

Biogeochemistry at the zone of intermittent saturation: Field-based study of the shallow alluvial aquifer, Rio Grande, New Mexico

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ABSTRACT

The Rio Grande in central New Mexico (USA) flows through a semiarid alluvial valley; the river is regulated by levees, river-side drain ditches, irrigation structures, and upstream dams. As a large river in a semiarid region, the Rio Grande experiences large variability in flows and solute concentrations due to riparian evapotranspiration, aquifer recharge, and upstream contributions. In order to characterize biogeochemical processes in this setting, surface water and groundwater from the shallow alluvial aquifer between the river and a parallel drain ditch were sampled from 1 to 13 m depth, including high-resolution multilevel sampling near the fluctuating water table, at a representative site on the middle Rio Grande. The zone of intermittent saturation is a region, ~50 cm in vertical extent at this site, in which the water table shifts in response to changes in river level and riparian evapotranspiration. Sediment extractions of iron and manganese oxides indicate that these solids are more prevalent in the zone of intermittent saturation, where oxic-anoxic cycling occurs. River water chemistry varies with time, strongly influencing influent waters to the alluvial aquifer. This chemistry evolves significantly in the ~100 m from the river to four wells.

River concentrations of dissolved oxygen (mean 6.9 mg L⁻¹) and nitrate (mean 2.8 mg L⁻¹) are reduced to near zero in the shallower wells (1–3 m depth), but are less reduced from the river in the deeper wells (5–13 m depth). Mn and Fe increase from near zero in the river to maximum concentrations from 1 to 3 m depth (mean 1.0 mg L⁻¹ and 2.1 mg L⁻¹, respectively), with lesser increases at 5 and 13 m depth. Sulfate concentration decreases relative to chloride in many samples, especially from 1 to 3 m depth, most likely due to sulfate reduction. Overall, patterns in water and sediment chemistry indicate that waters in the region of the shifting water table are more evolved from the river via terminal electron-accepting processes than deeper waters, including aerobic respiration, denitrification, manganese oxide reduction, iron oxide reduction, and sulfate reduction. This implies that a greater extent of organic carbon metabolism occurs at shallower depths. The influence of sulfate reduction on organic carbon oxidation is facilitated by sulfate concentrations of river water that varied from 31 to 83 mg L⁻¹ during the study. These results illustrate that sulfate reduction may constitute a significant portion of organic carbon metabolism in higher-sulfate shallow alluvial aquifers associated with freshwater rivers. Biogeochemical processes in the shallow alluvial aquifer depend on the river for solute inputs, and may in turn influence large-scale river chemistry.

Keywords: biogeochemistry, alluvial aquifer, zone of intermittent saturation, terminal electron-accepting process, redox, Rio Grande.

INTRODUCTION

Shallow, unconfined aquifers of alluvial rivers are dynamic, complex environments of interest to hydrologists, geologists, and ecologists (Woessner, 2000). Alluvial aquifers rapidly exchange water and solutes with the channel, creating a biogeochemically active area that has been called the hyporheic corridor (Stanford and Ward, 1993). This region hosts interactions between solutes and solids, including redox fluctuations, mineral precipitation-dissolution, and adsorption processes. These processes cause chemical evolution of water and sediment at a variety of spatial and temporal scales (Groffman and Crossey, 1999; Baker et al., 2000a). One location at which these interactions occur in shallow alluvial aquifers is the rapidly fluctuating water table, influenced by nutrient availability, redox conditions, phreatophytes, and the microbial community.

The region of the dynamic water table has been termed the zone of intermittent saturation (Groffman and Crossey, 1999) and the region of seasonal saturation (Baker et al., 2000b). Research along small forest streams has demonstrated that this zone hosts a higher level of biogeochemical activity than the permanently phreatic sediments below (Groffman and Crossey, 1999; Baker et al., 2000b). Intermittent saturation events may occur on diel, seasonal, annual, or irregular (anthropogenic) time scales; in the semiarid southwestern United States, examples of these events are riparian evapotranspiration (Dahm et al., 2002), summer monsoon rains, interannual differences in snowpack (Molles et al., 1992), and irrigation diversions, respectively. In dry areas in which rivers commonly recharge

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alluvial aquifers, these external events create a complex pattern of water table variations in the zone of intermittent saturation.

As surface water recharges an alluvial aquifer, a thermodynamically predictable sequence of terminal electron-accepting processes is expected to oxidize organic carbon to inorganic carbon: aerobic respiration, denitrification, Mn oxide reduction, Fe oxide reduction, sulfate reduction, and methanogenesis (Fig. 1; Champ et al., 1979; Jackson and Patterson, 1982; Baker et al., 2000a; Chapelle, 2001). Groundwater also encounters Fe and Mn oxides in the sediments, especially when the water table rises. These phases form at oxic-anoxic interfaces at lower water table levels (Groffman and Crossey, 1999). Reactive Fe and Mn oxyhydroxides attract trace metals and nutrients (such as phosphorous) and incorporate them via coprecipitation and adsorption. When anoxic groundwater encounters reactive Fe or Mn oxyhydroxides, reductive dissolution occurs, producing Fe^{2+} or Mn^{2+} . In addition, soluble trace metals and phosphate are released into solution if they were originally incorporated into the mineral (Ferris, 2000). Through this process, the reactivity of Fe/Mn oxyhydroxides influences trace metal and/or nutrient distribution (Boulton et al., 1998; Lovley, 2000). In shallow alluvial aquifers subject to the influence of phreatophytes, evapotranspiration exports water vapor from the aquifer and concentrates the residual groundwater (Dahm et al., 2002). Plant respiration may also influence dissolved organic and inorganic carbon.

The purpose of this research is to identify the relative importance of terminal electron-accepting processes in two dimensions: horizontally, to characterize chemical evolution across the alluvial aquifer from river to drain ditch (Fig. 1), and vertically, to identify the extent of the zone of intermittent saturation and its influence on the dominant biogeochemical processes in the alluvial aquifer.

Although these processes have been characterized in many settings, including in particular small forested streams in the Rio Grande headwaters (e.g., Valett et al., 1996; Groffman and Crossey, 1999; Baker et al., 2000b; Morrice et al., 2000), critical differences exist between those settings and a large river floodplain in a semiarid area. These include (1) strong gradients in solute supply due to the basin's rock types and tectonic activity (e.g., Phillips et al., 2003; Plummer et al., 2004; Newell et al., 2005) and hydrologic variability (Passell et al., 2004); (2) the potential importance of sulfate reduction rather than methanogenesis as a major pathway of anaerobic organic carbon decomposition in higher-sulfate waters (Capone and Kiene, 1988; Weston et al., 2006); (3) high variability in flows and disturbances on desert rivers (such as flooding and drying) compared to mesic temperate zone rivers; and (4) intense evapotranspiration overprinted on the well-known processes that govern the oxidation of organic carbon. These may introduce additional complexity to the biogeochemical structure of shallow aquifers through modifying flow paths, surface water-

groundwater connections, and salinity (e.g., Dahm et al., 2002; Shafroth et al. 2005; Cleverly et al., 2006).

HYDROLOGIC SETTING

This study focuses on a reach of the Rio Grande, the major river of central New Mexico, called the middle Rio Grande. The middle Rio Grande extends 320 km from Otowi to Elephant Butte, New Mexico, and drains an area of $\sim 39,000 \text{ km}^2$. The river basin contains Chihuahuan desert scrub at lower elevations ($\sim 1250 \text{ m}$), semiarid grasslands and woodlands, and forested mountain ranges more than 3000 m above sea level. The Rio Grande loses surface flow to evapotranspiration (Dahm et al., 2002) and aquifer recharge (Hansen and Gorbach, 1997; Plummer et al., 2004) as it flows through the Albuquerque Basin. Evapotranspiration occurs in the riverine corridor and in conjunction with agriculture in the adjacent floodplain. In addition, the Rio Grande contributes $\sim 3 \text{ cm yr}^{-1}$ of recharge to the deep basin-fill aquifer (Plummer et al., 2004). As a result of these losses, the Rio Grande tends to have lower discharge with increasing downstream distance, with a 10%–15% decrease in average discharge from Otowi to the study area (Passell et al., 2004). Within the shallow alluvial aquifer in the riverine corridor, groundwater consumption by phreatophytes lowers the water table during daylight. This depletion is recharged at night, producing a centimeter-scale diel fluctuation. This evapotranspiration-derived fluctuation is largest in mid-summer (Dahm et al., 2002).

Before the middle Rio Grande was regulated, floods caused large-scale aggradation on the floodplain, such as an estimated 5.8 cm yr^{-1} from 1936 to 1941 (Rittenhouse, 1944). Holocene valley-fill deposits are 15–29 m thick (Connell and Love, 2001). Historic flood sedimentation raised the water table, enabled flood-dependent trees to reproduce, and damaged farmland. During the twentieth century, the middle Rio Grande underwent flow regulation measures including upstream dam construction, bank stabilization, and levee construction (Crawford et al., 1993). These human-induced changes have increased the long-term stability of the middle Rio Grande hydrologic system and have decreased the amount of physical and ecological disturbance, particularly flooding. Water is diverted into irrigation canals parallel to the river at the upper edge of the floodplain, and smaller distribution ditches carry water to farms. Riverside drainage ditches, parallel to the river channel and lower than the irrigation system, intercept shallow groundwater. This system has been present for several decades (Theis, 1938),

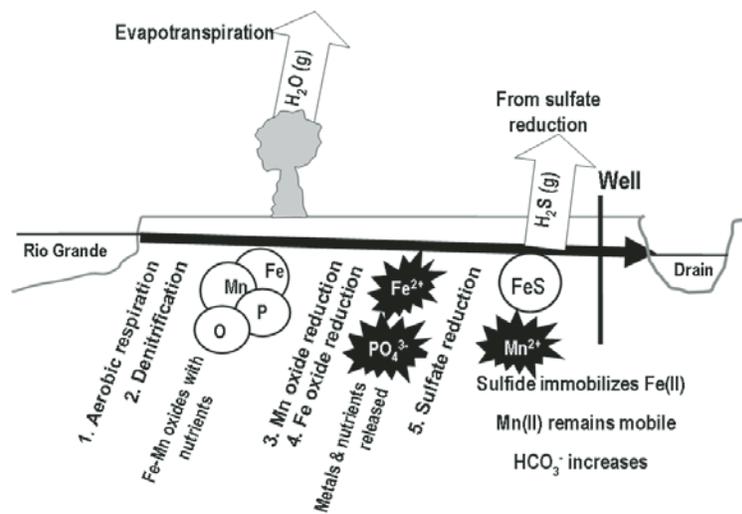


Figure 1. Summary of biogeochemical processes affecting groundwater traveling from river to study wells and the drainage ditch.

and pre-development hydrologic behavior of the shallow, intermittently saturated sediments must be inferred. The intended effect of the riverside drains is to steepen the hydraulic gradient beneath the floodplain and lower the water table, returning intercepted water to the river via surface flow (Theis, 1938; Hansen and Gorbach, 1997). Because the riverside drains have lower bed levels than the corresponding riverbed, the prevalent groundwater flow direction is from the river to the riverside drains (Peter, 1987).

