Hydrologic and Biogeochemical Controls of River Subsurface Solutes under Agriculturally Enhanced Ground Water Flow

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The relative influences of hydrologic processes and biogeochemistry on the transport and retention of minor solutes were compared in the riverbed of the lower Merced River (California, USA). The subsurface of this reach receives ground water discharge and surface water infiltration due to an altered hydraulic setting resulting from agricultural irrigation. Filtered ground water samples were collected from 30 drive point locations in March, June, and October 2004. Hydrologic processes, described previously, were verified by observations of bromine concentrations; manganese was used to indicate redox conditions. The separate responses of the minor solutes strontium, barium, uranium, and phosphorus to these influences were examined. Correlation and principal component analyses indicate that hydrologic processes dominate the distribution of trace elements in the ground water. Redox conditions appear to be independent of hydrologic processes and account for most of the remaining data variability. With some variability, major processes are consistent in two sampling transects separated by 100 m.

Agricultural practices can degrade ground water and surface water quality. Common impacts on aquifers include introduction of pesticides and herbicides (e.g., Puckett and Hughes, 2005) and nutrient enrichment (e.g., Harned et al., 2004). Surface water quality can be degraded by overland flow of agricultural runoff (e.g., McKergow et al., 2006) or by the increase of suspended and dissolved solids due to increased erosion (e.g., Montgomery, 2007). As demands on water in agricultural areas of the USA increase due to climate change, population growth (Anderson and Woosley, 2006), and protection of endangered species habitat (via increase of residual stream flows at the expense of agricultural diversions; Franssen et al., 2007), mitigation of agricultural impacts is an active area of research and watershed management.

Surface- and ground water quality are linked in the riverbed hyporheic zone, a region of exchange between riverbed ground water and surface water characterized by short-length scales (Findlay, 1995; Packman and Bencala, 2000). The hyporheic zone provides an environment for abiotic and biogeochemical reactions that may influence pore water redox chemistry and stream transport of nutrients (Haggard et al., 2005; Valett et al., 1996) and other inorganic solutes (Salehin et al., 2004; Bencala, 2000; Packman and Bencala, 2000). Ground water flow from affected aquifers through the hyporheic zone can be a major source of contaminants to surface water (Brown et al., 2007), and thus hyporheic degradation or sequestration (by biogeochemical reactions) or transport (by advection) of contaminants affect ground water and surface water quality.

Previous research has examined systems where surface water is the dominant source of riverbed ground water and hydrology is relatively unperturbed (e.g., Choi et al., 2000; Harvey et al., 2005). However, agricultural irrigation can substantially alter hydrologic regimes in aquifers and surface water. Extensive irrigation by interbasin water transfer (a common practice in the western USA) may raise the water table beneath agricultural fields and subsequently

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Abbreviations: CV, coefficient of variation; DOC, dissolved organic carbon; ICP–MS, inductively coupled plasma–mass spectrometry; PC, principal component; PCA, principal component analysis; SC, specific conductance; SD, standard deviation.

induce ground water discharge to river reaches that would otherwise lose water to the subsurface. Furthermore, storage of irrigation water in reservoirs often leads to downstream river flows that do not resemble those that occur in undammed rivers.

We examined such an agriculturally influenced system, a reach of the lower Merced River in the Central Valley of California. The Merced flows into the San Joaquin River, which feeds the Sacramento-San Joaquin Delta, a major drinking water source for Southern California and the western San Joaquin valley (Gronberg and Kratzer, 2007). The Delta is ecologically sensitive and home to the threatened delta smelt (*Hypomesus transpacificus*) and other declining fish species (Feyrer et al., 2007). The San Joaquin River, once habitat for a thriving Chinook salmon (*Oncorhynchus tshawytscha*) population, is a target for ecological restoration (Lucas et al., 2002).

This study builds on recent results that characterize hydrological and chemical processes beneath the Merced River. The objective of our study was to use chemical tracers of hydrologic processes (bromine [Br]) and redox conditions (manganese [Mn]) in the Merced River subsurface to assess the dominant influences on the distribution of four specific solutes (strontium [Sr], barium [Ba], uranium [U], and phosphorus [P]) in the subsurface. These "response elements" were chosen to represent a range of chemical behaviors from elements observed to have measurable concentrations in an initial survey.

The field site was a reach of the lower Merced River approximately 20 km above its confluence with the San Joaquin River (Fig. 1). This productive agricultural area is typical of the eastern San Joaquin Valley, California. The land surface, which is composed of highly permeable, low organic carbon, medium- to coarse-grained sand, slopes westward from the Sierra Nevada with a slope of about 1 to 4 m km^{-1} (Capel et al., 2008; Phillips et al., 2007). The semiarid Mediterranean climate delivers 31 cm yr^{-1} of rainfall, mostly during winter, and necessitates summertime crop irrigation (Capel et al., 2008; Gronberg and Kratzer, 2007). The yearly average flow of the Merced River at its confluence with the San Joaquin is 19.4 m^3 s^{-1} (Capel et al., 2008). The streambed sediment is sandy and subject to vigorous scouring and bedload transport (Zamora, 2008).

Regionally, crops cover 55% of the lower Merced Basin (Capel et al., 2008) and surround our field site. Consequently, agricultural practices have substantially altered the hydrology of the lower Merced River. Water is retained upstream of the field site in multiple reservoirs, diverted for agricultural use, and returned via five irrigation canals to the lower section of the river (Gronberg and Kratzer, 2007). Additional water is transported into the basin via canal and applied to fields and orchards. Thus, the local aquifer to the northwest of the field site experiences a net gain that is discharged to the Merced River and then transported out of the basin (Phillips et al., 2007). No ground water flow information is available about the local aquifer to the southeast of the study reach, but a similar irrigation scenario may exist there also. In other settings, altered hydrologic patterns affect solute transport and trace element mobility (e.g., Harvey et al., 2006; Kneeshaw et al., 2007), and the same may be true at the Merced River.

