# Groundwater Pollutant Transfer and Export from a Northern Mississippi Valley Loess Hills Watershed

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# ABSTRACT

Non-point source pollutant inputs are the most widespread and vexing contributors to ground and surface water, affecting the drinking water resources and the biotic integrity of many of the nation's water bodies. The relation between agriculture and nonpoint pollution is well established, and the contribution of pollutants from agricultural lands is significant. The increase in agricultural chemical use combined with the long residence time of groundwater suggests that groundwater transport of pollutants may not yet be in equilibrium with the current landscape; the consequences of which could mean that despite all of our current efforts to improve water quality pollutant export will continue to increase until equilibrium is reached.

This study assesses the role of groundwater in the export of nutrients and pesticides from the Fever River Watershed; an agriculturally dominated watershed in the Northern Mississippi Valley Loess Hills region. More than 100 water bodies in the NMVLH are listed as impaired on state 303(d) lists, and half of the land area is in impaired watersheds. About two-fifths of the area is in cropland and another fifth in permanent pasture. Streamflow is baseflow dominated with groundwater discharge occurring through well defined riparian springs, ill-defined riparian seeps, and streambed discharge.

Groundwater samples were obtained at 23 discharge locations and subjected to analyses for nutrients, dissolved gases (including denitrification and groundwater age-dating gases), and pesticide residues. Groundwater age-dates ranged from 1969 – 1989. Nitrate-N ranged from 4.7 to 23.5 mg $L^{-1}$ while dissolved reactive P ranged from 0.003 to 0.052 mg $L^{-1}$; both showed a positive relationship to groundwater age-date. Denitrified N ranged from 0 to 4.5 mg $L^{-1}$ and was negatively correlated to groundwater age-date. Metolachlor ESA was the most pervasive pesticide residue detected in groundwater samples, followed by de-ethylatrazine, alachlor ESA, atrazine, and de-isopropylatrazine, the summed concentration of pesticides ranged from 2.1 to 9.1 $\mu$g $L^{-1}$.

Baseflow accounted for approximately 86% of the total streamflow in the Fever River. Nitrate accounted for the largest nutrient loss with baseflow $NO_3$ alone accounting for 80% of the annual N loss (23.4 kg $ha^{-1}$ $yr^{-1}$). Even though runoff represented only a small portion of the annual streamflow, 85% of total P was transported during runoff events. Pesticide concentrations were generally highest during spring runoff events, however; concentrations of pesticides were present in baseflow year round and show that the amounts present and transported in groundwater can be significant.

The land-use practices, geology and hydrological settings in the Fever River watershed are representative of much of southwest Wisconsin. We conclude that the watershed is not yet in equilibrium with current land-use and denitrification within the aquifer is not capable of sufficiently denitrifying current $NO_3$ loading rates to groundwater. As a result, concentrations of $NO_3$ in the surface waters of these systems will likely increase before finally stabilizing because of the time it takes for groundwater to penetrate the aquifer and reach discharge locations. Understanding groundwater surface water relationships

are critical for interpreting stream water quality data and understanding past and future impacts of land management decisions.

# 1.0 INTRODUCTION

Pollutants such as $NO_3$, pesticide residues, and possibly P and others leak from agricultural landscapes to groundwater, and subsequently are transferred and discharged to surface water. This results in degradation of drinking water sources (Postle et al. 2004, Nolan et al. 2002, Fan and Steinberg 1996) and causes harms to aquatic ecosystems, both freshwater and marine (Rouse et al. 1999, Johnston et al. 1999, Howe et al. 1998, Hayes et al. 2002). This leakage (mass per area-time) has increased greatly over the last several decades, at least for $NO_3$ and pesticide residues, driven by increasing fertilizer and pesticide use particularly over the period of about 1960 to 1990 (e.g. Kraft et al., 2007; Hallberg et al. 1989, Böhlke and Denver 1995, Kellog et al. 2000).

The role of groundwater in transferring pollutants from agricultural lands to surface water and in exporting pollutants from watersheds has received little attention relative to runoff and shallow-subsurface flows in the midwestern US. We define "transfer" here as mechanisms that route pollutants from a landscape surface to surface water, and "export" as the mass of pollutant per time that leaves a portion of a watershed. We further use the term "runoff" to describe only the overland flow portion of water leaving the landscape, usually during precipitation periods, rather than as summed groundwater and overland flow, as is used by some authors. The USDA-initiated Management Systems Evaluation Area (MSEA) program of the 1990s (e.g., Onstad, 1991), seen by many as a pinnacle for agro-environmental systems research, did not address groundwater pollutant transfer to surface water, with possibly the sole exception of the Walnut Creek watershed. There, the groundwater transfer of pollutants was found negligible because heavy soils and tile drains caused pollutant transfer to be dominated by overland and shallow-subsurface flow processes (Schilling and Wolter, 2001; Eidem et al., 1999).

The Walnut Creek experience does not imply that groundwater pollutant transfer and export is always small in the midwestern US, however. Nitrate export from baseflow-dominated Wisconsin central sand plain was in the uppermost category of the classification scheme of Goolsby et al. (2001) for the Mississippi drainage (15-31 kg $ha^{-1}$ $yr^{-1}$) and increasing (Browne et al., 2007; Stites and Kraft, 2002. Substantial groundwater transfer of atrazine was demonstrated in the Cedar River Iowa watershed, amounting to 75% of the stream's atrazine load during baseflow periods (Squillace et al., 1993). The potential for large groundwater P leakage and transfer was demonstrated by the study of Brye et al. (2002) beneath corn in a silt loam typical of much of southeast Wisconsin where leachate exiting the root zone averaged about 0.09 mg/L dissolved P over a 21 month period, with loads to groundwater of 426 g $ha^{-1}$ (Brye et al., 2002).

Groundwater transfer and export of pollutants is an active area of research in the Chesapeake Bay watershed. Groundwater $NO_3$ export amounted to nearly 40% of the total N load to the Bay (Bachman and Phillips, 1996) and 60% during baseflow periods (Pionke et al. 1996). The Wye River estuary of the Chesapeake Bay exported 60 kg $yr^{-1}$ nitrate-N per ha of watershed via groundwater. Work continues there to estimate groundwater P export (e.g., Sims et al., 1998).

In this study, we estimated the groundwater pollutant transfer to a receiving stream, compared groundwater transfer and export with that from runoff, and determined whether groundwater transfer and export were likely at a steady-state or increasing. We used the following approach:

1. Groundwater pollutant transfer to the receiving stream was determined through repetitive sampling of stream water quality and discharge during the study period.
2. Comparisons with runoff transfer and export were made at a gauging and sampling station which measured water quality and discharge during runoff events.
3. Questions about steady-state vs. increase were inferred by sampling water quality and groundwater age-date at groundwater discharge features, such as riparian springs.

This study was conducted in the upper Fever River watershed (Figure 1.1), an area representative of the agriculturally-intensive portion of the Northern Mississippi Valley Loess Hills region (NMVLH; Major Land Resource Area 105; NRCS, 2000). We report here information gathered during calendar years 2003 and 2004. Compared to the past 30-yr climate record (1971-2000), year 2003 was slightly cooler (2,630 $GDD_{50}$ compared to 2,773 $GDD_{50}$), had a 5% longer growing season, and 0.7 in precipitation above normal. Year 2004 was also cooler than average (2,425 $GDD_{50}$ compared to the median of 2,773 $GDD_{50}$), with a 1% shorter growing season. Precipitation was 0.1 in. below normal.

## 2.0 STUDY AREA

The Northern Mississippi Valley Loess Hills covers 57,520 km$^2$; about one-fifth of Wisconsin (including most of the "driftless area") plus adjacent parts of Minnesota, Iowa, and Illinois. The area is characterized by rolling to hilly uplands dissected by tributaries of the Mississippi River. About two-fifths of the area is in cropland and another fifth in permanent pasture. More than 100 water bodies in the NMVLH are listed as impaired on state 303(d) lists, and half of the land area is in impaired watersheds (WDNR, 2001). Groundwater quality impairments include about 25% of wells exceeding the nitrate MCL (LeMasters and Baldock, 1995), 11% containing atrazine residues, 32% containing alachlor residues, and 34% contain metolachlor residues (after VandenBrook et al., 2002).

The study area is a 1,360 ha portion of the upper Fever River watershed containing about 11.4 km of perennial first and second order stream (Figure 2.1). It is representative of much of the more agriculturally-intensive portion of the NMVLH which in Wisconsin lies south of the Military Ridge running across northern Grant and central Iowa Counties, Wisconsin. Ninety-one percent of the land cover in this vicinity is in agriculture, dominantly row crops. The topography is gently rolling (6% slopes), with perennial streams occurring at 1-3 km intervals. The geology consists of 1-4 m of loess-derived soils overlying 30-60 m of Sinnippee Group dolostone and more than 100 m of other Ordovician and Cambrian rocks. The USGS gauging station #05414850 is located within the watershed. Mean annual precipitation is 36.1 in. Little of the study area is artificially drained through the subsurface. By comparison to the well-known Coon Creek watershed (north of Military Ridge), the study area is more gently rolling, contains a greater proportion of agricultural land cover and less forest and grassland, and is subject to more intensive cultivation (more row crops, less forage and pasture). Groundwater movement in the upper Fever watershed is probably dominated by flow through solution-enlarged fractures and bedding planes (work in progress). Much of the Fever River is in a degraded state in this vicinity. Riparian areas usually consist of actively grazed animal pasture or grass buffers (generally < 5 m) adjacent to row crops and virtually no tree cover. Streambank erosion and siltation are prevalent.

## Upper Fever Morphology and Groundwater Discharge Patterns

We investigated upper Fever River characteristics through aerial photography, field surveys, and detailed synoptic surveys conducted on 8 Dec 2003 and 7 April 2004 (Appendix A).

Perennial flow in the upper Fever originates slightly south of the newly reconstructed State Highway 151 at a set of springs (spring set 1005.001; Figure 2.1). The spring set there consisted of three 0.5 to 1.0 m diameter sand-boils surrounded by smaller and diffuse discharge features. The main channel of the upper Fever has three short (about 200-600 m long) permanent tributaries (T1, T2, and T3; Figure 2.2) that also originate at springs and appear well connected to watershed-scale groundwater flow systems. A fourth, smaller tributary (T4) also exists, but is likely an expression of a localized perched water table. Stream discharge during baseflow periods (July 2003 to Dec 2004; section 3.0) averaged 0.8 $ft^3 s^{-1}$ at location A, 1.6 $ft^3 s^{-1}$ at location B, 2.1 $ft^3 s^{-1}$ at location C, and 3.6 $ft^3 s^{-1}$ at location D. During runoff events discharges can be much greater; and reached 75 cfs at station C during the 2003-4 period (See section 4.0).

Groundwater enters the upper Fever through well defined stream-bottom springs (sand boils and other concentrated groundwater discharge) that feed tributaries or the main channel of the Fever, ill-defined riparian seeps that contribute little to streamflow, and diffuse streambed seepage. Though diffuse streambed seepage areas are much more common than riparian spring areas, they apparently contribute little to the upper Fever's baseflow. This is due to the low permeability of most of the streambed, which usually consists of dolomite rubble contained in a silt and clay matrix. We identified three artificial groundwater discharges in the form of short (perhaps 30-50 m) drains that appear to convey water from what were once springs adjacent to the riparian zone.

Synoptic surveys characterized discharge and water quality during baseflow conditions in individual stream segments, tributaries, and the two artificial drainages (Table 2.1). The baseflow contribution for each segment was computed. Streamflow contribution from tributaries was treated separately from the main channel stream streamflow contribution. In addition, a "groundwater discharge intensity" was calculated by dividing the baseflow contribution of an individual segment by its length (Table 2.1). This analysis indicates that baseflow discharge is not uniformly distributed along the stream. Baseflow intensity averaged 7.2 x $10^{-5}$ $ft^3$ $s^{-1}$ $ft^{-1}$, but reached 8.3 x $10^{-4}$ $ft^3$ $s^{-1}$ $ft^{-1}$ in segment T2. Segment 5 had a negative intensity on both dates, indicating it is a losing stretch. During synoptic surveys, $NO_3$-N concentrations declined with distance from the headwaters, while Cl increased slightly.

