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Diel patterns in coastal-stream nitrate concentrations linked to evapotranspiration in the riparian zone of a low-relief, agricultural catchment

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Abstract:

Evapotranspiration (ET) can cause diel fluctuations in the elevation of the water table and the stage in adjacent streams. The diel fluctuations of water levels change head gradients throughout the day, causing specific discharge through near-stream sediment to fluctuate at the same time scale. In a previous study, we showed that specific discharge controls the residence time of groundwater in streambed sediment that, in turn, exerted the primary control on NO_3^- removal from groundwater passing through the streambed. In this study, we examine the magnitude of diel specific discharge patterns through the streambed driven by ET in the riparian zone with a transient numerical saturated–unsaturated groundwater flow model. On the basis of a first-order kinetic model for NO_3^- removal, we predicted diel fluctuations in stream NO_3^- concentrations. Model results indicated that ET drove a diel pattern in specific discharge through the streambed and riparian zone (the NO_3^- removal zones). Because specific discharge is inversely proportional to groundwater travel time through the NO_3^- removal zones and travel time determines the extent of NO_3^- removal, diel changes in ET can result in a diel pattern in NO_3^- concentration in the stream. The model predictions generally matched observations made during summertime base-flow conditions in a small coastal plain stream in Virginia. A more complicated pattern was observed following a seasonal drawdown period, where source components to the stream changed during the receding limb of the hydrograph and resulted in diel fluctuations being superimposed over a multi-day trend in NO_3^- concentrations. Copyright © 2013 John Wiley & Sons, Ltd.

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INTRODUCTION

The flux of nitrogen (N) from groundwater contaminated by agricultural or waste-disposal practices has been implicated in the degradation of numerous surface-water bodies by eutrophication (Lowrance *et al*., 1983; Burt *et al*., 1993). The degree to which NO_3^--rich groundwater interacts with the biologically active subsurface and experiences the ameliorating process of denitrification (microbial reduction of NO_3^- to N_2) depends upon a number of hydrological attributes (Cirmo and McDonnell, 1997; Clément *et al*., 2003). For denitrification to decrease the flux of NO_3^- to surface waters, groundwater must reside for some time in an oxygen-depleted, organic-rich zone of biological activity (Lowrance, 1992). Under these conditions, increasing residence time, or decreasing flow rate, reduces the amount of NO_3^- entering the stream (Willems *et al*., 1997; Tesoriero *et al*., 2005; Gu *et al*., 2007).

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The balance between the rates of microbial denitrification and of groundwater flow determines the extent of NO_3^- reduction (Ocampo *et al*., 2006). *Gu et al*. (2007) found that specific discharge through intact streambed sediment cores strongly controlled the breakthrough of NO_3^- from the cores; slower rates of simulated groundwater seepage resulted in lower NO_3^- concentrations discharged from the sediment. At the field scale, variability of NO_3^- concentrations in streambed seepage water has been clearly tied to the magnitude of specific discharge through the streambed (Flewelling, 2009; Flewelling *et al*., 2011).

Because temporal patterns in specific discharge affect the residence time of groundwater in denitrification zones, processes, such as the passage of flood waves, that cause transient shifts in head relationships have been shown to affect the export of NO_3^- from groundwater systems (Gu *et al*., 2008a). Using flood pulses of the magnitude seen in long-term stage hydrographs (Mills *et al*., 2008), reactive-transport modelling demonstrated that these changes in stream stage were adequate to alter the magnitude of NO_3^- flux from streambed sediment (Gu *et al*., 2008a). Given the demonstrated effect of transient hydraulic gradients through experimental columns and reactive-transport modelling on the extent of denitrification in streamed sediment, the question of how other mechanisms of hydraulic change might impact N cycling arose.

Transient processes other than storms can also influence stream stage (Gribovszki *et al.*, 2008). Vegetative water demand causes lowering in water-table elevation in a daily cycle (White, 1932; Tabacchi *et al.*, 2000; Schilling, 2007). Generally, water-table elevation reaches its lowest point near sunset and rebounds to its highest elevation by early morning (White, 1932). The resulting alteration in hydraulic head gradients has been quantitatively linked to diel patterns in stream discharge (Czikowsky and Fitzjarrald, 2004). We sought to determine if diel changes in groundwater discharge that are driven by evapotranspiration (ET) were of sufficient magnitude to generate a diel oscillation in NO_3^- concentration in the Cobb Mill Creek (CMC).

Modest diel patterns in stream NO_3^- concentrations have been observed in concert with diel cycles in temperature and dissolved oxygen and chlorophyll-*a* concentrations and attributed to high rates of water-column algal productivity and nutrient uptake (Pellerin *et al.*, 2009). Extreme diel O_2 and CO_2 dynamics have been documented in streams and recently connected to diel NO_3^- patterns as well, but only under the extreme situations of subtropical, eutrophic streams (Harrison *et al.*, 2005) or in a hot, semi-arid, sewage-impacted river (Pellerin *et al.*, 2009). More subtle diel patterns in stream chemistry have been reported, but those patterns have not been elucidated clearly to be results of water-column or sediment processes. Diel patterns in stream NO_3^- concentrations have been found in a forested catchment (Burns, 1998) and in a mixed land-use moorland catchment (Scholefield *et al.*, 2005), and both studies concluded some degree of NO_3^- uptake by photoautotrophs in the water column through relationships to temperature and light availability. Although Scholefield *et al.* (2005) pointed to the possible additional relationship of the patterns in NO_3^- concentrations with the magnitude of stream discharge, diel patterns of stream NO_3^- chemistry have not been linked convincingly in the literature to the temporal patterns of stream discharge or groundwater flow. A review article by Nimick *et al.* (2011) implied that physical processes may modify or nullify diel NO_3^- cycles caused by in-stream processes but did not consider the possibility that physical processes could be the primary cause of such cycles.