In the center of the upstream transect (described below) at the study reach, flux across the streambed was estimated to range from -1.1×10^{-7} to 5.9×10^{-7} m^3 m^{-2} s^{-1}, where positive values indicate flow from the riverbed into the Merced River (Essaid et al., 2008). Ground water generally flows slowly to the Merced River (mean flux, 1.8×10^{-7} m^3 m^{-2} s^{-1}) when summertime irrigation raises the water table (Phillips et al., 2007; Domagalski et al., 2008). This small flow of ground water into the river results from small differences in hydraulic head between surface water and ground water, and it can vary or reverse in the center of the river due to variations in river stage caused by to storms or dam releases (Puckett et al., 2008; Essaid et al., 2008). The residence time of surface water that infiltrates into the subsurface can be approximately 2 mo (Puckett et al., 2008).

Puckett et al. (2008) inferred spatial hydrological processes beneath the Merced River from data collected at "upstream" and "downstream" transects (approximately 100 m apart; Fig. 1) during March and October 2004 (Fig. 2 and 3). Briefly, specific conductance (SC), hydraulic head data, and the 2004 river hydrograph suggest that three distinct sources contribute water to the Merced River subsurface: surface water, the local aquifer to the northwest, and that to the southeast. Surface water infiltration to the hyporheic zone is variable, generally occurring in the center of the river and rarely penetrating deeper than 0.5 m below the sediment–water interface. At the upstream transect, the local aquifers contribute equally from both sides of the river; however, 70% of the riverbed ground water appears to come from the southeast side at the downstream transect (Domagalski et al., 2008).

Domagalski et al. (2008) used trace solutes to determine that the riverbed is much more reducing than the aquifer to the northwest; denitrification has been observed as ground wa-

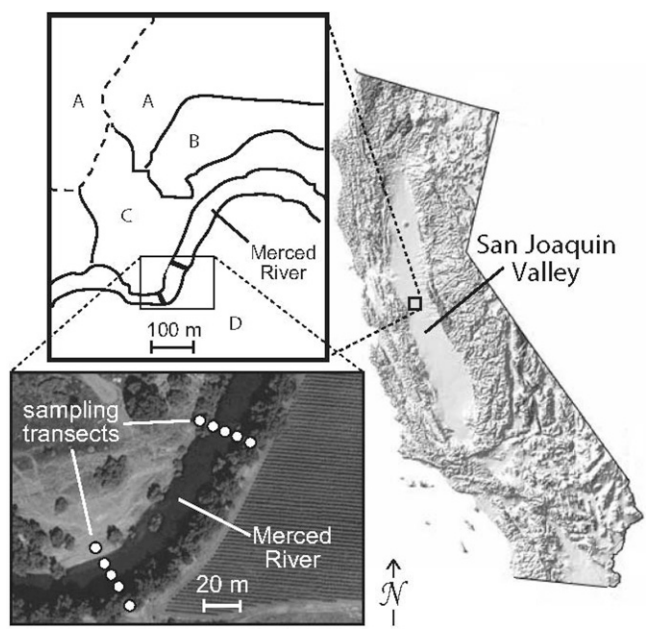

Fig. 1. Right: State of California, USA. Upper inset: Proximal land uses of the Merced River field site. Dashed line represents the Highline Canal; solid lines crossing the river represent the sampling transects. (A) Almond orchards. (B) Feed corn. (C) Native vegetation. (D) A vineyard (after Phillips et al., 2007). Lower inset: Drive point locations in sampling transects across the Merced River (image from Google Earth). The river flows from northeast to southwest in both insets.

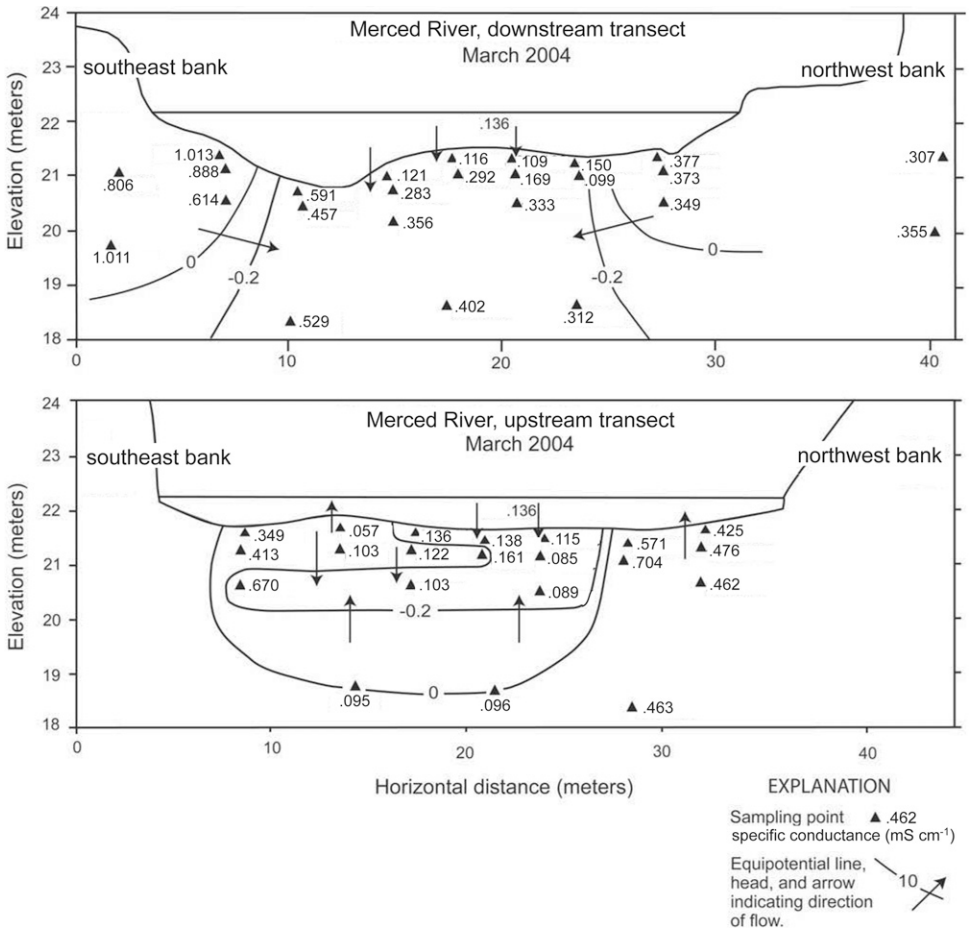

Fig. 2. Profile view specific conductance in ground water beneath the Merced River, March 2004 (data and figure adapted from Puckett et al., 2008).

ter flows from the local aquifer into the riverbed, and metal reduction was prevalent at nearly all sampling locations and times. There were no robust spatial patterns in the reduction of Mn- and Fe-oxide minerals, possibly due to pockets of high organic carbon in the aquifer material, but reducing conditions appeared to be stronger in the summertime.