# 3.0 BASEFLOW PERIOD DISCHARGE, WATER QUALITY, AND POLLUTANT LOADS

## Overview

Monthly measurements of stream water quality and discharge during baseflow periods were used to estimate pollutant loads and yields in order to make inferences about groundwater pollutant transfer and export. Sampling for inorganic parameters and discharge was done at four sites (A, B, C, and D; Figure 1.1) between July 2003 and December 2005. Inorganic analytes included specific conductance, N species (filtered $NO_3$, $NH_4$, and total Kjeldahl), P (filtered dissolved reactive and total dissolved), Cl, and suspended sediment. A pesticides analytical suite was performed on samples taken August 2003, July 2004, and September 2004. Pesticide residue analysis included the residues of atrazine (parent atrazine and the chlorinated degradates deethyl-, deisopropyl-, and diamino-atrazine), and the chloroacetanlides alachlor, acetochlor, and metolachlor (parents plus their ethane sulfonic acid (ESA) and oxanilic acid (OA) degradates). These are common groundwater pollutants in much of the midwestern US (Postle et al. 2004, Kalkhoff et al. 1998). Details of analytical methods are summarized in the Appendix C.

As part of an effort to address how potential instream transformations might alter streamwater quality between a groundwater discharge point and a surface water sample point (and hence possibly hinder the ability to make groundwater transfer and export inferences), baseflow was sampled hourly for a 24 hour period at site C on 31 Aug 2004 and analyzed for temporal trends in $NO_3$-N, Cl, and DRP. We intentionally picked a warm (maximum temp = 25.6°C) sunny day during late summer for this sampling as it ought to represent baseflow conditions under which maximum potential for biological transformations would occur.

## Results

Nitrate-N was the dominant N species in stream baseflow, averaging 13.6 mg $L^{-1}$ in the uppermost monitoring site and 9.4 mg $L^{-1}$ in the lowermost. Other N species were small, 0.07 and 0.73 mg $L^{-1}$ (average of sites A,B,C,D) for $NH_4$-N and TKN respectively (Table 3.1; Figure 3.1). Nitrate varied slightly from month to month, but absolute differences between sample sites were consistent through the study period. Average Cl at individual sites ranged 17.3 to 19.1 mg $L^{-1}$, Table 3.1, Figure 3.1). Initially, Cl differed among sample sites systematically, with concentrations increasing from the headwaters downstream. But during the last half of the monitoring period, Cl differences among sites disappeared. No apparent patterns were observed in baseflow concentrations of DRP, TP, $NH_4$-N and TKN which averaged about 0.45, 0.11, 0.08, and 0.80 mg $L^{-1}$.

Pesticide analyses revealed common detections of atrazine, de-ethylatrazine and metolachlor ESA, and spotty detections of alachlor ESA and metolachlor. Detections were usually small, less than 0.5 μg $L^{-1}$, except for metolachlor ESA, which was commonly detected in the 2.7 to 4.4 μg $L^{-1}$ range (Table 3.2).

Results from the hourly sampling are shown in Figure 3.2. These demonstrated little variation over time in analyte concentrations and no diurnal pattern.

### Evaluation of instream transformation effects on pollutant transfer and export estimates

Could instream transformation confound making inferences about groundwater transfer and export by altering analytes? The potential for Cl transformations seems unlikely since mechanisms for sorption, uptake, or degradation are lacking. Nitrate presents a more difficult question; because though it tends not to sorb, it is subject to transformations due to biological uptake. A lack of a strong seasonal trend (Figure 3.1) in $NO_3$ provides prima facie evidence that instream transformations are lacking, as transformations should be great under warm summer conditions and small under cold winter conditions. Bolstering this is that diurnal fluctuations were not observed during 24 hour monitoring during the warmest, sunniest time of the year. Finally, baseflow $NO_3$ concentrations were similar to concentrations measured in groundwater discharge features (see section 5.0). The apparent lack of instream $NO_3$ transformations is consistent with other studies that have shown instream denitrification was not an efficient N sink compared to the $NO_3$ concentrations in the water column in agricultural watersheds (Kemp and Dodds, 2002; Royer et. al., 2004; Schaller et. al., 2004). Hence we conclude that instream transformation does not greatly affect $NO_3$ concentrations, and baseflow $NO_3$-N concentrations are representative of groundwater discharge $NO_3$-N concentrations.

Phosphorus is a still more difficult problem since P sorbs and is subject to biological uptake. Concentrations of DRP at sampling stations were quite consistent through the study period and fairly consistent during the hourly sampling experiment. However, both could be artifacts of desorption from stream sediments. Median P from groundwater discharge features was only half that measured in baseflow samples (see section 5.0). Hence we conclude that baseflow DRP is not a good indicator of groundwater P transfer and export.

The pesticide residues found in baseflow were consistent with those common to groundwater in this region (Postle et al., 2004) and are also consistent with the pesticide content of groundwater discharge features. Hence we conclude that instream transformation likely did not greatly affect groundwater pesticide discharge concentrations, and that baseflow pesticide concentrations are therefore representative of groundwater discharge concentrations.

## Pollutant loads and yields at baseflow and estimates of groundwater transfer and export

We calculated inorganic pollutant loads at baseflow by multiplying average baseflow concentrations by average annual baseflow discharge for each site. Yields were determined by dividing pollutant loads by the watershed area determined for each site. Results are shown in Table 3.1. Baseflow yields, which estimate the groundwater-driven transport and export , for $NO_3$-N and Cl (sampling site D) were about 22 and 46 kg $ha^{-1}$ $yr^{-1}$ , respectively. For pesticide residues we averaged analyses among sample dates and multiplied by annualized baseflow to approximate baseflow pesticide yield (and transfer / export) (Table 3.3). This amounted to less than 1 g $ha^{-1}$ $yr^{-1}$for all detected residues but metolachlor ESA, which was 5.7 g $ha^{-1}$ $yr^{-1}$ at the most downstream location. TP and DRP yields at baseflow were about 0.25 and 0.10 kg $ha^{-1}$ $yr^{-1}$, but these cannot be attributed to groundwater transfer because of confounding by stream processes.

## Summary

Baseflow concentrations of $NO_3$, Cl, and certain pesticide residues are likely representative of concentrations in groundwater discharge, and hence can be used to estimate the groundwater transfer and export of these pollutants from the landscape.

Observed differences in concentrations among sample sites A,B,C and D are due to spatial variability of concentrations in groundwater discharge, not instream transformation.  This spatial variability is likely due to spatial variability in groundwater discharge age (section 5.0).

Baseflow concentrations of P were variable between stream sites, and were greater than average concentrations found in groundwater discharge samples.  Hence baseflow concentrations are not an accurate representation of groundwater P discharge concentrations.

## 4.0 GROUNDWATER VS RUNOFF POLLUTANT TRANSFER AND EXPORT

We compared groundwater vs runoff pollutant transfer and export at sampling site C. This site contains USGS gauging station 05414850, which is instrumented with automated flow and sampling systems for monitoring streamwater quality. The sampling system can obtain discrete samples during runoff events that are flow-weight composited and analyzed to provide event-based average pollutant concentrations and loads.

### Water budget and baseflow separation for 2003-4

Precipitation and mean daily streamflow at site C is shown for years 2003 and 2004 (Figure 4.1). During these years, there were 11 and 29 runoff events that were sampled in 2003 and 2004 respectively. Flow-weight composite runoff samples were analyzed for inorganic analytes including specific conductance, N species (filtered $NO_3$, $NH_4$, and total Kjeldahl), P (filtered dissolved reactive and total P), Cl, and suspended sediment. A pesticide analytical suite was performed on runoff samples representing 9 events (Table 4.1).

Hydrograph separation was performed for 1 Jan 2003 to 31 Dec 2004 using the daily hydrograph values from the USGS gauging station and a computer baseflow separation tool (Figure 4.1, see also Appendix D). Hydrograph separation determined that overland runoff accounted for 14% of streamflow over the study period, or an average of 0.3 $ft^3 s^{-1}$ (1.4 in $yr^{-1}$). Average baseflow at site C was determined to be 2.0 $ft^3 s^{-1}$ (8.9 in $yr^{-1}$). (Mean annual precipitation for this region is 36.1 in $yr^{-1}$).

Sampled overland runoff events accounted for 8% of the total discharge over the study period. The difference sampled and total runoff is mainly due to (1) some smaller runoff events not being sampled, and (2) sampling of larger events may have ceased before the hydrograph completely returned to baseflow.

### $NO_3$, Cl, and P concentrations and loads

Inorganic pollutant export at site C for baseflow and runoff periods can be found in Table 4.2. Average concentrations of $NO_3$ and Cl were greater during baseflow periods, while concentrations of $NH_4$, TKN, TP, DRP, and suspended sediment were greater during runoff periods.

The annual pollutant load summary is summarized in Table 4.2. Results show that baseflow accounted for 97 and 93% for $NO_3$ and Cl export respectively. Baseflow $NO_3$ alone accounted for 80% of the total N ($NO_3$ + TKN) export (29.2 kg $ha^{-1}$ $yr^{-1}$) from the watershed, indicating groundwater $NO_3$ is the most important vector for N delivery to surface waters in this system.

The total P export resulted in a yield of 1.31 kg $ha^{-1}$ $yr^{-1}$. Approximately 85% of all P loss occurred during runoff events. Dissolved reactive P fraction accounted for 19% of the total P export. Based on mean groundwater discharge feature concentrations of total P (See section 5.0), the groundwater contribution of P export (0.04 kg $ha^{-1}$ $yr^{-1}$) is only 3% of the total P export at this site. Runoff period flow also accounted for 94% of the total suspended sediment loss.

Eight pesticide residues were detected during runoff events (Table 4.1) compared with four in baseflow samples at site C (Table 3.2). Atrazine, deethylatrazine, metolachlor and metolachlor ESA were detected in both baseflow and runoff event sampling. Acetochlor, metribuzin, and simazine were only detected in runoff event samples. Acetachlor ESA was detected in baseflow but not runoff. While concentrations of atrazine and its metabolites in baseflow were small compared to those measured in runoff, they may represent a significant export since baseflow is such a large percentage of annual streamflow particularly during dry years when little runoff occurs. Concentrations of metolachlor ESA in baseflow actually appeared to be diluted by runoff and show that groundwater is a significant vector for export.

Concentrations of parent compounds (atrazine, acetochlor, metribuzin, and metolachlor) during runoff periods were generally greatest shortly following planting when pesticides are typically applied. Concentrations gradually declined to detection levels by July for most compounds. Pollutant load as a percent of baseflow or runoff could not be calculated since pesticide analysis was only performed on a limited number of runoff events.

# 5.0 WATER QUALITY OF GROUNDWATER DISCHARGE FEATURES

Groundwater discharge features (springs, sand boils, and others) in and adjacent to the Fever River were sampled to help develop an understanding of the groundwater geochemistry; help determine whether stream water quality at baseflow could be accurately attributed to groundwater discharge, or alternatively, that instream transformations were altering groundwater discharge quality; and make inferences about whether groundwater pollutants, particularly $NO_3$ and pesticide residues, were at a steady-state or increasing.

