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SYNTHESIS AND EMERGING IDEAS

Seasonal biogeochemical hotspots in the streambed around restoration structures

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Abstract Rapid exchange of stream water and groundwater in streambeds creates hotspots of biogeochemical cycling of redox-sensitive solutes. Although stream–groundwater interaction can be increased through stream restoration, there are few detailed studies of the increased heterogeneity of water and solute fluxes through the streambed and associated patterns of biogeochemical processes around stream restoration structures. In this study, we examined the seasonal patterns of water and solute fluxes through the streambed around a stream restoration structure to relate patterns of water flux through the streambed to morphology of the channel and biogeochemical processes occurring in the bed. We characterized different biogeochemical zones in the streambed using principal component analysis (PCA) and examined the change in spatial patterns of these zones during different seasons. The PCA results show that two principal components summarized 83% of the variance in the original data set. Streambed pore water was characterized as oxic (indicating production of nitrate), anoxic (indicating sulfate, iron and manganese reduction), or stream-like (indicating there was minimal change in the stream water chemistry in the bed). Regardless of season of the year, anoxic zones were predominantly located upstream of the structure, in a low-velocity pool, and oxic zones were predominantly located downstream of the structure, in a turbulent riffle. We expect structures that span the full channel, are impermeable, and permanent, such as those installed in natural channel design restoration will similarly impact biogeochemical processing in the streambed. The installation of these types of restoration structures may be a way to increase the degree of biogeochemical cycling in stream ecosystems.

Keywords Hyporheic zone · Principal component analysis · Redox processes · Stream restoration · Surface water–groundwater interaction

Introduction

Streambeds are the interface between stream water and groundwater where water, heat and solutes from these two end-members mix and transform (Brunke and Gonser 1997). Streambeds are hotspots of biogeochemical processing of redox-sensitive solutes (Boulton et al. 1998). The rapid exchange of stream water with the streambed increases the residence time of stream water as it is diverted to relatively low velocity flow paths through streambed sediments. The increased residence time corresponds to increased exposure of stream solutes to geochemically active

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sediments and microbial communities in the bed (Baker et al. 2000; Findlay 1995; Valett et al. 1996). As a result, nutrients and other solutes are cycled rapidly through inorganic and organic pools as stream water is continuously flushed through the streambed during transport.

Rapid exchange of stream water and groundwater in the streambed is driven by stream hydrology and morphology (Harvey and Wagner 2000). Spatial variability of stream water–groundwater (SW–GW) mixing in the bed is strongly controlled by channel morphological features, such as pool-riffle sequences (Harvey and Bencala 1993), small dams (Hester and Doyle 2008; Lautz and Siegel 2006), step-pool sequences (Kasahara and Wondzell 2003), and meanders (Wroblicky et al. 1998), because these features create spatially variable hydraulic head gradients that drive water in and out of the subsurface. Sediment characteristics of the bed can also impact SW–GW mixing in the streambed, with more permeable sediments allowing a more rapid exchange of water between the stream and the bed (Brunke and Gonser 1997; Morrice et al. 1997; Valett et al. 1996).

Patterns of water flux between the stream and its bed can be highly heterogeneous in space (Brunke and Gonser 1997; Conant 2004) and heterogeneity of SW–GW interaction in the streambed can be increased through stream restoration (Hester and Doyle 2008; Kasahara and Hill 2006b; Kasahara and Hill 2007). The active restoration of streams by channel modification and installation of structures is becoming increasingly popular, with billions of dollars spent annually (Bernhardt et al. 2005; Malakoff 2004). A primary factor driving restoration is the desired return of stream ecosystem functions (Palmer et al. 2005) and in-stream restoration efforts, including reference reach approaches, often include the addition of structures to the channel (Rosgen 1996, 2001). These structures are designed to mimic or assist in maintaining natural bedform features such as pool-riffle sequences and increase physicochemical and biological heterogeneity inherent in natural stream systems (Rosgen 1997). Because a primary goal of many stream restoration projects is to increase bedform heterogeneity, stream restoration projects are expected to enhance hyporheic exchange (Boulton 2007; Kasahara and Wondzell 2003).

There are very few detailed studies of the increased heterogeneity of water and solute fluxes through the streambed and the associated patterns of biogeochemical processes around stream restoration structures. Field and modeling experiments clearly indicate that the step in the water surface profile over in-stream structures generates head gradients in the streambed that drive rapid fluxes of water through the bed around the structure (Fanelli and Lautz 2008; Gooseff et al. 2006; Hester and Doyle 2008; Kasahara and Hill 2006b; Lautz and Siegel 2006). The rates of water flux across the streambed interface around in-stream structures are primarily controlled by the height of the step and the sediment characteristics (Hester and Doyle 2008; Lautz and Siegel 2006). In some settings, the streambed around restoration structures acts as a sink for dissolved oxygen and nitrate (Kasahara and Hill 2006a), but other settings show the streambed acts as a net source of nitrate (Fanelli and Lautz 2008). The spatial distribution of source and sink regions of the streambed are tightly linked to spatial patterns of hydrologic characteristics, such as vertical hydraulic gradient and seepage flux (Fanelli and Lautz 2008; Kasahara and Hill 2006a).

We examined the seasonal patterns of water, heat and solute fluxes through the streambed around a stream restoration structure to test whether the hydrologic and geomorphic setting around the structure generated zones of enhanced biogeochemical cycling that persisted across seasons. Our objectives were to (1) relate patterns of water fluxes through the streambed around a restoration structure to morphology of the channel and biogeochemical processes occurring in the bed, (2) characterize biogeochemical zones in the streambed around the structure using multivariate statistical methods, and (3) examine the change in patterns of these zones during different seasons.

Methods

Site description

The Red Canyon Creek (RCC) Watershed, located near Lander, WY, USA, is a third-order semi-arid watershed that is owned and managed by The Nature Conservancy of Wyoming (TNC) for recreation, education and livestock ranching (Fig. 1). Livestock overgrazing in the intermountain semi-desert ecoprovince (Bailey 1995) has accelerated erosion of topsoil, bank failure, and stream incision, lowered

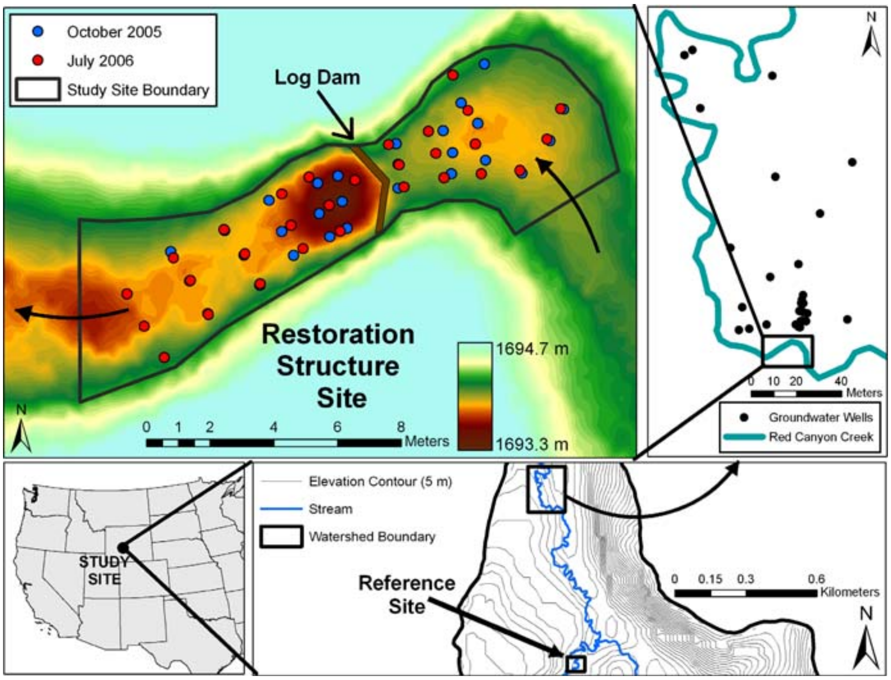


Fig. 1 Map of the restoration site and its location in central western Wyoming and the Red Canyon Creek watershed (bottom). The map to the right shows the locations of groundwater wells adjacent to the restoration site. On the color map to the upper left, blue and red points indicate sampling locations for October 2005 and July 2006, respectively. Where only July 2006, points are visible, October 2005, points are not shown because they are in the same location. Direction of water flow is as shown with the black arrows. Color shading on the site map indicates streambed elevation

water tables, and dried out landscapes (Chaney et al. 1990; Rosgen 1996). More specifically, induced stream incision causes destruction of point bars and meanders, stream shortening, and increased downcutting (Bledsoe et al. 2002; Leopold and Maddock 1953), which locally lowers the water table, causing riparian wetlands and meadows to disappear (Richards et al. 2002; Rosgen 1996).

