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The seasonal dynamics of the stream sources and input flow paths of water and nitrogen of an Austrian headwater agricultural catchment

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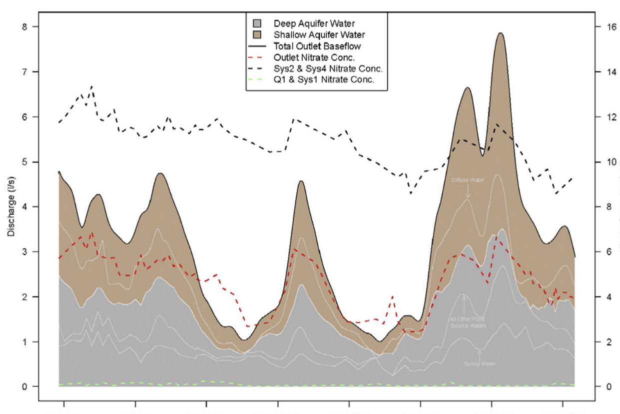
HIGHLIGHTS

- There is nitrogen seasonality in streams in headwater agricultural catchments.
- We measured the major nitrogen point inputs contributing to the stream.
- We applied an endmember mixing model for the source water seasonal dynamics.
- Tile drainage and the diffuse groundwater inputs had significant seasonal variability.
- Seasonality of the nitrate was due to the alternating aquifer source contributions.

GRAPHICAL ABSTRACT



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ABSTRACT

Our study examines the source aquifers and stream inputs of the seasonal water and nitrogen dynamics of a headwater agricultural catchment to determine the dominant driving forces for the seasonal dynamics in the surface water nitrogen loads and concentrations. We found that the alternating aquifer contributions throughout the year of the deep and shallow aquifers were the main cause for the seasonality of the nitrate concentration. The deep aquifer water typically contributed 75% of the total outlet discharge in the summer and 50% in the winter when the shallow aquifer recharges due to low crop evapotranspiration. The shallow aquifer supplied the vast majority of the nitrogen load to the stream due to the significantly higher total nitrogen concentration (11 mg-N/l) compared to the deep aquifer (0.50 mg-N/l). The main stream input pathway for the shallow aquifer nitrogen load was from the perennial tile drainages providing 60% of the total load to the stream outlet, while only providing 26% of the total flow volume. The diffuse groundwater input to the stream was the largest input to the stream (39%), but only supplied 27% to the total nitrogen load as the diffuse water was mostly composed of deep aquifer water.

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1. Introduction

Excessive discharges of nutrients to the aquatic environment have been found to adversely affect human health and aquatic ecosystems (Romstad et al., 1997; Walling et al., 2002). Mass algal blooms in rivers and lakes from an abundance of nitrogen and phosphorous can produce harmful toxins and encourage bacteria that subsequently reduce oxygen levels for fish stocks. This eutrophication of lakes, rivers, and coastal zones is currently one of the primary issues facing surface water environmental policy (Clercq, 2001). In response to public concern and the scientific evidence of the hazards of water pollution, many developed countries, including the European countries and the European Union (EU) as a whole, have enacted environmental legislation to combat the growing problem of water pollution.

Agricultural management and catchment conditions regulate the nutrient conversions and release into the groundwater and surface water. These include fertilizer application rates and timing, crop type and growth periods, soil type and composition, precipitation rates and seasonality, the size of the riparian area, and many others. Improved knowledge on these important conditions and processes will improve the accuracy of nutrient transport models and ultimately better target those processes that can best reduce excessive nutrients to the water bodies. Natural systems are inherently difficult to isolate and test specific processes to determine the effect and sensitivity of those specific processes to the response of the entire system. Consequently, identifying and determining the causes of recurring changes in the nutrient concentrations and loads over several years in a single catchment where many of the catchment conditions are kept the same (e.g. soils, land management, etc.) may be more appropriate than comparing multiple different catchments with varying catchment conditions over the same period.

One of these recurring nutrient changes over several years that many researchers have observed is the seasonal pattern of nitrogen concentration in streams that increase in winter and decrease in summer. This phenomenon has been observed on all sizes of streams and rivers from headwater streams to major rivers. There are several explanations in the scientific literature for the apparent seasonality of nitrate loads and concentrations. One explanation is attributed to higher in-stream nitrogen uptake and denitrification rates during the summer as compared to the winter (Mulholland et al., 2008; Peterson et al., 2001; Alexander et al., 2009). The second explanation is attributed to increased leaching from seasonal biochemical changes in the vegetation and soil microorganisms associated with certain source waters (Holloway and Dahlgren, 2001; Ocampo et al., 2006; Molenat et al., 2008; Arheimer et al., 1996; Burns et al., 2009). Many of these studies have attributed the riparian zone as the primary source of the seasonal biochemical changes and uptakes. Others have found that the seasonality is caused by changes in the relative source water contributions throughout the year without a clear impact from seasonal biochemical reactions (Martin et al., 2004; Grimaldi et al., 2004; Pionke et al., 1999). A final possible candidate is the seasonal agricultural land management associated with fertilizer application timing and crop growth when direct surface runoff is significant.

There are wide varieties of catchments. Some have unique characteristics that only exist in a few isolated locations, while others have typical catchment characteristics representative of broader regional catchments. We have chosen to investigate a headwater agricultural catchment that has typical characteristics of soils, land use, and precipitation for the region. These seasonal nitrate and total nitrogen concentrations have also been observed at our small headwater agricultural catchment called the Hydrologic Open Air Laboratory (HOAL) in Petzenkirchen, Austria (Fig. 1).

The goal of our study is to determine the primary mechanisms that cause the seasonal dynamics of the nitrogen loads and concentrations at the surface water outlet of a headwater agricultural catchment. We accomplished this goal through analyses of monthly input and output totals of water and nitrogen loads entering and exiting the catchment, point and diffuse input contributions of water and nitrogen to the surface waters, and finally the source water contributions to the catchment outlet.

2. Field site

The study was performed at the Hydrologic Open Air Laboratory (HOAL) catchment located in Petzenkirchen in Lower Austria, approximately 100 km west of Vienna (Fig. 2) (Blöschl et al., 2015). The catchment is about 66 ha in area with about 82% of arable land, 3% riparian forest, 5% planted trees with grass undergrowth, 8% grassland, and 2% impermeable surfaces (e.g. paved roads, buildings, etc.). It also has a first order stream that runs about 620 m through the catchment (Fig. 2).

The catchment area of 66 ha is defined as the topographic region where rainfall would flow over the surface and converge to the stream outlet gauge. The stream outlet gauge is named MW. 631 mm and 742 mm of precipitation fell during 2011 and 2012 respectively, while 133 mm and 124 mm left the catchment from surface waters for 2011 and 2012 respectively. The average discharge during these two years was 2.8 l/s and 2.6 l/s. There are six tile drainage systems along the stream named Sys1, Sys2, Sys3, Sys4, Frau1, and Frau2. Additionally, there are four known springs with two measured directly at the source (Q1 and K1) and two springs measured at a location 40 m down gradient of the actual springs before they enter the main stream (A1 and A2). There are also two locations on the edge of the riparian area that drain much of the overland flow during heavy rainfall events from the adjacent fields called erosion gullies (E1 and E2). Although the term spring may also refer to tile drainages that have perennial flow, springs in this study are defined as locations along the riparian area of the stream where water is visibly flowing out of the soil.

During normal baseflow conditions, water entering the stream at Sys4 will take approximately 3 to 4 h to reach the catchment outlet. During this time, the riparian area provides almost continuous shading for the stream. The depth of the water in the stream ranges from 5 cm in the upper end to 20 cm at the outlet. The HOAL exhibits general properties which are typical throughout the range of catchments of the prealpine area alongside the eastern Alps with intensive agriculture associated with the seasonality of rainfall, runoff, and drainage density (Merz and Blöschl, 2007).

