

# Influence of hydrological, biogeochemical and temperature transients on subsurface carbon fluxes in a flood plain environment

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**Abstract** Flood plains play a potentially important role in the global carbon cycle. The accumulation of organic matter in flood plains often induces the formation of chemically reduced groundwater and sediments along riverbanks. In this study, our objective is to evaluate the cumulative impact of such reduced zones, water table fluctuations, and temperature gradients on subsurface carbon fluxes in a flood plain at Rifle, Colorado located along the Colorado River. 2-D coupled variably-saturated, non-isothermal flow and biogeochemical reactive transport modeling was applied to improve our understanding of the abiotic and microbially mediated reactions controlling carbon dynamics at the Rifle site. Model simulations considering only abiotic reactions (thus ignoring microbial reactions) underestimated  $\text{CO}_2$  partial pressures observed in the unsaturated zone and severely underestimated inorganic (and overestimated organic)

carbon fluxes to the river compared to simulations with biotic pathways. Both model simulations and field observations highlighted the need to include microbial contributions from chemolithoautotrophic processes (e.g.,  $\text{Fe}^{+2}$  and  $\text{S}^{-2}$  oxidation) to match locally-observed high  $\text{CO}_2$  concentrations above reduced zones. Observed seasonal variations in  $\text{CO}_2$  concentrations in the unsaturated zone could not be reproduced without incorporating temperature gradients in the simulations. Incorporating temperature fluctuations resulted in an increase in the annual groundwater carbon fluxes to the river by 170 % to  $3.3 \text{ g m}^{-2} \text{ d}^{-1}$ , while including water table variations resulted in an overall decrease in the simulated fluxes. We conclude that spatial microbial and redox zonation as well as temporal fluctuations of temperature and water table depth contribute significantly to subsurface carbon fluxes in flood plains and need to be represented appropriately in model simulations.

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## Introduction

The quantification of carbon fluxes in soils and groundwater is critical for closing key biogeochemical cycles and for developing a predictive understanding

of climate change scenarios. Soil CO<sub>2</sub> dynamics are difficult to predict because of the presence of several carbon sources and sinks, as well as different hydrological and biogeochemical mechanisms that affect its uptake and release (Suchomel et al. 1990; Hope et al. 1994; Hanson et al. 2000; Andrews et al. 2011). CO<sub>2</sub> fluxes in near-surface environments are primarily affected by atmospheric exchange, root zone biogeochemical processes, and microbial respiration (e.g., Wood and Petraitis 1984; Schlesinger and Andrews 2000; Crow and Wieder 2005). The origin of CO<sub>2</sub> at depth has been attributed to aerobic and anaerobic degradation of dissolved organic carbon, inorganic processes involving carbonate minerals, and the effects of vertical temperature gradients and water table fluctuations (Keller and Bacon 1998; Etiope 1999; Walvoord et al. 2005; Fan et al. 2014). Among these processes, the rates of organic matter degradation and production of CO<sub>2</sub> are strongly dependent on microbial community structure and function (Waldrop et al. 2000; Schmidt et al. 2011; Southwell and Thoms 2011; Steefel et al. 2014). Abiotic reactions, such as precipitation and dissolution of calcite, have a significant effect on pH and solution chemistry (Stumm and Morgan 1993; Macpherson 2009). Given the complex and coupled nature of hydrological and biogeochemical processes controlling CO<sub>2</sub> fluxes in the subsurface, soil carbon budgeting can benefit from reactive transport simulations that can be used to identify the contributions of the different processes within both unsaturated and saturated zones (e.g., Simunek and Suarez 1993; Thornton and McManus 1994; Doussan et al. 1997; Druhan et al. 2014b)

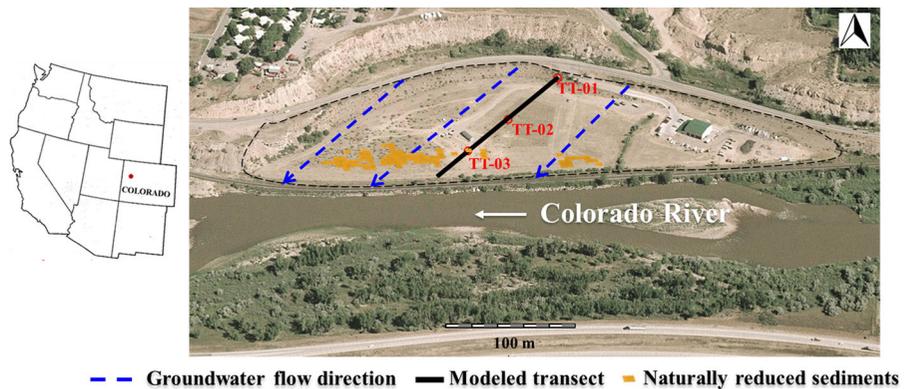
Although atmospheric CO<sub>2</sub> exchanges are thought to be several times greater than subsurface exports (Pulliam 1992; Richey et al. 2002), groundwater exports from terrestrial sources and flood plain environments to aquatic ecosystems also constitute an important part of the global carbon cycle. Several studies have debated the role of rivers as passive or active transporters of carbon to the ocean (Cole and Caraco 2001; Richey et al. 2002; Cole et al. 2007; Aufdenkampe et al. 2011). In either case, inorganic and organic carbon exports exert an important control on aquatic respiration, carbonate buffering and pH control, as well as CO<sub>2</sub> degassing in rivers and other aquatic environments (Brunke and Gonser 1997; Aufdenkampe et al. 2011). However, significant uncertainty is associated with the prediction of these

subsurface exports, particularly due to the influence of climatic variations, land-use changes, and human disturbances. The spatiotemporal variability of subsurface carbon fluxes thus needs to be better understood.

Temporal variability in carbon concentrations has been linked to rainfall events, seasonality of flow, evapotranspiration, and temperature fluctuations (e.g., Hinton et al. 1997; Arora et al. 2013; Kang et al. 2014). For example, Leirós et al. (1999) stressed the importance of seasonal variability on soil carbon and nitrogen mineralization rates. Changes in microbial community structure and activity have also been correlated with seasonal and annual temperature and precipitation variability and with the fate of carbon (Parton et al. 1987; Zogg et al. 1997; Waldrop et al. 2000; Wilhelm et al. 2014). There are thus several drivers of temporal variability in carbon fluxes, such as hydrological processes and climatic variables (Kalbitz et al. 2000; Dai et al. 2012; Atkins et al. 2013; Jansen et al. 2014). However, many studies have argued that temperature and soil moisture are two primary controls on CO<sub>2</sub> production rates (Raich and Potter 1995; Smith et al. 2003; Stielstra et al. 2015). In particular, several studies have conducted soil warming experiments to suggest that changes in microbial biomass and resulting soil CO<sub>2</sub> fluxes are due to these controls (Eliasson et al. 2005; Dermody et al. 2007; Frey et al. 2008).

Spatial variability in carbon concentrations has been linked to landscape patterns, hydrological connectivity, and heterogeneous subsurface properties (e.g., Dick et al. 2014; Southwell and Thoms 2011; Tockner et al. 1999). For example, Andrews et al. (2011) suggested that swales had higher solid and dissolved organic carbon content across the Shale Hills Catchment, Pennsylvania due to their landscape position and hydrological connectivity. Similarly, reduced zones in alluvial aquifers adjacent to rivers are known to exert a strong control on the transformation and redox dynamics of carbon and nutrients in flood plain environments due to their distinct biogeochemical properties (e.g., Bourg and Bertin 1993). In this context, emphasis has been given to the role of reduced zones in river bank filtration (e.g., Doussan et al. 1997; Hiscock and Grischek 2002; Tufenkji et al. 2002) and metal assimilation (e.g., Gandy et al. 2007; Lynch et al. 2014). Albeit involving similar biogeochemical concepts, the present study focuses instead

**Fig. 1** Rifle site map with the location of the modeled “TT” transect and the spatial distribution of naturally reduced zones (NRZ). The mapping of NRZs using a combination of induced polarization methods and Bayesian techniques is presented in more detail by Wainwright et al. (2015)



on the persistence and impact of reduced zones on subsurface carbon exports during conditions of aquifer discharge to a river.

Here we focus on the U.S. Department of Energy (DOE) site at Rifle, Colorado (USA) (Fig. 1), where reduced zones have been observed within the alluvial aquifer beneath the Rifle flood plain (described in more detail below) and are associated with the accumulation of Fe(II) and non-volatile sulfides in sediments close to the stream banks of the Colorado River (Lovley and Phillips 1986; Bargar et al. 2011; Lynch et al. 2014). Such areas are commonly referred to as “naturally reduced zones” (NRZs) within the Rifle site community to distinguish them from areas where reducing conditions have developed from bio-stimulation experiments. These NRZ’s have the ability to scavenge metals and oxidants due to their typically elevated levels of sediment-associated organic matter as compared to non-reduced flood plain sediments (Campbell et al. 2012; Qafoku et al. 2014). Because these NRZs occur primarily down-gradient of the site (roughly paralleling the Colorado River) (Wainwright et al. 2015), the study of their spatial distribution presents a unique opportunity to test conceptual models of redox dynamics at the field-scale using reactive transport simulations.

In this study, we test a conceptual model where the spatial organization of a naturally reduced zone is dependent on the interactions between oxygenated groundwater and initially homogeneous (reduced) flood plain sediments. Although the NRZs have been studied at the Rifle site in the context of understanding their geochemical characteristics and/or uranium sequestration abilities, to our knowledge, this is the first study in which a numerical model is applied to simulate the persistence of these NRZs in the presence

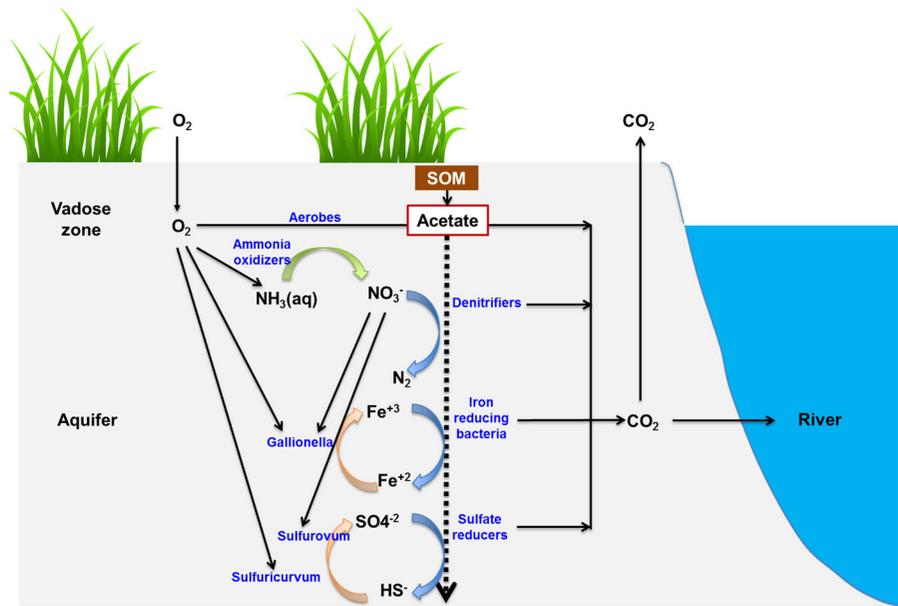
of a constant up-gradient oxic recharge, beginning initially from uniformly reducing conditions throughout the modeled domain. Furthermore, these simulations provide a foundation for detailed assessment of the relative contributions of abiotic and biotic processes as well as the primary factors (soil moisture, temperature) controlling the spatiotemporal variability of carbon fluxes from the site to the atmosphere and the Colorado River.

