Chapter 6

HYDROLOGIC AND BIOGEOCHEMICAL CONTROLS OF RIVER SUBSURFACE SOLUTES UNDER AGRICULTURALLY-ENHANCED GROUNDWATER FLOW

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(accepted by *Journal of Environmental Quality*)

ABSTRACT

The relative influences of hydrologic processes and biogeochemistry on minor solutes were compared using groundwater samples collected beneath and adjacent to a reach of the Merced River (California, USA) that receives subsurface discharge enhanced by seasonal agricultural irrigation. Filtered groundwater samples were collected beneath the riverbed from 30 wells at different depths and riverbed locations in March, June, and October 2004. Hydrologic processes were inferred from specific conductance (SC) and bromine (Br) concentrations; manganese (Mn) was used as an indicator of redox conditions. The separate responses of the minor solutes strontium (Sr), barium (Ba), uranium (U), and phosphorus (P) to these influences were examined. Correlation and principal component analyses (PCA) indicate that hydrologic processes dominate the distribution of trace elements in the groundwater. 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 well transects separated by 100 m.

INTRODUCTION

Agricultural practices can degrade groundwater 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 United States 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 both research and watershed management.

Surface- and groundwater quality are linked through exchange in the riverbed. Hydraulic connection in the shallow river subsurface provides an additional pathway for surface water degradation. This region of active mixing between riverbed groundwater and surface water, known as the hyporheic zone, is characterized by short length scales of exchange with overlying water and oxygenation of surface sediment (Findlay, 1995; Packman and Bencala, 2000). Hyporheic subsurface advection transports minor solutes, while biogeochemical reactions can sequester or mobilize them, making the hyporheic zone important for the fate and transport of aqueous contaminants.

Both abiotic (Kennedy et al., 1984) and biogeochemical (e.g., Harvey and Fuller, 1998) processes can retard or enhance subsurface solute transport. Many studies detail the sorption of trace elements to solid iron (Fe), Mn, and aluminum oxides (e.g., Beauchemin and Kwong, 2006; Han et al., 2006; Tonkin et al., 2004). Both Fe and Mn oxides dissolve under reducing conditions, potentially mobilizing elements sorbed onto the surfaces of these solids (e.g., van Griethuysen et al., 2005). Such reactions are especially likely at interfaces between parcels of water with different geochemical characteristics (Kneeshaw et al., 2007; McGuire et al., 2002). Microbial redox reactions are important in the hyporheic zone, where dissimilatory microbial reduction of Fe and Mn oxides is likely (Harvey and Fuller, 1998). The river subsurface provides an environment for enhanced abiotic and biogeochemical reactions that may influence porewater 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).

Agricultural irrigation can substantially alter hydrologic regimes in aquifers and influence the behavior of subsurface solutes. Previous research has examined hyporheic systems where surface water is the dominant source of riverbed groundwater and hydrology is relatively unperturbed (e.g., Choi et al., 2000; Harvey et al., 2005). In areas with extensive irrigation, local groundwater advection may compress or eliminate the hyporheic zone by inducing a dominant flow from the subsurface into the river. Groundwater flow from impacted aquifers can be the major source of contaminants to surface water (Brown et al., 2007). Furthermore, groundwater from the local aquifer may differ from the river subsurface in redox potential. So, in addition to influencing mixing of groundwater and surface water, an irrigation-driven flow regime may also affect subsurface redox chemistry.

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 field site is a focus of the U.S. Geological Survey National Water Quality Assessment (NAWQA) program, Cycle II. Cycle I of this program was designed to assess national water quality and understand trends and influential factors (Gilliom et al., 1995). Cycle II of NAWQA emphasizes processes and trends controlling water quality and features an Agricultural Chemicals Transport (ACT) study that has been carried out in five different river basins (Capel et al., 2008).

The goals of this study were to evaluate chemical tracers for hydrologic processes and redox conditions in the Merced River riverbed and to use these tracers to assess the dominant influences on the distribution of four specific solutes (Sr, Ba, U, and P) in the subsurface. These “response elements” were chosen to represent a range of chemical behaviors from elements observed to have measurable concentrations by an initial survey. Each solute is expected to be influenced by hydrologic processes to some extent. In addition, 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 are expected to sorb to solid Fe- and Mn-oxides and enter the dissolved phase when these oxide minerals dissolve. The transport of Sr is expected to be conservative and independent of redox processes, in contrast to that of U, Ba, and P.

FIELD SITE: THE MERCED RIVER

The geography of the Merced River is typical of the eastern San Joaquin Valley, California. Below two water-storage reservoirs, the lower Merced River flows west through productive agricultural land (Gronberg and Kratzer, 2007). The field site was a reach approximately 20 km above the confluence with the San Joaquin River (Figure 1). In this area, the land surface slopes westward from the Sierra Nevada with a slope of about 1-4 m km^{-1} (Phillips et al., 2007). The semi-arid 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 is 19.4 m^3 s^{-1} at the confluence of the Merced and San Joaquin Rivers (Capel et al., 2008).

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 and applied to fields and orchards. Crops cover 55% of the lower Merced Basin (Capel et al., 2008);

our field site is surrounded by an almond orchard, a field of feed corn, native vegetation, and a vineyard (Figure 1).

Groundwater near the Merced River lies in a < 43 m thick surface aquifer that is composed of highly permeable, low organic carbon, medium- to coarse-grained sand (Capel et al., 2008). The water table is approximately 6.5 m below ground surface (Domagalski et al., 2008b). After entering the water table, irrigation water applied 1 km from the river has been observed to flow towards the Merced River with a travel time of about 30 years (Domagalski et al., 2008b). A groundwater flow model for the lower Merced River region in the year 2000 (which was based on groundwater elevation measurements) indicates that surface recharge, mostly from irrigation, accounts for 76% of the total aquifer recharge and that 65% of the groundwater is discharged to the river. Thus, local groundwater experiences a net gain that is discharged to the Merced River and then transported out of the basin (Phillips et al., 2007). 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.

The streambed sediment is sandy and subject to vigorous bedload transport (Zamora, 2008). Flux across the streambed between groundwater and the Merced River ranges from $-1.1 \cdot 10^{-7}$ to $5.9 \cdot 10^{-7}$ m^3 m^{-2} s^{-1}, where positive values indicate flow from the riverbed into the river. Groundwater generally flows to the Merced River (mean $1.8 \cdot 10^{-7}$ m^3 m^{-2} s^{-1}) except during increased river flow (Essaid et al., 2008). Hydraulic conductivity was calculated to be $1.2 \cdot 10^{-5}$ m^3 m^{-2} s^{-1} (Essaid et al., 2008). Hyporheic exchange is not consistent spatially or temporally (Domagalski et al., 2008b).

In the groundwater beneath the Merced River, reduction of O_2, denitrification, and reduction of Mn^{4+} and Fe^{3+} have been characterized (Puckett et al., 2008). The riverbed is much more reducing than the surrounding aquifer; denitrification has been observed as groundwater flows from the local aquifer into the riverbed (Domagalski et al., 2008b). Reduction of electron acceptors occurs because the residence time in the subsurface is long (Puckett et al., 2008). There are no robust spatial patterns in the reduction of Mn- and Fe-oxide minerals (Domagalski et al., 2008b), possibly due to pockets of high organic carbon in the aquifer material (Puckett et al., 2008), but reducing conditions appear stronger in the summertime (Domagalski et al., 2008b).