Materials and Methods

Field and Laboratory Procedures

Samples for this study were collected from infrastructure described in previous studies of this site (see Capel et al. [2008] for details). Briefly, upstream and downstream transects consisted of three drive point locations in the riverbed and a location beneath both the northwest and southeast riparian areas. At these locations, stainless steel drive point tips with 2-cm screened openings were installed 0.3 to 3 m below the riverbed. These drive point tips were connected to nylon tubing that was routed to the river bank. The set of drive point locations selected for this study (Fig. 2–5) overlaps partially with that used by Puckett et al. (2008).

Ground water samples were collected by attaching a peristaltic pump to the nylon tubes that led to each screened drive point opening. A volume of water (approximately 1 L) greater than the tube volume was pumped before any samples were collected. Specific conductance, pH, and temperature were measured with a YSI probe (Geotech Environmental Equipment, Denver, CO). When these parameters had stabilized, approximately 2-L samples were collected for various analyses. For collection of filtered samples, 0.45-μm cartridge filters (Supor model; Pall Corporation, East Hill, NY) were pre-rinsed with 1 L of distilled, deionized water and connected in-line with the peristaltic pump tubing. Samples were collected in high-density polyethylene bottles that had been washed with 3% HCl and rinsed with distilled, deionized water before use. Within 2 h of collection, samples were acidified with concentrated HNO_3 to a final concentration of 2%. Samples were open to the atmosphere during collection. Routine field and equipment blanks were collected and showed no evidence of carryover or cross contamination. Sampling was performed on 29 to 31 March, 28 to 30 June, and 5 to 7 Oct. 2004 to assess the effects of seasonal ground water and river flow conditions on ground water solute transport.

Samples were returned to the laboratory and analyzed on a 4500 model inductively coupled plasma mass spectrometer (ICP-MS) (Agilent Technologies, Inc., Santa Clara, CA). Concentrations of Br, Mn, Sr, Ba, U, and P were quantified based on multi-element calibration solutions prepared from ICP-grade single element standards for Mn, Sr, Ba, U, P and an ion chromatography standard for Br (EMD Chemicals, Darmstadt, Germany). Analytical detection limits (μmol L^{-1}) were 0.03 for Br, 0.004 for Mn, 0.02 for Sr and Ba, 0.008 for U, and 0.07 for P.

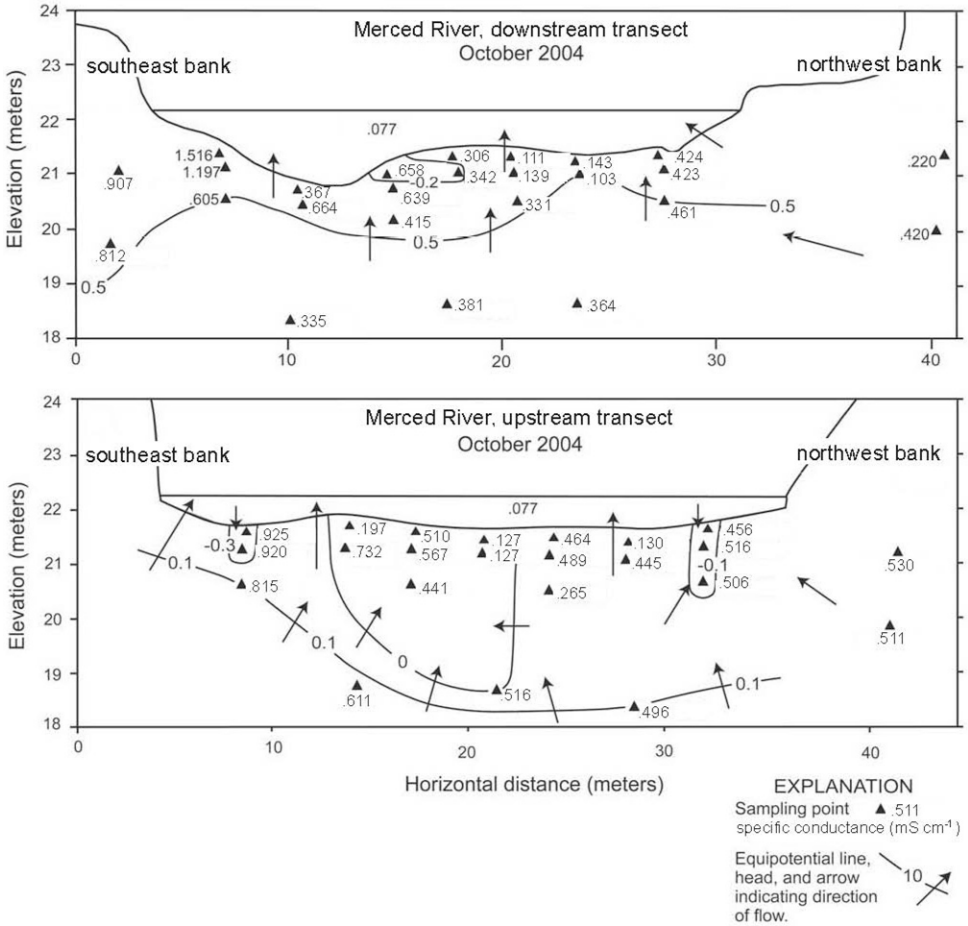

Fig. 3. Profile view specific conductance in ground water beneath the Merced River, October 2004 (data and figure adapted from Puckett et al., 2008).