To address these problems at RCC, TNC has installed a series of small log dams, or restoration structures, to restore stream habitat and improve riparian wetlands along the creek. These restoration structures block in-channel flow, locally raise the water table and create step-wise subsurface flow paths between the stream and water table (Lautz and Siegel 2006). These subsurface hydrologic "steps" enhance the lateral dispersal of recharge, re-saturation of dry soils, and redevelopment of wet meadows. During October of 2005 and July of 2006, we instrumented a reach surrounding one of the restoration structures installed by TNC along RCC (Fig. 1). In July of 2006, we also instrumented a reference site, without any restoration structure, in the same watershed within 1 km of the restoration site. The reference site is located on Cherry Creek, the largest tributary in the watershed, contributing 50% of the total RCC stream flow (Fig. 1).

The restoration structure was installed about 15 years ago and our experimental reach during both field seasons extended approximately 8 m upstream and 10 m downstream of the structure (Fig. 1). Previous work at this site has characterized the hydrology and geomorphology around the restoration structure in detail. MODFLOW simulations of the groundwater system show that the RCC dam creates large negative hydraulic gradients upstream of the structure, driving surface water into the subsurface in large and deep hyporheic zones, enhancing hyporheic exchange. The dam also creates localized sections of the subsurface with relatively high concentrations of stream water (Lautz and Siegel 2006). Field observations at multiple restoration structures in the RCC watershed show that flux into the streambed upstream of structures is generally vertical and limited in magnitude by low permeability sediments while fluxes downstream can be horizontal and large in magnitude due to the coarser substrate downstream of the structure (Fanelli and Lautz 2008).

The small log dam along RCC establishes a clear sequence of morphological features or channel units, which are segments of the stream that are smaller in scale than stream reaches and relatively homogeneous in terms of depth, velocity and streambed sediment characteristics, relative to adjacent units

(Bisson et al. 2006; Fig. 1). The morphology around TNC restoration structures is described in more detail in Fanelli and Lautz (2008) and summarized here.

Upstream of the dam is a pool (approximately 0.5–1.0 m in depth) where stream water is slow moving and silts and clays have settled out of the water column, reducing the streambed hydraulic conductivity. Vertical head gradients are up to −1.2 m/m and associated seepage flux rates from the stream into the bed average approximately 2 cm/day (Fanelli and Lautz 2008). The impoundment is impermeable and at the spill stream water velocity increases as the bed ramps up to the crest of the dam, creating a narrow band of coarse sands and gravels immediately upstream of the dam. The high water velocity, shallow depth (<0.5 m) and less turbulent flow here are characteristic of runs or glides. Here, vertical gradients average approximately −1.0 m/m and seepage flux rates from the stream into the bed average approximately 30 cm/day (Fanelli and Lautz 2008).

Immediately downstream of the dam, water falls about 1.5 m vertically over the impoundment onto the streambed, scouring out a plunge pool. Flow in this channel unit is fast and turbulent, mobilizing sediments and leaving coarse gravel in the streambed. A few meters downstream of the dam the streambed ramps up into a riffle unit, which is characterized by relatively shallow depths (less than 0.25 m) and moderate-sized streambed sediments that are a mixture of coarse silts, sands and gravel. Vertical gradients in both the pool and riffle are generally between 0.0 and −0.5 m/m and seepage flux rates from the stream into the bed average approximately 12–13 cm/day (Fanelli and Lautz 2008). About 6–7 m downstream of the dam, the streambed slopes downward and the channel transitions to the next pool, although this pool is shallower than the upstream pool and more characteristic of the naturally-occurring pool-riffle sequences that are found throughout the basin.

At the Cherry Creek reference site there are no restoration structures and the channel morphology is more uniform. The streambed is predominantly sand and gravel and the morphology includes a series of two small step-pool sequences. The steps consist of cobbles that create shallow pools (<0.5 m in depth). The steps are smaller in height than the step over the dam at the restored site (0.2 vs. 1.5 m, respectively).

Field and laboratory methods

Similar field and laboratory methods were used to analyze the streambed pore water geochemistry and vertical hydraulic gradients during October of 2005 and July of 2006. In the field, in-stream mini-piezometers were used to measure the vertical hydraulic gradient and to collect a sample of the streambed pore water (Woessner and Sullivan 1984). For this study, mini-piezometers installed in backwater areas or the riparian zone were excluded to only consider those installed within the active channel (i.e. where water is actively flowing). Mini-piezometers were constructed of 2.5 cm inner diameter PVC with the bottom 10 cm screened. Screens in the PVC were made by drilling ~1 mm diameter holes throughout the 10 cm interval. The mini-piezometers were installed to a depth of 30 cm and arranged in a series of transects between 1 and 2 m apart, with spacing of approximately 1 m between mini-piezometers along individual transects.

During October of 2005, 27 in-stream mini-piezometers were installed in the streambed around the restoration structure, with 13 mini-piezometers installed upstream of the dam and 14 installed downstream (Fig. 1). In July of 2006, mini-piezometers were reinstalled using approximately the same spacing as October of 2005. Sampling was extended farther downstream of the structure by adding an additional transect. In July of 2006, 29 in-stream mini-piezometers were installed, with 13 installed upstream of the dam and 16 installed downstream. In July of 2006, 22 in-stream mini-piezometers were installed at the Cherry Creek reference site, extending through the two step-pools.

The vertical hydraulic gradient is the difference between the water height inside the piezometer and the water height in the stream, relative to the distance between the streambed interface and the average screen depth (in this case, 25 cm). Vertical hydraulic gradients were measured at least 24 h after the mini-piezometers were installed. Pore water samples were extracted for geochemical analysis a minimum of 24 h after the hydraulic gradients were measured. The pore water samples were extracted using a syringe and flexible plastic tubing to minimize disturbance in the bed at the location of the mini-piezometer screen.

Stream water samples were collected at the same date and time as the streambed pore water samples during both seasons. Groundwater samples at the restoration site were collected from a network of over 33 wells and piezometers installed 5–50 m from the channel, in the floodplain adjacent to the stream (Fig. 1). A groundwater sample at the Cherry Creek reference site was collected from a groundwater well located approximately 5 m from the channel, in the adjacent floodplain. The groundwater wells and piezometers have 0.6–3.0 m long screens that are located between 0.8 and 3.7 m below the land surface. Although streambed pore waters are also subsurface waters, we restrict our definition of groundwater to water recently derived from the relatively large floodplain aquifer. Groundwater samples were not available for October 2005, so measurements taken in July of 2005 were used.

In both October of 2005 and July of 2006, samples were filtered through a 0.45 μm filter following extraction and then split. Samples for anion analysis (SO_4^{2-}, NO_3^- and Cl^-) were frozen in the field until analysis on a Dionex ICS-2000. Samples for metal analysis (soluble Fe, Mn, and Si) were acidified with 15 mol nitric acid and refrigerated until analysis on a Perkin-Elmer OPTIMA 3300DV inductively coupled plasma optical emission spectrometer. For the July 2006 sampling, pH of the pore water was measured in the field using a WTW 340i multi-parameter probe. Also, to measure alkalinity, an additional sample was collected and stored without head space and titrated within 12 h with 0.02 mol HCl to a pH of approximately 4.3.

Streambed temperature measurements during October of 2005 and July of 2006 were made using different techniques. In October of 2005, a hand-held thermistor thermometer was inserted into the mini-piezometers to record the temperature of the streambed pore water. Streambed temperature measurements were taken in the morning, between 9 and 10 am, and during the later afternoon, between 3 and 4 pm. The difference between the morning and afternoon temperature measurement is reported as the daily temperature fluctuation. In July of 2006, the mini-piezometers were removed from the streambed and replaced with iButton temperature data loggers (Dallas Semiconductor, Corp, CA). The iButtons were installed at a depth of 25 cm and recorded the temperature every 10 min for approximately 96 h. We used records for three complete days (72 h) for each data logger to determine the minimum and maximum temperatures each day in the streambed. The average difference between the minimum and maximum temperatures is reported as the daily temperature fluctuation. Caution should be used when interpreting the October 2005 temperature data because morning and afternoon temperature readings alone may not reflect the full magnitude of the diel temperature swing in the streambed, as recorded in July 2006. Despite this limitation, the change in streambed temperature over a fixed time interval is still useful as a qualitative measure, particularly when used with detailed temperature data, such as the data recorded in July 2006.

Multivariate statistical analysis

Principal Component Analysis (PCA) is a statistical method commonly used in environmental applications to interpret relationships between variables within large data sets and to reduce dimensionality of data tables (Johnson and Wichern 2001). The goal of PCA is to describe geochemistry using a small number of linear combinations of the original variables that summarize a majority of the variability contained in the original data set (i.e. Cloutier et al. 2008; Mencio and Mas-Pla 2008; Woocay and Walton 2008). We used the PRINCOMP procedure in SAS to do the analysis for the restoration site chemistry data (SAS Institute Inc., Cary, NC). Diagonalization of the correlation matrix of the data transformed the original five variables that showed spatial variation (SO_4^{2-}, NO_3^-, Fe, Mn and Si) into five linear combinations. The coefficients, or loadings, for each variable in the linear combinations were derived from the eigenvectors of the correlation matrix. The eigenvalues of the principal components indicate the data variance summarized by each principal component and these values can be expressed as a percentage of the total data variance.