Fourteen groundwater discharge features (Figure 2.1) were sampled on 19 Nov 2004 and 15 were sampled on 12 May 2005 (See Appendix B). Six features were common to both samplings, and provide information as to the variability of water quality with time. Groundwater discharge features included 13 streambed springs (sand boils and smaller features) and 1 drain tile. Analytes for the November 2004 samples included field parameters (pH, dissolved oxygen, specific conductance), N species ($NO_3$, $NH_4$, excess $N_2$-N, filtered total Kjeldahl N), P (filtered dissolved reactive , filtered total), Cl, dissolved gasses for age date estimation (Ar, CFC 11, 12, and 113), and pesticide residues. Pesticide residue analyses included the residues of atrazine (parent atrazine and the chlorinated degradates deethyl-, deisopropyl-, and diamino-atrazine), and the chloroacetanlides alachlor, acetochlor, and metolachlor (parents plus their ethane sulfonic acid (ESA) and oxanilic acid (OA) degradates). Analytes for the May 2005 sampling included field parameters, N and P species, dissolved organic C, alkalinity, Ca, Mg, K, Na, Fe, Mn, S, As, Cu, Pb, and Zn. Details on analytical methods and CFC age date interpretation are provided in the Appendix C.

## Results

Groundwater from discharge features was the Ca – Mg – $HCO_3$ type with a median pH of 7.2 (Table 5.1). Most water was well oxygenated (average dissolved oxygen = 4.7 mg $L^{-1}$), and signs of reducing conditions (e.g., large Fe and Mn) were absent. Apparent groundwater discharge age-dates ranged 1968 to 1990 (average = 1978) (Table 5.2). Sites sampled twice showed good agreement of age dates and other analytes common to both sample dates suggesting that the discharge features are not heavily influenced by short term variation.

N, Cl, P, pesticides and relations to groundwater age-date

Nonatmospheric N in groundwater discharge was predominantly $NO_3$-N and denitrified-N (excess $N_2$-N). Nitrate-N ranged 4.7 to 23.5 mg $L^{-1}$, denitrified-N from < 0.20 mg $L^{-1}$ to 4.5 mg $L^{-1}$, with initial $NO_3$-N (summed NO3 + denitrified N) ranging 7.9 to 23.5 mg $L^{-1}$. Denitrified N comprised 4 to 48% of initial $NO_3$-N. Ammonium-N and TKN were only about 1% of total groundwater N. The median groundwater discharge $NO_3$-N (10.6 mg $L^{-1}$) was consistent with that measured in the stream during baseflow conditions (see section 3.0).

Nitrate-N increased with groundwater age-date (0.6 mg $L^{-1}$ $yr^{-1}$, $r^2$=0.48, p<0.001); with the Maximum Contaminant Level (MCL; the US drinking water standard) of 10 mg $L^{-1}$ being exceeded in groundwater younger than about 1979 (Fig. 5.1). Initial $NO_3$-N increased similarly (0.4 mg $L^{-1}$ $yr^{-1}$, $r^2$=0.38, p<0.001). Denitrified N decreased linearly with groundwater age-date ($r^2$=0.65, p<0.001). Dissolved $O_2$ declined as denitrified N increased ($r^2$=0.56, p<0.001) (Fig. 5.2), which is consistent with the existence of subsurface reducing agents that would consume both electron acceptors.

Groundwater discharge Cl ranged 10.0 to 33.5 mg $L^{-1}$, and showed no relation to age date ($r^2$=0.06, p=0.263) nor to $NO_3$ ($r^2$=0.10, p=0.135), contrary to what has been found in some other groundwater studies (Kraft et al., 2007).

Concentrations of DRP and total dissolved P (TDP) ranged from 0.007 to 0.052 mg $L^{-1}$ and <0.012 to 0.050 mg $L^{-1}$, respectively. Most groundwater P (83%) was DRP, and DRP and TDP correlated well ($r^2$=0.74, p<0.001). As groundwater discharge total P concentrations were approximately half of stream baseflow total P, baseflow P is apparently a poor indicator of P concentrations contributed by groundwater to this receiving body. Dissolved reactive P increased with groundwater age-date at a rate of 0.001 mg $L^{-1}$ $yr^{-1}$ ($r^2$= 0.58, p<0.001) (Figure 5.3).

Five pesticide residues were found in 14 groundwater samples (Table 5.3). Metolachlor ESA was the most common, detected in all 14 samples, at concentrations of 1.13 to 7.06 μg $L^{-1}$, followed by de-ethylatrazine, alachlor ESA, atrazine, and deisopropylatrazine (Table 5.3). The sum of all pesticide residues had a maximum concentration of 8.34 µg $L^{-1}$ and a median concentration of 3.95 µg $L^{-1}$. Total atrazine residues had a median concentration of 0.38 µg $L^{-1}$ and a maximum of 1.01 µg $L^{-1}$, which were below the Wisconsin groundwater enforcement standard of 3 µg $L^{-1}$ for total atrazine. There are currently no groundwater standards for alachlor ESA or metolachlor ESA. No relationship between pesticide concentration and groundwater age-date were apparent ($r^2$=0.10, p=0.271) (Figure 5.4).

Denitrification kinetics

Denitrification could be a significant control for decreasing the groundwater transfer and export of $NO_3$. We investigated denitrification kinetics using a first-order model:

$$N_t = N_i \exp(-kt)$$

or

$$\ln\frac{N_t}{N_i} = -kt$$

where t is time, $N_t$ is the $NO_3$-N concentration we measured in 2004 and 2005, $N_i$ is the initial $NO_3$-N concentration (sum of measured and denitrified $NO_3$-N), $t$ is the groundwater age, estimated as the difference between sampling year and the groundwater age date (2004 or 2005 minus age-date) and $k$ is the first order decay constant. For this analysis, we averaged results for sites that were sampled twice, though considering them separately produced only small changes in rate-constant estimates.

We used two approaches to estimating k. In the first approach, for each sample we calculated $-\ln(N_t/N_i)$, and then regressed this quantity against the sample's groundwater age. The value of $k$ is given by the slope of the regression. This approach would be consistent with a presumption that groundwater parcels moving through subsurface flow paths would encounter uniform geochemical conditions which would produce uniform denitrification rates. The first-order constant for all data (Figure 5.5) is 0.028 $yr^{-1}$ (SE = 0.004; $r^2$= 0.73, p = 0.0003), which corresponds to a half-life of about 25 years. Note that Figure 5.5 suggests that two denitrification domains may be present; one for relatively young (< 20 years) and another for older waters. Regressing these separately suggests $NO_3$ is stable in young groundwater ($k$ not different than 0; p = 0.63) and is 0.042 $yr^{-1}$ (SE = 0.0078; $r^2 = 0.68$, $p = 10^{-6}$) in older groundwater, which corresponds to a half-life of about 17 years. Two denitrification domains would be consistent with dual domain groundwater flow paths, one rapid and shallow, the other slow and deep.

In the second approach we estimated a $k$ for each sample, as

$$k = \ln \frac{N_t}{N_i} \times t^{-1}$$

Doing thusly allows for a possibility that each groundwater parcel sampled traveled along a flowpath encountering unique geochemical circumstances that might affect denitrification. The average across all samples yields $k = 0.10$ (sd = 0.005). Neglecting samples with groundwater ages of < 20 years results in a slightly larger $k = 0.012$ $yr^{-1}$ (sd = 0.005). These suggest denitrification half lives of 57 to 60 years.

In summary, all methods of estimating denitrification indicate it is slow, and unable to attenuate a substantial amount of $NO_3$ being transferred from the landscape to surface water by groundwater.

## Summary

Groundwater discharge in the upper Fever was the Ca-Mg-$HCO_3$ type typical of a carbonate bedrock system. Groundwater was oxidizing. Groundwater had a mean age date of 1979 which ranged 1968 to 1989. Nitrate concentrations were consistent with those observed in stream baseflow, bolstering hypotheses that instream processes have little effect on $NO_3$ after it discharges from ground to surface water. Hence baseflow $NO_3$ concentrations appear to be a valid estimator of groundwater discharge loads. Nitrate increased greatly with age-date, from about 5 mg $L^{-1}$ in 1970 to around 15 mg $L^{-1}$ by 1990. Denitrified $N_2$-N was 48% of initial $NO_3$-N in old groundwater, but <10% in younger groundwater. Inferred denitrification rates were small, corresponding to half-lives of 25 years or more. Denitrification is insufficient to substantially control $NO_3$ transport and export from ground to surface water.

Chloride and pesticide residues in discharging groundwater were also consistent with stream baseflow water quality. However, P concentrations in discharging groundwater were only about half those in baseflow. This is evidence that desorption or other mechanisms in the stream channel are adding to P discharged from groundwater. Groundwater P showed signs of increasing over time.

# 6.0 CONCLUSIONS

**We estimated the groundwater pollutant transfer to a receiving stream, compared groundwater transfer and export with that from runoff, and determined whether groundwater transfer and export were likely at a steady-state or increasing.**

1. Groundwater pollutant transfer to the receiving stream was determined through repetitive sampling of stream water quality and discharge during the study period.
2. Comparisons with runoff transfer and export were made at a gauging and sampling station which measured water quality and discharge during runoff events.
3. Questions about steady-state vs. increase were inferred by sampling water quality and groundwater age-date at groundwater discharge features, such as riparian springs.

Groundwater was the chief agent responsible for the transfer to surface water and subsequent export of $NO_3$, Cl, and the residues of Metolachlor ESA and Deethylatrazine. Annual groundwater transfer and export of $NO_3$ and Cl were 23.4 and 42.9 kg $ha^{-1}$ $yr^{-1}$ (at site C) respectively. This amounted to 97 and 93% of the total. Pesticides groundwater export was estimated to be 0.20, 0.42, 0.71 and 9.0 g $ha^{-1}$ $yr^{-1}$ for atrazine, deethylatrazine, alachlor ESA and metolochlor ESA. Runoff was chiefly responsible for P and sediment transfer and export with 1.1 and 792 kg $ha^{-1}$ $yr^{-1}$. This amounted to 85 and 94% of the total. Summed concentrations of pesticides ranged from 4.24 ug $L^{-1}$ during baseflow periods up to 53.3 ug $L^{-1}$ in one particular runoff event period sample.

The groundwater transport of $NO_3$ in this system has yet to reach equilibrium with leakage from the landscape. This is due to two factors, increasing leakage from fields to groundwater over time, presumably caused by increasing rates of N inputs, and the inability of denitrification to degrade substantial amounts of $NO_3$ prior to groundwater being discharged to surface waters. Groundwater samples showed no age-date relationship for Cl or pesticides; however it is unknown from this data whether an equilibrium has been reached with current land-use practices.

Currently runoff events represent the largest source of P delivery to the Fever River and likely contribute to baseflow P levels in excess of groundwater water quality, however, groundwater phosphorus also showed signs of increasing over time.  In addition, pesticides and pesticide breakdown components are persistent in the groundwater and surface water.  Due to the substantial inertia of the groundwater system, the full extent of pollutant loading from groundwater discharge to surface waters is not yet reflected in current water quality found in our rivers and streams.

