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LANDSCAPE AND WATERSHED PROCESSES

Groundwater and Surface-Water Exchange and Resulting Nitrate Dynamics in the Bogue Phalia Basin in Northwestern Mississippi

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During April 2007 through September 2008, the USGS collected hydrogeologic and water-quality data from a site on the Bogue Phalia to evaluate the role of groundwater and surface-water interaction on the transport of nitrate to the shallow sand and gravel aquifer underlying the Mississippi Alluvial Plain in northwestern Mississippi. A two-dimensional groundwater/surface-water exchange model was developed using temperature and head data and VS2DH, a variably saturated flow and energy transport model. Results from this model showed that groundwater/surface-water exchange at the site occurred regularly and recharge was laterally extensive into the alluvial aquifer. Nitrate was consistently reported in surface-water samples (n = 52, median concentration = 39.8 μmol/L) although never detected in samples collected from in-stream piezometers or shallow monitoring wells adjacent to the stream (n = 46). These two facts, consistent detections of nitrate in surface water and no detections of nitrate in groundwater, coupled with model results that indicate large amounts of surface water moving through an anoxic streambed, support the case for denitrification and nitrate loss through the streambed.

Groundwater/surface-water (GWSW) exchange processes provide many ecosystem services such as maintaining baseflow in streams, regulating stream temperature regimes for aquatic biota, and buffering the transport of contaminants through the streambed interface (Hayashi and Rosenberry, 2002; Hester and Gooseff, 2010). The ability of GWSW exchange processes to provide these ecosystem services is dependent on the hydrologic and physiochemical characteristics of each GWSW system. One such ecosystem service that has received extensive research is the role that GWSW exchange processes play in nitrogen cycling and the transport of nitrate through the streambed (Tesoriero et al., 2005; Bernot et al., 2006; Gu et al., 2007; Mehnert et al., 2007; Duff et al., 2008; Puckett et al., 2008; Kennedy et al., 2009). In agricultural settings, nitrate is a ubiquitous contaminant due to both the application of inorganic and organic fertilizers to agricultural fields and nitrate's general persistence in oxygenated aqueous environments (Nolan and Stoner, 2000; Coupe, 2001; Puckett and Hughes, 2005; Domagalski et al., 2008; Green et al., 2008; Denver et al., 2010).

Studies examining the transport of nitrate through the streambed typically couple estimates of flux through the streambed interface and water-quality data to assess the total mass of nitrate moving through the streambed and the processes affecting nitrate transport, such as nitrification and denitrification. For the most part, these studies have focused on the role of groundwater in transporting nitrate to the stream and the role the streambed plays in the removal of nitrate from groundwater before it discharges to the stream (Hinkle et al., 2001; Mehnert et al., 2007; Puckett et al., 2008; Kennedy et al., 2009). To date, few, if any, agricultural studies have been located in a setting where nitrate was almost always present in the stream but rarely detected in groundwater. The Bogue Phalia, a stream in northwestern Mississippi, located in an agricultural area, has these characteristics. Nitrate is almost always detected in the Bogue Phalia but has never been detected in shallow groundwater samples within the basin (Coupe, 2001; Landreth, 2008). This finding would suggest either a lack of GWSW exchange (or predominantly gaining rather than

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Abbreviations: CC, central channel; GWSW, Groundwater/surface water; HEC-RAS; Hydrologic Engineering Centers River Analysis System; LB, east bank ; LC, east channel; NWQL, National Water-Quality Laboratory; PVC, polyvinyl chloride; RB, west bank ; RC, west channel; TEAP, terminal electron acceptor process.

losing stream conditions) or that the conditions in the aquifer and/or streambed permit the removal of nitrate as surface water moves through the streambed during losing periods.

This paper documents GWSW exchange for 18 mo at one site on the Bogue Phalia and presents results of a study to determine the influence of this exchange on the fate and transport of nitrate. GWSW exchange was modeled using heat as a tracer and then coupled with water-quality data collected from the stream, as well as from near-stream and in-stream piezometers installed along a flowpath perpendicular to the stream.

Background

In 2005, the USGS National Water Quality Assessment Program (NAWQA) began an Agricultural Chemical Transport Study within Mississippi's Bogue Phalia Basin with the objective of gaining a better understanding of the fate and transport of agricultural chemicals (Capel et al., 2008). The Bogue Phalia Basin is located in northwestern Mississippi in the Mississippi Alluvial Plain, locally referred to as the Delta (Fig. 1). The Mississippi Delta, once a floodplain to the Mississippi River covered with hardwoods and marshland, is now a highly productive agricultural region of large economic importance to the state. Fertile soils, a long growing season, more than 132 cm average annual rainfall, and a productive alluvial aquifer make this region a prime area for agriculture. Primary crops grown in this region include soybean [*Glycine max* (L.) Merr.], corn (*Zea mays* L.), cotton (*Gossypium hirsutum* L.), and rice (*Oryza sativa* L.).

The principal aquifer of interest in this region is the Mississippi River alluvial aquifer. This aquifer is considered to be a confined aquifer, with the confinement penetrated locally by streams. Recharge from infiltration typically is low due to the overlying clay and fine-grained material in the upper part of the aquifer. Previous studies reported recharge rates of 6.6 cm yr^{-1}, or 5% of the average annual rainfall that falls on this region (Arthur, 2001). Historically, the regional groundwater flow path was composed of two flow components, flowing from the north to the south and from the east and west peripheries toward the center of the Delta. These flow paths generally followed the topography of the alluvial plain, which slopes from north to south and is bounded by the levees of the Mississippi River on the west and Bluff Hills on the east, both topographic highs relative to the interior of the Delta (Arthur, 2001). Presently, the regional groundwater flow path is intercepted by a large cone of depression in the middle of the Delta, formed as a result of groundwater pumping for irrigation. Within the Bogue Phalia Basin, which lies to the west of the cone of depression, groundwater generally moves from the west to the east toward the cone of depression.

The Bogue Phalia flows from north to south to its confluence with the Sunflower River, which ultimately discharges into the Mississippi River (Fig. 1). Most of the nearly 100-km length of the Bogue Phalia is incised through the surficial clay

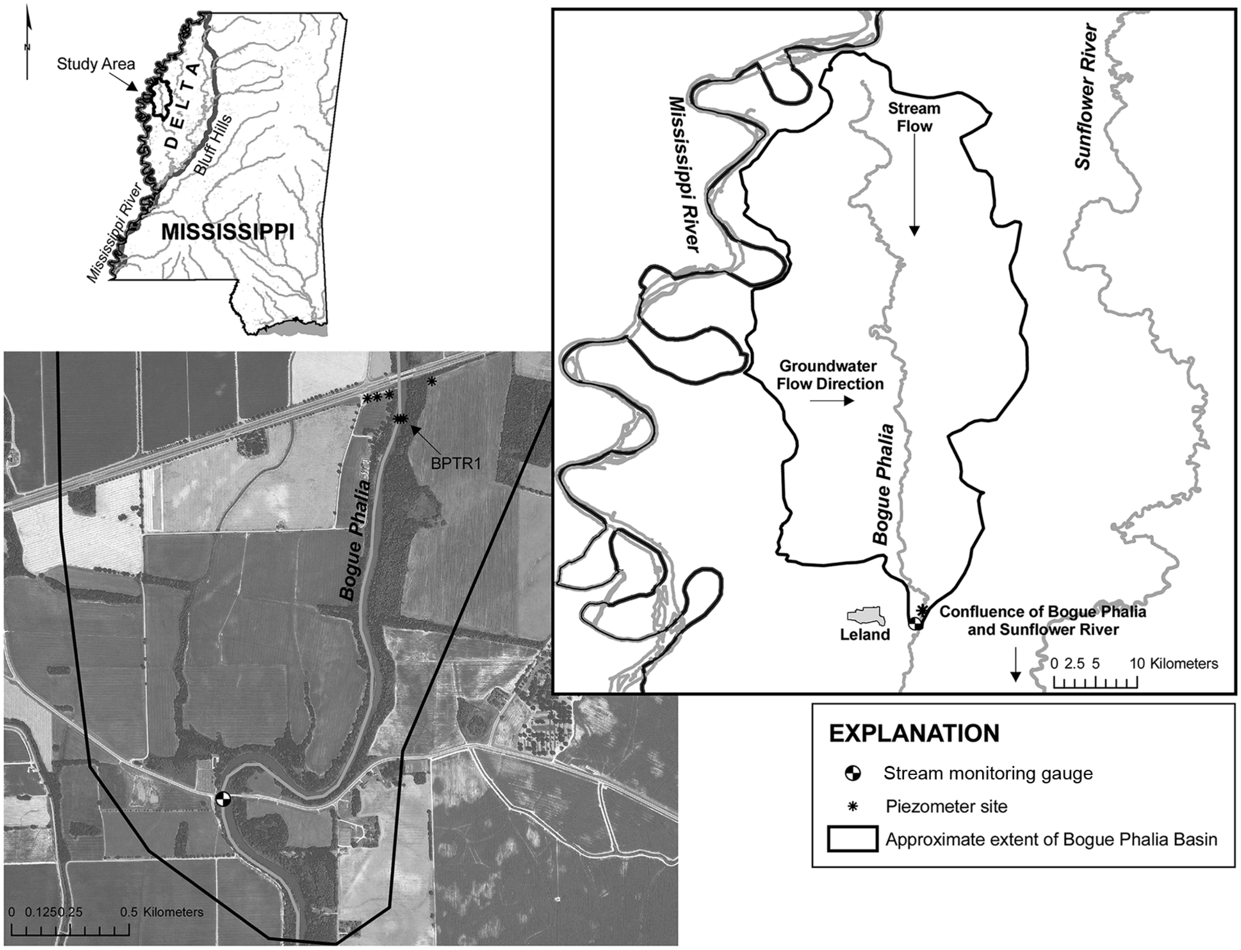


Fig. 1. Location of the study area within the Bogue Phalia Basin in northwestern Mississippi.

layer; however, hydraulic connection with the alluvial aquifer is dependent on the incised depth of the stream channel and water level in the alluvial aquifer. The study area transect is located within a reach of the stream in which the channel is incised through the surficial clay layer and is hydraulically connected to the alluvial aquifer. Previous surveys of GWSW interaction near the study transect have confirmed that the stream is hydraulically connected for at least 2 km upstream (north) and downstream (south) of the study transect. Streambed sediments in this area consist of loamy clays, with some loess at the surface, grading to fine-to-medium sands about 2 m below land surface. In the absence of rainfall or overland runoff, groundwater heads generally are higher than the stream stage, and the reach is gaining. The study site is further described by Barlow and Coupe (2009).