Loadings for the principal components indicate the relative importance of each individual variable for computing the principal component scores and are used to interpret the meaning of the principal components. Correlations between the principal components and the variables in the original data set are also used to interpret the meanings of each principal component. Each principal component was used to compute a principal component score for each individual observation and these scores were used to describe combined patterns for multiple variables simultaneously.

Results

Hydrology at the restoration site

Spatial patterns of the vertical hydraulic gradient and the diurnal temperature signal in the streambed can be used to infer the rate and direction of water flux to and from the stream in the various channel units around the dam (i.e. Stonestrom and Constantz 2004; Woessner and Sullivan 1984). At the restoration site, the hydraulic gradients at all sites were negative (indicating flux downward into the bed) or static (indicating zero vertical flux or only horizontal flow) during both seasons (Fig. 2). The hydraulic gradients were slightly more negative during July 2006, but the spatial patterns in October 2005 and July 2006 were consistent. Upstream of the dam, in the backwater pool and the run, gradients were large and negative, between −1.25 and −0.5 m/m. Downstream of the dam, in the plunge pool and riffle, gradients were generally much smaller in magnitude, but also negative during both seasons.

Recent advances in the application of heat as a tracer in groundwater systems have made the technique a cost-effective, accurate and generalizable method for assessment of SW–GW interactions in streams (Anderson 2005; Stonestrom and Constantz 2004). Stream temperatures change dramatically on daily time scales while groundwater temperatures remain fairly constant. The propagation of the diurnal stream temperature signal into the streambed reflects the vertical flux rate of water to or from the stream (Conant 2004; Lapham 1989). Daily temperature changes in the streambed were measured differently during October of 2005 versus July of 2006. Also, temperature fluctuations in the stream itself were larger in July versus October, generating greater temperature fluctuations in the bed during July. So, the two measurements cannot be compared directly in terms of their magnitude. But, in both cases, we

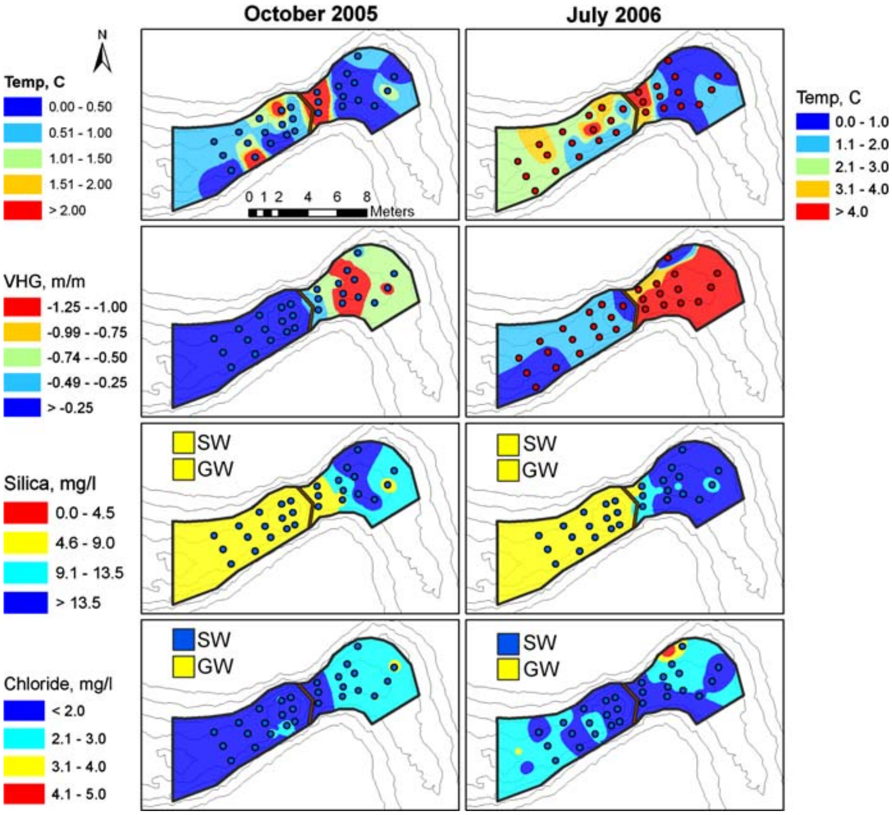


Fig. 2 Contour maps of the temperature fluctuations, vertical hydraulic gradients, silica concentrations and chloride concentrations in the streambed pore water at the restoration site. Contour maps were generated using inverse-distance weighting. Color-coded boxes representing the concentrations in the stream (SW) and groundwater (GW) are also shown, where applicable. Grey contour lines in the background are 20 cm topographic contours showing streambed elevation

expect a positive relationship between the relative magnitudes of daily fluctuations in streambed pore water temperature and rates of water flux into the bed, so the spatial patterns can be compared between seasons. Indeed, the spatial patterns between the two seasons are consistent (Fig. 2)

Streambed temperature fluctuations were highly variable during October of 2005 and ranged from −0.1 to 4.7°C (Fig. 2). Temperatures in the upstream pool changed by about 0.5°C or less at most sites, indicating a relatively low rate of water flux into the bed. The greatest observed temperature changes in the bed occurred in the upstream glide, where temperatures changed by greater than 2°C. Temperature signals in the downstream plunge pool and riffle were highly variable, but generally moderate (between 0.5 and 1.5°C). Streambed temperature fluctuations during July 2006 were larger in magnitude due to the greater change in the surface water temperature in the summer and the difference in methodology, although spatial patterns remain consistent from season to season. The signal ranged from 0.3 to 9.2°C. Previous modeling of seepage flux across the streambed from the July 2006 temperature records produced very similar values when compared to Darcy flux calculations, showing the temperature records provide good estimates of water flux through the bed (Fanelli and Lautz 2008). A spatial pattern similar to October 2005 was observed in July of 2006, with the temperature signal in the upstream pool relatively low and consistently less than 2°C. The greatest observed temperature changes in the bed occurred, again, in the upstream glide, where the temperature signal was up to 9.2°C. Temperature signals in the downstream plunge pool and riffle were, again, more variable in space but generally moderate (between 1.0 and 4.0°C).

Water chemistry at the restoration site

Summary statistics for the chemical analyses for the stream, groundwater and streambed pore water at the restoration site are given in Table 1. The spatial patterns of all solutes in the streambed pore water were similar during both October of 2005 and July of 2006 (Figs. 2, 3).

Dissolved silica concentrations were remarkably similar during the two field seasons, with concentrations higher in the streambed pore water than either the stream or groundwater (Table 1). The silica concentrations in the stream were 6.3 mg/l during both October of 2005 and July of 2006 and concentrations in the neighboring aquifer were 8.3 and 7.5 mg/l for the two seasons, respectively. Dissolved silica concentrations in streams and groundwater are generally uniform and constant because silica is buffered by its association with the surfaces of fine-grained materials (Langmuir 1997). We observed elevated silica concentrations in the streambed pore water upstream of the dam, with silica concentrations reaching 22.6 mg/l in October of 2005 and 27.2 mg/l in July of 2006 (Fig. 2).

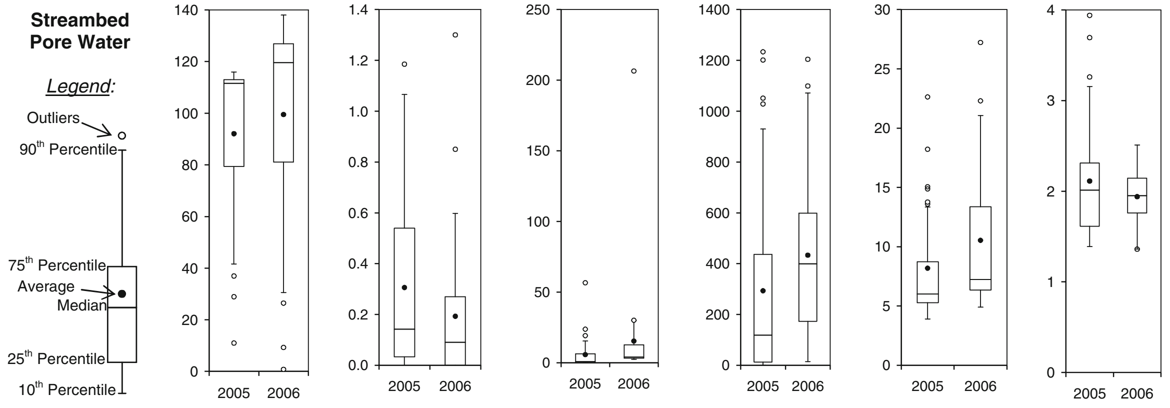
Chloride concentrations were generally low and less variable than the other solutes (Table 1). Stream water chloride concentrations were the lowest observed, at 1.4 mg/l during October of 2005 and 1.2 mg/l during July of 2006. Groundwater concentrations were the highest observed, at 3.3 mg/l during October of 2005 and 3.4 mg/l during July of 2006. Chloride concentrations in the streambed pore water generally fell between these two values and were more similar to the stream water concentrations during both seasons. In October of 2005, the chloride concentrations in the downstream channel units were virtually identical to the stream but in July of 2006, the most downstream sampling sites showed slightly elevated chloride concentrations (Fig. 2).

