeochemical hot spots near surface. Strong correlations were found between upland slope length and nitrate inputs at field perimeter (Vidon and Hill 2004b).

Riparian sediment permeability and depth to a confining layer also influence groundwater flow paths with consequent effects on the width of the riparian zone required for nutrient removal (Vidon and Hill 2004a, c). The size and seasonality of hydrologic connections with adjacent uplands aquifer depend on slope of upland-riparian margin, hydraulic conductivity, depth of permeable soil. In general, when the depth to the confining layer in the upland exceeds 2-3 m, it is more likely to create a permanent subsurface hydrologic link between uplands and riparian zones (Vidon and Hill, 2006). When the permeable soil depth is >6 m, ground water may bypass the riparian zone at depth. Although the depth of permeable sediments in uplands and adjacent riparian zones are commonly similar in settings where a confining layer lies within a few meters of surface, valley incision in landscapes with thick surficial aquifers can cause considerable differences in permeable sediment depth between upland and riparian zones. In this case, for riparian zones with a confining layers less than 2 m, ground water at the field perimeter may be forced to the surface as seeps or overland flow, which strongly constraints the potential of this type of riparian zone as a nitrate sink. Therefore, the depths of permeable soil and confining layers influence the fluctuations of riparian zone water table and the extent of surface saturation, with consequent effects on soil redox potential and microbial processes (Devito and Hill, 1997). Nitrate fluxes to riparian areas increase gradually with increasing permeable sediment's depth, upland slope length and the slope gradient of uplands (Vidon and Hill, 2004b).

In general, a riparian width of <20 m wide is often sufficient for effective nitrate removal. However, studies from multiple riparian sites in the United States, Canada and European countries support that more than 25 m width is needed for 90 percent nitrate removal for riparian sites with sand and gravel sediments. Another exception is that, for

riparian sites with more than 4 m permeable sediments, a 90% percent of nitrate removal requires a distance larger than 40 m (Vidon and Hill, 2006). Vidon and Hill (2004b) reported that, at the Boyne river site, a nitrate plume extended at depth in the sands beneath the peat for a horizontal distance of more than 150 m before declining to less than 5 mg/L near the bank. Soil attributes also influence water residence time, and therefore, poorly drained soils often have low redox potentials, while well drained soils tend to have higher redox potentials under the same hydrological conditions (Vidon and Hill 2006). Hydrological conductivity of sediments within riparian zones affects the residence time and flow path, which influences the development of anaerobic conditions and the duration of flooding soil conditions. To be more specific, the progressive decrease in redox potential after aerobic soils are flooded is analogous to the change in redox potential with depth. Vidon and Hill (2004b) reported that nitrate removal dropped from >90 to 60% as the water table rose and groundwater fluxes increased in a riparian zones in southern Ontario. They found that a gravel layer near the soil surface allowed water to bypass organic rich sediment in the riparian zone during episodic high water table periods.

When it comes to the effect of soil texture on nutrient transport and transformation for multiple contaminants, entire soil profile needs to be considered in order to objectively examine biotransformation in riparian zones. Gold et al. (1998) and Jacinthe et al. (1998) both found that the occurrence of denitrification in small patches of OC in the C horizon of riparian soils. Hill et al. (2000) observed the occurrence of denitrification at interfaces between sands and peats or buried channel deposits in a southern Ontario riparian zone. Although denitrification rate is the highest in surficial soil horizons and a strong vertical gradient in soil profile (Clément et al., 2002), they found that significant nitrate removal occurs in the lower portion soil profile at the interface of field edge and riparian zones. More recently, Gurwick et al. (2008) showed that 10

buried patches of organic carbon in riparian zones in glaciated landscapes were zones of preferential microbial activity. All of these studies suggested that studies of nitrate removal should pay attention to the entire soil profile instead of the surface soil layer only, and they may also lend insight to other contaminant removal in the soil profile. The biogeochemical processes can become complicated with added spatial heterogeneity of natural environments in consideration of its inherent temporal variations. 70% of the N_2O emission and coupled nitrification and denitrification in terrestrial ecosystems during a year may only occur during a period of 5-10 days (Groffman et al., 2009). Although sulfate, P and mercury might be less volatile in comparison to N dynamics, the general pattern of high heterogeneity applies as well. In order to capture those spatial and temporal variations in riparian zones, a mechanistic understanding of processes controlling the biogeochemical cycling of the four contaminants would be necessary.

The geologic characteristics of the landscape surrounding the riparian zone have a direct impact on groundwater chemistry flowing through the riparian zone. For instance, the type of bedrock (limestone, dolomite, granite or schist) will partially control the acidity (pH) of subsurface water and its mineral composition, which will influence the biogeochemical reactions occurring within the riparian soil profile. Reflecting bedrock composition in the US Southwest (Utah and Arizona), groundwater sulfate concentrations are much higher than in the Midwest where glacial till is the predominant soil parent material.

Vegetation participates in the distribution of incoming waters intercepted in riparian buffers. Most significantly, through evapotranspiration, vegetation substantially impact water table fluctuations during the growing season. Riparian zone vegetation plays other roles in maintaining stream-bank stability, and providing food for aquatic life (Dosskey et al., 2010). Grassy riparian buffers have also been shown to produce a great deal of the DOC in adjacent streams because of their high OM content, among other

factors (Hill, 2000). In particular, grass buffers are more efficient in phosphorus retention because the grass retards overland flow and allows the deposition within the buffer of phosphorus adsorbed to particles (Lowrance et al., 1997; Benoit et al., 1999; Dosskey et al., 2001). Vegetation may play an important role in enhancing denitrification by providing carbon deposit at longer time scale (channel deposit) but current surface vegetation has little to no impact on nitrate removal in many riparian zones. By comparing the effect of different vegetation cover on denitrification, a study in France also suggested that topography is more important than vegetation cover regarding nitrate removal (Clément et al., 2002). In a study comparing 14 riparian sites across Europe, Sabater et al. (2003) reported that no correlation existed between nitrate removal and vegetation. Vidon and Hill (2004a, c) showed that nitrate removal profiles at eight southern Ontario riparian sites did not vary significantly with seasons. Therefore, we assume that vegetation play insignificant role in biogeochemical cycles of multiple contaminants in riparian zones.

Land use also has significant and even dominant impact on nutrient input within a catchment. Studies indicate that the increase in groundwater nitrate over time was approximately proportional to the documented increase in regional N fertilizer use, and could be accounted for by oxidation and leaching of about 25-30% of the fertilizer N (Böhlke and Denver, 1995). A landscape model including metrics of hydrogeomorphology, riparian/wetland area, and open water, explains about 66% to >90% of spatial variation in THg and MeHg in spring and summer samples. Among all landscape factors, wetland area is typically the strongest correlate with THg and MeHg concentrations and loads at watershed scale (Burns et al., 2012). However, some studies showed that DOC and Hg concentrations are weakly correlated in some surface water (Schelker et al., 2011). Although P transport by overland flow accounts for a majority of annual P exports in agricultural settings (Peterjohn and Correll, 1984), P

leaching via subsurface flow could become significant in artificially drained agricultural settings (McDowell et al., 2001).

In a natural environment, climate and landscape characteristics form a variety of combinations to affect biogeochemical transformations of contaminants. Depending on the climate (precipitation) and the hydrogeomorphic characteristics of the watershed in which the riparian zone resides, the proportion of groundwater, precipitation and surface water recharging the riparian zone will vary (Vidon and Smith, 2007).

Due to temporal heterogeneity of solute fluxes through riparian zones, large fractions of annual solute loadings often occur during brief portions of the year such as rainfall and snowmelt (called hot moments). Hot moments are defined as short periods of time that displayed disproportionately high reaction rates (biogeochemical hot moments) or high flux (transport hot moments) relative to longer intervening time periods (McClain et al., 2003; Vidon et al., 2010). A hot spot is an area displaying disproportionately high reaction rates (biogeochemical hot spots) or high solutes flux (transport hot spots) (McClain et al., 2003; Vidon et al., 2010). A basic understanding of the possible co-occurrence of hot phenomena (hot moments and hot spots) for multiple contaminants in riparian systems will certainly add to our understanding of the influence of riparian zones on water quality and air quality, which will help land management strategies at the landscape scale (Vidon et al., 2010; Vidon, 2010).

Studies have proven that landscape characteristics like slope, topography, sediment depth, soil texture and vegetation types can be used to predict site hydrology and nitrate removal efficiency at the watershed scale (Lowrance et al., 1997; Hill, 2000; Baker et al., 2001; Gold et al., 2001; Vidon, 2004a,b). A conceptual and semi-quantitative model incorporating these controlling factors has been developed and successfully applied in predicting N removal capacity of riparian buffers from various geological settings, and validated by studies in temperate regions of United States,

Canada and European countries (Gold et al., 2001, Rosenblatt et al., 2001; Hill, 2000; Vidon and Hill 2004b; Vidon and Hill, 2006).

Those reactions occurred in narrow redox ranges, so they are theoretically mutual exclusive (Naiman et al., 2005). But we need to accept this with caution because highly heterogeneous subsurface environment might provide small anoxic patches within oxic environments (Jacinthe et al., 1998). Natural environments are not isolated into separate containers, nor do they simply contain a mixture of components. Those variables controlling the biogeochemical function of riparian zones are universal, but operate in different combinations and in different orders of importance in both space and time (Schlesinger, 1991). Therefore, we should also be aware of that, due to high spatial heterogeneity and high temporal variation of biogeochemical transformation for contaminants and because of discrepancies between biogeochemical hot phenomena (reaction rate) and transport hot phenomena (flux), it could be challenging enough to identify hot spot and hot moment for a single contaminant on an annual basis (McClain et al., 2003; Groffman et al., 2009; Vidon et al., 2010). Needless to say, we try to simultaneously study multiple contaminants regarding their spatial and temporal patterns of biogeochemical cycles. However, literature review suggests that knowledge of the possible co-occurrence of hot spots and moments for a variety of contaminants is much needed for the optimization of riparian zone management (Groffman et al., 2009; Vidon et al, 2010). Because our three sites are representatives of landscape types in central Indiana, our findings may help to better optimize riparian zone management on improving water quality and to provide insights for land management in this region.

MATERIAL AND METHODS

Hydrogeomorphic settings of the study sites

Three representative riparian zones, White River (WR), Scott Startling (SS), and Leary-Weber Ditch (LWD) were selected for this study. The three sites are representatives of three main types of landscape at the White River watershed on the basis of GIS analysis. To minimize potential environmental heterogeneity, our research sites were randomly chosen for each type of hydrogeomorphic (HGM) setting. The three sites are located in central Indiana (Figure 1), with the climate classified as temperate continental and humid. The average January temperature is -3°C whereas the average for July is 23°C (Indiana State Climate Office, 2005). The average annual precipitation ranges from 96.5-101.6 cm (Newman, 1997). The hydrological wet period is December to May and the dry period is July to November. The wettest period is late spring and the coldest month is February. The highest stream discharge is observed in March while the lowest discharge generally occurs in September. Rainfall variations affect the timing and magnitude of groundwater recharge and surface runoff (Clark, 1980). About 68% of precipitation is lost to evapotranspiration, 9% serves as groundwater recharge, and 23% becomes surface runoff (Clark, 1980). Therefore, overall water input is larger than water output in this region, and excess water will be consumed by growth of agriculture and human population.

The Leary Webber Ditch (LWD) is a drainage site on the flat Tipton Till Plain northeast of downtown Indianapolis, and it is adjacent to a stream been artificially deepened and straightened. This site is a typical agriculturally dominated riparian zone. Soil at the site is dominated by poorly drained loamy to clay-loam soils and surface water ponding is often observed in the days following precipitation events (USDA proposal). Soil at LWD belongs to Crosby- Brookston associations which are generally deep, very poorly drained or somewhat poorly drained with a silt clay loam texture in the

first 30 cm soil profile (Vidon and Cuadra, 2010). Glacial till deposits and low conductivity sediments underneath are features of this site. Saturated soil hydraulic conductivity estimated by the Hvorslev water recovery method is 16.39 cm/day which is equivalent to magnitude of 10^{-4} cm/s. The flat topography between the upland and the riparian zone is very common for this setting. The slope gradient at the upland-riparian margin is less 3%, but the slope gradient at riparian and stream margin is close to 1. The steep slope of the stream and riparian margin area allows high input from outflow of tile drainage. Vegetation in the riparian buffer is a mixture of annual and perennial grasses and forbs.

The Scott Starling (SS) site is located in a glacial till valley with alluvial deposits near the Fishback Creek, an ancient stream created by glacial melting water. The geologic setting is composed of two layers of glacial till with a thin layer of outwash in between. The lower till is pre-Wisconsin in age, and the upper Trafalgar till is Wisconsin in age (Harrison, 1963). Typical till in this area has coarse silt to fine sand texture, and is high in carbonates because of high percentages of limestone and dolomite bedrock that was eroded by glacial melt water (Harrison, 1963). Topography in the study area is characterized as steep concave topography at field edge, with a flat riparian area directly adjacent to the stream. The groundwater in the riparian zone is mainly from seeps between the two glacial till layers. A thin layer of alluvium (approximate 2 m deep) overlying the lower till unit that restrict water flow to the first 2 m of the soil profile forms the riparian zone between the stream and the slope bottom (Vidon and Smith, 2007). Soil saturated hydraulic conductivity measurements indicate an average soil hydraulic conductivity (K_s) of 63 cm/day for areas where loamy soil dominates, 132 cm/day for areas sandy loam dominates, and 158 cm/day for the sand and gravel layer at depth (Vidon and Smith, 2007), which is equivalent to the magnitude of 10^{-4} to 10^{-3} cm/s . Vegetation in the riparian zone is herbaceous except near the stream where hardwood

species dominate. The upland is a managed forest land with low density residential housing development, which has low nitrate input. The riparian zone could be divided into two regions on the basis of vegetation and soil hydrologic conditions. The region close to the upland is a wetland area, and the one close to the stream is covered by mixed shrubs and trees.

The White River (WR) site, an alluvium / outwash area, has 2 m of silt loam soil overlaying a gravel layer, then 50 cm thick alluvium deposits at greater depth. This is an agriculturally dominated riparian zone with soybean and corn rotation upland, and is typical of large valley bottoms in the US Midwest landscape. The slope gradients between upland and field perimeter are 8-11%. The WR site is adjacent to the White River, which is a fourth order river. The margin between river and riparian zone is steep (3 m deficit). The soil in the riparian zone is mainly sand and gravel, which is highly conductive and well drained. It is reasonable to assume that soil hydraulic conductivity (K_s) at WR site is at the magnitude of 10^{-3} cm/s, and this type of soil is not favorable for the development of long periods of anoxic conditions.



Figure 1: Geographical location of the three study sites in Indiana - Leary Webber Ditch (LWD), Scott Starling (SS) and White River (WR).

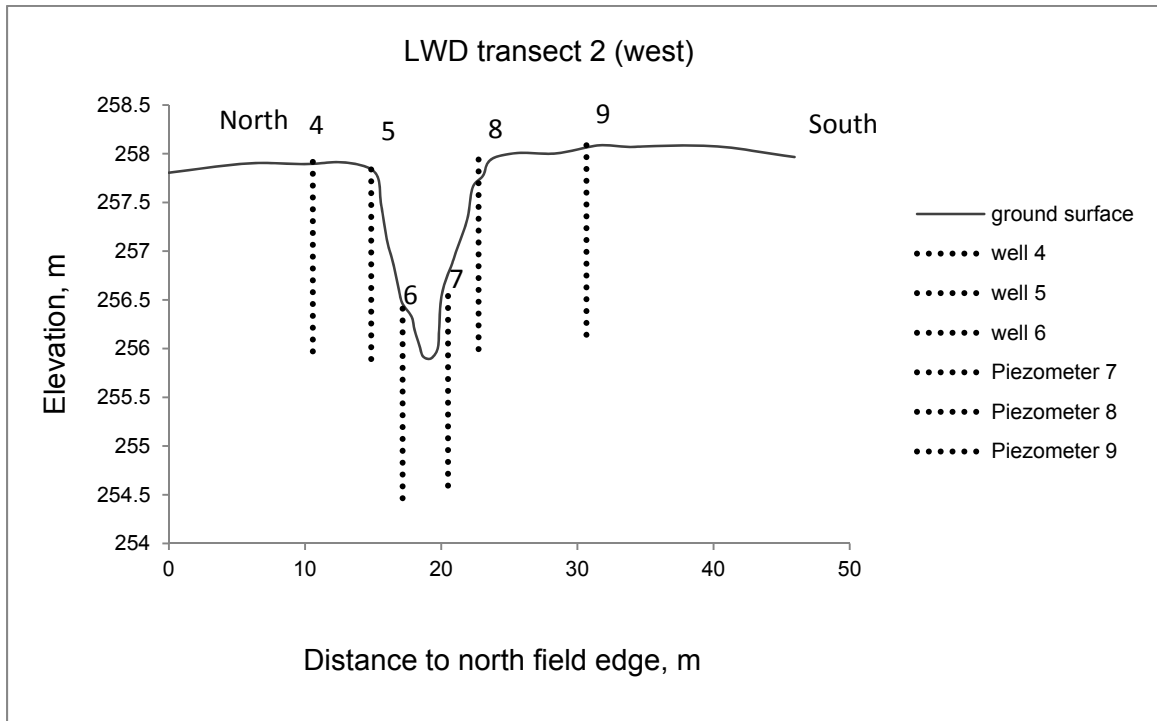
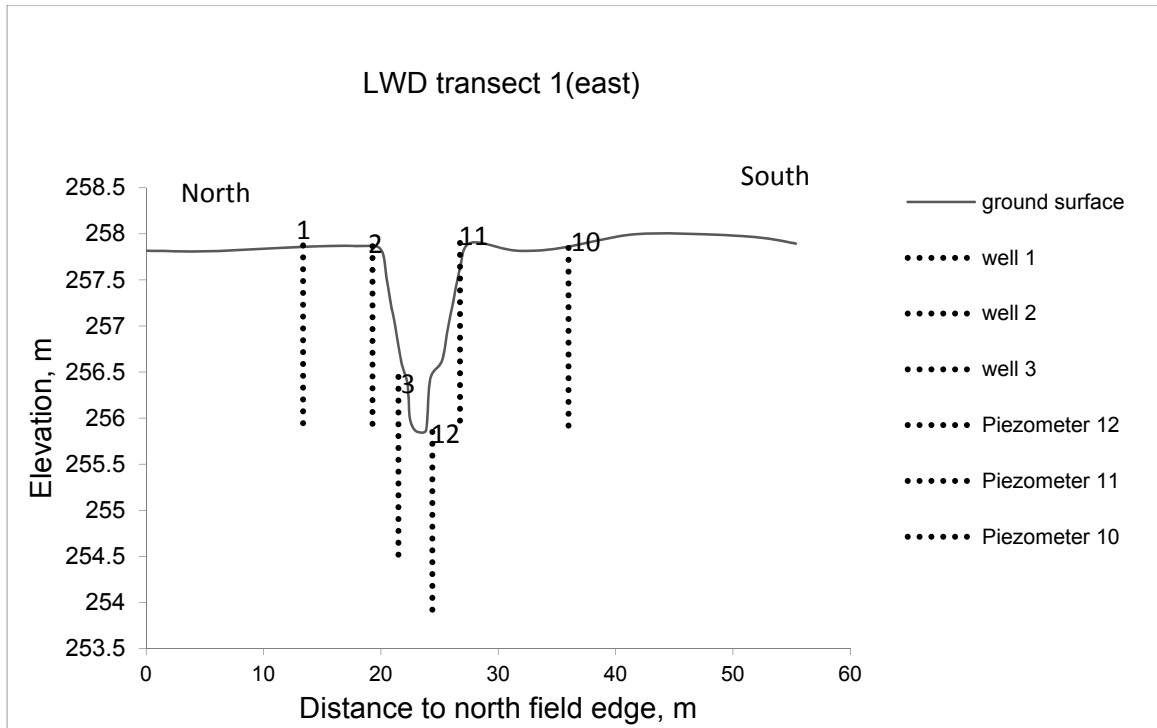
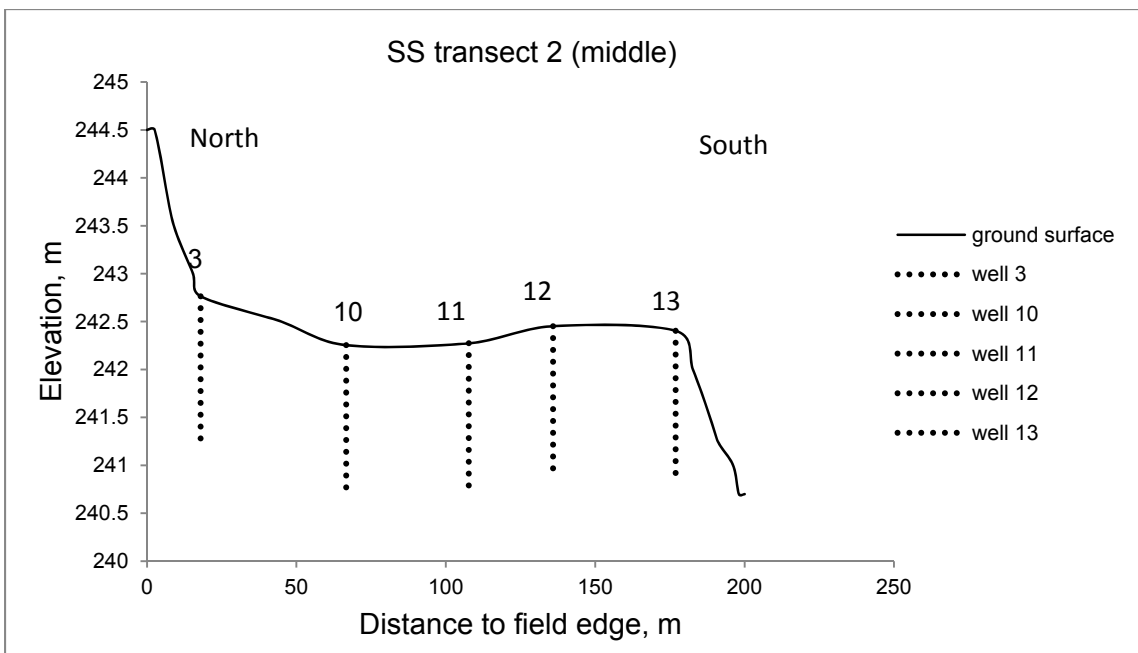
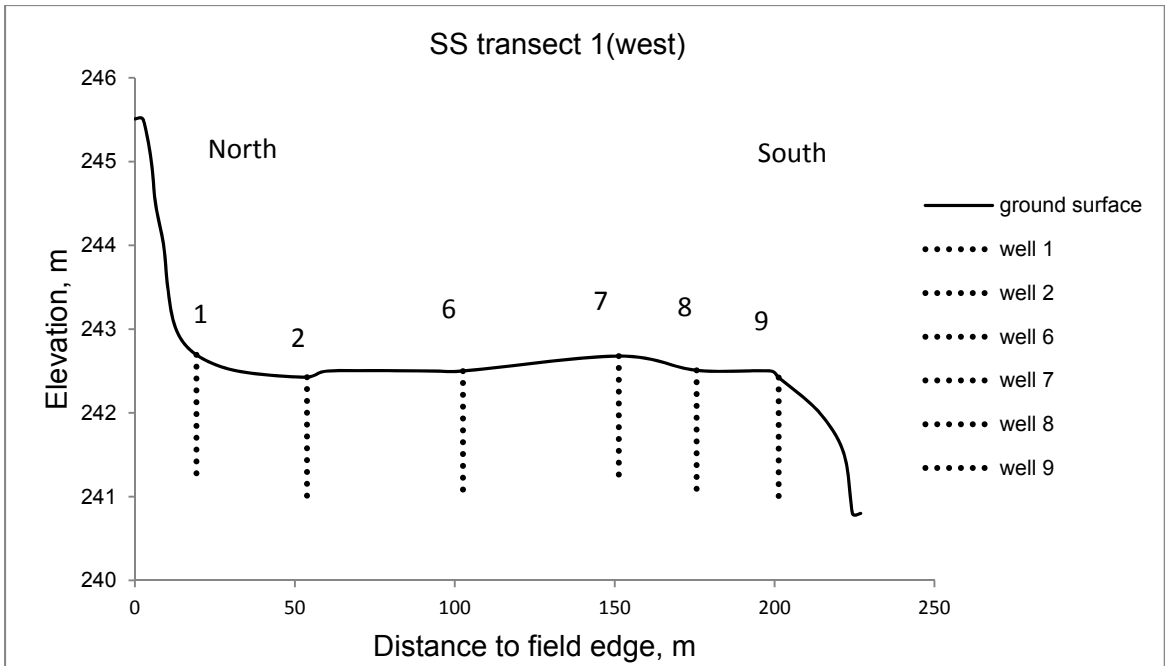


Figure 2A: Location of groundwater wells along transects 1 and 2 at the Leary Webber Ditch (LWD) site.