Based on a detailed soil survey conducted in 2010, the soils throughout the catchment are generally classified as silt loam or more specifically as Cambisols that have 7.2% sands (0.51 coefficient of variation (CV)), 68.7% silts (0.11 CV), and 24.1% clays (0.30 CV) (Deckers et al., 2002). The Cambisols also have hydromorphic characteristics such as Stagnosols and Gleysols, and these types of soils cover almost 50% of the land of the federal province of Lower Austria. The soil survey found that the silt loam extends vertically at least 0.7 m below the surface throughout the catchment. A detailed geologic survey has not been performed in this catchment, but based on core samples from piezometers placed in and around the riparian area and production wells installed by the local farmers the silt loam extends down approximately 5 to 7 m below the surface where it meets a fractured siltstone unit. There is neither information about the thickness of the fractured siltstone unit nor what geologic units are below it. Due to the high clay and silt content of the soil, cracking of the soil occurs frequently during the dry summer months.

The deep aquifer is defined as the water contained within the fractured siltstone unit, while the shallow aquifer is associated with the water draining the shallow subsurface soil (i.e. the silt loam) (Fig. 3). The origin of the Q1 spring can be seen visually as this fractured siltstone, and subsequently the water from Q1 is used to define the water from the fractured siltstone unit. The chemical and hydrologic dynamics of the deep aquifer are distinctly different from water draining the shallow aquifer. The shallow aquifer water is primarily identified by the baseflow water from the perennial tile drainages (i.e. Sys2 and Sys4) as most of the tile drainages were installed between 1 to 1.5 m below

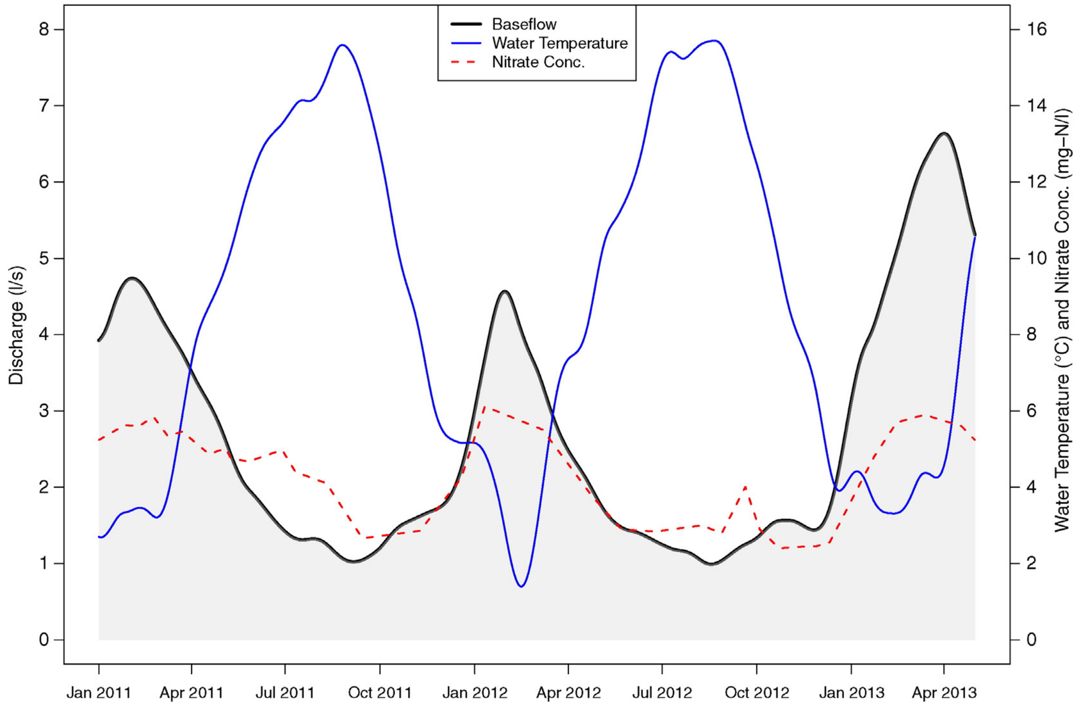

Fig. 1. The baseflow discharge, nitrate concentration, and water temperature of the HOAL catchment surface water outlet from early 2011 to mid 2013.

the surface. Distinct chemical characteristics of the deep aquifer as compared to the shallow aquifer include a much lower nitrate concentration, generally higher chloride concentration, much lower dissolved oxygen concentration, higher dissolved silica concentration, and higher ammonium concentration. The other distinct difference between the two aquifers is that the deep aquifer has a lack of hydrograph dynamics during rainfall events. At most discharge inputs to the stream, the associated hydrographs during rainfall events show clear increases

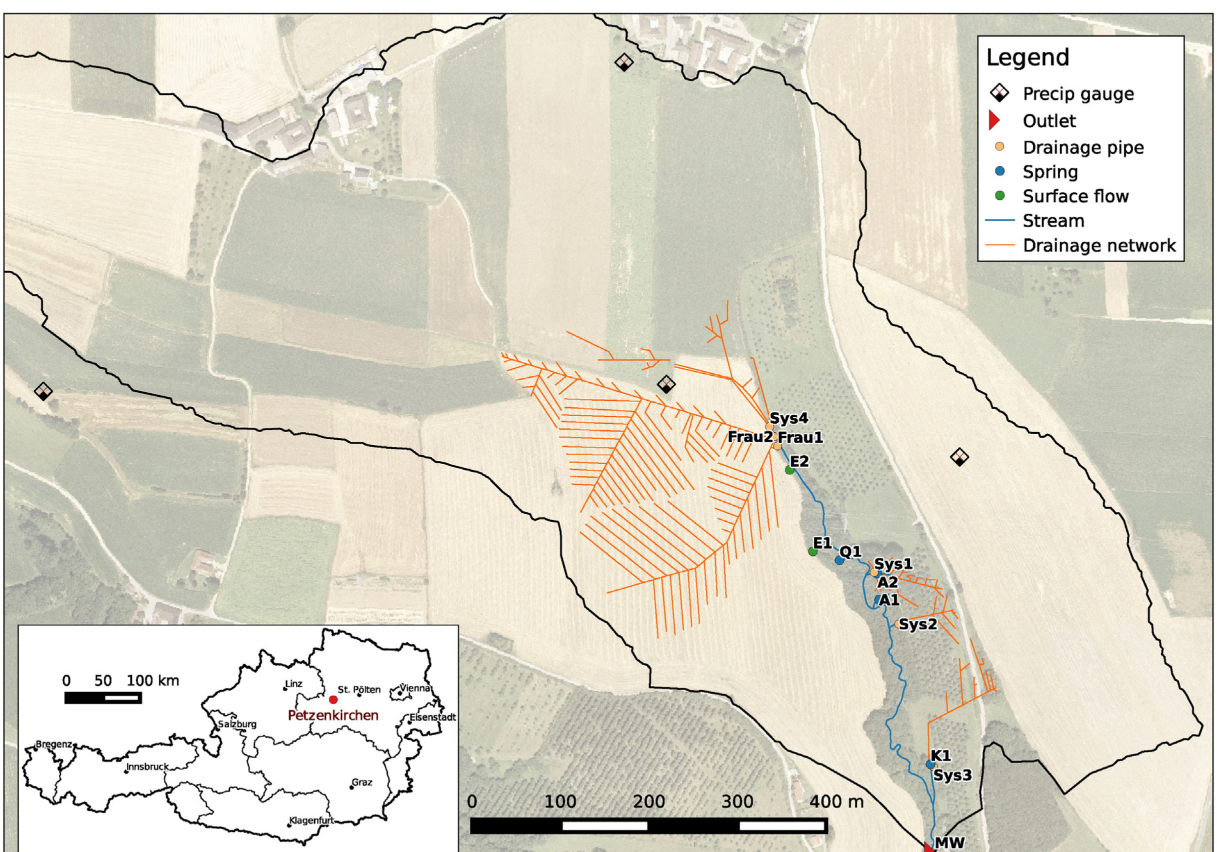

Fig. 2. Overview map for the HOAL catchment in Petzenkirchen, Austria.