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# 8.0 TABLES AND FIGURES

Table 2.1. Results of Fever River synoptic survey.

| **Location** | **Measured Flow** | **Segmented baseflow contribution** | **Groundwater discharge intensity** | **Conductivity** | **$NO_3$-N** | **$NH_4$-N** | **Dissolved Reactive P** | **Cl** |
|---|---|---|---|---|---|---|---|---|
| | **-------$ft^3$ $s^{-1}$-------** | | **$ft^3$ $s^{-1}$ ft** | **µs/cm** | **----------------------mg $L^{-1}$---------------------** | | | |
| S1 | 0.54 | 0.54 | $1.6 \times 10^{-4}$ | 697 | 13.9 | 0.06 | 0.037 | 17.0 |
| S2 | 0.72 | 0.00 | 0.0 | 723 | 11.2 | 0.01 | 0.036 | 18.0 |
| S3 | 1.18 | 0.46 | $1.1 \times 10^{-4}$ | 696 | 10.9 | 0.08 | 0.043 | 17.8 |
| S4 | 1.66 | 0.28 | $5.7 \times 10^{-5}$ | 718 | 10.0 | 0.07 | 0.031 | 19.0 |
| S5 | 1.48 | -0.18 | $-5.6 \times 10^{-5}$ | 712 | 9.8 | 0.06 | 0.033 | 19.0 |
| S6 | 2.53 | 0.79 | $1.1 \times 10^{-4}$ | 709 | 9.4 | 0.17 | 0.041 | 19.0 |
| S7 | 2.79 | 0.22 | $2.8 \times 10^{-5}$ | 671 | 9.2 | 0.12 | 0.033 | 18.8 |
| T1 | 0.18 | 0.18 | $1.7 \times 10^{-4}$ | 698 | 9.8 | 0.03 | 0.046 | 25.3 |
| T2 | 0.20 | 0.20 | $8.3 \times 10^{-4}$ | 743 | 4.5 | 0.04 | 0.007 | 19.5 |
| T3 | 0.26 | 0.26 | $1.7 \times 10^{-4}$ | 756 | 9.7 | 0.03 | 0.040 | 16.8 |
| T4 | 0.04 | 0.04 | $2.9 \times 10^{-5}$ | 539 | 8.3 | <0.01 | 0.031 | 12.0 |
| D1 | 0.01 | 0.01 | - | 872 | 24.2 | 0.02 | 0.020 | 34.8 |
| D2 | 0.01 | 0.01 | - | 709 | 11.6 | 0.01 | 0.035 | 15.0 |

Table 3.1  Summary of monthly baseflow measurements and inorganic water quality at sites A,B,C, and D.

| Site | Streamflow | $NO_3$-N | $NH_4$-N | TKN | Total P | DRP | Cl |
|---|---|---|---|---|---|---|---|
|  | $m^3 s^{-1}$ | -------------Concentration (mg $L^{-1}$)------------------ |  |  |  |  |  |
| A | 0.02 | 13.6 | 0.06 | 0.61 | 0.09 | 0.043 | 17.3 |
| B | 0.04 | 11.1 | 0.09 | 0.86 | 0.13 | 0.053 | 18.1 |
| C | 0.06 | 10.3 | 0.06 | 0.55 | 0.09 | 0.044 | 18.9 |
| D | 0.10 | 9.4 | 0.08 | 0.90 | 0.13 | 0.040 | 19.1 |
|  | $m^3 yr^{-1}$ | -----------------------Load (kg $yr^{-1}$)---------------------------- |  |  |  |  |  |
| A | 625,100 | 9,145 | 43 | 381 | 56 | 29 | 11,632 |
| B | 1,428,800 | 15,932 | 126 | 1,229 | 186 | 76 | 25,990 |
| C | 1,875,300 | 19,616 | 105 | 1,032 | 169 | 83 | 35,905 |
| D | 3,214,800 | 30,644 | 255 | 2,894 | 418 | 132 | 62,358 |
|  | mm $ha^{-1}$ $yr^{-1}$ | --------------------Yield (kg $ha^{-1}$ $yr^{-1}$)-------------------------- |  |  |  |  |  |
| A | 240 | 35.2 | 0.17 | 1.46 | 0.22 | 0.11 | 44.8 |
| B | 227 | 25.3 | 0.20 | 1.95 | 0.30 | 0.12 | 41.3 |
| C | 243 | 25.5 | 0.14 | 1.34 | 0.22 | 0.11 | 46.6 |
| D | 236 | 22.5 | 0.19 | 2.13 | 0.31 | 0.10 | 45.8 |

* Watershed areas for A,B,C, and D were 260, 629, 770 and 1,360 ha respectively.

Table 3.2 Concentrations of pesticide and metabolites in baseflow from study sites along Fever River sampled on 8 August 2003, 24 July and 14 Sept 2004.

| Date | Site | Atrazine | De-Ethyl Atrazine | Alachlor ESA | Metolachlor | Metolachlor ESA |
|---|---|---|---|---|---|---|
| | | **-------------------------------Concentration (ug $L^{-1}$)---------------------------------** | | | | |
| 8 Aug 2003 | A | 0.10 | 0.33 | <LOD | <LOD | 4.6 |
| | B | 0.15 | 0.41 | <LOD | <LOD | 4.4 |
| | C | <LOD | <LOD | <LOD | <LOD | 4.0 |
| | D | 0.11 | 0.31 | <LOD | <LOD | 3.9 |
| 24 July 2004 | A | <LOD | 0.18 | <LOD | <LOD | 4.2 |
| | B | 0.14 | 0.24 | 0.3 | <LOD | 4.4 |
| | C | 0.15 | 0.21 | 0.4 | <LOD | 4.3 |
| | D | 0.10 | 0.21 | <LOD | <LOD | <LOD |
| 14 Sept 2004 | A | 0.11 | 0.29 | <LOD | <LOD | 4.0 |
| | B | 0.22 | 0.30 | <LOD | 0.13 | 3.0 |
| | C | <LOD | 0.30 | 0.47 | <LOD | 2.7 |
| | D | <LOD | 0.24 | <LOD | <LOD | 3.3 |

<LOD Less than limit of detection.

Table 3.3. Mean concentration, load and yield measurements of baseflow period pesticide residues.

| Site | Atrazine | Deethyl-atrazine | Alachlor ESA | Metolachlor | Metolochlor ESA |
|---|---|---|---|---|---|
| | ----------------------------Concentration (ug $L^{-1}$)------------------------------ | | | | |
| A | 0.10 | 0.27 | <LOD | <LOD | 4.3 |
| B | 0.17 | 0.32 | 0.10 | 0.04 | 3.9 |
| C | 0.08 | 0.17 | 0.29 | <LOD | 3.7 |
| D | 0.09 | 0.25 | <LOD | <LOD | 2.4 |
| | --------------------------Load (g $yr^{-1}$)----------------------------- | | | | |
| A | 67 | 180 | 0 | 0 | 2,881 |
| B | 244 | 455 | 144 | 62 | 5,631 |
| C | 152 | 323 | 550 | 0 | 6,982 |
| D | 293 | 825 | 0 | 0 | 7,775 |
| | ------------------------Yield (g $ha^{-1}$ $yr^{-1}$)---------------------------- | | | | |
| A | 0.26 | 0.69 | 0 | 0 | 11.1 |
| B | 0.39 | 0.72 | 0.23 | 0.10 | 9.0 |
| C | 0.20 | 0.42 | 0.71 | 0 | 9.0 |
| D | 0.22 | 0.61 | 0 | 0 | 5.7 |

* Watershed areas for A,B,C and D were 260, 629, 770 and 1,360 ha respectively.

Table 4.1  Concentration of pesticide residues detected in runoff events.

| **Year** | **Date** | **Compounds**<br>**Atrazine** | **De-ethyl atrazine** | **De-isopropyl atrazine** | **Acetochlor** | **Metribuzin** | **Metolachlor** | **Metolachlor ESA** | **Simazine** |
|---|---|---|---|---|---|---|---|---|---|
| | | ------------------------------------------------------------------- | | | **µg $L^{-1}$** | ------------------------------------------------------------------- | | | |
| **2003** | **8 May** | 16 | 1.2 | 0.5 | <LOD | 1.2 | <LOD | NA | <LOD |
| | **10 May** | 41 | 3.5 | 1.1 | 3.3 | 4.4 | <LOD | NA | <LOD |
| | **14 May** | 11 | 1.2 | 0.5 | 0.4 | <LOD | <LOD | NA | 1.1 |
| | **6 July** | 1.5 | 0.5 | <LOD | <LOD | 0.1 | <LOD | NA | <LOD |
| **2004** | **17 May** | 3.3 | 0.4 | <LOD | 1.2 | <LOD | 4.6 | 3.8 | <LOD |
| | **21 May** | 1.0 | 0.4 | <LOD | 0.4 | <LOD | 1.7 | <LOD | <LOD |
| | **21 July** | <LOD | 0.2 | <LOD | 1.1 | <LOD | 1.4 | 1.9 | <LOD |
| | **23 Aug** | <LOD | 0.2 | <LOD | <LOD | <LOD | <LOD | 2.0 | <LOD |
| | **15 Sep** | <LOD | 0.3 | <LOD | <LOD | <LOD | <LOD | 2.7 | <LOD |

<LOD Less than limit of detection
NA Not available

Table 4.2  Comparison of streamflow and pollutant export during baseflow and runoff event periods at site C.

| | Flow | $NO_3$-N | $NH_4$-N | TKN | TP | DRP | Cl | Suspended Sediment |
|---|---|---|---|---|---|---|---|---|
| | $ft^3 s^{-1}$ | --------------------------------Concentration ($mg L^{-1}$)---------------------------------------- | | | | | | |
| Baseflow | 1.9 | 10.3 | 0.06 | 0.55 | 0.09 | 0.04 | 18.9 | 21 |
| Runoff | 0.3 | 1.8 | 1.02 | 11.14 | 3.15 | 0.42 | 9.6 | 2,237 |
| | $ft^3$ | ------------------------------------------Load ($kg yr^{-1}$)------------------------------------------------ | | | | | | |
| Baseflow | $1.23 \times 10^8$ | 18,006 | 105 | 3,041 | 154 | 77 | 33,041 | 37,062 |
| Runoff | $1.93 \times 10^7$ | 497 | 278 | 965 | 859 | 116 | 2,620 | 610,532 |
| Total | $1.42 \times 10^8$ | 18,503 | 383 | 4,006 | 1,013 | 193 | 35,661 | 647,594 |
| | in $yr^{-1}$ | ----------------------------------------Yield ($kg ha^{-1} yr^{-1}$)---------------------------------------------- | | | | | | |
| Baseflow | 8.9 | 23.4 | 0.14 | 3.95 | 0.20 | 0.10 | 42.9 | 48 |
| Runoff | 1.4 | 0.6 | 0.36 | 1.25 | 1.11 | 0.15 | 3.4 | 792 |
| Total | 10.3 | 24.0 | 0.50 | 5.20 | 1.31 | 0.25 | 46.3 | 840 |
| | ---------------------------------------------------------%-------------------------------------------------------------- | | | | | | | |
| Baseflow | 86 | 97 | 27 | 24 | 15 | 40 | 93 | 6 |
| Runoff | 14 | 3 | 73 | 76 | 85 | 60 | 7 | 94 |

Table 5.1 Summary of inorganic analyses for groundwater discharge.

| Analyte | Mean | Median | Max | Min |
|---|---|---|---|---|
| | ------- mg $L^{-1}$ except pH ------- | | | |
| $Ca^1$ | 84.1 | 82.4 | 96.2 | 76.0 |
| $Mg^1$ | 47.1 | 46.3 | 54.8 | 42.5 |
| $Na^1$ | 8.6 | 7.6 | 15.6 | 4.6 |
| $K^1$ | 1.5 | 0.7 | 3.7 | 0.4 |
| $Cl^1$ | 19.4 | 18.0 | 33.5 | 10.0 |
| $SO_4{}^1$ | 39.1 | 32.8 | 72.9 | 17.4 |
| $O_2{}^3$ | 4.7 | 4.3 | 9.2 | 1.8 |
| $Fe^1$ | 0.009 | 0.006 | 0.045 | 0.002 |
| $Mn^1$ | 0.008 | 0.002 | 0.046 | <0.001 |
| Organic $C^1$ | 2.1 | 1.5 | 6.9 | 0.9 |
| ANC (as $HCO_3$)$^1$ | 305 | 300 | 376 | 288 |
| $pH^2$ | 7.2 | 7.2 | 7.3 | 7.0 |
| Dissolved Reactive $P^3$ | 0.021 | 0.021 | 0.050 | <0.012 |
| Total $P^3$ | 0.020 | 0.015 | 0.052 | 0.007 |
| | ------- mg $L^{-1}$ N ------- | | | |
| $NO_3{}^3$ | 10.7 | 10.6 | 19.0 | 5.5 |
| Denitrified $NO_3{}^3$ | 2.3 | 2.2 | 4.5 | <0.20 |
| Initial $NO_3{}^3$ | 12.5 | 11.6 | 23.2 | 7.9 |
| Total Kjeldahl$^3$ | 0.12 | 0.10 | 0.20 | 0.05 |
| $NH_4{}^3$ | <0.01 | 0.01 | 0.02 | <0.01 |

[1] From 12 May 2005 sampling.