We undertook an evaluation of the diel behaviour of the CMC that drains a small catchment on the Eastern Shore of Virginia, USA, specifically to examine the plausibility that diel changes in groundwater discharge rates could result in observable changes in NO_3^- concentrations. Here, we report an exploration of how diel patterns in stream stage and groundwater discharge through the streambed may be driven by ET in the riparian zone. Our central question focused on whether such diel patterns in groundwater and stream flow were temporally associated with measurable diel patterns in streamwater NO_3^- concentrations. Given that a diel variation in streamwater NO_3^- concentration could be measured, we sought confirmation that the patterns and magnitude of those changes were consistent with the proposed mechanism of streambed denitrification being limited in extent by the ET-driven residence time of groundwater in the streambed sediment. Our approach relied upon a combination of the collection of stream flow and chemistry data and of the application of a numerical model of 2D, time-dependent, saturated–unsaturated groundwater flow and reaction for a cross section of the CMC and an adjacent forested hillslope. Modelled diel variations in stream discharge were consistent with variations in observed stream stage. The magnitude, timing, and shape of modelled stream NO_3^- concentration patterns were consistent with observations during a typical summertime base-flow period; however, a more complicated pattern was found on the receding limb of the hydrograph in early summer. On the basis of the consistency between model results and observations, we conclude that diel flow patterns driven by ET are sufficient to account for the observed diel pattern in stream NO_3^- concentrations in the CMC during the summertime.

METHODS

Research site description

Our field observations and modelling scenario were based on a hillslope transect in the CMC watershed, located within the Anheuser-Busch Coastal Research Center on Virginia's Coastal Plain. The watershed is $4.96\,km^2$ and has low topographic relief. The CMC is one of many coastal streams whose discharge supplies NO_3^- to the seaside lagoons of the Atlantic Ocean. The primary source of NO_3^- is agriculture. Approximately 50% of Virginias Eastern Shore is agricultural land, with 80% of agricultural area in row crops (USDA, 2002). Commercial fertilizer use and manure application to land account for essentially all of the nitrogen load to catchments on the Delmarva Peninsula (Brakebill and Preston, 1999). Cropland is preferentially situated on well-drained soils (Phillips *et al.*, 1993) where NO_3^- fertilizers readily leach to the unconfined Columbia aquifer (Denver, 1989). As a result, groundwater NO_3^- concentrations often exceed the US EPA drinking water standard of $10\,mg\ NO_3^-\text{-N}\,l^{-1}$ (Denver *et al.*, 2003).

The Columbia aquifer is composed of Pleistocene-aged unconsolidated sands (generally 8–30 m thick; Calver, 1968; Mixon *et al.*, 1989) with high hydraulic conductivity (on the order of $10^{-5}\,m\,s^{-1}$; Hubbard *et al.*, 2001). The aquifer is generally aerobic and is very low in organic matter, resulting in little attenuation of NO_3^- concentrations during transport through groundwater. Groundwater discharge supplies the majority of flow to streams on the Delmarva Peninsula (Bachman *et al.*, 1998) and represents a potentially large source of nitrogen to downgradient systems.

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Previous measurements of hydraulic head in the subsurface of the CMC watershed have indicated a typical pattern of groundwater flow from a hillslope to a downgradient floodplain and stream (Gu *et al*., 2008b) and allowed us to develop a model that reasonably represents the groundwater flow regime there. The stream's floodplain has a very low gradient, is forested, and remains saturated throughout the year. The width of the forested floodplain varies but is on the order of tens of metres on each side of the stream. The catchment is generally flat except for a prominent slope (less than a 10-m elevation change) that separates the water-logged floodplain areas from the better drained upland farm areas.

Measurement of stream solute concentrations and stream stage

We collected stream water from the CMC at hourly intervals with an ISCO automatic sampler during three 72-h campaigns in March, June, and August 2008. Water samples collected for chemical analysis were filtered through sample-rinsed 0.45-μm filters in a field lab and refrigerated prior to analysis. Analysis of Cl^- and NO_3^- was performed on a Dionex® Ion Chromatograph equipped with a Dionex IonPac AS4A® 4×250-mm analytical column preceded by a Dionex IonPac AG4A-SC® 4×50-mm guard column. All NO_3^- concentration data are expressed as NO_3^--N.