METHODS

Field and Laboratory Procedures

Wells in “upstream” and “downstream” transects were installed 100 m apart at this field site (Figure 1). Each transect consists of five well locations (Figure 2), three of which, “northwest river”, “center”, and “southeast river”, are evenly spaced across the river. Two additional well locations, “northwest riparian” and “southeast riparian”, are about 5 m from the riverbank. At these locations, stainless steel drive point tips with 2 cm screened openings were installed 0.3 m, 0.5 m, and 3 m below the riverbed. These drive point tips were connected to Nylon tubing that was routed to the river bank (Capel et al., 2008).

Groundwater samples were collected by attaching a peristaltic pump to the Nylon tubes that led to each screened well opening. Approximately 1 L of water was pumped before any samples were collected. Specific conductance, pH, and temperature were measured with a YSI probe (Geotech Environmental Equipment). 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) 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 prior to 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 sample collection. Routine field and equipment blanks were collected and showed no evidence of carryover or cross-contamination. Sampling was performed on March 29-31, June 28-30, and October 5-7, 2004 to assess the effects of seasonal groundwater and river flow conditions on groundwater solute transport.

Samples were returned to the laboratory and analyzed using inductively-coupled plasma mass spectrometry (ICP-MS; Agilent 4500). 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). Analytical detection limits (μM) were: 0.008 for U, 0.02 for Ba and Sr, 0.03 for Br, and 0.07 for P.

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 an Oceanography International (OI) Model 700 carbon analyzer (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 M 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 using the software package R (The R Project for Statistical Computing). Errors of correlation estimates are assumed to have a normal distribution, which implies that the standard deviation (σ) of these errors is $1/\sqrt{n}$, where n is the number of samples. Correlations were deemed significant when they differed from zero by at least 2σ, 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 4σ or more are interpreted as strong correlations.

The parameters included in the correlation analysis were fit to a linear regression model (created with R) 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 quantifies the extent to which different parameters explain the variability of a data set (e.g., Báez-Cazull et al., 2008). More general than analysis of residuals, 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), 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 standard deviation for that parameter, a step that compensates for varying parameter ranges.

RESULTS AND DISCUSSION

Extensive agricultural irrigation in the Merced River basin has altered its hydrologic regime. The variability of the measured parameters in Merced River groundwater is illustrated by the summary of results shown in Table 1. Statistical analyses help explain the effect of local hydrology on groundwater mixing, redox chemistry, and trace solutes in the riverbed subsurface. Groundwater mixing patterns and redox chemistry are inferred from SC, Br, and Mn data; these relationships will be explained here as a conceptual framework for the data that are presented and discussed in the following subsections.

Although synoptic sampling provides information only at fixed time points, comparison of groundwater chemistry at three sampling times and multiple locations within the study reach provides insight into separate groundwater sources and their mixing patterns. Specific conductance data can be used to characterize the major element composition of groundwater during each sampling event. 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). Taken together, these data can be used to infer hydrologic processes beneath the Merced River.

Manganese is used as an indicator of redox state, which results from biogeochemical processes in the riverbed. 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. The kinetics of aqueous and surface-bound oxidation of Mn(II) by $O_2(aq)$ are very slow compared to the time required for groundwater sampling (Morgan, 2005; Davies and Morgan, 1989). Hence, exposure to the atmosphere should not lead to artifacts in the Mn data.

In the aquatic environment, oxidized Mn exists as solid oxide minerals. These species dissolve upon accepting electrons from reduced chemical species, generally DOC. On the basis of thermodynamics, microbes should reduce Mn oxides after dissolved oxygen and nitrate are depleted, though this sequence of electron-accepting processes is not always distinct (McGuire et al., 2002). This redox chemistry controls dissolved Mn concentrations across oxic-anoxic gradients, which often correspond to depth gradients and are well-understood in the general case. Based on free-energy calculations and field measurements in marine and lake sediments, dissolved Mn is generally expected to be low in surficial (oxygenated) sediment and then to increase with depth as dissolved oxygen decreases.

Decreases in dissolved Mn at greater depths may result from precipitation of Mn minerals, such as rhodocrocite, $MnCO_3$, and albandite, MnS (e.g., Trefry and Presley, 1982; Canfield et al., 1993). However, precipitation reactions are not expected to influence observed Mn concentrations in this study. Groundwater samples were determined to be undersaturated by several orders of magnitude with respect to rhodocrocite ($K_s = 7.94 \times 10^{-5}$; Foulliac and Criaud, 1984) based on carbonate concentrations calculated from measured pH and alkalinity (Table A1). Sediment samples have very low concentrations of acid-volatile sulfide (Puckett et al. 2008), and thus we expect that minimal precipitation of albandite, which is usually undersaturated even in sulfidic porewaters (e.g., Naylor et al., 2006), has occurred.

Specific Conductance, Bromine, and Advective Patterns

Specific conductance values in Merced River groundwater ranged from 72 to 907 $\mu S\ cm^{-1}$ at 298 K, and Br concentrations ranged from below the detection limit to 23.5 μM (Table 1). Values of SC in the river (i.e., surface water) were 136 $\mu S\ cm^{-1}$ in March, 222 $\mu S\ cm^{-1}$ in June, and 72 $\mu S\ cm^{-1}$ in October; Br was not measured in surface water (Table 2). The deepest wells range in SC from 96 to 611 $\mu S\ cm^{-1}$ (mean = 374 $\mu S\ cm^{-1}$) upstream and from 80 to 812 $\mu S\ cm^{-1}$ (mean = 443 $\mu S\ cm^{-1}$) downstream. Upstream, northwest riparian wells ranged in Br from 2.6 to 4.4 μM (mean = 3.2 μM), whereas southeast riparian Br values ranged from 18.3 to 23.5 μM (mean = 20.5 μM). Similarly, downstream, northwest riparian wells range in Br from 0.7 to 2.8 μM (mean = 2.1 μM) and in SC from 220 to 420 $\mu S\ cm^{-1}$ (mean 333 $\mu S\ cm^{-1}$), whereas southeast riparian wells range in Br from 9.1 to 15.4 μM (mean = 11.9 μM) and in SC from 700 to 907 $\mu S\ cm^{-1}$ (mean = 796 $\mu S\ cm^{-1}$).

Spatial patterns in SC and Br data indicate significant differences between water sources. Values of SC in surface water are significantly lower (t-test, $p < 0.05$) than the deepest groundwater samples in each transect, an observation consistent with previous work showing that the Merced River generally gains water from local groundwater

(Essaid et al., 2008; Phillips et al., 2007). Furthermore, comparisons of riparian Br in each transect and of riparian SC in the downstream transect indicate that groundwater entering the riverbed from the northwest is significantly different (t-test, $p < 0.01$) from that entering from the southeast. While it is possible that surface water infiltration may dilute conservative tracers in the riparian wells, this process does not blur the differences between surface water and local aquifer groundwater. Thus, three separate sources appear to contribute water to the Merced River subsurface: surface water, the local aquifer to the northwest, and that to the southeast. During these comparisons, it is assumed that SC signature of groundwater entering the riverbed from the local aquifer does not change significantly in time during the sampling period, which is supported by measurements in the local aquifer northwest of the river (Domagalski et al. 2008b; Table A2).