[2] From 16 November 2004 sampling.

[3] From both sampling dates.

Table 5.2 Results of groundwater age-date analyses with depth below water table. Blank cells were invalid. Gray cells were deemed environmentally contaminated (see Appendix C).

| **Date** | **Site** | **CFC11** | **CFC12** | **CFC113** | **Best** |
|---|---|---|---|---|---|
| 19 Nov 2004 | 1005.001 | 1970 | 1971 | 1974 | 1972 |
| | 1005.002 | 1977 | 1976 | 1980 | 1978 |
| | 1005.004 | 1988 | 1989 | 1987 | 1988 |
| | 1040.004 | 1974 | 1974 | 1978 | 1975 |
| | 1040.008 | 1975 | 1977 | 1978 | 1977 |
| | 1040.009 | 1975 | 1974 | 1977 | 1975 |
| | 1045.001 | 1973 | 1973 | 1972 | 1973 |
| | 1065.002 | 1983 | 1982 | 1987 | 1984 |
| | 1065.003 | 1987 | 1982 | 1988 | 1986 |
| | 1130.002 | 1988 | 1984 | 1988 | 1987 |
| | 1130.003 | 1989 | 1984 | 1987 | 1987 |
| | 1318.008 | 1979 | 1978 | 1982 | 1980 |
| | 1318.009 | 1976 | 1976 | 1980 | 1978 |
| | 1318.010 | 1972 | 1969 | 1968 | 1970 |
| 12 May 2005 | 1005.001 | 1976 | 1975 | | 1976 |
| | 1005.004 | 1986 | 2001 | | 1986 |
| | 1005.005 | 1983 | 1988 | | 1986 |
| | 1005.006 | 2001 | 1990 | | 1989 |
| | 1015.005 | 1976 | 1978 | | 1977 |
| | 1015.006 | 1977 | 1976 | | 1977 |
| | 1040.006 | 1974 | 1976 | | 1975 |
| | 1130.001 | 1981 | 1983 | | 1982 |
| | 1130.002 | 1985 | 1982 | | 1983 |
| | 1130.003 | 1982 | 1983 | | 1983 |
| | 1318.007 | 1976 | 1979 | | 1978 |
| | 1318.009 | 1972 | 1976 | | 1974 |
| | 1318.010 | 1969 | 1968 | | 1969 |
| | 1318.020 | 1972 | 1973 | | 1973 |
| | 1318.021 | 1967 | 1969 | | 1968 |

Table 5.3 Pesticide residue concentrations detected in groundwater samples taken on 16 Nov 2004.

| **Pesticide Residue** | **Detects (No.)** | **Detection Limit** | **Median Detection** | **Maximum Detection** |
|---|---|---|---|---|
| | | **Concentration (µg $L^{-1}$)** | | |
| Atrazine | 6 | 0.1 | 0.15 | 0.24 |
| Deethylatrazine | 10 | 0.2 | 0.26 | 0.61 |
| Deisopropylatrazine | 3 | 0.2 | 0.29 | 0.36 |
| Total atrazine residues | 11 | 0.1-0.2 | 0.38 | 1.01 |
| Alachlor ESA | 10 | 0.16 | 0.59 | 1.36 |
| Metolachlor ESA | 14 | 0.12 | 2.97 | 7.06 |
| Summed residues | 14 | 0.1-0.16 | 4.03 | 9.15 |

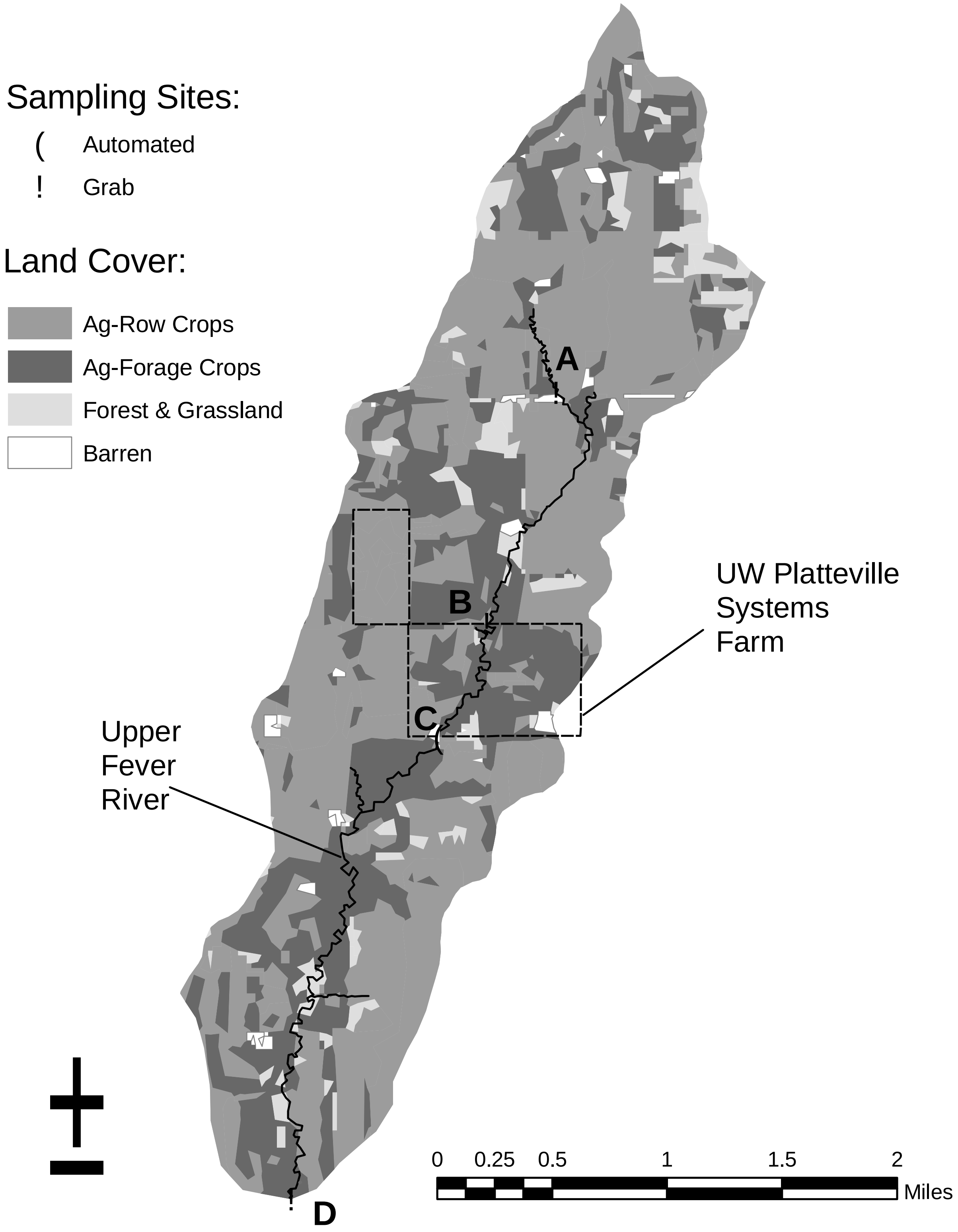


Figure 1.1 Study watershed, land cover and stream sampling locations.

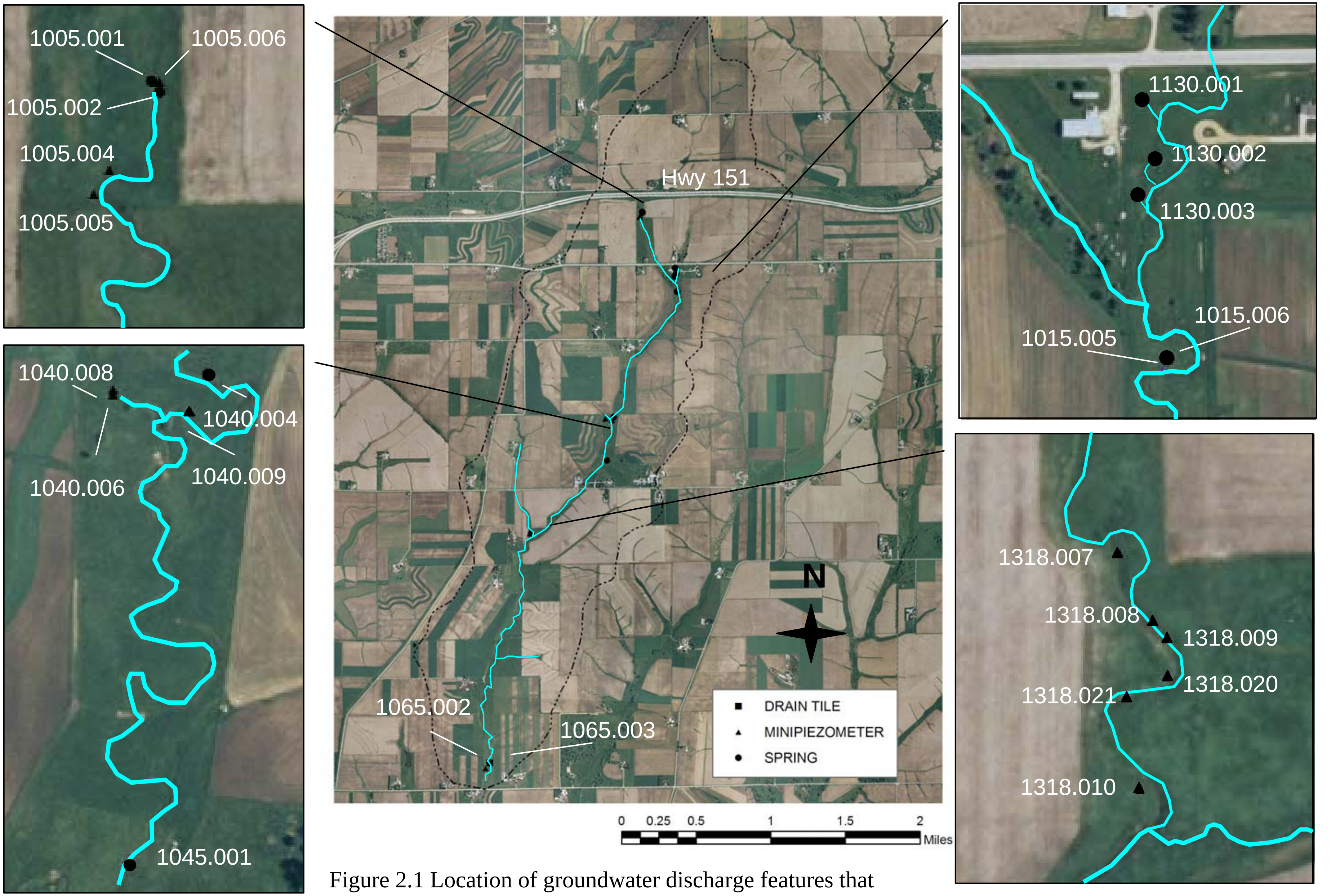


Figure 2.1 Location of groundwater discharge features that were sampled for water quality