Materials and Methods

Water-Level and Temperature Data

Beginning in late June 2005, five in-stream piezometers were installed along a transect within the stream channel of the Bogue Phalia (BPTR1; Fig. 1, 2). The in-stream piezometers were installed to depths of about 2 m below the streambed interface and located on the west bank (RB), west channel (RC), central channel (CC), east channel (LC), and east bank (LB) of the stream. In-stream piezometers were made from polyvinyl chloride (PVC) with an inner diameter of 5.20 cm and a screened interval of 15.24 cm. In April 2007, four additional shallow monitoring wells were installed at depths from 9.8 to 12.2 m below land surface along potential flow paths on the west and east side of the stream to assess the extent of GWSW exchange and its affect on groundwater quality adjacent to the Bogue Phalia. Three of the near-stream shallow wells (FS1, FS2, and FS3) were located on the west side of the stream and one (AR1) on the east side of the stream (Fig. 2). Near-stream shallow wells were also made from PVC with an inner diameter of 2.5 cm and a 1.5-m screened interval at the bottom of each well. The in-stream piezometers and near-stream shallow wells were sealed to prevent the inflow of surface water during high flow and precipitation.

All wells and piezometers were instrumented with pressure transducers, which measured groundwater level and temperature at 15-min intervals. Temperature dataloggers were installed at fixed depths within the in-stream piezometers and recorded temperature of the streambed at 15-min intervals. According to the manufacturer's specifications, the temperature dataloggers have an accuracy of ± 0.2°C; dataloggers were also tested for quality assurance in the laboratory using a water bath and National Institute of Standards and Technology thermometer to ensure that each met the manufacturer's specifications (StowAway Tidbit Data Logger; Onset, Bourne, MA). The stream water-level gauge, Bogue Phalia near Leland, MS (USGS station number 07288650), located downstream

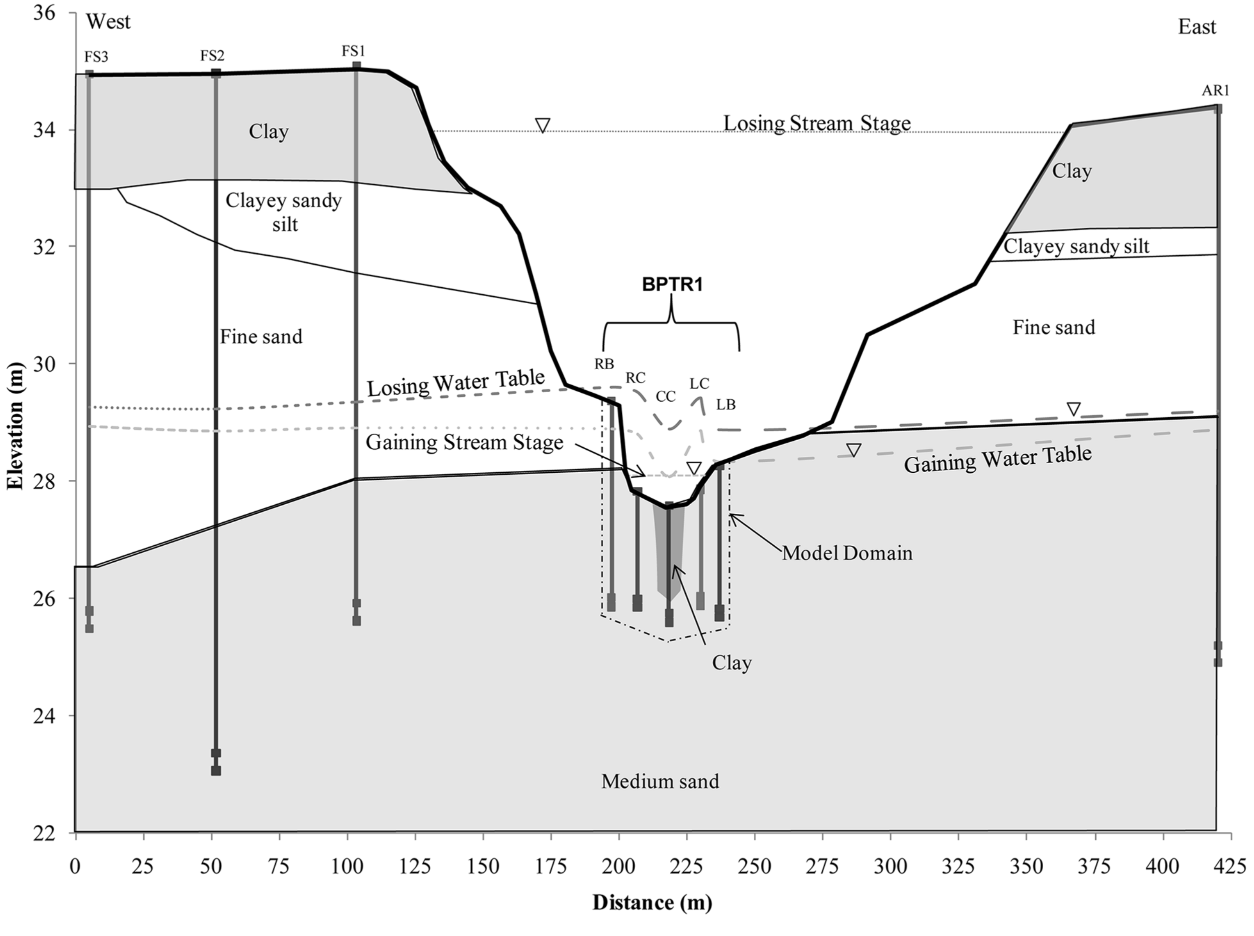


Fig. 2. Study area cross-section showing piezometer depths, screened interval, and examples of gaining and losing water table and stream stage profiles. CC, central channel; LB, east bank; LC, east channel; RB, west bank; RC, west channel.

approximately 2.3 km, measured and recorded stream stage and temperature every 15 min.

Water-Quality Data

Samples for water-quality analysis were collected from the stream, in-stream piezometers, and near-stream wells using nationally consistent sampling protocols (Koterba et al., 1995). To sample the streambed during high flow, drive points with an inner diameter of 1.5 cm and a 2.3-cm-length screen were installed adjacent to the screened interval of the right and left channel in-stream piezometers. Teflon tubing with a 0.5-cm diameter was attached to these drive points and extended to the bank so that they would be accessible during high flow.

Samples for inorganic and nutrient analysis were filtered through a 0.45-μm pore-size capsule filter, and cations were preserved with 7.5 M nitric acid. Samples were chilled on ice and shipped for next-day delivery for analysis using approved analytical methods at the USGS National Water-Quality Laboratory (NWQL) in Denver, CO. Dissolved inorganic constituents were determined at the NWQL using atomic absorption, inductively-coupled plasma, ion-chromatography, ion specific electrode, and colorimetric methods, as described in Fishman and Friedman (1989) and Fishman (1993). Alkalinities were determined in the field at the time of sample collection using incremental titrations. During sampling, field properties including temperature, pH, specific conductance, and dissolved oxygen were measured using a multiparameter sonde. Water-quality analysis results for all constituents analyzed are available in Dalton et al. (2010). This study focused primarily on nitrate and constituents related to reduction–oxidation (redox) processes.

Quality-control data, including field blanks, replicate samples, and field-spiked samples, were collected along with routine samples to ensure that unintended contamination did not occur at any point in the sample collection and laboratory analysis. Quality-control samples were collected for approximately 10% of all routine samples, and data indicate that unintended contamination did not occur throughout the study period.

Groundwater/Surface-Water Model Development

The use of heat as a natural tracer has proven to be an effective method for identifying and quantifying GWSW interactions (Lapham, 1989; Constantz, 1998; Stonestrom and Constantz, 2003; Anderson, 2005; Burow et al., 2005; Constantz, 2008; Essaid et al., 2008). Although heat is a nonconservative tracer, the physics of heat and water transport through sediments is well defined and predictable for a range of hydrologic settings (Blasch et al., 2007). Temperature data are relatively easy to collect and provide insight into streambed processes, such as infiltration rates and groundwater discharge to the stream. Numerical models, such as VS2DH used in this analysis, that use a form of the advection–dispersion equation to simulate energy transport, make analysis of temperature data relatively simple (Healy and Ronan, 1996). VS2DH is a modification of VS2DT (Healy, 1990), which was developed for simulating solute transport in variably saturated porous media such as ephemeral streambeds or through the unsaturated zone (Constantz et al., 2001; Blasch et al., 2006). Recent studies also have shown the effectiveness of using heat to model energy transport to derive hydraulic properties of alluvial aquifers and wetlands (Su et al., 2004; Burow et al., 2005; Eddy-Miller et al., 2009). A previous study at the Bogue Phalia study site developed one-dimensional models using VS2DH, which verified GWSW exchange, but did not include transport processes (Barlow and Coupe, 2009).

For this study, a two-dimensional groundwater flow and heat transport model was developed using VS2DH to quantify GWSW exchange for the period from 11 Apr. 2007 through 30 Sept. 2008. The model domain extends through the in-stream piezometers, extending horizontally from the RB piezometer on the west side of the stream to LB piezometer on the east side of the stream and vertically to the depth of each in-stream piezometer (approximately 2 m below the streambed interface) (Fig. 2 and 3). Total area for the model domain was approximately 40 m wide by 3 m deep with grid spacing of 0.15 m by 0.15 m.