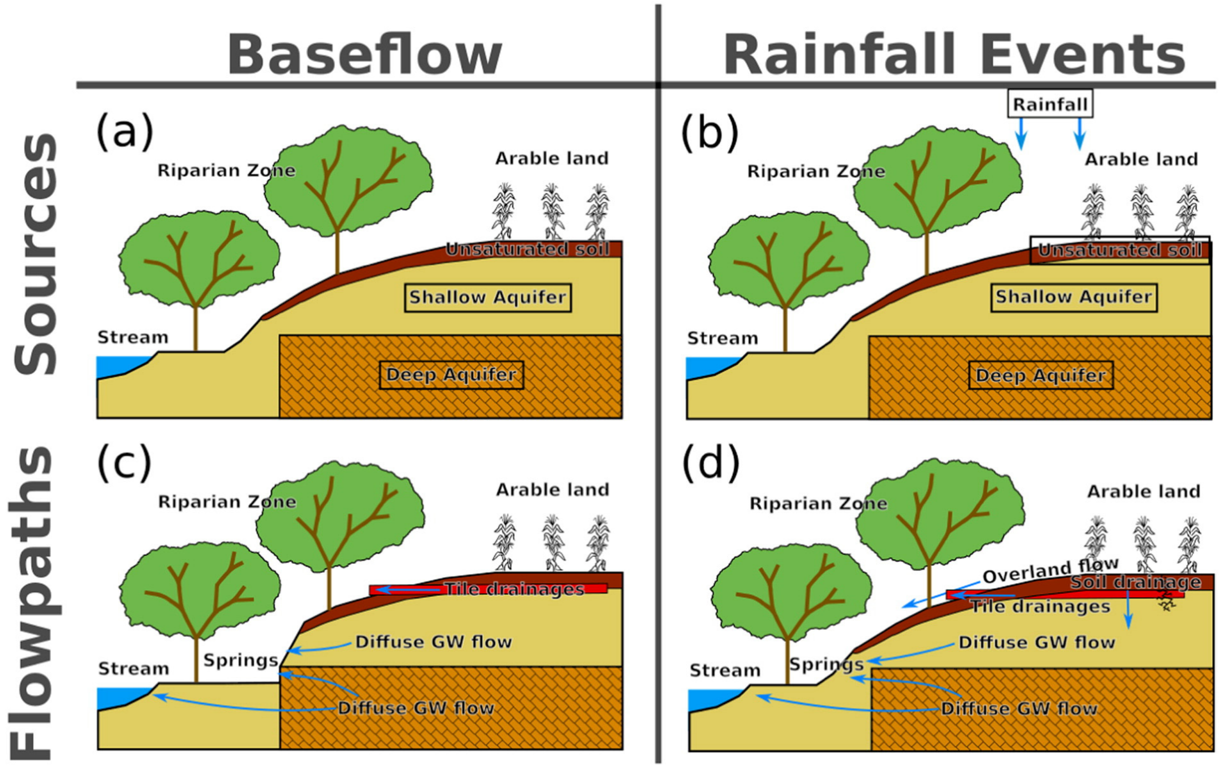

Fig. 3. A schematic diagram of the sources and pathways of water and nitrogen during baseflow and rainfall conditions in the HOAL catchment. Diagrams (a) and (b) illustrate the source reservoirs during baseflow and rainfall event conditions, and diagrams (c) and (d) illustrate the flowpaths of the water and nitrogen from the reservoirs to the stream during baseflow and rainfall event conditions. The main reservoirs for stream baseflow are the shallow aquifer and the deep aquifer, and in addition to the previously mentioned aquifers the unsaturated soil and the rainfall are the source reservoirs during rainfall events. Diagram (c) illustrates a slightly different cross-section where the deep aquifer outcrops into the riparian zone and manifests as a spring. This cross-section is representative of the location of the Q1 spring found in Fig. 2. In both (c) and (d), diffuse groundwater (GW) flows through the soil matrix and macropores are important flowpaths in addition to tile drainage discharge.

associated with the rainfall event magnitude. The inputs to the stream that are purely deep aquifer water (e.g. Q1) show no such dynamics during rainfall events and only change gradually associated with monthly or seasonal hydrologic conditions.

3. Methods

3.1. Available data

Manual grab samples were collected at all point discharge inputs along the stream including MW (Fig. 2). These water samples were collected once every 1–4 weeks during 2010–2013 and were analyzed for many physical and chemical parameters. The parameters used in this study include nitrate nitrogen (NO_3-N), total nitrogen (TN), total phosphorus (TP), dissolved silica, and discharge. Two 24-bottle autosamplers were installed at MW to collect samples of flow during rainfall events.

MW has all flow routed through an H-flume to capture both baseflow and runoff events. Water level was measured continuously using two independent devices that included a pressure sensor installed in a submerged pipe connected below the H-flume and an ultrasonic water level sensor installed within the H-flume. Both were used to estimate discharge from calibrated water level to discharge relationships (Shaw, 2011). The two independent water level devices were used to assess the uncertainty in the discharge estimation associated with the water level measurements.

In addition to discharge, MW was measured continuously for nitrate using an ion sensitive electrode (ISE). Other physical and chemical parameters were measured at MW and other sites, but are unrelated to this study. The ISE device had an offset calibration performed approximately once a month and a 2-point calibration was performed twice a year. Sys1, Sys2, Sys4, and Q1 flow at least 0.05 l/s throughout the year, while all of the other stations run dry or below 0.01 l/s for some time during the year. The piezometers installed along the riparian zone had water samples taken four times between 2011 and 2012 in addition to water samples in the stream in close proximity to the piezometer groups.

Three precipitation gauges located within the catchment used precision weighting systems to measure precipitation during 2011 and 2012. The precipitation gauges are distributed evenly throughout the catchment. The gauges measure near real-time (nRT) precipitation at 1 min intervals. No post-processed corrections to the precipitation data were performed. A meteorological station is located within the town of Petzenkirchen less than 1 km from the catchment and is maintained by the Federal Agency for Water Management, Institute for Land and Water Management Research (IKT). From 2011 to 2012, this station measured incoming solar radiation, sunshine hours, minimum and maximum temperature, minimum and maximum relative humidity, wind speed, wind direction, and precipitation at daily intervals.

Detailed land management information from a survey of the land owners was obtained for 2011–2012 and this information included the plowing, fertilization, sowing, and harvesting schedules for all parcels within the catchment.

3.1.1. Missing data

Every continuous measurement device had some periods without measurements. This can be attributed to device failure, transmission failure, or data storage failure. Regardless of the type of failure, data are either completely missing or of such low quality that they are unusable. The missing data were estimated to complete the analyses for this study.

During the period from 2011 to 2012, there were 126 runoff event hydrographs captured at MW that exceeded a rise in discharge above baseflow of 2 l/s. There were 9 additional runoff events that were not captured at MW due to equipment failure and identified based on the rainfall time series. There were 37 runoff events at MW that captured both water chemistry (i.e. chloride and nitrate) and discharge continuously out of the 135 total runoff events.