METHODS

Study Site

The study location is along the eastern bank of the Rio Grande south of Belen, New Mexico, at 34°35'25" N, 106°45'02" W, and elevation 1460 m (Fig. 2), one of eight representative hydrologic research sites in the middle Rio Grande (Dahm et al., 2002). At the site, sediments are sand dominated below the unsaturated soil zone (Block, 2002; Vinson, 2002). The unsaturated zone soils have been described as Entisols, containing alternating sand and silt-clay layers. The poorly developed soil contains an A horizon <20 cm thick, and B horizons are virtually absent. Below are multiple buried soils, with minor or absent B horizons, reflecting

repeated deposition by historical floods of the Rio Grande (Bailey, 2004). Four wells, located a few meters apart at the location shown in Figure 2, were installed with discrete screened intervals. BLN2, BLN3, and BLN4 were installed using a motorized drilling rig. BLNC, containing a pressure transducer, is screened from 208 to 300 cm depth, and was installed by hand-augering. The pressure transducer was used to determine the level of the water table every 30 min during the study period. BLN2, used for multilevel sampling, is 462 cm deep and is continuously screened. BLN3 is screened from 348 to 500 cm below the surface. BLN4 is screened from 1219 to 1371 cm depth. BLN9, a hand-augered well used for sediment sampling and studies of mineral growth on incubated surfaces (Vinson, 2002), is ~200 cm deep and is screened from ~50 to 200 cm below the surface. All wells are constructed of ~5-cm-diameter PVC.

Water Sampling and Analytical Methods

BLNC, BLN3, and BLN4 were sampled regularly to establish the coarse vertical chemistry of the site. Prior to sampling, BLN3 and BLN4 were purged with a bailer; BLNC could not be bailed because it contained a pressure transducer. Samples were collected for major anions, cations, and alkalinity with a peristal-

tic pump into acid-washed bottles. Cation and anion samples were filtered during collection with in-line 0.45 μm Millipore filters, and the cation sample was acidified immediately with nitric acid. The pH was determined in the field using an Orion model 290A meter with automatic temperature compensation. Dissolved oxygen was determined down-well using a YSI model 55 meter with nominal precision of ± 0.3 mg L⁻¹. Surface water samples were collected by holding an acid-washed bottle from shore into the stream. These samples were filtered (0.45 μm , Millipore) and split into cation and anion subsamples in acid-washed bottles in the lab, and the cation subsample was acidified. Although the wells were sampled on several additional occasions (Block, 2002; Vinson, 2002), only dates on which both the river and groundwater (conventional wells or multilevel sampler) were sampled are presented here.

Water samples were collected from BLN2 with the dialysis multilevel sampling system for continuously screened wells (Ronen et al., 1986; Magaritz et al., 1989). This system collects samples passively with 30 dialysis cells along a 1.5 m plastic column. We established 14 sampling intervals at ~9 cm resolution, providing a 30 mL sample per interval. Intervals are separated by gaskets that fit against the well casing, preventing vertical exchange. Dialysis cells

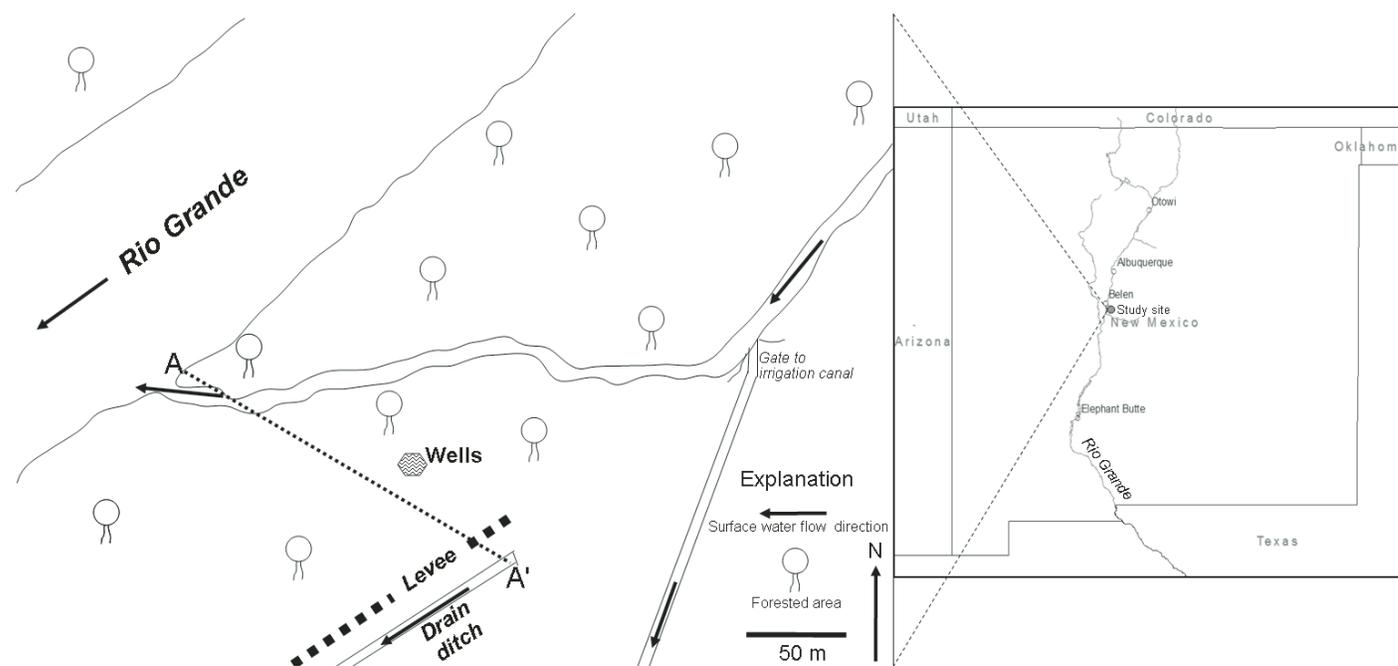


Figure 2. Map of the study site. Gradient between Rio Grande and drain ditch water surfaces was surveyed between points A and A'. Surface flow directions are shown by arrows. (Geographic information system layers for regional map obtained from www.nationalatlas.gov; site map traced from U.S. Bureau of Reclamation aerial photograph.)

were fitted with 0.2 μm nylon membranes that passively filtered samples. Dialysis cells were filled with deionized water having resistivity of at least 18 $\text{M}\Omega$. The sampling column was inserted into the well; cells equilibrated with their surroundings by diffusion across chemical gradients. The sampling rod was left in the aquifer far in excess of the equilibration time. Equilibration time, determined by a tracer dilution experiment, is less than one day at the Belen site (Vinson, 2002); thus, samples taken represent approximately daily averaging of solute concentrations. Only multilevel sampling data from below the water table and between 100 and 240 cm depth are reported.

Decisions regarding analytical methods were influenced by the limited sample volume provided by the multilevel sampler (30 mL per depth interval as configured). Some procedures were modified to accommodate smaller sample volumes. A 1.5 mL subsample was drawn from each interval into a clean syringe, which was stoppered without air bubbles and kept cold. Upon return to the lab (travel time ~ 1 h), sulfide was determined colorimetrically on this subsample by the methylene blue method (American Public Health Association, 1995) modified for small volumes. A 3 mL subsample was taken from each sampling interval for immediate electrode analysis for pH; the pH subsample was then discarded. Cation and anion subsamples from each passively filtered multilevel sampling cell were poured into acid-washed bottles in the field. The cation subsample was immediately acidified with nitric acid. Dissolved oxygen (DO) and temperature were not analyzed from the cells, but were determined in the same well at 10 cm depth intervals and matched to the closest sampling depth. DO was measured just before the sampling column was reinstalled. The well was not specifically purged prior to DO measurement, but the well water had been disturbed previously by removal of the multilevel sampler.

Major cations, Fe, and Mn were determined by flame atomic absorption spectrometry. The Fe analysis has a detection limit of ~ 0.01 mg L^{-1} , and the Mn detection limit is ~ 0.025 mg L^{-1} . Other cation concentrations are always far above instrumental detection. In previous work in the same lab, replication of cation analyses had precision of better than $\pm 5\%$ (Groffman and Crossey, 1999). Anions were determined by ion chromatography. The method of anion analysis used on the Dionex DX-500 ion chromatograph has a detection limit of < 0.01 mg L^{-1} and a precision of $\pm 1\%$ (Dionex Corporation technical note 133, http://www1.dionex.com/en-us/webdocs/4083_AN_133_V23.pdf). Due to severely limited sample volume, alkalinity

was determined by a Gran titration on only 4 of the 14 multilevel sampling intervals using a 5 mL subsample and a Hach digital titrator. For conventional well samples, the Gran titration was performed on a 40 mL sample. Dissolved organic carbon (DOC) concentration was determined by a Shimadzu TOC-5050A organic carbon analyzer on filtered, HCl-preserved 5 mL samples stored in acid-washed glass vials with Teflon seals. Thermodynamic modeling of saturation indices and $p\text{CO}_2$ was performed using the PHREEQC code (Parkhurst and Appelo, 1999; Post, 2006). Simple statistical tests (t-tests for difference of means) were performed using the R software package (R Development Core Team, 2006).