Sulfate concentrations were highest in the groundwater and lowest in streambed pore water upstream of the dam during both seasons (Table 1, Fig. 3). Groundwater concentrations averaged 435 and 543 mg/l during October of 2005 and July of 2006, respectively. Sulfate concentrations in the stream water were substantially lower at 115 mg/l during October of 2005 and 123 mg/l during July of 2006. The major ion geochemistry of stream water and groundwater at the site is dominated by gypsum dissolution (Fanelli and Lautz 2008) and, as a result, sulfate concentrations throughout the system are relatively high. Stream water and groundwater samples typically fall along the gypsum dissolution line, with carbonate dissolution providing an additional source of calcium (Fig. 4). In contrast, samples of streambed pore water do not fall along the gypsum dissolution line and the sulfate concentrations in the streambed are generally lower than the stream and groundwater concentrations (Fanelli and Lautz 2008). Indeed, the streambed pore water concentrations of sulfate are the lowest observed throughout the system.

Table 1 Geochemistry results for stream water, groundwater and streambed pore water at the restoration site for October 2005 and July 2006

RESTORATION SITE	SO_4^{2-} *mg/l*		NO_3^- *mg/l*		Fe *µg/l*		Mn *µg/l*		Si *mg/l*		Cl^- *mg/l*	
Sample Date	*Oct 2005*	*July 2006*	*Oct 2005*	*July 2006*	*Oct 2005*	*July 2006*	*Oct 2005*	*July 2006*	*Oct 2005*	*July 2006*	*Oct 2005*	*July 2006*
Stream Water (n=1, 7) [a]	115.3	122.5 (10.9)	0.02	0.11 (0.05)	1.2	2.9 (3.4)	17.3	19.2 (3.6)	6.3	6.3	1.4	1.2
Groundwater (n=1, 33) [b]	434.7 (211.4)	542.8 (341.6)	0.18 (0.35)	0.33 (0.49)	42.0 (74.6)	2.1	277.8 (144.2)	86.5	8.3 (1.4)	7.5	3.3 (1.1)	3.4

Streambed Pore Water



For stream water and groundwater samples, means and standard deviations (in parentheses) are reported when more than one measurement is available. Box plots are as shown in the legend. Concentrations not detected in the chemical analysis are considered to be zero

[a] For October, 2005, $n = 1$. For July, 2006, $n = 7$ for sulfate, nitrate, iron and manganese values and $n = 1$ for silica and chloride values

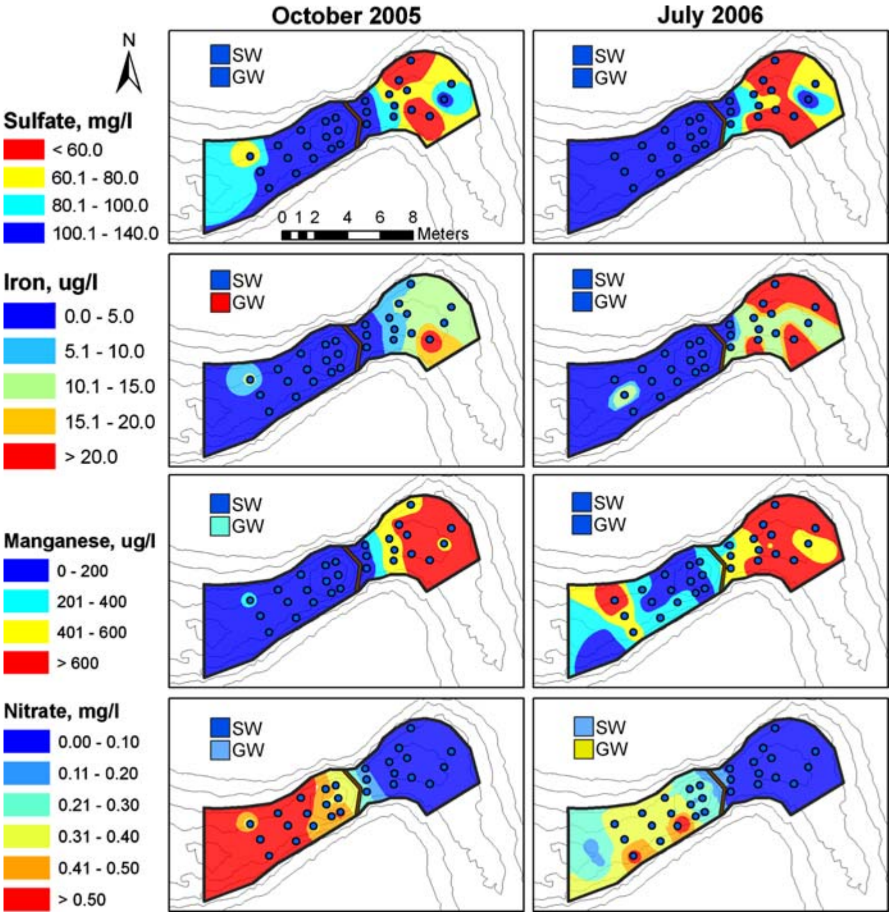
[b] For October, 2005, $n = 33$ and samples were collected in July 2005. For July, 2006, sulfate and nitrate concentrations are from the same set of 33 well and piezometers. For iron, manganese, silica and chloride values, $n = 1$

We attribute the apparent loss of sulfate in the upstream pool sediments to sulfate reduction, as has been observed elsewhere (Morrice et al. 2000). To confirm the plausibility of sulfate reduction occurring in the streambed, we compared differences in sulfate concentrations between the stream and streambed to differences in alkalinity and pH between the stream and streambed during July of 2006. Alkalinity, in meq/l, is significantly, negatively correlated to sulfate, in meq/l, in the streambed ($r = -0.97$, $p < 0.001$, $n = 29$). The oxidation of organic matter by sulfate reduction produces CO_2 (Table 2) (Baker et al. 2000) and, subsequently, HCO_3^- under circumneutral pH conditions (pH of 7–9), such as those found in RCC. We expect alkalinity to be elevated by a predictable magnitude in regions of the streambed where sulfate reduction is occurring. For every equivalent loss of sulfate, we expect a corresponding twofold increase in equivalents of alkalinity.

We used simple stoichiometric relationships for sulfate reduction, as presented by Baker et al. (2000), to compare changes in sulfate concentrations with corresponding changes in alkalinity. Assuming the loss of sulfate via sulfate reduction can be estimated as the difference between the sulfate concentration in the stream and the sulfate concentration in the bed, we can then compute the expected change in alkalinity, per the stoichiometric relationship shown in Table 2, and compare that change to the observed alkalinity patterns in the streambed. Predicted changes in alkalinity are similar in magnitude to observed changes in alkalinity and fall along the 1:1 line (Fig. 5). This supports our hypothesis that losses of sulfate are associated with sulfate reduction occurring in the streambed.

Sulfate reduction also produces a net decrease in pH. Although sulfate reduction consumes H^+, as shown in Table 2, it also produces CO_2, which releases H^+ during the formation of bicarbonate. The rate of CO_2 production is twice the rate of H^+ consumption, resulting in a net decrease in pH. There

Fig. 3 Contour maps of the sulfate, iron, manganese and nitrate concentrations in the streambed pore water at the restoration site. Contour maps were generated using inverse-distance weighting. Color-coded boxes representing the concentrations in the stream (SW) and groundwater (GW) are also shown. Grey contour lines in the background are 20 cm topographic contours showing streambed elevation



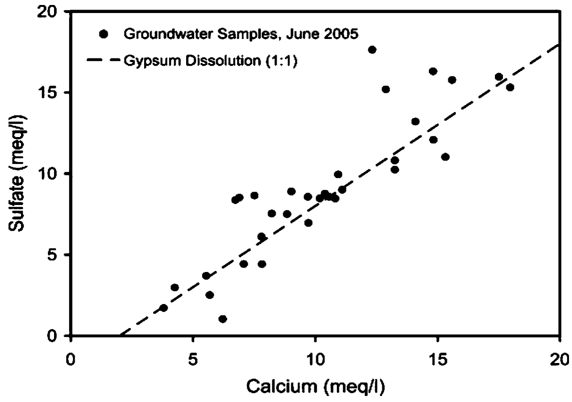


Fig. 4 Bivariate plot of calcium versus sulfate concentrations, in milliequivalents per liter, for groundwater samples collected in wells and piezometers immediately adjacent to the restoration site during July 2005. The 1:1 line, representing gypsum dissolution, is also shown

is a strong correlation between alkalinity and pH and between sulfate concentrations and pH, suggesting that sulfate reduction is likely responsible for changes in both of these parameters in the streambed (Fig. 6). Comparable alkalinity and pH data were not available from October of 2005, but we anticipate similar processes occurring during both seasons, as we observed similar patterns in the magnitude and spatial patterns of sulfate concentrations.