Rainfall data was missing from 2012-02-10 to 2012-03-25. Missing rainfall data were estimated from the daily rainfall data from the Petzenkirchen meteorological station. Missing event runoff volume data at MW were estimated from a log–log linear regression to the total rainfall associated with the event. Missing data of the rainfall and event runoff volumes did not overlap.

Missing data for baseflow parameters of any station (i.e. discharge and water chemistry) were estimated based on a normal linear regression to the outlet baseflow. Missing data for the runoff event parameters of any station were estimated based on a log–log linear regression to the event runoff volumes of the outlet. These differences in the type of regressions were used to ensure that the correlation had a relatively equal distribution throughout the range of the values.

3.2. Monthly water and nitrogen input and output components

The primary water and nitrogen inputs and outputs of the catchment were estimated for the years 2011 and 2012. The water components include precipitation, evapotranspiration (ET), and surface water discharge. Other water components like deep groundwater seepage were not included due to lack of data. The nitrogen components include fertilizer applications, crop harvests, and surface water nitrogen load. Other nitrogen components like denitrification were not included due to lack of data.

Precipitation was measured using the precipitation gauges described in Section 3.1. Discharge was aggregated at the catchment outlet for the total volume of water leaving the catchment per month. Daily ET was estimated using the procedures developed by the Food and Agricultural Organization of the United Nations (FAO) for crop ET (ET_c) (Food and Agriculture Organization of the United Nations, 1998). Daily reference ET (ET_o) was estimated for 2011 and 2012 from the meteorological data of the Petzenkirchen station from Section 3.1 using the FAO procedures. A daily time series of crop coefficients (K_c) were assigned to each parcel of land within the catchment based on the land management data and the procedures outlined in the (Food and Agriculture Organization of the United Nations, 1998).

The event runoff volumes were separated from the complete hydrograph from 2011 to 2012 by constructing a straight line from the initial rise of the hydrograph to the inflection point at the trailing limb of the hydrograph on a semi-log plot (Shaw, 2011). Baseflow nitrate loads were estimated by assuming that the baseflow nitrate concentrations during the events were the same as the baseflow concentrations before the events. The prior baseflow nitrate concentrations were multiplied by the extracted baseflow discharges to estimate baseflow nitrate loads.

Fertilization and harvest data were gathered about the land management within the catchment and converted to kg of TN (Wendland et al., 2011). Pig manure slurries were applied to the fields in addition to mineral fertilizers. The surface application of manure slurry as performed in the HOAL catchment volatilizes significant amounts of ammonia from the slurry into the atmosphere. Many studies have measured or estimated the ammonia volatilization from manure slurry and have found that there is a wide range in the rates (Huijsmans et al., 2003; Misselbrook et al., 2004; Mkhabela et al., 2009; Gordon et al., 2001; Chantigny et al., 2004; Moal et al., 1995). We decided to assume that 35% of the manure application was lost as ammonia volatilization based on both (Huijsmans et al., 2003; Misselbrook et al., 2004), because the value is consistent and fairly average throughout the literature. Ammonia volatilization losses were removed from the total fertilizer estimate presented in the manuscript.

Total nitrogen was measured for the manual grab samples, but only nitrate was measured continuously during the bulk of the rainfall events. The grab sample total nitrogen data was then correlated to nitrate using a normal linear regression. The resulting equation from the linear regression was used to estimate total nitrogen from the continuous nitrate data for rainfall events. The R2 and normalized root mean square error (NRMSE) of the linear regression was 0.996 and 0.045 respectively. The mean ratio of nitrate load to total nitrogen in the grab samples was 0.93 from 58 samples.

3.3. Flowpath input assessment

The flowpaths were categorized by how the water physically flows into the stream. Some flowpath inputs are self-explanatory to the descriptions given in earlier sections (i.e. tile drainages, springs, surface waters, and the erosion gullies). The one additional stream input is the diffuse groundwater flowpath. The net diffuse groundwater input was defined as the residual difference of the total discharge from the outlet (MW) to the sum of all the point inputs to the stream. The net diffuse input calculation makes the assumption that no water is flowing from the stream to the groundwater.

Mean yearly concentrations were estimated for all of the inputs by dividing the total yearly loads by the total yearly discharge. The seasonal flowpath input contribution assessment used grab samples from 2010 to 2013 for all input locations and an estimated baseflow time series extracted and smoothed from the continuously monitored discharge at MW.

In both the yearly lumped baseflow assessment and the seasonal flowpath input contribution assessment, water samples were taken at locations directly before these inputs would enter the stream. As the stream is approximately 620 m long, some inputs may spend longer or shorter periods of time in the stream than others. For example, Sys4 is the initial inflow to the stream and subsequently the water from Sys4 spends the longest period in the stream, while A1 and A2 enter at approximately halfway. Past tracer experiments within the stream (unpublished) and much scientific literature has shown that streams frequently exchange water between the groundwater and the stream water itself (Covino et al., 2011; Harvey and Bencala, 1993; Payn et al., 2009; Lowry et al., 2007; Covino and McGlynn, 2007; Briggs et al., 2012; Westhoff et al., 2007). Consequently, the pathway assessment may sum all of the masses at the input locations and subtract that from the total mass at the outlet to determine a net diffuse groundwater input to the stream, but in reality the true proportions of the input pathways to the outlet will be lower in proportion to the distance the water has traveled. The diffuse groundwater input contribution to the outlet on the other hand will be higher due to the losses of the other pathways and the gains from the groundwater.

Tile drainages are typically installed in the shallow subsurface, consequently in our catchment they would normally drain the shallow aquifer water. This appears to be true at all locations except one. Although the water at Sys1 flows out of a drain pipe, the water flowing out of Sys1 is chemically and dynamically water from the deep aquifer rather than the shallow aquifer. Likewise, not all springs are from the deep aquifer. Chemically and dynamically, the water from K1 is distinct from the shallow aquifer. From the historic maps, the location of K1 has a corresponding drainage system associated with it. The original outflow drainage pipe of K1 may have either collapsed or had been removed in the past, nevertheless flow is still routed to the original outlet location and currently manifests as a spring. A1 and A2 appear to be chemically and dynamically a combination of both the shallow and deep aquifer.

3.4. Baseflow source separation assessment

The end member mixing analysis (EMMA) performed on the outlet baseflow used mass balance equations for a two end member EMMA (Exner-Kittridge et al., 2014). The aggregated nitrate concentrations of known deep aquifer inputs (i.e. Q1 and Sys1) and the perennial tile drainages (i.e. Sys4 and Sys2) were used as the two end-member concentrations for the deep aquifer and the shallow aquifer respectively.

$$Q_{DA} = Q_{MW}\left(\frac{C_{MW} - C_{SA}}{C_{DA} - C_{SA}}\right) \tag{1}$$

where Q_{DA} is the deep aquifer water contribution at MW in l/s, C_{MW} is the concentration of nitrate at MW in mg-N/l, C_{SA} is the end-member concentration of nitrate of the shallow aquifer water in mg-N/l defined above as the aggregated flow proportional concentration of the perennial tile drainages, and C_{DA} is the end-member concentration of nitrate of the deep aquifer water in mg-N/l defined above as the aggregated flow proportional concentration of the deep aquifer point discharges. Eq. (1) was applied at every time period when grab sample data with discharges and nitrate concentrations were available.