VS2DH requires three main input categories for model development: boundary conditions, textural information, and the location of observation points. Daily head (groundwater level and stream stage) and temperature values were specified for each boundary (Fig. 3). Daily head and temperature values were derived by averaging the 15-min data collected by the stream gauge, transducers, and temperature recorders. Temperature data for the upper streambed boundary were obtained from the stream gauge. Barlow and Coupe (2009) determined that stream temperatures at the stream gauge and BPTR1 did not differ significantly from one another. Stream stage at BPTR1 was determined using the U.S. Army Corps of Engineers Hydrologic Engineering Centers River Analysis System (HEC-RAS; U.S. Army Corps of Engineers, 2010) to model the stream reach between a bridge crossing just upstream of BPTR1 and the stream gauge located 2.3 km below BPTR1. The slope for this reach of the relatively flat Bogue Phalia is about 5 cm/km^{-1}. Stream channel geometry data for the HEC-RAS model were gathered from acoustic Doppler current profiler measurements and stream habitat surveys conducted on this reach of the stream. Head data for the horizontal side and bottom boundaries of the heat transport model were from the pressure transducers located within the screened interval of each in-stream piezometer (RB, RC, CC, LC, and LB). Temperature data from the pressure transducers were used for the bottom boundaries, and temperature data from the temperature recorders in RB and LB were used for the horizontal side boundaries, which were divided into three segments to simulate the vertical temperature gradient along these boundaries.

Textural information was obtained from visual observations of the streambed material at the time of piezometer installation. The streambed is primarily fine-to-medium sand with some silt and clay. A clay unit was observed in the middle of the stream channel and extended vertically to almost 1.5 m below the streambed interface. Fluctuations of temperature and head data from the center piezometer appear dampened relative to the other in-stream piezometer data, evidence of the lower thermal and hydraulic properties of the clay in this part of the streambed. Default values for medium sand and clay from VS2DH's graphical user interface, VS2DI, were used as initial values for all flow-related parameters. Thermal transport-related parameters were obtained from published reports (Table 1).

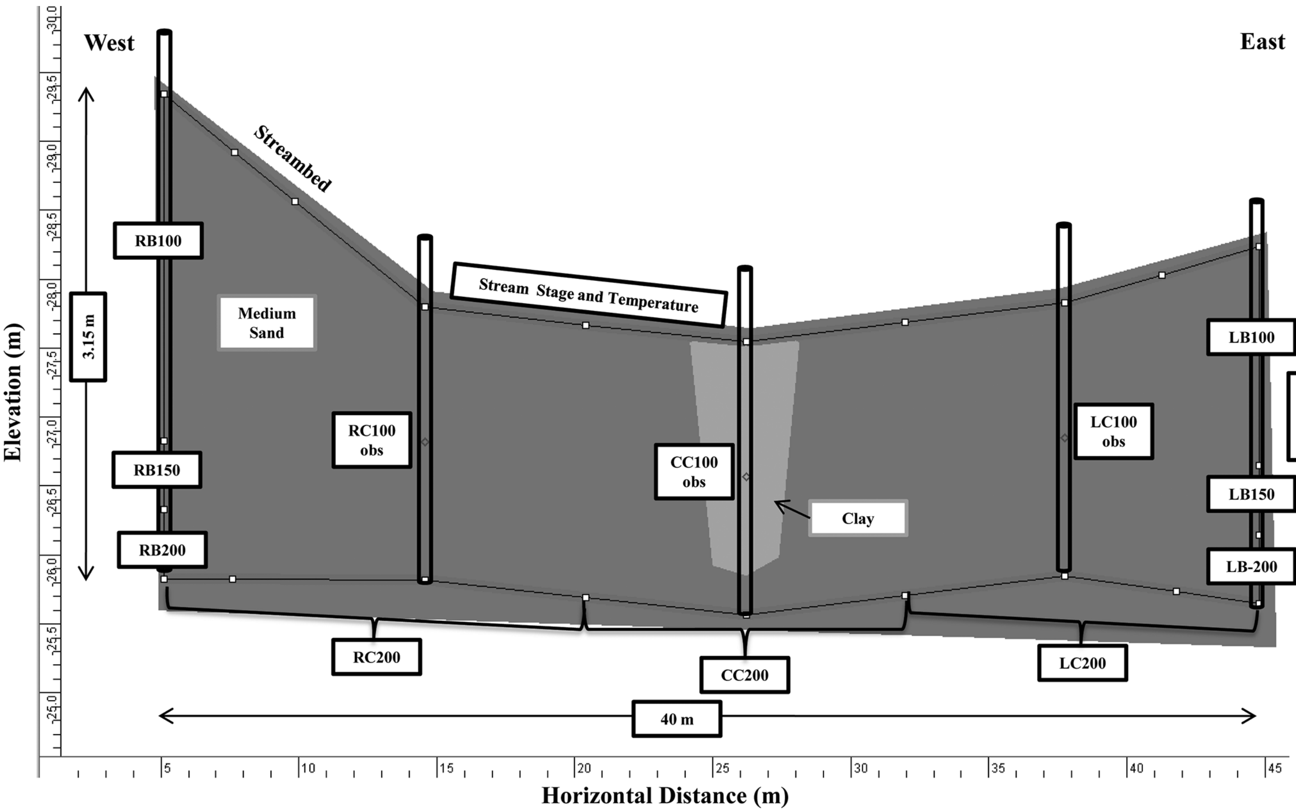


Fig. 3. VS2DH model domain, boundary conditions, textural distribution, and location of observation points. Horizontal and bottom boundary labels denote in-stream piezometer from which head data were obtained and depth of temperature recorder in cm (e.g., RB100 refers to RB piezometer head and 100-cm temperature. Observation point labels denote in-stream piezometer and depth of temperature recorder from which observation data was obtained. CC, central channel; LB, east bank; LC, east channel; RB, west bank; RC, west channel.

Observation points were set within the model domain at locations of known temperature to ascertain model performance and uncertainty, as well as to estimate parameters that are most sensitive within the model. Observation points within the model domain are located coincident with the temperature dataloggers set at 100 cm below the streambed interface within RC, CC, and LC piezometers (Fig. 2). Model calibration was performed by adjusting horizontal hydraulic conductivity (*K*hh) and anisotropy, or the ratio of vertical conductivity, *Kzz*, to horizontal conductivity, *K*hh (*Kzz*/*K*hh) using the nonlinear parameter estimation software package PEST (Doherty 2004) to achieve the best match between simulated temperatures and observed temperatures (Table 1). Both parameters, *K*hh and *Kzz*/*K*hh, were chosen for parameter estimation because they both have the greatest sensitivity relative to other parameters within the VS2DH model (Niswonger and Prudic, 2003).

Using the best-fit values for *K*hh and *Kzz*/*K*hh, the measured-to-simulated temperature can be compared both graphically and statistically (Fig. 4). The correlation coefficient, Pearson's *r*, and the Nash–Sutcliffe (Nash and Sutcliffe, 1970) efficiency coefficient (*E*) were calculated to compare simulated and observed temperature values (Fig. 4). The correlation coefficient measures the covariance between the simulated results from each scenario and the observed results recorded by the temperature recorders (Helsel and Hirsch, 1992). The Nash–Sutcliffe efficiency coefficient measures how well the model is able to predict the observed temperature by comparing the differences between measured and simulated temperatures (Nash and Sutcliffe, 1970). A perfect model is indicated by a

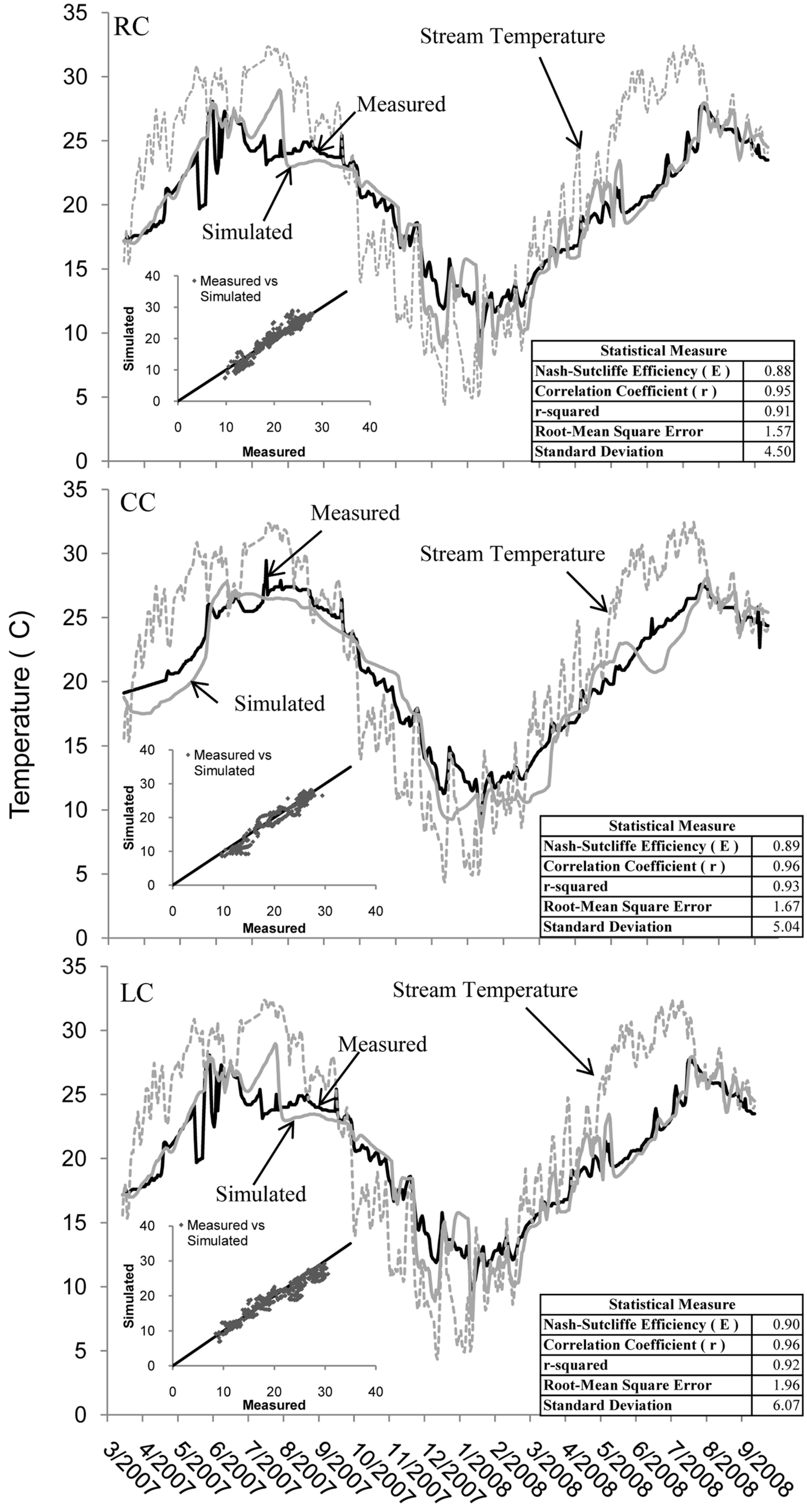
Table 1. Final flow and transport parameter values used in VS2DH model; lower and upper 95% confidence limits in parenthesis for parameters estimated using PEST.