Stream stage was recorded at 10-min intervals by Levelogger™ pressure transducers installed in stilling wells in the CMC at upstream and downstream locations, separated by 225 m of stream length. A transducer suspended above the water in the downstream stilling well was used to correct the raw pressure data to water pressure above the submerged transducer to yield stage, in terms of elevation above mean sea level. Because of gauge malfunction, the downstream stream-stage data were necessarily estimated from the upstream gauge in the CMC. Stage data from a period in 2009 (early March to mid-June) in which good data from both gauges were available were compared to determine the quality of the relationship between the two stations. A total of 13 828 contiguous and simultaneous points (about 96 consecutive days) from each gauge were compared by linear regression. The equation obtained was $s_{\text{down}} = 1.6s_{\text{up}}^3 - 8.4s_{\text{up}}^2 + 15s_{\text{up}} - 8.3$, where s is stage, and r^2 for the regression line was 0.98.

Model of groundwater and stream flow

A 2D, time-dependent, saturated–unsaturated groundwater flow equation was solved numerically to examine the effect of ET on groundwater discharge to the CMC. The groundwater flow model was developed in earlier studies (Gu, 2007; Gu *et al*., 2008b), so we provide only a brief description here. The model solves the transient 2D saturated–unsaturated groundwater flow equation for an unconfined aquifer, as described by Bear (1972), using the Galerkin finite element approximation. The time derivative is treated with a fully implicit finite-difference scheme and solved with the Douglas–Jones predictor–corrector method (Gu *et al*., 2008b). Here, we applied the model to a 2D cross section of the CMC, the adjacent floodplain, and a portion of the upland farm area. Hydraulic properties of the aquifer and streambed (specific storage, hydraulic conductivity, and porosity) were the same as those used previously for the CMC (Gu, 2007; Gu *et al*., 2008b). This model includes a 30-cm-thick layer that extends from the channel centre to the top of a streambank seepage face and has half the hydraulic conductivity of the rest of the model domain. The width of the cross section was 227.5 m, and the thickness varied from 15 m at the upslope boundary to 10 m at the channel centre. This model configuration represents a typical cross section of the catchment and includes the stream, floodplain, and adjacent hillslope. We varied the cross section width from 50 to 227.5 m and found that the domain sizes in this range do not noticeably affect the model results. We ultimately chose a domain size of 227.5 m, because it fully encompassed the landscape elements (i.e. the stream, floodplain, and adjacent hillslope) that are relevant to our research questions. The domain was divided into a mesh of 4356 triangular shaped elements and 2271 nodes. Horizontal grid spacing varied from 0.15 to 10 m, and vertical grid spacing varied from 0.15 to 1 m, with finer resolution near the water table and streambed. The upslope boundary was assigned a constant head, representing a static water-table elevation at 12.2 m above the confining layer; the confining layer and channel centre were no-flow boundaries; the model included a seepage face that allowed for groundwater to discharge from the streambank above the static stream stage, and the seepage face was assigned land surface elevation as its boundary condition; and below stream stage, the area of the streambed was assigned a constant-head boundary condition of 10.2 m above the confining layer. Stream stage varies with time, and therefore, the effect of using static stream stage in the model was evaluated by comparing the patterns of modelled stream discharge to observed stream stage.

Potential evapotranspiration (PET) was estimated with the Penman–Monteith equation (as in Campbell and Norman (1998)) and was used as a specified flux condition distributed evenly at the land surface. The assignment of unamended PET as a flux boundary condition is reasonable for the fully saturated floodplain but is an overestimate for upland segments of the hillslope under variably saturated conditions. Aquifers behave as low-pass filters and will dampen the PET pressure pulse far from the stream. Thus, an overestimate of the surface flux condition there will not have a significant effect on calculated diel patterns of groundwater flux to the stream. Rather, the unamended PET flux will only affect long-term stream recession in the model (Czikowsky and Fitzjarrald, 2004), which is not the focus of this study. Meteorological data from two weather stations near the CMC watershed were used in PET calculations during June and August 2008. Total incoming solar irradiance was measured hourly in Cape Charles, VA (National Oceanic and

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Atmospheric Administration Environmental Satellite, Data, and Information Service website, accessed on 21 January 2011; http://www.ncdc.noaa.gov/crn/products.html). Air temperature, horizontal wind speed, barometric pressure, and relative humidity were measured at 6-min intervals in Weirwood, VA (http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KVAWEIRW1), which we subsequently averaged to hourly intervals. Precipitation was measured at 6-min intervals in an open field adjacent to the downstream sampling location as part of routine sampling conducted by the Virginia Coast Reserve Long-Term Ecological Research site staff. Complete details of the PET calculations were described by Flewelling (2009).

The numerical simulations provided head values for the modelled cross section, which we used to develop time-series predictions of specific discharge through the streambed and stream bank driven by PET in the vadose zone. The head gradient was computed across a 15- to 20-cm-thick layer of sediment (depending on grid spacing) directly beneath or adjacent to the stream. Specific discharge for all streambed and seepage-face nodes was calculated from Darcy's law and then integrated across the width of the groundwater discharge zone (streambed plus seepage face) to determine the total groundwater flux per unit stream length, q_w. To compare these estimates to measured stream stage required extrapolation of q_w for this one cross section to the approximately 1800-m-long stream channel that is upstream of the sampled location in order to calculate discharge (Q). We assumed that the unit flux was constant for the entire stream length. Stream discharge was computed as the sum of all unit upstream inputs, $Q = \int_0^x q_w\left(t - \frac{x}{u}\right) dx$, where X is the total stream length (1800 m) and u is the flow velocity in the stream channel. Stream velocity was selected on the basis of the visual agreement between the pattern of modelled stream discharge and observed stream stage.