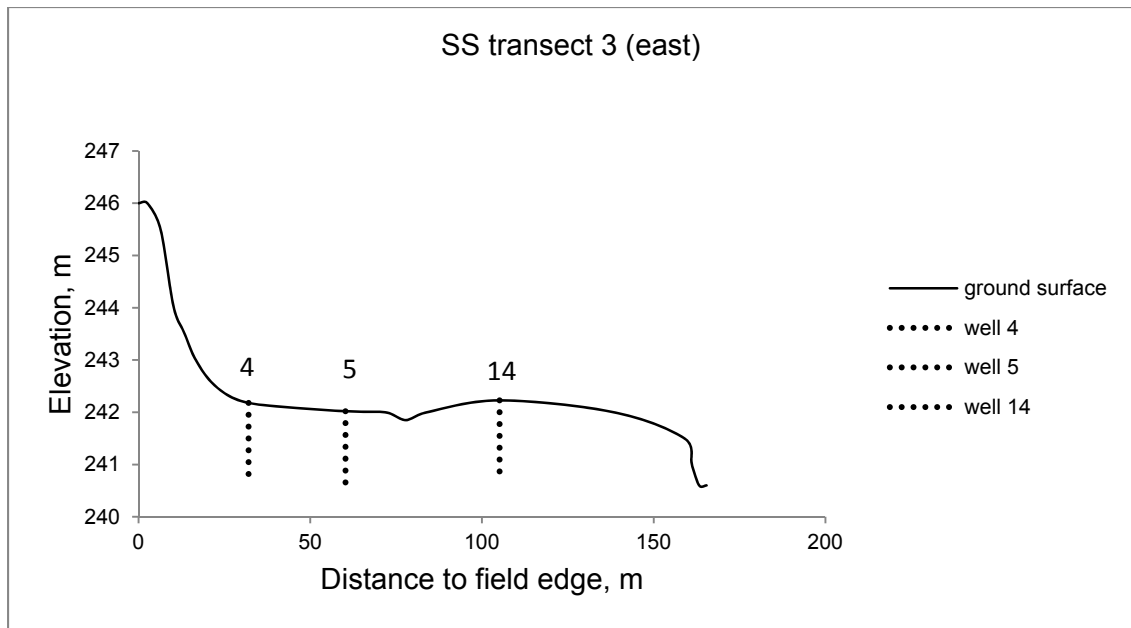


Figure 2B: Location of groundwater wells along transects 1, 2 and 3 at the Scott Starling site.

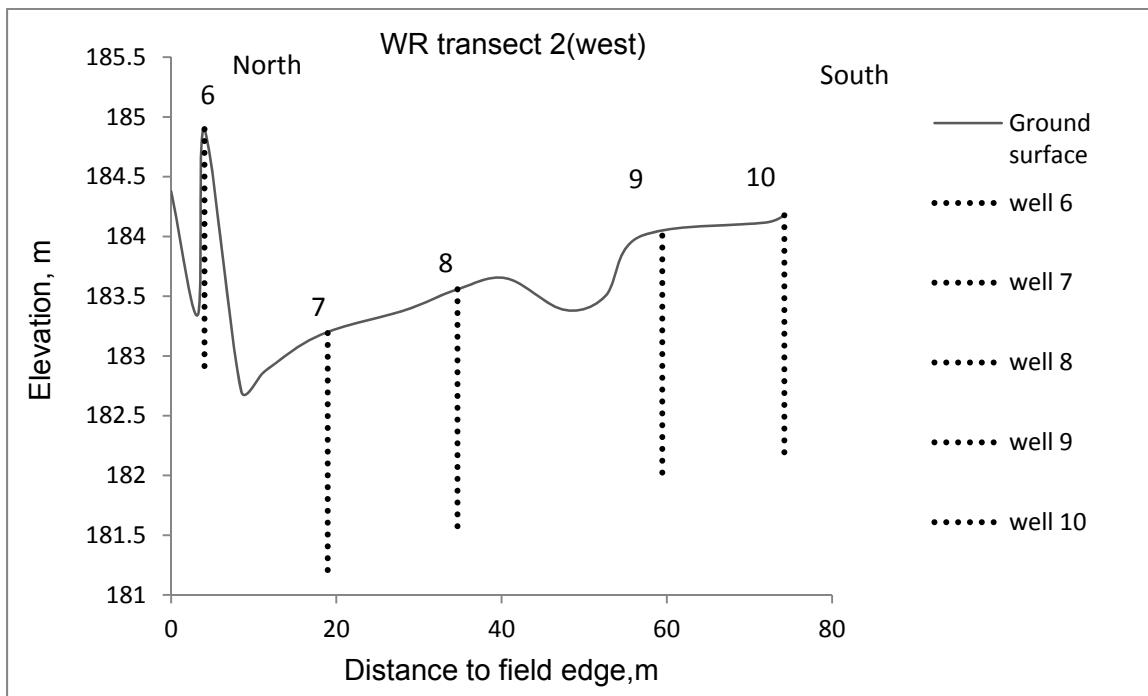
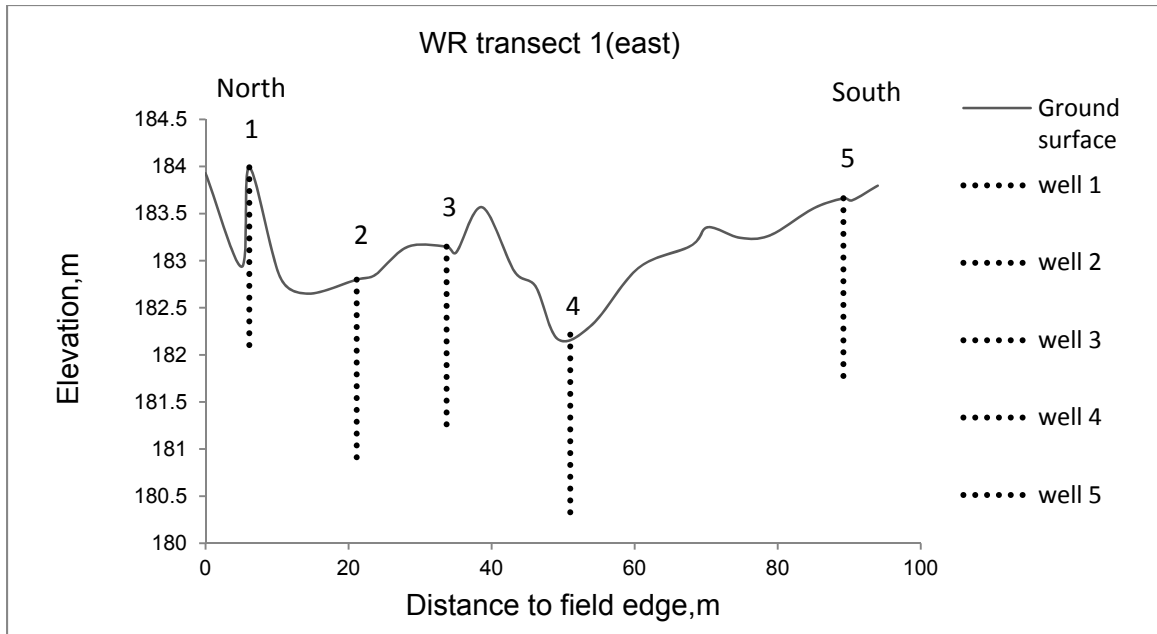


Figure 2C: Location of groundwater wells along transects 1 and 2 at the White River site.

Hydrological networks and topography

At LWD site, an extensive network of well and piezometer nest was set up from the field-riparian zone margin to the stream (Figure 2A). Two separate transects of piezometers were installed 6-10 m apart on the north and south sides of the stream in order to assess site variability and subsurface flow paths at the riparian zone scale. Each piezometer nest consisted of piezometers constructed from 1.27 cm ID PVC pipe with 20 cm long slotted ends installed at depth between 0.5, 1 and 2 m. Groundwater wells (ID 5.1 cm ABS pipe 2-2.5 m long) perforated throughout their length were installed at each piezometer nests on the north sides of the stream.

At the Scott Starling site, a total of three transects perpendicular to stream flow composed of 14 wells (130-170 cm deep, 5 cm diameter, PVC screened on entire depth) were installed during a previous project (Figure 2B). The wells were installed 30-50 m apart in order to assess site variability and subsurface flow paths at the riparian zone. Saturated soil hydraulic conductivity was measured for each well in LWD and SS site using the Hvorslev water recovery method (Freeze and Cherry, 1979).

At the WR site, ten thin wells (200-250 cm deep, 0.5 inch diameter PVC screened on entire depth) had been installed in the fall of 2009 in two separate transects with a distance of 300 m in between (Figure 2C). A nylon mesh sleeve was placed over the screened intervals to minimize obstruction of wells by fine grained particles. Holes were filled with sand along the screened intervals, and a bentonite clay seal was used near the ground level to prevent contamination from surface runoff. Riparian zone lithology was first determined from visual inspection of cores collected by hand augers during piezometer and well installation.

Topography of the WR site and the elevation and position of all wells and piezometers were determined using a total station in the winter of 2010. Topography of the LWD site was determined using a total station in previous research conducted in

spring 2009. Topography of the SS site was characterized using the same method in 2006-2007. Cross section profiles for each site were drawn using the topography measurements (Figure 2A, 2B and 2C).

Cross sections were used to visualize the groundwater flow direction and flow path, which gave us information about the sources of contaminants. Bird view topography maps showed groundwater elevations, hydraulic gradients, and potential interactions between groundwater and river (e.g. flow reversals). Water table depths for each sampling date at each site were used to capture the seasonal changes in water flow path. Soil conductivity and hydraulic gradients were used to determine the amount of the chemical input into the riparian zone from the upland, or from the stream to the riparian zone. We expect to see a relationship between water table fluctuations and changes in DO and ORP in groundwater.

There are differences between water table measured with loggers and that of the whole site. To calculate water table at the whole site using logger data, we used the difference between average elevation and well elevation with data logger as the factor X. Therefore, water table of the site is equal to logger data plus X. The sign of X could be positive or negative depending on which is higher. For example, if the elevation of the well with data logger is lower than the average elevation for the site, the sign of factor X is negative because we overestimated the actual depth of the water table for the site if we only used logger data. In an opposite case, if the elevation of the well with logger is higher than the average elevation of the site, the sign of the factor X is positive because we underestimate the water table for the site. On the basis of this calculations,, water table at LWD was equal to logger level +0 cm; water tables at SS was equal to logger +(-14) cm, and water tables at WR was equal to logger +(-135) cm.

Precipitation and discharge

Water year 2010 was from 10/1/2009 to 9/30/2010, and water 2011 year was from 10/1/2010 to 9/30/2011. For matching our study period, we used the cumulative precipitation from 10/1/2009 to 9/30/2010 to represent the annual precipitation of 2010.

Precipitation data was obtained from:

http://climate.agry.purdue.edu/climate/data_archive_v3.asp?rdatatype=cp.

For precipitation data during the study period, we used weather stations located in Greenfield, Indianapolis Eagle creek and Martinsville 2 SW, for the LWD, SS and WR sites, respectively. Also note that data from 12-22-2009 to 4-30-2010 at Indianapolis Eagle Creek station was replaced by a nearby station—Castleton station because no data was available for Indianapolis Eagle Creek station during that period.

Stream discharge data were obtained from <http://waterdata.usgs.gov/nwis/sw> for the LWD site, there is one station at the outlet of the bridge with intermittent data (no long-term data) (station #03361638 at Mohawk). For long term discharge data at LWD, we used data from station #03361650 in New Palestine. For the SS site, we used data from station #03353200. For the WR site, we used data from station #03354000 located upstream (Centerton, Indiana) from the study site.

Field measurements and water chemistry characterization

Water level in wells was measured approximately once a month from November 2009 to May 2011. The well bottoms were used as the water table elevation on dates when no water was present in the monitoring well. Water table elevation maps for each sampling date were constructed by Surfer (Golden Software, 1999). Water samples were collected from wells, piezometers, and streams from three sites, and all wells were purged before the first collection of samples was made. Field parameters, such as water table depth, ORP, dissolved oxygen (DO), pH and temperature of groundwater, were measured on the spot during sample collection. Water samples were collected in 118 ml

polypropylene containers with tygon tubes connected to a three-way stopcock, and kept on ice until returning to the laboratory where all samples were filtered using 0.7 μm GF/F filters (Whatman, Florham Park, NJ) within 12 hours of sampling. Filtered samples were kept frozen until analysis. Electrical conductivity was measured in the lab before sample filtering. Samples were analyzed for NH_4^+ , NO_3^- , PO_4^{3-} , SO_4^{2-} , Cl^- and Si, using an Aquakem 20 Photometric analyzer. Analysis of samples for mercury was conducted at the University of Toronto. To ensure data quality, we calibrated the DO meter and the ORP meter each time before going to the field and make sure that meter reading was stable and accurate. Due to the difficulty of achieving equilibrium for ORP in the field, we took our readings only when meter reading fluctuations were within 10 mV. For lab analysis, we used a control sample for every ten samples to ensure data accuracy and made triplicate measurements of randomly-selected samples to make sure the data precision was within expected range (STDEV < 10%).

The study was conducted over a 19-months period, a little less than two hydrologic years. To reduce inconsistency in sampling date among study sites, sampling was conducted at each riparian zone within a window of 10 days or less. Greenhouse gas fluxes were also measured at the field at the same time when the groundwater samples were collected. Mercury sampling started in April 2010, and subsequently followed in June, August, December of 2010 and March 2011. Major events like freeze-thaw, snow and rain storms that can affect riparian hydrology in a rapid way were documented. Therefore, our field measurements were conducted biweekly during those periods of significant variations in hydrology. Data regarding seasonal variations in precipitation and the timing of major hydrological events during the study period were downloaded from the Noaa.gov website. Barologgers and levelloggers were installed to document in detail the soil temperature and water table dynamics at 20 minute interval at WR and SS, 15 minute interval at LWD. The water table depth in wells without logger

was determined by extrapolation based on relationships developed using field-measured water table depths of all wells. Soil moisture and temperature sensors were installed at depth of 20 and 70 cm below ground surface to monitor changes in soil moisture and temperature at the research sites.

Removal efficiency is defined as the decline in chemical concentration across the riparian zones, expressed as a percentage of the concentration at the riparian zone margin (Correl et al., 1997). The width of the riparian zone necessary to deplete inputs was used to assess the chemical removal effectiveness of riparian zones (Lowrance, 1998). Having the concentrations of each contaminant at the field edge and in the riparian zones, the removal efficiency can then be calculated. This information helped us identify the features of riparian zones with high removal efficiency, which can be used to optimize best management practice or watershed management strategies. Specifically, for LWD, field edge included well 1, well 3, well 9 and well 10 (Figure 2A), and stream edge included well 3, well 6, well 7 and well 12 (Figure 2A). For SS, field edge included well 1, well 3 and well 4 (Figure 2B), and stream edge included well 9, well 13 and well 14 (Figure 2B). For WR, field edge included well 2 (Figure 2C), and stream edge included well 4 (Figure 2C). The reason we did not include wells in transect 2 is that no consistent groundwater flow through wells on this transect was observed during our study period except for some periods of very high water table.

For assessment of temporal variation, we define wet period as December to June, and dry period as July to September. In general water tables rise after winter precipitation and snowmelt in early spring, and water tables drop quickly due to high evapotranspiration in summer. Fall and winter are usually transition time of low water tables to high water tables. We expect to observe clear anaerobic changes in those two hydrologic extremes and associated biogeochemical transformations of contaminants.

Data analysis

Before any comparison was conducted, equal variance test and normality test for data sets was performed to determine whether parametric or nonparametric statistical methods should be used. Because most variables (DO, ORP, WT) in the dataset did not simultaneously satisfy the requirements for normal distribution (Ander-Darling Normality test) and equal variance (F test), we could choose nonparametric statistical analysis to compare site differences. But the catch was that we had to compare the average of site on each date instead of each well on each data due to equal length requirement for Minitab, such a limitation might lead to loss of certain sensitivity of the differences. For removal efficiency comparison, this limitation was accepted because it involves the calculation of averaging wells at field and stream edge. But for N, P, S data with large and unequal sample size, it was not possible to use non-parameter methods. Because most of our sample sizes were >100 , an approximate normal distribution was assumed. Because the sample size was small (between 19 and 52 samples) for DOC and Hg, we interpreted these results with caution. One way ANOVA was used to detect significant differences among sites with respect to the biogeochemical fates of contaminants in the riparian zones. Without assuming equal variance, two sample t-test was used to compare the difference in solute concentration between field and stream edge.

RESULTS

A: Site hydrology

Water table

The mean water table depths during study period were 87 cm BGS in LWD, 57 cm BGS in SS and 141 cm BGS in WR. Water table at each site was significantly different to the other two sites ($\alpha = 0.05$, $P < 0.05$). Pearson correlation analysis showed water tables at three sites positively were correlated to each other ($\alpha = 0.1$, $P < 0.1$). During the study period, water table depths (WTD) in Leary Webber Ditch (LWD) varied between 62 cm (April 21, 2011) and 136 cm (Oct 28, 2010). In general, water table in Scott Starling (SS) remained close to the ground surface during wet period (Figure 3), and it remained in the 20-30 cm depth between February and May in both 2010 and 2011. The average water table in White River site (WR) during the sampling period was 141 cm BGS. Standing water as high as 320 cm at WR site well 4 during the wet season (Mar 1, 2011), and water table as deep as 300 cm at WR site well 1 during the dry season (October 2010) were observed.

At all three study sites, the water table exhibited clear seasonal variation which was manifested by distinctive dry period (July to November) and wet period (December to June), but the degree of variability was site-specific. While at SS the water table was more stable during the wet season (35 ± 11 cm), marked fluctuations in water table depth were observed at LWD and WR during the same wet period (Figure 4). In all three sites, WT reached the lowest level in dry period of 2010, averaging 180, 140 and 250 cm bgs in LWD, SS and WR, respectively (Figure 3). Seasonal fluctuations in WTD generally followed rainfall and snowmelt events. Shallow water table occurred during the wet season (December-June), but in spring 2011 WTD was much closer to land surface (Figure 4) than in 2010. However, this trend was not observed at LWD. Despite a 4% increase in rainfall in 2010 relative to 2010 at LWD, mean WTD at LWD was similar

during the wet season in both years (2010:109 cm BGS; 2011:112 cm BGS). Thus, water table variation at the SS and WR sites was more responsive to precipitation, but less so at LWD. Although both the SS and LWD sites are located in the Till plain, drop in water table position occurred more rapidly at LWD than at SS (Figure 3).

The rise and duration of high water tables behaved differently among sites. Rises in water tables were observed after intensive summer rainfall and snowmelt events in early spring, but the hydrologic response to these events varied with site (Figure 4, 5 and 6). At LWD, the water table was flashy with a lag of about one day between a rainstorm and major swing in water table position. After a 51.31 mm rainfall on June 19, 2010, the water table at LWD rose from 111 cm to 52 cm and then dropped to 100 cm in a 2-day span. A similar pattern was also observed at LWD after a 118 mm rainfall on April 19-20, 2011 (Figure 4). The water table immediately rose from 130 m to near surface (12 cm BGS), and then dropped 100 cm less than 2 days later. Compared to the other sites, the WR site had the highest water table fluctuations, displaying responses to snowmelt in winter and intensive rainfall events in the spring and early summer (Figure 6). Overall, large water fluctuations in WT were observed at the WR site. For example, decreases in snow depth in February-March 2010 (loss of 15.30 cm) and in early February 2011 (loss of 10 cm) resulted in significant variations in water table depth (80 and 250 cm, respectively). While no flooding was observed at the other sites during the study period, five flood events (2 in 2010 and 3 in 2011) were recorded at WR (Figure 6). Ponding duration can be relatively brief (Ex. June 12-16, 2010; Figure 6), but during the floods of Spring 2011, the water table remained above ground or close to ground surface for several days due to extensive and persistent rainfall at WR (10.74 cm from Apr 25 to May 6, 2011). At the SS site, water table responded quickly to snowmelt and precipitation events, often resulting in ponding in the wetland area (Figure 5).

Groundwater flow

Groundwater flow direction at the three sites displayed clearly different patterns. At LWD, groundwater flow was constantly from field edge to stream (Figure 8), while at SS (Figure 9) and WR (Figure 10), groundwater flow direction was seasonally variable. At all three sites, hydraulic gradients were generally high in the spring, but low in summer and early autumn. In general, the highest hydraulic gradient was found at LWD and the lowest at WR, with intermediate gradient at SS (Figure 8, 9, 10).

There was a clear seasonal pattern in groundwater flow at SS (Figure 9). During the high water table period (winter/spring), groundwater flow was predominantly perpendicular to the adjacent stream. However, this flow direction weakened during the dry period, and lateral flow prevailed. During the fall/winter transition (as seen in Nov 30, 2010), groundwater flow pattern in the wetland portion of the SS site was clearly from field edge toward stream edge. No flow reversal or flooding was observed at this site; however, during the spring season, water table remained close to land surface and ponding in the wetland area was not uncommon.

The groundwater flow direction at WR was more complicated: floods and flow reversals were observed (Figure 10C). Groundwater flow was from field edge to river during the wet season (Figure 10D) but, during the dry period, groundwater flow was below well bottom (250 cm). Instances of flow reversal at WR site were observed three times (Nov 9, 2009; Jan 21, 2010; Mar 4, 2010, Figure 10).

B: Site Biogeochemical conditions

The mean ORP values during study period were 22 mV for LWD, 73 mV for SS and 75 mV for WR (Table 1). LWD had the most reducing condition, and significant lower than at SS and WR. However, ORP was not statistically different between SS and WR. At site scale, water table depth and OPR were positively correlated at the LWD ($r^2 = 0.45$, $P < 0.05$) and SS sites ($r^2 = 0.63$, $P < 0.05$), but not at WR ($r^2 = 0.09$). At well scale,

however, a much more complex pattern was observed. Water table depth and ORP were negatively correlated at SS, but no correlation was found at WR and LWD.

Strong seasonal patterns in ORP were observed at all sites, higher ORP in early spring and lower ORP in the summer when water table was deep (Figure 12). The highest ORP at WR was 285 mV when water table was 149 cm BGS (May 20, 2010), and the lowest was -79 mV when water table was 167 cm BGS (Sep 12, 2010). ORP at LWD was overall relatively lower comparing to SS and WR (Figure 11). The highest average ORP at LWD was 186 mV (May 3, 2010) when the water table was at the highest level, and the lowest was -153 mV (Sep 22, 2010) during the dry summer in 2010. The highest ORP at SS was 303.4 mV in 2010 when water table was 37 cm BGS (Apr 14, 2010), and the lowest was -46.50 mV when water table was 143 cm BGS from April 2010 to April 2011.