Parameter		Textural class	
		Medium sand final value	Clay final value
Flow	Anisotropy (*Kzz*/*K*hh)†	1.3×10^{-3} (6.9×10^{-4} – 1.8×10^{-3})	1.0 (0.76 – 1.2)
	Horizontal saturated hydraulic conductivity (*K*hh), m/d†	96 (80 – 1.1×10^{1})	0.16 (0.11 – 0.22)
	Effective porosity‡	0.38	0.43
Transport	Saturated thermal conductivity, W/m°C‡	2.2	1.4
	Residual thermal conductivity, W/m°C‡	0.25	0.22
	Heat capacity (dry sediment) ‡	2.6×10^{6}	2.6×10^{6}
	Heat capacity (water) ‡	4.2×10^{6}	4.2×10^{6}

† *K*hh, horizontal hydraulic conductivity; *Kzz*, vertical hydraulic conductivity. Parameter value was estimated using PEST.

‡ Based on literature values (Stonestrom and Blasch, 2003; Niswonger and Prudic, 2003).

coefficient value equal to 1 in both cases. Values for r and E ranged from 0.95 to 0.96 and 0.88 to 0.90, respectively.



Statistical Measure	
Nash-Sutcliffe Efficiency (E)	0.88
Correlation Coefficient (r)	0.95
r-squared	0.91
Root-Mean Square Error	1.57
Standard Deviation	4.50

Statistical Measure	
Nash-Sutcliffe Efficiency (E)	0.89
Correlation Coefficient (r)	0.96
r-squared	0.93
Root-Mean Square Error	1.67
Standard Deviation	5.04

Statistical Measure	
Nash-Sutcliffe Efficiency (E)	0.90
Correlation Coefficient (r)	0.96
r-squared	0.92
Root-Mean Square Error	1.96
Standard Deviation	6.07

Fig. 4. Simulated and observed temperatures for the 100-cm depth observations points within west channel (RC), central channel (CC), and east channel (LC) piezometers.

Discrepancies between the observed and measured temperatures are probably a result of simplifications within the model, especially in regards to the distribution of textural zones within the streambed. Keeping with the idea of parsimony, the streambed was modeled as two homogeneous but anisotropic zones. In reality, the streambed is more likely composed of heterogeneous gradational layers with varying hydraulic properties. Another possible explanation for the observed-to-measured discrepancies is that a significant flow component exists perpendicular to the model domain or along the stream in the direction of stream flow. VS2DH is a two-dimensional model; therefore, only flow in the vertical and horizontal directions are considered. Although the model domain was positioned perpendicular to the stream length and along groundwater flow lines also perpendicular to the stream length, it is possible that there is a flow component perpendicular to the model domain and not represented in the two-dimensional model.

Estimates of Nitrate Loads in the Bogue Phalia

Daily values for stream nitrate concentrations were determined using LOADEST, a program developed by the USGS to estimate constituent loads in streams (Runkel et al., 2004). The Bogue Phalia has a long record of water-quality and flow data (1997 to present), a prerequisite for the use of the LOADEST program. Nitrate loads for this study were determined using a previously developed LOADEST model, described in detail in Rebich and Demcheck (2007). The 95% confidence intervals determined by LOADEST were used to ascertain the uncertainty of the model and provide an upper and lower estimate of the average annual nitrate load within the stream during the study period.

Results and Discussion

Groundwater/Surface-Water Exchange

Stream and piezometer water-level and temperature data aid in developing a conceptual model of GWSW exchange processes and validate that GWSW exchange occurs throughout the simulation (Fig. 2 and 5). Gaining and losing water table profiles (Fig. 2) indicate that the groundwater level changes in response to stream stage and that a horizontal gradient exists, which generally slopes from the west side of the stream to the east side of the stream toward a cone of depression in the central Delta. In-stream piezometer head distributions across the stream are more complex and likely reflect both the west-to-east gradient and heterogeneity of streambed hydraulic properties (i.e., lower heads beneath a clay zone in the center of the streambed). Based on head gradients between stream and near-stream and in-stream groundwater levels, the stream transect is gaining during low flows and losing during high flows (Fig. 5). Head gradients during losing periods are significantly larger than head gradients during gaining periods (mean head gradient = -1.4 m m^{-1} during losing periods versus mean head gradient = 0.44 m m^{-1} during gaining periods). These large gradients indicate greater movement of water through the streambed interface. Changes in hydraulic gradient from positive (indicating gaining conditions) to negative (indicating losing conditions) are accompanied by rapid temperature changes in the in-stream piezometers due to streamwater moving through the streambed; however, temperature changes in the near-stream shallow wells are seasonal due to the nonconservative nature of heat transport in groundwater. As groundwater moves along a flow path, heat is transferred to the solid matrix, which has larger heat capacities. This results in both a dampening and lag time in groundwater temperature fluctuations as the length of the flow path from the stream (the source of temperature perturbations) increases (Constantz, 2008).

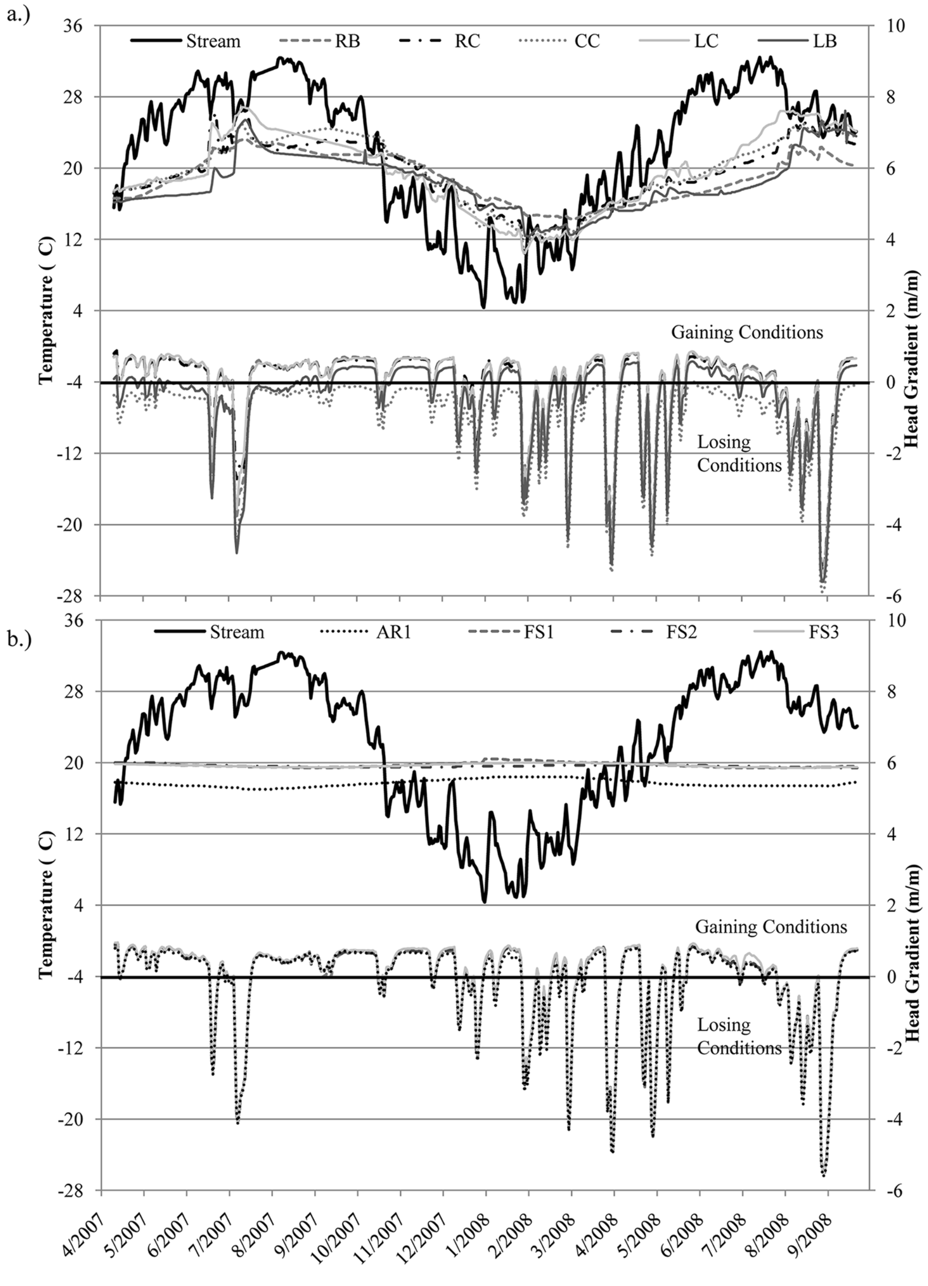


Fig. 5. Thermographs and head gradient for (a) in-stream piezometers and stream and (b) near-stream piezomters and stream. CC, central channel; LB, east bank ; LC, east channel; RB, west bank ; RC, west channel.