Dissolved organic carbon (DOC) measurements were made with a persulfate wet oxidation method that used a reaction in a gas-tight vessel and analysis by a Model 700 carbon analyzer (OI Analytical, College Station, TX) (Aiken, 1992). Samples were introduced into the reaction vessel by means of a fixed-volume sample loop. Linear instrument response was maintained by limiting sample mass to 50 µg C. A 0.5-mL aliquot of 5% v/v H_3PO_4 was added to the sample, which was then purged with N_2 for 2.0 min and treated with 0.5 mL of 0.42 mol L^{-1} sodium persulfate solution for 5 min.

Statistical Analyses

Three statistical methods were used to evaluate the data collected. A matrix of correlation estimates ("correlations") for the six measured elements was constructed for all the samples in a given transect using R 2.1.1 (R Development Core Team, 2005). Errors of correlation estimates were verified to have a normal distribution, which implies that the standard deviation (SD) of these errors is $1/\sqrt{n}$, where n is the number of samples. Based on the number of samples in each transect (Table 1), correlations were deemed significant when they differed from zero by at least 2 SD, creating thresholds of ±0.324 and ±0.316 for the upstream and downstream transects, respectively. For simplicity, only values exceeding these thresholds are reported. Values differing from zero by 4 SD or more are interpreted as highly significant.

The parameters included in the correlation analysis were fit to a linear regression model (created with R 2.1.1) in which Br was the single predictor variable and Mn, Sr, Ba, U, and P were the response variables. Regressions were not forced to pass through the origin. The set of model residuals, which constitutes the variability not associated with Br, was added to the correlation analysis.

Principal component analysis (PCA) quantifies the extent to which different parameters explain the variability of a data set (e.g., Báez-Cazull et al., 2008). More general than an analysis of residuals from a linear model, PCA does not require the initial assignment of a predictor variable. Instead, principal component vectors, linear combinations of parameters that are orthogonal to one another, describe the variance of the data set. Correlations of principal component scores are interpreted on the basis of scientific background knowledge. Before PCA (using R 2.1.1), the data for the six measured elements were centered around zero by subtracting the mean of a parameter from every value of that parameter. They were then divided by the SD for that parameter, a step that compensates for varying parameter ranges.

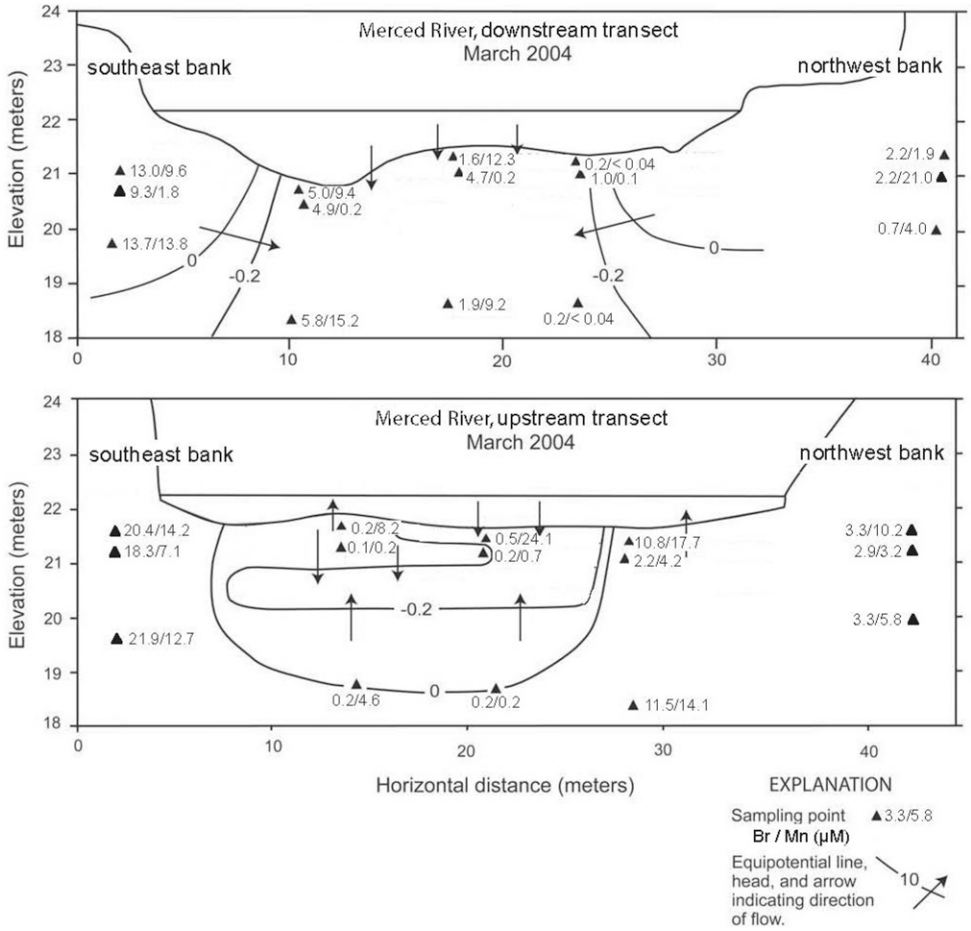

Fig. 4. Profile view of bromine and manganese in ground water beneath the Merced River, March 2004 (data from this study; figure adapted from Puckett et al., 2008).

Results and Discussion

Hydrologic Patterns

Bromine measured by ICP–MS is assumed to correspond to bromide, a common conservative and non-reactive tracer (e.g., Green et al., 2005; Harvey et al., 2005). Thus, Br is used to represent hydrologic processes because it was measured in the same samples as the other trace solutes in this study. Overall variation of Br is reported in Table 1.

Upstream, northwest riparian drive point locations ranged in Br from 2.6 to 4.4 µmol L^{-1} (mean, 3.2 µmol L^{-1}), whereas southeast riparian Br values ranged from 18.3 to 23.5 µmol L^{-1} (mean, 20.5 µmol L^{-1}). Downstream, northwest riparian drive point locations rangeed in Br from 0.7 to 2.8 µmol L^{-1} (mean, 2.1 µmol L^{-1}), and southeast riparian drive point locations ranged in Br from 9.1 to 15.4 µmol L^{-1} (mean, 11.9 µmol L^{-1}). Consistent with previous work suggesting that the local aquifers to the northwest and southeast of the Merced River provide chemically distinct water to the riverbed, concentrations of Br were significantly higher (*t* test, $p < 0.01$) in both sets of southeastern drive point locations relative to northwestern drive point locations. Furthermore, higher Br (*t* test, $p < 0.01$) in both sets of upstream riparian drive point locations relative to those downstream was consistent with differences in flow between these two transects.