Sediment Sampling and Analytical Methods

Sediments were collected from BLN2 and BLN9. BLN2 was constructed and sampled using a motorized drilling rig, whereas BLN9 was hand-augered. Sediment samples were taken at 15 cm vertical resolution and oven dried ($40\text{--}65$ $^\circ\text{C}$). Samples from these adjacent wells were combined to make a single depth profile. BLN9 sediments were used for the

upper part of the profile, because hand-augering left them less disturbed, and BLN2 sediments were used for the lower portion of the profile to 550 cm depth. Selective extraction techniques were performed nonsequentially on separate samples to assess the availability of reactive Fe and Mn oxides on mineral surfaces. Amorphous iron oxides were estimated by extraction in oxalate (McKeague and Day, 1966). Amorphous Fe phases were extracted from separate samples with 0.5N HCl (Roden and Edmonds, 1997). To assess the relationship between easily extracted iron, manganese, and phosphorus, Mn and P were also analyzed from the 0.5N HCl extracts: 0.5N HCl dissolves amorphous Fe oxides and sulfides and associated P (Roden and Edmonds, 1997), although the effectiveness of this extraction method for Mn was not stated by Roden and Edmonds (1997). P was analyzed colorimetrically by the ammonium molybdate method (American Public Health Association, 1995). Fe and Mn were analyzed by flame atomic absorption spectrometry. In addition to the extractions of amorphous iron, the citrate-dithionite extraction method (Mehra and Jackson, 1960; McKeague and Day, 1966) was employed to approximate total nonsilicate iron, including crystalline and amorphous Fe.

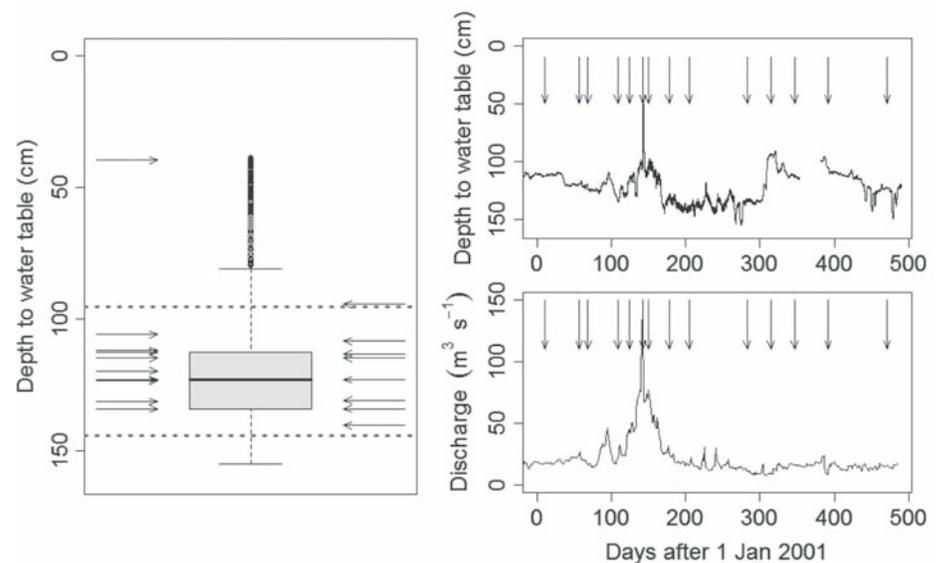


Figure 3. Water table depths at the study location (top right) and Rio Grande discharge at Albuquerque, 60 km upstream (lower right). Discharge data obtained from U.S. Geological Survey Web site (www.usgs.gov). At left, box plot depicting half-hourly water table elevation measurements from 1 January 2001–1 May 2002, indicating the vertical extent of the zone of intermittent saturation during the study period (dotted line). Arrows indicate dates and water table elevations at which samples were collected. Arrows from left are for conventional well sampling dates; arrows from right are for multilevel sampling dates.

RESULTS

Site Hydrology

At the site, the water table responds rapidly to changes in river level. Because only daily discharge data are available for the Rio Grande, this response time can only be estimated at daily resolution. River pulses are observed in study wells a perpendicular distance (minimum travel distance) of ~100 m from the channel in about one day (Vinson, 2002). At the Belen site, the gradient across the floodplain from the Rio Grande water surface to the riverside drain ditch water surface was surveyed (Fig. 2), and is 0.012 (the riverside drain is 1.7 m lower than the river). This measurement, approximately perpendicular to the river channel, is a maximum hydraulic gradient, assuming that groundwater travels perpendicular to the channel. We present water table data collected at 30 min resolution in BLNC with a pressure transducer and define the zone of intermittent saturation as the middle 95% of water table elevations. During the study period, the zone was ~49 cm in vertical extent (Fig. 3).

Water Chemistry

River and groundwater data of chemical parameters for dates on which the river and either conventional wells or multilevel sampler were sampled are summarized in Table 1

and presented in full in GSA Data Repository Table DR1¹. For all solutes, temporal variability is large in both river water and groundwater. Groundwater DO concentrations are low, although somewhat higher concentrations of oxygen were sometimes detected in the 20 cm immediately below the water table (overall range 0.1–1.5 mg L⁻¹) and usually detected in the deeper conventional wells (0.3–1.7 mg L⁻¹). River concentrations of DO are consistently higher (3.1–7.9 mg L⁻¹; Fig. 4). In general, groundwater nitrate concentrations are low but measurable (<1 mg L⁻¹) a few tens of centimeters below the water table and lowest at the bottom of the multilevel sampler. In the conventional wells, nitrate concentrations are higher than in the multilevel sampling depths. An increase in nitrate is visible between the two deepest wells BLN3 and BLN4; there is a mixed relationship between BLNC and BLN3. Groundwater nitrate concentrations are consistently lower than average river nitrate concentrations of >2 mg L⁻¹ as NO₃⁻ (Fig. 4). Manganese usually exhibits an increase to ~3 m depth, resulting in the highest groundwater concentrations of Mn being found at the bottom of the multilevel sampler and in BLNC (Fig. 4). However, the highest Mn values on the site (as high as 2 mg L⁻¹) are seen in surface water samples from the riverside drain ditch located down-gradient from the wells (Vinson, 2002). Mn concentrations decrease with depth below BLNC, and river samples have low or

nondetectable concentrations of Mn (<0.25 mg L⁻¹; Fig. 4). Iron exhibits a spatially irregular vertical profile on most dates, sometimes with elevated concentrations a few tens of centimeters below the water table, and decreases with depth in the conventional wells. Iron is always low or nondetectable in river samples (<0.5 mg L⁻¹; Fig. 5). Depth trends for sulfate and chloride are depicted together. Because sulfate can be affected by evapotranspiration and microbial sulfate reduction, whereas chloride is conservative, variations in the sulfate/chloride ratio provide a means of separating the two processes. On most sampling dates, sulfate and chloride follow roughly parallel depth trends in the multilevel sampling waters and the conventional well samples; a striking exception is the multilevel sampling profile of 5 May 2001. On other sampling dates, more subtle divergence between sulfate and chloride is seen in the multilevel sampling profiles. In the conventional wells, several dates exhibit a divergence between sulfate and chloride in the 3-m-deep well BLNC (Fig. 5). For samples for which alkalinity titrations were performed, groundwater bicarbonate is often higher at shallower depths and generally higher in groundwater than in the river (Fig. 6). Aquifer pH is typically lower than that of the river. Although depth trends are not apparent in the multilevel sampling waters, pH becomes closer to river pH with increasing depth in the conventional wells (Fig. 6). Overall, the deeper samples (especially the 13-m-deep

¹GSA Data Repository item 2007236, Table DR1, is available at <http://www.geosociety.org/pubs/ft2007.htm>. Requests may also be sent to editing@geosociety.org.

TABLE 1. SUMMARY OF RIVER AND GROUNDWATER CHEMISTRY DATA

	Ca	Fe	Mg	Mn	K	Na	Cl ⁻	NO ₃ ⁻ (as NO ₃)	SO ₄ ²⁻	Sulfide	pH	Temperature (°C)	HCO ₃ ⁻	DO
River water														
Mean	44	0.07	8.0	0.03	5.7	40	20.8	2.83	59.5	0.02	8.0	16.6	160	6.94
Median	43	ND	7.5	0.02	5.0	43	22.6	3.06	60.8	ND	8.1	16.4	166	7.57
Minimum	27	ND	6.0	ND	3.1	20	8.1	0.32	30.8	ND	7.5	6.9	111	3.10
Maximum	63	0.28	12.3	0.11	10.8	60	28.5	5.08	83.3	0.07	8.6	24.6	210	9.07
2 standard deviations	18	0.21	3.4	0.08	4.5	20	12.5	2.93	34.2	0.07	0.7	12.1	61	3.48
Analyses	14	14	14	14	14	14	14	14	14	4	13	10	14	10
Conventional wells														
Mean	57	0.63	9.9	0.85	4.6	42	23.1	0.88	66.2		7.4	10.6	185	0.78
Median	55	0.09	9.5	0.89	4.0	41	23.8	0.77	63.9		7.4	10.6	181	0.58
Minimum	42	ND	5.8	0.02	3.0	33	10.8	ND	32.8		6.8	7.8	107	0.17
Maximum	78	2.70	18.0	1.79	11.0	55	41.0	3.13	111.1		7.8	14.6	289	1.94
2 standard deviations	17	1.84	4.6	1.19	3.4	12	11.7	1.64	36.8		0.5	3.5	97	1.10
Analyses	30	30	30	30	30	30	30	30	30		27	21	27	24
Multilevel sampling														
Mean	59	2.19	9.1	0.98	5.0	46	23.8	0.20	65.4	0.08	7.6	13.9	219	0.35
Median	59	2.22	9.3	0.95	4.0	43	22.8	0.11	59.4	0.04	7.7	14.3	206	0.27
Minimum	37	ND	6.3	ND	3.0	30	14.1	ND	24.1	ND	6.4	8.9	146	0.11
Maximum	200	6.71	12.8	1.70	15.9	100	41.1	1.42	118.3	1.29	8.2	17.7	388	1.48
2 standard deviations	35	1.97	4.1	0.63	4.8	21	13.3	0.52	41.4	0.42	0.7	4.9	124	0.53
Analyses	102	103	102	103	102	102	100	99	100	86	81	96	30	95

Note: Concentrations in mg L⁻¹. See Table DR1 for full data set (see footnote 1). ND—not detected. DO—dissolved oxygen. Concentrations below detection limits were computed as zero values for summary statistics.