The mean DO values during study period were 2.7 mg/L for LWD, 2.9 mg/L for SS and 2.5 mg/L for WR (Table 1). There was no statistical difference in DO among the three sites. A similar seasonal pattern in DO was observed across the three research sites (Figure 13). DO was high when water table was near ground surface and start to decrease quickly when water table was low.

The mean DOC concentration during study period was 7.9 mg/L at LWD, 5.4 mg/L at SS and 9.9 mg/L at WR (Table 1). A seasonal pattern in DOC concentration was also observed at all three sites (Table 1) with elevated groundwater DOC concentrations measured in the summer lowest DOC concentration in the spring (Figure 21). At the WR site, groundwater DOC concentrations showed the largest variation, ranging from 4 mg/L to 14 mg/L. The lowest DOC concentration was measured at SS (range: 4 mg/L to 8 mg/L) followed by LWD (range: 6 mg/L to 10 mg/L). In general, groundwater DOC >5 mg/L in was common at all three sites. The timing of DOC concentration decrease at LWD was in parallel with the period of nitrate depletion (Figure 14 and Figure 21). From

September 2010 to November 2010, decreases in DOC concentration and nitrate depletion were also observed at the WR site (Figure 14 and Figure 21). However, no such pattern was observed at the SS site.

There was no statistically difference in groundwater temperature (GWT) among the sites ($\alpha = 5\%$, $p > 0.05$), with mean groundwater temperature 11.4 °C at LWD and SS, 12.3 °C at WR. However, strong seasonal patterns were constantly observed for all three sites, with high groundwater temperature during the dry period and low temperature during the wet period.

C: Contaminant dynamics

Mineral N in riparian groundwater

During the study period, mean N concentrations were 1.1 mg N/L at LWD, 0.37 mg N/L at SS and 3.5 mg N/L at WR (Table 1). The difference in N concentrations among the study sites was statistically significantly ($p < 0.05$). Groundwater NO_3^- was generally lowest at SS and highest at WR (Figure 14), and NO_3^- concentrations at WR were generally 5-20 times higher than that at SS. At LWD, NO_3^- concentration during the 2011 wet period was 1.7 mg N/L in comparison to 0.86 mg N/L during the 2010 wet period. No such distinctive annual patterns were observed at the SS and WR sites.

During the study period, groundwater NO_3^- concentration at LWD and WR tended to be the highest in the spring after snowmelt and lowest in summer. No clear seasonal pattern was observed at SS. At LWD, groundwater NO_3^- ranged from 0.15 mg N/L during the dry summer season and up to 4 mg N/L during the early spring. High NO_3^- at the field edge during these periods was likely due to N mineralization following freeze-thaw or simply groundwater coming close to soil surface. Groundwater NO_3^- was highest at WR, ranging from 0.2 mg N/L to 13.7 mg N/L. High NO_3^- concentrations were generally observed during the early spring.

At LWD and WR, there was also a distinct pattern in the spatial variation of groundwater NO_3^- , with a general decline in concentration from field edge to stream (Table 5). During several wet periods (March 2010; fall 2010 to spring 2011), groundwater NO_3^- concentration near the stream was only 10-40% of the concentration at field edge. As flow direction during these periods was perpendicular to the stream channel (Figure 7), field edge and stream edge could represent the input and output, respectively. During the study period, mean N concentration at field edge was 1.3 mg N/L at LWD, 0.6 mg N/L at SS and 3.7 mg N/L at WR, indicating different loading rates from uplands.

On an annually basis, N removal efficiency 2%, 34% and 69% for the LWD, SS, and WR sites, respectively. N removal efficiency at WR was consistent throughout the year except during flow reversals. The LWD was a N sink in the spring, with high N removal efficiency between 60-90%. However, the LWD riparian zone was a source of N to the adjacent ditch in the summer. At the SS site, N concentrations were generally low, and there was no significant difference ($p > 0.05$) between field edge and stream edge with regard to NO_3^- concentration (Table 5). N removal ranged from 10-90% during wet period and 10-30% during dry period. At the WR site, NO_3^- removal as high as 96% was observed, but negative removal was also indicated by the data. For instance, during flow reversal at the end of January 2010, NO_3^- concentration at stream edge was higher than at the field edge. These results show that assessment of NO_3^- removal may become complicated in such a hydrological-complex riparian zone as the WR site.

NO_3^- concentrations at LWD site were positively correlated with water table depth BGS, DO, ORP, and negatively correlated with WT at well scale. NO_3^- concentrations at SS were not correlated with any the parameters investigated in the study. NO_3^- concentrations at the WR site were positively correlated with WT depth, DO, ORP, and were negatively correlated with DOC and WT at the well scale. NO_3^- concentrations were

constantly correlated with water table depths, DO, ORP and groundwater temperature ($P < 0.05$). For the LWD site, the correlation was significant between NO_3^- and DOC at $\alpha = 10\%$ level. Considering the small sample size for DOC at LWD, it is reasonable to use $\alpha = 10\%$ in order to increase statistical power.

Mean NH_4^+ concentrations were 0.18 mg N/L at LWD, 0.08 mg N/L at SS and 0.31 mg N/L at WR (Table 1), and significant difference ($P < 0.05$) among sites were detected with respect to NH_4^+ concentration. During the study period, NH_4^+ concentrations at field edge were 0.07 mg N/L at LWD, 0.07 mg N/L at SS and 0.19 mg N/L at WR, which indicates similar loading from uplands. However, NH_4^+ concentrations at stream edge were 0.41 mg N/L at LWD, 0.08 mg N/L at SS and 0.89 mg N/L at WR, which indicates that the LWD and WR sites were net NH_4^+ sources to adjacent rivers.

Across study sites, strong seasonal patterns in NH_4^+ dynamics were observed. NH_4^+ concentration increased 2 to 10 times in the summer compared to spring (Figure 15). NH_4^+ at LWD ranged from 0.04 to 1.6 mg N/L. Higher NH_4^+ concentration was found in the summer months at WR, averaging 0.79 mg N/L compared to 0.15 mg N/L during the wet periods. In the summer, there was an increase in NH_4^+ from field edge to stream edge - which was opposite of the pattern observed for NO_3^- . At SS, groundwater NO_3^- was very low (< 1 mg N/L, Figure 14). NH_4^+ at SS was also very low (< 0.2 mg N/L, Figure 15) although there was a slight increase in the summer.

NH_4^+ concentrations at LWD site were positively correlated with WT, and negatively correlated with DO at the well scale. NH_4^+ concentrations at SS site were positively correlated with WT and DOC, and negatively correlated with ORP at the well scale. NH_4^+ concentrations at the WR site were positively correlated with DOC and WT, and negatively correlated with DO, ORP and WT at well scale. Across sites, NH_4^+ production was positively related to groundwater temperature and DOC availability (Table 2, 3, 4).

Soluble reactive Phosphorous

Significant difference ($P < 0.05$) among the study sites was found with respect to SRP concentration. During the study period, SRP averaged 0.03 mg/L at LWD, 0.04 mg/L at SS and 0.08 mg/L at WR (Table 1). There were significant differences in SRP concentrations between field edge and stream edge at WR and LWD.

In general, there was no clear seasonal pattern in SRP concentration at LWD and SS, but a weak seasonal pattern in groundwater SRP was observed at WR (Figure 16). At the WR site, SRP concentration increased from April to May in both 2010 and 2011. The higher SRP concentration in wells 2 and 7 (closest to field edge) suggests P input from the agricultural field, The decrease in SRP concentration from field to stream edge suggests adsorption net SRP retention at WR. At LWD, the highest SRP at field edge matches the timing of high water table after snowmelt. Three spikes in field edge were caused by high SRP concentrations in well 1 (Mar 26, 2010 and Apr 22, 2011), well 9 (Feb 18, 2010), and two spikes in stream edge were caused high concentration of SRP in well 7 (Nov 4, 2009 and Oct 28, 2011). Due to the highest SRP (0.42 mg/L on Nov 4, 2009 and 0.43 mg/L on Oct 28, 2010) in well 7, the average SRP concentration at stream edge was elevated, averaging 0.11 mg/L and 0.12 mg/L, respectively on those dates. These averages are slightly above the limit of 0.1 mg/L set by USEPA for preventing eutrophication. At the SS site, isolated spikes in SRP were observed for well 9 (0.82-0.85 mg/L) in, well 2 (0.37 mg/L), well 7 (0.49 mg/L), well 11 (0.42 mg/L) and well 12 (0.34 mg/L). These elevated SRP concentrations in isolated wells lead to high average SRP at stream edge (0.28 mg/L on Dec 11, 2009 and 0.30 mg/L on March 8, 2010) much higher than the USEPA recommended limit of 0.1 mg/L SRP.

At the WR site and for the whole study period, SRP concentration at field edge (0.08 mg/L) was higher than that at stream edge (0.04 mg/L) (Table 5), which indicates a 40-50% removal of SRP. In contrast, at the SS and LWD sites, difference in groundwater

SRP between the field and stream edge was not statistically significant (Table 5), although SRP concentration at field edge (0.02 mg/L) was lower than that of stream edge (0.04 mg/L) at the LWD site. On an annual basis, SRP concentration in spring 2011 at LWD was higher (0.38 mg/L) than that in spring 2010 (0.27 mg/L). In contrast, SRP concentration in spring 2011 at SS was lower (0.26 mg/L) than that in spring 2010 (0.42 mg/L). No such year to year difference was observed at WR. Although average SRP concentrations at WR were higher than at LWD and SS (Figure 16), stream edge SRP concentrations never exceeded 0.1 mg/L. Thus, in terms of SRP discharge to stream, the WR site poses a lower risk of water quality impairment in comparison to the LWD and SS sites. Positive correlations were found between SRO and DO at LWD, but SRP concentrations were not correlated with any other parameters measured during the study.

Groundwater sulfate

There was no significant difference in ground water sulfate concentrations for three sites ($P > 0.05$) during the study period, with mean SO_4^{2-} concentrations 34 mg/L at LWD, 28 mg/L at SS and 43 mg/L at WR site (Table 1). However, there were seasonal patterns in SS and WR. SO_4^{2-} concentrations were 25-40 mg/L during spring high water table period but only 10-20 mg/L during summer low water table period at SS. Similar temporal pattern of SO_4^{2-} concentrations were also observed at WR site, 30-60 mg/L in spring and 15-30 mg/L in summer. No such temporal pattern was found at LWD, but it had a clear spatial pattern from field edge to stream edge.

Overall, groundwater SO_4^{2-} concentration decreased sharply after May and slowly but constantly decreased in summer at the study sites, although the degree of decrease in concentration varied with site (Figure 17). The sharp decrease of SO_4^{2-} concentration in ground water was slightly after the sharp decrease of NO_3^- concentrations. On May 26, 2010, Well 7,8,9,13 (Figure 2B), ORP was below 110 mV, which might explain a drop in

SO₄²⁻ concentration at SS. From June to November 2010 ORP in well 4 at WR (stream edge) (Figure 2C) was below -150 mV with SO₄²⁻ concentration decreasing, implying that sulfate reduction had occurred during this period. The spatial patterns of groundwater SO₄²⁻ also varied considerably with sites. At most of sampling dates, the spatial variation in SO₄²⁻ concentration at LWD suggested a net release of SO₄²⁻ from field edge to stream edge. SO₄²⁻ concentrations were generally less than 10 mg/L at field edge but more than 50 mg/L at stream edge. However, SO₄²⁻ concentrations in the ditch were one magnitude lower than that in the groundwater. No such large difference in SO₄²⁻ concentration between groundwater and surface water were observed at SS and WR. Although there was no clear difference in sulfate concentrations between field edge and stream edge, huge spike in SO₄²⁻ concentration was observed at the SS site (field edge) and the WR site (stream edge) in mid-winter 2011 during rewetting events. The SO₄²⁻ removal efficiency varied significantly among sites, with -1114% for LWD, 11% for SS and 38% for WR, respectively. However, there was no significant difference in SO₄ concentration between field edge and stream edge for WR and SS.

Concentrations of SO₄²⁻ decreased when concentrations of NH₄⁺ increased in summer across the three sites. Negative correlations between concentrations of SO₄²⁻ and NH₄⁺ were found at LWD and WR site. If examining this pattern by wells at LWD site, we can see 4 highest averaged SO₄²⁻ in the wells near stream: well 3, 6, 7 and 12. And well 12 has the highest averaged sulfate concentration (135 mg/L) and the highest NH₄⁺ (0.53 mg/L) for entire sampling period. The highest NH₄⁺ production (0.89 mg/L) was in well 4 at WR site which was in depression area with low ORP in general. The variation of SO₄²⁻ and NH₄⁺ concentrations at SS was negligible.

SO₄²⁻ concentrations at LWD site were negatively correlated with water tables at well scale. SO₄²⁻ concentrations at SS site were positively correlated with groundwater temperature at well scale. SO₄²⁻ concentrations at WR site were positively correlated

with DOC and negatively correlated with groundwater temperature at well scale. Basically, correlations are randomly distributed across three sites (Table 2, 3, 4).

Total mercury and methyl-mercury

During the study period, THg concentrations were 0.53 ng /L for LWD, 0.37 ng/L for SS and 1.48 ng/L for WR, respectively (Table 1). THg concentration at WR were significantly different from LWD and SS ($P < 0.05$), but there was no significant difference between LWD and SS ($P > 0.05$). During study periods, MeHg concentrations were 0.06 ng /L at LWD, 0.09 ng /L at SS and 0.23 ng /L at WR, respectively (Table 1). MeHg concentration at WR are significantly different from LWD and SS ($P < 0.05$), but not significantly different between LWD and SS ($P > 0.05$). During the study period, the highest THg (5.95 ng/L) and MeHg (1.74 ng/L) concentration in groundwater was observed at the WR between July and August 2010. One snow sample at WR has the highest THg concentration (11.8 ng/L), which was 10-20 folds higher than that in groundwater collected for the same sampling event.

Clear seasonal variation of THg and MeHg were observed (Figure 19). MeHg concentrations were elevated in summer for three sites (Figure 20). MeHg ranged up to 0.48 ng/L at WR, 0.13 ng/L at LWD and 0.12 ng/L at SS. Both WR and LWD increased nearly two folds regarding MeHg in groundwater in summer. While the peak MeHg production occurred early summer at SS, the highest MeHg concentrations were measured in the late summer at LWD and WR (Figure 19 and 20). The peaks of MeHg production matched well with its lowest ORP for these sites (Figure 11). The MeHg concentration gradient (field to stream) at LWD and WR suggested a net release of MeHg from these sites although there was no statistically difference between field edge and stream edge (Figure 18).

THg concentrations at field edge were also not significantly different to that at stream edge for all sites, but MeHg concentrations at field edge lower than that at

stream edge for LWD and WR (Figure 18, Table 5). Because so few sampling dates and large variations, we have very limited statistical power to detect the difference between field edge and stream edge. Those results are more from mathematical comparisons and have less statistical meanings at this point.

THg concentrations were positively correlated with DOC at well scale for LWD, positively correlated with groundwater temperature for SS, and positively correlated with groundwater temperature and negatively correlated with DO at well scale for WR (Table 2, 3, 4). Therefore, no constant parameters were found correlated to THg across sites.

MeHg concentrations at LWD site were positively correlated with groundwater temperature at well scale. MeHg concentrations at SS site were positively correlated with groundwater temperature and THg concentrations at well scale. MeHg concentrations at WR site are positively correlated with groundwater temperature, DOC, THg and negatively correlated with water tables, DO and ORP at well scale. MeHg dynamics were constantly correlated to groundwater temperature across sites. Except for WR site where we could observe thermodynamic constraint on MeHg, our results indicated thermodynamic constraints have less control on MeHg at watershed scale (Table 2, 3, 4).

DISCUSSION

Riparian HGM, riparian hydrology and biogeochemistry

Previous studies at the tile-drained LWD site (Vidon and Cuadra, 2010) and at the moderately incised valley SS site (Vidon and Smith, 2008) have shown marked difference in water table fluctuation, groundwater flow and response to precipitation. Additional work at the WR site (floodplain on glacial outwash) has shown more dramatic water table fluctuation in response to snow melt and summer rainfall, as manifested by floods and flow reversals. For the SS site, Vidon and Smith (2006) reported mean WT of 40 cm BGS during wet periods and 122 cm BGS during dry periods. These results are comparable to the mean WT depths measured in the present study (26 cm and 109 cm during wet and dry periods, respectively). In order to determine whether measured WT variations correctly reflect variations in site hydrology, precipitation and stream discharge during the study period was compared to long-term hydrology data in the region. This comparison showed that the present investigation was conducted in a relatively normal water year at LWD and WR, and during a slightly wetter year at SS. During the period of study, stream discharges were 2% and 17% higher than the 40-year normal at LWD and at SS, respectively. At WR, daily discharge was near the 40-year normal (NOAA 2010). Cumulative precipitation during the 2010 water year was near average at LWD, and below average at WR and SS (Figure 7). During the 2011 water year, precipitation was still below average at WR, but above average at LWD and SS (Figure 7). The trends of cumulative precipitation were in line with annual average daily discharge from 2001 to 2011 (Figure 7). However, such small variations in daily discharge cannot explain the large variations of water table for three sites. Therefore, observed fluctuations in water table are likely real, and reflect typical hydrologic conditions at the study sites. These results confirmed the selection of the three sites as representing different HGM classes of riparian buffers.

How major events affect site hydrology? Regardless of differences in HGM settings, the largest variations in WT depth were observed after snow melt events (Figure 4, 5, 6). Across the three study sites, WT rose more quickly in early spring and responded slower to summer rainfall events, which might indicate that antecedent soil conditions affect water table response to precipitation. In a previous study in the LWD watershed, Vidon and Cuadra (2010) showed that the same amount of precipitation generated a stream discharge of 1500 l/s in May, but only 8 l/s in August. These findings therefore indicate that the response of tile drainage flow to bulk precipitation varies with season.

Major events also affected groundwater flow directions. Before large storm events, water flow was mainly perpendicular to stream at SS (Vidon and Smith, 2008). However, within a day after a storm, a flow reversal occurred, and groundwater flowed in a down valley direction (Vidon and Smith, 2008). Similar temporal variations in groundwater flow direction were also observed at SS during the present study. As reported by Vidon (2012), high water tables lasting 2-5 days after the cessation of rainfall events were also observed at the SS site.

To what extent difference in hydrology can be translated into difference in site biogeochemistry? Many studies pointed out that redox conditions in wetland soils are strongly influenced by water table fluctuations (Hill, 1996; Hedin et al., 1998; Clement et al., 2002; Hefting et al., 2004). However, there is no significant difference in DO and no difference in ORP between WR and SS although ORP in LWD is significantly lower than the other two sites. This study supported this general conclusion, but also showed that the relationship was seasonally variable. Results showed that high WT corresponded to high ORP after snow melt in spring and after large storms in fall. An interpretation of these results is that increase in groundwater ORP might be due to relatively high oxygen in rainwater, or limited consumption of dissolved oxygen by soil microbes during cooler

periods. These results might also indicate that hydrology alone cannot explain short-term variations in redox condition. However, at seasonal scale, changes in water table play a dominant role in driving ORP variations. Other studies proposed that water table height controls the balance of anaerobic and aerobic processes in wetlands and other periodically flooded systems (Blodau, 2002; Reddy and DeLaune, 2008). Regardless of site differences, a consistent pattern in ORP and DO was observed in this study: both parameters increased when groundwater was near the surface in early spring and decreased in the summer.

In addition to seasons, other factors (soil texture, drainage, land use) are also important to the development of redox conditions. For instance, mean ORP was higher at WR than at LWD although the average water table was higher at LWD. Lastly, we must also be aware of limitation of our sampling interval which might have failed to capture the rapid changes in soil redox condition after rainfall events. Catallo (1999) reported that in a closed, hydrostatic system (separation with oxygen supply), the development of anaerobic condition proceeded rapidly (>370 mV ORP decreased under 48 hours).

Significantly difference among study sites was found with respect to DOC concentrations. However, the ranking of sites for DOC was the reverse of their ranking in terms of WT depth. In other words, with the highest water table and the wettest condition, the SS site had the lowest groundwater DOC concentration. In contrast, the WR site had the lowest water table and the highest DOC concentration. This is contrary to the high DOC concentration and reducing condition typically found in wetlands and riparian zones with water table close to soil surface. These findings suggest that, despite well recognized controls of hydrology on riparian functions, biogeochemical conditions are difficult to predict on the basis of hydrology alone. Other factors such as land use history,

vegetation cover, soil texture, natural and artificial drainage may play additional role in defining biogeochemical conditions in riparian zones.

Oxidation-reduction processes are linked to the availability of both electron donors and acceptors (Szogi et al., 2004), so ORP might be related to DOC concentrations in groundwater. Results showed that ORP was significantly correlated to DOC at SS and LWD. Although we did not detect significant correlation between ORP and DOC at WR ($r = -0.20$, $n = 36$) (Table 4), the result might be due to the small sample size of DOC and the lack of statistical power. ORP was strongly correlated with WT at all three sites, indicating strong temperature influence on microbial activities in summer. Decomposition of organic matter in saturated areas may have led to rapid consumption of available oxygen, and thus causing microbes to switch to alternative electron acceptors (Hedin et al., 1998; Hill, 2000). In terrestrial environments where organic matter is the primary electron donor, redox potentials drop as organic matter is oxidized (donates an electron) and oxygen, nitrate, and other electron acceptors are used in sequence (Mitch and Gosselink, 2000). In the absence of large amounts of organic matter, decomposition may be insufficient for the development of strongly reducing conditions.

Contaminant dynamics

Water table, ORP and DO generally rise as rainfall becomes more abundant in late fall. These parameters reach their peak level after snowmelt in the spring, and then drop in the summer due to low rainfall and high evapotranspiration. DOC and groundwater temperature are lower in winter and spring, but higher in summer and fall. Rewetting of soil in the fall and ORP increase may favor oxidative processes including nitrification and reoxidation of reduced S species. This interpretation is supported by the gradual increase in nitrate concentration in the field edge. The nitrate produced was

probably consumed within the riparian buffer given the constant decline in nitrate concentration from field edge to stream edge at WR and LWD.

The N transport by snowmelt could come from different sources, such as accumulation of atmospheric N deposition in the snowpack, active nitrification in the snowpack or N mineralization during the freeze-thaw change or N eluted from snowpack interacting with surface soil layer (Kendall et al., 1995). Snowmelt water interacting with surface soil in agricultural uplands and carrying nitrate out thereafter might explain the high nitrate input after snowmelt at LWD and WR site. The application of anhydrous ammonia may contribute a large portion of the nitrate pool during the following spring. During corn years, ammonia is applied to the farmland. In 2010, ammonia was applied to the corn field located upland from the riparian buffers. The transport of residual N during the dormant season may have contributed to the huge increase in nitrate observed in spring 2011. Although corn was planted for three consecutive years at the WR site, year to year variation in spring NO_3^- concentration was not observed. This was probably due to the high nitrate removal capacity observed at the WR site in winter and early spring when the water table was high and ORP was high. This finding agreed with the results of Mayer et al. (2010) who observed the highest groundwater NO_3^- concentrations when WT depth was highest. These results are indicative of high groundwater-surface water exchange. This consistent pattern might indicate major events and the hydrology might be the strongest one among the factors controlling ORP variations in a wide range of natural settings. However, considering highest nitrate input during this period, the length of groundwater resident time would therefore become especially critical.