3.5. Uncertainty estimations

Uncertainty in yearly and monthly rainfall aggregates are due primarily to the spatial heterogeneity of rainfall distribution (Grayson and Bloschl, 2001). Assuming that the available rainfall gauges are distributed evenly throughout the catchment, a basic estimate of spatial uncertainty in rainfall distribution is the standard deviation of the yearly totals of the individual precipitation gauges. As described in Section 3.1.1, the missing rainfall data was filled from rainfall data from the Petzenkirchen weather station. As the amount of missing data was a little over a month, the uncertainty estimates associated with the Petzenkirchen data was determined by aggregated monthly comparisons of the HOAL data to the Petzenkirchen data for 2012. The root mean square error (RMSE) between the HOAL data and the Petzenkirchen data of these months was used for the uncertainty values.

ET_c uncertainty was estimated by comparing the yearly and monthly ET_c and ET aggregates from estimates of an eddy covariance station (ET_{eddy}) installed within the catchment. The eddy covariance station was not installed until August 2012, so ET_c and ET_{eddy} could be compared for the end of 2012 through 2013. The RMSE between the monthly totals of the ET_c and ET_{eddy} for the available months were used for the uncertainty values.

The discharge uncertainty for the monthly aggregations was estimated from duplicate continuous water level measurements acquired at MW. The estimated discharge from the pressure sensor water level was compared to the ultrasonic sensor estimated discharge, and the average normalized difference between the estimates of the two devices was used as the value of uncertainty.

The uncertainty for the continuous measurements of nitrate were estimated by comparing the field calibrated measurements of nitrate to the periodic grab sample nitrate concentrations from laboratory measurements. Differences in the concentrations were made at all grab sample times and linear interpolations were performed during the periods between the grab sample times to create a continuous series of nitrate concentration differences. These differences were normalized to the continuous nitrate measurements from the ISE devices and aggregated monthly to estimate the monthly nitrate concentration uncertainty.

Uncertainty for the fertilizer applications and crop uptake were not estimated due to a lack of information on the uncertainty of the associated data.

4. Results

The air temperature at the Petzenkirchen weather stations and the outlet water temperature from mid-2010 to the end of 2013 are shown in Fig. 4. Superimposed onto the temperatures are the nitrate concentrations of the deep aquifer point inputs (i.e. Q1 and Sys1), the shallow aquifer point inputs (i.e. Sys2 and Sys4), and the catchment outlet (i.e. MW). The outlet discharge during the summer and winter periods are about 1.0 and 4.5 l/s respectively, and the nitrate concentrations are about 2.7 and 6.0 mg-N/l. The yearly cycles of temperature are clearly seen and are consistent throughout the several years and range from 2 to 16 °C. Linear regressions of nitrate concentrations to discharge and water temperature for all available data from mid-2010 to the end of 2013 are shown in Fig. 4. A smaller subset of the data is also illustrated for the nitrate to water temperature regression from early 2011 to April 2013.

The monthly totals of the main water budget components are shown in Fig. 6. Precipitation is generally distributed around the summer months, but winter months can also provide significant amounts of precipitation. Baseflow dominated the total surface water outflow from 2011 to 2012 with 82% as compared to event flow from 2011 to 2012. Two rainfall events in mid-January of both years accounted for 56% of total event flow volume for both years. ET_c tends to follow the incoming solar radiation intensity and the number of sunshine hours throughout the year. Discharge on the other hand is highest around winter and spring when ET is low and precipitation is moderate and slowly diminishes through to autumn.

Fig. 7 shows the three main nitrogen components that were aggregated monthly. Fertilizer applications primarily occur in spring and autumn and crop nitrogen uptake follows the pattern of ET_c. Similarly, the total monthly outlet nitrogen load followed the seasonal pattern of the total monthly runoff volume. Similar to the baseflow water volume contribution, the contribution of the baseflow TN load was 73% compared to event TN load from 2011 to 2012. During most of the year, the baseflow accounts for nearly all of the total discharge and nitrate load.

The yearly pathway nitrogen concentrations and contributions to the outlet for 2011 and 2012 are shown in Table 1. For both years, the net diffuse discharge has the highest contribution to the outlet with about 38%, while the perennial tile drainages and the deep aquifer point discharges contribute an equal amount to the outlet and most of the remaining water (i.e. about 26%). The perennial tile drainages contribute most of the TN load to the outlet (i.e. about 60%) followed by the diffuse discharge (i.e. about 26%). The high contribution of the perennial tile drainages are attributed to the relatively high TN concentrations of over 11 mg/l compared to the other water pathways.

The outlet baseflow dynamics from mid-2010 to the end of 2013 is shown in Fig. 8. As can be inferred from the discharge in Fig. 8, the summers of 2010 and 2013 were substantially wetter than 2011 and 2012. The precipitation amounts from the Petzenkirchen meteorological station for 2009, 2010, and 2013 were 1020, 735, and 930 mm. While 2009 and 2013 were exceptionally wet years, 2010 had approximately the same amount of precipitation as 2012 only distributed differently within both years. The nitrate concentration at the outlet oscillates closely to the rise and fall of the baseflow during these years. The nitrate concentrations of the tile drainages and deep aquifer point pathways (i.e. Q1 and Sys1) do not show a similar distinctive oscillation. Although the input pathway nitrate concentrations do not show a seasonal trend, the baseflow contributions of these input pathways do show a change associated with the magnitude of the outlet baseflow. Both the tile drainages and the net diffuse discharge input dominate the baseflow contribution changes over the years. While the contribution of the tile drainages to the total discharge changes very little throughout the year (i.e. 25–30%), the contribution of the diffuse input has a substantially larger range (i.e. 0–50%).

The results of the baseflow EMMA from the perennial tile drainages and the deep aquifer point pathways end-member concentrations are

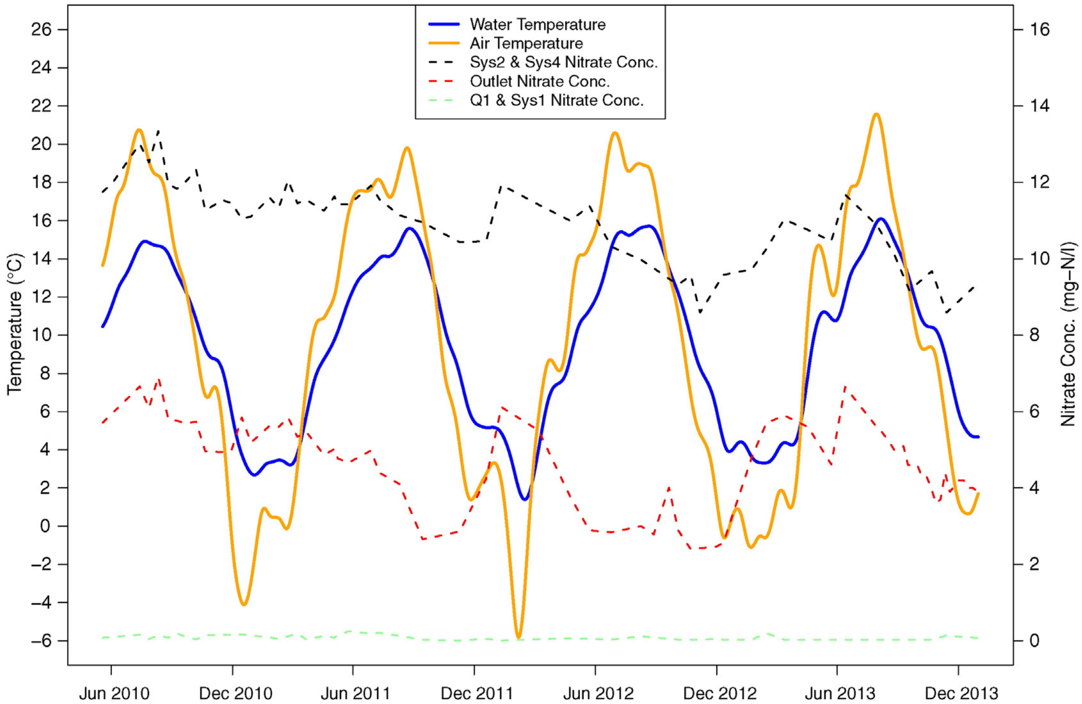

Fig. 4. Air and stream water temperature overlaid with the nitrate concentrations of the end-members and MW during mid-2010 to the end of 2013.