The combined effect of the horizontal and vertical gradients causes variability in the head gradients from the west side to the east side of the stream because the groundwater levels are higher on the west side than on the east side of the stream (Fig. 2). Assuming homogeneous hydraulic conductivity throughout the streambed, the relatively larger vertical gradients observed on the east side of the stream indicate that during losing conditions, the potential exists for more water to move downward through the streambed interface on the east side of the stream than on the west side. During gaining conditions, the vertical gradient is smaller on the east side than the west side, indicating that under homogeneous conditions more water potentially could move upward through the streambed interface on the west side than on the east side.

Using the calibrated model, the flux rate and cumulative flux can be determined through specified sections of each model boundary (Fig. 6). Flux is expressed here as m^3 d^{-1} and represents the movement of water through the entire width of each boundary multiplied by a 1-m unit length of streambed. Positive flux indicates water moving through the boundary into the model domain, and negative flux indicates water moving through the boundary out of the model domain. For example, the streambed flux is positive during losing conditions (surface water moving down through the streambed interface into the model domain) and negative during gaining conditions (groundwater moving up through the streambed interface out

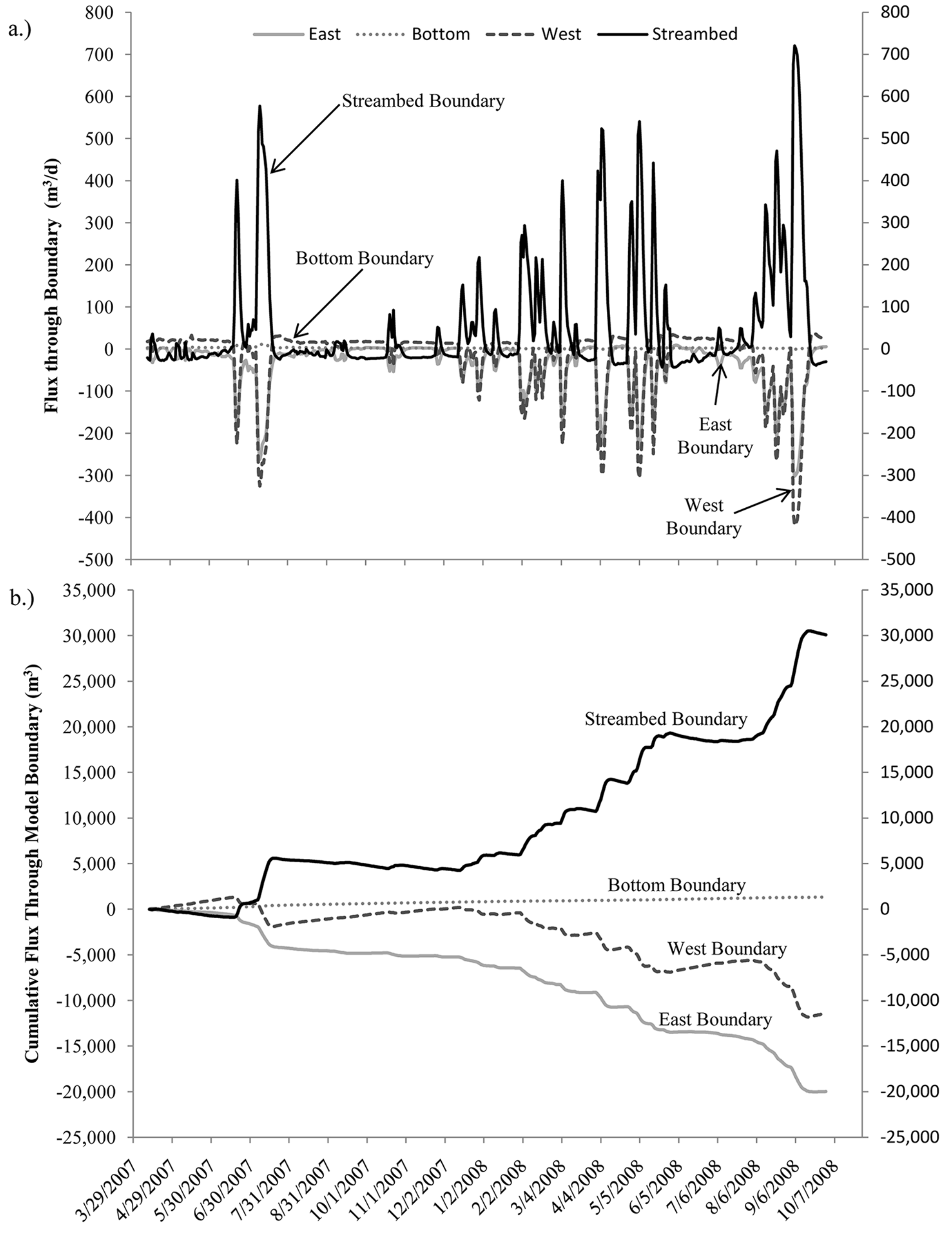


Fig. 6. Graphs showing (a) flux rate through each boundary throughout the simulation period and (b) cumulative flux through each boundary for the simulation period.

of the model domain). In general, most of the water moves through the horizontal and streambed interface boundaries, whereas less water moves through the bottom boundary. This predominance of horizontal flux versus vertical flux likely is due to the anisotropy of the fine sand that makes up most of the streambed sediments within the model domain (Table 1).

Streambed flux rates agree with the qualitative analysis of the head gradients and thermographs with larger flux rates occurring during losing conditions (mean flux rate = 151 m^3 d^{-1}) than during gaining conditions (mean flux rate = −18 m^3 d^{-1}). Cumulatively, the stream transect is losing (total flux into streambed per 1-m length stream channel = 30,091 m^3) for the simulation period, although the stream transect is gaining for a larger percentage of time than it is losing (56 and 44%, respectively). Mean residence times per unit streambed were determined for gaining and losing conditions using the mean flux rate and dividing it by 2 m, the average streambed thickness throughout the model domain. Gaining and losing mean residence times per unit streambed were 4.4 d (106 h) and 0.5 d (12 h), respectively.

The horizontal boundary flux output also agrees with the conceptual model in that although cumulatively, water moves out of both the east and west boundaries, more water moves out through the east boundary than out of the west boundary (−19,990 m^3 and −11,430 m^3, respectively) (Fig. 6). This is due to the hydraulic gradient of the water table, which slopes from the west side of the stream downward toward the east side of the stream, inducing larger vertical gradients on the east side of the stream and creating a heterogeneous flux pattern across the streambed interface (Fig. 7). Because of the heterogeneous flux rates across the streambed interface, it is possible for the total streambed flux to be a negative value, indicating gaining conditions, whereas the flux rates through the eastern part of the streambed interface are positive, indicating losing conditions. During gaining periods, groundwater from the west side of the stream supplies most of the groundwater discharging to the stream. During losing periods, nearly equal amounts of water move down through the east and west sections of the streambed interface and through the horizontal boundaries. Therefore, the total amount of water moving out of the east horizontal boundary is higher than the total amount moving out of the west boundary due to the gradient-induced heterogeneous flux across the streambed interface during gaining periods.

Results and estimates from VS2DH can be used with increased confidence to assess the transport and fate of nitrate associated with GWSW exchange if water-quality data support the streambed flux results. A qualitative means of assessing GWSW mixing is to examine the relation of major anions and cations in the water (Fig. 8). The Piper diagram is an effective tool for indicating the extent of mixing occurring between stream, streambed, and east and west near-stream groundwater. During gaining periods, stream water chemistry shifts toward the water chemistry groupings of the streambed and near-stream groundwater on the west side of the stream. Most streambed samples were collected