Model of stream nitrate concentrations

We modelled NO_3^- removal in the streambed (NO_3^- reduction zone) as a first-order kinetic process, which is appropriate for settings such as the CMC where organic matter is not limiting (Reddy and Patrick, 1984; Ocampo *et al.*, 2006), $N = N_0 e^{-kt}$, where N is the NO_3^- concentration and k is the first-order rate coefficient. The groundwater travel time through the streambed is calculated as $t = nL/q$, where L is the thickness of the NO_3^- reduction zone, n is the porosity, and q is the specific discharge. The analysis of streambed sediment at the CMC by Galavotti (2004) and Gu *et al.* (2007) indicated that L and n could reasonably be assumed constant at 30 cm and 0.3, respectively, so that t is a function of time-varying q only. The initial NO_3^- concentration entering the streambed, N_0, was held constant at 12.2 mg l^{-1}, the average NO_3^- concentration in four piezometers (12.2 ± 0.2 mg l^{-1}, mean $\pm$ 1 standard error of the mean, $n = 52$) open at 40–80 cm beneath the streambed that were repeatedly sampled between October 2003 and May 2005. A single k value was selected for each of the modelled periods from the range previously measured in the CMC streambed sediment by Flewelling *et al.* (2011), namely, 0.15–7 d^{-1}. This range of k values was derived from 57 seepage-metre measurements made throughout several hundred metres of the CMC and is expected to bound the average effective rate coefficient for the streambed as a whole. The flow weighted average rate coefficient (0.29 d^{-1}) for all seepage-metre measurements is at the low end of that range.

Predicted NO_3^- concentrations are for groundwater as it discharges from the streambed. Stream NO_3^- concentrations would be an integration of all such upstream NO_3^- inputs over the time it takes for water to travel downstream to an observation point. The approach that we used to account for such in-stream averaging is analogous to the method used to estimate stream flow. First, the NO_3^- flux per unit stream length (J_w) was calculated by integrating the modelled NO_3^- flux (qN) across the stream's width. Assuming that the unit flux is constant along the length of the CMC, the stream NO_3^- flux at our sampling station (J) was calculated by summing the NO_3^- fluxes per unit stream length (J_w) upstream of the observation point using the additional assumption of only advective transport in the stream, $J = \int_0^x J_w\left(t - \frac{x}{u}\right) dx$. Lastly, we calculated the stream NO_3^- concentration (N_s) from the ratio of the NO_3^- flux to stream flow ($N_s = J/Q$).

We selected model parameters (stream velocity and denitrification rate coefficient) for June and August simulations on the basis of visual inspection of the agreement between predicted discharge and observed stage patterns as well as agreement between predicted and observed NO_3^- concentration patterns. In June simulations, we set the denitrification rate coefficient at 0.43 d^{-1} and stream velocity at 0.038 m s^{-1}; in August simulations, we set the denitrification rate coefficient at 0.36 d^{-1} and stream velocity at 0.026 m s^{-1}. Selected stream velocities are consistent with prior measurements of stream velocity on the order of 0.01 m s^{-1} during similar base-flow conditions.

RESULTS

March observations were used as a baseline to determine whether diel stage or NO_3^- fluctuations occurred prior to leaf emergence. There were no diel fluctuations in stage or NO_3^- during this period. June observations were made during the early summer seasonal drawdown period and were also preceded by several precipitation events, including 14 mm of rain on 16 and 17 June and 1 mm on June 22 (Figure 1). Diel stage fluctuations were superimposed over the seasonal recession curve through-

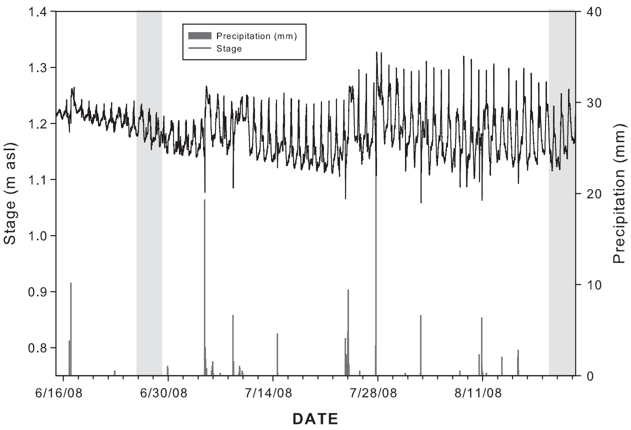

Figure 1. Precipitation and stage record for the Cobb Mill Creek from mid-June to late August. The periods in which the detailed observations and modelling were carried out are represented by the grey bars. The slight overlap of the stream stage and precipitation record on about 7/28 corresponds to a precipitation of 27 mm

out June. August observations were made during typical late summertime base-flow conditions. Large diel stage fluctuations are the most dominant features in this portion of the hydrograph. On 10 and 11 August, 11 mm of precipitation fell, followed by 2 mm on 13 August and 5 mm on 15 August (Figure 1).