Concentrations of Br are significantly higher (t-test, $p < 0.01$) in both sets of upstream riparian wells relative to those downstream. This implies that, while each transect has three distinct groundwater sources, riverbed mixing patterns will be clearer upstream because of larger differences in Br between surface water and aquifer-derived groundwater. Furthermore, regional groundwater models confirm differences in flow between these two transects. At the upstream transect, water contributions are equal from both sides of the river; however, 70% of the riverbed groundwater comes from the southeast side at the downstream transect (Domagalski et al., 2008b). Hence, riverbed groundwater mixing will be discussed separately for each transect here.

At all sampling times in the upstream transect, the center, shallow well has an SC value that is far closer to that of surface water than to that of any riparian well. Thus, water in this well must come from surface water, and surface water can be assumed to have Br values of < 2 μM. Bromine correlates strongly with SC ($r = 0.715$), allowing these two variables to be used as conservative tracers interchangeably. In the upstream transect, SC was not measured at several locations, so Br will be used to describe riverbed mixing here.

Surface water infiltration to the hyporheic zone at this site has been observed to be spatially variable (Domagalski et al., 2008b; Essaid et al., 2008), yet some trends can be isolated. Several well depths at the center and southeastern riverbed locations show Br values < 2 μM, which are significantly lower (t-test, $p < 0.01$) than those in riparian wells. This trend is notably more prevalent in March than in October, where only the shallow well in the center of the river has SC and Br values nearer to those of surface water than to riparian wells. The opposite trend is true in the northwest river location, where Br concentrations are < 2 μM only in October. Thus, surface water infiltration occurs in the center and southeast river locations in March, only in the center location in June, and in the center and northwest river locations in October.

In the downstream transect, SC and Br again correlate strongly ($r = 0.914$). Here, lower concentrations of Br in the riparian wells complicate differentiation between surface water and local aquifer groundwater from the northwest. However, riparian SC data are more plentiful in this transect, so SC will be used to evaluate riverbed mixing. Only a few SC measurements in the riverbed wells are much closer to the surface water than to either riparian location (Table 2). Otherwise, SC values in the northwest and southeast river locations are generally between those of the surface water and the corresponding riparian locations, indicating significant contributions of local aquifer water to these locations. This indicates that riverbed groundwater is derived roughly equally from three sources in this transect, with none prevailing consistently in many well locations.

Seasonal hydraulic patterns of the local aquifer groundwater are overlain on these spatial variations. In the 2004 growing season, irrigation in the almond orchard and the corn field to the northwest of the river (Figure 1) raised the local groundwater table by approximately 0.7-0.8 m and as much as 1.5 m, respectively, beginning in early May and persisting throughout the study period (Phillips et al., 2007). The observations of SC show that the signature of surface water in the shallow riverbed wells is present before the irrigation season (March) but not after it (October), consistent with data reported elsewhere (Domagalski et al., 2008b). Irrigation patterns and groundwater composition of the vineyard to the southeast of the river are not known, but data from the southeast river and riparian wells indicate no clear seasonality.

This pattern is perturbed by varying river flows. During calendar year 2004, flow averaged 7.76 $m^3 s^{-1}$ with a depth of 1.0-1.5 m at the center of the river (Essaid et al., 2008). Stream stage increased for about four weeks between mid-April and mid-May, with depth reaching a maximum of 3.0-3.5 m for about 1 week. While the Merced River generally experiences a net gain from the surrounding aquifers, this increase in surface water hydraulic head led to surface water infiltration into the subsurface during this 4-week period (Essaid et al., 2008). Riverbed groundwater has a long residence time due to low head differences with surface water (Puckett et al., 2008, Essaid et al., 2008). Thus, specific conductance in the subsurface did not recover for nearly two months after the spring high flow event. Furthermore, the decrease in SC at the 3 m depth due to surface water infiltration lags that at the 0.3 m depth by two months (Puckett et al., 2008).

This slow groundwater response to variations in flux across the sediment-water interface can explain seemingly anomalous riverbed SC values. In the upstream transect, the SC value at the upstream center well location in June is closer to the surface water SC value in March than to that measured in June. In addition, the June SC measurement in the deep, downstream, center well resembles the March surface water SC value more than the June SC value. These low riverbed SC values probably indicate signatures of remnant surface water that infiltrated into the subsurface some time before the sampling event. Consistent surface water flows after May 2004 (Essaid et al., 2008) imply a midsummer return of steady groundwater flux from the riverbed to the river during the late summer; the October sampling is not expected to be affected by the late-spring flow reversal. While they do not directly imply directions of groundwater flow, conclusions drawn from our SC and Br data match those drawn by studies based on thermal and chemical tracers, groundwater flow modeling, and hydraulic head measurements at this site (Essaid et al., 2008; Domagalski et al., 2008b; Phillips et al., 2007).

Manganese and Redox Conditions

In filtered samples, Mn ranges from below detection limit to 206.7 μM with high standard deviations and coefficients of variation in both transects (Table 1), suggesting substantial heterogeneity in redox conditions. Its spatial and temporal patterns do not resemble those of the conservative tracers, but are generally similar to DOC, which ranges from 0.06 to 0.54 mM C (Table 4). Subsurface dissolved oxygen is expected to be supplied by diffusion and infiltration from surface water. Manganese concentrations in filtered groundwater samples (Tables 1, 4) are generally greater than 1 μM, implying consumption of dissolved oxygen and reductive dissolution of Mn-oxide minerals. This is consistent with data showing total consumption of oxygen, denitrification, and reduction of Mn- and Fe-oxides (Puckett et al., 2008). Denitrification appears to remove the vast majority of nitrate entering the river subsurface from the northwest (Domagalski et al., 2008b), implying that Mn and Fe reduction may be the dominant terminal electron accepting processes in much of the riverbed.

Maximum Mn frequently occurs in shallow wells, even though their proximity to the river bottom should allow for the maximal introduction of dissolved oxygen via diffusion or infiltration of surface water. Lower Mn concentrations in deeper wells are more likely to reflect decreased microbial activity since precipitation of reduced Mn solids is not expected (discussed above). However, DOC (Table 4) is usually highest in the shallow wells, suggesting that infiltration of surface water is important for supply of DOC to the subsurface. DOC may be supplied as a dissolved component of surface water, or it may originate from degradation of particulate organic carbon deposited to the river bottom. DOC in shallow wells may provide a substrate for microbial respiration and reductive dissolution of Mn-oxides. However, DOC and Mn do not correlate significantly and linear models based on DOC predict Mn poorly, indicating that the enhancement of Mn oxide dissolution by DOC may be a localized phenomenon.

Concentrations of Mn are strikingly high in the center shallow well of both transects in June and in the center and southeast river wells of the upstream transect in October. These extreme cases of Mn oxide reduction probably result from enhanced microbial activity due to high ambient temperatures coupled with ample DOC supply.

This finding is consistent with previous research that shows the hyporheic zone as an area of increased microbial activity (e.g., Harvey and Fuller, 1998).

In March, the lowest Mn concentrations were observed in the wells at 1 m depth, except in the center of the river in the upstream transect. Data are not available for this depth in June, but in October, this trend is observed only in the center of the river. At all other wells, the lowest observed Mn concentrations are in the deepest (3 m) wells.

The northwest wells of the downstream transect contradict observed Mn depth trends. At the downstream northwest riparian location, the maximum observed Mn concentration occurs at 0.5 m in March and at 3 m in June and October. At the northwest river location, anomalously low Mn concentrations were observed at all depths and sampling times.