Soluble iron concentrations were ubiquitously low through the system during both seasons, with concentrations generally less than 25 μg/l (Table 1). Iron concentrations in the stream were less than 3 μg/l during both field seasons. Iron concentrations in the streambed pore water were higher, but generally less than 25 μg/l in October of 2005 and in July of 2006, with two exceptions. In October of 2005, the iron concentration in US-1 was 57 μg/l and in July of 2006, the iron concentration in US10 was 206 μg/l. Both of these sites are located near the edge of the channel in the backwater pool upstream of the dam. Although soluble iron concentrations in the upstream bed pore waters are generally low, they are consistently higher

Table 2 Stoichiometry of redox processes occurring in the streambed (adapted from Baker et al. 2000)

	Reaction	Reductive process equation
Increasing ΔG° ↓	Aerobic respiration	$CH_2O + O_2 = CO_2 + H_2O$
	Denitrification	$CH_2O + (4/5)NO_3^- + (4/5)H^+ = (7/5)H_2O + (2/5)N_2 + CO_2$
	Mn(IV) reduction	$CH_2O + 2MnO_2 + 4H^+ = 2Mn^{2+} + 3H_2O + CO_2$
	Fe(III) reduction	$CH_2O + 4Fe(OH)_3 + 8H^+ = 4Fe^{2+} + 11H_2O + CO_2$
	Sulfate reduction	$CH_2O + (1/2)SO_4^{2-} + (1/2)H^+ = (1/2)HS^- + H_2O + CO_2$

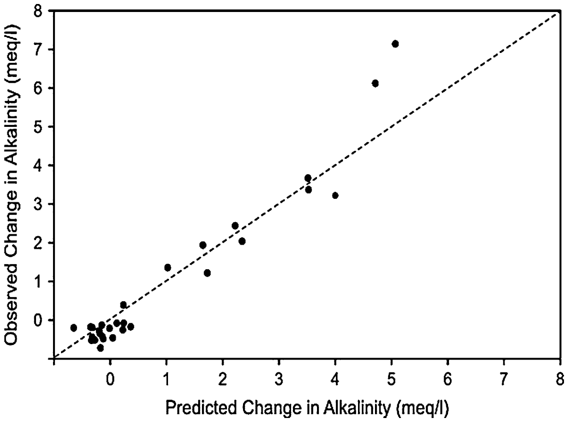


Fig. 5 Predicted versus observed alkalinity in the streambed pore water at the restoration site, based on stoichiometry relationships for sulfate reduction (for July 2006 data only)

than the iron concentrations in the stream and in the pore waters downstream of the dam (Fig. 3).

During both seasons, soluble manganese concentrations were much more variable than the soluble iron concentrations and the maximum concentrations observed were much higher (Table 1). In the stream, manganese concentrations were generally low, at 17 and 19 µg/l during October 2005 and July 2006, respectively. Although groundwater manganese concentrations were higher than the stream (278 and 87 µg/l during October 2005 and July 2006, respectively), the highest soluble manganese concentrations were observed in the streambed. Streambed manganese concentrations ranged from non-detectable to 1,233 µg/l in October of 2005 and 14 to 1,204 µg/l during July of 2006. In general, manganese concentrations were elevated in the pool upstream of the dam during both seasons (Fig. 3). In October of 2005, the manganese concentrations in the downstream channel units were generally uniform and low (Fig. 3). In July of 2006, the manganese concentrations in the most downstream sampling sites were elevated, although still generally lower than observed in the upstream pool (Fig. 3).

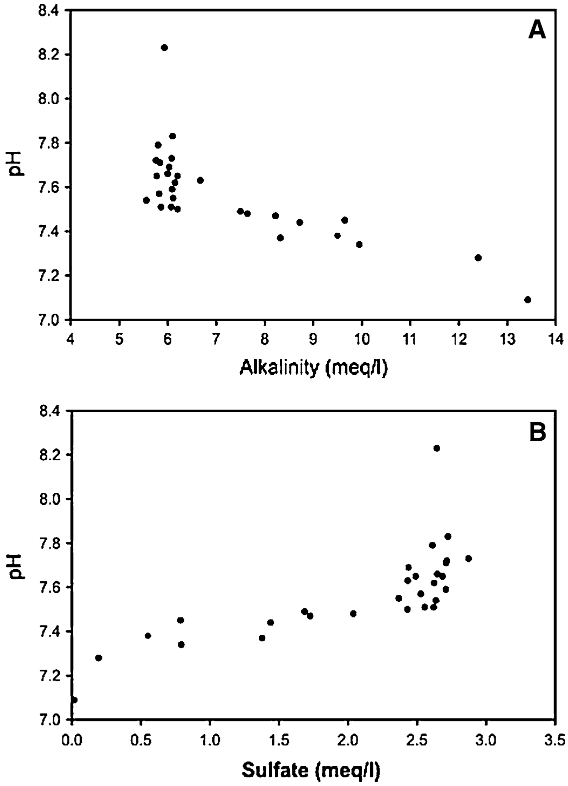


Fig. 6 Bivariate plots showing the relationships between pH and (**a**) alkalinity and (**b**) sulfate concentrations in streambed pore waters from the July 2006 data for the restoration site

Observed nitrate concentrations in the stream water and groundwater in Red Canyon are typically very low (Lautz and Siegel 2007). The watershed is semi-arid and nutrient-limited, as evidenced by the presence of *Nostoc* colonies along various segments of the streambed. *Nostoc*, a blue-green algae common in aquatic habitats, has the ability to fix atmospheric N_2, which can make it more competitive in nitrogen-poor environments (Dodds et al. 1995). We observed very low stream and groundwater nitrate concentrations during October 2005 (0.02 and 0.18 mg/l, respectively) and during July 2006 (0.11 and 0.33 mg/l, respectively). In contrast, nitrate concentrations in the streambed were highly variable and higher than the stream and groundwater concentrations at many locations. Nitrate concentrations in the streambed pore water ranged from non-detection to 1.18 mg/l in October of 2005 and from non-detection to 1.30 mg/l in July of 2006. The highest nitrate concentrations were found in the downstream riffle unit during both field seasons (Fig. 3).

PCA and typing of water chemistry at the restoration site

Principal Component Analysis (PCA) is appropriate for the restoration site data set because many of the solute concentrations are highly correlated and the patterns of these correlations are consistent across both seasons (Table 3). Sulfate and nitrate are positively correlated with one another and both are negatively correlated with iron, manganese and silica concentrations.

We combined the seasonal data sets at the restored site and performed one PCA analyses (Table 4). We selected two linear combinations (or principal components) because, together, they account for 83% of the variance within the data set, which contained five original variables (sulfate, nitrate, iron, manganese and silica concentrations) (Table 4). The first linear combination (PC1) accounted for 68% of the variance within the data set and is most strongly correlated with sulfate, iron, manganese and silica concentrations. Therefore, PC1 is termed the “redox function” because it represents the loss of sulfate due to sulfate reduction and the generation of soluble iron and manganese due to iron and manganese reduction. PC1 also represents the increase in silica associated with deposition of particulate matter. The second linear combination (PC2) accounted for 16% of the data variance. PC2 is most strongly correlated with nitrate concentrations. Therefore, PC2 is termed the “nitrate function” because it represents the elevated nitrate concentrations at some sites.

Table 3 Correlation matrix for the five geochemical parameters considered in the PCA analysis

		SO_4^{2-}	NO_3^-	Fe	Mn	Si	
SO_4^{2-}	July, 2006 (n=29)	1.00	0.49 (<0.01)	-0.70 (<0.01)	-0.82 (<0.01)	-0.92 (<0.01)	October, 2005 (n=27)
NO_3^-		0.40 (0.03)	1.00	-0.39 (0.05)	-0.57 (<0.01)	-0.48 (0.01)	
Fe		-0.61 (<0.01)	-0.20 (0.31)	1.00	0.74 (<0.01)	0.57 (<0.01)	
Mn		-0.83 (<0.01)	-0.23 (0.25)	0.58 (<0.01)	1.00	0.85 (<0.01)	
		-0.97 (<0.01)	-0.43 (0.02)	0.67 (<0.01)	0.83 (<0.01)	1.00	

Correlations from the October, 2005, data are shown in the upper right and correlations from the July, 2006, data are shown in the lower left. *p*-values are provided in parantheses

Table 4 Principal component loadings, eigenvalues and explained variance for the PCA. Correlations reported are the correlations between the principal components and the individual variables in the original data set

	PC1 loadings Redox function	ρ	PC2 loadings Nitrate function	ρ
$[SO_4^{2-}]$	−0.49	−0.91	−0.10	ns*
$[NO_3^-]$	−0.31	−0.58	0.87	0.77
[Fe]	0.39	0.72	0.47	0.42
[Mn]	0.48	0.89	0.00	ns
[Si]	0.52	0.95	0.07	ns
Eigenvalue	3.38		0.78	
% Variance explained	67.7%		15.7%	
% Cumulative variance	67.7%		83.3%	