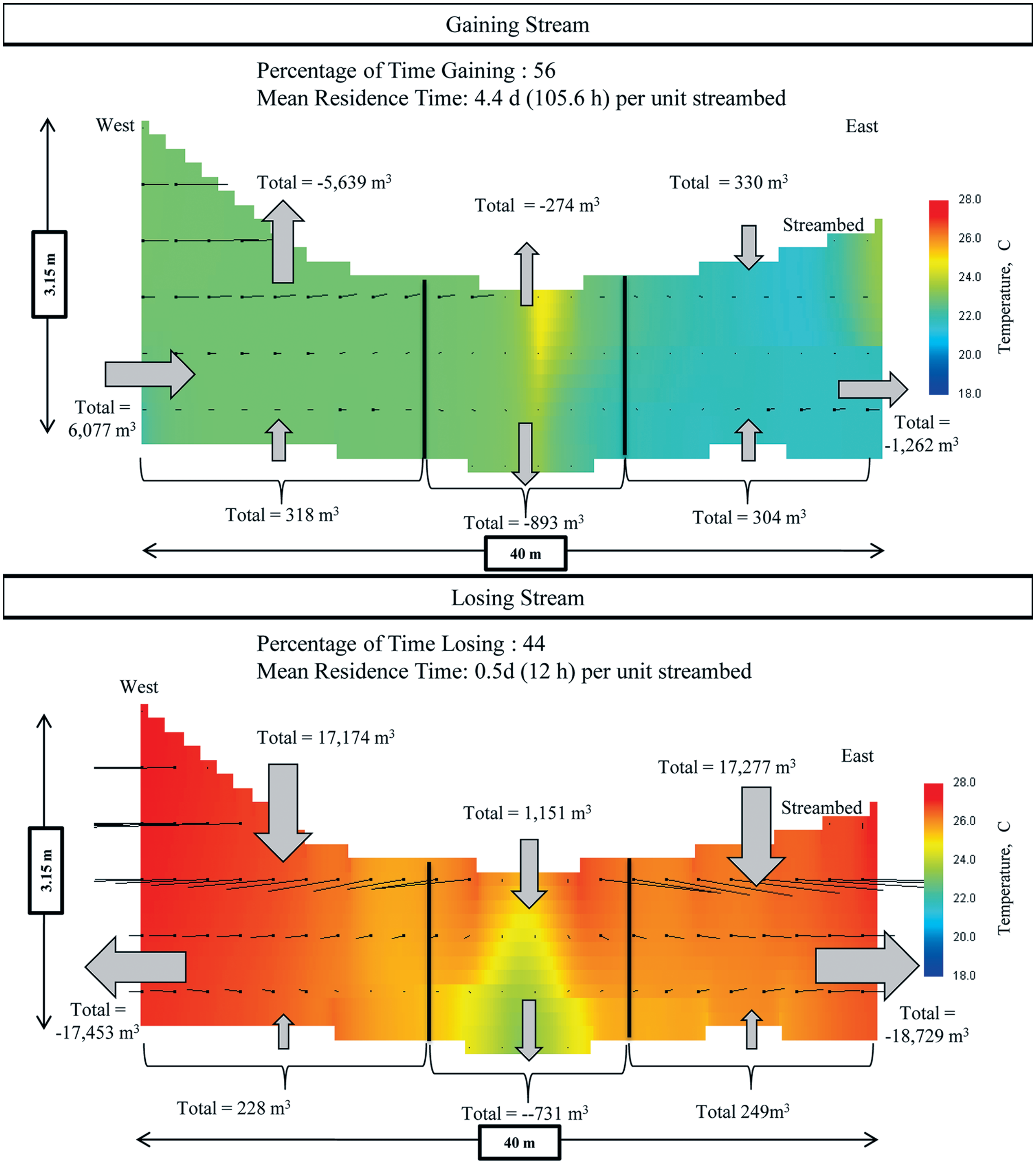


Fig. 7. Cumulative flux moving through each boundary section for gaining and losing periods. Arrows indicate direction of flow; negative numbers indicate water moving out of the model domain, positive numbers indicate water moving into the water domain.

from the in-stream piezometers during gaining periods due to accessibility; however, this shift in stream water chemistry is in agreement with VS2DH results in that most of the water discharging to the stream is from the west side of the stream through the streambed interface. Near-stream groundwater samples from the east side of the stream show a different chemical signature, dominated more by sulfate than the other groupings. Results from VS2DH indicate that surface water moves predominantly out toward the east side of the stream. One explanation for the higher sulfate concentrations measured in near-stream samples from the east side of the stream could be that the movement of oxygenated stream water to the east side of the stream causes the oxidation of HS^- or pyrite. A by-product of these oxidation reactions is $SO_4^=$, and over time, accumulation of $SO_4^=$ can occur, which would explain higher concentrations in groundwater on the east side of the stream than on the west side of the stream. This would require anoxic or oxygen-limited conditions within the aquifer, which are present at this site and discussed further in the following section.

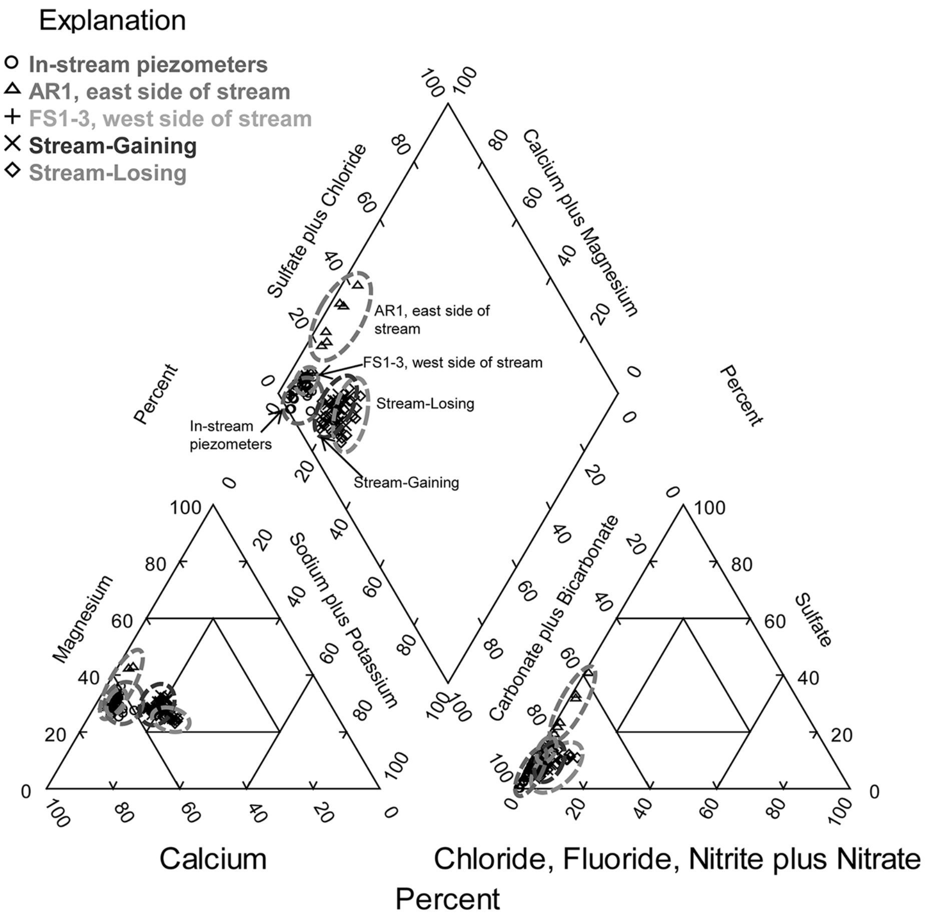


Fig. 8. Piper diagram of stream and groundwater chemistry, April 2007 through September 2008.

Fate and Transport of Nitrate through the Streambed

A significant amount of surface water has been shown to be moving into the streambed and then into the groundwater system. Nitrate is detected in nearly all stream samples (*n* = 52, median concentration = 39.8 μmol L^{-1}; Table 2), although never detected above laboratory reporting levels (<2.8 μmol L^{-1}) in any of the in-stream or near-stream piezometer samples (*n* = 46). Stream nitrate concentrations typically were higher during losing conditions than gaining conditions for the simulation period, which suggests dilution of stream nitrate concentrations by groundwater, or that the major transport mechanism of nitrate to the stream is overland runoff occurring during precipitation-driven high flow events (Table 2). An explanation for the lack of nitrate in the streambed and groundwater samples is denitrification. Denitrification is a complex process and can be difficult to measure and quantify; however, certain conditions must be present for denitrification to occur, and if denitrification is occurring, chemical endpoints will occur that can be measured. Denitrification, or the reduction of NO_3^- to N_2O or N_2, requires anoxic or oxygen-limited conditions, appropriate bacteria to oxidize organic and inorganic compounds for energy, and available electron donors such as organic carbon. The reduction of NO_3^- to N_2O or N_2 is an example of the preferential sequence of reduction reactions, commonly referred to as the terminal electron acceptor processes or TEAPs (Korom 1992; Chapelle et al., 1995). The TEAPs typically progress in the following order: O_2 reduced to H_2O, NO_3^- reduced to N_2, Mn(IV) reduced to Mn(II), Fe (III) reduced to Fe(II), $SO_4^{=}$ reduced to HS^-, and finally, CO_2 reduced to CH_4 (methanogenesis) (Korom, 1992; Chapelle et al., 1995).

Redox conditions of the streambed and adjacent aquifer typically are anoxic, and the dominant TEAP was determined to be either iron or sulfate reducing (McMahon and Chapelle, 2007; Jurgens et al., 2009) (Fig. 9). Hydrogen sulfide, which is needed to distinguish between iron- and sulfate-reducing conditions, was not measured; however, all near- and in-stream piezometers had a H_2S odor during all sampling events, indicating the presence of HS^- and sulfate-reducing conditions. Available redox constituent data (NO_3^-, Mn, Fe, and SO_4) from RB (in-stream piezometer on west side of stream), LC (in-stream piezometer on east side of stream), and the stream were compared with streambed flux

Table 2. Summary of nitrate and redox-related data for the Bogue Phalia near Leland, MS, surface-water data-collection site throughout simulation period (11 Apr. 2007–30 Sept. 2008). Concentrations are shown as the median value with the maximum value in parentheses.

Stream condition	Gaining	Losing
Percentage of time gaining/losing	56	44
Mean residence time (days per unit streambed)	4.4	0.5
No. of samples	22	28
Dissolved oxygen (μmol/L)	222 (432)	217 (372)
pH‡	7.7 (8.2)	7 (7.7)
Specific conductance (μS/cm)‡	481 (705)	210 (636)
Nitrate (μmol/L)†	26.6 (104.7)	44.4 (212.9)
Manganese (μmol/L)‡	0.5 (3.3)	0.15 (2.95)
Iron (μmol/L)‡	0.1 (0.4)	0.4 (1.4)
Sulfate (μmol/L)‡	625 (981)	203 (863)

† Indicates difference between gaining and losing concentrations are statistically significant at the 0.05 level.

‡ Indicates difference between gaining and losing concentrations are statistically significant at the 0.01 level.