shown in Fig. 9. The deep aquifer diffuse water, contrary to the deep aquifer point pathways, does follow a similar pattern to the overall baseflow, but the pattern is less pronounced than the shallow aquifer water. Most of the additional deep aquifer water originates in the net diffuse discharge, while the additional shallow aquifer water originates from both the other point discharges and the net diffuse discharge. In the baseflow of the summers of 2011 and 2012, the deep aquifer constitutes almost all of the other point discharges including the net diffuse discharge. The deep aquifer water typically contributes 75% of the total outlet discharge in the summer and 50% in the winter.

5. Discussion

Agricultural land management could impact the seasonal nitrogen concentrations and loads by fertilization flowing directly from the soil surface shortly after application. Direct discharge of fertilizer from the unsaturated zone into the surface waters occurs mainly by heavy rain events shortly after fertilizer applications. Catchments that have flashy hydrographs and have little to no baseflow throughout the year would have the majority of the yearly nitrogen load from runoff events and subsequently the fertilizer discharge into the surface waters may have a significant contribution (David et al., 1997; Cirmo and McDonnell, 1997). Although runoff events directly after fertilizer applications do occasionally occur in the HOAL, runoff events do not contribute the majority of the TN load to the outlet, and the seasonality of the fertilizer applications do not fully coincide with the nitrogen loads (Fig. 7). Rather in the HOAL, the fertilizer applications supply the long term load into the solute reservoirs, and only multi-year reductions in the fertilizer applications would gradually reduce the solute mass in the reservoirs and subsequently the load into the stream.

If in-stream and/or seasonal biochemical reactions would be a source or sink for the nitrogen, then the seasonal temperature and vegetation growth should be the primary factors for these biochemical reactions. The summers of 2010 and 2013 were unusually wet, but they were not unusually cool (Fig. 4) and had normal crop and riparian growth patterns. Nevertheless, the summers of 2010 and 2013 did have relatively high nitrate concentrations more closely associated with the typical winter periods. In-stream denitrification has been shown to be dominant in streams with very low nitrate concentrations (e.g. less than 0.1 mg/l), while in-stream biochemical reactions in agricultural streams with elevated nitrate concentrations (e.g. greater than 1 mg/l) would have a substantially lower impact on the total nitrogen load and subsequently the in-stream nitrate concentrations (Peterson et al., 2001; Mulholland et al., 2008).

The seasonal baseflow dynamics from mid-2010 to the end of 2013 are dominated by changes in the contributions by the tile drainage water and the net diffuse water (Fig. 8). The deep aquifer point discharges show little seasonal changes other than a slight increase in mid-2013. Although the pathway contributions change seasonally, the concentrations of the perennial tile drainages and the deep aquifer point discharges have little seasonality.

The evidence indicates that the seasonal volatility of the outlet nitrate concentration is attributed primarily to the changing input pathway and source contributions rather than the earlier explanations (e.g. fertilizer applications, in-stream denitrification, biochemical reactions, etc.). This is especially clear from the wet summers of 2010 and 2013. 2011 and 2012 had relatively normal seasonal patterns of temperature and precipitation, which caused a more typical pattern of high baseflow discharges in the winter and spring and low baseflow

Table 1
The baseflow contributions of the various input pathways to the outlet for 2011–2012. Additionally, the yearly average concentrations of nitrate, total nitrogen, and chloride are listed for each pathway category. The ratio values are the yearly loads of the input types normalized to the yearly load of MW (unitless). The concentrations are in mg/l-N. Other point discharges include all of the point inputs to the stream excluding Sys2 and Sys4.

			MW	Sys2 + Sys4	Deep aq	Other point inputs	Diffuse
2011	Ratios	Flow	1.00	0.26	0.27	0.10	0.39
		NO_3	1.00	0.60	0.01	0.12	0.27
		TN	1.00	0.59	0.03	0.12	0.27
	Conc	NO_3	4.81	11.09	0.11	5.44	3.36
		TN	5.00	11.40	0.48	5.82	3.49
2012	Ratios	Flow	1.00	0.25	0.28	0.10	0.38
		NO_3	1.00	0.62	0.01	0.11	0.26
		TN	1.00	0.61	0.03	0.11	0.26
	Conc	NO_3	4.46	10.81	0.12	5.00	3.00
		TN	4.64	11.09	0.49	5.30	3.19

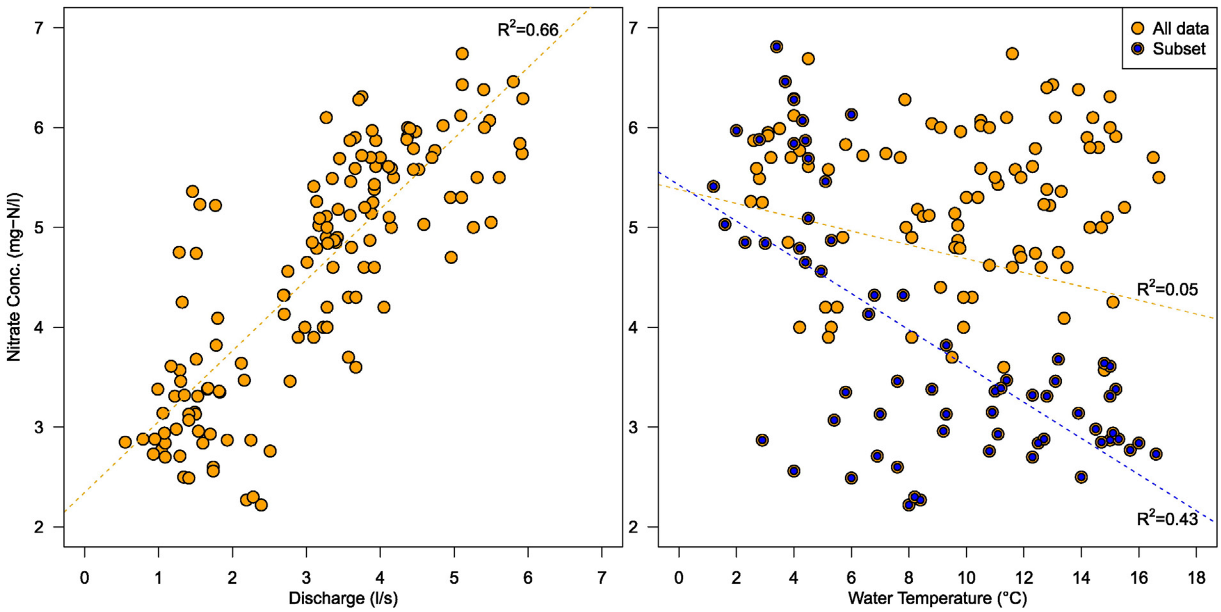

Fig. 5. Linear regressions of nitrate concentrations to discharge and water temperature. All data includes the years from mid-2010 to the end of 2013, while the subset includes only data from early 2011 to April 2013 represented by Fig. 4.

discharges in summer and autumn. 2010 and especially 2013 had exceptionally wet summers, yet the outlet nitrate concentrations were similarly high as they were in the winters of 2011/2012 and 2012/2013.