The objectives of this study are to develop and apply the conceptual modeling framework to: (1) quantify the release of carbon dioxide via abiotic processes, heterotrophic pathways, and autotrophic microbial oxidation of both reduced aqueous species (e.g.,  $\text{Fe}^{+2}$ ,  $\text{HS}^-$ ) and minerals (e.g., pyrite), and (2) investigate the effects of reduced zones as well as water table variations and temperature gradients on subsurface carbon dynamics at the Rifle site. To reach these objectives, a biogeochemical reaction network (Fig. 2) was built based on knowledge from previous modeling and experimental efforts at the site. The current modeling study targets a portion of the Rifle field site unaffected by previous groundwater remedial activities (e.g., Williams et al. 2011), incorporates new information on chemolithoautotrophs using a reduced-order geochemical reaction network, and tests the spatial extent of naturally reduced zones adjacent to the river under continued influx of oxygenated groundwater.

## Study site

Comprehensive descriptions of the Rifle site have been presented elsewhere (U.S. Department of Energy 1999; Anderson et al. 2003; Vrionis et al. 2005;

**Fig. 2** Schematic representation of the biogeochemical reaction network included in model simulations. Some microbially-mediated pathways are explicitly represented in the reaction network (such as *Sulfuricurvum* as sulfide oxidizer) while the broader diversity of species for other functions (such as sulfate reducers) is captured by simplified, overall reactions and rates (Table 5)



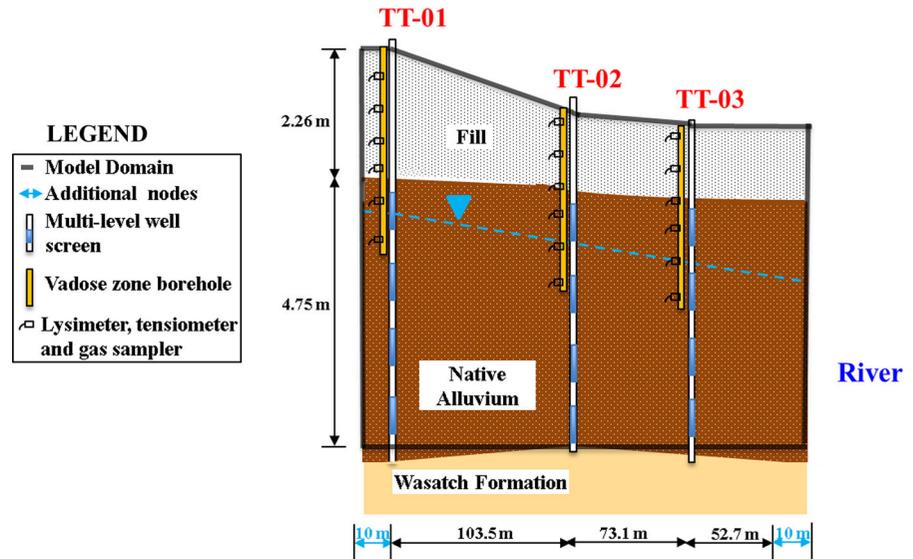
Williams et al. 2011) and thus the environmental conditions of the site are only briefly summarized here. The Rifle site is a former uranium and vanadium ore processing facility in western Colorado that operated from 1924 through 1958 (U.S. Department of Energy 1999). Subsequently, the mill tailings and impacted alluvial sediments were removed and the site was capped with a locally-derived fill material, and then revegetated. In spite of these near-surface cleanup efforts, groundwater at the site has remained contaminated with uranium at the micromolar level (Fang et al. 2009; Li et al. 2010; Fox et al. 2012).

Groundwater at the site flows through alluvial flood plain deposits, which are mainly comprised of unconsolidated gravel and cobbles, but are also interspersed with fine grained silt and clay and locally organic-rich sediments (U.S. Department of Energy 1999; Campbell et al. 2012; Tokunaga et al. 2015). The alluvial deposits are 6–7 m thick and include approximately 2 m of the fill material underlain by the relatively impermeable Wasatch formation (Figs. 1, 3). The depth to groundwater averages between 3 and 4 m depending on the Colorado River stage (Fang et al. 2009; Yabusaki et al. 2011). The variability in groundwater flow and direction is short-lived and has been linked to Colorado River stage fluctuations as well as seasonal precipitation, which averages approximately 300 mm annually (Arora et al. 2015a).

Groundwater flows generally southwest to the river because of significant aquifer recharge by rainfall, snow melt, and irrigation ditches up-gradient of the site (U.S. Department of Energy 1999). The hydraulic conductivity ( $0.06\text{--}20\text{ m day}^{-1}$ ) and pore water velocity ( $0.1\text{--}0.6\text{ m day}^{-1}$ ) vary across the site depending upon the local lithology (Williams et al. 2011; Yabusaki et al. 2011). Minerals reported in the sediments include quartz and calcite with lesser amount of clays and iron-bearing minerals, such as goethite, magnetite, and hematite (Campbell et al. 2012). Both the physical properties and geochemical characteristics of these sediments, including the abundance of the Fe-oxyhydroxides vary spatially across the site. Whereas NRZ sediments are associated with elevated concentrations of natural organic matter and reduced mineral phases such as framboidal pyrite, the abundance of these phases is much lower outside the NRZ sediments (Qafoku et al. 2009; Kukkadapu et al. 2010; Qafoku et al. 2014).

The biogeochemical interactions of uranium, iron, sulfate and carbon species in NRZ sediments at the site are markedly different from those observed in background aquifer sediments (Flores Orozco et al. 2011; Campbell et al. 2012; Bao et al. 2014; Qafoku et al. 2014). The dissolved oxygen uptake rates in these two contrasting zones also differ significantly (Long 2009; U.S. Department of Energy 2012). Arora et al. (2015a)

**Fig. 3** 2-D cross section of the model domain (modified from Tokunaga et al. (2015))



reported that geochemical hot moments (McClain et al. 2003) associated with both conservative and reactive species in the NRZ's occur at different dominant frequencies than those found in other zones at the site. Because of this spatial variability and complexity, we model a well-instrumented transect of the Rifle site (two-dimensional  $x$ - $z$  model domain) that is approximately parallel to the general groundwater flow direction and which includes both the saturated and unsaturated zones as well as a naturally reduced (NRZ) location.

The transect (referred to as the "TT" transect) includes three wells, TT-01, TT-02, and TT-03 installed in 2013 (Figs. 1, 3). Well TT-01 is located furthest north, hydrologically up-gradient from the river, TT-02 is within the central flood plain, and TT-03 is a down-gradient well situated within a previously characterized NRZ within ca. 50 m of the Colorado River (Campbell et al. 2012). A detailed description of the TT transect and the well instrumentation was given by Tokunaga et al. (2015) and Williams et al. (2011). Our model relies in large part on hydrologic and geochemical data from these authors. Tokunaga et al. (2015) and Williams et al. (2011) installed separate boreholes to sample the unsaturated and saturated zones. For vadose zone sampling, instrumentation sets were installed at various depths up to 3.5 m and included tensiometers, thermistors (at TT-03 only), and soil water and gas samplers. For CO<sub>2</sub> analysis, pore gas from all ports above the water table samples were

collected using a peristaltic pump and injected into evacuated serum vials capped with blue butyl rubber septa. CO<sub>2</sub> concentrations were quantified on a GC-2014 Shimadzu gas chromatograph. Using a gas tight syringe, 4.5 mL of sample aliquot was injected into a 1 mL stainless steel loop mounted on a 10-port valve (Valco). CO<sub>2</sub> was separated on a packed HayeSep-D column (4 m × 1/8 inch). CO<sub>2</sub> was reduced to CH<sub>4</sub> in a methanizer. Reduced CO<sub>2</sub> was quantified using a flame ionization detector (FID). Groundwater sampling was carried out at three discrete levels—an upper zone in the capillary fringe which becomes saturated during the annual peak height of the water table, a zone about 1 m below the typical minimum water table depth, and the deepest portion of the aquifer. In particular, bicarbonate was measured as TIC (total inorganic carbon) directly from the pore water samples using a Shimadzu TOC-V<sub>CPH</sub> analyzer.

### Model development

Our biogeochemical model for carbon fate and transport was built in a domain of the Rifle site that is generally representative of a flood plain environment. A conceptual model is adopted in which the lateral extent of the reduced zone adjacent to the river is controlled by the influx of oxygenated groundwater up-gradient from the river bank along the lateral flood plain accretion boundary, as described further below.