Average modelled specific discharge was 2.2×10^{-4} cm s^{-1} for June simulations and 2.4×10^{-4} cm s^{-1} for August simulations. During both periods, the model produced diel patterns in stream discharge that were similar in shape to the observed stream stage (Figure 2). The modelled discharge values were in the appropriate range for measured discharge in similar summer periods in the past (we could not compare modelled and measured discharge during the study period because our stilling well had been damaged). The timing of modelled and observed peaks and troughs generally agreed, although modelled discharge maxima occurred in late morning and slightly preceded observed stage maxima. Observed stage often had broader troughs than model predictions. In June, stream stage trended downward over several days, whereas in August, stream stage trended upward. Overall, the modelled forcing due to ET did a reasonable job of reproducing the pattern in stream flow, even with the simple fixed-head upslope and stream-stage boundary conditions used in the model.

Modelled stream NO_3^- concentrations were consistent with the observed diel pattern in August, but a more complicated pattern was found in June (Figure 3). Simulated NO_3^- concentrations in August agreed very well with observations in terms of the magnitude, timing, and shape of the diel variations (Figure 3B) with peak NO_3^- concentrations at about 10:00–14:00 h and minima at about 22:00–2:00 h. Simulated NO_3^- concentrations in June showed a diel variation, as did observations, but there were several noticeable differences. The magnitude of observed diel variations (~2 mg l^{-1} peak to trough) was about twice the simulated values (~1 mg l^{-1}), and the

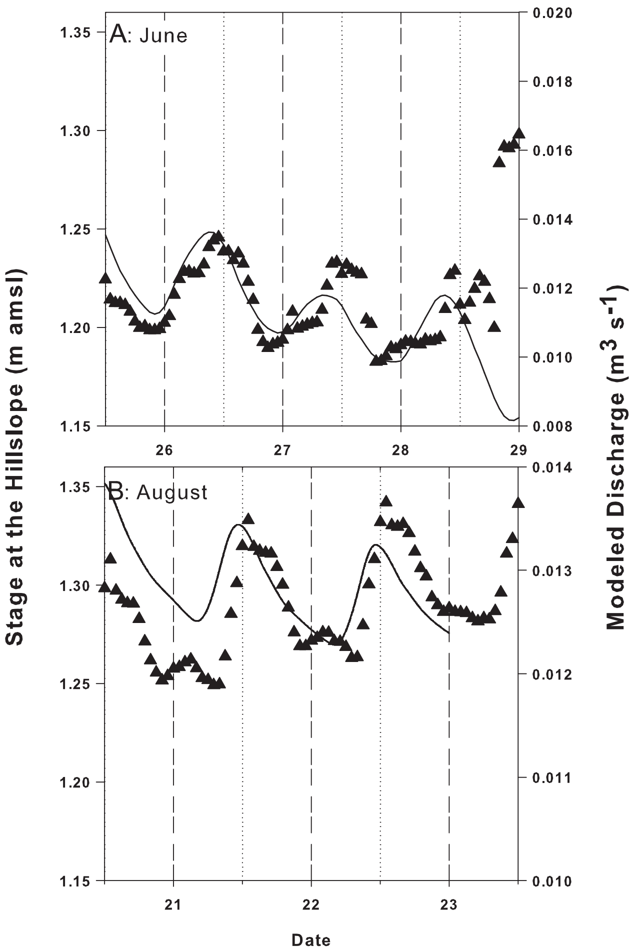

Figure 2. Modelled discharge and observed stage in the Cobb Mill Creek for A: 26–29 June 2008 and B: 20–23 August 2008. Dashed lines indicate midnight of the designated date, and the dotted lines represent the following noon. The symbols represent the observed stages, whereas the solid line represents the modelled discharge

multi-day trend in observed NO_3^- concentrations was upward, whereas the model trend was downward (Figure 3A).

DISCUSSION

General

Our field observations clearly show diel variation in stream stage and therefore discharge, as well as in NO_3^- concentration (Figures 2 and 3). The modelled specific discharge (2.2×10^{-4} cm s^{-1} for June and 2.4×10^{-4} cm s^{-1} for August) was close to the geometric mean of specific discharge measurements (1.8×10^{-4} cm s^{-1}) made by Flewelling *et al.* (2011) during similar summertime base-flow conditions. The predicted travel time through the 1800-m stream channel of the CMC was 13 h for June and 19 h for August, based on the stream velocities used in model simulations. Wondzell *et al.* (2007) showed that stream velocity affects the amplitude and lag time for an ET pulse travelling down a stream network, and varying stream velocity within our modelling framework produced similar results. By combining the 2D groundwater flow model with an accounting scheme for in-stream averaging of