But NO_3^- concentrations were not correlated with any parameter abovementioned in SS. The rise of NO_3^- and SRP concentrations in SS followed by several rewetting events, as it is indicated by rapid changes in water table levels (Figure 5). In addition, NO_3^- and SRP were not correlated to WT, GWT, DO, ORP and DOC in SS, suggesting

that biogeochemical conditions were probably not the primary driver of dynamics of NO_3^- and SRP in this setting. Instead, the co-occurrence of NO_3^- and SRP peaks on select dates following intense rewetting events in late fall and winter, and the location of the study site down slope from low density housing development on septic systems suggest that NO_3^- and SRP concentrations at the SS site are likely source-driven, as opposed to being regulated by seasonal changes in local biogeochemical conditions in the subsurface at the site (Vidon et al., 2013 manuscripts). It seems that biogeochemical conditions drive the NO_3^- dynamics at the sites near cultivated fields (LWD and WR), but have little influence at the riparian site surrounded by forest and residential developments. This finding suggests that land use probably is an important factor of NO_3^- dynamics at watershed scale.

There was a slight increase in SRP transport after snowmelt events at WR, but the transport and fate of SRP did not generally follow major events and variations in ORP. Royer et al. (2006) reviewed 10 years of N and P export in three watersheds in Illinois, and found that 56% of the NO_3^- and 84% of the soluble reactive phosphorus (SRP) in runoff occurred during only 10% of the time (>90 percentile storm events). From 1994-1997, Kovacic et al. (2000) monitored P removal rates from wetlands receiving tile drain water in Illinois, and reported a 2% reduction for TP. The authors (Kovacic et al., 2000) suggested that the wetland performed poorly in terms of P retention. However, that study focused only on nutrient in tiles and did not measure sediment-associated P entering the wetland with surface runoff (Kovacic et al., 2000).

In another study conducted in LWD, Vidon et al. (2012) found that SRP flux in tile drainage could explain SRP flux in stream, and that SRP flux in overland flow did not translate into SRP flux in stream. Therefore, best management practice to control SRP export would be most effective if P flux in tile drainage can be reduced. This could explain the limited variation in groundwater SRP at the LWD site. However, at the WR

site, it is likely that P was transported from the crop field into the river via surface runoff instead of groundwater. Peterjohn and Correl (1984) suggested that vegetated riparian zones are not effective for the removal of P in groundwater, although they are effective with regard to P in surface runoff. Our field observations that overland flow occurred at the WR site in spring of 2010 and 2011 were consistent with their findings. Due to its timing, an alternative explanation is that the increase in groundwater SRP at the WR site in April 2010 and 2011 was due to planting activities. The range (0.10-0.20 mg/L) of SRP measured at the WR site during that period was similar to groundwater dissolved P (DP) concentrations (0.15-0.3 mg/L) reported by Osborne and Kovacic (1993) during the planting season in Illinois. Further, Osborne and Kovacic (1993) found that the forest buffer removed more phosphorus initially, but also released more phosphorus during the dormant season. In the present study (Figure 16), a slow rise in SRP at WR was observed during the fall season, which might also indicate a release of SRP during dormant season. While Nitrate removal in riparian systems can be complete (emitted as nitrogen gases), P removal may still result in P accumulation in the system and subsequent P loss (Carlyle and Hill, 2001). Therefore, it remains unclear how riparian systems function with regard to P retention on a longer time scale. For the SS site, it is more likely that P dynamics was source-driven given the location of that site down-slope from a low-density housing development on septic systems.

Contrary to expectations, SRP did not follow ORP variations. In a study of constructed wetlands in Indiana, Smith (2011) showed that inorganic P concentration in floodwater and pore water was not correlated with dissolved Fe, suggesting that reductive dissolution was not the dominant process controlling P release in US Midwest mineral soils developed from calcareous glacial till (Smith, 2011). Another finding in the similar tile drainage system is that SRP was transported into stream by macro pore flow during large storms and matrix flow during small storm events (Vidon and Cuadra, 2011).

Reoxidation of reduced sulfur accomplished fast and reach its peaks right after rewetting events in late fall. Sulfate reduction and other reactions requiring more reducing conditions are suppressed in the spring when water table is high. The slight decrease in SO_4^{2-} might suggest an autotrophic denitrification processes, or SO_4^{2-} reduction in anaerobic microsites. In summer, sulfate reduction reached its maximum. Sulfate concentration was significantly correlated with WT and DOC at the SS and WR sites. This result is consistent with the findings by Lazerte (1993) and Eimer et al. (2004) that wetland could be a sink of SO_4^{2-} in wet years and a source in dry years.

When water tables, OPR and DO dropped in late spring and summer, reducing conditions developed in the groundwater due to the long residence time and low hydraulic gradient (Figure 8, 9, and 10). As ORP dropped below 100 mV, NH_4^+ started to increase in late spring to reach a maximum in the summer. The accumulation of NH_4^+ might result from inhibition of nitrification due to low oxygen availability (Heffting et al., 2003). This is likely because low ORP does not preclude mineralization of soil organic matter, and NH_4^+ production. Using NaMoO_4 to selectively inhibit SO_4^{2-} reduction, Jacinthe and Groffman (2006) demonstrated the linkages between sulfate reduction and the release of NH_4^+ by salt marsh sediment. Support for this interpretation can be found from the positive correlations between NH_4^+ and DOC observed at both the WR ($r = 0.67$, $n = 38$) and the SS sites ($r = 0.37$, $n = 52$). However, this explanation does not hold for the LWD site because such a correlation was not found.

Although SO_4^{2-} concentration was not significantly correlated to DO, ORP, DOC or groundwater temperature at LWD, SO_4^{2-} concentration significantly correlated with DOC and WT at SS and at WR. In addition, lower SO_4^{2-} concentrations (<25 mg/L) were generally associated with low water table in summertime. This pattern suggests intense SO_4^{2-} reduction in groundwater, a process that preferentially occurs in the -100 mV to -200 mV range (Mitch and Gosselink, 2000). Sulfate reduction likely occurred more

actively in anoxic micro-sites or at individual well locations during the dry period (July to November) than during the wet period.

The co-occurrence of NH_4^+ increase and SO_4^{2-} decrease occurs approximately at the same period under low ORP condition in summer across all three sites, which is further evidence that sulfate reduction might take over the denitrification under extremely anoxic condition. Increased number of methanogens correlated with increased amounts of available ammonia - the form of nitrogen that methanogens require for growth (Bryant et al., 1971).

MeHg was positively correlated with DOC, but negatively correlated with WT, DO, ORP at the WR site. The influence of temperature on MeHg production is consistent with other findings. THg concentrations were commonly associated with high flow (Shanley et al., 2008), while MeHg often decreased during high flow periods such as snowmelt due to low sediment methylation rates during the cold season. Because MeHg but not THg was associated with sulfate reduction, the divergent behavior of these two forms of Hg was expected. These results are consistent with a study that showed strong seasonal variability in MeHg in glaciated riverine systems (Burns et al., 2012).

MeHg concentration at WR (0.23 ng/L) was significantly higher than that at LWD (0.06 ng/L) and SS (0.09 ng/L). These findings suggest that, compared to hydrology, land use and ground water temperature might be stronger controls of MeHg production. This interpretation contrasts with the conclusion of Burns et al. (2012) who argued that hydrogeomorphology, riparian area, and open water could explain 60-90% of the variation in both THg and MeHg. However, the study of Burns et al. (2012) was an analysis at the watershed scale, which is different from our site scale study. At site scale, land use or point source might be more important factors.

Why THg concentration in WR is the highest? One possible reason is its high flooding frequency. Since flooding facilitated the development of anaerobic conditions

favorable for mercury methylation and exchange of stream water and groundwater, it could explain high MeHg production at the WR site. The other possible explanation is related to DOC concentration in the groundwater. Previous research established that organic matter is an important factor controlling THg entry into aquatic systems. However, we did not find correlation between THg and DOC except at LWD. The SS had a lower DOC concentration, which might be because it is a recently restored wetland instead of well-preserved wetland. However, the difference in DOC concentration still cannot explain the much larger difference between SS and WR. Atmospheric depositions are believed to be the principal source of Hg to most aquatic ecosystems, and correlations between Hg deposition loads and concentrations in fish have been identified across the U.S. (Hammerschmidt and Fitzgerald, 2006), with some exceptions in areas with large point sources such as heavily mined regions, and near industrial/urban emissions sources (Waldron et al., 2000; Evers et al., 2008). Studies conducted in the Adirondacks also revealed several of the factors likely to promote high rates of Hg mobilization methylation, and bioaccumulation in the Adirondacks. These factors include abundant wetlands, predominantly forested land cover, low pH waters, and a location downwind from coal-fired power plants in the Ohio River valley (Driscoll et al., 1994; Simonin et al., 2008). The WR site is less than 1 mile northeast to a coal power plant. In Indiana, wind comes from north during winter and Southwest during summer, so there is a great possibility that south west wind in the summer may have caused greater THg deposition at the WR site than at the other sites. From another mercury study in central Indiana, Hatcher and Filippelli (2011) reported that the coal power plant close to our WR site is one of the top emitters accounting for 99% atmospheric emission in Indiana. The electric power plant can explain 50% of mercury in Indiana (Indiana 2004-2005), which could partly explain the high THg and MeHg at the

WR site. Especially considering the high demand of electricity due to the heavy use of air conditioning in the summer, this might be the case.

Hatcher and Filippelli (2011) found that urban areas have high concentration Hg, owing to local sources and/or rapid runoff from impervious surface. For LWD, the highest THg (4.54 ng/L on Feb 18, 2011) in the ditch could be possibly due to drainage pipe which functions similarly to impervious surface in urban areas. The highest THg concentration at SS was only 1.17 ng/L (March 11, 2011) after snowmelt, as indicated by a rapid rise in WT depth. We did not observed high concentration of Hg in the river section near the WR site, which has the highest THg 1.51 ng/L in summer (August 30, 2010) and the second highest 0.85 ng/L (February 16, 2010) following rapid rise of water tables. These findings regarding THg behavior at the three sites have several implications. First, it indicates strong point source influence such as coal power plant near WR site. Second, THg export to streams was generally associated with major events in spring. Third, drainage pipe has the potential to facilitate THg transport to stream, and riparian zones where tile drains are present could act as sources of THg for adjacent streams.

The increase in MeHg from field edge to stream edge at the WR and LWD sites is in agreement with the study hypothesis. However, the hypothesis was not supported by the trend observed at the SS site - decrease in MeHg from field edge to stream edge. These seemingly contradictory results actually were caused by wells in the wetland area at SS. These sampling points are therefore potential hot spots for MeHg production. Well 4 at WR, wells 3, 6, 7 and 12 at LWD and well 1, 3, 4, and 5 at SS are all potential hot spots for MeHg production (Figure 2A, 2B, 2C).

The peak of MeHg production at the study sites occurred at different periods (Figure 18). At the SS site, the peak was in early summer, but at LWD and WR MeHg peaks were in mid-summer. These findings suggest that MeHg production could be

more sensitive to ORP changes rather than temperature. High sulfate concentration is not favorable to mercury methylation, because the production of sulfide inhibits the methylation process (Eimers et al., 2004). That might explain why MeHg was produced in summer after most of the sulfate pool had been reduced and transformed. Our results revealed a strong seasonal pattern of THg/MeHg ratio (Figure 20), which was different from another study in which they found relatively constant THg/MeHg ratio (Shanley et al., 2008). However, the THg and MeHg concentrations in our study are consistent with the study conducted by Shanley et al., 2008) in which they reported that baseflow THg was generally less than 1 ng/L and MeHg was less than 0.2 ng/L. THg and MeHg concentrations increased with stream flow.

Although a thermodynamic approach might oversimplify the complex interactions among multiple contaminants in riparian groundwater, it is still valid at a large temporal scale. Our results supported this thermodynamic theory by the following evidence. First, both nitrate and sulfate concentrations were high in spring, but denitrification occurred earlier (early spring) than sulfate reduction (late spring and summer) (Figure 14, 15). Second, MeHg concentrations increased at SS earlier than at LWD and WR, which is consistent with the result that ORP in SS dropped earlier than LWD and WR (Figure 11, 18). Although groundwater temperature likely plays a more important role, the earlier increase in MeHg cannot be explained by groundwater temperature. Third, on an annual scale, the use of electron acceptors in the subsurface followed such a sequence, O_2 , NO_3^- , SO_4^{2-} , CH_4 which is supported by the results that increased concentrations in nitrate and sulfate in fall and winter, reduction of nitrate in spring, reduction of SO_4^{2-} in late spring and early summer, and MeHg accumulation in summer (Figure 14, 15, 17, 18). However, this theory fails to explain the SRP dynamics in the groundwater regardless of temporal or spatial variations (Figure 16). In addition, this theory has less

power to explain the dynamics of solutes driven by source, for example, NO_3^- and SRP concentrations at SS.

Removal efficiency and riparian functions as a source or sink

The conceptual model developed from a study in Ontario, Canada, could be used with minimum modification to predict nitrate removal in most glacial till and outwash landscapes (Vidon and Hill, 2004b, 2006). The model groups riparian zones into six categories. According to the model classification criteria, the LWD site falls in the first category that is a site exhibiting small N sink potential due to low soil hydraulic conductivity and restricted subsurface flow. The SS site belongs to the second category, a small sink with a thin upland aquifer, and level to gently sloping topography (<4-5%). For this second category, water input ceases during dry periods, as observed at the SS site. The WR riparian zones approximately belong to the fifth category that includes riparian zones linked to upland aquifer with intermediate thickness and steeper topography (>4-5%). Sites in this category show considerable seasonal variations in groundwater inputs but maintain a continuous upland-riparian zone hydrological connection. Sites in this category are generally medium to large nitrate sinks.

Among the three study sites, the WR site exhibited the highest nitrate removal efficiency. The upland of SS is a residential and forested area with low nitrate input; therefore, no clear nitrate removal pattern was observed in both wet and dry season. No obvious pattern of nitrate removal was observed at LWD during the dry season. Although some nitrate removal was noted during the dry season at WR, it decreased greatly compared to the peak in N removal observed in the spring season. The relatively constant nitrate input at WR compared to LWD might be due to the steep slope at the interface between the upland and riparian zones, and also to the coarse outwash deposit that underlies the WR site. This 2-year study showed that riparian zones at LWD and WR could serve as reliable nitrate sinks in the early spring. Taking flow direction and the

spatial variation in ground water NO_3^- (lower concentration at stream edge) into consideration, it can be concluded that the SS site had a relatively high NO_3^- removal efficiency despite a low NO_3^- input. The removal efficiency was higher and more consistent at the WR site (80-96%) than at LWD (50-90%). These N removal estimates are consistent with studies conducted on glaciated or outwash/alluvial landscapes of Ontario, Canada (Vidon and Hill, 2004a, b, c). High nitrate removal efficiency at WR might also be due to its low hydraulic gradient during the spring, thus resulting in increased groundwater residence time and more efficient denitrification by soil microbes. Another factor contributing to the high removal efficiency might also be the topography of the riparian zone at WR which allows groundwater to come in contact with the surface soil layers. With high organic matter, and higher microbial population, the 0-30 cm soil layer is the most active zone of denitrification in the soil profile (Clements et al., 2002).

Although large amounts of nitrate may have been exported from the crop fields at LWD, this nitrate was probably delivered directly to the stream via the drainage pipes. As a result of the limited contact between groundwater and riparian buffers, nitrate removal efficiency was low for this site, as a whole. This result is similar to that of Osborne and Kovacic (1993) who concluded that riparian buffers were not effective when tile drainage is present.

Because we did not include flux calculation, we would not be able to evaluate the magnitude of a sink or source. Therefore, our discussion on sink or source with respect to riparian functions would be qualitative at best. However, considering the highly conductive soil and high water input, the WR site is expected to either be a relative large sink or source of contaminants. As to SS, nutrient transport mainly occurred during high water table period considering its flat topography and the small amount of upland groundwater input in the summer. Therefore, SS is expected to be a small sink or source. Because of the steep slope (8-11%) at the interface between field edge and upland and

deep outwash deposit at WR, we observed the nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (SRP) input from upland are relatively constant in comparison to LWD and SS. Strong connection between river and riparian zones at WR during flood events lead to flow reversal, as well as contaminant input from river onto riparian zones.

SRP concentrations decreased considerably from field edge to stream edge during major events at the WR site, which might indicate the adsorption rather than release of SRP to the stream, but no notable seasonal and spatial changes were observed in groundwater SRP concentrations at the LWD and SS sites (Figure 16, Table 5). Nevertheless, this is contrary to our hypothesis that SRP release may increase when water tables rise and rewet riparian soil during wet periods. We found that groundwater is a not major sink or source of SRP for all the study sites.

Our results suggest that LWD was a SO_4^{2-} source but WR and SS were neither a source or sink with respect to sulfate. The SO_4^{2-} removal efficiency varied significantly among sites, with -114% for LWD, 11% for SS and 38% for WR. SO_4^{2-} concentration was below the EPA standard of 250 mg/L for secondary contaminant in drinking water.

Because of the small sample size, analysis of the Hg data had limited statistical power, and most of the discussion is based on numerical differences between concentrations at field edge and stream edge. THg concentrations at field edge were also not significantly different to that at stream edge for all sites, but MeHg concentrations at field edge was lower than that at stream edge for LWD and WR which indicates potential source to streams. At the SS site, MeHg concentrations at field edge were higher than at stream edge, which indicates a potential sink. However, one needs to be cautious with this interpretation because inherent differences in vegetation and soil between the field edge (wetlands) and stream edge (woody species in alluvial soil).

Conclusions and implications for management

The dynamics of six groups of solutes were examined in riparian buffers at three contrasting HGM settings- till plain, incised valley in glacial landscapes, and floodplain underlain by glacial outwash. In addition to HGM difference, the study results were influenced by major hydrological events, seasonal and land use (residential vs agricultural); the latter being an important controller of the amount and timing of contaminants delivered to the riparian zone.

Major events and HGM settings have significant implications for riparian management. In the Midwest, rapid changes in water table depth occurred during snowmelt events, and this particular period could potentially be hot moments of biogeochemical activities for nitrate removal. A large nitrate input in the soil profile in the early spring has important implications for water quality, because N uptake by plants is almost non-existent in early spring, accumulation of NO_3^- N in soil during that period poses a potential threat to water quality (Jacinthe et al., 2002). WR was a potential intermediate or large nitrate sink because of constant hydrological connection with uplands and high removal efficiency. This type of HGM should be promoted to mitigate high nitrate loading in spring from agricultural landscapes. From their water table management technique studies, Jacinthe et al. (2000) suggested that a high water table close to soil surface with a prolonged period could lead to higher denitrification rates. Another study pointed out that declines in water level likely increased subsurface mixing (Mayer et al., 2010), which led to low ORP conditions that sustained NO_3^- removal via denitrification. This might provide some insight in terms of how to regulate water tables through better design of drainage pipes in artificial drained landscape.

Past studies have reported inverse relationships between DOC and NO_3^- concentration (Hedin et al. 1998; Vidon and Hill, 2004c; Mayer et al. 2010). Our results at the LWD and WR sites (agricultural uplands) are consistent with these past findings.

The groundwater-surface water interface is a zone of active nitrogen transformation. Hedin et al. (1998) also suggest that DOC availability might be the limiting factor for denitrification in the interface between stream and groundwater. High DOC concentrations also support the development of more reducing condition and production of MeHg. This would support the strong positive correlations between DOC and MeHg and strong negative correlations between ORP and MeHg.

MeHg is a highly toxic and bio-accumulative contaminant in aquatic systems and, in a 1983-2006 survey, mercury was detected in 90% of fish tissues in Indiana (Stahl, 1997). Therefore, the timing of MeHg production and entry on streams and rivers is important to ecosystem health and human health in the region. Our results imply that MeHg is produced primarily during dry periods (base flow period), and almost no dilution should be expected for MeHg entering aquatic in the summer months in comparison to the spring. Due to water stress in summer for wildlife, this amplifies the risk for bioaccumulation for aquatic organisms, wild birds and mammals that would rely on MeHg-laden waters.

EPA standards for mercury in freshwater is 12 ng THg/L (Risch and Fowler, 2008). During the present study, the highest THg concentration of 5.95 ng THg/L was measured at WR. It should be pointed out that higher THg in snow water (11.78 ng THg/L) was recorded at that site. This value is similar to the average THg in precipitation (10.6 ng/L) reported for Indiana between 2004-2005 (Risch and Fowler, 2008). Considering the relevance of Hg transport with geographic locations and the favorable condition for MeHg production in riparian zones during summer, decision regarding the location of regional power plants should take these factors into account.

Whether or not the higher concentration of THg at LWD was caused by artificial drainage pipe is unclear, but decreased contact time between percolating water with the soil matrix may have caused a quick discharge into the ditch. Although concentration of

THg in the groundwater was low, an increase of MeHg from field to stream edge was observed. So, the selection of coal power plants should also consider whether or not it is in an area with high percentage of drainage pipe in use to drain water quickly.

Overall, our results revealed that difference in HGM translated into distinctive site hydrology, but significant difference in site hydrology did not lead to different biogeochemical conditions. Nitrate reduction, sulfate reoxidation were associated with major events, while sulfate reduction, ammonia and methylmercury production were associated with seasonal changes in biogeochemical conditions. Land use and point source played more important role in magnitude of solute loading and solute dynamics as well. Our thermodynamic theory probably oversimplified the complex patterns of solute dynamics which were also impacted by land use and point source. The LWD site was a small sink for nitrate and a small source for sulfate and MeHg. The SS site was a small sink for MeHg and no effect on NO_3^- , sulfate and SRP. The WR site was an intermediate to large sink for nitrate, an intermediate sink for SRP, and a small source of MeHg. Overall, this study demonstrates that analysis of multiple contaminants control in riparian zones must be conducted on a case by case basis. Generalizable conclusions regarding the dynamics of multiple contaminants must await further investigations.

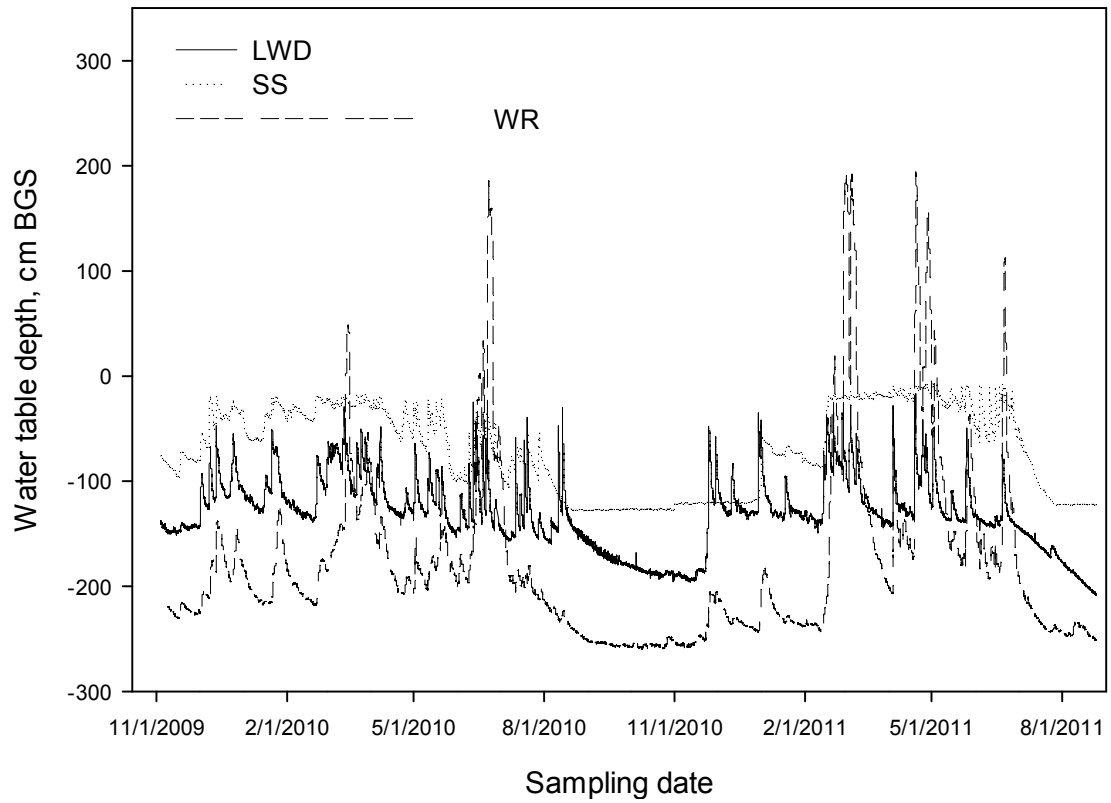


Figure 3: Water table depth below ground surface (BGS) (cm) during the study period (December 2009-May 2011) at Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR).