## Conceptual model

The Rifle flood plain site is situated where a former river channel left behind a crescent-shaped meander scar and several meters of flood plain alluvium (U.S. Department of Energy 1999) (Fig. 1). Flood plain sediments originating from overbank deposition, channel deposition, or flood events are widely known to accumulate organic matter that include surficial plants and woody debris (Miall 2001; Blazejewski et al. 2009; Wójcicki 2012). Although the composition and abundance of organic matter may vary from one depositional environment to another, the accumulation and degradation of organic matter is known to create reducing conditions adjacent to rivers (e.g., Bourg and Bertin 1993) and accumulation of trace metals (e.g., van Griethuysen et al. 2005; Wójcicki and Marynowski 2012; Helz and Adelson 2013). Similarly, naturally reduced sediments along the river at the Rifle site are enriched with organic matter, U, and reduced Fe and S phases. Campbell et al. (2012) compared these reduced zones to roll-type uranium ore deposits, where sharp redox fronts develop when oxidizing recharge groundwater meets reducing conditions induced by organic matter degradation (e.g., Harshman 1972; Spirakis 1996). The lateral extent of the NRZs along the stream banks of the Colorado River are likely controlled by similar processes, including the rate of oxidation by groundwater recharge up-gradient of the shore and the

deposition of organic matter. Note that no correlation was found between spatial distribution of NRZs and clay content or lower permeability zones at the Rifle site (Wainwright et al. 2015). Following this conceptual model, we simulate the persistence and lateral extent of an NRZ next to the river margin starting with uniformly distributed organic matter and reducing conditions across the modeled transect, then simulating the recharge of more oxidizing groundwater up-gradient of the transect (as well as minor precipitation above it) towards the river. Thus, in our model the NRZ develops over time from an initially homogeneous distribution of carbon and reduced phases. We test this conceptual model as a generic representation of redox-transitional zones which can be easily transferred to other flood plain environments.

## Modeling approach

To represent the geochemical system, the reactive transport code TOUGHREACT V3-OMP (Xu et al. 2011; Sonnenthal et al. 2014) was used. Several reactive transport simulations were run in which the degradation and oxidation of organic matter was simulated with increasing levels of complexity (Table 1; Fig. 2). The simulations were divided into two categories—the first set of simulations (S1, S2 and S3) focused on steady water table and temperature conditions. One goal with these simulations was to

**Table 1** Reactive transport simulations considered in this study

Simulation	Description	Reactions considered	Water level	Temperature
Steady water table and fixed temperature simulations				
S1	Base case simulation (no microbial reactions)	Table 4	Constant levels	Constant T (12 °C)
S2	S1 + microbial contributions from heterotrophic processes	S1 + Table 5 ( $R_{O_2}$ , $R_{NO_3^-}$ , $R_{NO_2^-}$ , $R_{NH_3}$ , $R_{Fe^{+3}}$ , and $R_{SO_4^{2-}}$ )	Constant levels	Constant T (12 °C)
S3	S1 + microbial contributions from heterotrophic and chemolithoautotrophic processes	S2 + Table 5 ( $R_{O_2-HS^-}$ , $R_{O_2-Fe^{+2}}$ , $R_{NO_3^-HS^-}$ and $R_{NO_3^-Fe^{+2}}$ )	Constant levels	Constant T (12 °C)
Simulations to capture short-term water table rise and temperature gradients				
S3.1	S3 + water table rise in the April–June 2013 time frame	Same as S3	Fluctuating	Constant T (12 °C)
S3.1'	S3 + water table fluctuations in the April 2013–April 2014 time frame	Same as S3	Fluctuating	Constant T (12 °C)
S3.2	S3 + temperature gradient on June 2013	Same as S3	Constant levels	Fixed gradient
S3.2'	S3 + temperature fluctuations in the April 2013–April 2014 time frame	Same as S3	Constant levels	Fluctuating

obtain nearly steady chemical conditions that are generally representative of the field data (average pH, aqueous and gaseous concentrations, etc.) and result in the persistence of the NRZ near the TT-03 well location. The second set of simulations (S3.1 and S3.2) was restarted from the selected base case simulation (S3) to evaluate CO<sub>2</sub> fluxes under seasonal water table variations (S3.1) and temperature gradients (S3.2). An estimate of carbon exports from the Rifle site to the Colorado River under steady (S1, S2, S3) and transient conditions (S3.1', S3.2') is also reported. Simulations S3.2 and S3.2' were run in a manner so as to clearly distinguish temperature effects from abiotic and biotic processes. A detailed description of the different simulations is provided in [Biotic reactions with chemolithoautotrophic pathways \(S3\)](#) section.

## Numerical model

**TOUGHREACT was used together with the EOS9 equation of state module (Pruess et al. 1999) for isothermal simulations. The EOS9 module implements Richards' equation (Richards 1931) for variably saturated flow of a single aqueous phase with air treated as a passive phase under conditions of constant pressure and temperature. Simulations considering variable temperature were run using the EOS3 module (Pruess et al. 1999), which simulates non-isothermal, multi-phase (water, air) flow processes in variably saturated porous media. The model discretization, inputs and boundary conditions are summarized below.**

### Model domain and discretization

The modeling domain consists of a two-dimensional (x–z) cross-section about 230 m long (along the regional direction of groundwater flow) and 7 m deep (Fig. 3). The domain was discretized using a total of 8050 grid blocks with a uniform grid spacing of 1 m along the horizontal direction and 0.2 m along the vertical direction. The fill and alluvium stratigraphic units were represented, and the top of the underlying, much less permeable, Wasatch Formation was chosen as the lower boundary of the domain. Homogeneous geochemical and hydrogeological properties were initially assumed within each unit (as described in the next section). A maximum time step of 1 day was used for all simulations.

## Hydrological, thermal and transport properties

The average hydrological properties of the fill and alluvium were estimated using pedotransfer functions from textural data of sediments from the site. These values are summarized in Table 2.

An aqueous phase diffusion coefficient of  $1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  was used for all aqueous species in all the simulations. The diffusion coefficient of gaseous CO<sub>2</sub> was dynamically computed as a function of temperature and molecular diameter (Lasaga 1998, Eq. 322), yielding values ranging from  $1.74 \times 10^{-5}$  to  $1.87 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  between 10 and 24 °C. In all simulations, these diffusion coefficients are multiplied by a tortuosity factor (ranging between 0 and 1) to yield effective diffusion coefficients, and the tortuosity factor is dynamically (and locally) computed as a function of liquid saturation and porosity following the Millington-Quirk model (Millington and Quirk 1961). Tortuosity factors computed in this way are quite sensitive to liquid saturation and lower the gas diffusivity by about 1, 2, and 3 orders of magnitude at liquid saturations of 0.4, 0.7, and 0.85 respectively (Fig. A1, Appendix 1). Relevant thermal properties used in the simulations are listed in Table 3.

## Geochemical system

The key geochemical processes included in this study are aqueous speciation, mineral precipitation/dissolution reactions, and microbially mediated redox reactions. The primary species in the modeled reaction network include H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, Al<sup>+3</sup>, Ca<sup>+2</sup>, Cl<sup>-</sup>, Fe<sup>+3</sup>, Fe<sup>+2</sup>, K<sup>+</sup>, Mg<sup>+2</sup>, NH<sub>3</sub>(aq), NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Na<sup>+</sup>, N<sub>2</sub>(aq), O<sub>2</sub>(aq), HS<sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, SiO<sub>2</sub>(aq), and acetate. The aqueous speciation reactions and their equilibrium constants are listed in Table 10 in the Appendix.

The mineralogy of the aquifer sediments was assigned on the basis of previous studies at the site (Li et al. 2009; Fang et al. 2009; Campbell et al. 2012; Qafoku et al. 2014). Based on these studies, calcite, siderite, goethite and pyrite were included in the reaction network. The precipitation and dissolution of these minerals were modeled using kinetic rate laws (Table 4). The equilibrium constants for mineral precipitation/dissolution reactions are listed in Table 11 in the Appendix.

Although the biodegradation of organic carbon is usually simulated through several reactive fractions

**Table 2** Physical model parameters used in the simulations

Hydrostratigraphic unit	Porosity, $\Phi$ (–)	Permeability, $k$ ( $\text{m}^2$ )	van Genuchten parameter, $\alpha$ ( $\text{kg}^{-1} \text{m s}^2$ )	van Genuchten parameter, $m$ (–)	Residual liquid saturation, $S_r$ (–)
Fill	0.21	$4.52 \times 10^{-12}$	$5.07 \times 10^{-4}$	0.18	0.07
Alluvium	0.20	$9.67 \times 10^{-12}$	$8.46 \times 10^{-4}$	0.31	0.13

**Table 3** Average soil thermal properties for different materials from Farouki (1982) considered in simulations S3.2 and S3.2'

Hydrostratigraphic unit	Formation heat conductivity, CWET ( $\text{W m}^{-1} \text{ }^\circ\text{C}^{-1}$ )	Formation heat conductivity under desaturated conditions, CDRY ( $\text{W m}^{-1} \text{ }^\circ\text{C}^{-1}$ )	Rock grain specific heat, SPHT ( $\text{J kg}^{-1} \text{ }^\circ\text{C}^{-1}$ )
Atmosphere	0.025	0.025	1010
Fill	1.5	0.5	800
Alluvium	2.5	2	1000
Bedrock <sup>a</sup>	1.5	0.5	$1 \times 10^6$

<sup>a</sup> An additional material at the bottom of the domain was added with an infinite specific heat to keep the bottom temperature constant at 12 °C

**Table 4** Kinetic parameters for mineral dissolution/precipitation reactions<sup>a</sup>

Mineral	Neutral mechanism		Acid mechanism			Additional mechanism		
	$k_{nu}$ ( $\text{mol kg}_{\text{H}_2\text{O}}^{-1} \text{ m}^{-2} \text{ s}^{-1}$ )	$E_{nu}$ ( $\text{kJ mol}^{-1}$ )	$k_a$ ( $\text{mol kg}_{\text{H}_2\text{O}}^{-1} \text{ m}^{-2} \text{ s}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	$x^b$	$k_{ex}$ ( $\text{mol kg}_{\text{H}_2\text{O}}^{-1} \text{ m}^{-2} \text{ s}^{-1}$ )	$E_{ex}$ ( $\text{kJ mol}^{-1}$ )	Species involved, $a_{ij}^y$
Goethite <sup>c</sup>	$1.15 \times 10^{-8}$	86.5						
Calcite <sup>d</sup>	$1.55 \times 10^{-6}$	23.5	$5.01 \times 10^{-1}$	14.4	1	$3.31 \times 10^{-4}$	35.4	$[\text{CO}_3^{-2}]$
Siderite <sup>e</sup>	$2.24 \times 10^{-9}$	48.0	$1.79 \times 10^{-4}$	48.0	0.75			
Pyrite <sup>f</sup>	0.0	56.9				$2.63 \times 10^{-8}$	56.9	$[\text{Fe}^{+3}]^{0.3}$ , $[\text{Fe}^{+2}]^{-0.47}$ , $[\text{H}^+]^{-0.32}$
						$7.94 \times 10^{-8}$	56.9	$[\text{O}_2]^{0.5}$ , $[\text{H}^+]^{-0.11}$
SOM <sup>g</sup>	$1.0 \times 10^{-10}$ <sup>h</sup>	72.3 <sup>i</sup>						