Relative Influence of Hydrologic and Biogeochemical Processes

Since Mn is expected to reflect *in situ* biogeochemical processes, it is reasonable that its concentration in filtered samples does not correlate with that of Br, which represents hydrologic processes (e.g., conservative groundwater advection and mixing). 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 correlate positively and very strongly with Mn (Table 3).

Principal component analysis (Table 5) shows that Br and Mn correspond to distinct contributions to the data variability. In the upstream well transect, principal component (PC) 1 accounts for about 56% of the variability and shows a high score for Br and a score near 0 for Mn. In PC 2, the magnitude of these scores is reversed, though this PC accounts for ~24% of the variability. This trend is similar, but weaker, in the downstream transect. There, Br scores highly on PC 1 and Mn on PC 2. However, Mn and Br are not as close to 0 in PC 1 and PC 2, respectively, as in the upstream transect. PC 1 accounts for ~50% of the variability and PC 2 for ~29% of the data variability, a slightly diminished difference from upstream. In the upstream and downstream transects, PC 3 accounts for ~11% and ~14% of the variability, respectively, and the magnitude of the Mn score is much greater than that of the Br score in each case.

Thus, hydrologic processes do not predict reducing conditions in this system. Reducing conditions correlate very strongly with the data variability for which a linear model based on hydrologic processes do not account. Correlation analyses indicate that these two factors describe separate and exclusive portions of the data set. Furthermore, PCA suggests that hydrologic processes drive 50-56% of the variability and redox conditions influence 35-42% of the variability. Together, these two factors explain > 90% of the variability in the data set. Hydrologic processes appear to be slightly more important in the upstream transect, where conservative tracers indicate more surface water infiltration and less riverbed mixing than in the downstream transect.

Responses of Sr, Ba, U, and P

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

Bromine correlates with Sr, Ba, and U in both transects and also with P in the downstream transect (Table 3). Principal component analyses (Table 5) also show the association of response elements with Br. In both transects, PC 1 shows moderately high scores of matching sign for Br, Sr, Ba, and U. Downstream, P also matches Br in PC 1. Since PC 1 accounts 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 correlate positively with P in both transects and with Ba in the downstream transect (Table 3), 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 has high scores of matching sign for Mn and P, indicating that this PC accounts for variability due to redox conditions and that P responds to this variability. Upstream, P in PC 3 shows a notably high score with opposite sign from that of Mn. Downstream, U scores highly and Sr scores moderately on PC 2, and their signs are 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 none 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 ($CaCO_3$, e.g., Tesoriero and Pankow, 1996) in the study of Kennedy et al. (1984). This latter mechanism is 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 are controlled by hydrologic processes in both transects, and also 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). Well location is an important predictor variable for both elements: the aquifer groundwater entering the riverbed from the southeast contains high concentrations of each. Occasionally, U exceeds 0.126 μM (30 μg L^{-1}), the maximum drinking water contaminant level set by the United States 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, though they do appear to have some effect downstream, where concentrations significantly exceed those of the upstream transect (t-test, $p < 0.05$; Tables 1, 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 PCs 2 and 3 in the analysis corresponding to each transect. However, the signs of the scores are the same in PC 2 and the opposite in PC 3. This indicates that reductive dissolution of Mn-oxide minerals may also 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). 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 than organic matter decomposition in this river reach.

CONCLUSIONS

Results presented in this study show that hydrological processes, which are probably closely related to regional irrigation patterns (Phillips et al., 2007), dominate subsurface distribution of Sr, Ba, and U beneath a reach of the lower Merced River. Their influence is strongest on Sr, which shows a minor response to biogeochemical redox conditions. Upstream, hydrological processes also control Ba and U, but, downstream, redox trends are also relevant. Phosphorus transport is controlled by hydrological processes at high concentrations and redox conditions otherwise. Comparison among these elements is useful because they have different sorption and redox properties in addition to different probable sources in this system.

Overall, hydrological processes account for a little more than 50% of the variance in data collected from Merced River groundwater samples. The influence of redox conditions is less important, accounting for 35-42% of the variability. Trends are not consistent between two transects separated by 100 m; redox chemistry influences minor solutes more in the downstream transect. This is a curious finding that is worthy of future research.

These results complement prior reports on the behavior of nutrients and pesticides at this field site (Gronberg et al., 2004; Domagalski et al., 2008a, 2008b; Puckett et al. 2008) by suggesting that changes in groundwater flow derived from agricultural irrigation control inorganic solute transport in river subsurface. Differences in the controls of Ba, U, and P in the two proximal transects suggest a complex connection between aquifer flowpaths and the riverine subsurface.

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 natural tracer concentrations and groundwater redox indicators provide insight into subsurface systems subject to a combination of lateral advection, hyporheic exchange, and mixing of surface water and ground water.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Steven Phillips and Celia Zamora (USGS) for field assistance. Laboratory analysis would have been impossible without Nathan Dalleska, Megan Ferguson, Kate Campbell, and Giehyeon Lee (Caltech). Tapio Schneider and Drew Keppel (Caltech) gave advice at key points during statistical analysis. The manuscript was improved with the help of Claire Farnsworth (Caltech), Peter Reichert (Eawag), Laura Sigg (Eawag), and 2 anonymous reviewers. This work was partially supported by the U.S. Geological Survey National Water Quality Assessment Program (ACT study). NSF SGER grant EAR-0408329 funded sample analysis and Rich Wildman's graduate study.

REFERENCES

Aiken, G.R. 1992. Chloride interference in the analysis of dissolved organic carbon by the wet oxidation method. Environ. Sci. Technol. 26:2435-2439.

Anderson, M.T. and L.H. Woosley, Jr. 2006. Water availability for the Western United States – Key scientific challenges. U.S. Geological Survey Circular 1261, Reston, VA.

Arias, M., J. Da Silva-Carballal, L. Garcia-Rio, J. Mejuto, and A. Nunez. 2006. Retention of phosphorus by iron and aluminum-oxides-coated quartz particles. J. Coll. Int. Sci. 295:65-70.

Báez-Cazull, S.E., J.T. McGuire, I.M. Cozzarelli, M.A. Voytek. 2008. Determination of dominant biogeochemical processes in a contaminated aquifer-wetland system using multivariate statistical analysis. J. Environ. Qual. 37:30-46.

Beauchemin, S. and Y.T.J. Kwong. 2006. Impact of redox conditions on arsenic mobilization from tailings in a wetland with neutral drainage. Environ. Sci. Technol. 40:6297-6303.

Bencala, K.E. 2000. Hyporheic zone hydrological processes. Hydrol. Processes 14:2797-2798.

Brown, B.V., H.M. Valett, and M.E. Schreiber. 2007. Arsenic transport in groundwater, surface water, and the hyporheic zone of a mine-influenced stream-aquifer system. Wat. Resour. Res. 43: W11404, doi:10.1029/2006WR005687.

Canfield, D.E., B. Thamdrup, and J.W. Hansen. 1993. The anaerobic degradation of organic matter in Danish coastal sediments: Iron reduction, manganese reduction, and sulfate reduction. Geochim. Cosmochim. Acta 57:3867-3883.

Capel, P.D., K.A. McCarthy, and J.E. Barbash. 2008. National, holistic, watershed-scale approach to understand the sources, transport, and fate of agricultural chemicals. J. Environ. Qual. 37:983-993.

Choi, J., J.W. Harvey, and M.H. Conklin. 2000. Characterizing multiple timescales of stream and storage zone interaction that affect solute fate and transport in streams. Wat. Resour. Res. 36(6):1511-1518.