These interpretations match those of Puckett et al. (2008), who used SC as a tracer. Where samples were collected at the same times and locations, correlations between SC and Br were highly significant in both the upstream ($r = 0.715$) and downstream ($r = 0.914$) transects.

Manganese and Redox Conditions

In natural soils and sediments, Mn occurs nearly exclusively as solid Mn(III, IV) oxide minerals or as dissolved Mn(II) species. Generally, Mn data from acidified samples analyzed by ICP–MS can be assumed to correspond to Mn^{2+} concentrations. On the basis of thermodynamics, microbes should reduce Mn oxides after dissolved oxygen and nitrate are depleted (Stumm and Morgan, 1996). Although this sequence of electron-accepting processes is not always distinct (McGuire et al., 2002), dissolved Mn is thermodynamically unstable in the presence of oxygen, and thus Mn can be used as an indicator of redox state in ground water samples. In the Merced River subsurface, precipitation of reduced Mn minerals is not expected to confound interpretations based on dissolved Mn. Ground water samples were determined to be undersaturated by several orders of magnitude with respect to rhodocrocite ($K_s = 7.94 \times 10^{-5}$, where K_s is the equilibrium solubility product constant) (Foulliac and Criaud, 1984) based on carbonate

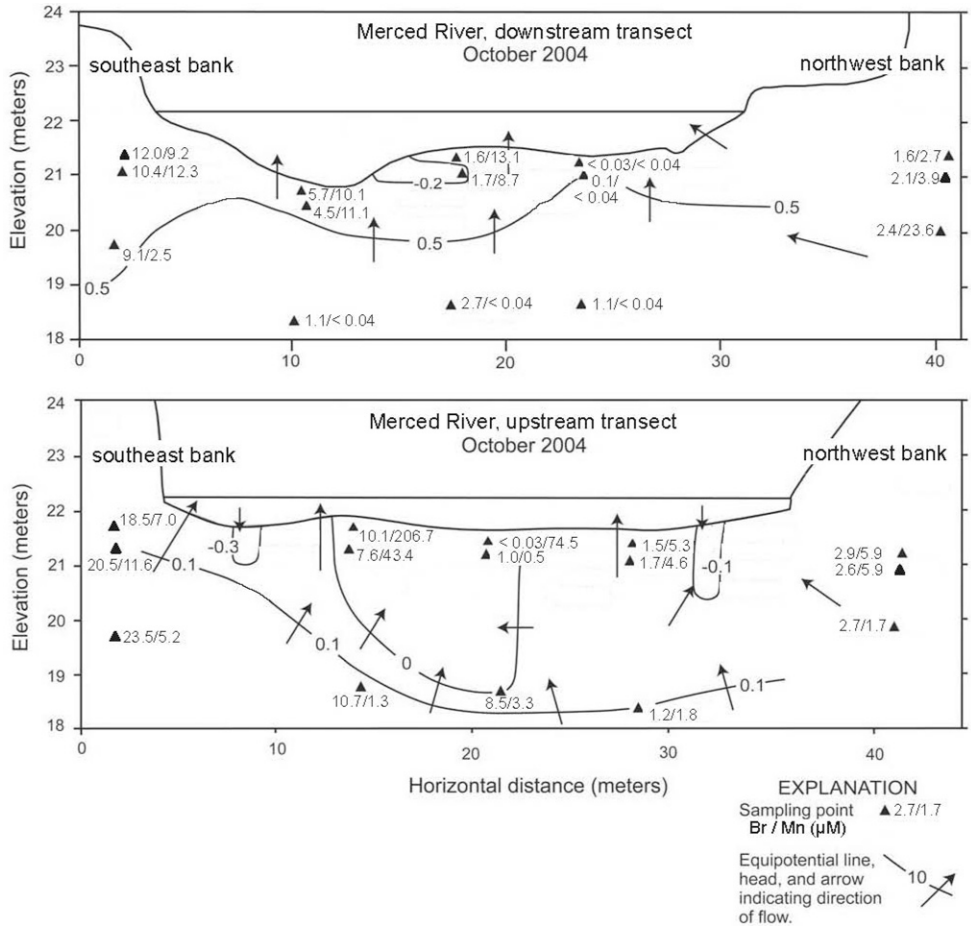

Fig. 5. Profile view of bromine and manganese in ground water beneath the Merced River, October 2004 (data from this study; figure adapted from Puckett et al., 2008).

concentrations calculated from measured pH and alkalinity (Wildman, 2009). Sediment samples have very low concentrations of acid-volatile sulfide (Puckett et al., 2008), and thus we expected that minimal precipitation of albandite, which is usually undersaturated even in sulfidic pore waters (e.g., Naylor et al., 2006), had occurred.

Our measurements of Mn in ground water beneath the Merced River (Fig. 4 and 5; Tables 1 and 2) support results described by previous researchers. The riverbed is an area where active and heterogeneous oxygen consumption, denitrification, and reduction of Mn- and Fe-oxides occurs (Puckett et al., 2008; Domagalski et al., 2008). In filtered samples, Mn ranged from below detection to 206.7 μmol L^{-1}, with high SDs and coefficients of variation (CVs) in both transects (Table 1), suggesting substantial heterogeneity in redox conditions. Its spatial and temporal patterns did not resemble those of Br (Fig. 4 and 5; Table 2), and thus dissolved Mn concentrations probably represented in situ redox biogeochemical processes that are independent of hydrologic processes.

Spatial and temporal variations in ground water Mn were generally similar to those of DOC, which ranged in concentration from 0.06 to 0.54 mmol L^{-1} C (Table 3). This suggests that the availability of DOC, which acts as an electron donor for Mn(III/IV) reduction, may partially control the concentration of Mn in ground water. Specifically, concentrations of Mn and DOC were generally highest in shallow depths, an observation consistent with previous research showing that the hyporheic zone is an area of increased microbial activity (e.g., Harvey and Fuller, 1998). Although it is notably heterogeneous across the sampling locations and times, microbial deg-

Table 1. Descriptive statistics for full data set.