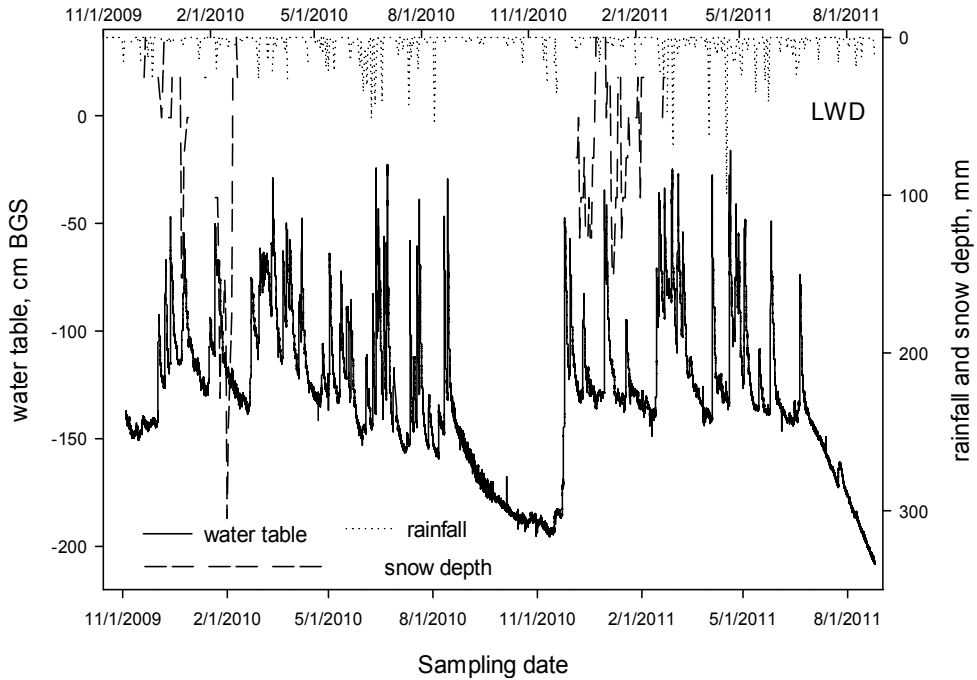


Figure 4: Precipitation (mm), snow depth (mm) and water table depth (cm below ground surface) at the Leary Webber Ditch (LWD) site. Precipitation (mm) and snow depth are on the right side of Y-axis; and water table depths (cm) are on the left side of Y-axis. Note that snow depth refers to the depth of snow left on the ground - not total snowfall.

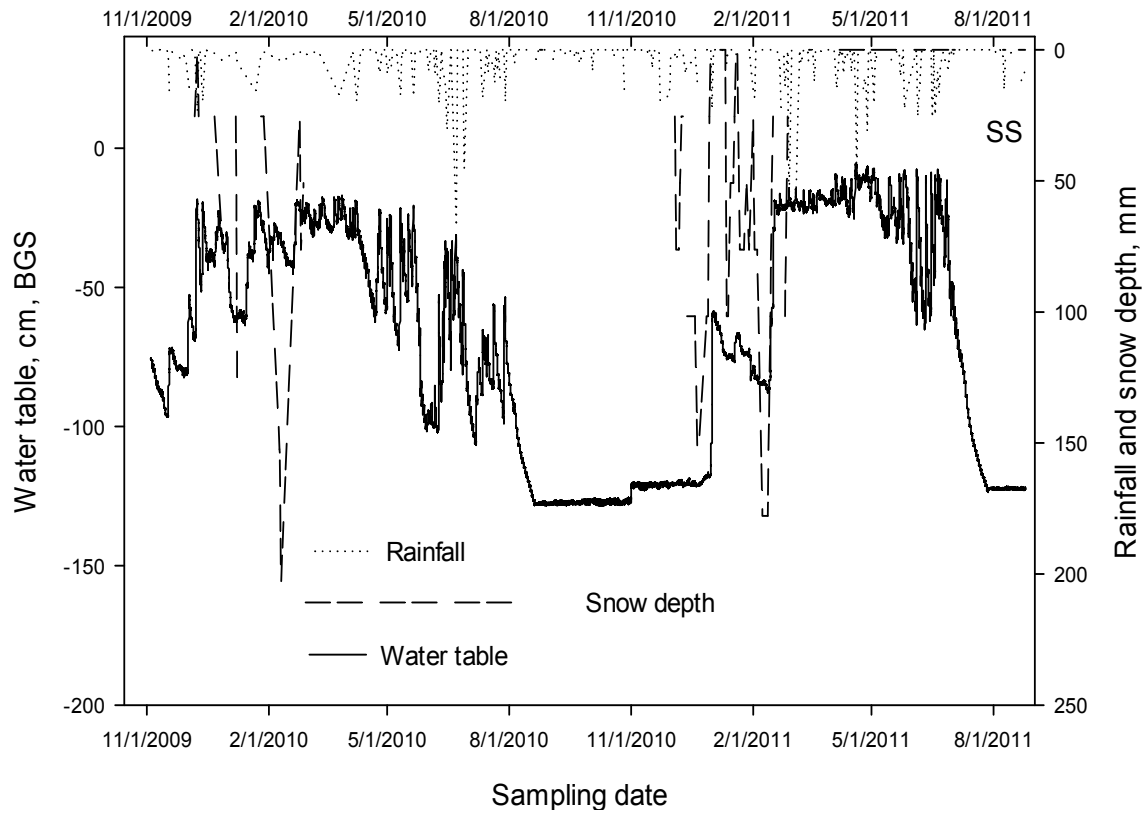


Figure 5: Precipitation (mm), snow depth (mm) and water table depth (cm below ground surface) at the Scott Starling (SS) site. Precipitation (mm) and snow depth are on the right side of Y-axis; and water table depth (cm) is on the left side of Y-axis. Note that snow depth refers to the depth of snow left on the ground - not total snowfall.

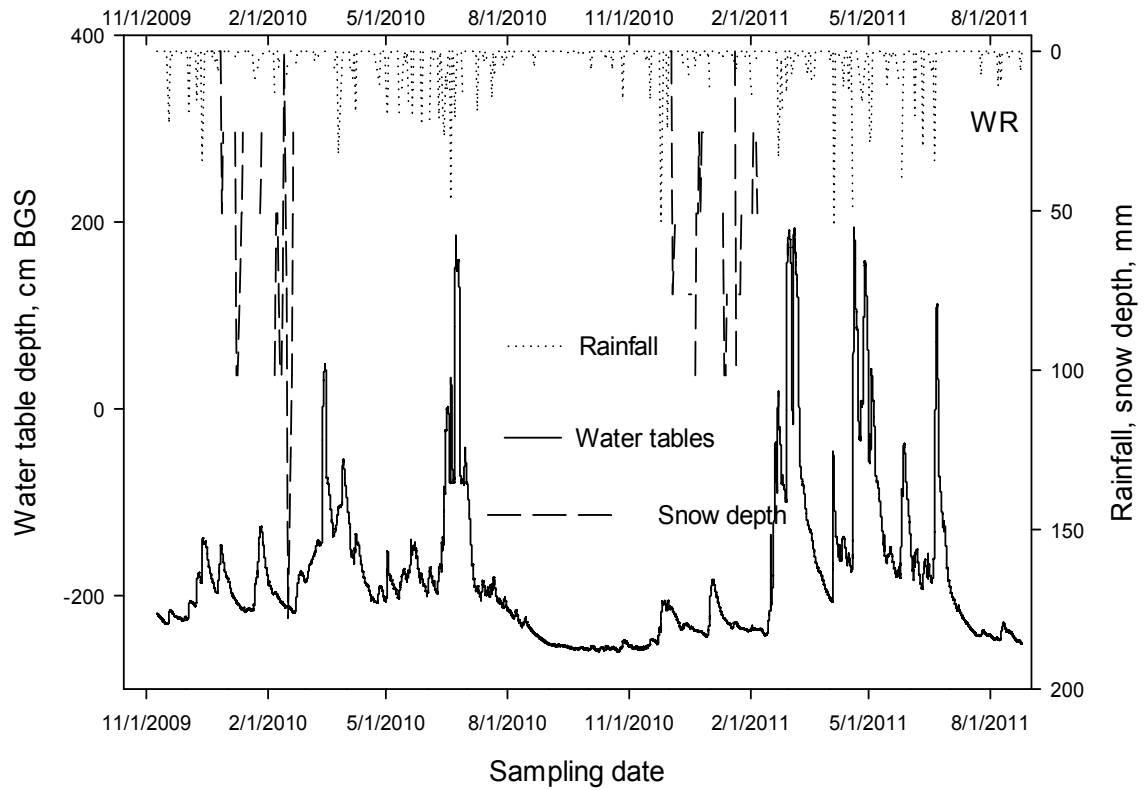


Figure 6: Precipitation (mm), snow depth (mm) and water table depth (cm below ground surface) at the White River (WR) site. Precipitation (mm) and snow depth are on the right side of Y-axis; and water table depth (cm) is on the left side of Y-axis. Note that snow depth refers to the depth of snow left on the ground - not total snowfall.

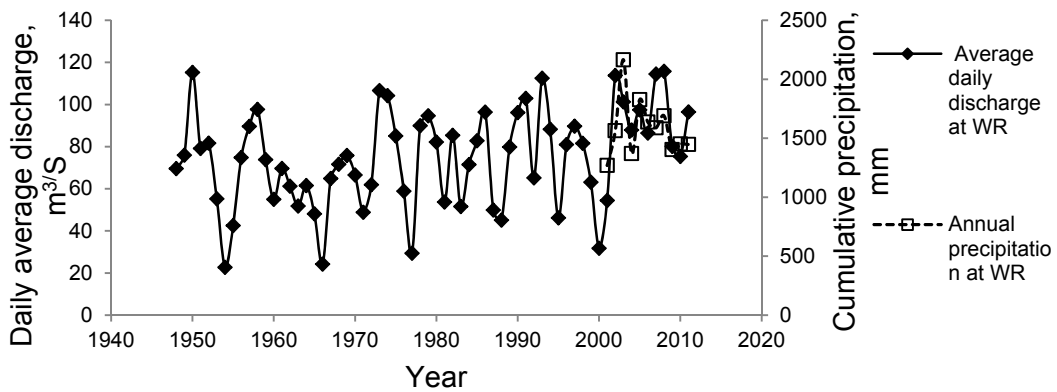
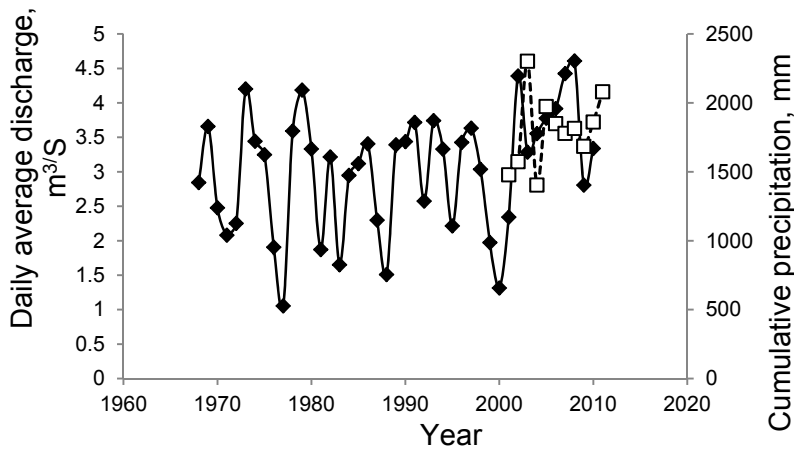
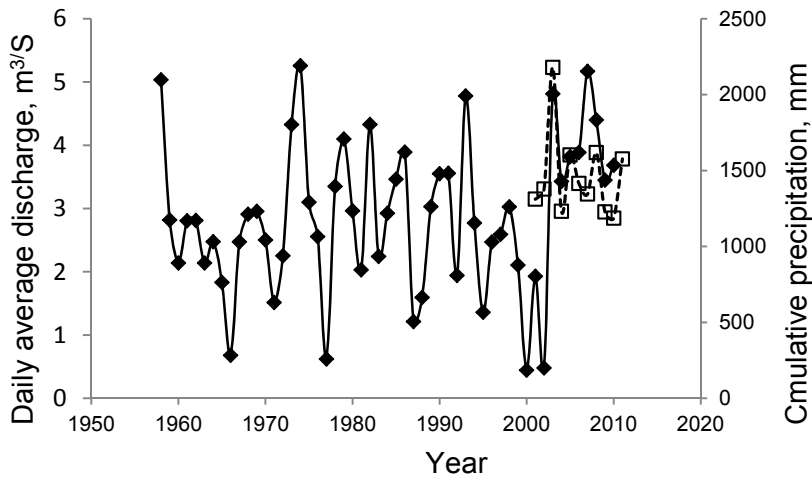
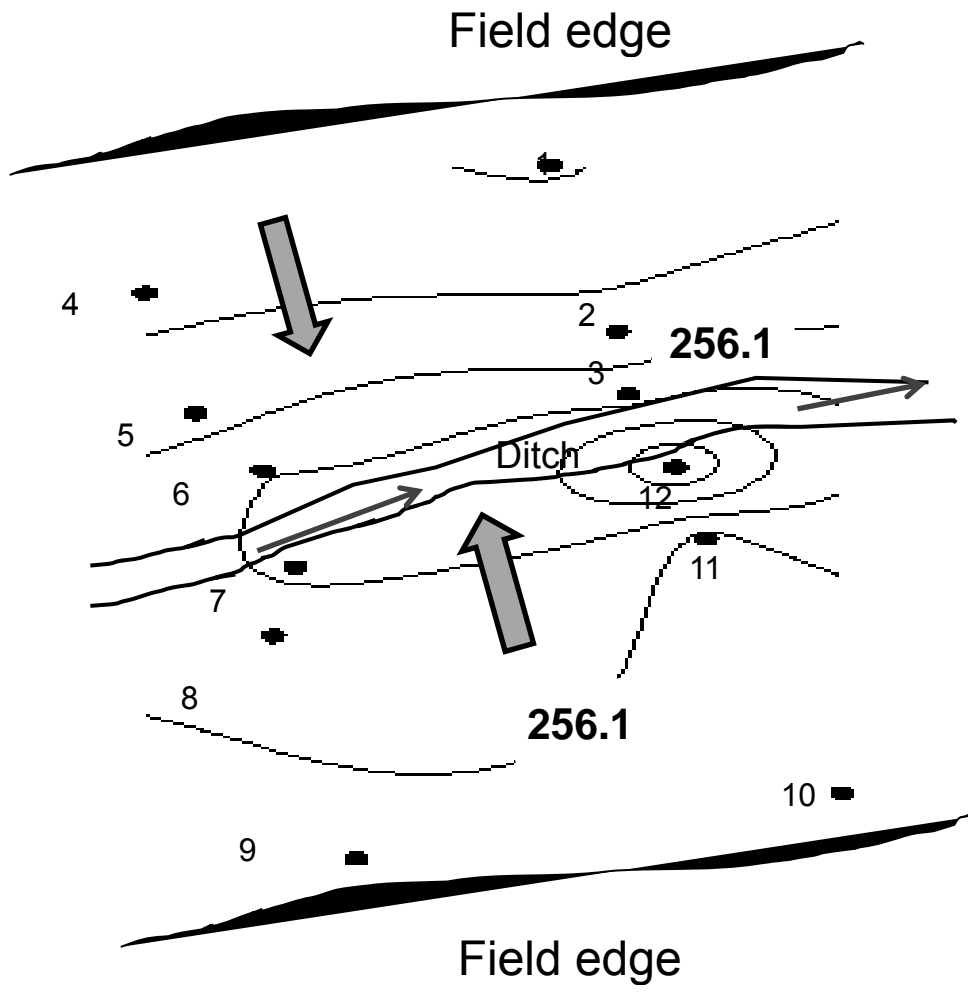


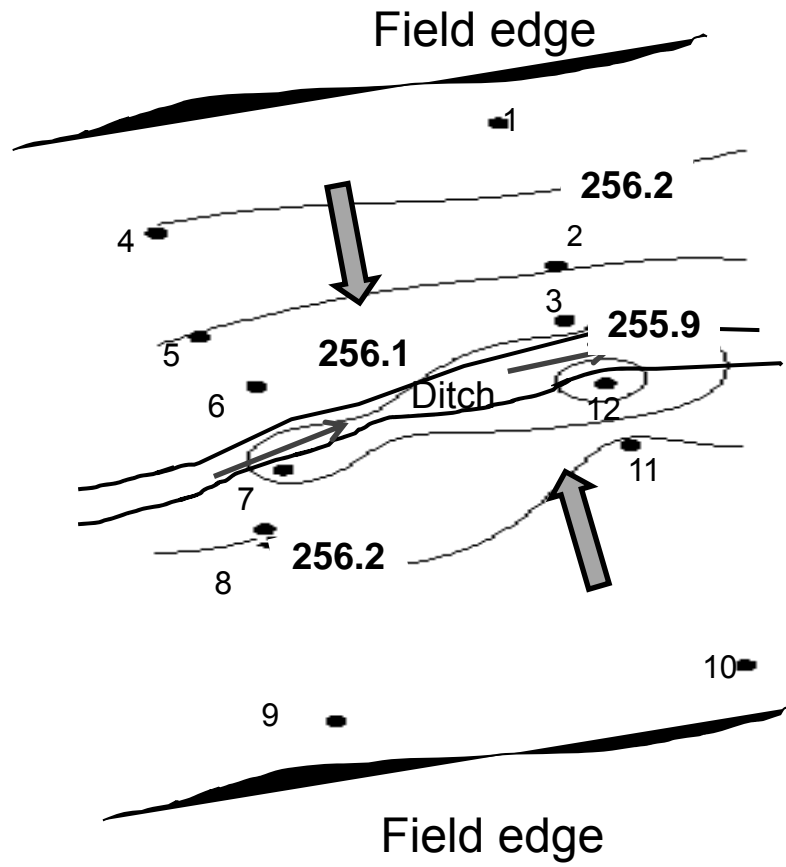
Figure 7: Average daily discharge and cumulative precipitation at the Leary Webber ditch, Scott Starling and White River sites. The discharge data was obtained from USGS website, and precipitation data was obtained from the Indiana climate database (Purdue University).

A) 11-4-2009 LWD



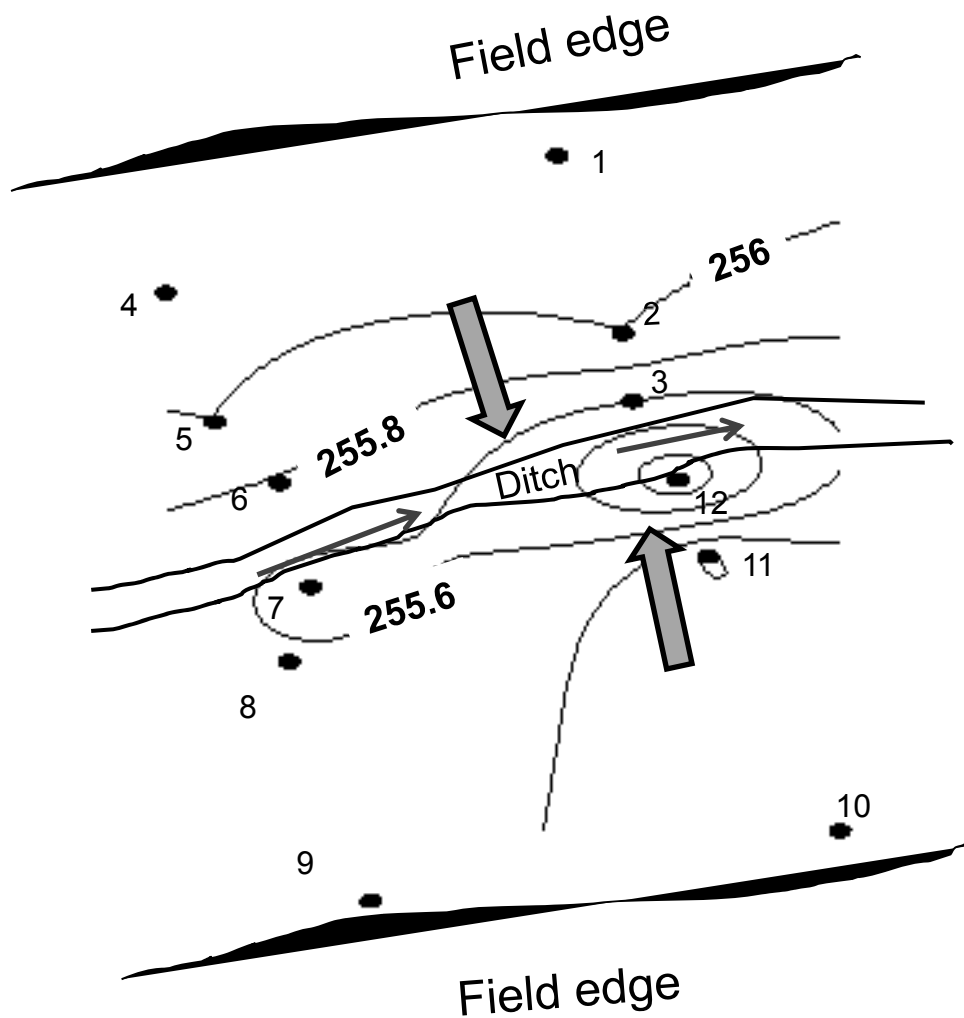
B)

4-14-2010 LWD



c)

9-22-2010 LWD



D)