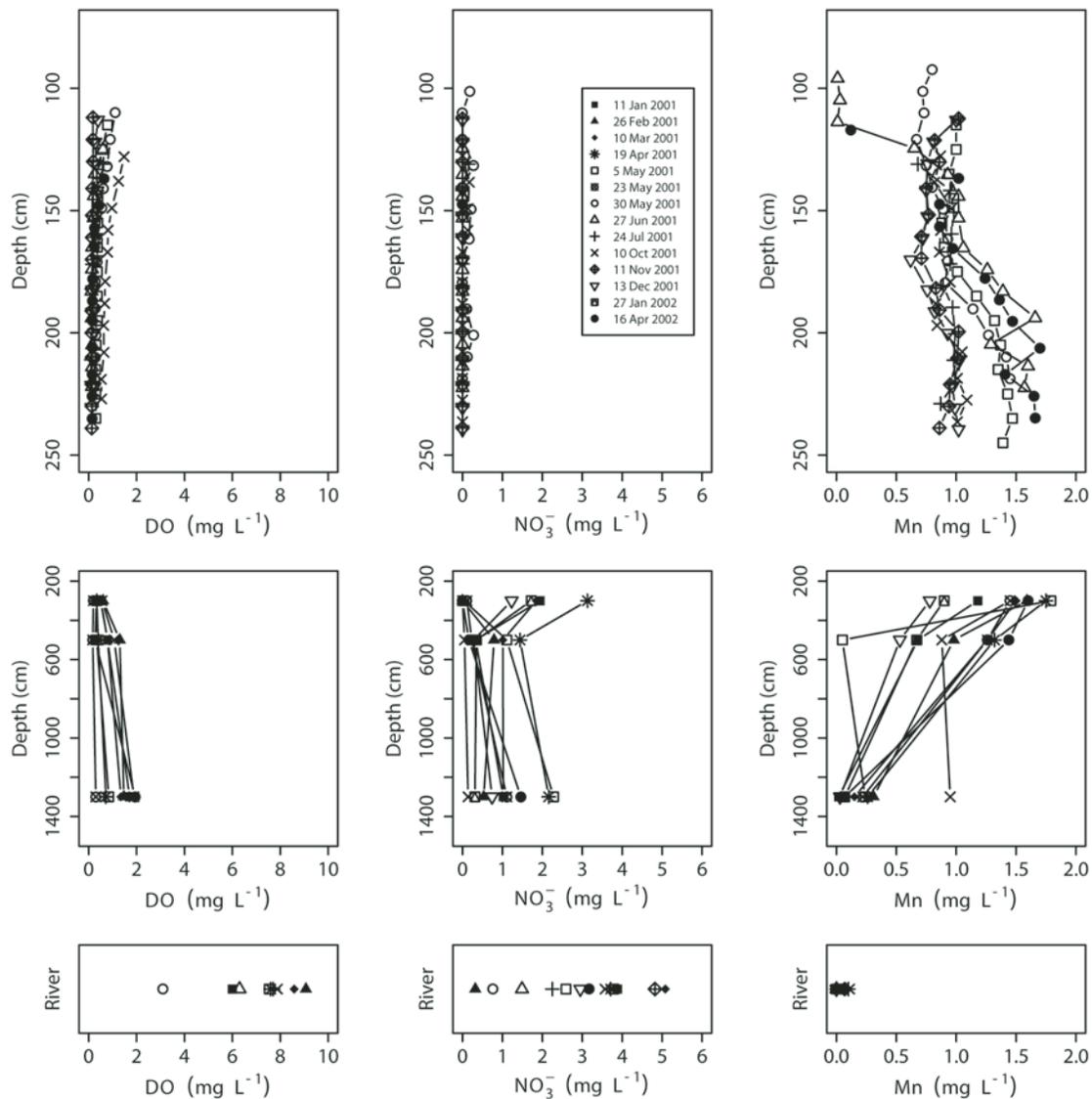


Figure 4. Vertical profiles of dissolved oxygen (DO), nitrate, and manganese concentrations in multilevel sampler (top), conventional wells (middle), and river (bottom). Not all sampling dates are represented in both conventional wells and multilevel sampling.

BLN4) are more river-like in their composition than the multilevel sampling depth range of 1.0–2.4 m and the 3-m-deep BLNC.

Sediment Extractions

Both oxalate-extractable Fe and dithionite-extractable Fe are enriched in the zone of intermittent saturation relative to the permanently saturated sediments below (Fig. 7). *P*-values of *t*-tests are 0.03 for oxalate-extractable Fe and 0.00004 for dithionite-extractable Fe, indicating that the intermittently saturated sediments have significantly different means. If available dithionite data are used for the entire depth of BLN2

(Block, 2002), sediments that are believed to be more disturbed during sampling than the BLN2-BLN9 combination used for the above analysis, the depth trend is less significant ($p = 0.09$). Fe and P extracted with 0.5N HCl are also enriched in the zone of intermittent saturation, with *p*-values of 0.002 and 0.04, respectively. The 0.5N HCl-extractable Mn is not significantly higher at this depth ($p = 0.24$; Fig. 8). All three elements are highest in the fine-grained unsaturated zone soils. Below the zone of intermittent saturation, extractable Fe and Mn reach a baseline level; extractable Fe increases slightly at below 400 cm depth. In samples for which both oxalate-extractable Fe and 0.5N HCl-extractable

Fe were determined, the methods were comparable. The HCl method recovered, on average, 16% more Fe than the oxalate method.

DISCUSSION

Water and Sediment Chemistry

Although the data exhibit relative similarity between river and groundwater chemistry on each date, the absolute concentrations do not demonstrate seasonal or systematic temporal variability. High solute concentrations are not confined to the high-evapotranspiration summer season and can occur throughout the year,

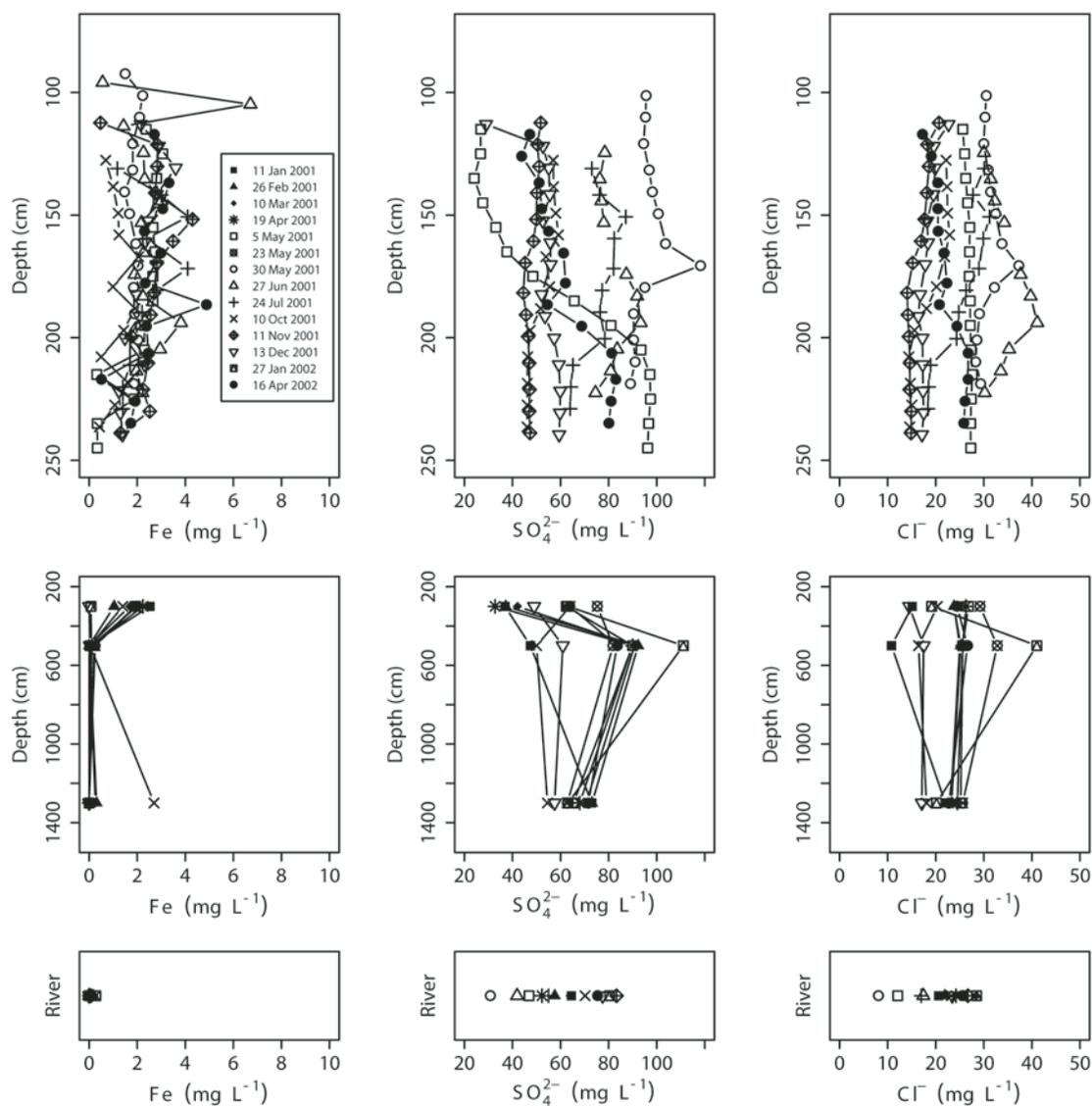


Figure 5. Vertical profiles of iron, sulfate, and chloride concentrations in multilevel sampler (top), conventional wells (middle), and river (bottom). Not all sampling dates are represented in both conventional wells and multilevel sampling.

driven by upstream processes in the Rio Grande. Higher Rio Grande discharge is associated with lower dissolved solids (Passell et al., 2004), and the Albuquerque sewage treatment plant is a significant contributor of discharge and salinity year-round (Phillips et al., 2003; Passell et al., 2004). Although discharge is typically highest during spring snowmelt, other dilution events may occur at irregular, nonseasonal intervals. These events may include dam releases, irrigation returns, and summer storms.