* ns = not significant at $p < 0.05$

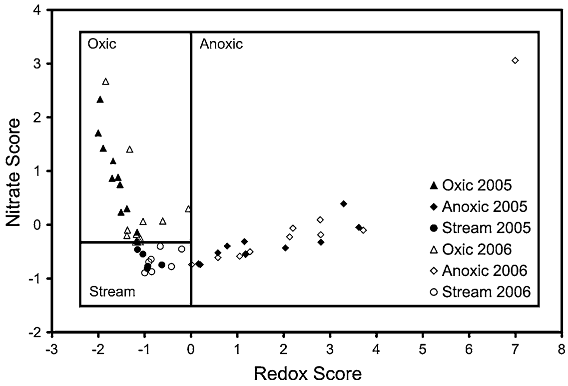
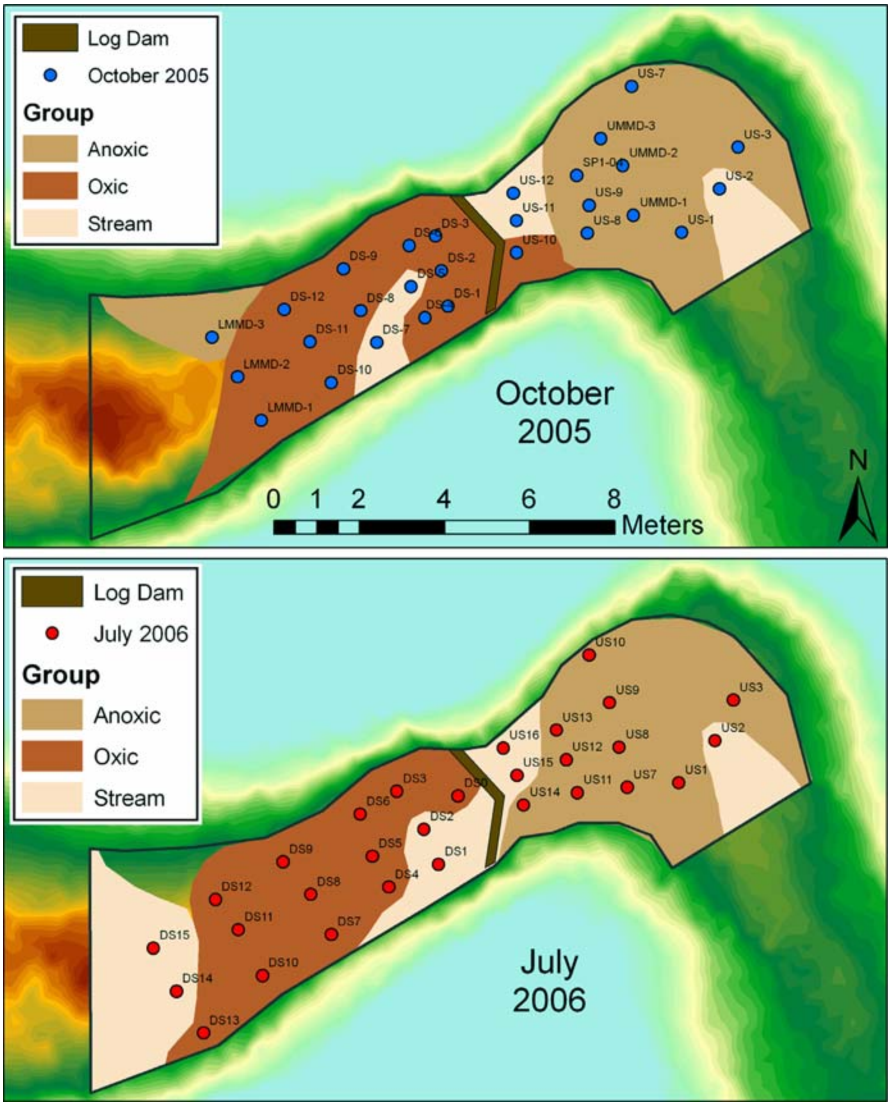


Fig. 7 Nitrate and redox scores from the two principal components for October 2005 and July 2006 for the restoration site. Boxes indicate the type of streambed pore water (oxic, stream or anoxic) based on PCA results

Fig. 8 Delineations of streambed pore water types at the restoration site derived from PCA for October 2005 and July 2006



The two principal components were used to calculate "redox scores" and "nitrate scores" for each pore water sample (Fig. 7). The two scores can be used to distinguish three streambed pore water types, which we term *anoxic*, *stream* and *oxic* (Fig. 7). *Anoxic* water samples received high redox scores, indicating they had a combination of low sulfate concentrations and elevated iron and/or manganese concentrations. These sites also had elevated silica concentrations. *Stream* water samples received low redox and nitrate scores, indicating that the water chemistry was similar to the stream water in terms of sulfate, iron, manganese and nitrate concentrations. *Oxic* water samples received high nitrate scores and low redox scores, indicating elevated nitrate concentrations, relative to the stream samples, and no evidence of alternate electron accepting processes, such as sulfate and manganese reduction. We mapped the spatial patterns of these pore water types for the October 2005 season and the July 2006 season to see whether a similar spatial pattern persisted across seasons (Fig. 8).

Hydrology and water chemistry at the reference site

Results of temperature measurements, vertical hydraulic gradient measurements and chemical analysis at the Cherry Creek reference site are provided in Fig. 9. Temperature measurements were only available for 11 of the 22 sites, as shown in Fig. 9, due to equipment

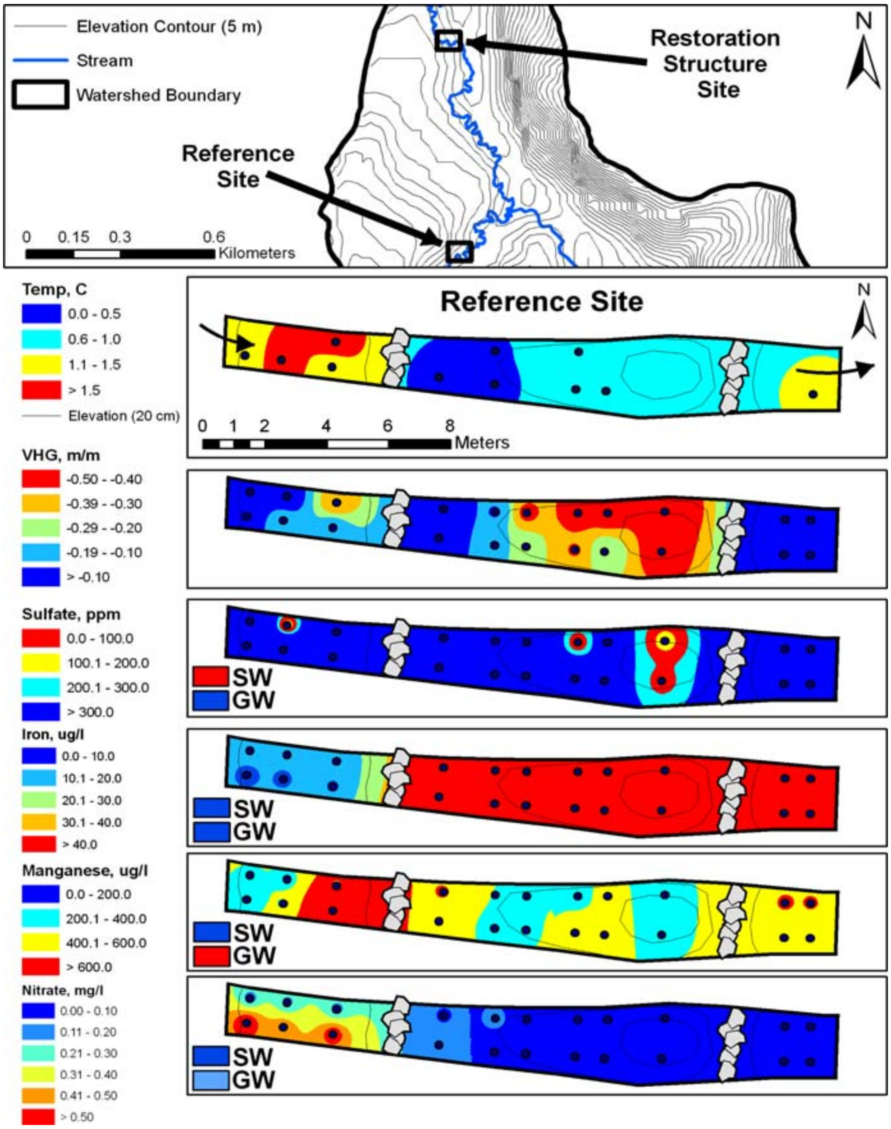


Fig. 9 Site map and contour maps of the reference reach along Cherry Creek. Site map shows the location within the Red Canyon Creek watershed (top). Contour maps show the temperature fluctuations, vertical hydraulic gradients and concentrations of redox-sensitive solutes (sulfate, iron, manganese and nitrate). Contour maps were generated using inverse-distance weighting. Note that the temperature contour maps were shown from the subset of points indicated on the map. Color-coded boxes representing the stream and groundwater concentrations are shown, if applicable. Blue points indicate sampling locations for July 2006. Direction of water flow is shown with arrows

malfunction, but the spatial distribution of the available data is fairly comprehensive. Overall, temperature fluctuations in the streambed at the reference site were smaller in amplitude (maximum = 1.7°C) than the observations at the restoration site (maximum = 9.2°C), indicating an overall lower rate of water flux into the bed. The July 2006 temperature measurements are directly comparable in terms of magnitude because iButtons were used at both sites and data were collected during the same season. Temperature fluctuations in the streambed are larger upstream of the steps, relative to immediately downstream. The vertical hydraulic gradients were generally negative or static, similar to the restored site, and ranged from −0.51 to 0.06 m/m. Although the pools upstream of the steps have slightly more negative gradients than areas immediately downstream of the steps (Fig. 9), the magnitude of the gradients overall were about half of those measured at the restored site (maximum gradient of −0.51 vs. −1.22 m/m, respectively). The combination of smaller temperature fluctuations and hydraulic gradients suggests an overall lower rate of water flux into the streambed at the reference site.