<sup>a</sup> Rates are reversible (unless otherwise noted) and computed as  $R_i = \left[ k_{nu} + k_a a_H^x + \sum_i k_{ex} \prod_j a_{ij}^y \right] (1 - \Omega)$  with  $k = k_{298.15} \exp[-E/R(1/T - 1/298.15)]$

<sup>b</sup> Reaction order with respect to  $\text{H}^+$

<sup>c</sup> Palandri and Kharaka (2004)

<sup>d</sup> Palandri and Kharaka (2004)

<sup>e</sup> Duckworth and Martin (2004)

<sup>f</sup> Williamson and Rimstidt (1994)

<sup>g</sup> Only dissolution is allowed

<sup>h</sup> Rate determined by the assumption of a non-limiting dissolved organic carbon (acetate) supply

<sup>i</sup> Davidson et al. (2012)

(Bosatta and Ågren 1995; Van Breukelen et al. 2004; Riley et al. 2014), for simplicity this study considers a single solid phase carbon source (cellulose) as the source of dissolved organic carbon at the site. This solid phase carbon will be henceforth referred to as SOM for Soil Organic Matter. SOM is assumed to react kinetically with the pore water, and is present in the model in amounts sufficient to provide an essentially unlimited supply of dissolved organic carbon in the form of acetate (Table 4):



Although simplistic, this representation of SOM and dissolved organic carbon has been used in other reactive transport studies (Hunter et al. 1998; Van Breukelen et al. 2004; Arora et al. 2015b), and it is considered sufficient here as a first-order, semi-quantitative approach to investigate the dominant controls on carbon dynamics at the site.

The microbially mediated redox reactions implemented in the simulations were based on previous studies at the site (Table 5). Several studies have documented iron and sulfate reduction to be important biogeochemical processes occurring at the Rifle site (Kukkadapu et al. 2010; Williams et al. 2011; Druhan et al. 2014a; Long et al. 2015). In addition, a field survey of the microbial populations indicated the presence and activity of chemolithoautotrophic bacteria (*Gallionella*, *Sulfurovum*, and *Sulfuricurvum*) responsible for the

oxidation of  $\text{Fe}^{+2}$  and  $\text{HS}^-$  in reduced zones (Handley et al. 2013). Based on this information, chemolithoautotrophic pathways for the oxidation of  $\text{Fe}^{+2}$  and  $\text{HS}^-$  were explicitly represented in the reaction network (Fig. 2). These reactions were tested in various model simulations to evaluate their relative importance in affecting carbon fluxes at the site, with acetate being the source of chemical energy (Table 5). The biodegradation of acetate was coupled to several terminal electron acceptors, which follow the hierarchical sequence of aerobic respiration, nitrate reduction, iron reduction, and sulfate reduction. These biotic pathways were implemented using single Michaelis–Menten kinetics, and the sequence of TEAs was realized using inhibition terms that impede lower energy-yielding redox reactions when higher energy-yielding electron acceptors are present (e.g., Van Cappellen and Gaillard 1996; Doussan et al. 1997) (Table 6). It should be noted that the rate law parameters of the biotic reaction network considered here differ from those used in previous modeling studies at the site (e.g., Li et al. 2010; Druhan et al. 2014a) because the simulations cover a non-biostimulated zone. Hence, several orders of magnitude lower biodegradation rates are adopted. Characterizations of pore-water and solid phase chemistry at the site were used to calibrate some of the kinetic parameters given in Table 6. For simulations S3.2 and S3.2', the temperature dependence of microbial reaction rate constants was also incorporated.

**Table 5** Microbially mediated redox reactions and their thermodynamic parameters considered in the reactive transport model. See Table 6 for kinetic rate laws and parameters

Reaction stoichiometry	Rate Equation	$\log K$ (25 °C) <sup>a</sup>
Redox reactions with heterotrophic pathways		
$\text{CH}_3\text{COO}^- + 2\text{O}_2 \rightarrow 2\text{HCO}_3^- + \text{H}^+$	$R_{\text{O}_2}$	146.76
$\text{CH}_3\text{COO}^- + 4\text{NO}_3^- \rightarrow 2\text{HCO}_3^- + 4\text{NO}_2^- + \text{H}^+$	$R_{\text{NO}_3^-}$	89.04
$\text{CH}_3\text{COO}^- + 2.667\text{NO}_2^- + 1.667\text{H}^+ \rightarrow 2\text{HCO}_3^- + 1.33\text{N}_2 + 1.33\text{H}_2\text{O}$	$R_{\text{NO}_2^-}$	200.52
$\text{NH}_3(\text{aq}) + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+$	$R_{\text{NH}_3}$	62.23
$\text{CH}_3\text{COO}^- + 8\text{Fe}^{+3} + 4\text{H}_2\text{O} \rightarrow 8\text{Fe}^{+2} + 2\text{HCO}_3^- + 9\text{H}^+$	$R_{\text{Fe}^{+3}}$	79.0
$\text{CH}_3\text{COO}^- + \text{SO}_4^{-2} \rightarrow 2\text{HCO}_3^- + \text{HS}^-$	$R_{\text{SO}_4^{-2}}$	8.40
Redox reactions with chemolithoautotrophic pathways		
$0.5\text{HS}^- + \text{O}_2 \rightarrow 0.5\text{H}^+ + 0.5\text{SO}_4^{-2}$	$R_{\text{O}_2-\text{HS}^-}$	68.90
$\text{Fe}^{+2} + 0.25\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{+3} + 0.5\text{H}_2\text{O}$	$R_{\text{O}_2-\text{Fe}^{+2}}$	8.47
$\text{HS}^- + 1.6\text{NO}_3^- + 0.6\text{H}^+ \rightarrow \text{SO}_4^{-2} + 0.8\text{N}_2 + 0.8\text{H}_2\text{O}$	$R_{\text{NO}_3^--\text{HS}^-}$	11.52
$\text{Fe}^{+2} + 0.2\text{NO}_3^- + 1.2\text{H}^+ \rightarrow \text{Fe}^{+3} + 0.1\text{N}_2 + 0.6\text{H}_2\text{O}$	$R_{\text{NO}_3^--\text{Fe}^{+2}}$	-7.32

<sup>a</sup> Calculated from  $\log K$  values for half redox reactions reported by Morel and Hering (1993)

**Table 6** Kinetic rate laws and parameters for redox reactions

Rate law	Rate law parameters <sup>a</sup>	Reference
$R_{O_2} = K_{\max}^{O_2} \frac{[O_2]}{[O_2] + K_s^{O_2}}$	$K_{\max}^{O_2} (s^{-1}) = 5 \times 10^{-12}$ $K_s^{O_2} (molal) = 2.41 \times 10^{-5}$ $E_a^{O_2} (KJ/mol) = 50$	Calibrated <sup>b</sup> Maggi et al. (2008) Thamdrup et al. (1998)
$R_{NO_3^-} = K_{\max}^{NO_3} \frac{[NO_3^-]}{[NO_3^-] + K_s^{NO_3}} \frac{K_{O_2}^{in}}{K_{O_2}^{in} + [O_2]}$	$K_{\max}^{NO_3} (molal) = 2 \times 10^{-10}$ $K_s^{NO_3} (molal) = 1.13 \times 10^{-4}$ $K_{O_2}^{in} (molal) = 1.61 \times 10^{-8}$ $E_a^{NO_3} (KJ/mol) = 68$	Parkhurst and Appelo (1999) Maggi et al. (2008) Widdowson et al. (1988) McKenney et al. (1984)
$R_{NO_2^-} = K_{\max}^{NO_2} \frac{[NO_2^-]}{[NO_2^-] + K_s^{NO_2}} \frac{K_{O_2}^{in}}{K_{O_2}^{in} + [O_2]}$	$K_{\max}^{NO_2} (molal) = 3 \times 10^{-8}$ $K_s^{NO_2} (molal) = 1.13 \times 10^{-4}$ $K_{O_2}^{in} (molal) = 1.61 \times 10^{-8}$ $E_a^{NO_2} (KJ/mol) = 30$	Calibrated <sup>c</sup> Maggi et al. (2008) Widdowson et al. (1988) Wang et al. (1995)
$R_{NH_3} = K_{\max}^{NH_3} \frac{[NH_3]}{[NH_3] + K_s^{NH_3}} \frac{[O_2]}{[O_2] + K_s^{O_2}}$	$K_{\max}^{NH_3} (s^{-1}) = 5.27 \times 10^{-4}$ $K_s^{NH_3} (molal) = 1.48 \times 10^{-5}$ $K_s^{O_2} (molal) = 2.41 \times 10^{-5}$ $E_a^{NH_3} (KJ/mol) = 87.1$	Calibrated <sup>c</sup> Wu et al. (2011) Maggi et al. (2008) Kim et al. (2008)
$R_{Fe^{+3}} = K_{\max}^{Fe^{+3}} \frac{K_{O_2}^{in}}{K_{O_2}^{in} + [O_2]} \frac{K_{NO_3}^{in}}{K_{NO_3}^{in} + [NO_3^-]}$ <sup>d</sup>	$K_{\max}^{Fe^{+3}} (s^{-1}) = 1 \times 10^{-13}$ $K_{O_2}^{in} (molal) = 1.61 \times 10^{-8}$ $K_{NO_3}^{in} (molal) = 1 \times 10^{-7}$ $E_a^{Fe^{+3}} (KJ/mol) = 100$	Calibrated <sup>e</sup> Widdowson et al. (1988) Doussan et al. (1997) Arndt et al. (2013)
$R_{SO_4^{2-}} = K_{\max}^{SO_4} \frac{[SO_4^{2-}]}{[SO_4^{2-}] + K_s^{SO_4}} \frac{K_{O_2}^{in}}{K_{O_2}^{in} + [O_2]} \frac{K_{NO_3}^{in}}{K_{NO_3}^{in} + [NO_3^-]} \frac{K_{Fe}^{in}}{K_{Fe}^{in} + [Fe^{+3}]}$	$K_{\max}^{SO_4} (s^{-1}) = 3 \times 10^{-12}$ $K_s^{SO_4} (molal) = 1 \times 10^{-3}$ $K_{O_2}^{in} (molal) = 1.61 \times 10^{-8}$ $K_{NO_3}^{in} (molal) = 1 \times 10^{-7}$ $K_{Fe}^{in} (molal) = 1 \times 10^{-12}$ $E_a^{SO_4} (KJ/mol) = 77.5$	Calibrated <sup>f</sup> Li et al. (2010) Widdowson et al. (1988) Doussan et al. (1997) Calibrated <sup>g</sup> Amos et al. (2004)
$R_{O_2-HS^-} = K_{\max}^{O_2-HS^-} \frac{[HS^-]}{[HS^-] + K_s^{HS^-}} \frac{[O_2]}{[O_2] + K_s^{O_2}}$	$K_{\max}^{O_2-HS^-} (s^{-1}) = 2.38 \times 10^{-8}$ $K_s^{HS^-} (molal) = 1 \times 10^{-5}$ $K_s^{O_2} (molal) = 2.41 \times 10^{-5}$ $E_a^{O_2-HS^-} (KJ/mol) = 65$	Luther et al. (2011) Handley et al. (2013) Maggi et al. (2008) Ahonen and Tuovinen (1990)
$R_{O_2-Fe^{+2}} = K_{\max}^{O_2-Fe^{+2}} \frac{[Fe^{+2}]}{[Fe^{+2}] + K_s^{Fe^{+2}}} \frac{[O_2]}{[O_2] + K_s^{O_2}}$	$K_{\max}^{O_2-Fe^{+2}} (s^{-1}) = 5.25 \times 10^{-11}$ $K_s^{Fe^{+2}} (molal) = 1 \times 10^{-5}$ $K_s^{O_2} (molal) = 2.41 \times 10^{-5}$ $E_a^{O_2-Fe^{+2}} (KJ/mol) = 30.9$	Calibrated <sup>e</sup> Mayer et al. (2002) Maggi et al. (2008) Oba and Poulson (2009)
$R_{NO_3^-HS^-} = K_{\max}^{NO_3^-HS^-} \frac{[HS^-]}{[HS^-] + K_s^{HS^-}} \frac{[NO_3^-]}{[NO_3^-] + K_s^{NO_3^-}} \frac{K_{O_2}^{in}}{K_{O_2}^{in} + [O_2]}$	$K_{\max}^{NO_3^-HS^-} (s^{-1}) = 7 \times 10^{-8}$ $K_s^{HS^-} (molal) = 1 \times 10^{-5}$ $K_s^{NO_3^-} (molal) = 1.13 \times 10^{-4}$ $K_{O_2}^{in} (molal) = 1.61 \times 10^{-8}$ $E_a^{NO_3^-HS^-} (KJ/mol) = 65$	<sup>h</sup> Handley et al. (2013) Maggi et al. (2008) Widdowson et al. (1988) <sup>i</sup>