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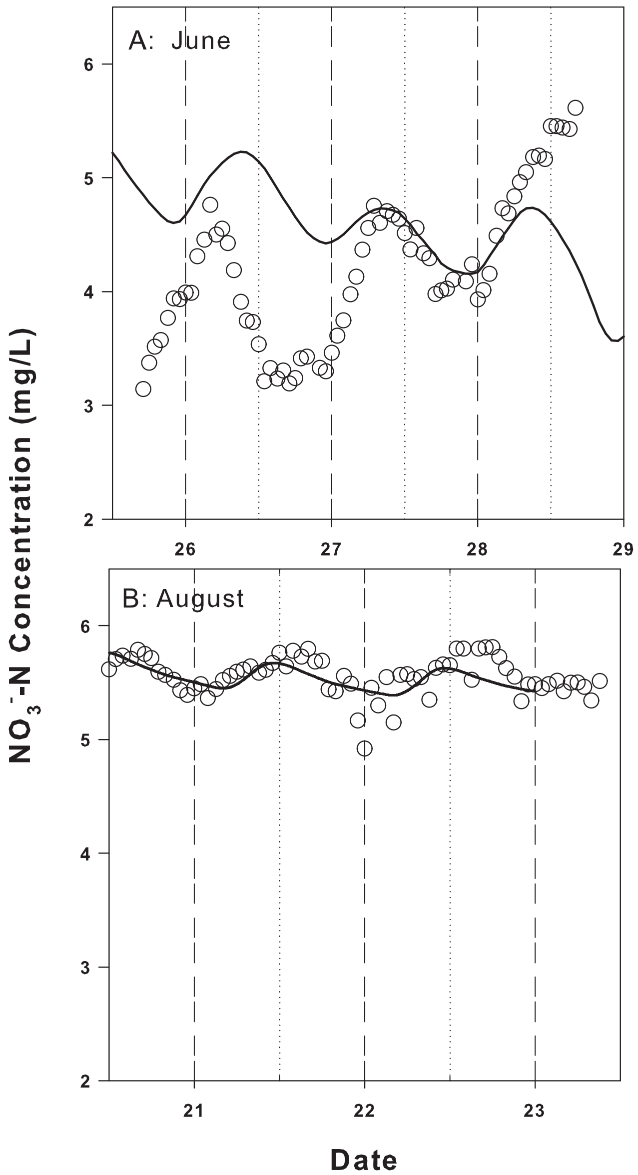

Figure 3. Modelled (line) and observed (symbol) NO_3^- concentration in the Cobb Mill Creek for A: 26–29 June 2008 and B: 20–23 August 2008

ET-driven signals, our modelling approach took into account the effects of the ET pulse and of signal attenuation in the stream network on stream flow and NO_3^- concentrations.

Although the modelled responses to varying velocity were similar in our study and in the study by Wondzell *et al.* (2007), the watershed characteristics were quite different. The CMC is a very simple case, where a perennially gaining stream resides in a single channel that drains a relatively thick, homogeneous, and transmissive aquifer, with little or no hyporheic exchange (Mills, unpublished data). Wondzell *et al.* (2007) examined a more complex montane system, where the watershed includes tributaries, active hyporheic exchange, greater variability in aquifer properties, and potential breaks in hydraulic connectivity between the upland and riparian areas during seasonally dry periods. Despite these markedly different systems, diel stream flow patterns were observed in both cases. The only apparent similarity between these two systems is with regard to travel time through the stream network. Travel time is equal to the ratio of channel length to stream velocity, and in our study, the range of travel times for June and August (13–19 h) was similar to the range of base-flow travel times for the stream network studied by Wondzell *et al.* (2007) (7 h to more than 24 h). Thus, it seems likely that the most important factor in determining whether ET signals are observable is travel time through the stream network and that other complexities in the watershed play a secondary role.

The ability of our model simulations to produce diel stream behaviour with realistic model inputs indicates that the physical processes embodied in the model can account for these variations. That is, ET-driven change in groundwater discharge was able to explain the diel NO_3^- variation we observed. In close examination, the August modelling results agree very well with observed NO_3^- concentrations (Figure 3B). We previously found that the residence time of NO_3^- in streambed sediment is a dominant control on stream NO_3^- concentrations (Gu *et al.*, 2007; Flewelling *et al.*, 2011). Because ET-driven flow patterns will affect the residence time of NO_3^- in biologically active zones (i.e. the organic-rich sediment underlying the streambed), ET must have an indirect effect on stream NO_3^- concentrations. Previous studies have shown many instances of diel patterns in stream discharge (Troxell, 1936; Burt, 1979; Bond *et al.*, 2002), and the diel streamflow signal is strongest in small watersheds (Czikowsky and Fitzjarrald, 2004). Our study demonstrates that the ET-driven hydrological behaviour of groundwater–surface–water interaction is sufficient to result in diel patterns in streamwater NO_3^- concentration.

Impact of antecedent moisture conditions

Upon closer inspection of the June data, we note some differences between model results and field observations of stream NO_3^- concentrations (Figure 3A). There were diel fluctuations in NO_3^- concentrations in both the model results and measurements, yet the 3-day trends in magnitude of NO_3^- concentration go in opposite directions; the observed NO_3^- concentrations trended upward overall, whereas the modelling results trended downward (Figure 3A). Although the goal of our field campaign was to make observations under base-flow conditions, in fact, the antecedent moisture conditions were different. June samples were taken when stream stage was undergoing a seasonal decline as a result of increasing ET in early summer. Although some rain fell in the weeks before our field work, the long-term hydrograph shows that we sampled during a seasonal decline in stage that is typical of drawdown brought about by increasing rates of ET during early summer (Figure 1). Thus, measurements were made on the receding limb of the hydrograph during a period when the riparian-zone water table would have been declining from its elevated position in spring relative to its drawn down position

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during late summertime. In contrast, August sampling occurred in late summer, when ET has drawn down the water table and created more typical summertime base-flow conditions. As opposed to June, stream stage in August increased over the 3-day sampling event, possibly as a result of recent precipitation events (Figure 1).