Statistic	Element					
	Br	Mn	Sr	Ba	U	P
	μmol L^{-1}					
Upstream transect						
Number†	38	38	38	38	38	38
Max	23.5	206.7	11.4	2.0	0.15	16.6
Min	<0.03	<0.04	<0.02	0.1	<0.008	<0.07
Median	2.9	5.8	2.7	1.0	0.01	0.6
Mean	6.1	17.8	3.6	1.0	0.03	2.0
SD	7.1	39.9	3.0	0.6	0.04	3.8
CV	116.4	224.2	83.3	60.0	133.3	190.0
Downstream transect						
Number†	40	40	40	40	40	40
Max	15.4	168.8	6.4	1.9	0.16	40.8
Min	<0.03	<0.04	0.1	<0.02	<0.008	<0.07
Median	2.3	3.7	2.3	0.6	0.01	2.4
Mean	4.2	10.5	2.8	0.7	0.02	8.0
SD	4.3	26.8	1.6	0.5	0.04	10.6
CV	102.4	255.2	57.1	71.4	200.0	132.5

† The number of samples analyzed from each transect.

Table 2. Bromine and manganese in filtered Merced River ground water, June 2004. Table layout matches Fig. 2–5.

Depth	Southeast riparian		Southeast river		Center		Northwest river		Northwest riparian	
	Br	Mn	Br	Mn	Br	Mn	Br	Mn	Br	Mn
	μmol L^{-1}									
Downstream transect										
0.3 m	15.4	11.4	0.9	4.2	2.6	168.8	1.4	<0.04	2.6	3.5
3.0 m	12.2	2.9	6.2	0.1	0.1		1.5	<0.04	2.8	34.7
Upstream transect										
0.3 m			2.8	13.0	1.5	135.8	3.1	9.8	4.4	7.3
3.0 m			4.4	<0.04	1.8	<0.04	2.7	2.7	3.1	3.3

radation of organic matter appeared to consume nearly all oxygen that may reach the subsurface due to surface water infiltration.

Relative Influence of Hydrologic and Biogeochemical Processes

The independence of in situ biogeochemical processes from hydrologic processes (e.g., ground water advection and surface-subsurface exchange) is consistent with statistical results that show no significant correlation between Mn and Br (Table 4). The variability in the data set due to hydrologic processes was removed by assigning Br as the predictor variable in a linear regression model. Model residuals correlated positively and highly significantly with Mn (Table 4). Thus, Br and Mn can be interpreted as representing two separate and unrelated influences on trace solutes in the Merced River riverbed.

Principal component analyses (Table 5) also showed that Br and Mn corresponded to distinct contributions to the data variability, and this statistical method provided a quantitative estimate of their relative importance. In the upstream drive point transect, principal component (PC) 1 accounted for about 56% of the variability and showed a high score for Br and a score near 0 for Mn. In PC 2, the magnitude of these scores was reversed, although this PC accounted for approximately 24% of the variability. This trend was similar, but weaker, in the downstream transect. There, Br scored highly on PC 1 and Mn on PC 2. However, Mn and Br were not as close to 0 in PC 1 and PC 2, respectively, as in the upstream transect. Principal component 1 accounted for approximately 50% of the variability and PC 2 for approximately 29% of the data variability, a slightly diminished difference from upstream. In the upstream and downstream transects, PC 3 accounted for approximately 11% and approximately 14% of the variability, respectively, and the magnitude of the Mn score was much greater than that of the Br score in each case.

Table 3. Dissolved organic carbon in filtered Merced River ground water. Table layout matches Fig. 2–5.

Depth	Southeast riparian	Southeast river	Center	Northwest river	Northwest riparian
	mmol L^{-1} C				
Downstream transect, March 2004					
0.3 m	0.22	0.17	0.15	0.12	0.10
3.0 m	0.11	0.10	0.07	0.08	0.10
Downstream transect, June 2004					
0.3 m	0.16	0.28	0.13		
3.0 m	0.12	0.06	0.08	0.06	0.07
Upstream transect, March 2004					
0.3 m		0.14	0.54	0.12	
3.0 m		0.11	0.07	0.13	
Upstream transect, June 2004					
0.3 m		0.11	0.22	0.10	
3.0 m			0.12	0.07	

These statistical analyses strengthen a central conclusion drawn from direct observations of ground water data: Hydrologic processes and redox biogeochemistry operate independently in this system. Correlation analyses indicate that these two factors describe separate portions of the data variability. Furthermore, PCA of data from each transect suggests that hydrologic processes, represented by Br, drive 50 to 56% of the variability and that redox conditions, represented by Mn, influence 35 to 42% of the variability. Hydrologic processes appear to be slightly more important in the upstream transect, where more surface water infiltration and less ground water discharge occurs than in the downstream transect.

Responses of Strontium, Barium, Uranium, and Phosphorus

Each of the four response elements considered in this study is expected to be influenced by ground water flow to some extent. In addition, uranium (U) is redox active, and its solubility is dependent on its oxidation state. Changes in oxidation state are not expected for Ba and P, but their dissolved concentrations are likely to be influenced by the precipitation or dissolution of other redox-active species, particularly Fe and Mn. Specifically, these elements were expected to sorb to solid Fe- and Mn-oxides and enter the dissolved phase when these oxide minerals dissolved. The transport of Sr was expected to be conservative and independent of redox processes, in contrast to that of U, Ba, and P.

The response elements (Sr, Ba, U, P; Tables 6 and 7) showed considerable variation across sampling locations and times, with very large CVs (Table 1). Generally, a gradient across the drive point transects, with highest concentrations in the southeast, especially upstream, was consistent with the contribution of different water sources to the riverbed.

Bromine correlated with Sr, Ba, and U in both transects and with P in the downstream transect (Table 4). Principal component analyses (Table 5) also showed the association of response elements with Br. In both transects, PC 1 showed moderately high scores of matching sign for Br, Sr, Ba, and U. Downstream, P matched Br in PC 1. Because PC 1 accounted for the majority of the data variance and shows Mn scores of lower magnitude than those of Br, these statistical analyses indicate a principal influence of hydrologic processes on these response elements.