**Table 6** continued

Rate law	Rate law parameters <sup>a</sup>	Reference
$R_{NO_3^- - Fe^{+2}} = K_{\max}^{NO_3^- - Fe^{+2}} \frac{[Fe^{+2}]}{[Fe^{+2}] + K_s^{Fe^{+2}}} \frac{[NO_3^-]}{[NO_3^-] + K_s^{NO_3^-}} \frac{K_{O_2}^{in}}{K_{O_2}^{in} + [O_2]}$	$K_{\max}^{NO_3^- - Fe^{+2}} (s^{-1}) = 7 \times 10^{-8}$ $K_s^{Fe^{+2}} (molal) = 1 \times 10^{-5}$ $K_s^{NO_3^-} (molal) = 1.13 \times 10^{-4}$ $K_{O_2}^{in} (molal) = 1.61 \times 10^{-8}$ $E_a^{NO_3^- - Fe^{+2}} (KJ/mol) = 22$	Palmer et al. (2010) Mayer et al. (2002) Maggi et al. (2008) Widdowson et al. (1988) Westerhoff (2003)

<sup>a</sup> For simulation S3.2, the rate constant is temperature-dependent and dynamically calculated as  $K_{\max} = K_{25} \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right]$  where  $E_a$  is the activation energy

<sup>b</sup> Lowered by three orders of magnitude starting from the value in Russell (1973), to yield computed  $Fe^{+2}$  concentrations close to measured values while maintaining pyrite oxidation in the system

<sup>c</sup> Adjusted from Maggi et al. (2008) so as to drive the redox zonation to iron/sulfate reduction while not de-stabilizing the system with overly fast reaction rates

<sup>d</sup> Assumes an unlimited  $Fe^{+3}$  supply (from abundant solid Fe hydroxides)

<sup>e</sup> Calibrated to stabilize pH in groundwater close to measured values

<sup>f</sup> Adjusted several orders of magnitude lower than the values reported by Li et al. (2010) and Druhan et al. (2014a) for acetate-amended experiments

<sup>g</sup> Adjusted to yield background dissolved  $Fe^{+2}$  concentrations reasonably close to measured values

<sup>h</sup> Kept to yield similar maximum reaction rate as  $R_{NO_3^- - Fe^{+2}}$

<sup>i</sup> Kept to yield similar activation energy as  $R_{O_2 - HS}$

It should be noted that the inorganic reaction system is coupled to the biotic reaction network through the kinetic constraints on the multiple TEAs used by the simulated microbial consortium that includes heterotrophs and chemolithoautotrophs. Thus, the stoichiometries of redox sensitive aqueous species and minerals are decoupled in the input thermodynamic database and elements with different redox states are treated as separate primary variables i.e., as individual “basis” species (e.g., all Fe(III) minerals and aqueous species are written in terms of  $Fe^{+3}$ , all Fe(II) minerals in terms of  $Fe^{+2}$ ).

#### Initial and boundary conditions

Following the conceptual model described above, fixed concentrations of dissolved species were applied at the top and left (up-gradient) model boundaries (Table 7). The fixed water composition at the up-gradient boundary was taken as that measured in well TT-01, and is considered representative of oxic recharge. The initial concentrations of (undetected) S(-2) and Fe(III) were set by equilibration with pyrite and goethite, respectively, and pH was recalculated to yield equilibrium with calcite, resulting in a pH consistent with field data (Table 7). For simplicity, the

same water composition was also assumed for infiltration at the top model boundary, although in this case the infiltration water was re-equilibrated with atmospheric  $O_2$  and  $CO_2$  concentrations (Table 7).

The groundwater composition at well TT-01 contrasts with the composition at down-gradient well TT-03, which is suboxic and representative of the more reducing conditions within NRZs at the site. The composition of this more reduced water, also equilibrated with pyrite and goethite to yield initial concentrations of S(-2) and Fe(III), respectively, was chosen as initial conditions over the entire model domain (Table 7). The sediments throughout the entire domain were set with an initial mineral composition representative of NRZs (Table 8). The proxy SOM phase was given an equilibrium constant calculated to yield acetate concentrations (at equilibrium with this phase, Reaction 1) representative of measured concentrations (Table 7).

A closed (no-flux) bottom model boundary was applied to represent the top of the low permeability Wasatch formation. The first sets of simulations (S1, S2 and S3) were run with a fixed water table height and hydraulic gradient (April 2013; averaging 0.0025), maintained by fixed pressures at up-gradient and down-gradient boundaries, with the latter set at the

**Table 7** Pore water compositions (molal) for initial and boundary conditions

Species	Left (oxic) boundary <sup>a</sup>	Top (oxic) boundary <sup>a</sup>	Concentration (molal) for (reduced) initial conditions <sup>b</sup>
pH	7.01 <sup>c</sup>	7.99 <sup>c</sup>	6.98 <sup>c</sup>
Cl	$6.08 \times 10^{-3}$	$6.08 \times 10^{-3}$	$2.57 \times 10^{-3}$
HCO <sub>3</sub>	$8.24 \times 10^{-3}$	$7.80 \times 10^{-4}$ <sup>d</sup>	$9.53 \times 10^{-3}$
Al	$3.48 \times 10^{-6}$	$3.48 \times 10^{-6}$	$9.74 \times 10^{-10}$
Ca	$5.59 \times 10^{-3}$	$5.59 \times 10^{-3}$	$4.48 \times 10^{-3}$
Mg	$6.16 \times 10^{-3}$	$6.16 \times 10^{-3}$	$4.06 \times 10^{-3}$
O <sub>2</sub> (aq)	$7.83 \times 10^{-6}$	$3.23 \times 10^{-4}$ <sup>e</sup>	$1.00 \times 10^{-10}$ <sup>f</sup>
Fe(II)	$7.49 \times 10^{-5}$	$7.49 \times 10^{-5}$	$7.85 \times 10^{-5}$
Fe(III)	$6.15 \times 10^{-13}$ <sup>g</sup>	$3.74 \times 10^{-13}$ <sup>g</sup>	$6.28 \times 10^{-13}$ <sup>g</sup>
K	$3.48 \times 10^{-4}$	$3.48 \times 10^{-4}$	$2.00 \times 10^{-4}$
Na	$1.25 \times 10^{-2}$	$1.25 \times 10^{-2}$	$7.56 \times 10^{-3}$
S(-2)	$1.07 \times 10^{-10}$ <sup>h</sup>	$4.93 \times 10^{-10}$ <sup>h</sup>	$1.07 \times 10^{-10}$ <sup>h</sup>
SO <sub>4</sub>	$1.18 \times 10^{-2}$ <sup>i</sup>	$1.48 \times 10^{-2}$ <sup>i</sup>	$6.94 \times 10^{-3}$ <sup>i</sup>
SiO <sub>2</sub> (aq)	$3.30 \times 10^{-4}$	$3.30 \times 10^{-4}$	$4.04 \times 10^{-4}$
NO <sub>3</sub>	$2.31 \times 10^{-5}$	$2.31 \times 10^{-5}$	$1.00 \times 10^{-10}$ <sup>f</sup>
NO <sub>2</sub>	$1.05 \times 10^{-6}$	$1.05 \times 10^{-6}$	$1.00 \times 10^{-10}$ <sup>f</sup>
N <sub>2</sub> (aq)	$1.00 \times 10^{-10}$ <sup>f</sup>	$1.00 \times 10^{-10}$ <sup>f</sup>	$1.00 \times 10^{-10}$ <sup>f</sup>
Acetate	$1.00 \times 10^{-10}$ <sup>f</sup>	$1.00 \times 10^{-10}$ <sup>f</sup>	$9.94 \times 10^{-4}$
NH <sub>3</sub> (aq)	$6.67 \times 10^{-6}$	$6.67 \times 10^{-6}$	$2.22 \times 10^{-4}$
P <sub>CO<sub>2</sub>(12 °C)</sub>	0.028 bar	0.004 bar	0.035 bar

<sup>a</sup> Measured concentrations in pore water at TT-01 in May 2013, unless indicated otherwise

<sup>b</sup> Measured concentrations in pore water at TT-03 in May 2013, unless indicated otherwise

<sup>c</sup> Fixed by equilibrium with calcite

<sup>d</sup> Fixed by P<sub>CO<sub>2</sub></sub> (g) of  $10^{-3.5}$  bar

<sup>e</sup> Fixed by P<sub>O<sub>2</sub></sub> (g) of  $10^{-0.7}$  bar

<sup>f</sup> Small assumed value (below detection)

<sup>g</sup> Fixed by equilibrium with goethite

<sup>h</sup> Fixed by equilibrium with pyrite

<sup>i</sup> Adjusted for charge balance

average annual river level. These simulations were also run for a constant temperature (12 °C) representative of the mean measured aquifer temperature in April 2013. Because simulations S2 and S3 were restarted from S1, their initial conditions were taken from the inherited modeled state of simulation S1.