It is possible that the ET-driven changes in groundwater discharge could be the primary factor in determining stream NO_3^- concentration through its control on groundwater flow velocity and residence time in the biologically active streambed sediment in the CMC (Flewelling *et al*., 2011). Yet, in June, it appears that another process is contributing to streamwater composition. Knowing that ET is of such a magnitude to influence water-table elevation, we also expect it is sufficient to influence conservative solute concentrations; therefore, we compared relative behaviours of the biologically modified NO_3^- with the conservative Cl^-. Chloride and NO_3^- concentration patterns were essentially mirror images during June; when Cl^- concentration was high, NO_3^- concentration was low, and vice versa (Figure 4). This generalization holds true for the multi-day trend where NO_3^- goes up and Cl^- goes down, as well as for the diel pattern where NO_3^- and Cl^- variations are out of phase.

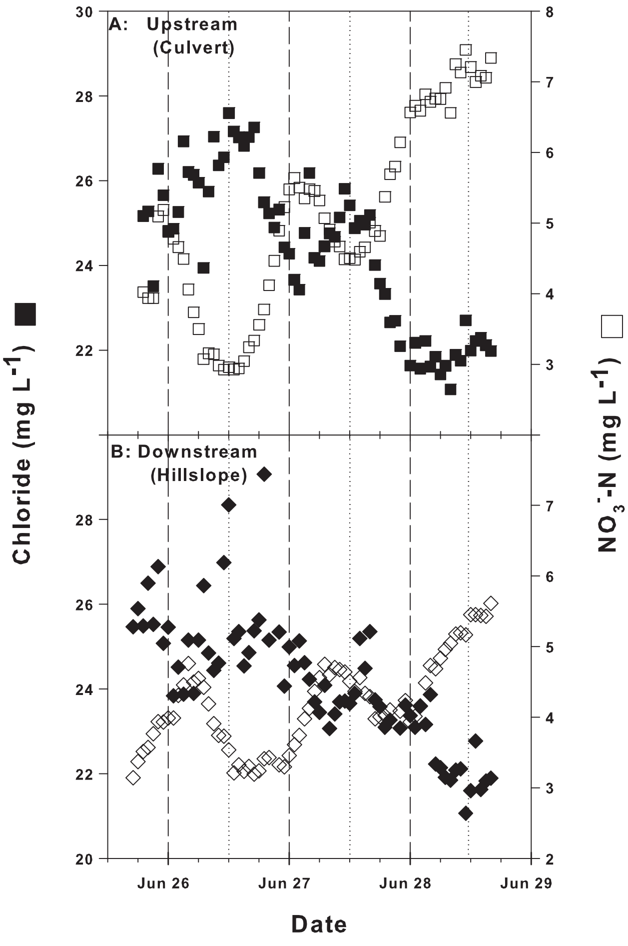

Figure 4. Observed NO_3^- and Cl^- concentration at A: upstream and B: downstream monitoring locations in the Cobb Mill Creek for 26–29 June 2008. Days are set to begin at midnight (as indicated by the dashed lines). Noon is indicated by the dotted line

This behaviour is most clearly seen at the upstream sampling location (Figure 4A), but it also occurred at the downstream sampling location (Figure 4B). The opposing trends in NO_3^- and Cl^- concentrations were not readily explained with the ET-driven diel changes in groundwater discharge alone.

Shifts in contributions for two distinct groundwater sources

In our previous study of spatial distribution of NO_3^- concentration and groundwater discharge (Flewelling *et al*., 2011), we identified two different groundwater source components contributing NO_3^- to the stream – a high-NO_3^-, low-Cl^- water and a low-NO_3^-, high-Cl^- water. The mixing of these waters may occur via dispersion in the heterogeneous streambed or in the stream channel following exfiltration of the two groundwater sources. Other investigators have pointed to spatially varying source components as causes of the observed patterns in streambed porewaters (Kennedy *et al*., 2009). At the CMC, previous data and model simulations by Gu *et al*. (2008b) have shown the presence of these two distinctive waters (see Figure 5 in Gu *et al*., 2008b). In this work, we concluded that a deep groundwater carrying NO_3^- from upland recharge areas was characteristically high in NO_3^- concentration but low in Cl^- concentration, consistent with the composition of leachate expected from the upland farm areas. The composition of this deep groundwater was essentially unchanged from when it recharged because it resided deeply enough below the water table to be relatively uninfluenced by processes in the riparian zone that can alter solute concentrations (see low-chloride, high-nitrate region directly beneath the stream channel shown in Figure 5 in Gu *et al*., 2008b). A contrast in solute ratios is expected in the shallow subsurface underlying the forested hillslope riparian zone owing to the different ways in which processes affect NO_3^- and Cl^- concentrations. Here, Cl^- concentration was high, and NO_3^- concentration was low (see high-chloride, low-nitrate region just beneath the water table in the riparian zone of the hillslope in Figure 5,Gu *et al*., 2008b). Deeply circulated groundwater has been shown to typically discharge in the centre of a stream channel, whereas shallow, proximal groundwater is likely to discharge near stream margins (Kennedy *et al*., 2009; Flewelling *et al*., 2011).