2-18-2011 LWD

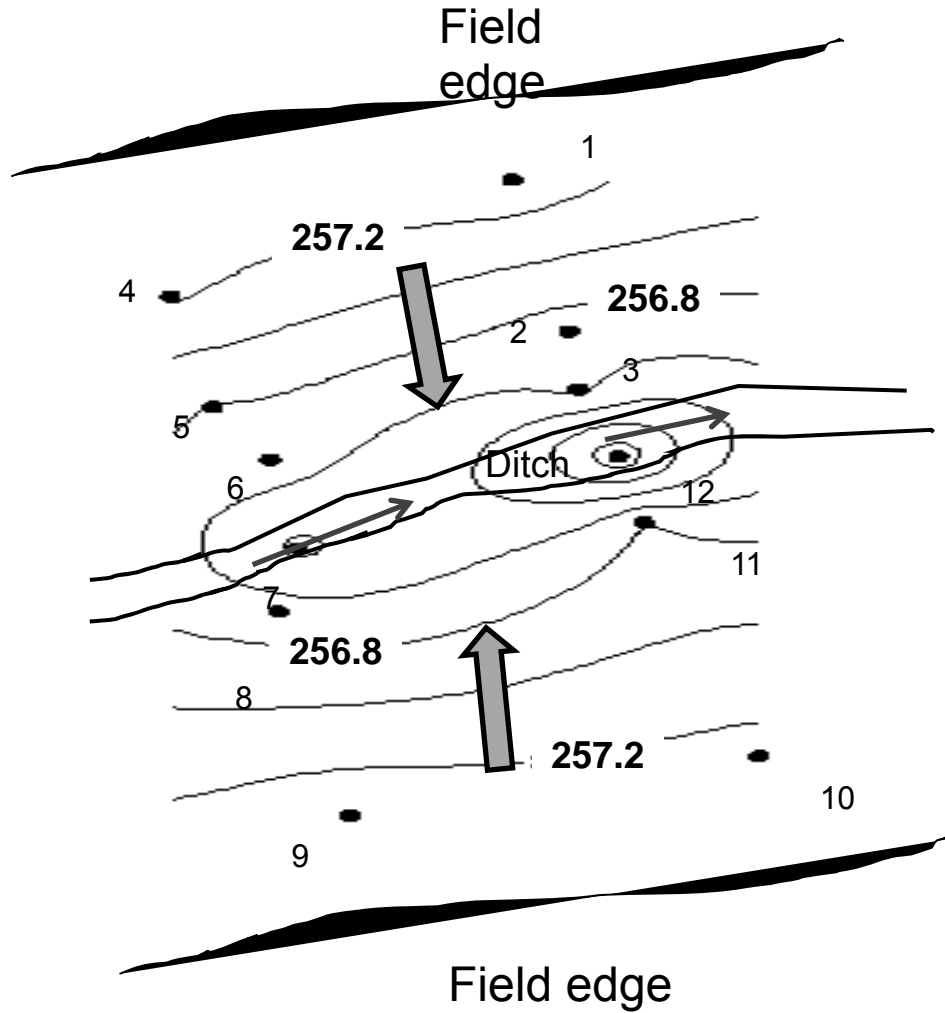
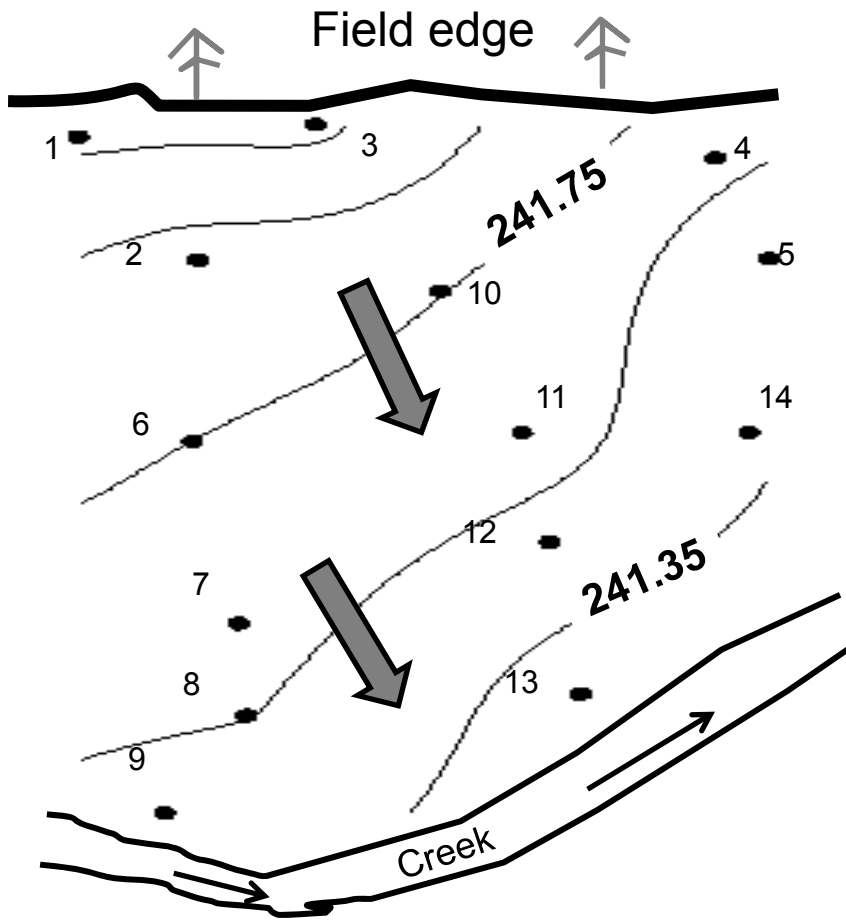


Figure 8: Groundwater flow direction and hydraulic gradient contour maps at the Leary Webber Ditch site. Contour interval is 0.2 m. Black dots represent locations of wells. Thin arrows and wider arrows represent the directions of ditch flow and groundwater, respectively.

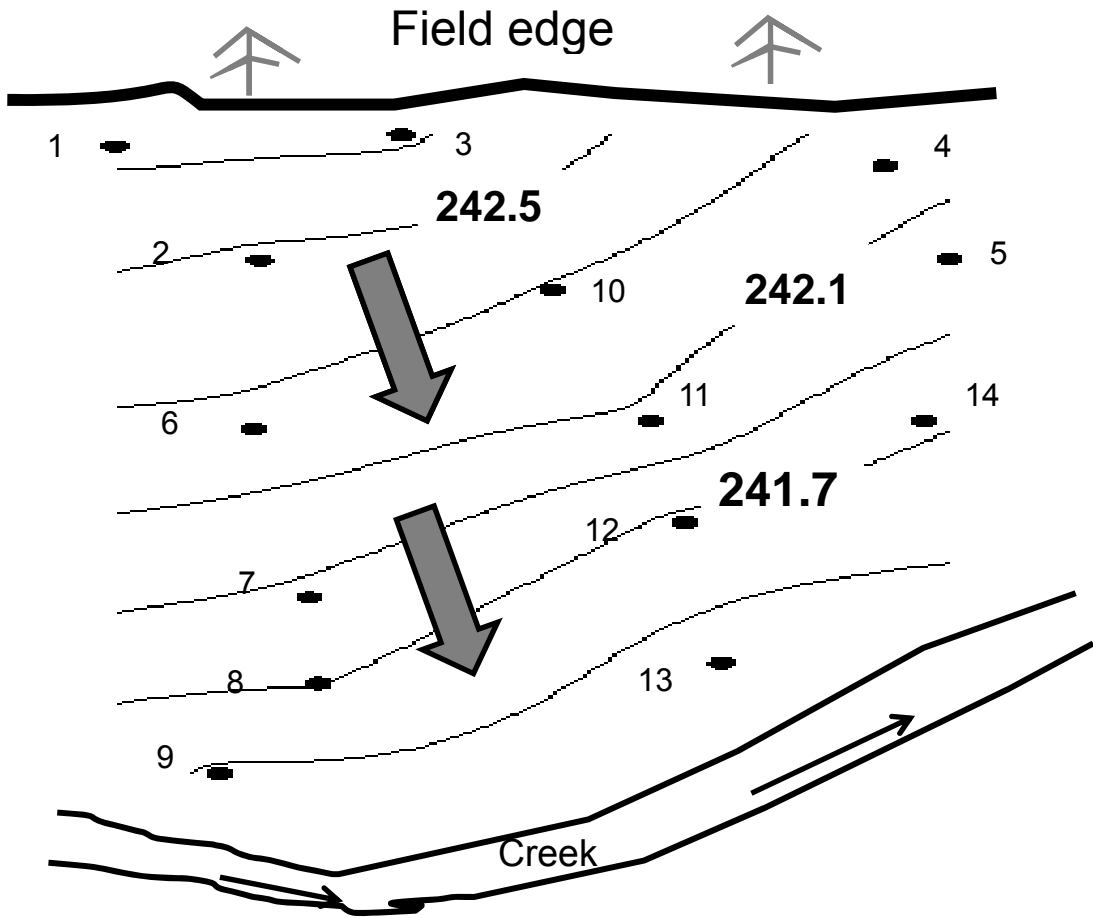
A)

11-04-2009 SS



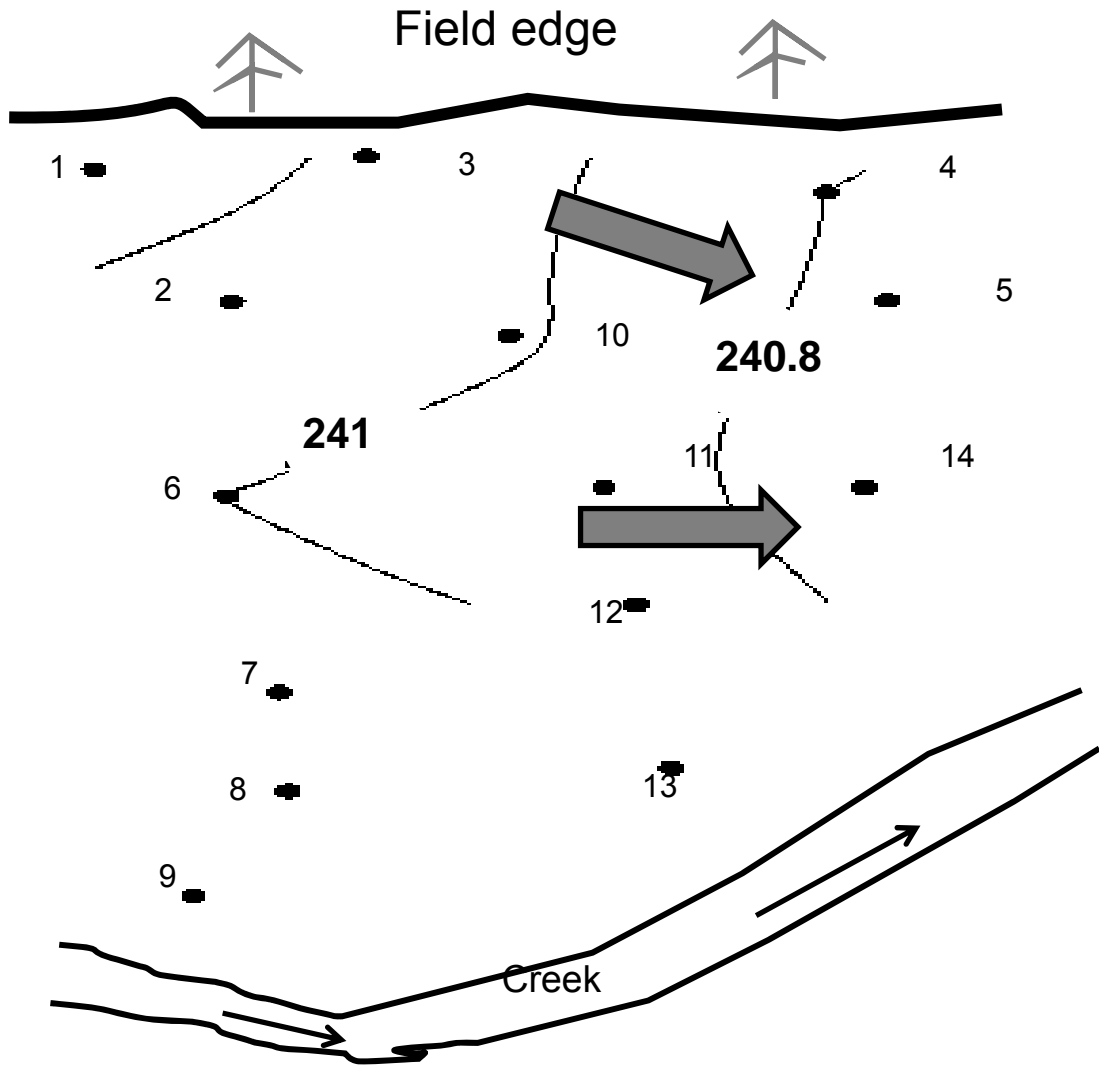
B)

4-14-2010 SS



C)

9-22-2010 SS



D)

4-13-2011 SS

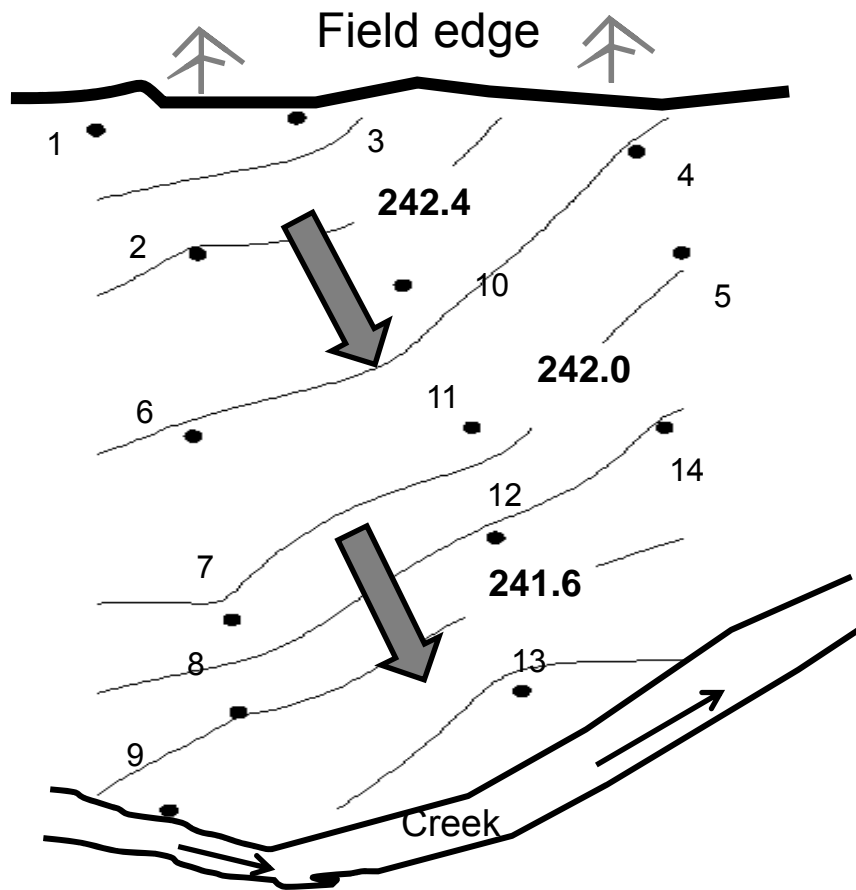
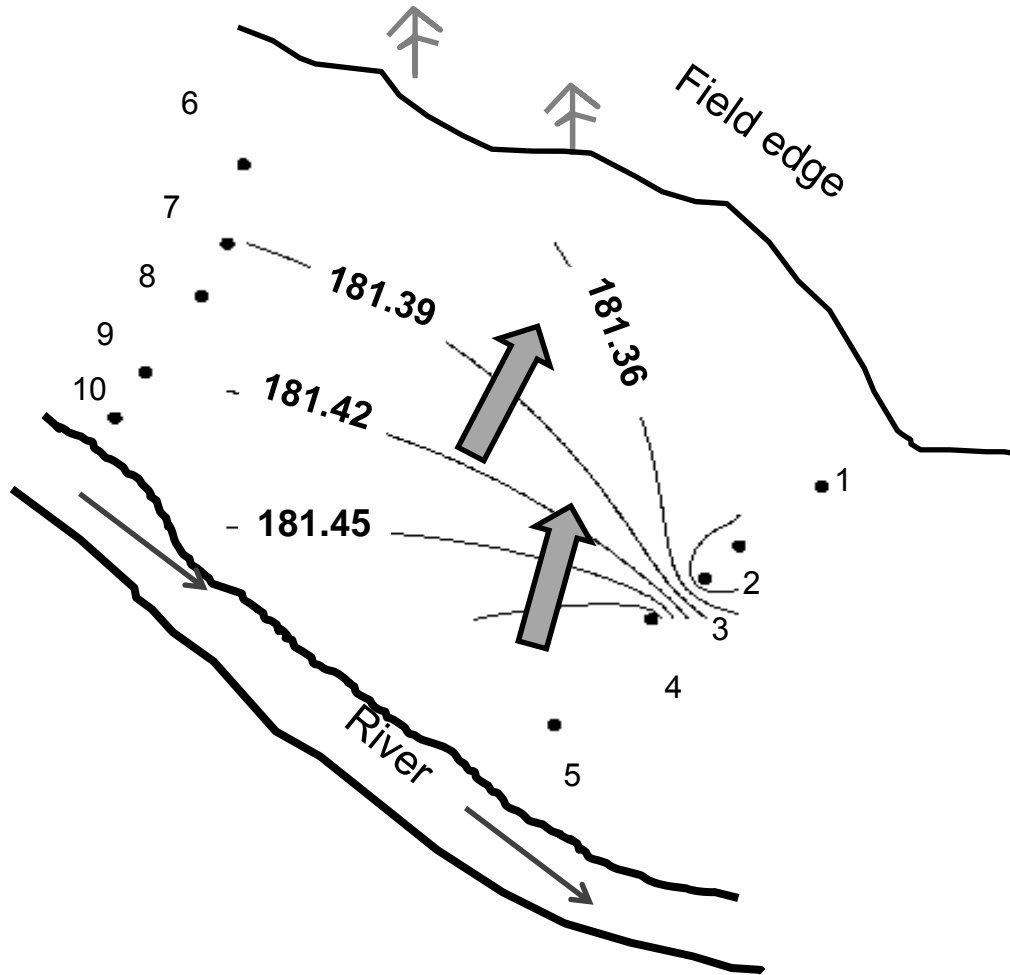


Figure 9: Groundwater flow direction and hydraulic gradient (0.2m intervals) contour maps at the Scott Starling (SS) site. Thin arrows and wider arrows represent the directions of ditch flow and groundwater, respectively. Black dots represent locations of wells (numbers 1-14).

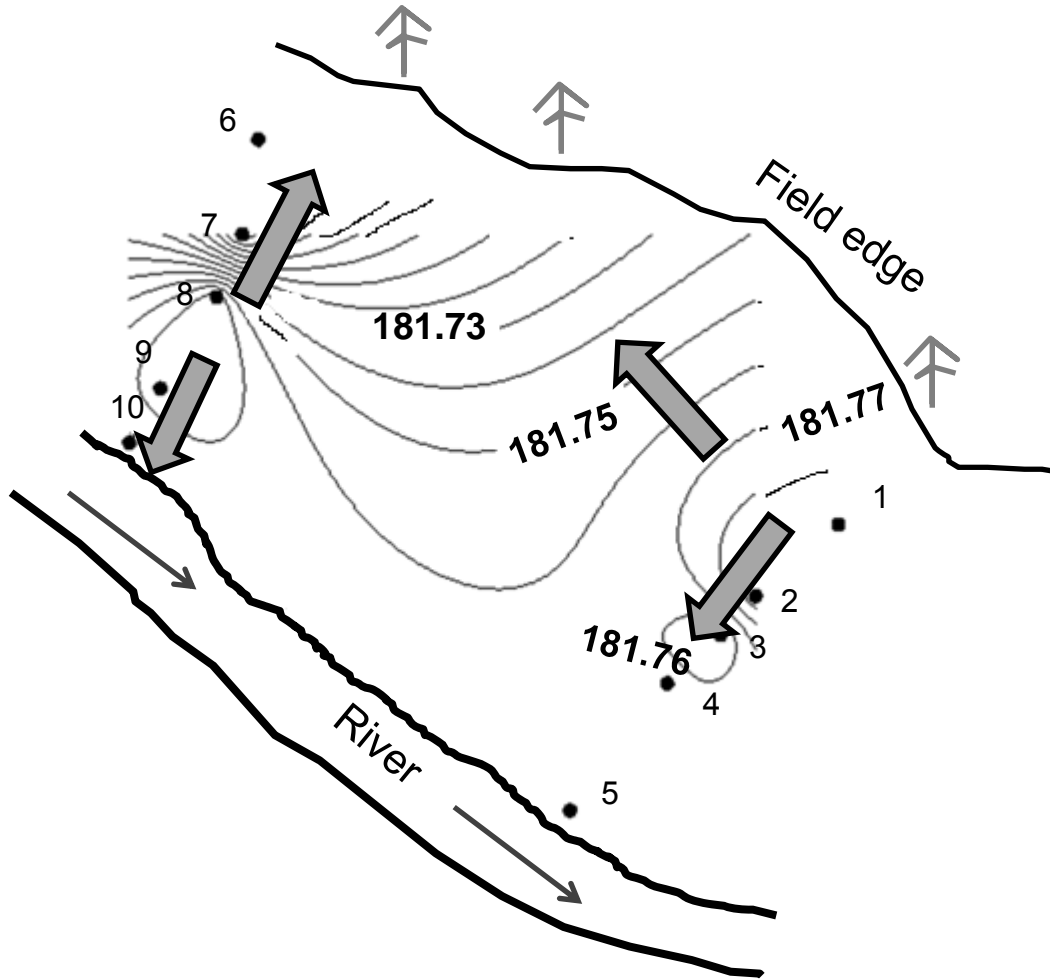
A)

11-9-2009 WR



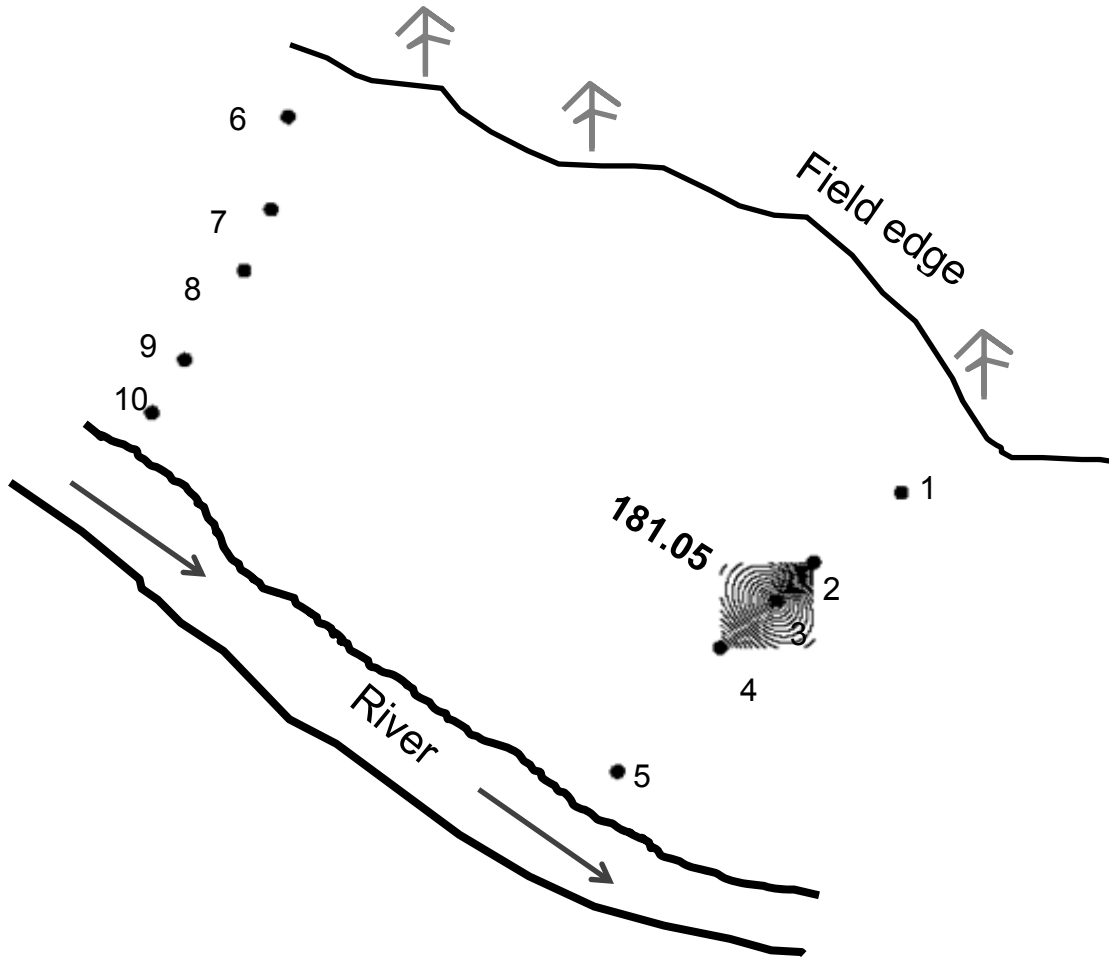
B)