Because of external temporal variability in the solute concentrations of surface-water inputs to the aquifer (Table 1; Passell et al., 2004, 2005), groundwater chemistry should be considered

in relation to river chemistry on each date. Increases or decreases of redox-sensitive solutes from river values indicate the net effects of terminal electron-accepting processes. In general, nitrate present in the river has been reduced substantially in the conventional wells and to near zero in the multilevel sampling cells. Dissolved manganese increases from river concentrations at all depths, and the highest increase occurs at ~2–3 m depth. However, some enrichment of Mn is observed in all wells. Enrichment of iron above river values is seen primarily at 3 m depth and shallower, especially in some multilevel sampling waters. Within the multilevel sampling depth range, the depth trends for Mn

and Fe do not agree. The disparity between Fe and Mn at less than 240 cm depth may be explained in terms of the different sinks for Fe²⁺ and Mn²⁺. There is no sulfide sink for Mn²⁺ in freshwater sediments (Bernier, 1981; Matsunaga et al., 1993), so accumulation of manganese in groundwater indicates a greater extent of Mn oxide reduction in anoxic groundwater. This could indicate somewhat more favorable conditions for Mn oxide reduction with depth and the possible effects of unsaturated zone oxygen oxidizing Mn at the water table. Although the reductive dissolution of Fe oxides is chemically similar to Mn oxide reduction, an added complication of Fe oxide reduction is the possibility

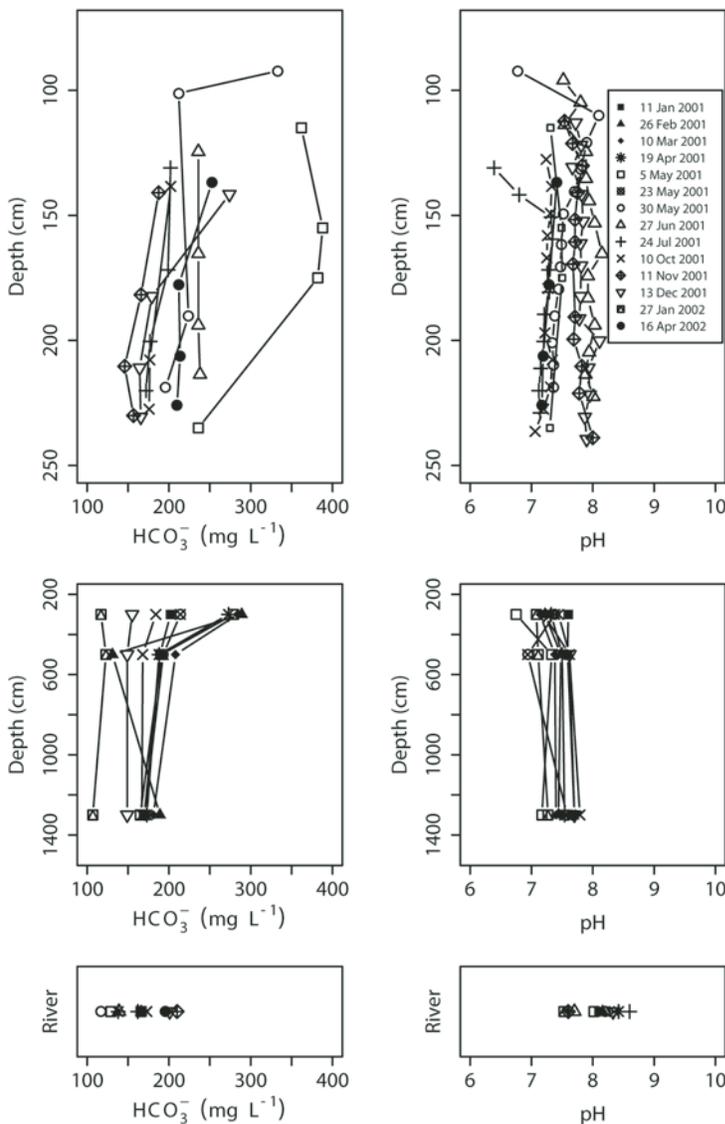


Figure 6. Vertical profiles of bicarbonate concentrations and pH in multilevel sampler (top), conventional wells (middle), and river (bottom). Not all sampling dates are represented in both conventional wells and multilevel sampling.

of Fe sulfide precipitation. Iron sulfide formation would remove Fe^{2+} from solution, removing evidence of Fe oxide dissolution from water samples. From this discrepancy between iron and manganese at shallow depths, it is inferred that a solid-phase sink for Fe^{2+} exists in the shallow alluvial aquifer.

It might be expected that terminal electron-accepting processes are more advanced with greater depth in the sediments due to the effects of oxygen at the water table (Groffman and Crosse, 1999) or the sediment-water interface of lake or marine sediments (Capone and Kiene, 1988; Nealson and Stahl, 1997), unless organic

carbon or nutrient availability limits the extent of these processes. The presence of elevated levels of extractable Fe in the zone of intermittent saturation (Figs. 7 and 8) may reflect the presence of DO at the shifting water table combined with microbial activity. However, below the water table, the groundwater is persistently anoxic to 3 m depth, then DO increases in the two deeper wells. Patterns in nitrate concentrations indicate that denitrification and/or nitrogen uptake by organisms are greater near the water table than at greater depths. However, at all depths, nitrate concentrations are lower than in the river, having been aggressively scavenged by microbes

or plants. The presence of nitrogen or oxygen from the unsaturated zone may contribute to the low but measurable concentrations of nitrate at the water table. The accumulation of dissolved Mn with depth reaches an apparent peak at ~3 m depth, and dissolved Fe is also highest in the relatively shallow multilevel sampling cells. The pH decrease between river and wells is consistent with a strong net signal from terminal electron-accepting processes, buffered by calcite (von Gunten et al., 1991). Thus, conditions are less evolved from the river at the deeper wells than in the region immediately below the water table to ~3 m depth.

In general, the vertical gradients of redox-sensitive solutes indicate (1) the presence of some oxygen in the deepest well, BLN4, combined with some nitrogen removal; (2) continued N removal and extensive Mn oxide reduction in BLN3; (3) Mn oxide and Fe oxide reduction, and possible sulfate reduction, in BLN2; and (4) Mn, Fe, and sulfate reduction, with likely FeS precipitation, in the multilevel sampling range above 240 cm depth. This interpretation assumes that the wells at the site are about equally connected to the river. There may be some influence on the shallower wells from the unsampled ditch shown in Figure 2. This ditch is a riverside drain being returned to the river. Although the ultimate source of this water is probably the river, this ditch may be chemically evolved in ways not accounted for by our sampling. However, at an upstream site without such a ditch sampled by Block (2002), the same general depth trends in DO, nitrate, Mn, and Fe were observed. Although a systematic trend in the sulfate/chloride ratio was not seen at that site, it might be due to the higher influent nitrate concentrations at that site or the less frequent sampling in the zone of intermittent saturation there.

Also, it is assumed that the multilevel sampling intervals are equally connected to the aquifer. This is reasonable given the consistent sand-dominated size distribution at these depths (Block, 2002) and the consistent, rapid equilibration of the multilevel sampler (Vinson, 2002). Furthermore, it is assumed that the conventional well samples can be directly compared to the multilevel sampling waters despite (1) the only partial overlap of sampling dates; (2) the difference in nominal pore size between the multilevel sampling (0.2 μm) and conventional well sampling (0.45 μm) methods; and (3) the different environments represented by the inside of a multilevel sampling cell and a well screen (including the passive, non-purged nature of the multilevel sampler). These interpretations alone do not indicate which terminal electron-accepting processes are most influential for the oxidation

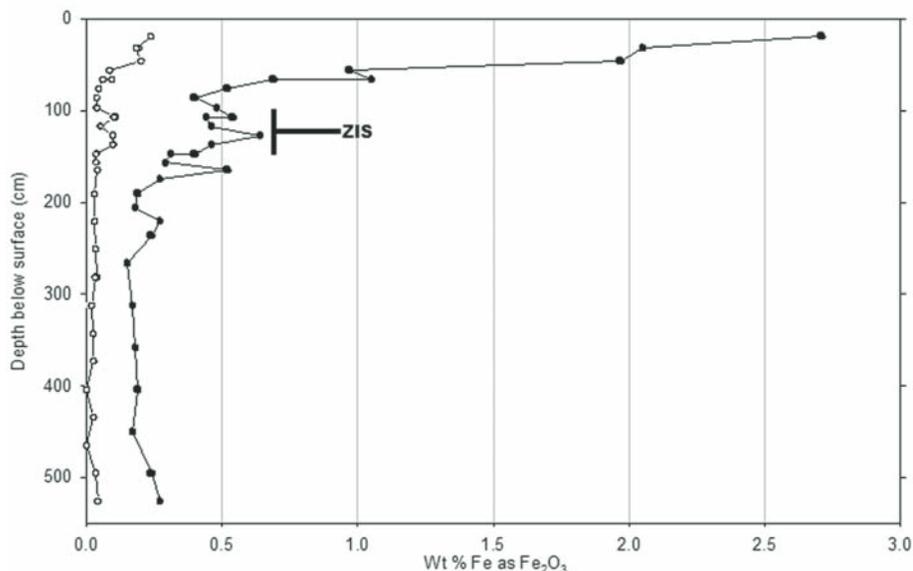


Figure 7. Oxalate-extractable Fe (open circles) and dithionite-extractable Fe (filled circles). Zone of intermittent saturation (ZIS) is from 95 to 144 cm below the surface.