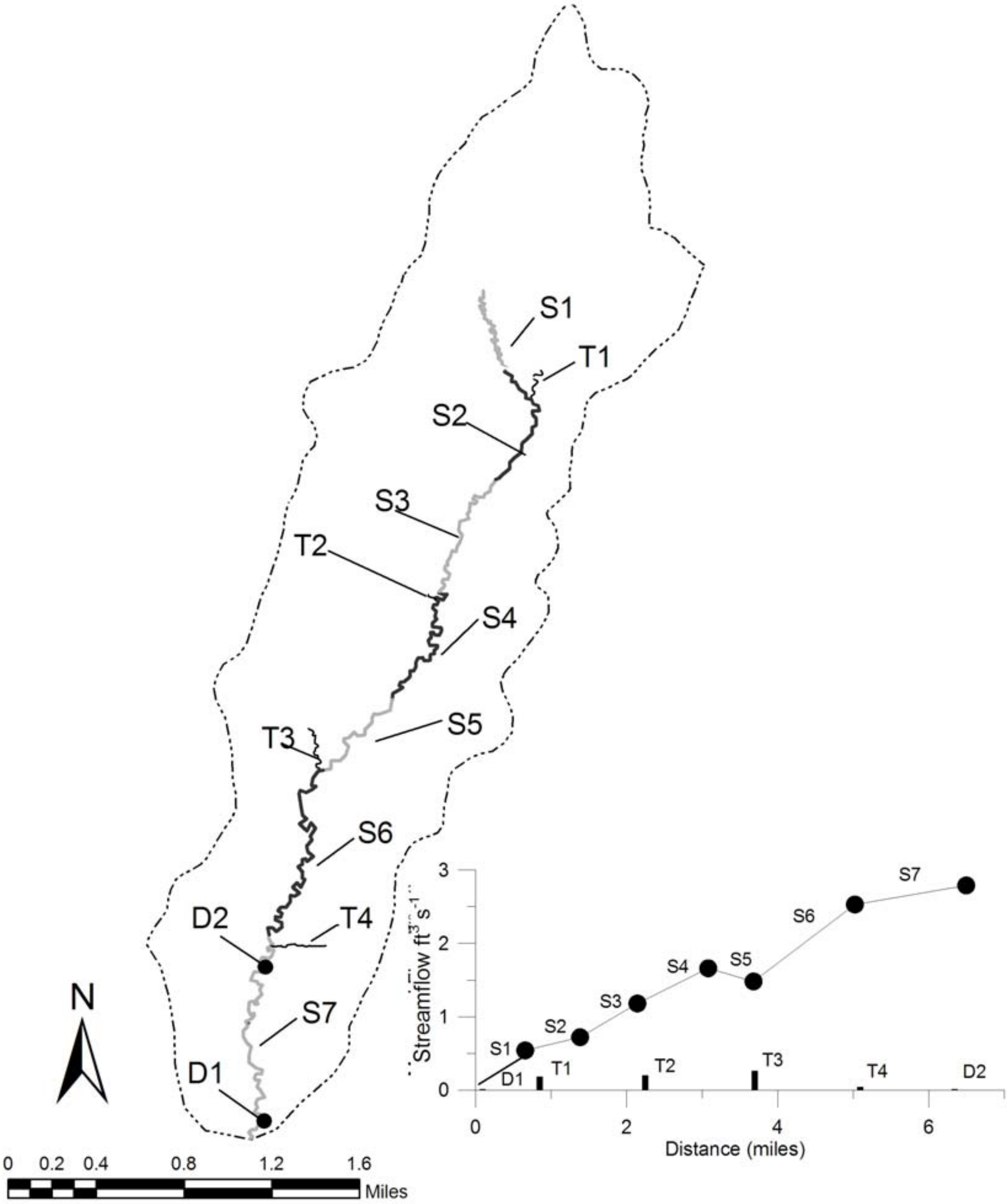


Figure 2.2 Segments and features investigated during synoptic surveys performed on 8 Dec 2003 and 7 April 2004. S1-S7 identify stream segments of the main channel. T1-T4 identify tributaries. D1-D2 identify drain tiles that provided flow during sampling dates. Graph depicts streamflow as a function of distance from headwater springs. Note S5 is a losing stretch.

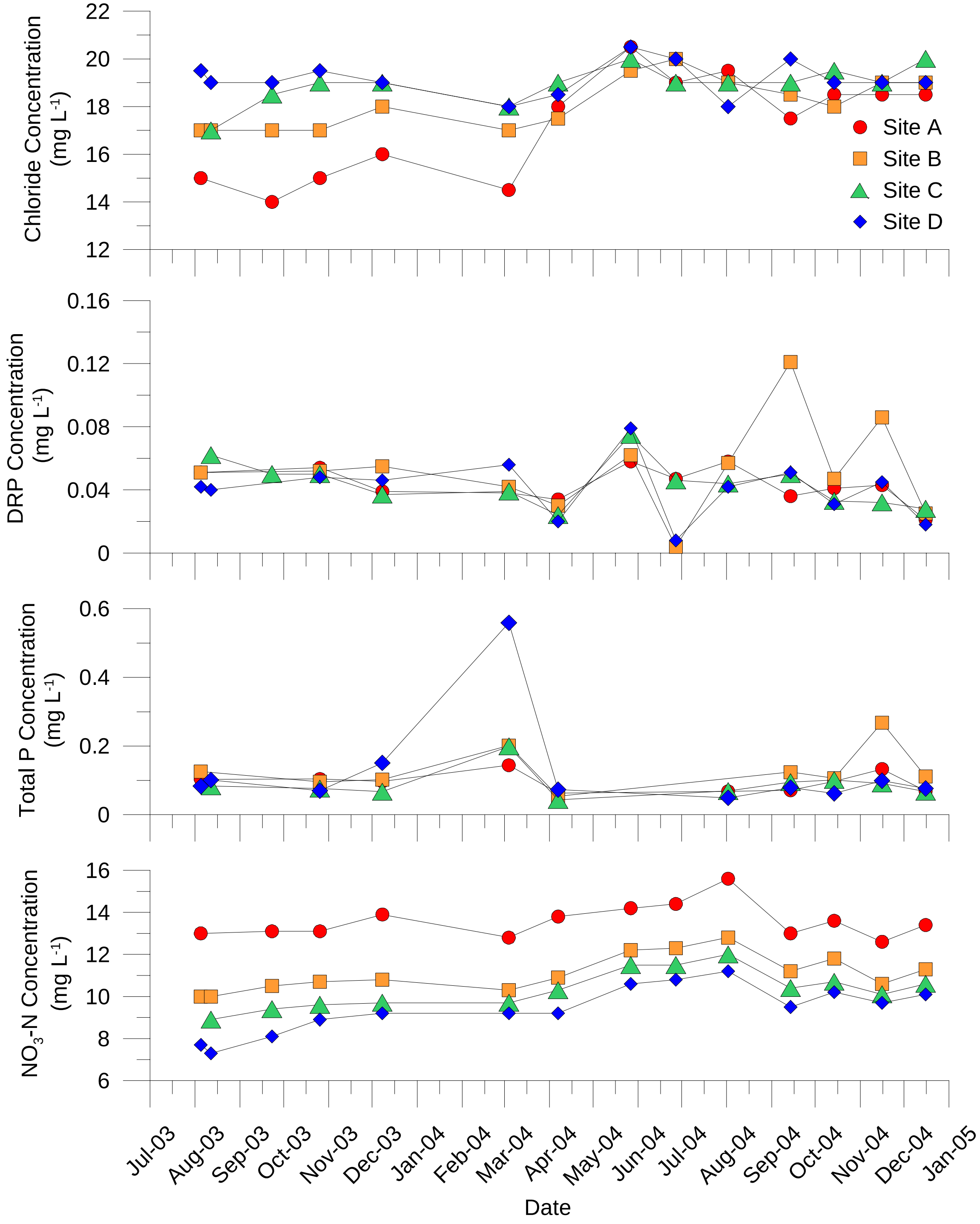


Figure 3.1 Monthly baseflow water quality at sites A, B, C, and D.

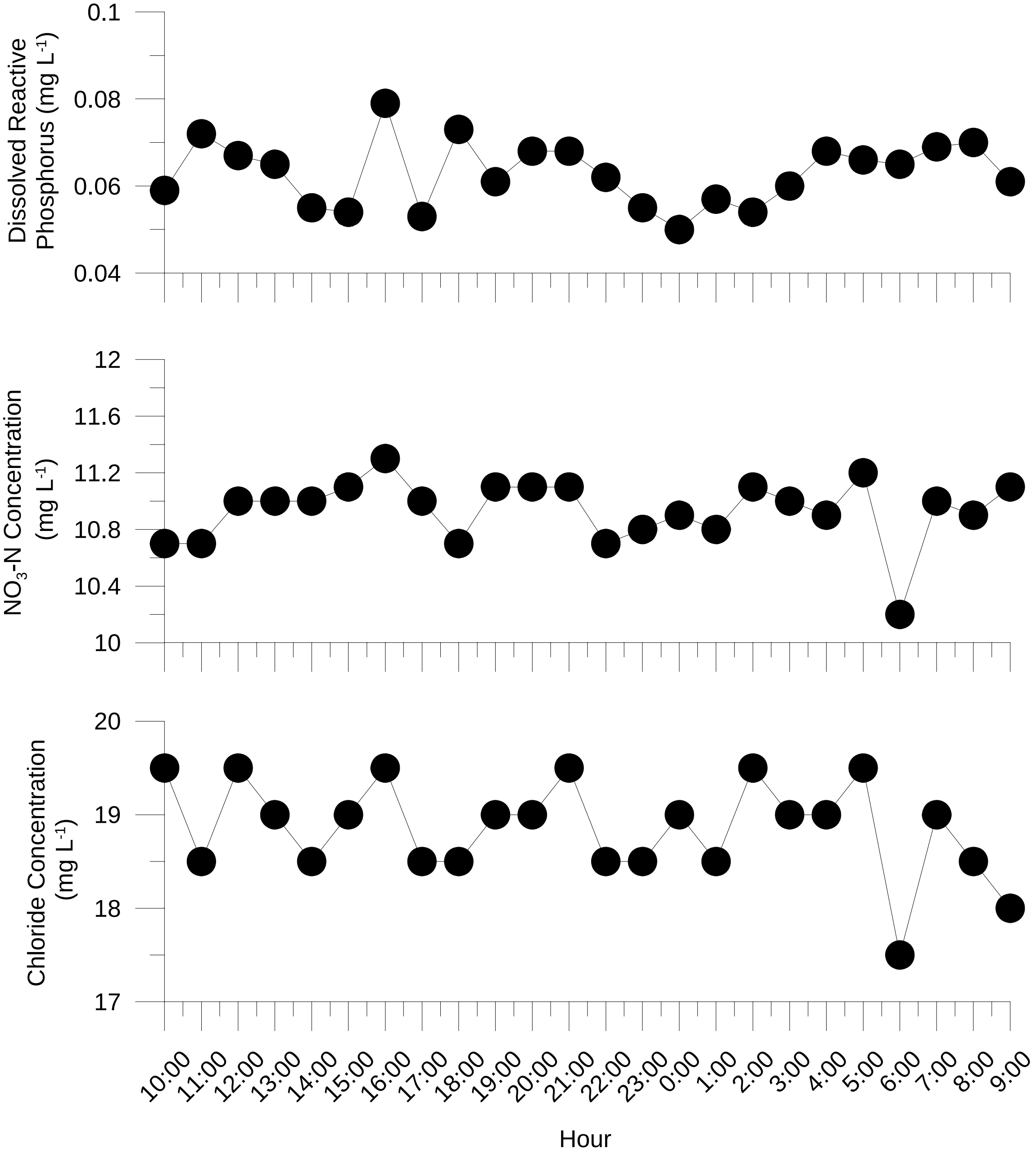


Figure 3.2 Hourly streamflow concentrations of DRP, $NH_4$-N, and $NO_3$-N during baseflow conditions over a 24-h period.