The second set of simulations (S3.1, S3.1', S3.2, and S3.2') were run to assess the effect of variable groundwater levels and subsurface temperatures on model results. For simulations S3.1 and S3.1', a variable flux was imposed at the left boundary (at the edge of the model domain) to simulate observed water table fluctuations (Fig. 4). Heat flow was

considered in simulation S3.2 by imposing a vertical temperature gradient at the left model boundary and using soil thermal properties (Table 3) that were chosen to reproduce the maximum temperature gradient observed with depth in well TT-03 (Fig. 5). In contrast, to simulate observed temperature fluctuations with simulation S3.2' (Fig. 5c), a variable heat boundary was imposed at the top of the model domain and a constant temperature of 12 °C was imposed along the bottom model boundary. For simulations S3.2 and S3.2', the right model boundary corresponding to the river was kept at a constant 12 °C average temperature, and the location of the

**Table 8** Initial mineral volume fractions considered in the simulations

Mineral	Density (g cm <sup>-3</sup> )	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )	Volume fraction (–)	Specific surface area (m <sup>2</sup> <sub>mineral</sub> m <sup>-3</sup> <sub>mineral</sub> ) <sup>a</sup>
Goethite	4.268	20.82	1.2 × 10 <sup>-3</sup> <sup>b</sup>	60,000
Calcite	2.710	36.934	0.01 <sup>c</sup>	60,000
Siderite	3.944	29.378	4.09 × 10 <sup>-3d</sup>	60,000
Pyrite	5.012	23.94	3.6 × 10 <sup>-5</sup> <sup>e</sup>	60,000
SOM	1.500	108.059 <sup>(f)</sup>	0.0626	1.13 × 10 <sup>5</sup> <sup>g</sup>

<sup>a</sup> Reactive surface area are calculated assuming 100 micron spherical grains unless otherwise noted

<sup>b</sup> Based on 3.8 × 10<sup>-5</sup> mol/g hydroxylamine-extractable Fe(III) content in fine grained (<2 mm) Rifle sediments (Li et al. 2010; Campbell et al. 2012)

<sup>c</sup> Assumed low value from visual observation of calcite in sediments

<sup>d</sup> Based on 0.5 M HCL Fe(II) content in fine grained (<2 mm) Rifle sediments (Campbell et al. 2012) yielding a value largely dominating the amount of Fe(II) sulfide in the sediment (see <sup>e</sup>)

<sup>e</sup> Based on 7 × 10<sup>-7</sup> mol/g acid volatile sulfide content in fine grained (<2 mm) Rifle sediments (Campbell et al. 2012)

<sup>f</sup> Fixed by density and molecular weight

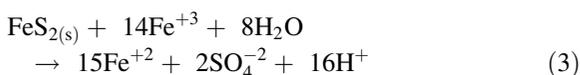
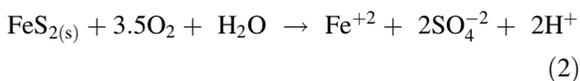
<sup>g</sup> Based on the smallest particle size fraction (53 micron) with reported organic matter content in Rifle sediments (Campbell et al. 2012)

water table was kept constant as was the case for simulation S3.

## Simulated cases

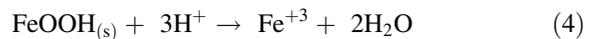
### Base case simulation (S1)

The base case simulation was designed to consider abiotic reactions so as to gain insight into the interpretation of processes controlling the self-organization of naturally reduced zones associated with reduced Fe and S phases. In this study, several iron minerals (goethite, siderite, and pyrite) are associated with the sediments and can influence the redox cycling of Fe and S as well as affect C fluxes. For example, two independent and parallel pathways for pyrite dissolution are considered:

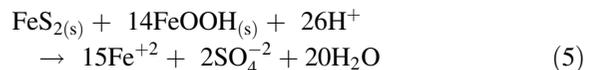


Because different rate laws are used for the two reactions (see Table 4), the overall pyrite dissolution reaction depends on whether Fe<sup>+3</sup> or O<sub>2</sub>(aq) is the dominant oxidant (Williamson and Rimstidt 1994;

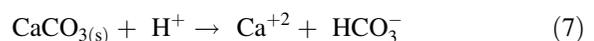
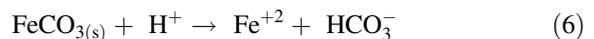
Steefel 2000). The second pathway (Reaction 2) is coupled to the dissolution of goethite, which is modeled using a kinetic rate law (Table 4):



The overall effect of Reactions 3 and 4 yields the reductive dissolution of Fe<sup>+3</sup> by sulfide:

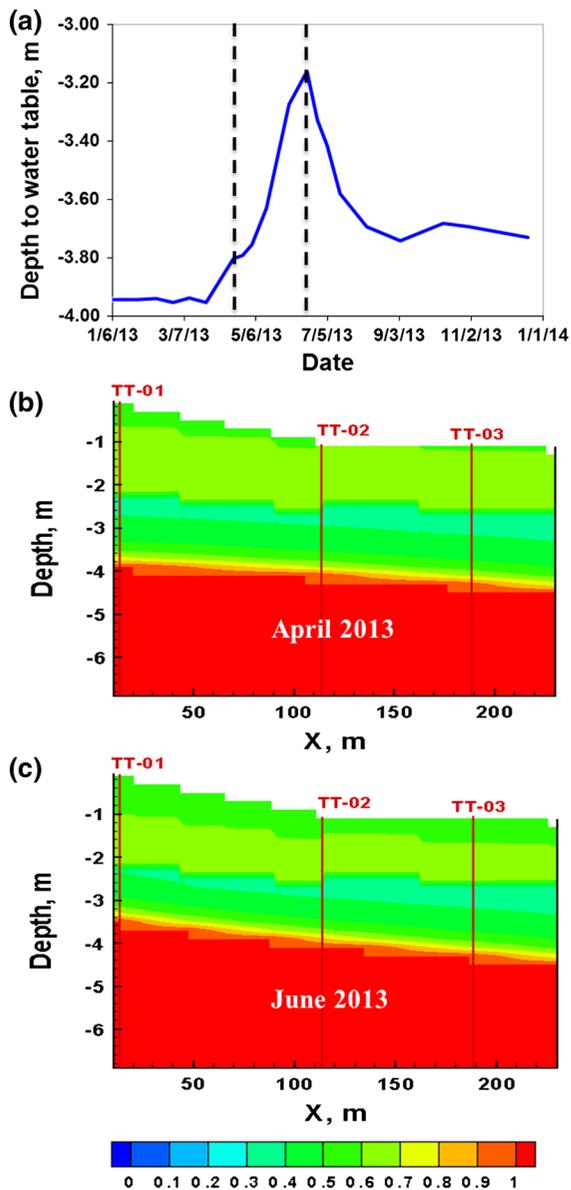


Among the minerals considered here, siderite and calcite dissolution directly affect CO<sub>2</sub> geochemistry:



Note that Reaction 5 strongly affects pH, which indirectly impacts bicarbonate alkalinity through Reactions 6 and 7. Thus, for simulation S1, carbon fluxes and the spatial extent of the NRZ in the system are controlled by these mineral reactions only (with rates as listed in Table 4).

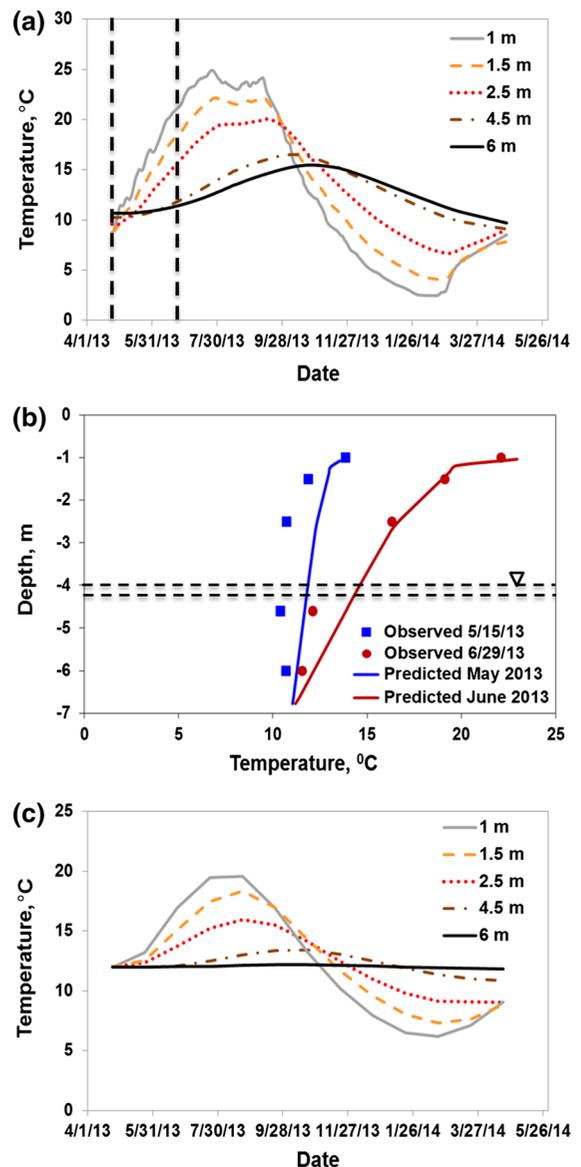
Simulation S1 was run for 15 years with a fixed water table height and fixed temperature (12 °C) until steady chemical conditions were reached that matched approximately the field observations. Note that a mean groundwater residence time of 6 years was computed from the model input parameters.