Davies, S.H.R. and J.J. Morgan. 1989. Manganese(II) oxidation kinetics on metal oxide surfaces. J. Col. Int. Sci. 129(1):63-77.

Domagalski, J.L., S. Ator, R. Coupe, K. McCarthy, D. Lampe, M. Sandstrom, and N. Baker. 2008a. Comparative study of transport processes of nitrogen, phosphorus, and herbicides to streams in five agricultural basins, USA. J. Environ. Qual. 37:1158-1169.

Domagalski, J. L., S. P. Phillips, R. E. Bayless, C. Zamora, C. Kendall, R. A. Wildman, and J. G. Hering. (2008b). Influences of the unsaturated, saturated, and riparian zones on the transport of nitrate near the Merced River, California. Hydrogeol. J. 16(4):675-690.

Essaid, H.I., C.M. Zamora, K.A. McCarthy, J.R. Vogel, and J.T. Wilson. 2008. Using heat to characterize streambed water flux variability in four stream reaches. J. Environ. Qual. 37:1010-1023.

Feyrer, F., M.L. Nobriga, and T.R. Sommer. 2007. Multidecadal trends for three declining fish species: habitat patterns and mechanisms in the San Francisco Estuary, California, USA. Can. J. Fish. Aquat. Sci. 64:723-734.

Findlay, S. 1995. Importance of surface-subsurface exchange in stream ecosystems: The hyporheic zone. Limnol. Oceanogr. 40(1):159-164.

Foulliac, C. and A. Criaud. 1984. Carbonate and bicarbonate trace metal complexes: Critical reevaluation of stability constants. Geochem. J. 18:297-303.

Franssen, N.R., K.B. Gido, and D.L. Propst. 2007. Flow regime affects availability of native and nonnative prey of an endangered predator. Biol. Conserv. 138:330-340.

Gächter, R. and B. Wehrli. 1998. Ten years of artificial mixing and oxygenation: No effect on the internal phosphorus loading of two eutrophic lakes. Environ. Sci. Technol. 32:3659-3665.

Gilliom, R.J., W.M. Alley, M.E. Gurtz. 1995. Design of the National Water-Quality Assessment Program: Occurrence and distribution of water-quality conditions. U.S. Geological Survey Circular 1112, Sacramento, CA.

Green, C.T., D.A. Stonestrom, B.A. Bekins, K.C. Akstin, and M.S. Schulz. 2005. Percolation and transport in a sandy soil under a natural hydraulic gradient. Wat. Resour. Res. 41:W10414, doi: 10.1029/2005WR004061.

Gronberg, J.M. and C.R. Kratzer. 2007. Environmental setting of the lower Merced River Basin, California. U.S. Geological Survey Scientific Investigations Report 2006-5152, Sacramento, CA.

Gronberg, J.M., C.R. Kratzer, K.R. Burow, J.L. Domagalski, and S.P. Phillips. 2004. Water-quality assessment of the San Joaquin-Tulare Basins: Entering a new decade. U.S. Geological Survey Fact Sheet 2004-3012, Sacramento, CA.

Haggard, B.E., E.H. Stanley, and D.E. Storm. 2005. Nutrient retention in a point-source enriched stream, J. Nor. Amer. Benthol. Soc. 24(1): 29-47.

Han, R., W. Zou, Z. Zhang, J. Shi, and J. Yang. 2006. Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand I. Characterization and kinetic study. J. Haz. Mat. B137: 384-395.

Harned, D.A., J. B. Atkins, and J.S. Harvill. 2004. Nutrient mass balance and trends, Mobile River Basin, Alabama, Georgia, and Mississippi. J. Amer. Wat. Resour. Assoc. June 2004:765-793.

Harvey, C.F., K.N. Ashfaque, W. Yu, A.B.M. Badruzzaman, M.A. Ali, P.M. Oates, H.A. Michael, R.B. Neumann, R. Beckie, S. Islam, and M.F. Ahmed. (2006). Groundwater dynamics and arsenic contaminations in Bangladesh. Chem. Geol. 228(1-3):112-136.

Harvey, J.W. and C.C. Fuller. 1998. Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance. Wat. Resour. Res. 34(4):623-636.

Harvey, J.W., J.E. Saiers, and J.T. Newlin. 2005. Solute transport and storage mechanisms in wetlands of the Everglades, south Florida. Wat. Resour. Res. 41: W05009, doi:10.1029/2004WR003507.

Kennedy, V.C., A.P. Jackman, S.M. Zand, G.W. Zellweger, and R.J. Avanzino. 1984. Transport and concentration controls for chloride, strontium, potassium and lead in Uvas Creek, a small cobble-bed stream in Santa Clara County, California, U.S.A. J. Hydrol. 75:67-110.

Kneeshaw, T.A., J.T. McGuire, E.W. Smith, and I.M. Cozzarelli. 2007. Evaluation of sulfate reduction at experimentally induced mixing interfaces using small-scale push-pull tests in an aquifer-wetland system. Appl. Geochem. 22:2618-2629.

Krom, M. D. and R.A. Berner. 1981. The diagenesis of phosphorus in a nearshore marine sediment. Geochim. Cosmochim. Acta 45:207-216.

Lovley, D. R. and E.P. Phillips. 1992. Reduction of uranium by Desulfovibrio desulfuricans. App. Env. Microbiol. 58(3):850-856.

Lucas, L.V., J.E. Cloern, J.K. Thompson, and N.E. Monsen. 2002. Functional variability of habitats within the Sacramento-San Joaquin Delta: Restoration implications. Ecol. App. 12(5):1528-1547.

McGuire, J.T., D.T. Long, M.J. Klug, S.K. Haack, and D.W. Hyndman. 2002. Evaluating behavior of oxygen, nitrate, and sulfate during recharge and quantifying reduction rates in a contaminated aquifer. Environ. Sci. Technol. 36:2693-2700.

McKergow, L.A., I.P. Prosser, D.M. Weaver, R.B. Grayson, and E.G. Reed. 2006. Performance of grass and eucalyptus riparian buffers in a pasture catchment, Western Australia, part 2: water quality. Hydrol. Processes 20:2327-2346.

Montgomery, D.R. 2007. Soil erosion and agricultural sustainability. Proc. Nat. Acad. Sci. USA 104(33):13268-13272.

Morgan, J.J. 2005. Kinetics of reaction between O_2 and Mn(II) species in aqueous solutions. Geochim. Cosmochim. Acta 69(1):35-48.

Naylor, C., W. Davison, M. Motelica-Heino, G.A. Van Den Berg, L.M. Van Der Heijdt. 2006, Potential kinetic availability of metals in sulphidic freshwater sediments. Sci. Tot. Environ. 357:208-220.

Packman, A.I. and K.E. Bencala. 2000. Modeling Surface-Subsurface Hydrological Interactions. p. 45-80. In J.A. Jones and P.J. Mulholland (ed.) Streams and Ground Waters. Academic Press: San Diego.

Phillips, S.P., C.T. Green, K.R. Burow, J.L. Shelton, and D.L. Rewis. 2007. Simulation of multiscale ground-water flow in part of the Northeastern San Joaquin Valley, California. U.S. Geological Survey Scientific Investigations Report 2007-5009, Sacramento, CA.

Puckett, L.J. and W.B. Hughes. 2005. Transport and fate of nitrate and pesticides: Hydrogeology and riparian zone processes. J. Environ. Qual. 34:2278-2292.