Our interpretation of the contrasting behaviour in June during the early summer recession period and August during a typical summertime base-flow period is based upon the presence of these two groundwater sources of differing composition and a physical interpretation of groundwater flow behaviour. When the water table elevation increases in response to a storm, the most prominent effect on groundwater discharge to the CMC is a large increase in the flow of shallow riparian-zone groundwater to the stream (Gu *et al*., 2008a). The same will be true during winter, spring, and early summer, when seasonal recharge patterns have elevated the water table. Thus, directly after a storm passes or during seasonally high water table conditions, it is reasonable to expect streamwater to most closely reflect shallow

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riparian-zone groundwater composition high in Cl^- and low in NO_3^-. Over time, as the water table relaxes, input of shallow riparian-zone groundwater declines and the streamwater shifts to reflect the high-NO_3^-, low-Cl^- composition of deep groundwater. Over the 3-day observation period in June, NO_3^- concentrations increased from approximately 3 to 5.5 mg l^{-1}, whereas Cl^- concentrations decreased from approximately 26 to 22 mg l^{-1} (Figure 4). All the while, diel fluctuations in NO_3^- concentrations continued to occur superimposed on the multi-day trend that was driven by time-varying groundwater source components to the stream.

The observations during the June recession period raise the question of whether the observed diel nitrate patterns could be due to time-varying source components driven by ET, i.e. a source-component hypothesis instead of a streambed travel-time hypothesis. The source-component hypothesis would predict that stream nitrate concentrations would be lowest when groundwater discharge is highest (i.e. when stream flow is most influenced by the lower nitrate shallow groundwater component). Conversely, the streambed travel-time hypothesis would predict that nitrate concentrations are lowest when groundwater discharge is lowest (i.e. when streambed travel time is longest). Therefore, the source-component hypothesis predicts precisely the opposite pattern as the streambed travel-time hypothesis and the pattern observed in the stream. Time-varying source components due to ET would therefore be expected to counteract the signal driven by time-varying travel time in the streambed. The fact that observed nitrate concentrations are in approximate agreement (in amplitude and timing) with the predictions based solely on ET-driven variations in groundwater travel time through the streambed suggests that diel variations in source components must not be very important in this stream.

Simple physical controls on reactive solute transport

Our simple physical model of groundwater discharge to a low-gradient stream draining an agricultural watershed being forced by dynamic changes in ET showed that diel patterns in NO_3^- concentration were expected and explicable. The model simulations showed greater consistency with observed stream discharge and NO_3^- concentrations for late summer base-flow conditions in August, but even those findings showed some small differences in behaviour. At least part of the discrepancy is likely due to our simplistic model assumption that stream velocity is constant. In reality, as stream stage and discharge vary throughout the day for a given stream channel, the stream velocity must vary also. Thus, minor differences in the timing and shape of peaks and troughs were expected. Nonetheless, our model results did capture the general patterns in stream NO_3^- concentrations, indicating that ET is indeed the most likely cause.

Other investigators have measured diel patterns in stream NO_3^- concentration in a range of environmental settings and offered speculation on water-column biological activity in the uptake of NO_3^-. Studies spanning multiple seasons have found that diel NO_3^- patterns are dampened in the summer relative to the spring in streams where the forest canopy creates dense shade and limits in-stream photoautotrophic activity (Roberts and Mulholland, 2007; Rusjan and Mikos, 2010). Given the lack of a diel NO_3^- pattern in our stream in the spring (when the open canopy would permit higher photoautotrophic activity) and the observations in prior studies that diel NO_3^- patterns attributed to photoautotrophs are dampened in summer relative to spring, it appears unlikely that in-stream photoautotrophic activity is a significant contributor to the NO_3^- patterns we observed. Nonetheless, diel NO_3^- patterns attributed to the uptake of NO_3^- by in-stream photoautotrophs would cause NO_3^- concentrations to reach a minimum in late afternoon (Burns, 1998), similar to our predictions based on a physical model of ET as the forcing mechanism (Figure 3). Scholefield *et al.* (2005) described diel patterns for a mixed-land-use watershed, but was unable to discriminate between possible biological and physical processes. Factors anticipated to be critical to the possibility or extent of water-column biological uptake such as water temperature and photosynthetically active radiation (Laursen and Seitzinger, 2004; Mulholland *et al.*, 2006) vary on a diel cycle roughly concurrent with the daily maxima and minima in ET, confounding an interpretation of time patterns as conclusive evidence of controlling processes. In fact, it seems entirely reasonable that multiple processes may actively influence streamwater NO_3^- concentrations. Our results do not demonstrate that ET alone is the cause of diel patterns in NO_3^- concentration in all situations, even in similar streams, but we have clearly shown ET to be the likely cause for the variation in NO_3^- concentrations observed for a small coastal stream in an agricultural watershed in the summertime.

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