The residuals from the Br-based linear regression model correlated positively with P in both transects and with Ba in the downstream transect (Table 5), indicating that variability in P (in both transects) and Ba (downstream) is not completely explained by hydrologic processes. Similar correlations of P and Ba with Mn further suggest that these two elements respond to changes in redox biogeochemistry. In the PCA from both transects (Table 5), PC 2 had high scores of matching sign for Mn and P, indicating that this PC accounted for variability due to redox conditions and that P responded to this variability. Upstream, P in PC 3 showed a notably high score with opposite sign from that of Mn. Downstream, U scored highly and Sr scored moderately on PC 2, and their signs were opposite from that of Mn. These last two observations suggest responses to redox conditions that are relevant, yet opposite, to that of Mn.

Strontium transport appears to be dominated by hydrologic processes with a slight influence of redox chemistry downstream. This contrasts a previous study in a cobble-bed stream, where retention of Sr relative to a conservative tracer was described (Kennedy et al., 1984). Nevertheless, no association between Sr and redox chemistry was expected, and no strong influence was observed. The discrepancy between these two studies may be explained by greater amounts of clay minerals in the riverbed sediment or by incorporation of Sr into calcite (e.g., Tesoriero and Pankow, 1996) in the study of Kennedy et al. (1984). This latter mechanism was not addressed in either of these studies, yet the strong association of Sr with hydrologic processes in our study may suggest that calcite precipitation does not control trace element mobility at the Merced River.

Barium and uranium appear to be controlled by hydrologic processes in both transects and by biogeochemical processes downstream. Redox influence on Ba can be explained in part by sorption to Mn oxides (Tonkin et al., 2004). Anti-correlation between U and Mn scores in downstream PC 2 are consistent with the opposite effects of redox conditions on the stability of Mn- and U-containing solids (Lovley and Phillips, 1992). Sampling location appears to be important for both elements: The aquifer ground water entering the riverbed from the southeast contains high concentrations of each. Occasionally, U exceeds 0.126 μmol L^{-1} (30 μg L^{-1}), the maximum drinking water contaminant level set by the US Environmental Protection Agency (California Department of Health Services: http://www.dhs.ca.gov/ps/ddwem/chemicals/MCL/EPAandDHS.pdf).

Phosphorus variability is not explained well by hydrologic processes in either transect, although they do appear to have some effect downstream, where concentrations significantly exceeded those of the upstream transect (t test, $p < 0.05$; Tables 1 and 7). Phosphorus is expected to enter the river subsurface by decomposition of dissolved organic matter (e.g., Krom and Berner, 1981) and by the transport and breakdown of fertilizer from the local aquifers. When P loads to a river are high, sediment P sorption capacity can be saturated (Haggard et al., 2005). Thus, higher concentrations may lead to hydrologic control of P transport in the downstream transect, whereas lower concentrations upstream are governed by redox processes.

The effect of redox conditions on P appears to be relevant, yet inconsistent. Principal component analysis scores of P and Mn are high in PC 2 and PC 3 in the analysis corresponding to each transect. However, the signs of the scores are the same in PC 2 and opposite in PC 3. This indicates that reductive dissolution of Mn-oxide minerals may release sorbed P but also that dissolved P may increase during oxidizing conditions that lead to Mn precipitation. Taken together, these contrasting signals lead to overall weakly significant correlations between P and Mn. Many dissolved forms of P, including most phosphate species, sorb to Fe and Mn oxides (Arias et al., 2006), which can control dissolved P concentrations through their response to redox conditions (e.g., Gächter and Wehrli, 1998).

Table 4. Correlation matrices† for trace elements and residuals from a linear model with Br as a predictor variable.

	Br	Mn	Sr	Ba	U	P	Residuals‡
Upstream transect							
Br			0.941	0.703	0.905		
Mn						0.353	0.996
Sr				0.733	0.828		
Ba					0.512		
U							
P							0.424
Residuals							
Downstream transect							
Br			0.673	0.747	0.441	0.599	
Mn				0.515		0.365	0.974
Sr				0.546	0.697		
Ba						0.726	0.534
U							
P							0.514
Residuals							

† Only correlations exceeding significance thresholds of ±0.324 (upstream) and ±0.316 (downstream) are shown.

‡ The parameter "residuals" is the set of residuals from the linear regression model using bromine as the predictor variable.

Table 5. Principal component analysis of measured parameters in Merced River ground water.

	PC1	PC2	PC3	PC4
Upstream transect				
Principal component score				
Br	−0.535	0.022	0.108	−0.133
Mn	−0.039	−0.704	−0.587	−0.381
Sr	−0.528	0.097	0.026	0.067
Ba	−0.437	−0.206	−0.275	0.728
U	−0.491	0.056	0.206	−0.533
P	0.040	−0.670	0.725	0.137
Importance of components				
Proportion of variance	0.556	0.235	0.112	0.074
Cumulative proportion	0.556	0.791	0.903	0.977
Downstream transect				
Principal component score				
Br	−0.519	0.125	−0.346	0.198
Mn	−0.196	−0.475	0.775	0.129
Sr	−0.442	0.398	0.137	−0.572
Ba	−0.523	−0.244	0.044	−0.345
U	−0.253	0.597	0.354	0.584
P	−0.399	−0.429	−0.365	0.395
Importance of components				
Proportion of variance	0.501	0.287	0.135	0.043
Cumulative proportion	0.501	0.788	0.923	0.965

Table 6. Strontium and barium in filtered Merced River ground water. Table layout matches Fig. 2–5.