Puckett, L.J., C. Zamora, H. Essaid, J.T. Wilson, H.M. Johnson, M.J. Brayton, and J.R. Vogel. 2008. Transport and fate of nitrate at the ground-water/surface-water interface. J. Environ. Qual. 37:1034-1050.

Qiu, S. and A.J. McComb. 1994. Effects of oxygen concentration on phosphorus release from reflooded air-dried wetland sediments. Australian J. Mar. Freshwat. Res. 45:1319-1328.

Salehin, M., A.I. Packman, and M. Paradis. 2004. Hyporheic exchange with heterogeneous streambeds: Laboratory experiments and modeling. Wat. Resour. Res. 40: W11504, doi: 10.1029/2003WR002567.

Tesoriero, A.J. and J.F. Pankow. 1996. Solid solution portioning of Sr^{2+}, Ba^{2+}, and Cd^{2+} to calcite. Geochim. Cosmochim. Acta 60(6):1053-1063.

Tonkin, J.W., L.S. Balistrieri, and J.W. Murray. 2004. Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. Appl. Geochem. 19:29-53.

Trefry, J.H. and B.J. Presley. 1982. Manganese fluxes from Mississippi Delta sediments. Geochim. Cosmochim. Acta 46:1715-1726.

Valett, H.M., J.A. Morrice, C.N. Dahm, and M.E. Campana. 1996. Parent lithology, surface-groundwater exchange, and nitrate retention in headwater streams. Limnol. Oceanogr. 41(2):333-345.

van Griethuysen, C., M. Luitwieler, J. Joziasse, and A.A. Koelmans. 2005. Temporal variation of trace metal geochemistry in floodplain lake sediment subject to dynamic hydrological conditions. Environ. Pollut. 137:281-294.

Zamora, C. 2008. Estimating water fluxes across the sediment-water interface in the lower Merced River, California. U.S. Geological Survey Scientific Investigations Report 2007-5216, Sacramento, CA.

FIGURE CAPTIONS

Figure 1: Regional and detailed setting and near-river land uses of the Merced River field site. In the inset, (A) represents almond orchards, (B) feed corn, (C) native vegetation, and (D) a vineyard (after Phillips et al., 2007). The river flows from right to left in the inset.

Figure 2: Schematic of well locations beneath the Merced River, looking upstream. Circles indicate locations where samples for analysis of specific conductance, manganese, strontium, barium, uranium, phosphorus, bromine, and dissolved organic carbon were collected in each transect. Dimensions are not to scale.

TABLES

Table 1: Descriptive statistics for full data set (SC in µS/cm at 298 K, all elemental concentrations in µM).

statistic	*element*						
	SC	Br	Mn	Sr	Ba	U	P
				upstream transect			
number[†]	25	38	38	38	38	38	38
max	732	23.5	206.7	11.4	2.0	0.15	16.6
min	72	<0.03	<0.04	<0.02	0.1	<0.008	<0.07
median	441	2.9	5.8	2.7	1.0	0.01	0.6
mean	343	6.1	17.8	3.6	1.0	0.03	2.0
σ[‡]	212	7.1	39.9	3.0	0.6	0.04	3.8
CV[§]	62	116.4	224.2	83.3	60.0	133.3	190.0
				downstream transect			
number[†]	33	40	40	40	40	40	40
max	907	15.4	168.8	6.4	1.9	0.16	40.8
min	72	<0.03	<0.04	0.1	<0.02	<0.008	<0.07
median	343	2.3	3.7	2.3	0.6	0.01	2.4
mean	400	4.2	10.5	2.8	0.7	0.02	8.0
σ[‡]	230	4.3	26.8	1.6	0.5	0.04	10.6
CV[§]	57	102.4	255.2	57.1	71.4	200.0	132.5

[†] The number of samples analyzed from each transect.

[‡] σ is the population standard deviation.

[§] CV is the coefficient of variation. CV = σ/mean * 100%.

Table 2: Specific conductance (µS/cm at 298 K) and Br (µM) in surface water and groundwater.

upstream transect

depth	northwest riparian		northwest river		center		southeast river		southeast riparian	
	SC	Br	SC	Br	SC	Br	SC	Br	SC	Br
March 2004										
river					136					
0.3 m		3.3	704	10.8	161	0.5	103	0.2		20.4
0.5 m		2.9		2.2		0.2		0.1		18.3
3.0 m		3.3	467	11.5	96	0.2	97	0.2		21.9
June 2004										
river					222					
0.3 m	490	4.4	441	3.1	117	1.5	171	2.8		
0.5 m										
3.0 m	483	3.1	450	2.7	123	1.8	262	4.4		
October 2004										
river					72					
0.3 m	530	2.9	445	1.5	127	<0.03	732	10.1		18.5
0.5 m		2.6		1.7		1.0		7.6		20.5
3.0 m	511	2.7	496	1.2	516	8.5	611	10.7		23.5

downstream transect

	northwest riparian		northwest river		center		southeast river		southeast riparian	
	SC	Br	SC	Br	SC	Br	SC	Br	SC	Br
March 2004										
river					136					
0.3 m	307	2.2	99	0.2	292	1.6	457	5.0	806	13.0
0.5 m		2.2		1.0		4.7		4.9		9.3
3.0 m	355	0.7	312	0.2	402	1.9	529	5.8	756	13.7
June 2004										
river					222					
0.3 m	297	2.6	340	1.4	326	2.6	175	0.9	793	15.4
0.5 m										
3.0 m	398	2.8	343	1.5	80	0.1	458	6.2	700	12.2
October 2004										
river					72					
0.3 m	220	1.6	103	<0.03	342	1.6	664	5.7	907	12.0
0.5 m		2.1		0.1		1.7		4.5		10.4
3.0 m	420	2.4	364	1.1	381	2.7	335	1.1	812	9.1

Table 3: Correlation matrices[†] for trace elements and residuals from a linear model with Br as a predictor variable.

upstream transect

	Br	Mn	Sr	Ba	U	P	residuals[‡]
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	Mn	Sr	Ba	U	P	residuals[‡]
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 4: Manganese (μM) and DOC (mM C) in filtered Merced River groundwater.

depth					*upstream transect*					
	northwest riparian		northwest river		center		southeast river		southeast riparian	
	Mn	DOC	Mn	DOC	Mn	DOC	Mn	DOC	Mn	DOC
					March 2004					
0.3 m	10.2		17.7	0.12	24.1	0.54	8.2	0.14	14.2	
0.5 m	3.2		4.2		0.7		0.2		7.1	
3.0 m	5.8		14.1	0.13	0.2	0.07	4.6	0.11	12.7	
					June 2004					
0.3 m	7.3		9.8	0.10	135.8	0.22	13.0	0.11		
0.5 m										
3.0 m	3.3		2.7	0.07	<0.04	0.12	<0.04			
					October 2004					
0.3 m	5.9		5.3		74.5		206.7		7.0	
0.5 m	5.9		4.6		0.5		43.4		11.6	
3.0 m	1.7		1.8		3.3		1.3		5.2	

					downstream transect					
	northwest riparian		northwest river		center		southeast river		southeast riparian	
	Mn	DOC	Mn	DOC	Mn	DOC	Mn	DOC	Mn	DOC
					March 2004					
0.3 m	1.9	0.10	<0.04	0.12	12.3	0.15	9.4	0.17	9.6	0.22
0.5 m	21.0		0.1		0.2		0.2		1.8	
3.0 m	4.0	0.10	<0.04	0.08	9.2	0.07	15.2	0.10	13.8	0.11
					June 2004					
0.3 m	3.5		<0.04		168.8	0.13	4.2	0.28	11.4	0.16
0.5 m										
3.0 m	34.7	0.07	<0.04	0.06		0.08	0.1	0.06	2.9	0.12
					October 2004					
0.3 m	2.7		<0.04		13.1		10.1		9.2	
0.5 m	3.9		<0.04		8.7		11.1		12.3	
3.0 m	23.6		<0.04		<0.04		<0.04		2.5	