In addition to the lower rates of water flux at the reference site, the redox-sensitive solutes (sulfate, iron, manganese, and nitrate) do now show complimentary spatial patterns. Low sulfate concentrations do not clearly coincide with elevated iron and manganese concentrations or low nitrate concentrations. Indeed, there were no significant correlations (at $p < 0.05$) between any of the redox-sensitive solute concentrations at the reference site, so no PCA was performed on the reference site data set.

The groundwater sulfate concentrations at the reference site were similar to the restored site at 433 mg/l, but the stream water sulfate concentration was lower at 75 mg/l. In contrast to the restoration site, sulfate concentrations in the streambed pore waters were higher than the stream concentrations in 90% of the samples, suggesting minimal sulfate reduction (Fig. 9). Although sulfate reduction appears minimal, iron concentrations throughout the streambed were higher than the stream or groundwater values. Manganese concentrations in streambed pore waters were also elevated relative to the stream manganese concentration, but much more spatially variable than the iron concentrations (Fig. 9). In contrast to the restored site, the spatial distribution of the high iron and manganese concentrations do not correspond to the spatial patterns of low sulfate concentrations. Nitrate concentrations in the stream and groundwater at the reference site are similar to the restored site at 0.09 and 0.13 mg/l, respectively. Most streambed pore water samples at the reference site (17 of 22) had nitrate concentrations less than 0.10 mg/l and only three samples of streambed pore water had nitrate concentrations greater than 0.5 mg/l, suggesting minimal nitrate production.

Discussion

Spatial patterns of biogeochemical hotspots in the streambed

The chemistry of streambed pore waters around the restoration structure reflects a complex interaction between the local hydrologic setting and numerous biogeochemical processes, including alternate electron accepting processes in anaerobic environments, nitrate production in aerobic environments and the accumulation of silica due to particulates settling out of the stream water column. These processes alter the chemical composition of the streambed pore water, which would otherwise represent a mixture of stream and groundwater. The rate of water influx to the streambed controls the replenishment of oxygen to the subsurface and, therefore, the distribution of these biogeochemical hotspots around the restoration structure.

The changes in water chemistry resulting from both aerobic and anaerobic biogeochemical cycling are highest in the streambed, relative to the stream or groundwater systems. These zones are biogeochemical "hot spots" because they are the only place in the system where nutrients and redox-sensitive solutes are rapidly transformed. The sulfate, manganese and nitrate concentrations observed in the bed are unique from both the stream and groundwater concentrations. The sulfate concentrations in the bed are the lowest observed anywhere in the system and the nitrate concentrations in the bed are the highest observed anywhere in the system. Although there are slight shifts in the spatial extent of these zones between seasons, those shifts are minor, indicating that the dam generates a predictable pattern of biogeochemical cycling in the bed that persists over time.

Anoxic hotspots in the streambed

Spatial patterns of the raw water chemistry data and the PCA water types clearly illustrate that anoxic conditions dominate in the upstream backwater pool during both seasons. These zones correspond to the channel unit with the lowest rate of seepage flux across the bed and associated replenishment of oxygen to the streambed. Redox reactions typically occur in a predictable sequence, starting with aerobic respiration when oxygen is available and then proceeding, in order through denitrification, manganese reduction, iron reduction and sulfate reduction, once oxygen has been depleted (Baker et al. 2000; Champ et al. 1979). Progressive decreases in dissolved oxygen, nitrate and sulfate, paired with increases in soluble iron along near stream flow paths have been attributed to the progression of microbial respiration of organic C by sequential alternate electron accepting processes (Morrice et al. 2000).

Nitrate concentrations in the upstream backwater pool are very low or not detectable. Because denitrification, or the dissimilatory reduction of nitrate, is the first alternate electron accepting process to occur following oxygen depletion, any nitrate present in the streambed would be quickly reduced in the backwater area. Spatial patterns also show elevated manganese concentrations in the backwater pool upstream of the dam during both seasons. Reduction of manganese generates soluble Mn^{2+} in these regions of the streambed. Spatial patterns of sulfate concentrations in the streambed also indicate that the lowest sulfate concentrations are found within the backwater pools during both seasons. The apparent loss of sulfate in the upstream pool sediments is attributed to sulfate reduction in anoxic segments of the streambed, as has been observed elsewhere (Morrice et al. 2000). The PCA typing of water chemistry summarizes these spatial patterns, clearly showing that they persist across seasons.

The low soluble iron concentrations are somewhat surprising because we expect iron reduction to proceed prior to sulfate reduction and, therefore, to find high concentrations of uncomplexed Fe^{2+} in the anoxic hotspots. However, sulfate concentrations in Red Canyon waters are high due to gypsum dissolution. When sulfate concentrations are high and conditions are anaerobic enough to cause sulfate reduction, Fe(II) will precipitate as sulfides (Langmuir 1997). As a result, in Red Canyon, iron is generally not soluble in either aerobic or anaerobic conditions due to the formation of either Fe(III) oxyhydroxides in aerobic environments or Fe(II) sulfides in anaerobic environments. Although iron concentrations in the streambed are generally low, the spatial patterns do indicate slightly higher soluble iron concentrations in the upstream backwater pools during both seasons (Fig. 3). The regions with elevated soluble iron correspond generally with zones of lower sulfate concentrations and we attribute the elevated soluble iron concentrations to iron reduction.

The extent of this anoxic zone is limited to the deep water section of the upstream area and streambed pore water becomes more similar to the stream in the glide immediately before the spill over the dam. Anoxic conditions are generated in the upstream pool because fine materials lower the streambed hydraulic conductivity and reduce the rate of water flux to the streambed, as demonstrated by the thermal patterns. Low rates of stream water infiltration to the bed limit the replenishment of oxygen and increase residence time. We expect that organic matter is also readily available for oxidation in the pool sediments because it accumulates with fine materials settling out of the water column. Rates of iron, manganese and sulfate reduction are expected to be higher in fine-grained streambed sediments because water residence time is relatively high, organic carbon is often more readily available and microbial densities are high (Baker et al. 2000). Elsewhere, low concentrations of dissolved oxygen and nitrate in bed pore water, relative to stream water, have revealed hotspots of nitrate reduction and ammonium production and these spatial patterns have also been linked to the inherent patchiness of the streambed sediment permeability (Pretty et al. 2006).

The zones of anoxia coincide with zones of silica accumulation in the backwater pool. Dissolved silica is taken up by diatoms, which then accumulate in stagnant pools with the settling out of fine-grained particulate matter. Siliceous remains of diatoms and radiolarian continue to dissolve after burial and silica concentrations in sediment pore waters are often elevated (Berner and Berner 1996). Elevated concentrations of silica in the upstream pool sediments suggest dissolution of diatoms that have accumulated with fine sediments in the slow-moving water.

Oxic hotspots in the streambed

Although the streambed can act as a sink for nitrate and other redox-sensitive solutes, the stream hydrology, and particularly water residence time in the subsurface, plays a strong role in the spatial patterns of biogeochemical reduction processes in the hyporheic zone (Findlay 1995; Valett et al. 1996). The riffle unit is moderate between the conditions found immediately around the dam (high streambed flux and short residence time) and the conditions found in the upstream pool (low water flux and long residence time). Relatively high velocity flow over the riffle creates a coarse sediment distribution, which has a relatively high permeability. Hydraulic gradients here are small and water flow is less turbulent compared to the glide, moderating the rate of water and oxygen flux into the bed. In this channel unit, flux rates into the bed are adequate to replenish the supply of oxygen and create aerobic conditions, but the residence time is long enough for the end products of aerobic processes, such as nitrification, to accumulate in the streambed pore waters.

Spatial patterns of the raw water chemistry data and the PCA water types clearly demonstrate that, in contrast to the upstream pool, oxic conditions dominate in the downstream riffle during both seasons. Elevated nitrate concentrations (greater than

0.20 mg/l) are found in the downstream riffle segment of the streambed where nitrate production dominates. The production of nitrate in the downstream segment of the channel is surprising, given the ubiquitously low nitrate concentrations found elsewhere in the system. Nitrate can be generated by either aerobic decomposition of organic matter or nitrogen fixation, followed by nitrification, which only occurs in the presence of available oxygen (Duff and Triska 2000). The downstream region of the bed is an area of moderate exchange of water between the stream and streambed, providing an ideal balance between adequate oxygen replenishment to maintain aerobic conditions and a long enough residence time to allow nitrate concentrations to increase in response to aerobic nitrate production.