Depth	Southeast riparian		Southeast river		Center		Northwest river		Northwest riparian	
	Sr	Ba	Sr	Ba	Sr	Ba	Sr	Ba	Sr	Ba
	μmol L^{-1}									
	Downstream transect									
March 2004										
0.3 m	4.1	1.5	4.8	0.9	3.0	0.5	1.1	0.2	2.1	0.5
0.5 m	6.1	0.9	4.7	0.5	2.7	0.3	1.6	0.2	1.9	0.7
3.0 m	3.7	1.7	6.4	1.3	3.4	<0.02	1.3	0.2	2.0	0.6
June 2004										
0.3 m	3.5	1.6	1.5	0.3	2.4	1.9	1.8	0.3	2.0	0.6
3.0 m	5.9	0.9	3.8	0.5	0.2	<0.02	2.2	0.2	2.3	1.0
October 2004										
0.3 m	3.8	1.6	5.6	1.2	2.8	0.6	1.0	0.2	1.5	0.5
0.5 m	3.0	1.4	4.7	1.2	2.9	0.6	1.3	0.2	1.8	0.7
3.0 m	5.4	0.8	2.1	0.3	2.3	0.3	1.8	0.2	2.0	0.8
	Upstream transect									
March 2004										
0.3 m	10.1	2.0	1.0	0.2	1.2	0.7	6.1	1.4	2.3	1.1
0.5 m	11.4	1.5	1.0	0.1	0.8	0.2	3.5	0.6	3.7	1.7
3.0 m	10.7	2.0	1.0	0.2	0.8	0.5	6.6	1.5	2.8	1.3
June 2004										
0.3 m			1.3	0.5	1.1	1.0	3.7	1.0	2.9	1.5
3.0 m			2.6	0.3	<0.02	0.1	3.3	0.6	3.4	1.7
October 2004										
0.3 m	6.3	1.6	4.1	1.6	0.6	1.2	1.7	0.5	2.1	0.8
0.5 m	7.5	1.5	4.2	1.3	0.8	0.4	1.9	0.6	2.1	0.8
3.0 m	9.4	1.4	5.5	0.9	3.6	1.4	2.4	0.4	2.1	1.1

Table 7. Uranium and phosphorus in filtered Merced River ground water. Table layout matches Fig. 2–5.

Depth	Southeast riparian		Southeast river		Center		Northwest river		Northwest riparian	
	U	P	U	P	U	P	U	P	U	P
	μmol L^{-1}									
	Downstream transect									
March 2004										
0.3 m	0.01	27.5	0.05	3.6	<0.008	6.1	<0.008	0.1	<0.008	0.1
0.5 m	0.12	3.0	0.07	0.2	0.02	0.7	0.01	0.6	<0.008	3.5
3.0 m	0.01	24.4	0.03	1.8	<0.008	7.7	<0.008	0.1	<0.008	1.1
June 2004										
0.3 m	0.01	31.3	0.02	13.0	0.01	24.1	0.02	1.2	0.01	0.7
3.0 m	0.16	4.8	0.06	1.7	0.01	7.7	0.02	1.3	0.01	9.5
October 2004										
0.3 m	<0.008	25.5	0.05	18.5	<0.008	12.5	<0.008	0.8	<0.008	<0.07
0.5 m	<0.008	40.8	0.01	6.7	<0.008	22.1	<0.008	<0.07	<0.008	1.5
3.0 m	0.12	0.7	0.02	<0.07	0.01	<0.07	<0.008	<0.07	<0.008	14.4
	Upstream transect									
March 2004										
0.3 m	0.11	4.1	0.02	<0.07	0.02	8.9	0.02	0.2	0.01	<0.07
0.5 m	0.10	<0.07	0.02	<0.07	0.02	0.1	0.02	<0.07	0.01	<0.07
3.0 m	0.13	<0.07	0.02	0.4	0.02	<0.07	0.02	<0.07	0.01	<0.07
June 2004										
0.3 m			0.01	0.7	<0.008	16.6	<0.008	2.6	<0.008	0.4
3.0 m			0.01	0.5	<0.008	3.8	0.01	1.5	<0.008	1.2
October 2004										
0.3 m	0.11	7.8	0.05	1.4	<0.008	3.5	<0.008	0.4	<0.008	0.2
0.5 m	0.15	3.4	0.02	3.9	<0.008	2.4	<0.008	2.8	<0.008	1.6
3.0 m	0.11	<0.07	0.06	<0.07	<0.008	8.1	0.01	9.4	<0.008	4.1

Oxic conditions may stimulate microbial breakdown of particulate organic matter, a process that mobilizes P (Qiu and McComb, 1994). Based on the relative importance of PC 2 and PC 3, sorption to metal oxides appears to be about twice as important for P mobility as organic matter decomposition in this river reach.

Conclusions

In a reach of the Merced River where subsurface hydrology has been perturbed by agricultural irrigation and variations in river stage, subsurface hydrological processes exert a stronger influence on the mobility of four trace solutes than redox biogeochemistry does. Previous work indicates that water is usually moving slowly

from the aquifers through the riverbed and into the river, although this is occasionally interrupted by pulses of river water into the riverbed (Puckett et al., 2008; Essaid et al., 2008). Bromine is assumed to be transported conservatively by hydrological processes, and this is supported by its close correlation with specific conductance, another conservative tracer. Strontium also appears to be transported nearly conservatively in this system.

Dissolved Mn concentrations are not dependent on hydrological processes in this system and are thus expected to be influenced by in situ redox processes. Redox biogeochemistry appears to control P mobility as well, although the different behavior of P in the two transects may suggest that higher concentrations of P lead to control by hydrological processes after the sorption capacity of aquifer materials is exceeded.

Upstream, hydrological processes control the mobility of Ba and U; downstream, redox trends are also relevant. Uranium appears to enter the riverbed subsurface only from the southeast, and it persists in the dissolved state despite reducing conditions in ground water, suggesting that it is not in thermodynamic equilibrium at our sampling locations. Although Mn is known to sorb Ba, the association of Ba with Br suggests that Ba sorption may be limited in this system.

Overall, hydrological processes accounted for a little more than 50% of the variance in data collected from Merced River ground water samples. The influence of redox conditions was less important, accounting for 35 to 42% of the variability. Spatial patterns were not consistent between two transects separated by 100 m; redox chemistry influenced minor solutes more in the downstream transect. This is a curious finding that is worthy of future research.

Previous research on transport and biogeochemical processes in the hyporheic zone has focused on streams with unperturbed hydrology. This study suggests that nearby agricultural irrigation influences the distribution of solutes in the subsurface. With riverbed hydraulic characteristics established by previous work, statistical analyses of a natural tracer and a ground water redox indicator provide insight into subsurface systems subject to a combination of lateral advection, hyporheic exchange, and mixing of surface water and ground water.

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