3-4-2010 WR



C)

9-12-2010 WR



D)

3-24-2011 WR

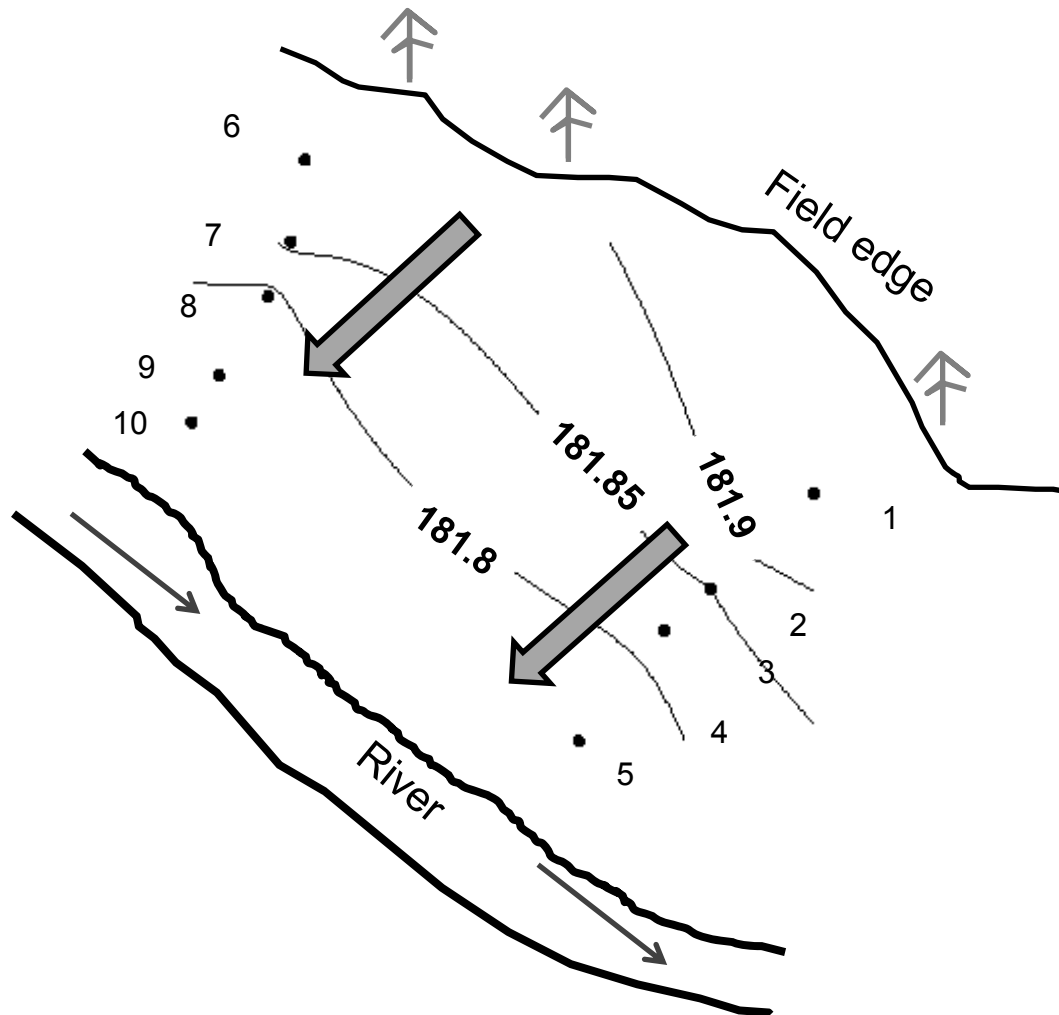


Figure 10: Groundwater flow direction and hydraulic contour maps at the White River site. Black dots white circle represent locations of wells (well 1 to well 10), respectively. Thin arrows and wider arrows represent the directions of stream flow and groundwater, respectively. Contour line interval is 0.01 m.

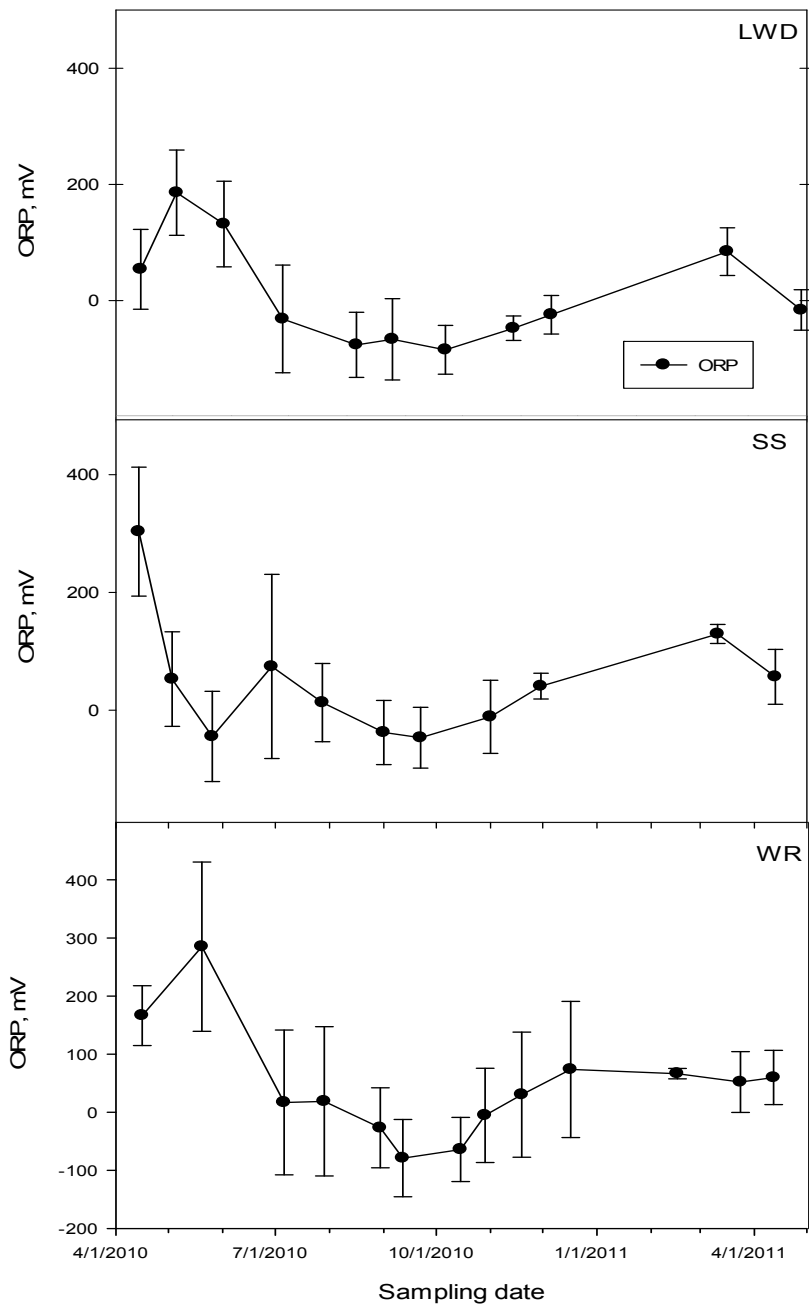


Figure 11: Mean ORP in groundwater at the Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR) sites. Each point is the average of 4-14 measurements. Error bars indicate standard deviation.

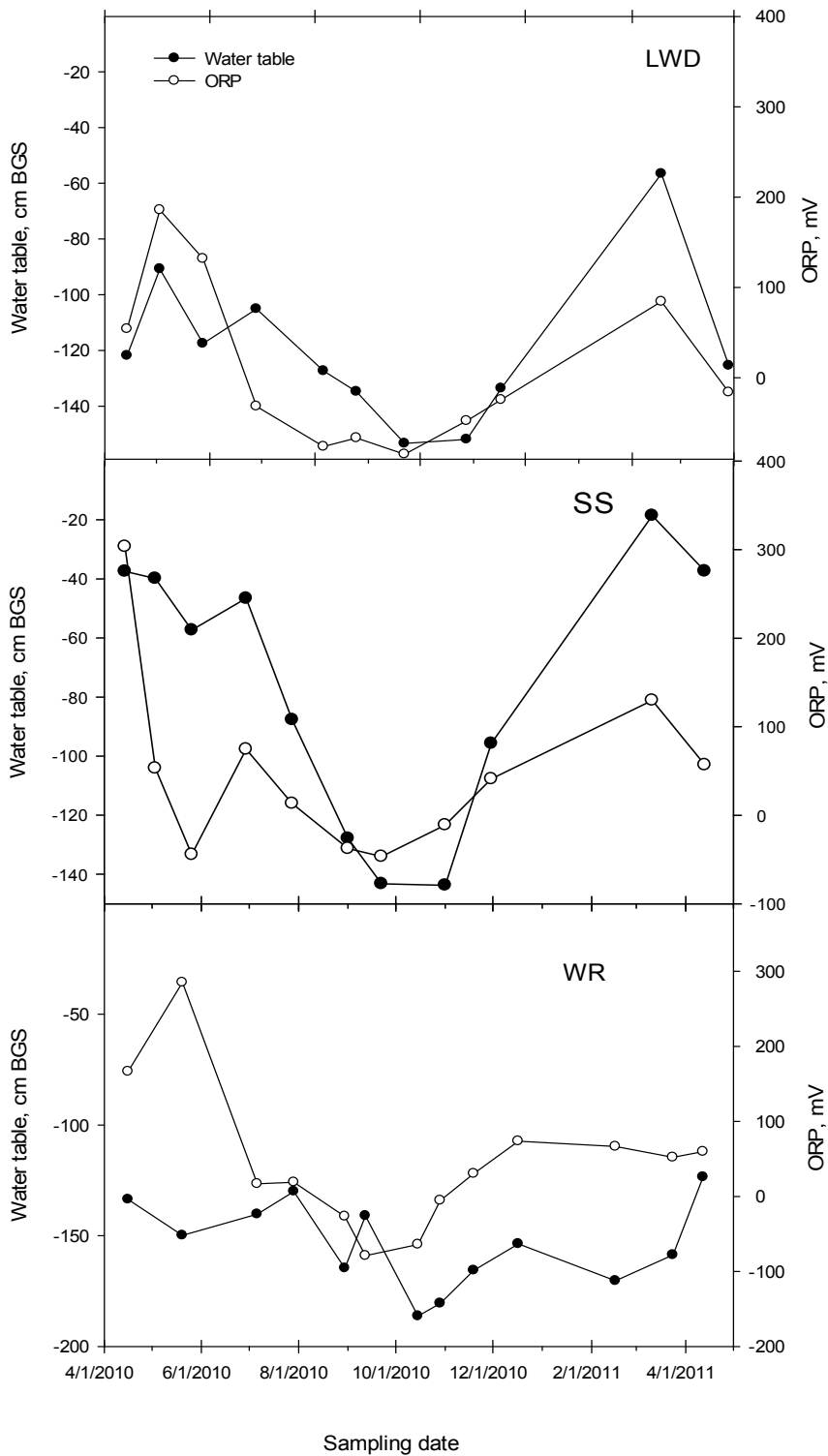


Figure 12: Seasonal trends in ORP and average water table depth at the study sites. Each point is the average of 4-14 measurements.

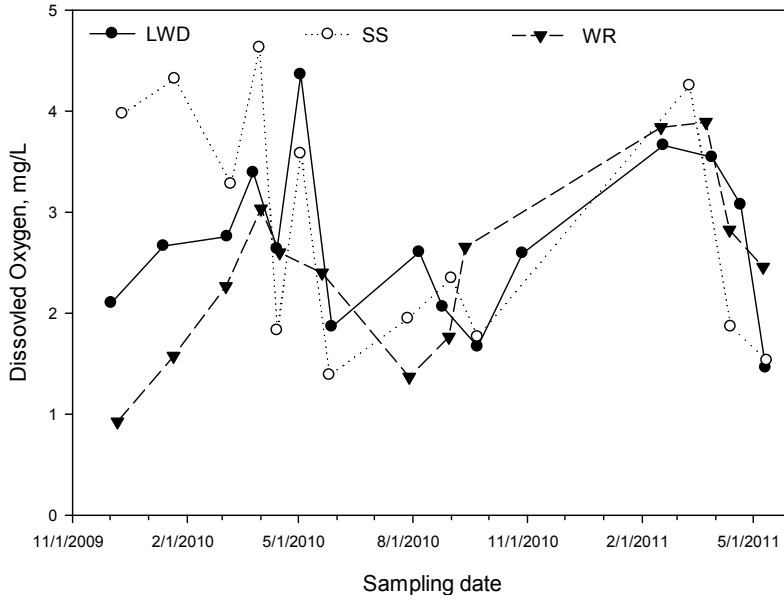


Figure 13: Mean dissolved oxygen (DO) in groundwater at the Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR) sites. Each point is the average of 4-14 measurements.

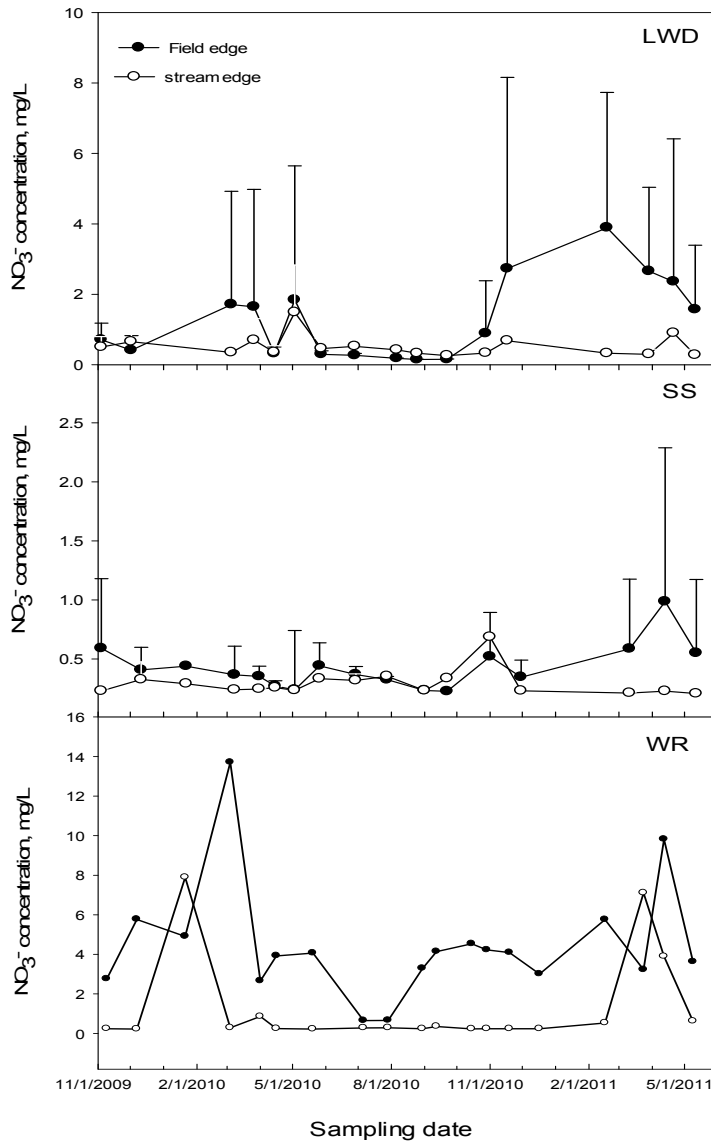


Figure 14: Mean nitrate concentrations in groundwater at field edge and stream edge in Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR). Note the scale difference of Y-Axis. Each point is the average of 4-5 measurements for LWD and SS and 1-3 measurements for WR.

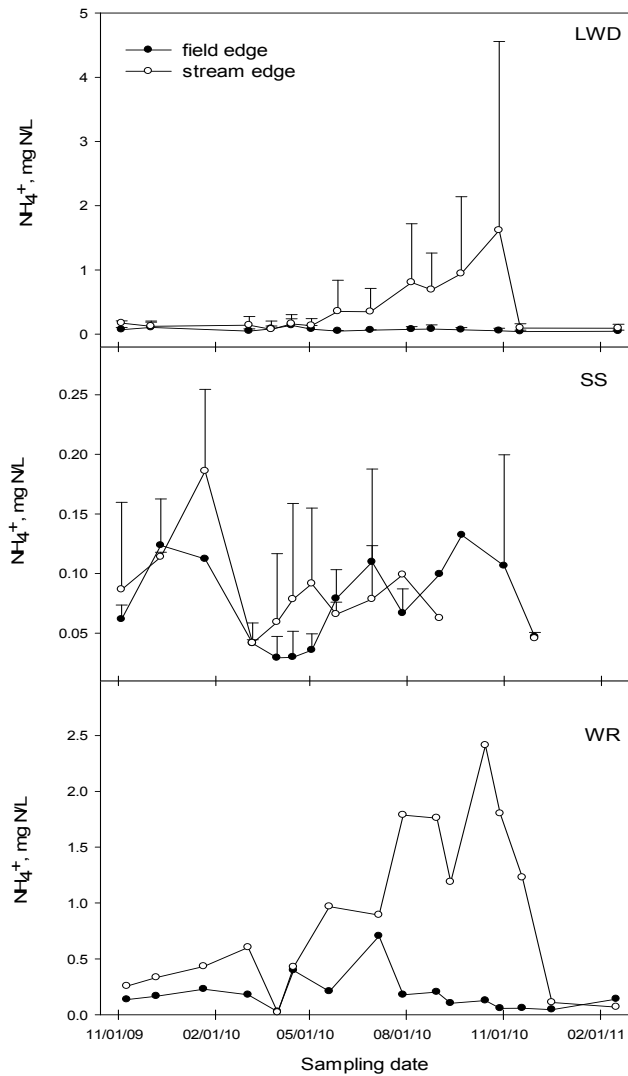


Figure 15: Mean NH_4^+ concentrations in groundwater at field edge and stream edge in Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR). Note the scale difference of Y-Axis. Each point is the average of 4-5 measurements for LWD and SS and 1-3 measurements for WR.

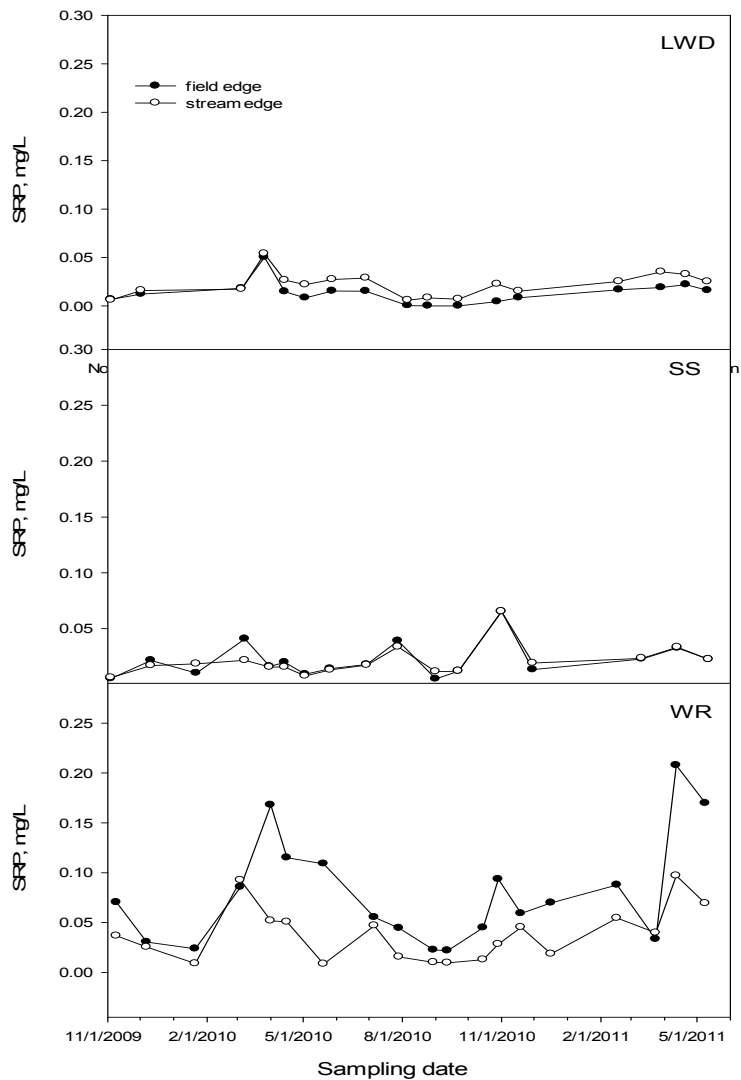


Figure 16: Mean SRP concentrations in groundwater at the field edge and stream edge in Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR). Note the scale difference of Y-Axis. Each point is the average of 4-5 measurements for LWD and SS and 1-3 measurements for WR.

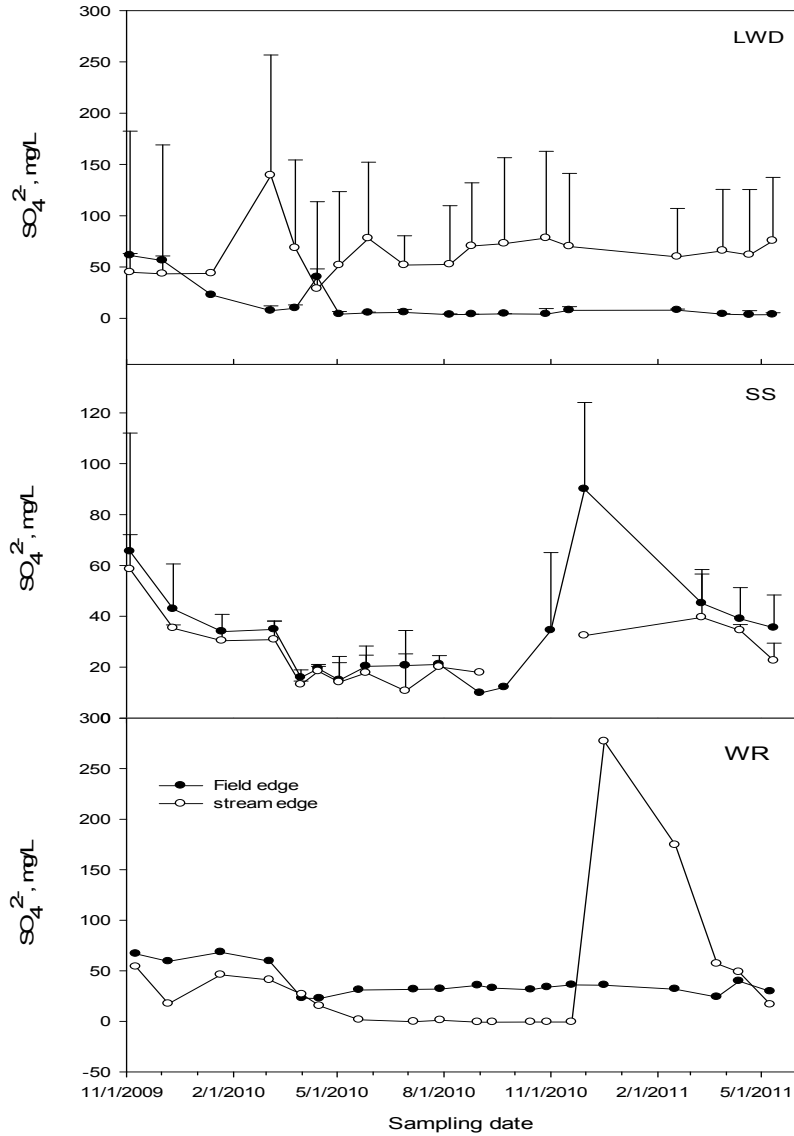


Figure 17: Mean SO_4^{2-} concentrations in groundwater at field edge and stream edge in at Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR). Each point is the average of 4-5 measurements for LWD and SS and 1-3 measurements for WR.