Linear regressions of nitrate concentrations to discharge and water temperature for all available data from mid-2010 to the end of 2013 show a clear positive correlation of nitrate concentration to discharge (R2 of 0.66) and practically no correlation to water temperature (R2 of 0.05) (Fig. 5). Although, if the period of data was from early 2011 to mid 2013 associated with Fig. 4 then the correlation of temperature to nitrate concentration would be more prominent with an R2 of 0.43. During years with typical seasonal patterns, discharge and water temperature can have a strong relationship, but at least in our catchment this correlation does not equate to causation.

It is important to emphasize that the net diffuse input was estimated as the residual amount of water and solute load from the total input pathways to the stream. These pathway results assume that diffuse discharge and solutes are only entering the stream as opposed to both diffuse discharge entering the stream and stream water exiting the stream into the groundwater. Based on unpublished tracer tests performed on this stream and from numerous studies on other streams, stream water is also flowing into the groundwater to some extent that changes throughout the year (Covino et al., 2011; Payn et al., 2009; Westhoff et al., 2007; Briggs et al., 2012; Lowry et al., 2007). One consequence of this interaction is that the gross diffuse groundwater input to the stream is higher than the net diffuse value published here and that the other point inputs have a lower gross contribution to the

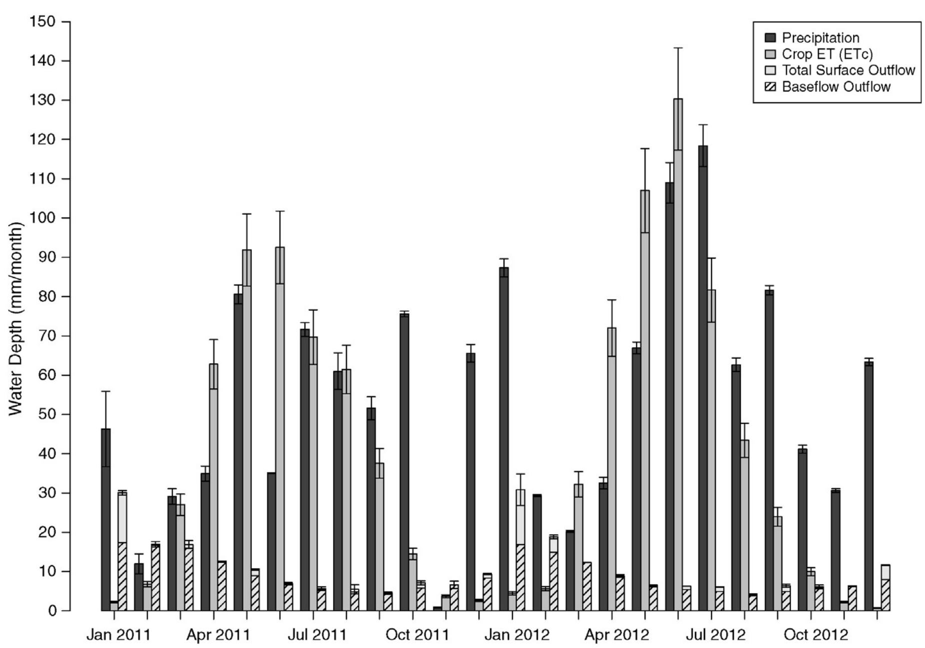

Fig. 6. The monthly totals of the water budget components (i.e. precipitation, crop ET, and surface water outflow) to the contributing area above the catchment outlet (MW). The bracketed lines at the top of each monthly bar are the uncertainties in the form of standard deviations.

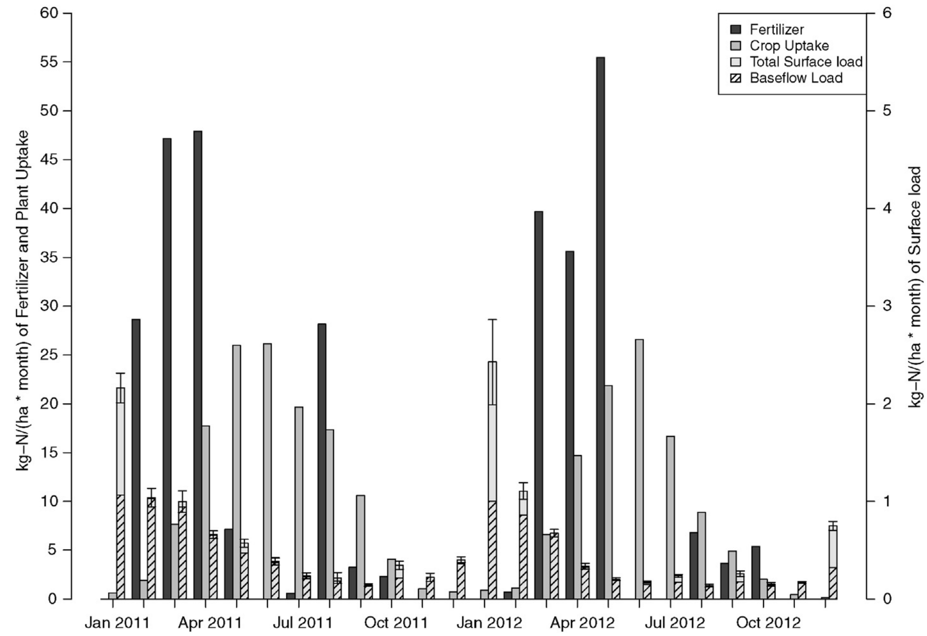

Fig. 7. The monthly totals of the nitrogen budget components that could be estimated on a monthly basis (i.e. fertilization, crop nitrogen uptake, and surface water load outflow) to the contributing area above the catchment outlet (MW). The bracketed lines at the top of the surface load bar are the uncertainties in the form of standard deviations.

stream as a function of distance from the outlet. The other consequence is that any biochemical reactions that do occur in the stream that reduce the nitrogen loads are manifested in the net diffuse load estimation.

The two end-member mixing analysis performed on the catchment outlet differentiates the two primary baseflow source components (i.e. deep and shallow aquifer). The results from Fig. 9 show that most of the contents of the net diffuse water is deep aquifer water. This can also be seen in the yearly average nitrate concentration of the net diffuse water in Table 1. Although we did not expect such substantial volatility in the deep aquifer water from our experience with the known point discharges of the deep aquifer water along the stream (i.e. Q1 and Sys1), the EMMA results do show that the total deep aquifer discharge throughout the year does change relative to the total baseflow. We do see some increases in the discharge of Q1 and Sys1 over the years, but significantly lower volatility than the estimated deep aquifer discharge from the EMMA. This result should not be surprising as a higher hydrostatic pressure exerted by the shallow aquifer on the deep aquifer should increase the discharge from the deep aquifer. Indeed, a correlation using a normal regression between the total baseflow and the