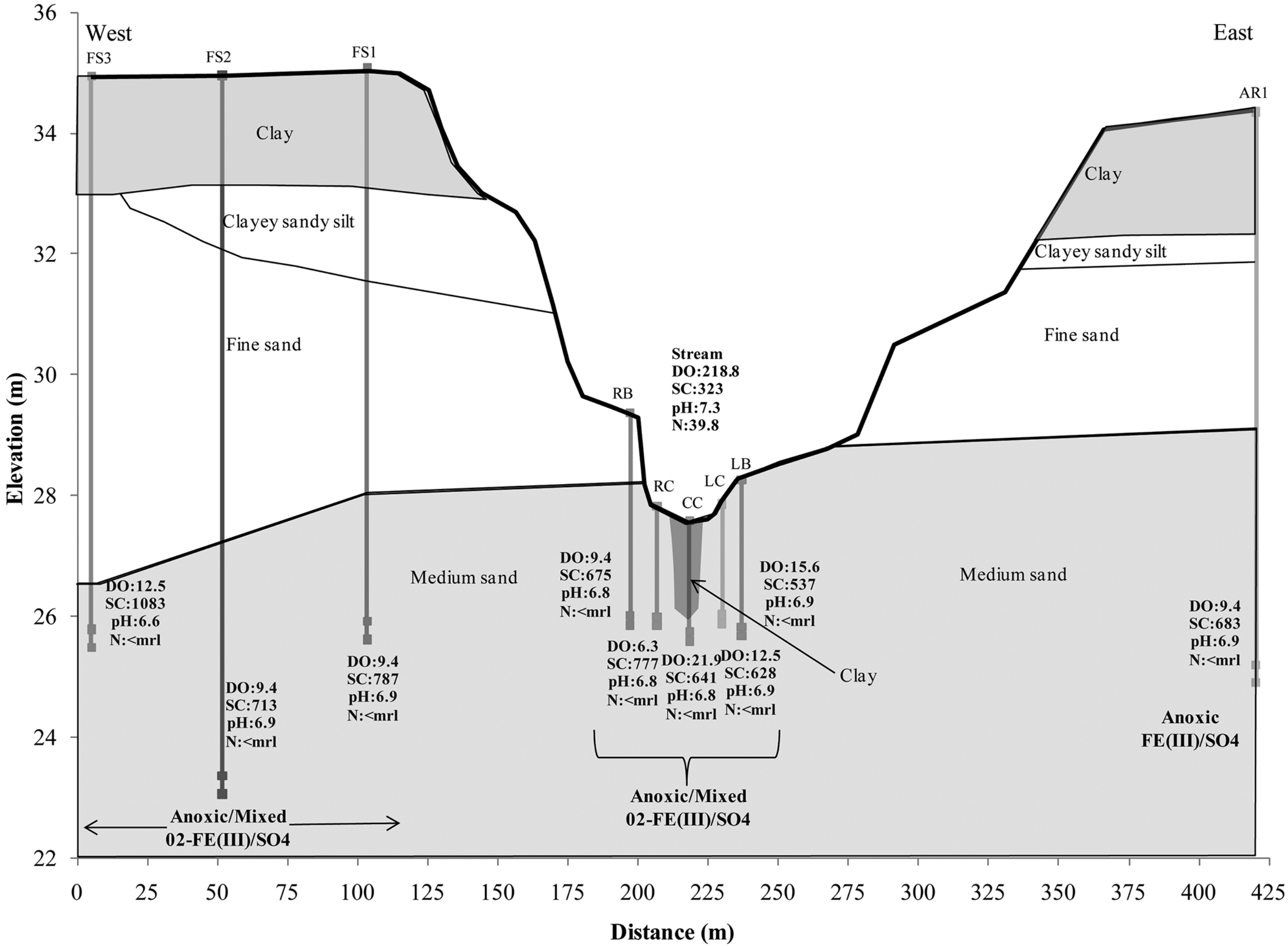


Fig. 9. Study area cross-section showing redox conditions, dominant terminal electron acceptor process, piezometer depths, and screened interval. Median concentrations of dissolved oxygen (DO in μmol L^{-1}), specific conductance (SC in μS cm^{-1}), pH (in standard units), and nitrate (N in μmol L^{-1}) shown for each piezometer and the stream.

throughout the simulation period to determine any relation between streambed flux and changes in redox constituent concentrations over time (Fig. 10). Stream concentrations of $SO_4^{=}$, and to a lesser degree, Mn, generally increase during gaining periods due to the higher concentrations of $SO_4^{=}$ and Mn in groundwater discharging to the stream. Iron concentrations in the stream remain relatively low because it is quickly oxidized to insoluble oxides and hydroxides of Fe(III) in the presence of oxygen. Similarly, Mn(II) oxidizes to Mn(IV) oxides in the presence of oxygen; however, the kinetics are not as rapid.

During periods when the stream transect is losing, concentrations of Mn and Fe increase in RB, whereas $SO_4^{=}$ concentrations generally decrease during losing conditions (Fig. 10). Increases in Mn and Fe concentrations can occur as a result of Mn(IV) and Fe(III) acting as oxidizing agents/electron acceptors during denitrification (Korom, 1992; McMahon and Chapelle, 2007). Decreases in $SO_4^{=}$ concentrations can occur as a result of the reduction of $SO_4^{=}$ to HS^- during denitrification. The changes in redox constituent concentrations observed in RB probably are related to streambed flux with the absence of O_2 and NO_3^- and concomitant increases in Mn and Fe concentrations and decreases in $SO_4^{=}$ concentrations corresponding to the reduction of O_2, NO_3^-, Mn(IV), Fe(III), and $SO_4^{=}$.

In contrast to RB, concentrations of Mn, Fe, and $SO_4^{=}$ decrease in LC when the stream transect is losing. The decrease in Mn and Fe concentrations suggests a lack of Mn(IV) oxides and Fe(III) oxide-hydroxides available for reduction within the streambed, leaving $SO_4^{=}$ reduction as the dominant terminal electron acceptor process (Chapelle and Lovely, 1992). One possible explanation for the differences between RB and LC in regards to the relation in redox constituents and streambed flux could be due to heterogeneous flux patterns through the streambed. The in-stream piezometer, LC, is located on the east side of the stream whereas RB is located on the west side of the stream. Based on the head gradients and streambed flux results, during losing conditions more stream water moves out through the east side of the stream, and during gaining conditions more groundwater from the west side of the stream discharges to the stream. Therefore, more streamwater interacts with LC and the east side of the streambed, over time potentially depleting the available Mn(IV) oxides and Fe(III) oxide-hydroxides in the streambed; whereas RB and the west side of the streambed receive more groundwater, with potentially more Mn(IV) oxides and Fe(III) oxide-hydroxides available as electron acceptors, moving along the west to east regional groundwater flow path and discharging to the stream. Ultimately, the case for denitrification through the streambed is supported by the

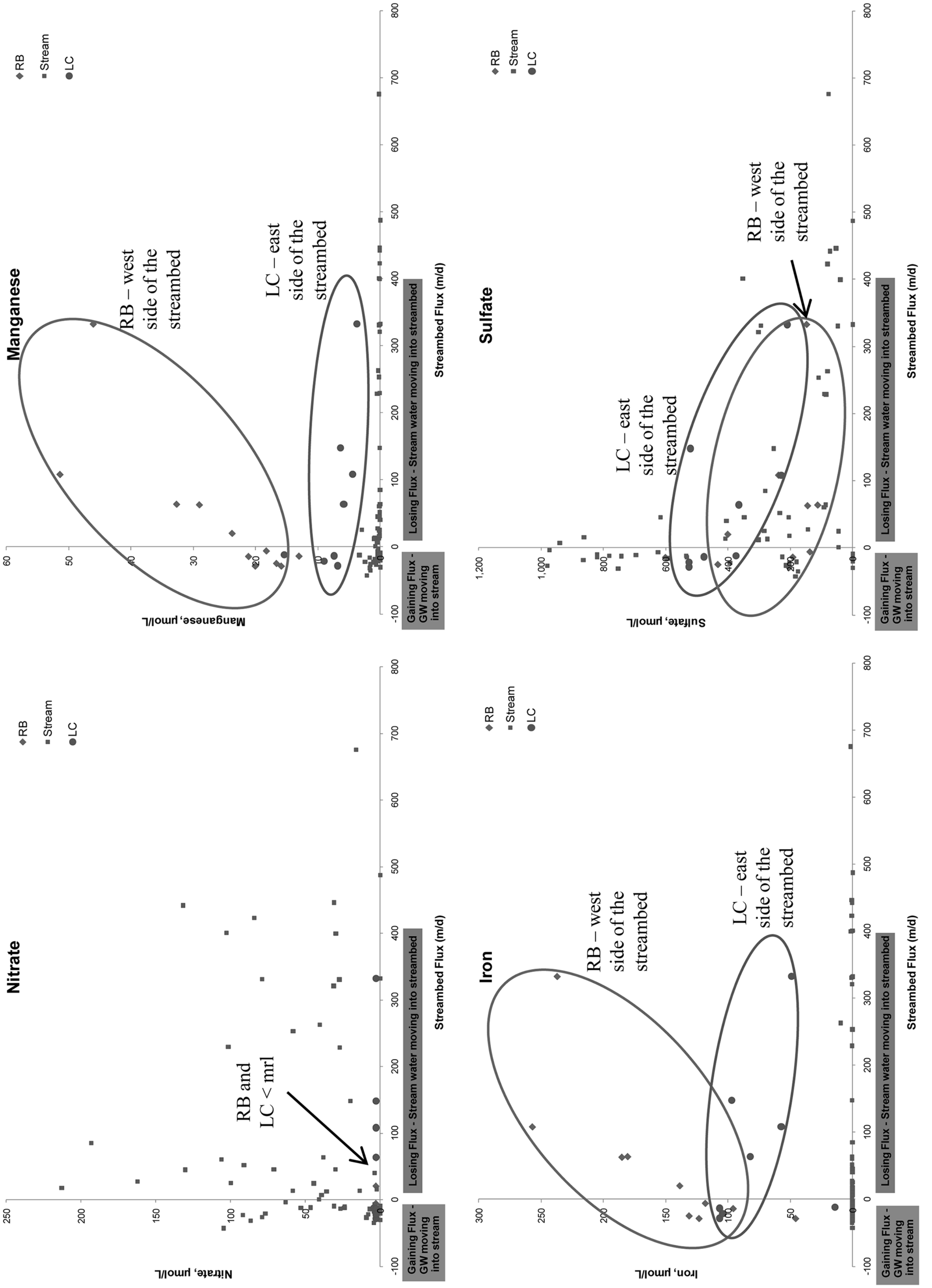


Fig. 10. Scatter plots showing the relationship between streambed flux and west bank (RB), east channel (LC), and stream redox constituents, NO_3^-, Mn(II), Fe(II), and $SO_4^=$. Negative streambed flux values indicate gaining conditions (groundwater [GW] discharging into stream), and positive values indicate losing conditions (streamwater moving into streambed).

changes in redox constituents relative to streambed flux, the anoxic conditions of the streambed and adjacent groundwater, and the lack of any observed transport of nitrate from the stream to the streambed during losing conditions.