**Fig. 4** **a** Time series of water table depth at a stilling well located upstream of the site, and **b**, **c** snapshots of simulated liquid saturation profiles for April and June 2013, respectively using S3.1. The dashed lines in **a** show the period of rising water table that was simulated in S3.1

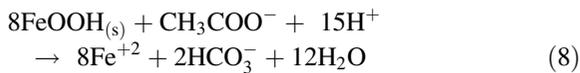
#### Biotic with heterotrophic pathways (S2)

Biotic pathways for the degradation of acetate and  $\text{CO}_2$  production (Table 5) were introduced in this simulation by restarting S1 and simulating for an additional 6 years. 6 years was sufficient to evolve to a quasi-steady state controlled by the balance between influxes



**Fig. 5** **a** Time series of temperature data at TT-03—dashed lines show the April–June 2013 time frame considered in short-term simulations (Table 1), **b** snapshots of simulated temperature gradients for May and June 2013 using S3.2—dashed lines show the water table level in April (low) and June 2013 (high), and **c** simulated annual temperature fluctuations using S3.2'. Note that the depth on the y-axis corresponds to the modeled domain and not true ground surface

and heterotrophic respiration rates. In addition to reaction 5, the reductive dissolution of goethite is now simulated as the rate-limited microbial reduction of  $\text{Fe}^{+3}$  (Table 5) coupled with kinetic dissolution of goethite (Table 4), with the overall reaction given by:



Note that reaction (8) also strongly affects pH and indirectly impacts bicarbonate alkalinity through reactions (6) and (7). Thus, for simulation S2, carbon fluxes and the spatial extent of the NRZ in the system are determined by both abiotic and biotic reactions.

#### Biotic reactions with chemolithoautotrophic pathways (S3)

Biotic reactions with both heterotrophic and chemolithoautotrophic pathways (Fig. 2) were introduced in this simulation by restarting S1 and simulating for an additional 6 years. A time frame similar to that of simulation S2 was chosen so as to clearly distinguish the contributions from chemolithoautotrophic processes. The aqueous concentrations are found to approach a quasi-steady state within this time frame. Therefore, in addition to the oxidation of acetate to CO<sub>2</sub> through several sequential pathways as in S2, oxygen- and nitrate-dependent oxidation of Fe<sup>+2</sup> and HS<sup>-</sup> were considered in this simulation (R<sub>O<sub>2</sub>-HS</sub><sup>-</sup>, R<sub>O<sub>2</sub>-Fe</sub><sup>+2</sup>, R<sub>NO<sub>3</sub>-HS</sub><sup>-</sup>, R<sub>NO<sub>3</sub>-Fe</sub><sup>+2</sup>, Table 5). Thus, for simulation S3, carbon fluxes and the spatial extent of the NRZ in the system depend on the tight coupling between transport, abiotic and biotic reactions as well as the biogeochemical recycling of SO<sub>4</sub><sup>-2</sup> and Fe<sup>+3</sup> through chemolithoautotrophic pathways.

#### Seasonal and annual water table fluctuations (S3.1 and S3.1')

S3.1 and S3.1' cases were derived directly from simulation S3 (with fixed water table conditions), except that water level fluctuations (Fig. 4) were included. Simulation S3.1 incorporates time-dependent boundary conditions to investigate the effect of seasonal water table variations (April–June 2013) on soil CO<sub>2</sub> concentrations at the site. Simulation S3.1' was run for a full year cycle of water level fluctuations (January 2013–January 2014) to assess the impact of annual water table variations on groundwater carbon exports to the river. Water table fluctuations observed at a stilling well (located 0.4 miles from the southeast boundary, upstream of the site) for an entire year at the Rifle site are shown in Fig. 4a and two representative snapshots of the simulated saturation profiles at both low and high

water levels in April and June 2013 are shown in Fig. 4b, c, respectively. Thus, for simulations S3.1 and S3.1', carbon fluxes in the system include the effect of water table fluctuations and the impact of these variations on abiotic and biotic reactions producing CO<sub>2</sub>.

#### Temperature gradients (S3.2) and annual temperature fluctuations (S3.2')

S3.2 and S3.2' cases were also derived from simulation S3, except that heat transport driven by temperature changes (Fig. 5) was included. Simulation S3.2 incorporates the temperature difference between the top and bottom of the modeled domain and investigates the effect of temperature gradients observed in June 2013 on soil CO<sub>2</sub> concentrations at the site. Simulation S3.2' was run for a full year cycle of temperature fluctuations (April 2013–April 2014) to assess the impact of annual temperature fluctuations on groundwater carbon exports to the river. In these cases, to clearly distinguish temperature effects from water level effects, the water table was kept at a constant level, as in simulation S3. In addition, the influence of temperature on abiotic and biotic processes was separately evaluated for each of these cases. Thus as with simulation S3.2, the simulated CO<sub>2</sub> dynamics are affected by temperature gradients during June 2013 (Fig. 5b) and in the case of simulation S3.2', carbon fluxes are impacted by annual temperature fluctuations (Fig. 5c). It should be noted that an increase in temperature results in decreasing CO<sub>2</sub> solubility (increasing volatility), decreasing calcite solubility (retrograde behavior), and increasing kinetic rates of both abiotic and microbial reactions.

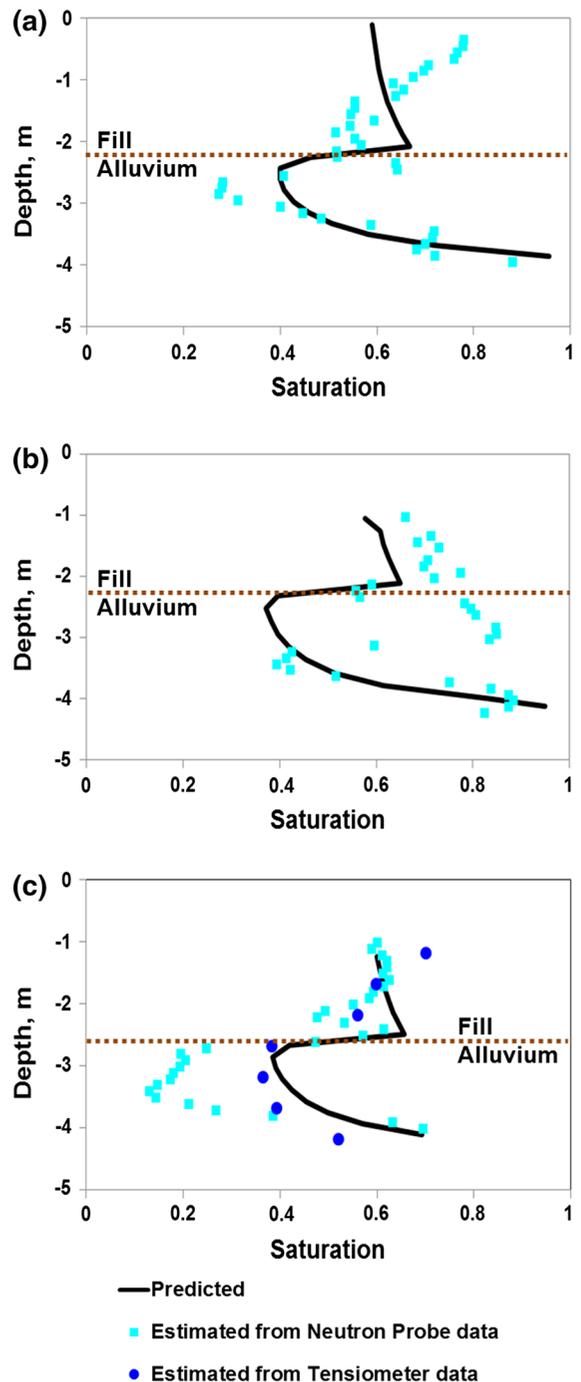
## Results and discussion

Results are presented for the two sets of simulations discussed above—the first set (S1, S2 and S3) focuses on understanding the relative contribution of different abiotic and biotic reactions on soil CO<sub>2</sub> concentrations under conditions of constant water table depth and temperature; the second set of simulations (S3.1 and S3.2) is used to evaluate CO<sub>2</sub> dynamics under conditions of variable water levels and subsurface temperatures. Groundwater carbon exports from the site to the river are evaluated using both sets of simulations (S1, S2, S3, S3.1', and S3.2').

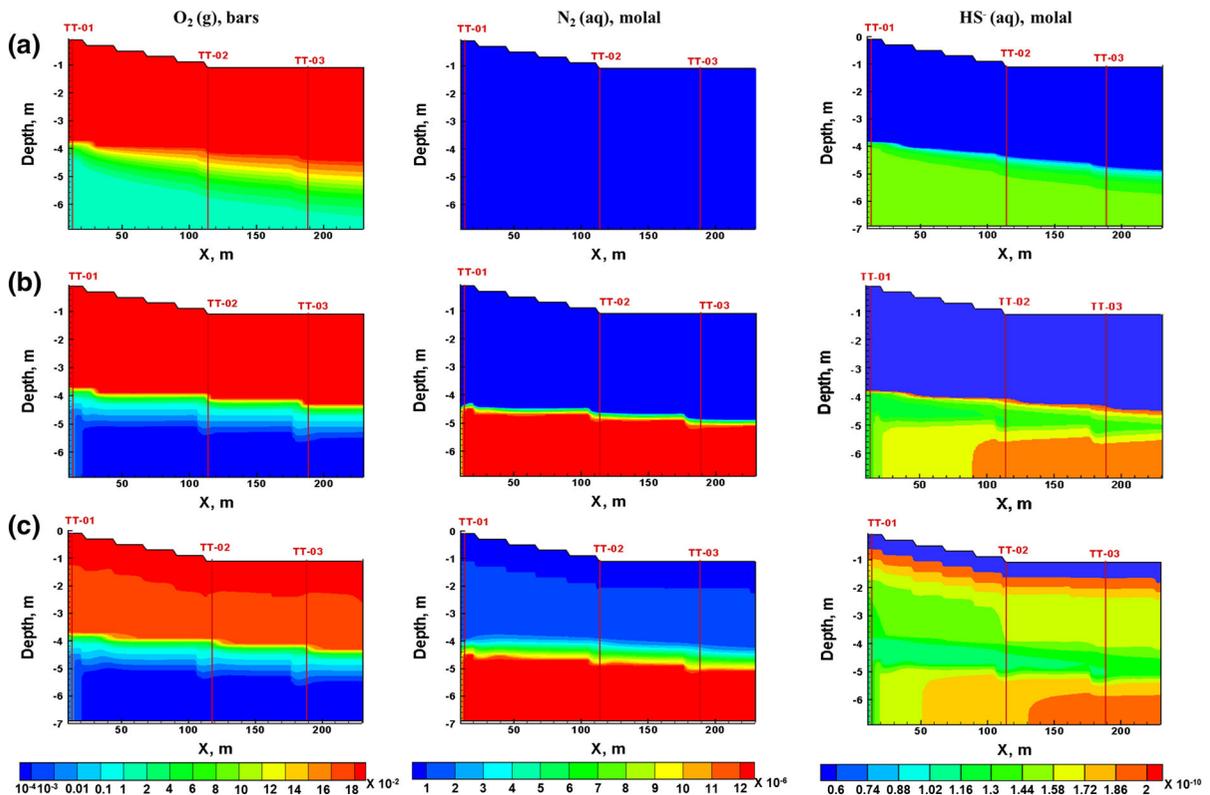
### Simulated liquid saturation and biogeochemical trends