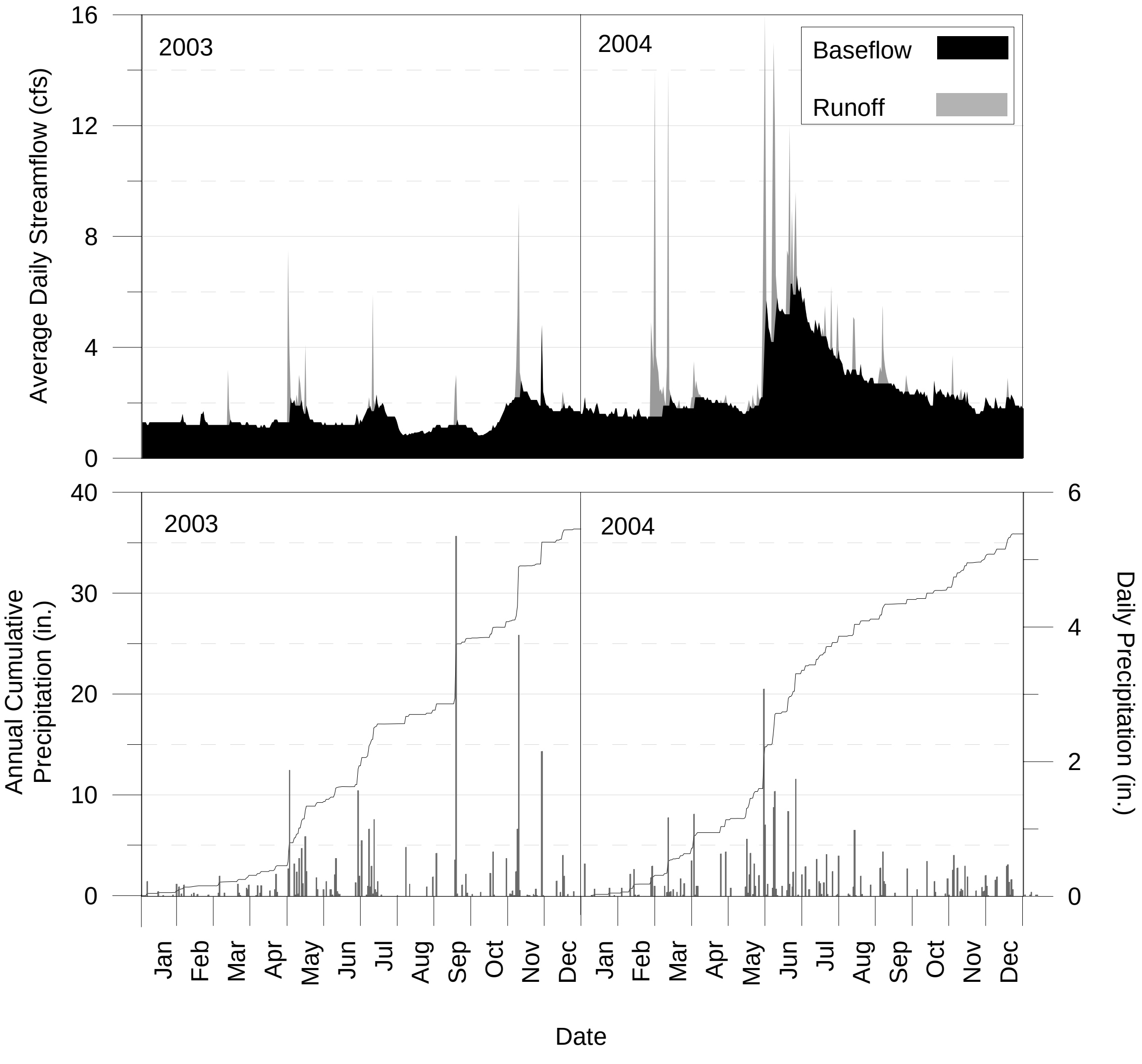


Figure 4.1. Precipitation and hydrograph separated into baseflow and runoff components for the period starting 1 Jan 2003 and ending on 31 Dec 2004.

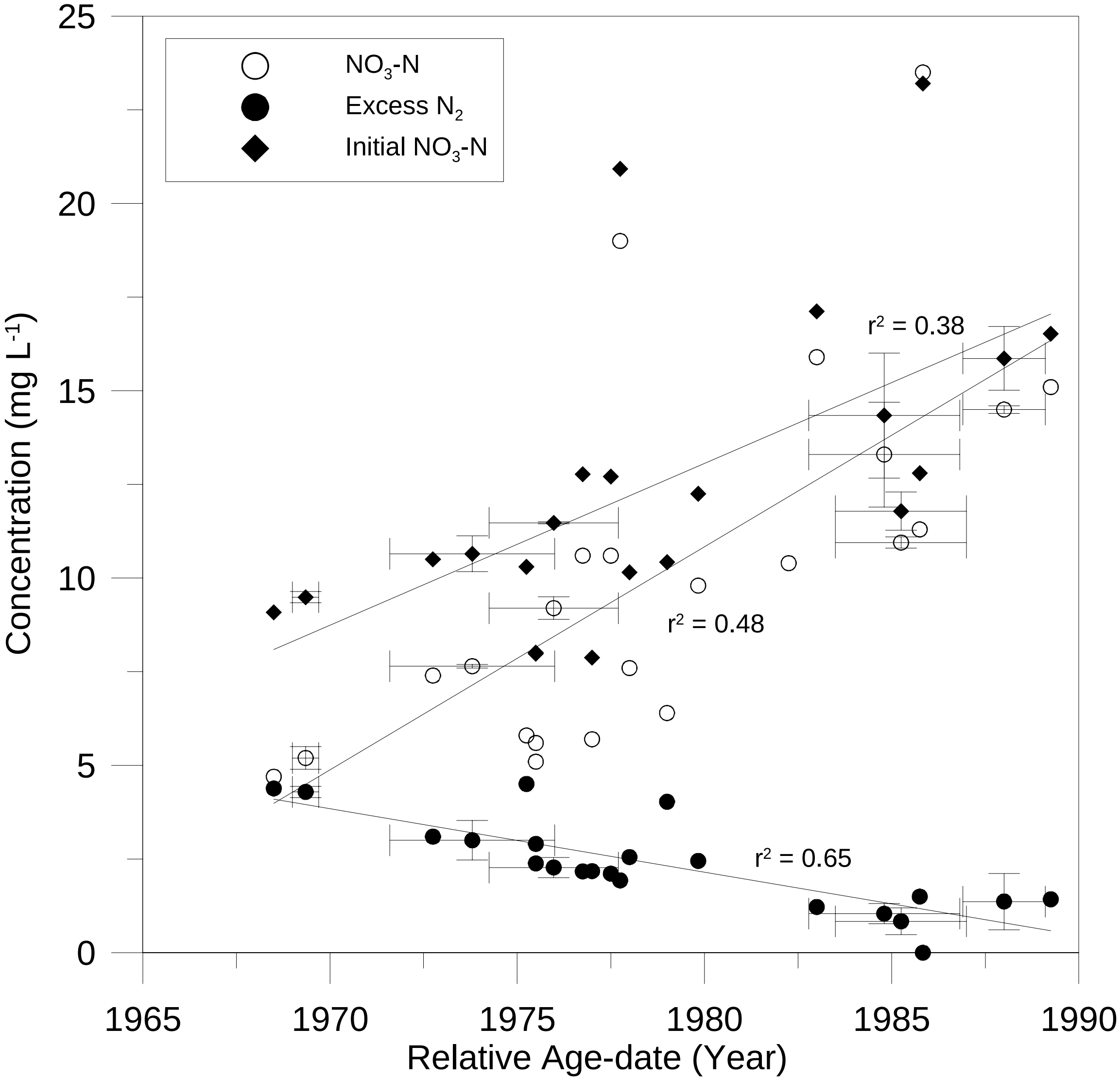


Figure 5.1. Measured $NO_3$-N and denitrified N from groundwater samples taken on 19 Nov 2004 and 12 May 2005 were used to reconstruct the initial $NO_3$-N concentration at the time of recharge. Sites that were sampled on both dates include standard error bars.

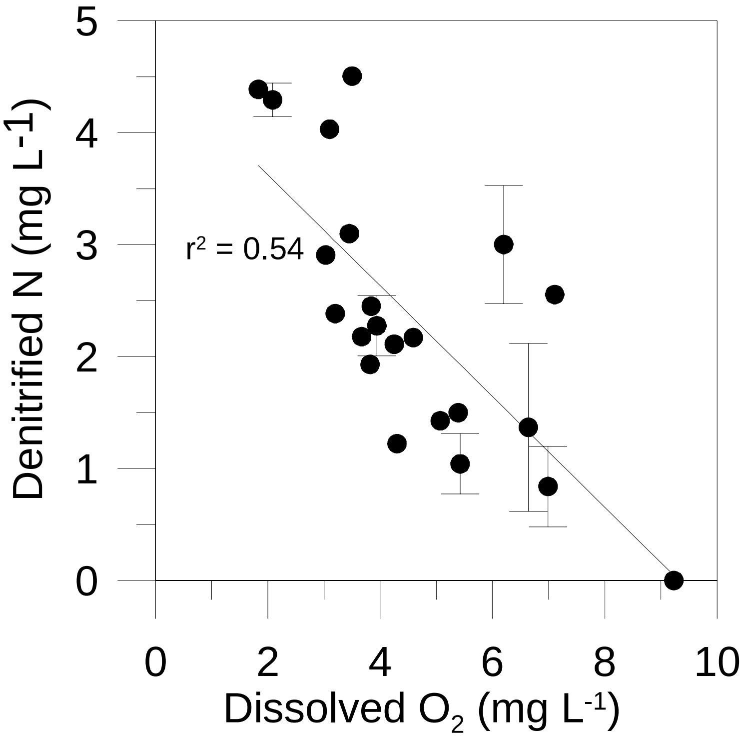


Figure 5.2 Relationship between dissolved $O_2$ levels and amount of denitrified N.

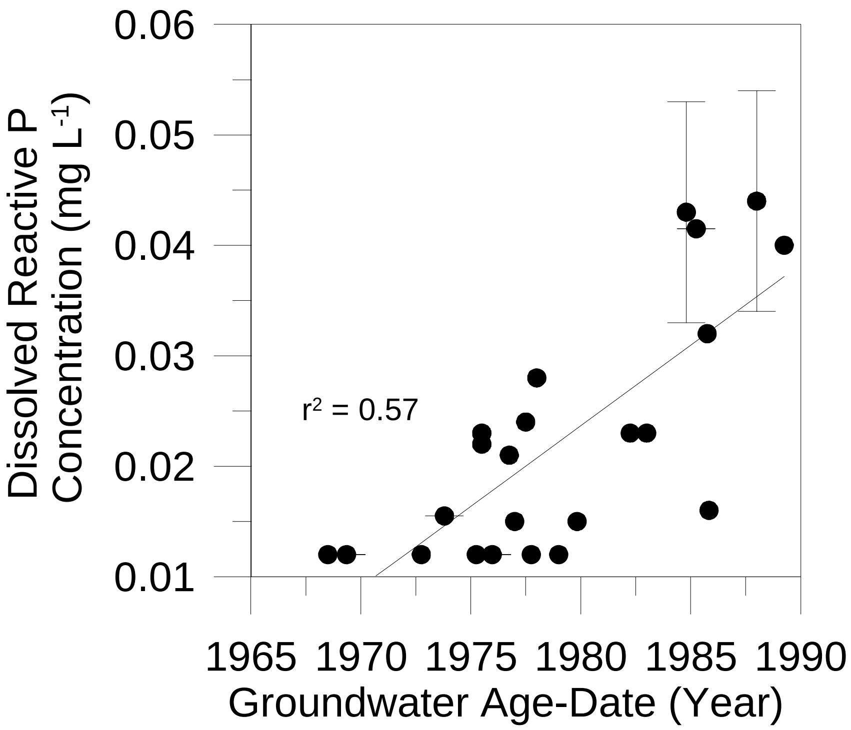
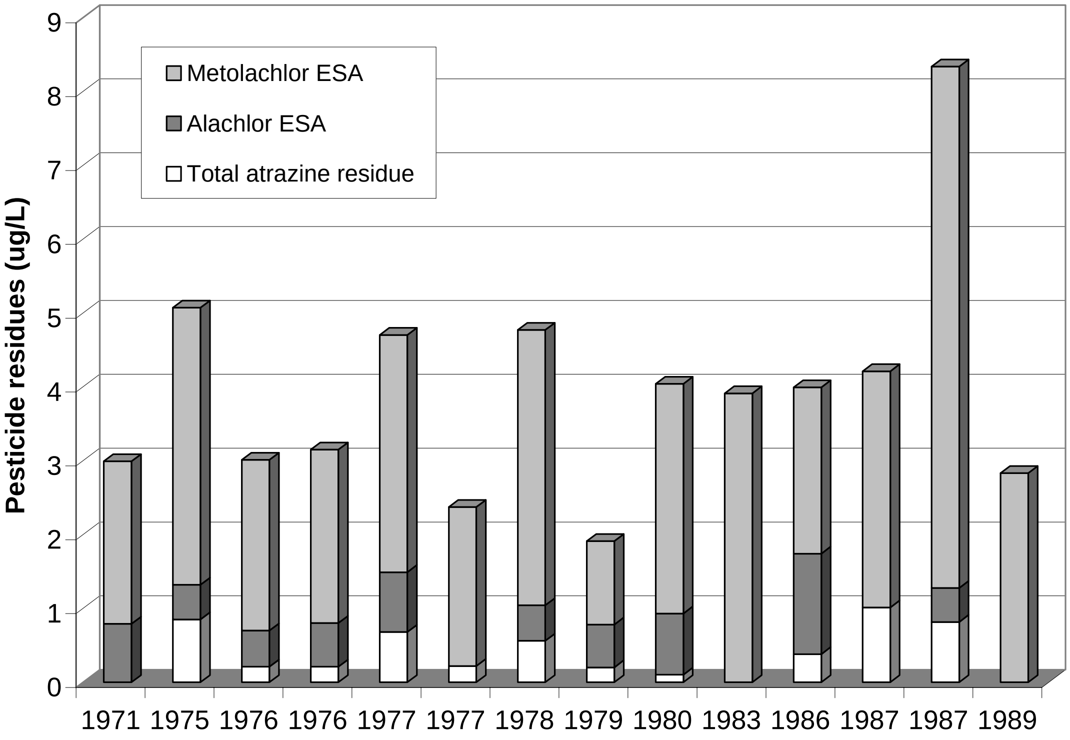