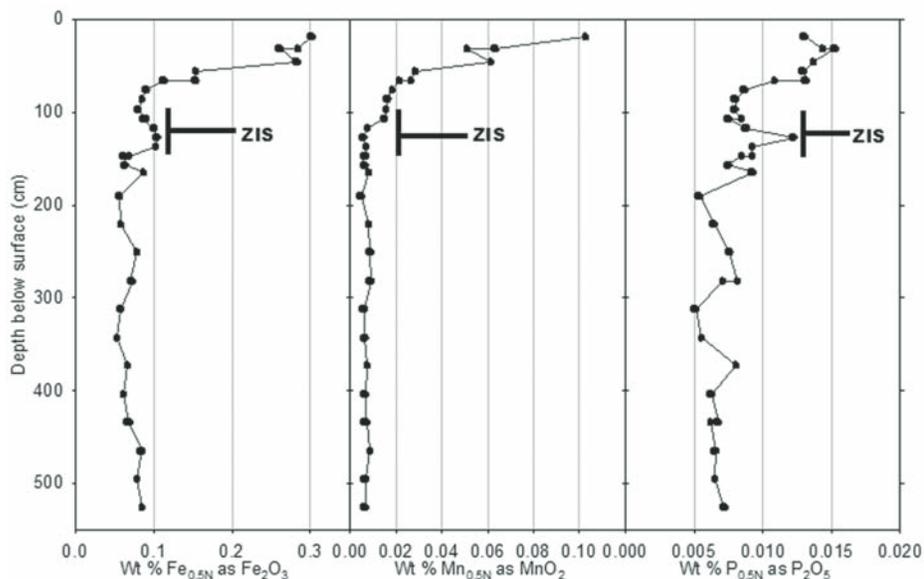


Figure 8. Extractable Fe, Mn, and P in 0.5N HCl. Zone of intermittent saturation (ZIS) is from 95 to 144 cm depth below the surface.

of organic carbon. This was accomplished using the reaction stoichiometry of these processes at near-neutral pH.

Organic Carbon Oxidation

Organic carbon oxidation due to inferred terminal electron-accepting processes has been estimated using the stoichiometry in Table 2 and presented in Figure 9. Where DO or nitrate concentrations are missing from the groundwater data, zero values were substituted to compute an assumed maximum organic carbon oxidation due to aerobic respiration or denitrification. Where DO concentrations are missing from river data, an average value was used in its place. These assumptions were made because of the large extent of net DO consumption and denitrification at all times. Aerobic respiration accounts for ~125–250 $\mu\text{mol L}^{-1}$ of organic carbon oxidation, with an exception occurring on a sampling date with low river DO. Denitrification accounts for up to 100 $\mu\text{mol L}^{-1}$ of organic carbon oxidation. Mn oxide reduction and Fe oxide reduction account for ~0–15 $\mu\text{mol L}^{-1}$ and 0–30 $\mu\text{mol L}^{-1}$ of organic carbon oxidation, respectively. Both transfers are higher in the shallower samples. Because of possible solid-phase sinks for Fe^{2+} , the estimate for Fe is a minimum. The total organic carbon oxidation from these four processes is from ~100 to 350 $\mu\text{mol L}^{-1}$ and decreases slightly with depth, except for one sampling date in which river DO was low. However, many of the samples for which alkalinity data are available exhibit a much larger bicarbonate increase (up to ~3950 $\mu\text{mol L}^{-1}$) than can be accounted for by these four processes alone. This unaccounted-for bicarbonate beyond Fe oxide reduction (Fig. 9) generally decreases with depth, even if three high HCO_3^- measurements on 5 May 2001 are neglected, although those three measurements coincide with the largest gradient in the sulfate/chloride ratio seen in the study, strongly suggesting a large extent of sulfate reduction on that date.

TABLE 2. STOICHIOMETRY OF TERMINAL ELECTRON-ACCEPTING PROCESSES

Process	Equation	Free energy at 25 °C, pH 7 (kJ)	Mol C oxidized per mol acceptor reduced
Aerobic respiration	$\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$	-501	1
Denitrification	$\text{CH}_2\text{O} + (4/5)\text{NO}_3^- + (4/5)\text{H}^+ = (7/5)\text{H}_2\text{O} + (2/5)\text{N}_2 + \text{CO}_2$	-476	1.25
Mn oxide reduction	$\text{CH}_2\text{O} + 2\text{MnO}_2 + 4\text{H}^+ = 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + \text{CO}_2$	-340	0.5
Fe oxide reduction	$\text{CH}_2\text{O} + 8\text{H}^+ + 4\text{Fe}(\text{OH})_3 = 4\text{Fe}^{2+} + 11\text{H}_2\text{O} + \text{CO}_2$	-107	0.25
Sulfate reduction	$\text{CH}_2\text{O} + (1/2)\text{SO}_4^{2-} + (1/2)\text{H}^+ = (1/2)\text{HS}^- + \text{H}_2\text{O} + \text{CO}_2$	-104	2
Methanogenesis	$\text{CH}_2\text{O} + (1/2)\text{CO}_2 = (1/2)\text{CH}_4 + \text{CO}_2$	-93	2

Note: Equations and free energy values from Jackson and Patterson (1982).

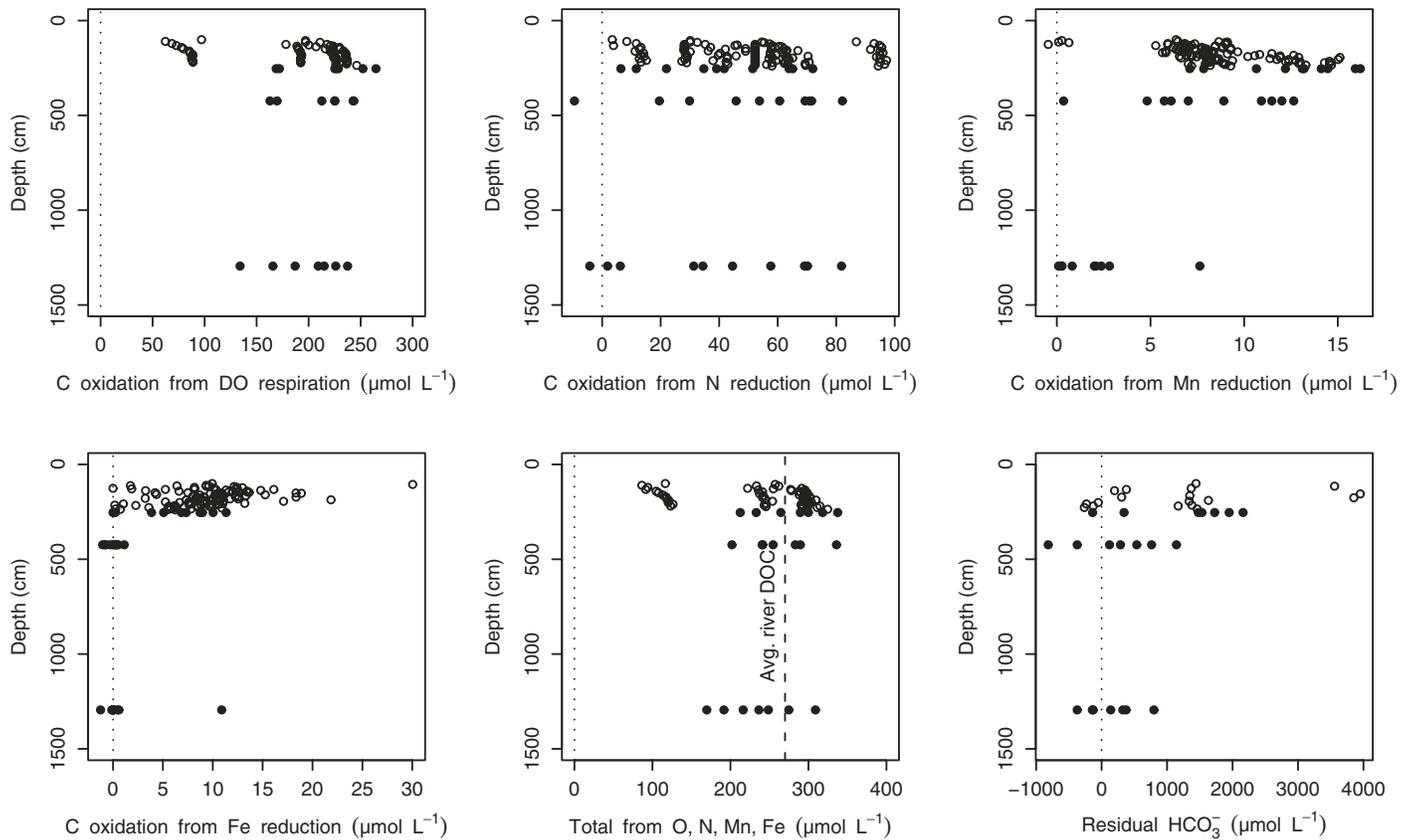


Figure 9. Organic carbon oxidation due to dissolved oxygen respiration, denitrification, Mn oxide reduction, and Fe oxide reduction; total organic C oxidation from these processes; and residual bicarbonate with depth. Open circles are from multilevel sampler; filled circles are from conventional well samples.