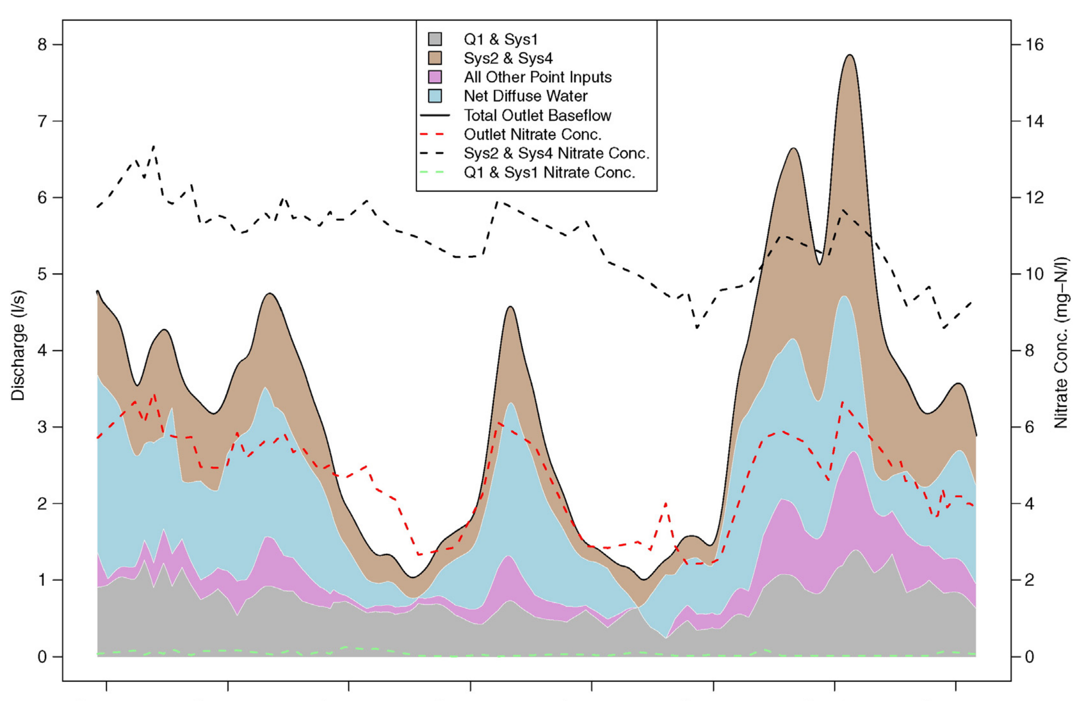

Fig. 8. The baseflow input pathways as a proportion of the total outlet baseflow. Strong seasonal dynamics are shown in the surface, tile drainage, and net diffuse waters. Q1 and Sys1 have less pronounced seasonal dynamics. The dominant end member nitrate concentrations of the perennial tile drainages and deep aquifer point discharges bound the outlet concentration.

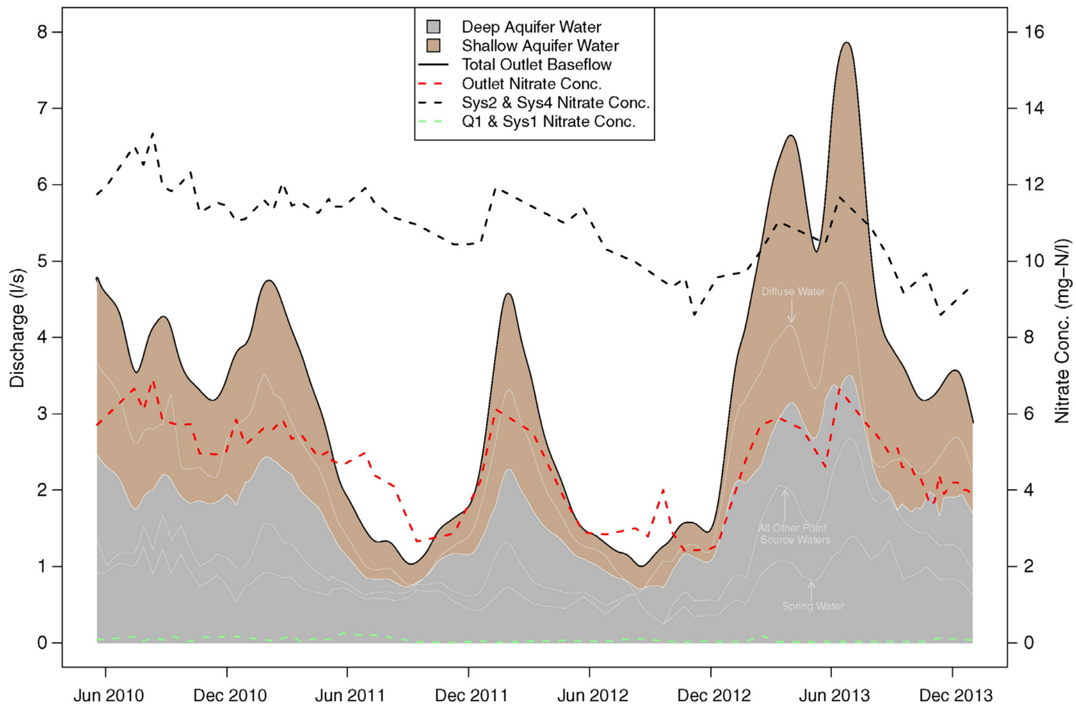

Fig. 9. The baseflow source components of the outlet assuming that the perennial tile drainage concentrations define the shallow aquifer concentration and the deep aquifer point discharges define the deep aquifer concentration. The outlines of the input pathways from Fig. 8 are shown in light gray for reference.

estimated deep aquifer water component has a very high positive correlation with an R2 and NRMSE of 0.98 and 0.06 respectively.

If the solute concentrations at the outlet of the catchment are primarily due to the changing source and pathway contributions, then the traditional hydrologic conceptual model of catchments that have large distinct reservoirs of contributing water is consistent with the low solute concentration fluctuations of the source waters. If the catchment source water reservoirs are large enough, then the impact of individual rainfall events, fertilization applications, and seasons on the total solute concentration of the entire reservoir should be minimal. In order to reduce the overall nitrogen load to the surface waters in these headwater agricultural catchments, long-term reductions in fertilizer applications would be needed rather than changes in the seasonal application rates.

The major source of uncertainty in interpretation is related to the impact of the riparian zone. In addition to some of the above studies related to the seasonal nitrate concentrations and loads, many studies have also found that riparian zones contribute significant amounts of water to the total surface water outflow (McGlynn and McDonnell, 2003; Hooper et al., 1998; Burns et al., 2001). Although, these studies tend to have study areas in more natural environments with well-developed riparian zones rather than agricultural areas with limited riparian zones. Water samples from within the piezometers installed within the riparian zone indicate that the riparian zone water has similar nitrate and dissolved oxygen concentrations as the deep aquifer water. From this nitrate concentration similarity, the identification of the source contributions of the net diffuse water from the deep aquifer or the riparian zone would be uncertain. A mixture of riparian zone water and deep aquifer water could explain the contradiction between the lack of significant seasonality in the measured deep aquifer point discharges and the clear seasonality of the estimated deep aquifer water from the EMMA. Nevertheless, other solutes measured in the riparian piezometers do not coincide with those of the estimated net diffuse water concentrations. For example, the average concentrations of TP and dissolved silica were 0.40 mg/l and 19.9 mg/l for the riparian piezometers, 0.04 mg/l and 30.0 mg/l for the net diffuse water, and 0.05 mg/l and 35.5 mg/l for the deep aquifer point discharges. Consequently, the contribution of the riparian water in the soil matrix to the stream water appears to be minimal.

The monthly nitrogen loads were dominated by the total monthly runoff volumes. The diffuse groundwater discharge into the stream had the highest contribution to the total yearly flow with 38% and was followed by the perennial tile drainages and deep aquifer point discharges with about 26% each. However, the majority of the nitrogen load contribution (60%) came from the perennial tile drainages due to their high nitrogen concentrations.

The monthly water and nitrogen volumes, the pathway contributions, and the source contributions indicate that the seasonality in the nitrate concentration is primarily due to the alternating input pathway contributions and ultimately the source contributions throughout the year. In-stream denitrification, biochemical reactions, and fertilizer application timings were not found to be the significant processes in the seasonality of the surface water nitrogen concentrations and loads.

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