Figure 5.3 Relationship between DRP concentration and groundwater age-date.

Figure 5.4 Groundwater pesticide residues with respective groundwater age-date.



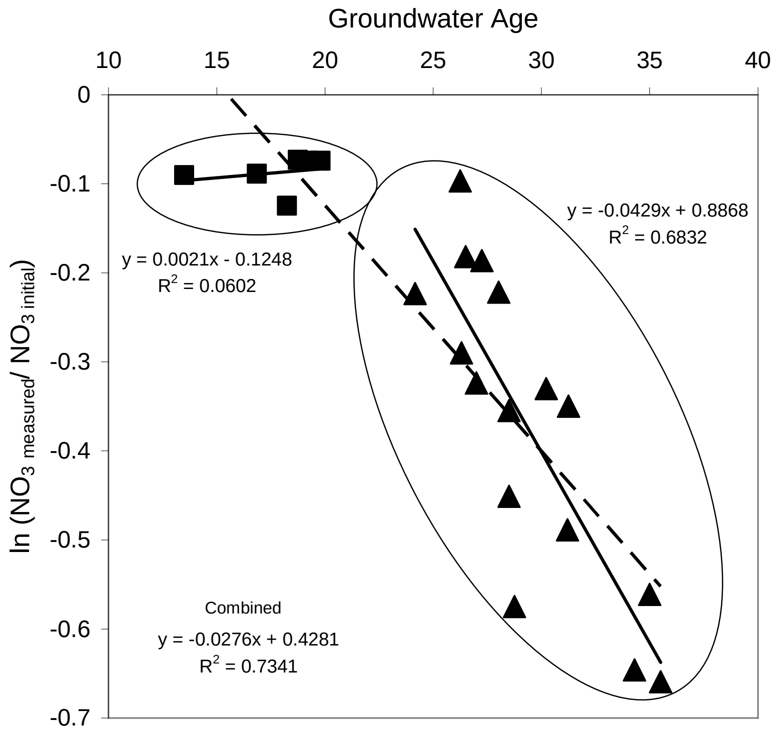


Figure 5.5 First order rate constants showing denitrification rates based on groundwater age-date, initial $NO_3$-N concentration and measured denitrified N. Dashed line represents regression analysis for combined data. Solid lines represent regression analysis of young and old denitrification domains.

## 9.0 APPENDIX

### A. Synoptic Survey

Detailed synoptic surveys of Fever River discharge and water quality were conducted in December 2003 and April 2004. We investigated 13 segments and features; seven in the main stream channel, four tributaries, and 2 drains (tiled-out riparian springs) that produced flow year round. Discharge and water quality were measured at the downstream end of each segment. In the main stream channel, discharge was measured using velocity - depth profile methods, with a Marsh McBierney flow meter. Where flows were small at tributary sites, a salt injection technique was used, and a 5 gallon bucket and stopwatch were used to measure flow from the drains. Grab samples were collected for inorganic water analysis ($NO_2$+$NO_3$-N, $NH_4$-N, total Kjeldahl N, total Kjeldahl N-filtered, dissolved reactive P-filtered, total P and Cl). Field filtered samples were collected for dissolved analysis, while raw water samples were collected for analysis requiring digestions. All samples were $H_2SO_4$ acidified and transported on ice and later stored at 4°C.

### B. Sampling Procedures

Groundwater discharge features

Major groundwater discharge features (springs, seeps, drains) were identified during synoptic surveys and a subset was chosen for sampling on 19 Nov 2004 and 12 May 2005. Twenty-three unique discharge features were sampled; 6 were sampled on both sample dates. Samples were obtained through mini-piezometers and stilling wells. Samples for inorganic analyses ($NO_2$+$NO_3$-N, $NH_4$-N, total Kjeldahl N-filtered, dissolved reactive P-filtered, total P-filtered and Cl) were field filtered and $H_2SO_4$ acid preserved. Samples for pesticide residue analysis (Nitrogen and Phosphorus Pesticides and Chloroacetanilide Herbicide Metabolites) were collected in 1L amber-glass bottle. All samples were stored on ice while transported from the field to the lab. Dissolved gasses were harvested in the field by pumping induced ebullition according to the method of Browne 2004. Gas was transferred using a gas-tight 60 mL plastic syringe from the PIE device into an evacuated 15 mL crimp top serum bottles fitted with 20 mm butyl stoppers. A total of 60 mL of harvested gas at atmospheric pressure was compressed into the serum bottles. Gas samples were maintained in their over-pressurized state until analyzed (< 48 hr).

Baseflow discharge and water quality

Stream discharge was measured and inorganic water quality samples were obtained monthly at sites A, B, C, and D. Discharge was again measured by velocity - depth profile methods using with a Marsh McBierney flow meter. Parameters for inorganic analyses included $NO_2$+$NO_3$-N, $NH_4$-N, total Kjeldahl N, total Kjeldahl N-filtered, soluble reactive P-filtered, total P, total P-filtered, Cl, and suspended sediment. Samples were again preserved and iced consistent with standard protocols for individual analyses. On three occasions samples were obtained for pesticide residue analyses. Samples were collected in a 1L glass bottle and stored on ice until transported to the lab where they were stored at 4°C.

Runoff

Runoff events were sampled by protocols instituted by the USGS and University of Wisconsin-Platteville Pioneer farm site C. Thirty-five runoff events were sampled during 2003 and 2004 with analyses for inorganic surface water parameters ($NO_2$+$NO_3$-N, $NH_4$-N, total Kjeldahl N, total Kjeldahl N-filtered, soluble reactive P-filtered, total P, total P-filtered, Cl, and suspended sediment). In addition, water samples from 9 runoff events were collected for pesticide analysis (N and P pesticides and Chloroacetanilide Herbicide Metabolites).

## C. Analytical Procedure

Inorganics

Field measurements (temperature, pH, specific conductance, dissolved $O_2$ and total dissolved gas pressure) were obtained using a Hydrolab sonde and a Common Sensing total dissolved gas pressure ($P_t$) monitor. Chloride, $NO_2$+$NO_3$-N, $NO_2$, $NH_4$, and total Kjeldahl N (TKN) were analyzed using automated colorimetry(APHA 1995 methods 4500 E, F, H, and G.). ANC (acid neutralizing capacity) was analyzed by titration (APHA, 1995; method 2320B). Metals (Al, Ca, Mg, K, Na, Mn, Fe), Si, and S (reported as $SO_4$) were analyzed by inductively coupled plasma AES (APHA, 1995 methods 311B, 3111D, and 3129 B). These analyses were run at the University of Wisconsin - Stevens Point WEAL facility, which is State of Wisconsin certified for these analyses.

### Pesticide residues

Atrazine, atrazine metabolites, and other parent herbicide residues were analyzed by GC/MS (modified EPA method 8270) at the WEAL facility with an extraction method developed by the Wisconsin State Laboratory of Hygiene to isolate the more water soluble atrazine metabolites. WEAL is state certified to analyze these residues. Chloroacetanilide herbicide metabolites were determined using solid-phase extraction and high performance liquid chromatography/diode array detection as described by Zimmerman et al. (2000).

### Dissolved gases and groundwater age date assignments

Dry mole fractions of dissolved gasses (CFCs, Ar, $N_2$, $N_2O$) within PIE harvested gas samples were determined by gas chromatography according to the procedure described in Browne 2004 and Browne et al. 2007. Denitrified $N_2$ was determined as the excess between dissolved atmospheric-source $N_2$ and measured dissolved total $N_2$,using a four-step Henrys Law approach (Vogel et al. 1981, Böhlke and Denver 1995, Martin et al. 1995) detailed in Browne et al. (2007). "Initial $NO_3$-N," the amount of $NO_3$ in a groundwater sample prior to denitrification, was calculated as the sum of measured $NO_3$-N and denitrified $N_2$-N concentrations.

Groundwater recharge age-dates were estimated from dissolved CFC concentrations. Briefly, dry air mole fractions of CFC11, CFC12, and CFC113 at the time of recharge were calculated from dissolved CFC concentrations using the Henry's Law approach described in Plummer and Busenburg (2000). Dry air mole fractions of CFCs were then referenced to chronological records of CFC atmospheric mixing ratios to determine groundwater recharge age-dates. CFC dry air mole fractions exceeding that possible for the modern atmosphere were attributed to local environmental contamination and were excised from the data set. Where age-date estimates derived by multiple CFCs for an individual sample agreed closely (<5 years), the estimates were averaged to produce a "best" age-date estimate. CFC-based groundwater age dates were inferred for 23 samples, 17 unique groundwater discharge features. There was good agreement between CFC11, CFC12, and CFC113 for the first sample date. On the second sample date, CFC113 data could not meet QA/QC standards. (Once analyzed samples cannot be rerun, issues resolving the baseline for CFC113 were not identified until after the sample run; therefore only CFC11 and CFC12 data were used to calculate age-date.) There was good agreement between CFC11 and CFC12 for all other samples collected on the second sample date with the exception of 2 samples. For one sample the CFC12 concentrations exceeded those in equilibrium with the modern atmosphere and provided a substantially younger apparent age (about 15years) than CFC11 for the other sample CFC11 was substantially younger than CFC12 (by about 11 years). Because all three CFCs are relatively resistant to biological degradation under nonreducing conditions, we attribute this discrepancy to environmental contamination.

### D. Baseflow versus Runoff Comparison

Streamflow separation was performed using the Web-based Hydrograph Analysis Tool (Lim et. al., 2005; **http://pasture.ecn.purdue.edu/~what/**). The local minimum method was used to quantify baseflow and runoff using daily streamflow values obtained directly from the USGS website. To calculate baseflow pollutant loads we used water quality data from monthly grab samples and flow data generated by the baseflow separation. Total pollutant loads for runoff events were calculated for individual storm events based on flow-weighted composite samples and detailed streamflow measurements collected at the USGS gauging station. This however only accounted for 7% of the total streamflow volume, because the total runoff event volume was determined to be 14% this left a difference of 7% of flow that was still unaccounted for. In order to account for the remaining 7% of flow, we used the median concentration from flow-weighted composite runoff events to calculate the remaining portion of the runoff event pollutant loads.