Estimates of Nitrate Loss and Denitrification through the Streambed

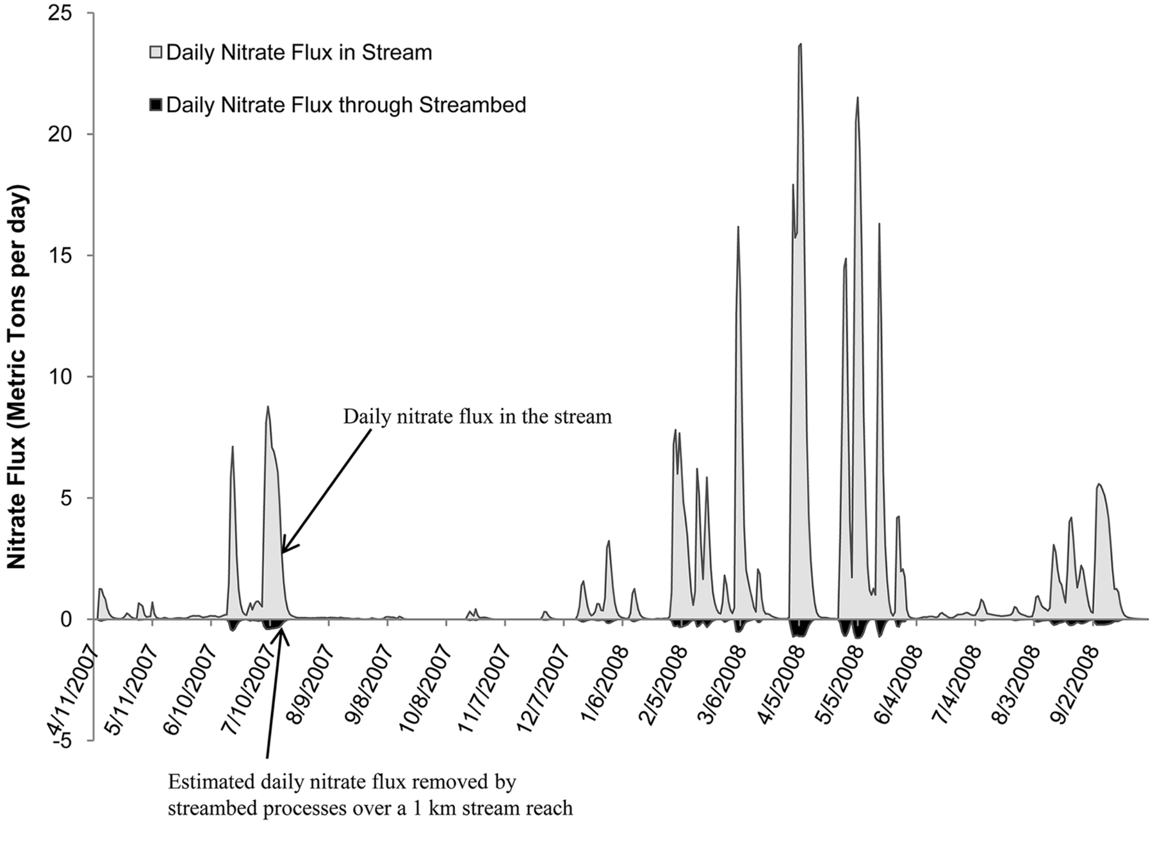
To date, most studies examining the role of GWSW interactions on nitrate transport reported that groundwater is contributing nitrate to surface water. These studies typically focused on the removal of nitrate from groundwater as it discharges to streams (Böhlke et al., 2004; Tesoriero et al., 2005; Gu et al., 2007; Duff et al., 2008; Kennedy et al., 2009; Puckett et al., 2008). However, results from this study of the Bogue Phalia show that groundwater in the Mississippi Delta does not contribute nitrate to surface water but instead is a factor in reducing the overall flux of nitrate in streams. The amount of nitrate removed by the streambed can be determined by multiplying the streambed flux by the nitrate concentration in the stream. Daily values for stream nitrate concentrations were determined using LOADEST, a program developed by the USGS to estimate constituent loads in streams (Runkel et al., 2004). Then, using the assumption that nitrate is completely removed to a depth of 2 m below the streambed interface, the nitrate flux into the streambed can be considered equal to the net mass of nitrate lost through the streambed.

The average annual load carried in the stream throughout the model simulation period (11 Apr. 2007 through 30 Sept. 2008) was 464 t with an upper and lower 95% confidence interval between 273 and 739 t. The average flux of water through a 1-m length by 40-m width of streambed was 151 $m^3 d^{-1}$, or approximately 0.005% of the total flow in the stream. This finding suggests that for this stream reach and study period, 0.005% of the total nitrate load in the stream was removed by streambed processes during losing conditions. Using this percentage, the average annual nitrate flux through the 1-m length by 40-m width of streambed was 0.023 t. Assuming that streambed conditions are homogeneous and stream nitrogen dynamics are static over a 1-km reach of stream, the average annual nitrate loss through the streambed would be about 5% of the total nitrate load in the stream throughout the simulation period. These results imply that streambed processes have the potential to significantly affect nitrate loads in the stream, and this potential increases as the amount of water and nitrate in the stream increase (Fig. 11).

Estimates of denitrification rates were determined using methods presented by Böhlke et al. (2009), which express denitrification as vertical denitrification flux per unit area of streambed using the following equation adapted for this study:

$$U_{\text{denit}} = v_{\text{sb}} \times (\text{NO}_3{}^-{}_{\text{sw}} - \text{NO}_3{}^-{}_{\text{sb}}) \qquad [1]$$

where U_{denit} is the vertical denitrification flux per unit area of streambed, v_{sb} is the vertical flux of water through 1-m^2 area of streambed, $\text{NO}_3{}^-{}_{\text{sw}}$ is the nitrate concentration of the stream, and $\text{NO}_3{}^-{}_{\text{sb}}$ is the nitrate concentration of the streambed. Assuming that nitrate is removed to a depth of 2 m below the streambed ($\text{NO}_3{}^-{}_{\text{sb}} = 0$ µmol) and using the LOADEST daily nitrate concentrations in the stream and VS2DH average daily streambed flux values per m^2 streambed, the maximum U_{denit}



Daily nitrate flux in the stream

Estimated daily nitrate flux removed by streambed processes over a 1 km stream reach

Fig. 11. Estimate of daily nitrate flux in the stream and through 1-km length of streambed.

value was 1,358,399 μmol N m^{-2} d^{-1} (56,600 μmol N m^{-2} h^{-1}), and the average U_{denit} value was 278,734 μmol N m^{-2} d^{-1} (11,614 μmol N m^{-2} h^{-1}). By comparison, U_{denit} values calculated by Böhlke et al. (2009) for agricultural streams in Illinois and Indiana draining the upper Mississippi River Basin ranged from 0 to 4000 μmol N m^{-2} h^{-1}, an order of magnitude lower than the rates estimated in this study. There are several possible explanations for the large differences in U_{denit} values estimated in this study and the values reported by Böhlke et al. (2009); one possible explanation is related to the geochemical setting of each study, in that this study is located in a setting with nitrate-free anaerobic groundwater, whereas the streams studied by Böhlke et al. (2009) are located in settings with aerobic groundwater that contains nitrate and has the potential to contribute nitrate to streams during baseflow. Another possible explanation is that flux rates through the streambed surface are larger in this study due to large gradient-induced fluxes. These two factors combined, anaerobic groundwater and higher flux rates through the streambed, could explain the larger U_{denit} values estimated in this study. Estimates of denitrification rates from this study likely are conservative estimates of the loss of nitrate in that they consider only the net loss of nitrate between the streambed interface and 2 m below the streambed interface and do not consider small-scale processes that occur at the streambed interface. The magnitudes of these rates indicate that rapid denitrification is occurring at or below the streambed interface and that this is an important pathway for nitrate loss.

Conclusions

Unlike many parts of the country, groundwater in northwestern Mississippi does not contribute nitrate to surface water but rather is a factor in reducing the overall flux of nitrate in streams. Estimates of streambed flux and water-quality data were coupled to assess the total mass of nitrate moving through the streambed and to gain a better understanding of the effect of GWSW exchange on the transport of agricultural constituents, such as nitrate. Streambed flux rates were determined to be higher during losing conditions than during gaining conditions, and cumulatively, the stream is a losing stream for the simulation period, although the stream was gaining for a larger percentage of time than it was losing (56 and 44%, respectively). Nitrate was detected in nearly all stream samples but never detected above laboratory reporting levels in any of the streambed or adjacent groundwater samples. Nitrate concentrations in the stream generally were higher during losing conditions than gaining conditions for the simulation period. The case for denitrification through the streambed is supported by the changes in redox constituents relative to streambed flux, the anoxic conditions of the streambed and adjacent groundwater, and the lack of any observed transport of nitrate from the stream to the streambed during losing conditions. The net loss of nitrate through the streambed over a 1-m length reach of stream for the time period 11 Apr. 2007 through 30 Sept. 2008 was on average 0.005% of the total nitrate load in the stream (almost 100 km in length). Assuming that streambed conditions are similar over a 1-km reach of stream, the average annual nitrate loss through the streambed was determined to be about 5% of the total nitrate load in the stream. These results imply that streambed processes have the potential to significantly affect nitrate loads in the stream and highlight the importance of stream–aquifer interaction, an issue that is manifesting itself in northwestern Mississippi, where reaches of many Delta streams go dry annually due to overuse of the alluvial aquifer for irrigation (Barlow and Clark, 2011). The Bogue Phalia is one of the larger rivers of the Yazoo River Basin, delivering water to the Mississippi River and ultimately to the Gulf of Mexico; therefore, stream nutrient loads and associated transport processes are an important issue locally and nationally.

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