Table 5: Principal component analysis of measured parameters and spatial variables in Merced River groundwater.

upstream transect

principal component scores:	PC1	PC2	PC3	PC4
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 scores:	PC1	PC2	PC3	PC4
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: Sr and Ba (µM) in filtered Merced River groundwater.

upstream transect

depth	northwest riparian		northwest river		center		southeast river		southeast riparian	
	Sr	Ba	Sr	Ba	Sr	Ba	Sr	Ba	Sr	Ba
March 2004										
0.3 m	2.3	1.1	6.1	1.4	1.2	0.7	1.0	0.2	10.1	2.0
0.5 m	3.7	1.7	3.5	0.6	0.8	0.2	1.0	0.1	11.4	1.5
3.0 m	2.8	1.3	6.6	1.5	0.8	0.5	1.0	0.2	10.7	2.0
June 2004										
0.3 m	2.9	1.5	3.7	1.0	1.1	1.0	1.3	0.5		
0.5 m										
3.0 m	3.4	1.7	3.3	0.6	<0.02	0.1	2.6	0.3		
October 2004										
0.3 m	2.1	0.8	1.7	0.5	0.6	1.2	4.1	1.6	6.3	1.6
0.5 m	2.1	0.8	1.9	0.6	0.8	0.4	4.2	1.3	7.5	1.5
3.0 m	2.1	1.1	2.4	0.4	3.6	1.4	5.5	0.9	9.4	1.4

downstream transect

	northwest riparian		northwest river		center		southeast river		southeast riparian	
	Sr	Ba	Sr	Ba	Sr	Ba	Sr	Ba	Sr	Ba
March 2004										
0.3 m	2.1	0.5	1.1	0.2	3.0	0.5	4.8	0.9	4.1	1.5
0.5 m	1.9	0.7	1.6	0.2	2.7	0.3	4.7	0.5	6.1	0.9
3.0 m	2.0	0.6	1.3	0.2	3.4	<0.02	6.4	1.3	3.7	1.7
June 2004										
0.3 m	2.0	0.6	1.8	0.3	2.4	1.9	1.5	0.3	3.5	1.6
0.5 m										
3.0 m	2.3	1.0	2.2	0.2	0.2	<0.02	3.8	0.5	5.9	0.9
October 2004										
0.3 m	1.5	0.5	1.0	0.2	2.8	0.6	5.6	1.2	3.8	1.6
0.5 m	1.8	0.7	1.3	0.2	2.9	0.6	4.7	1.2	3.0	1.4
3.0 m	2.0	0.8	1.8	0.2	2.3	0.3	2.1	0.3	5.4	0.8

Table 7: U and P (µM) in filtered Merced River groundwater.

depth	*upstream transect*									
	northwest riparian		northwest river		center		southeast river		southeast riparian	
	U	P	U	P	U	P	U	P	U	P
					March 2004					
0.3 m	0.01	<0.07	0.02	0.2	0.02	8.9	0.02	<0.07	0.11	4.1
0.5 m	0.01	<0.07	0.02	<0.07	0.02	0.1	0.02	<0.07	0.10	<0.07
3.0 m	0.01	<0.07	0.02	<0.07	0.02	<0.07	0.02	0.4	0.13	<0.07
					June 2004					
0.3 m	<0.008	0.4	<0.008	2.6	<0.008	16.6	0.01	0.7		
0.5 m										
3.0 m	<0.008	1.2	0.01	1.5	<0.008	3.8	0.01	0.5		
					October 2004					
0.3 m	<0.008	0.2	<0.008	0.4	<0.008	3.5	0.05	1.4	0.11	7.8
0.5 m	<0.008	1.6	<0.008	2.8	<0.008	2.4	0.02	3.9	0.15	3.4
3.0 m	<0.008	4.1	0.01	9.4	<0.008	8.1	0.06	<0.07	0.11	<0.07

	downstream transect									
	northwest riparian		northwest river		center		southeast river		southeast riparian	
	U	P	U	P	U	P	U	P	U	P
					March 2004					
0.3 m	<0.008	0.1	<0.008	0.1	<0.008	6.1	0.05	3.6	0.01	27.5
0.5 m	<0.008	3.5	0.01	0.6	0.02	0.7	0.07	0.2	0.12	3.0
3.0 m	<0.008	1.1	<0.008	0.1	<0.008	7.7	0.03	1.8	0.01	24.4
					June 2004					
0.3 m	0.01	0.7	0.02	1.2	0.01	24.1	0.02	13.0	0.01	31.3
0.5 m										
3.0 m	0.01	9.5	0.02	1.3	0.01	7.7	0.06	1.7	0.16	4.8
					October 2004					
0.3 m	<0.008	<0.07	<0.008	0.8	<0.008	12.5	0.05	18.5	<0.008	25.5
0.5 m	<0.008	1.5	<0.008	<0.07	<0.008	22.1	0.01	6.7	<0.008	40.8
3.0 m	<0.008	14.4	<0.008	<0.07	0.01	<0.07	0.02	<0.07	0.12	0.7