The origins of this residual bicarbonate may include concentration by evaporation, carbonate mineral dissolution, or sulfate reduction. Relationships between major solute trends may help to evaluate these possibilities. Bicarbonate (Fig. 10) and residual bicarbonate (Fig. 11) in groundwater have a linear relationship with the decrease in sulfate/chloride ratio from river to aquifer. The highest levels of bicarbonate are associated with samples most depleted in sulfate relative to chloride. In the multilevel sampling data set, the sulfate/chloride ratio decreases with depth within the upper 1–2 m of the aquifer (Fig. 12) and broadly agrees with the depth trend in residual HCO_3^- (Fig. 9). Near the water table, the ratio decreases more than 25% relative to river values. Below 200 cm depth, the ratio is approximately equal to that of the river. However, in the conventional wells, the data contain wide divergences of the sulfate/chloride ratio, indicating both decreases and increases in sulfate relative to chloride: these could indicate sulfate reduction and sulfide oxidation, respectively, although we have not collected data that could document sulfide oxidation here. In

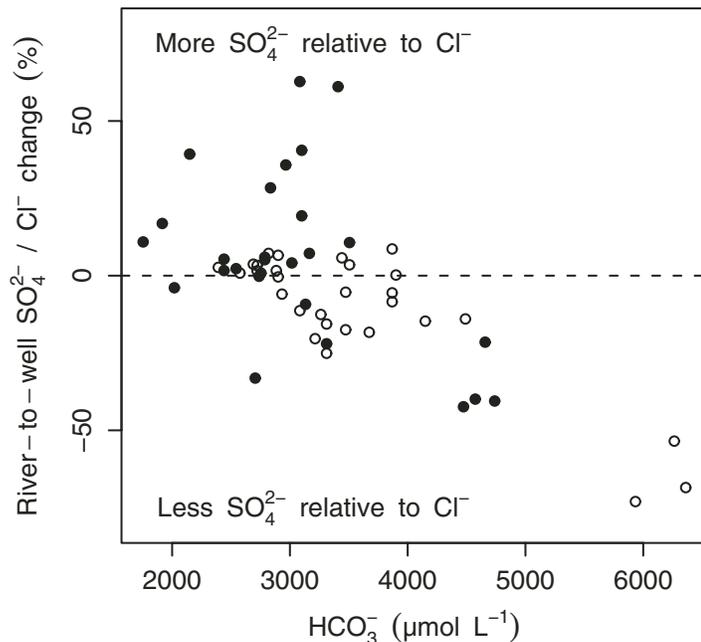


Figure 10. Bicarbonate in groundwater samples in relation to the sulfate/chloride ratio change between river and groundwater. Open circles are from multilevel sampler; filled circles are from conventional well samples.

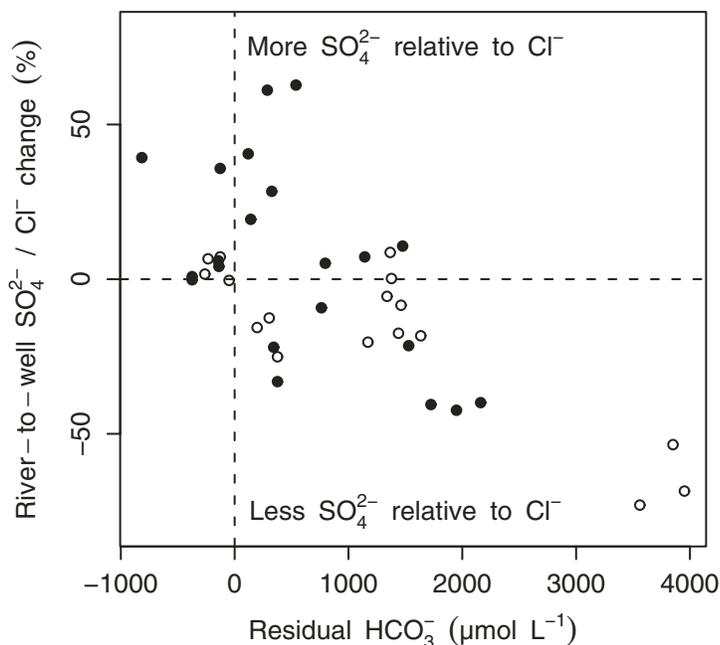


Figure 11. Residual bicarbonate in relation to the sulfate/chloride ratio change between river and groundwater. Open circles are from multilevel sampler; filled circles are from conventional well samples.

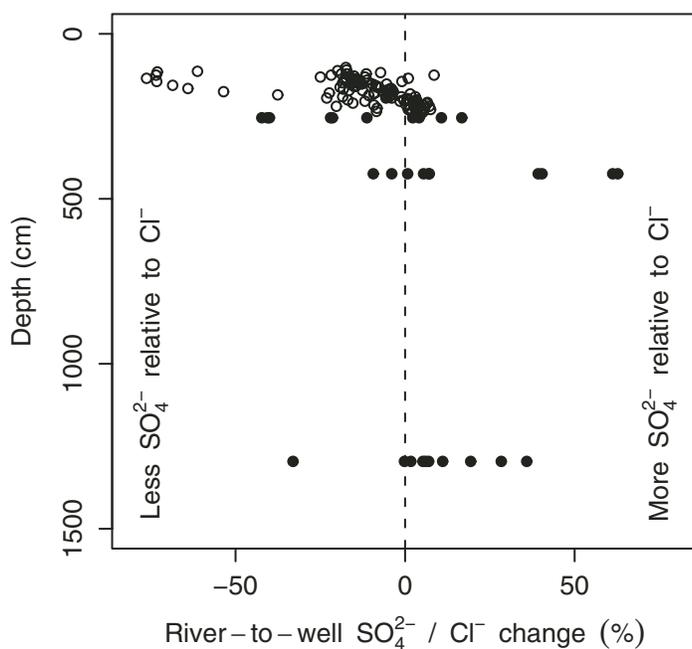


Figure 12. Change in sulfate/chloride ratio with depth. Open circles are from multilevel sampler; filled circles are from conventional well samples.

addition to the decreases in the sulfate/chloride ratio, additional evidence of sulfate reduction includes a sulfide odor when sampling the wells, measurable sulfide concentrations in shallow groundwater (Table DR1; see footnote 1), and iron-sulfur-containing growths on incubated surfaces observed by scanning electron microscopy (Vinson, 2002). Thus, at least some of the residual bicarbonate is attributable to sulfate reduction. However, several samples contain residual bicarbonate and exhibit a net increase in the sulfate/chloride ratio (Fig. 11). This might indicate alternating sulfate reduction and sulfur oxidation, with possible net sulfide oxidation. It might also indicate that residual HCO_3^- from those samples is due to mechanisms other than sulfate reduction.

One potential source or sink for inorganic carbon is carbonate minerals. The $p\text{CO}_2$, calculated using the PHREEQC code for samples with complete ion, pH, and temperature data, indicates that the waters are equilibrating with a higher $p\text{CO}_2$ (median $10^{-2.15}$ atm, range $10^{-2.93}$ to $10^{-1.16}$ atm) than that of the river (median $10^{-3.01}$ atm, range $10^{-3.44}$ to $10^{-2.35}$ atm) or the atmosphere ($10^{-3.5}$ atm; Drever, 1997). Thus, the aquifer contains $p\text{CO}_2$ a factor of ~ 7 higher than the river, on average. This is consistent with the pH decrease seen between river and wells and the expected accumulation of CO_2 from microbial respiration. Saturation index calculations indicate near-saturation with respect to calcite (median -0.20 , range -1.13 to 0.75). Thus, buffering by calcite may stabilize pH under these elevated $p\text{CO}_2$ conditions as a response to terminal electron-accepting processes. In such a case, some portion of bicarbonate could be from calcite dissolution, and the largest carbonate buffering would be from waters with the most advanced terminal electron-accepting processes. Also, evaporation and drying at the water table may cause calcite precipitation, suggested by one anomalously high calcium concentration (200 mg L^{-1}) in a sampling cell near the water table (Table DR1; see footnote 1). The aquifer is also supersaturated at times with siderite (median 0.17 , range -0.90 to 0.78) and rhodochrosite (median 0.50 , range -1.05 to 1.19), but their rapid precipitation in the sediments is less plausible given slow siderite and rhodochrosite precipitation in nature (Jensen et al., 2002) and the stronger affinity of sulfide than carbonate for Fe^{2+} , causing siderite to mostly precipitate in sulfide-free waters (Berner, 1981). Probable Fe sulfide precipitation was documented in experiments at the site (Vinson, 2002). Carbonate precipitation, if occurring, would lead to an underestimate of net organic C oxidation by removing biogenic HCO_3^- from solution. This effect would be most pronounced in the areas

near the water table subject to high evapotranspiration. The net effect of calcite is difficult to quantify. Given the other evidence at the site, the likely sources for a majority of residual HCO_3^- in these samples are sulfate reduction and concentration by evapotranspiration.

Another abiotic phase that might influence the interpretation of sulfate concentrations is gypsum. Precipitation of gypsum is implausible because groundwater never approaches saturation with respect to gypsum (median -1.85 , range -2.14 to -1.49), with the possible exception of drying at the shifting water table. This possibility is suggested by the salts observed in the unsaturated zone by Bailey (2004). The dissolution of gypsum, possibly at a rising water table, is evaluated in Figure 13. The increase of calcium and sulfate by evapotranspiration or gypsum dissolution would cause data to be on the 1:1 line. However, almost all of the data indicate a smaller increase in sulfate than in Ca, implying that sulfate is depleted relative to Ca. Although calcite buffering or sulfate reduction would disrupt the 1:1 relationship, these data suggest that gypsum dissolution is not a widespread influence on the saturated sediments.

Organic carbon oxidation due to sulfate reduction may exceed the preceding four terminal electron-accepting processes under many conditions, driven by high influent sul-

fate concentrations and the stoichiometric ratio of 2 moles carbon oxidized per mole of sulfur reduced (Table 2). This is especially true in the shallower wells: in the multilevel sampling depth range, where residual HCO_3^- averages $580 \mu\text{mol L}^{-1}$ (68% of the HCO_3^- increase from river to wells), and in BLNC, where it averages $1290 \mu\text{mol L}^{-1}$ (74% of the HCO_3^- increase). On average, the deeper wells BLN3 and BLN4 do not have residual bicarbonate, and on a few occasions, bicarbonate in wells is lower than in the river. Although other processes, such as buffering by calcite in response to other terminal electron-accepting processes and concentration from evaporation, may partially explain residual HCO_3^- , sulfate reduction is, at a minimum, a substantial terminal electron-accepting process in the shallowest part of the aquifer (1–3 m depth).