As expected, in oxygenated environments soluble iron concentrations in the downstream riffle are low because iron is present primarily as particulate Fe(III) oxyhydroxides that have a low solubility (Langmuir 1997). Relatively insoluble Mn oxyhydroxides also form in aerobic conditions and manganese concentrations were generally low in the downstream plunge pool and riffle during both seasons, although some regions of elevated manganese were observed in the most downstream sampling sites during July 2006 (Fig. 3). The elevated concentrations of manganese in the most downstream samples during the summer season may be an indication of discharging groundwater mixing with the streambed pore water. These locations coincide with areas that have slightly elevated chloride concentrations, which supports the hypothesis of groundwater discharge. Previous work along Red Canyon Creek has also suggested that the most downstream sections of riffles can be locations of groundwater discharge (Fanelli and Lautz 2008). An alternate explanation is that higher respiration rates during the summer reduce oxygen content in thebed at the downstream end of the riffle. Manganese reduction is one of the first alternate electron accepting processes to occur once oxygen is depleted, which would explain why manganese concentrations are elevated and iron and sulfate are not affected.

Stream water zones in the streambed

Immediately around the dam, some samples of streambed pore water from the upstream glide and downstream plunge pool had chemical signatures that were nearly identical to the stream. Due to the large negative hydraulic gradients and the high permeability sediments in the glide immediately before the spill, water and oxygen flux into the bed is highest at this location. The large daily temperature fluctuations in the upstream glide reflect the rapid influx of stream water into the bed. The rapid supply of oxygen creates aerobic conditions, but the low water residence time limits the ability of aerobic processes to alter the pore water chemistry. Similar conditions are found in the plunge pool immediately downstream of the dam. The energy available to transport fine materials away from the bed is very high and water flow is very turbulent. The turbulent flow through the plunge pool increases the rate of water and oxygen exchange with the bed, creating an aerobic streambed with low water residence time, similar to the glide.

Seasonal differences in streambed geochemistry

Although the pore water type distribution in the streambed around the restoration structure is remarkably consistent between seasons, there are some seasonal differences in the pore water geochemistry that are important to consider. The July 2006 sampling event indicates a greater degree of reduction of redox-sensitive solutes in the streambed while the October 2005 sampling event indicates a greater degree of oxidation of redox-sensitive solutes. In July 2006, the sulfate concentrations in the stream were slightly higher (122.5 mg/l) than during October 2005 (115.3 mg/l). Despite the higher sulfate concentration of infiltrating stream water in July 2006, sulfate concentrations in the streambed were lower in anoxic zones within the bed in July 2006 versus October 2005, indicating a greater degree of sulfate reduction in the upstream pool during the summer (Table 1, Fig. 3). In addition to increased sulfate reduction in anoxic zones in the bed, manganese reduction is more widespread in the streambed during July 2006, as compared to October 2005 (Fig. 3), and manganese concentrations are universally elevated. The greater loss of sulfate to sulfate reduction and the increase in soluble manganese during July 2006 are attributed to decreases in dissolved oxygen availability and increases in biological activity when water temperatures are high (i.e. during summer months). Seasonal and diel differences in anaerobic metabolism and accumulation of redox-sensitive solutes in the streambed have been observed elsewhere and been attributed to changes in water temperature (Brick and Moore 1996; Gunten et al. 1994, 1991; Gunten and Lienert 1993). The regions of elevated manganese in the downstream riffle also correspond to regions with elevated chloride concentrations, suggesting an increase in groundwater discharge at that location may be partially responsible for the elevated manganese concentrations.

In October of 2005, nitrate concentrations in oxic zones of the bed downstream of the dam are universally higher than observed in July 2006, suggesting a greater degree of nitrate production or less uptake of nitrogen by biota during the October season, allowing a greater accumulation of nitrate in the streambed pore water. Increases in dissolved oxygen availability in the cooler October season may fuel more nitrate production in the bed. Alternatively, lower rates of microbial activity in the bed during the cold season may limit biological assimilation of nitrogen. Diurnal changes in nitrate concentrations in stream water have been attributed to diurnal changes in rates of nitrogen uptake by photoautotrophs (Duff and Triska 2000). Although the magnitude of redox processing, both aerobic and anaerobic, appears to be different during the two seasons, the seasonally consistent spatial patterns show that morphology and hydrology play a significant role in the development of redox conditions in the bed.

Impacts of stream restoration structures

At the reference site, with no restoration structure, we did not see the development of biogeochemical hotspots in the streambed, as found at the restoration site. The small, naturally occurring step-pools did not clearly generate the same anoxic and oxic zones around the steps, as found at the restored site. There are no significant correlations between concentrations of redox-sensitivie solutes and no overlapping spatial patterns of these solutes in the streambed at the reference site. Investigations around other similar restoration structures in the RCC watershed do indicate that the spatial patterns of water, heat and solute fluxes described here are consistently found at other restoration sites, with sulfate, iron and manganese reduction occurring in upstream pools and nitrate production occurring in downstream riffles (Fanelli and Lautz 2008). Based on these results, the biogeochemical hotspots appear to be unique to restored sites and not apparent at other sites.

The Nature Conservancy has taken passive and active approaches to restoration of Red Canyon Creek (RCC). Although passive restoration at the site, including protecting the stream from heavy grazing pressure, has produced positive outcomes, recovery of severely degraded channels can take decades or longer, particularly when channels are severely incised with accelerated erosion of high banks, such as at RCC (Nagle 2007). Reestablishment of floodplain connectivity and riparian vegetation can be accelerated by adding structures that reduce bank erosion and locally raise the water table (Gordon et al. 2004; Nagle 2007). TNC has paired active restoration, including the installation of a series of small log dams, with their passive restoration approach to accelerate recovery of RCC.

Small in-stream obstructions like those installed along RCC are commonly used in active stream restoration projects, particularly in natural channel design (NCD) (Rosgen 1996). Structures, such as small wood debris dams, log jams, artificial weirs, current deflectors, dikes and groynes, are used in active restoration to restore the diversity of physical habitat (Gordon et al. 2004). Partial obstructions that do not span the full channel width can be used to protect eroding banks, create physical diversity in the stream, generate habitat for fish and macroinvertebrates (such as deep pools) and provide surfaces for attachment and growth of aquatic plants and invertebrates. Fully-spanning obstructions, such as low weirs and debris dams, are often used to re-establish pool-riffle morphology and pool-cascade sequences (Gordon et al. 2004). The morphology around the RCC structure indicates that the structure has been successful at creating a sequence of pools and riffles adjacent to the artificial step. These morphological features have developed over the 15 years since the structure was installed. Although the precise distribution of the pool-riffle transitions shift slightly in response to high spring runoff, the morphology is consistent from season to season and meets expectations for the structure impact.

We expect the morphology around the RCC structure to be characteristic of similar structures that span the full channel, are impermeable, and permanent, such as those installed as part of NCD restoration design projects. We anticipate that permanent, impermeable structures will generate a similar morphology that will similarly impact biogeochemical processing in the streambed. The installation of these types of restoration structures may be a way to increase the degree of biogeochemical cycling in stream ecosystems. Indeed, others have observed similar patterns of biogeochemical processing around similar restoration structures (Kasahara and Hill 2006a).

Conclusions

The significance of stream–groundwater interactions to the stream ecosystem is dependent on the activity in the streambed, including nutrient transformations, and the degree of connectivity between the stream and streambed (Boulton et al. 1998). In-stream obstructions, such as the small log dam in this study, increase connectivity between the stream and the streambed, generating spatially variable fluxes of water into the bed. These variable fluxes create closely spaced oxic and anoxic zones and rapid biogeochemical cycling of nutrients and other redox-sensitive solutes.

The spatial patterns of redox zones in the bed closely follow the morphology of the channel. Anoxic conditions are found in the upstream pool, where slow-moving water has allowed fine particulates to settle out, reducing the hydraulic conductivity of the bed material. In these zones, the influx of water to the bed is relatively low and the rate of oxygen consumption is greater than the rate of replenishment from the stream. As a result, the oxidation of organic material is proceeding via a series of alternate electron accepting processes, such as sulfate, manganese and iron reduction. Oxic conditions are found in the downstream riffle, where the moderate rate of stream water exchange with the bed supplies enough oxygen to maintain aerobic conditions, allowing for nitrate production. Residence times in the bed in this zone are long enough for the end products of nitrification to accumulate in the pore water. In regions of the bed where water flux into the bed is extremely high (i.e. the upstream glide), residence times are very short and stream water is not modified as it moves through the bed.

The spatial patterns of pore water geochemistry around the restoration structure are permanent across seasons, despite slight periodic changes in bed morphology. These spatial patterns are not present at unrestored sites. Therefore, the installation of small dams in restoration projects may be a mechanism to generate biogeochemical “hot spots” in the streambed that persist over time. These hotspots are geochemically unique from both stream water and groundwater and do not represent a simple mixing of these two end members. The rates of nitrate production, sulfate reduction and manganese reduction observed in the bed are higher than observed elsewhere in the system. The biogeochemical hotspots around restoration structures are important for stream nutrient spiraling and there presence may serve to improve stream function.

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