FIGURE 1

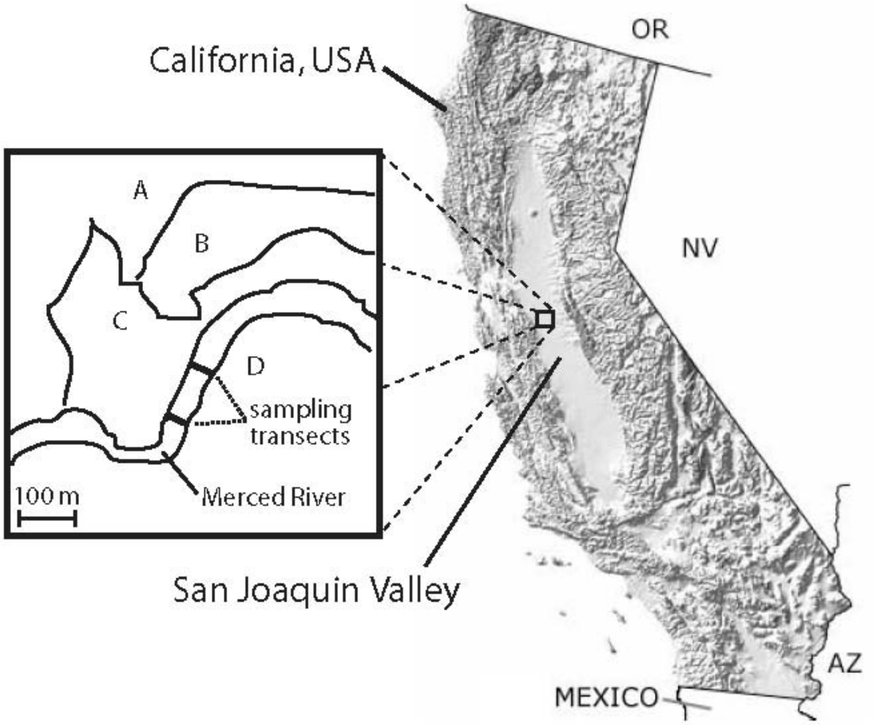
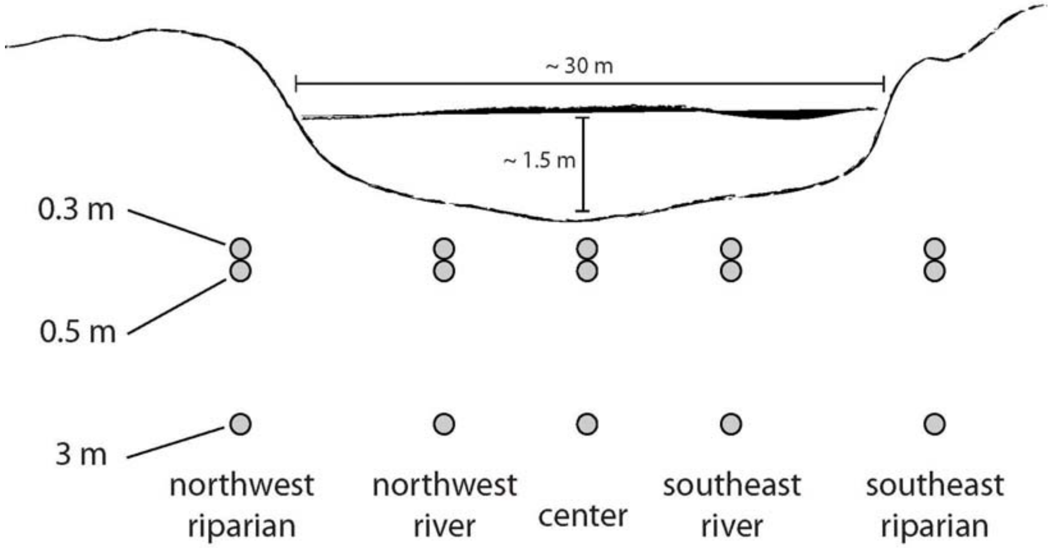

California, USA
OR
NV
A
B
C
D
sampling
transects
100 m
Merced River
San Joaquin Valley
AZ
MEXICO

FIGURE 2


~ 30 m
~ 1.5 m
0.3 m
0.5 m
3 m
northwest riparian
northwest river
center
southeast river
southeast riparian

APPENDIX

Table A1. pH and alkalinity[a] in the Merced River subsurface[b].

upstream transect

depth	northwest riparian		northwest river		center		southeast river		southeast riparian	
	pH	alk	pH	alk	pH	alk	pH	alk	pH	alk
March 2004										
0.3 m			6.49	150.2	6.70	58.8	6.87	34.3		
3.0 m			6.94	88.3	7.20	28.3	6.89	33.3		
June 2004										
0.3 m	6.30	72.6	6.70	71.7	6.30	33.7	6.60	40.0		
3.0 m	6.60	59.5	6.90	74.1	6.80	16.6	6.60	50.2		
Ocobter 2004										
0.3 m	6.87		6.78		6.90		6.79			
3.0 m	6.93		6.77		6.69		6.53			

downstream transect

depth	northwest riparian		northwest river		center		southeast river		southeast riparian	
	pH	alk	pH	alk	pH	alk	pH	alk	pH	alk
March 2004										
0.3 m	6.69	99.7	7.00	58.8	7.17	121.1	7.30	171.0	7.20	270.7
3.0 m	7.19	76.3	7.17	84.3	7.20	109.0	7.28	143.6	7.20	196.3
June 2004										
0.3 m	6.50	72.5	7.20	74.1	6.70	147.6	7.10	66.8	6.90	235.8
3.0 m	6.70	69.6	7.00	79.2	7.20	20.4	7.10	124.7	6.90	173.3
October 2004										
0.3 m	6.78		7.04		7.13		7.23		6.96	907.0
3.0 m	7.16		7.40		7.46		7.37		7.02	

[a] All data collected by the United States Geological Survey and shared by Joseph L. Domagalski.

[b] Alkalinity is reported as mg L^{-1} $CaCO_3$. It was measured in the field by a gran titration.

Table A-2. Specific conductance (in µS cm-1) and trace elements (in µM) in the local aquifer to the northwest of the Merced River[a].

well location[b] and depth		sampling month	specific conductance	Br	Mn	Sr	Ba	U	P
1 km	8.8 m	April	600	6.9	BDL	5.30	0.31	0.050	30.35
		June	571	5.4	BDL	5.25	0.34	0.046	11.49
		October	609	5.0	BDL	5.02	0.36	0.055	20.15
	13.9 m	April	597	3.1	1.09	8.40	0.08	0.034	132.35
		June	633	2.7	1.42	8.24	0.22	0.067	27.19
		October	648	1.9	BDL	7.64	0.15	0.059	32.39
	19.5 m	April	568	3.1	0.93	7.08	0.55	0.029	17.89
		June	550	3.4	0.69	6.62	0.60	0.034	11.85
		October	582	2.1	BDL	6.56	0.63	0.029	9.43
	25.9 m	April	585	2.7	0.24	6.90	0.92	0.042	6.59
		June	602	3.3	0.18	6.93	0.99	0.050	2.97
		October	596	2.8	BDL	6.63	0.93	0.042	5.23
0.5 km	13.9 m	April	308	1.5	BDL	3.24	0.21	BDL	26.28
		June	304	1.7	0.05	3.24	0.28	BDL	12.04
		October	293	0.8	BDL	2.93	0.31	BDL	10.82
	19.5 m	April	871	9.8	0.05	11.81	0.83	0.046	48.60
		June	878	11.2	0.07	12.12	1.10	0.055	15.63
		October	843	8.0	BDL	10.27	0.98	0.042	16.95
	25.9 m	April	365	1.9	BDL	2.93	0.23	BDL	31.09
		June	379	2.1	0.05	2.82	0.28	BDL	9.88
		October	385	1.7	BDL	2.98	0.31	BDL	15.63
0.1 km	8.8 m	April	552	2.5	1.22	3.97	0.66	0.017	3.13
		June	549	2.7	1.07	4.28	0.75	0.021	1.16
		October	573	2.2	BDL	4.35	0.69	0.017	2.68
	13.9 m	April	499	1.9	0.76	4.01	0.51	0.013	2.36
		June	506	2.1	0.76	4.17	0.55	0.013	0.90
		October	481	1.4	BDL	3.73	0.49	BDL	1.52
	25.9 m	April	290	1.2	0.07	1.27	0.17	BDL	2.58
		June	282	1.2	0.07	1.31	0.17	BDL	1.07
		October	286	0.8	BDL	1.28	0.16	BDL	1.13
	29.0 m	April	288	1.3	0.31	0.96	0.18	BDL	3.45
		June	284	1.3	0.25	0.96	0.19	BDL	0.61
		October	288	1.0	BDL	0.82	0.17	BDL	2.87
	53.3 m	April	463	3.6	1.49	1.29	0.17	BDL	10.40
		October	452	2.3	BDL	1.31	0.17	BDL	4.52
detection limit				0.025	0.04	0.02	0.01	0.008	0.06

[a] Specific conductance and trace elements were measured on unfiltered and filtered (0.2 µm) samples, respectively.

[b] Details of well installations described by Phillips et al. (2007).