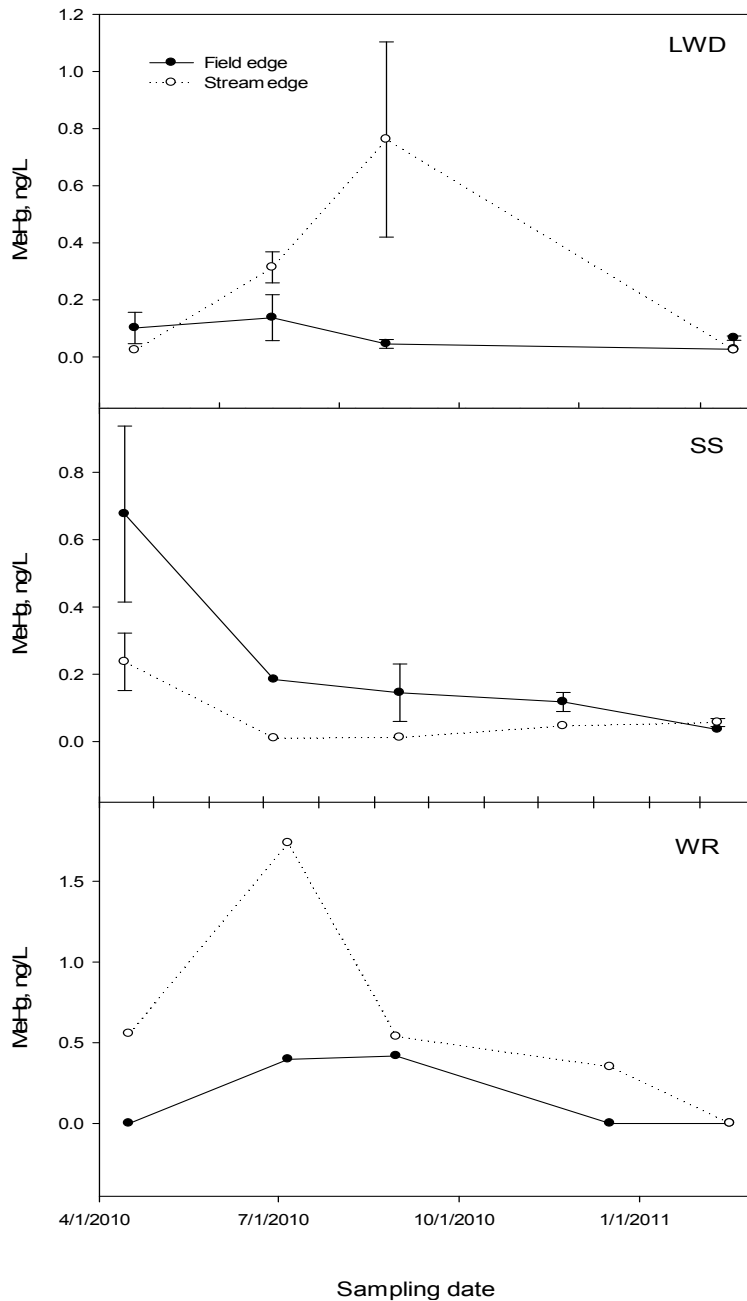


Figure 18: Mean MeHg concentrations in groundwater at field edge and stream edge at the Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR) sites. Each point is the average of 4-5 measurements for LWD and SS and 2 measurements for WR.

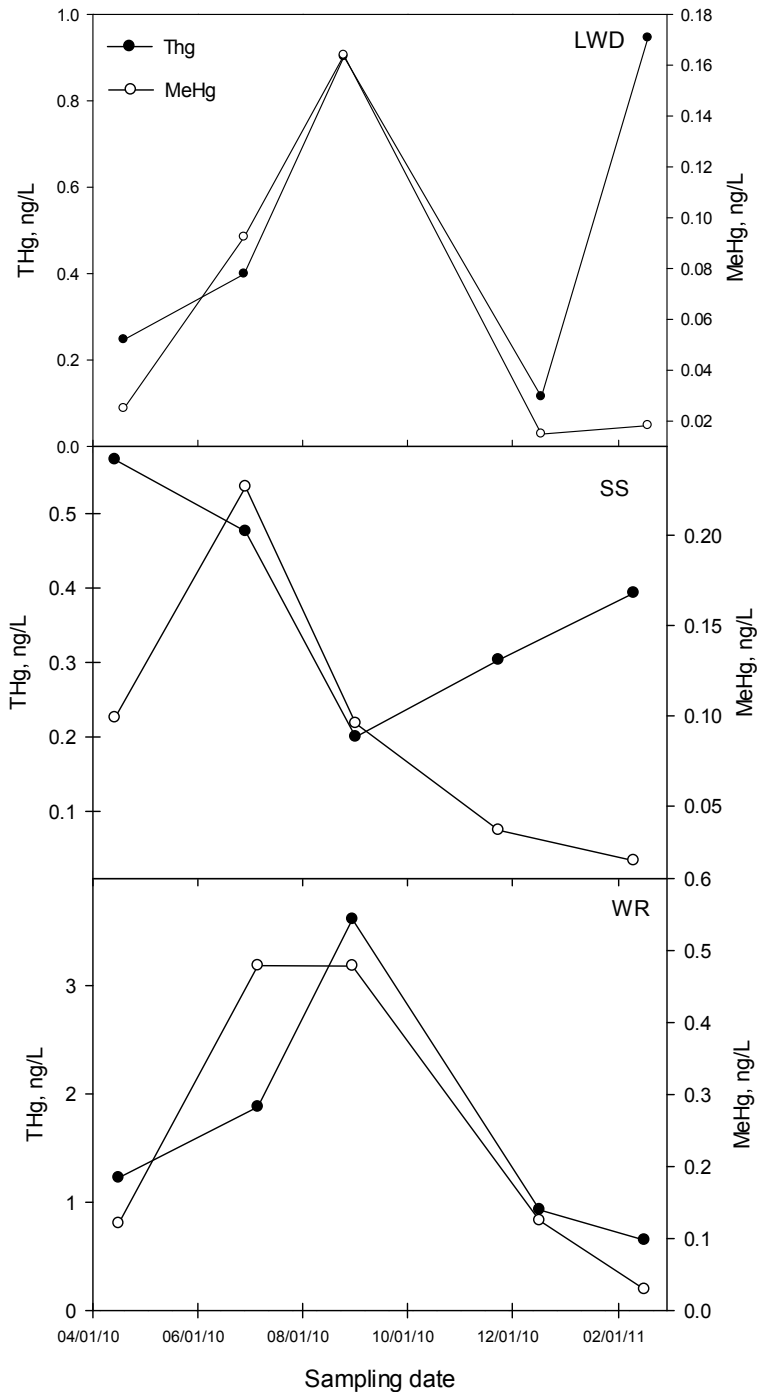


Figure 19: Mean THg and MeHg concentrations at the Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR) sites. Each point is the average of 4-5 measurements for LWD and SS and 1-3 measurements for WR.

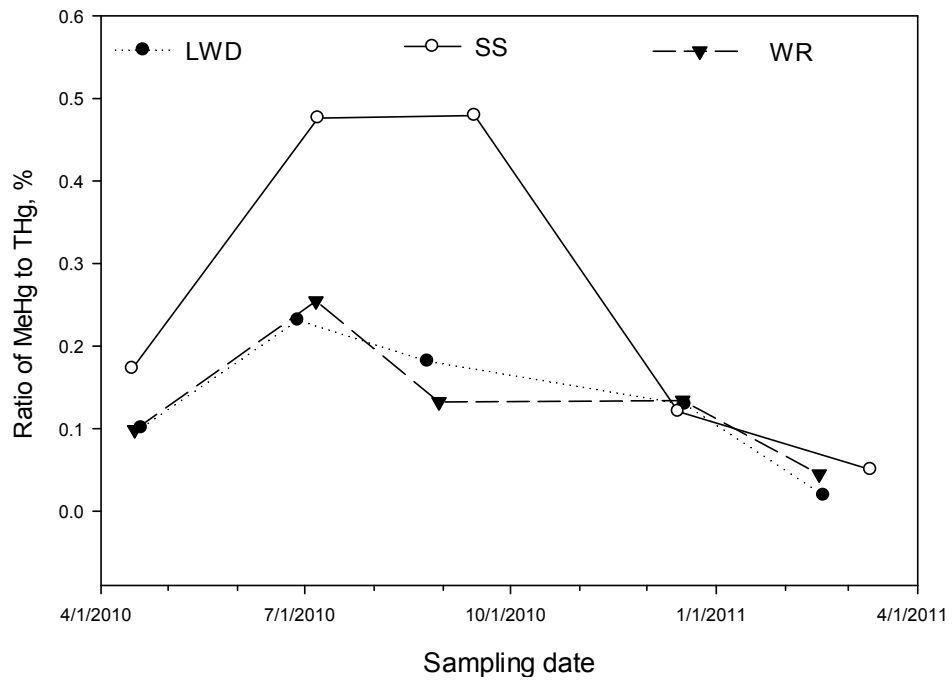


Figure 20: Ratio of MeHg to THg at the Leary Webber Ditch (LWD), Scott Starling (SS) and White river (WR) sites. Each point is the average of 4-14 measurements.

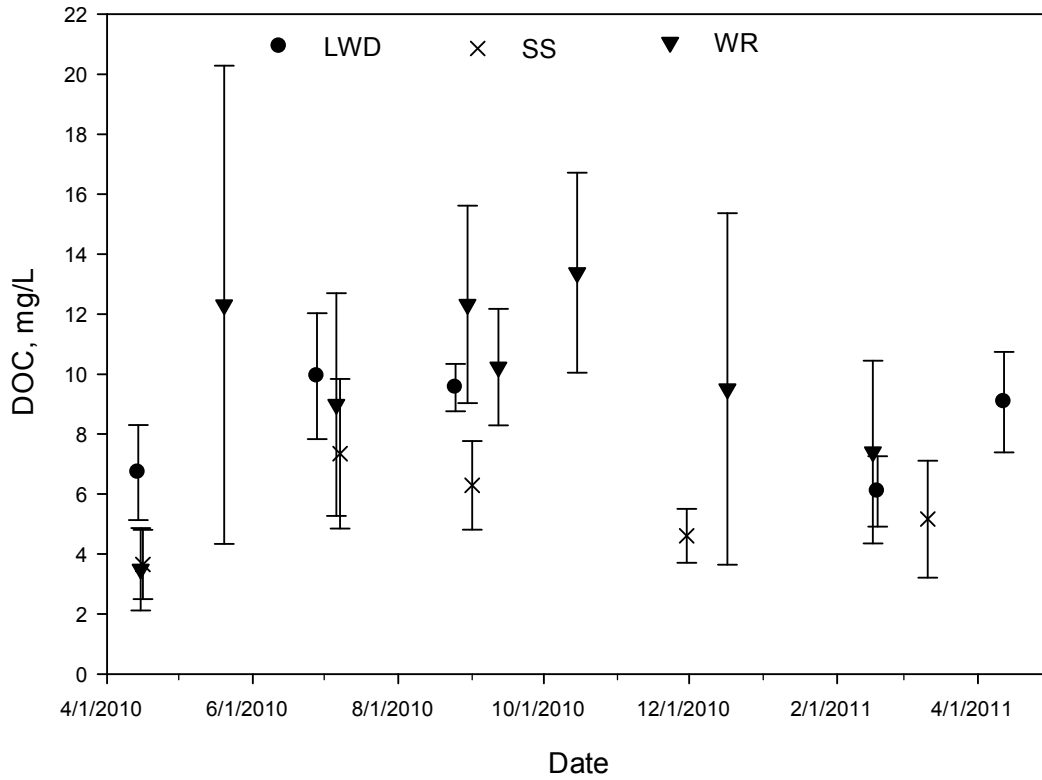


Figure 21: Mean DOC concentrations in groundwater at the Leary Webber Ditch (LWD), Scott Starling (SS) and White River (WR) sites. Each point is the average of 4-14 measurements.

Table 1: Mean Water table depth (cm below ground surface, BSG), oxidation-reduction potential (ORP), dissolved oxygen (DO), dissolved organic carbon (DOC), nitrate (NO₃⁻), ammonium (NH₄⁺), soluble reactive phosphorus (SRP), sulfate (SO₄²⁻), Total Mercury (THg) and Methylmercury (MeHg) concentration in groundwater at the Leary Webber Ditch (LWD), Scott Starling (SS) and White River(WR) sites.

	LWD (+/- stdev)	SS (+/- stdev)	WR (+/- stdev)	Significant difference of means (α = 0.05)
WT (cm BGS)	88 (64)	57(47)	141(61)	P<0.05, Significant
DO (mg/L)	2.7 (1.5)	2.9 (1.8)	2.5 (1.4)	P>0.05, NS for three sites
ORP (mV)	22 (107)	73 (131)	75 (132)	P<0.05, LWD differencnt from the other two sites
DOC (mg/L)	7.9 (2.3)	5.4(2.2)	9.9(5.1)	P<0.05, significant between any two sites
GWT	11.4(3.8)	11.4(4.9)	12.3(3.5)	P>0.05, NS for three sites
NO ₃ ⁻ (mg N/L)	1.1(1.8)	0.37(0.59)	3.5(4.1)	P<0.05, Significant for three sites
NH ₄ ⁺ (mg N/L)	0.18(0.5)	0.08(0.05)	0.31(0.49)	P<0.05, Significant for three sites
SRP (mg/L)	0.03(0.06)	0.04(0.1)	0.08(0.08)	P<0.05, Significant for three sites
SO ₄ ²⁻ (mg/L)	34(42)	28(19)	43(37)	P>0.05, NS for three sites
THg (ng/L)	0.52(0.53)	0.43(0.41)	1.48(1.3)	P<0.05, WR differeng from SS and LWD
MeHg (ng/L)	0.06(0.12)	0.09(0.16)	0.23(0.41)	P<0.05, WR differeng from SS and LWD

Table 2: Correlation coefficient between each solute concentration (NO_3^- , NH_4^+ , SRP, SO_4^{2-} , THg, MeHg) and key biogeochemical variables over the study period. Data presented are from the Leary Webber Ditch (LWD) site. (Legend: n/r = not relevant, WT = water table, DO = dissolved oxygen, ORP = oxidation-reduction potential, DOC = dissolved organic carbon GWT = groundwater temperature, NO_3^- = nitrate, NH_4^+ = ammonium, SRP = soluble reactive phosphorus, SO_4^{2-} = sulfate, THg = Total Mercury and MeHg = MethylMercury).

	NO_3^-	NH_4^+	SRP	SO_4^{2-}	THg	MeHg
Water table	0.14 *	-0.10	-0.13	-0.32 *	-0.35	-0.22
DO	0.31 *	-0.20 *	0.26 *	-0.07	0.43	0.30
ORP	0.22 *	-0.16	0.06	-0.12	-0.13	-0.26
DOC	-0.30	-0.002	0.211	-0.002	0.55 *	0.36
GW Temperature	-0.20 *	0.19 *	-0.11	0.05	0.07	0.44 *
NO_3^-	n/r	n/r	n/r	n/r	n/r	n/r
NH_4^+	n/r	n/r	n/r	n/r	n/r	n/r
SRP	n/r	n/r	n/r	n/r	n/r	n/r
SO_4^{2-}	n/r	n/r	n/r	n/r	0.34	0.005
THg	n/r	n/r	n/r	n/r	n/r	0.15

* indicates a significant positive correlation at $P < 0.05$.

Table 3: Correlation coefficient between each solute concentration (NO_3^- , NH_4^+ , SRP, SO_4^{2-} , THg, MeHg) and key biogeochemical variables over the study period. Data presented are from the Scott Starling (SS). (Legend: n/r = not relevant, WT = water table, DO = dissolved oxygen, ORP = oxidation-reduction potential, DOC = dissolved organic carbon GWT =groundwater temperature, NO_3^- = nitrate, NH_4^+ = ammonium, SRP = soluble reactive phosphorus, SO_4^{2-} = sulfate, THg = Total Mercury and MeHg = MethylMercury.

	NO_3^-	NH_4^+	SRP	SO_4^{2-}	THg	MeHg
Water table	-0.09	0.20*	0.08	-0.11	-0.34 *	0.0003
DO	0.006	-0.01	0.05	-0.08	0.06	-0.16
ORP	-0.004	-0.37 *	-0.01	0.09	0.16	-0.09
DOC	-0.004	0.36*	-0.001	-0.29 *	-0.01	-0.06
GW Temperature	-0.03	0.14	-0.11	-0.24	-0.03	0.36 *
NO_3^-	n/r	n/r	n/r	n/r	n/r	n/r
NH_4^+	n/r	n/r	n/r	n/r	n/r	n/r
SRP	n/r	n/r	n/r	n/r	n/r	n/r
SO_4^{2-}	n/r	n/r	n/r	n/r	-0.28	-0.18
THg	n/r	n/r	n/r	n/r	n/r	0.53 *

* indicates a significant positive correlation at $P < 0.05$.

Table 4: Correlation coefficient between each solute concentration (NO_3^- , NH_4^+ , SRP, SO_4^{2-} , THg, MeHg) and key biogeochemical variables over the study period. Data presented are from the White River (WR) site. (Legend: n/r = not relevant, WT = water table, DO = dissolved oxygen, ORP = oxidation-reduction potential, DOC = dissolved organic carbon GWT = groundwater temperature, NO_3^- = nitrate, NH_4^+ = ammonium, SRP = soluble reactive phosphorus, SO_4^{2-} = sulfate, THg = Total Mercury and MeHg = MethylMercury).

	NO_3^-	NH_4^+	SRP	SO_4^{2-}	THg	MeHg
Water table	0.26 *	-0.27 *	-0.14	0.17	-0.24	-0.65 *
DO	0.30 *	-0.27 *	0.11	0.1	-0.6 *	-0.84 *
ORP	0.23 *	-0.59 *	0.17	0.09	-0.36	-0.71 *
DOC	-0.32 *	0.67 *	-0.3	0.36 *	0.16	0.58 *
GW Temperature	-0.23 *	0.39 *	-0.12	-0.25 *	0.58 *	0.46 *
NO_3^-	n/r	n/r	n/r	n/r	n/r	n/r
NH_4^+	n/r	n/r	n/r	n/r	n/r	n/r
SRP	n/r	n/r	n/r	n/r	n/r	n/r
SO_4^{2-}	n/r	n/r	n/r	n/r	-0.16	-0.13
THg	n/r	n/r	n/r	n/r	n/r	0.53 *

* indicates a significant positive correlation at $P < 0.05$.

Table 5: Mean oxidation-reduction potential (ORP), dissolved oxygen (DO), dissolved organic carbon (DOC), nitrate (NO₃⁻), ammonium (NH₄⁺), soluble reactive phosphorus (SRP), sulfate (SO₄²⁻), Total Mercury (THg) and MethylMercury (MeHg) values or concentrations in groundwater, in field edge and stream edge for the Leary Webber Ditch (LWD), Scott Starling (SS) and White River (WR) sites. FE = field edge, SE = Stream edge, SIK = sink, SOR = source, ND = not significant. Difference between field edge and stream edge is deemed significant if P value is between 0.05-0.1. Sink or source notation is made when P<0.05..N/P = not applicable

	LWD			SS			WR		
	FE (+/- stdev)	SE (+/- stdev)	SIK, SOR, ND	FE(+/- stdev)	SE(+/- stdev)	SIK, SOR, ND	FE(+/- stdev)	SE(+/- stdev)	SIK, SOR, ND
ORP(mv)	1.3 (93.2)	12.4 (105.9)	ND	77.4 (130.4)	35.1 (95.3)	ND	88.2 (138.5)	-57.5 (81.1)	P<0.05
DO(mg/L)	2.8 (1.4)	2.2 (1)	ND	2.5 (1.1)	2.3 (1.2)	ND	2.7 (1.2)	1.5 (1.3)	P<0.05
DOC(mg/L)	7.52 (2.38)	8.34 (1.65)	N/A	5.1 (2.2)	6.3 (1.6)	N/A	8.21 (2.59)	13.70 (3.72)	N/A
NO ₃ ⁻ (mg N/L)	1.28 (1.13)	0.52 (0.31)	SIK	0.6 (0.66)	0.27 (0.05)	ND	3.7 (3)	0.7 (1.7)	SIK
NH ₄ ⁺ (mg N/L)	0.07 (0.02)	0.41 (0.43)	SOR	0.07 (0.03)	0.08 (0.04)	ND	0.19 (0.17)	0.89 (0.74)	SOR
SRP (mg /L)	0.02 (0.03)	0.04 (0.04)	ND	0.02 (0.01)	0.05 (0.10)	ND	0.08 (0.05)	0.04 (0.03)	SIK
SO ₄ ²⁻ (mg N/L)	8.8 (9.1)	69.6 (23.7)	SOR	33.9 (21.3)	26.4 (12.7)	ND	38.2 (14.3)	40.7 (70.6)	ND
THg (ug/L)	0.81 (0.71)	1.35 (1.02)	N/A	1.31 (1.06)	0.46 (0.44)	N/A	2.3 (2.2)	1.6 (1)	N/A
MeHg (ug/L)	0.08 (0.04)	0.23 (0.32)	SOR	0.23 (0.25)	0.07 (0.09)	Sink	0.17 (0.22)	0.64 (0.65)	SOR

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CURRICULUM VITAE

Xiaoqiang Liu

Education

Master of Science, Indiana University- Purdue University Indianapolis, May 2013
Ph.D. of Ecology, the Chinese Academy of Sciences, China, June 2006
Bachelor of Agronomy Education, Shandong Agricultural University, China, July 2001

Work experience

Instructional assistant, the Ohio State University, April 2013
Field manager, Grassroots voter outreach, June to October, 2012
Graduate research assistant, IUPUI, August 2009-Dec 2011
Volunteer technician, the Ohio State University, April, 2007 to June, 2007
Graduate research associate, Institute of Botany, the Chinese Academic of Sciences Beijing, China, September 2002-June 2006
Research technician, Institute of Botany, the Chinese Academic of Sciences, Beijing, China, July 2001-June 2002

Conference presentations

Baker, M., Jacinthe P.A., Vidon P., Panunto M., Fisher K., Liu X. 2012.
Hydrogeomorphic classification of riparian ecosystems in Central Indiana. AWRA Specialty Conference, Riparian Ecosystems, June 25-27, 2012, Denver, CO.

Jacinthe, P.A., Vidon P., Baker M., Liu X., Fisher K., Panunto M. 2012.
Hydrogeomorphic controls of nitrous oxide fluxes in riparian buffers of Central Indiana. AWRA Specialty Conference, Riparian Ecosystems, June 25-27, 2012, Denver, CO.

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Peer-reviewed articles

Wang, R.Z., W.W. Huang, L. Chen, L. Ma, C.Y., Guo, and X.Q. Liu. Anatomical and physiological plasticity in *Leymus chinensis* (Poaceae) along large scale longitudinal gradient in Northeast China. *PLoS ONE*. Nov 8th, 2011.

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Liu, X.Q., R.Z. Wang, and Y.Z. Li, 2004. Photosynthetic pathway types in rangeland plant species from Inner Mongolia, North China. *Photosynthetica* 42:339-344.

Academic Awards

2009-2011, Graduate research assistantship, Indiana University

2006, Outstanding graduate of Chinese Academy of Sciences

2004-2006, First-class scholarship of Institute of Botany, Chinese Academy of Sciences