In addition to the complexity of quantifying the extent of sulfate reduction, the actual extent of Fe oxide reduction is difficult to assess because Fe^{2+} is insoluble in the presence of sulfide, and the size of the FeS reservoir is unknown. Because the size of the Fe oxide reservoir is also unknown, the calculated extent of Fe oxide reduction from water chemistry alone (Fig. 9) may be an underestimate. Coupled Fe and sulfate oxidation to Fe sulfide would oxidize 2.25 moles of organic C per mole of iron

monosulfide precipitated (Table 2). Because of the low solubility of iron(III) and FeS, dissolved Fe concentrations should only be elevated in anoxic waters in which sulfate reduction has not yet become dominant, sulfide precipitation is slower than Fe oxide reduction, or sulfate is absent altogether. However, significant Fe concentrations were measured in many samples, and supersaturation was calculated with respect to Fe sulfides (Vinson, 2002). The reported Fe measurements may be supersaturated with respect to FeS because of slow FeS precipitation or may include colloidal Fe that dissolved when the samples were acidified.

Assuming that these processes occur according to their free energy values (Table 2), all other terminal electron-accepting processes probably occur completely to the extent that Mn and Fe oxides are easily reducible by microbes, but sulfate reduction, the least thermodynamically favorable of these processes, occurs incompletely. Because sulfate is never a limiting electron acceptor, the supply of labile organic carbon or nutrients, or the rates of biological processes, may vary with depth within the aquifer to explain the decreasing residual HCO_3^- and apparent sulfate reduction with depth. This suggests that the zone of intermittent saturation is the area of most active biogeochemical activity and that a less limiting supply of electron donors and/or nutrients is available there.

Additional constraints on the biogeochemical fates of sulfur and organic carbon in the middle Rio Grande system come from published stable isotope data presented by Plummer et al. (2004). Sulfate sources for the Rio Grande (precipitation and the Jemez River, with exposed evaporites in its watershed) contain generally positive $\delta^{34}\text{S}$ values, but the Rio Grande in the Albuquerque area (upstream from the study area) and river-recharged groundwater have mostly negative $\delta^{34}\text{S}$ values (Table 3). Although complicated by seasonal variability in river $\delta^{34}\text{S}$ that could originate upstream, these data suggest that recharging groundwater from the river has access to biotic, ^{34}S -depleted sulfide minerals in the shallow alluvial aquifer (Plummer et al., 2004). Our high-resolution vertical data indicate that sulfate reduction is most active in the upper 1–2 m of the saturated zone, and net sulfide oxidation is possible on some occasions at 5–13 m depth below the surface. In addition, some bicarbonate from terminal electron-accepting processes is probably present in groundwater near the Rio Grande, indicated by slightly lower $\delta^{13}\text{C}$ values than groundwater from other sources and river water (Table 3; Plummer et al., 2004). Finally, methane was not investigated as part of our research. Methanogenesis is normally a minor process as long as sulfate reduction remains

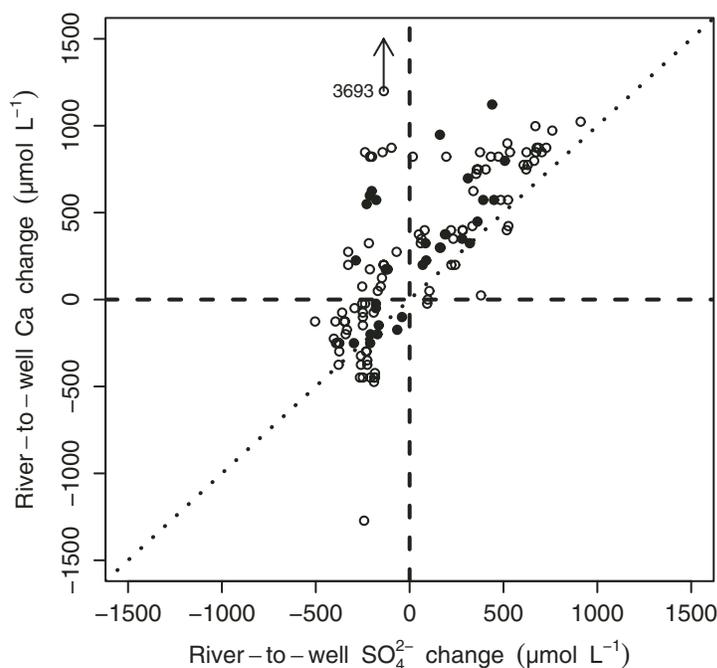


Figure 13. Sulfate concentration change and calcium concentration change from river to groundwater. Open circles are from multilevel sampler; filled circles are from conventional well samples. Dotted line is a 1:1 line.

TABLE 3. PUBLISHED SULFUR AND CARBON ISOTOPE DATA FOR THE MIDDLE RIO GRANDE

	$\delta^{34}\text{S}$ of SO_4^{2-}				$\delta^{13}\text{C}$ of DIC				Reference
	Median (‰)	Mean (‰)	2 std. dev. (‰)	<i>n</i>	Median (‰)	Mean (‰)	2 std. dev. (‰)	<i>n</i>	
Northern New Mexico snowpack	4.1	4.1	1.3	14					Mast et al. (2001)
Socorro, New Mexico, precipitation		2.9		11					Popp et al. (1986)
Jemez River	7.7	7.8	1.6	3	-3.3	-3.3		2	Plummer et al. (2004)
Rio Grande near Albuquerque	-1.3	-1.8	4.4	14	-6.4	-7.3	4.0	4	Plummer et al. (2004)
Wells near Rio Grande	-0.3	-0.2	10.9	78	-8.8	-9.1	2.1	83	Central Zone of Plummer et al. (2004)
Near-river wells <15 m only	-3.0	-2.9	4.9	12	-10.3	-10.4	4.2	3	Central Zone of Plummer et al. (2004)

Note: std. dev.—standard deviation. DIC—dissolved inorganic carbon.

active (Lovley and Klug, 1983; Capone and Kiene, 1988; Kirk et al., 2004). The high sulfate concentrations of the Rio Grande and active sulfate reduction suggest that methanogenesis is not a substantial process there.

River dissolved organic carbon (DOC) data collected during the study (mean 270 $\mu\text{mol L}^{-1}$ as C, $n = 3$) provide constraints on the river's ability to supply electron donors to the aquifer. Based on the stoichiometry of terminal electron-accepting processes (Table 2), river-based DOC alone could be adequate to (1) reduce the near-saturated dissolved oxygen concentration of the river to essentially zero; (2) reduce the significant nitrate concentration of the river to almost zero; and (3) reductively dissolve enough Mn and Fe oxides to produce the observed concentrations of Mn and Fe in groundwater (Fig. 9), but would not be adequate to (4) drive significant sulfate reduction; or (5) fully account for the bicarbonate increase seen from river to aquifer. Although higher average total organic carbon concentrations from unfiltered samples, averaging $\sim 580 \mu\text{mol L}^{-1}$ as C, were reported for this reach of river by Passell et al. (2005), it is not evident that the particulate organic carbon in river water would be able to significantly infiltrate through the alluvial aquifer under non-flooding conditions. During floods, this particulate organic carbon would be deposited onto the floodplain (Valett et al., 2005) and possibly buried, adding to the supply in the alluvial aquifer.

Additional evidence that down-flow DOC consumption is not the sole source of this electron donation is that DOC concentrations are higher in the down-gradient drain ditch (mean 360 $\mu\text{mol L}^{-1}$ as C, $n = 3$) than in the river on the dates that these samples were collected. These higher values might represent the release of less labile organic compounds produced by the partial oxidation of organic carbon in the aquifer. Because additional sources of organic carbon are present in the alluvial aquifer (e.g., soil organic matter, root exudates, and leaf litter), the cycling of organic carbon between the

river, floodplain, and aquifer may depend on high natural aggradation rates caused by flooding. With periodic flooding and aggradation, (1) a supply of organic carbon comes from flood debris deposition to the floodplain and (2) sulfide minerals from former water table levels are exposed to suboxic to oxic groundwater below 3 m depth and undergo oxidative dissolution. As many portions of the middle Rio Grande no longer flood due to river regulation measures (Crawford et al., 1993), this process likely does not function the same as it did prior to the twentieth century. For example, experimental flooding elsewhere in the middle Rio Grande deposited particulate organic carbon onto floodplain soils (Valett et al., 2005). As the water table has been lowered and flooding largely ended by flow regulation, contact between flood debris, flood waters, and groundwater has decreased. Sources of organic carbon to support microbial metabolism and biogeochemical processes in the shallow alluvial aquifer remain an area of needed research.

CONCLUSIONS

Sampling in two dimensions has revealed the relative importance of terminal electron-accepting processes in the alluvial aquifer. Sampling horizontal differences in chemistry between the river and the shallow alluvial aquifer has illustrated the net effects of evapotranspiration and several terminal electron-accepting processes: aerobic respiration, denitrification, Mn oxide reduction, Fe oxide reduction, and sulfate reduction. Vertically, the rapidly shifting water table creates a "rising tide" of groundwater with access to varying sources of electron donors, electron acceptors, and nutrients. In the 49-cm-tall zone of intermittent saturation, evidence of oxic-anoxic cycling suggests the influence of the fluctuating water table. Strongly anoxic conditions prevail from a few centimeters below the water table down to ~ 3 m below the surface. The chemical changes due to terminal electron-

accepting processes suggest that the shallowest portion of the aquifer is the most biogeochemically active depth horizon, and in particular that sulfate reduction appears to reach a maximum just below the water table. At these depths, sulfate reduction probably represents a large proportion of organic carbon oxidation. This is facilitated by high influent sulfate concentrations and is probably limited by organic carbon availability. At greater depth, waters are more river-like, with less evolution from river solute concentrations caused by terminal-electron accepting processes.

In investigating these biogeochemical processes, we have documented complex solute and mineral-solute interactions between the river and its alluvial aquifer that explain the chemical evolution observed between the river and the wells. Specifically, these results suggest that influxes of sulfate and organic carbon can have major effects on the biogeochemical behavior of the shallow aquifer. On a large scale, these interactions have the potential to influence overall solute processes in stream systems (Valett et al., 1996; Morrice et al., 2000). Although the physical hydrologic influences are very different in timing and magnitude than in the shallow alluvial aquifers of small headwater streams (e.g., Groffman and Crosse, 1999; Newman et al., 2006), effects of the chemical gradients at the zone of intermittent saturation are seen at many scales in river and aquifer systems. Biogeochemical processes, structured both vertically and horizontally, impart major controls on solutes and solid phases where surface waters recharge shallow alluvial aquifers in floodplains.

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