Simulated liquid saturation profiles from S1 (S2 or S3 could also have been used) were compared with data derived from neutron probe measurements under steady water table conditions (March 2014) at wells TT-01, TT-02 and TT-03 (Fig. 6). It should be noted that the neutron probe readings were likely affected by bentonite, which was used as backfill material for the surface-most regions (up to  $\sim 0.9$  m) of the TT wells, and for this reason no attempt was made to calibrate precisely flow model parameters to these data. To provide additional and likely better-constrained “observations”, liquid saturation profiles at well TT-03 were also estimated by fitting laboratory-determined van Genuchten parameters to tensiometer readings (March 2014) at various depths in this well (Fig. 6c). Figure 6 reveals a discontinuity in both the measured and simulated saturation profiles at the fill-alluvium interface (brown dotted lines) for all wells. Below the fill materials, the simulations capture reasonably well the trend of liquid saturations derived from these measurements; within the fill, the model appears to underestimate liquid saturation slightly, particularly in the shallower part of the modeled domain where bentonite was used. Note that this underestimation of the liquid saturation (if real) can affect the computed value of the gas diffusion coefficient (through the Millington-Quirk tortuosity formulation) and result in a system that is more open to gas flow, as discussed in the next section.

The conceptual model of NRZ persistence at the site was tested by comparing the predicted spatial distribution of important redox-sensitive species for the different modeled simulations: abiotic (simulation S1), biotic with heterotrophic (simulation S2) and chemolithoautotrophic pathways (simulation S3) (Fig. 7). Figure 7a shows that with simulation S1, oxidizing conditions develop in the vadose zone (as would be expected), whereas slightly reducing conditions are predicted to remain in the saturated zone. In this case, steady state redox conditions are determined by abiotic pathways alone and are controlled by the mass fluxes of redox species at the recharge boundary and the rates of mineral precipitation/dissolution reactions (e.g., reactions 5–7). Under this scenario, the reducing conditions initially imposed throughout



**Fig. 6** Simulated and observed profiles of saturation versus depth at wells **a** TT-01, **b** TT-02, and **c** TT-03. A consistent calibration of volumetric water content (VWC) =  $0.50 \times \text{counts ratio} - 0.05$  was used at all 3 wells for the neutron probe measurements. *Note* that the depth on the *y*-axis corresponds to the modeled domain and not true ground surface



**Fig. 7** Simulated spatial distributions of  $O_2(g)$ ,  $N_2(aq)$  and  $HS^-(aq)$  along the TT transect using **a** abiotic, **b** abiotic + biotic with heterotrophic pathways, and **c** abiotic + biotic with both

heterotrophic and chemolithoautotrophic pathways. The NRZ persists closer to the river when chemolithoautotrophs are taken into account

the model domain cannot be maintained at steady state, as shown with the simulated profiles for dissolved  $O_2$ ,  $N_2$  and  $HS^-$  (Fig. 7a). Note that the computed  $HS^-$  concentration in the presence of  $O_2$  is essentially zero. Evolving from these conditions, a redox zonation develops in the saturated zone when microbial reactions are considered in simulations S2 and S3 (Fig. 7b, c). In the vadose zone, oxidizing conditions are predicted to prevail with simulation S2 but not with S3. In the saturated zone, oxygen is depleted at a more rapid pace with both simulations S2 and S3 through the different microbially mediated pathways (Fig. 2). With simulations S2 and S3, denitrifying conditions cannot be maintained in the saturated zone because of the rapid rate of nitrate reduction through biotic pathways (Fig. 7b, c). Some elevated  $N_2$  concentrations are also observed in the vadose zone with simulation S3. In both cases, the predicted sulfide concentration ( $HS^-$ ) increases in the

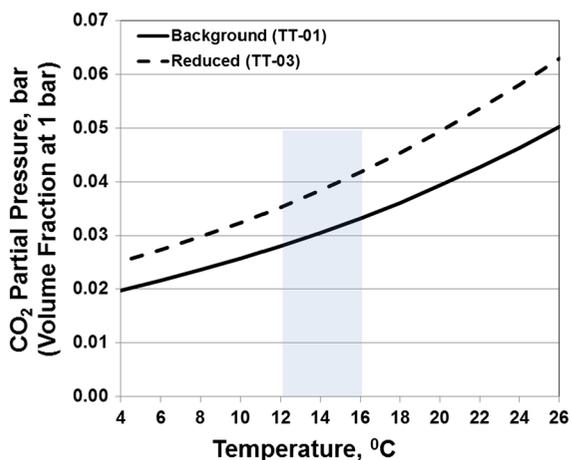
down-gradient portion of the cross section as a result of the interplay between the rate of dissolution of pyrite, heterotrophic reduction, and in S3, chemolithoautotrophic oxidation of iron and sulfide (Table 5) (Fig. 7b, c). When only heterotrophic processes are considered (Fig. 7b), the observed persistence of the NRZ near the river (right model boundary) cannot be reproduced as well as when chemolithoautotrophic oxidation is also included (Fig. 7c). This suggests that chemolithoautotrophic processes not only increase  $O_2$  and  $NO_3^-$  depletion, but also promote further heterotrophic reduction of  $Fe^{+3}$  and  $SO_4^{2-}$  through the cycling of these redox species. Thus, these processes control the spatial redox zoning observed in the saturated zone. An increase in acetate concentration in the down-gradient portion of the cross section in the case of both simulations S2 and S3 is further observed (not shown here). The lateral distribution of acetate also appears to be controlled by

the influx of up-gradient oxic recharge and microbial reactions.

These results suggest that abiotic pathways alone cannot account for the redox zonation observed at the site in the form of NRZs. The spatial extent of reduced zones near well TT-03 can be obtained by controlling the interactions between oxidizing recharge and homogeneous flood plain sediments, but more importantly by considering chemolithoautotrophic processes through the redox cycling of  $\text{Fe}^{+3}$  and  $\text{SO}_4^{-2}$ .

#### CO<sub>2</sub> concentrations from abiotic and multiple biotic pathways

2-D model simulations were used further to evaluate the effect of the different biogeochemical pathways on CO<sub>2</sub> efflux from the site. In the saturated zone, the transport of CO<sub>2</sub> (inorganic carbon) is dominated by advection, whereas CO<sub>2</sub> fluxes in the vadose zone are primarily diffusive (although advective effects from barometric pumping and/or water table fluctuations cannot be ruled out completely). The CO<sub>2</sub> partial pressure in groundwater at the water table (computed from the compositions shown on Table 7, reflecting equilibrium with calcite as suggested by field observation) is elevated and varies around 0.03 bar ( $\sim 30,000$  ppmV) in the range of groundwater temperatures recorded at the site (Fig. 8). Thus, the

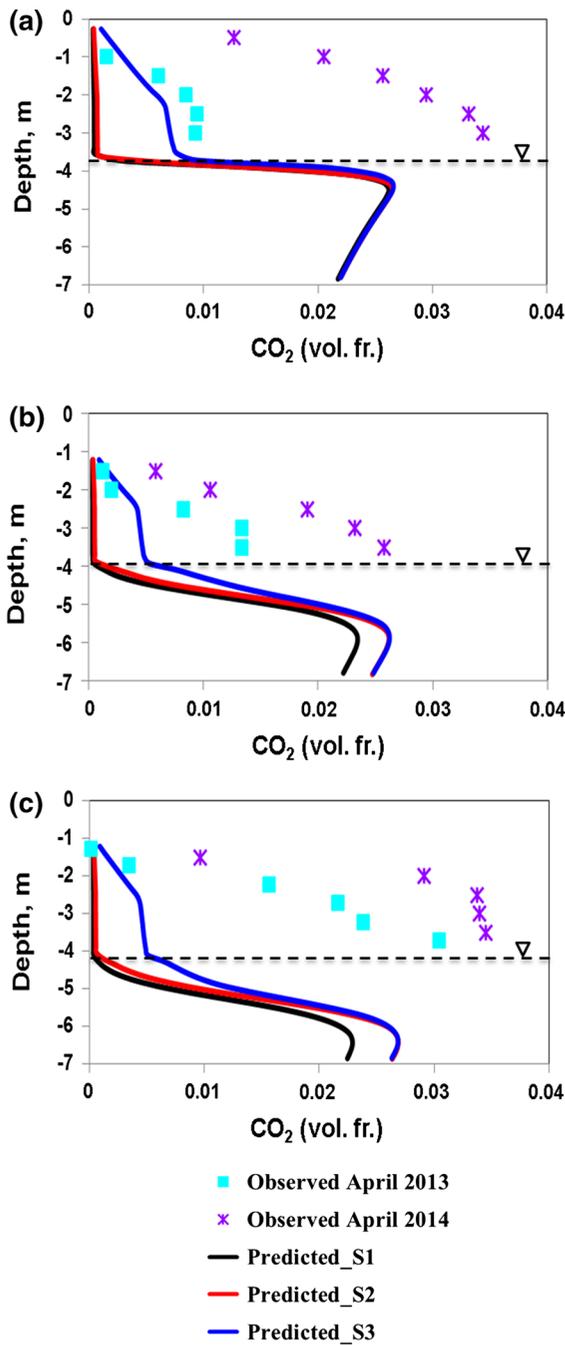


**Fig. 8** Computed CO<sub>2</sub> partial pressure in groundwater as a function of temperature at wells TT-01 and TT-03 (see Table 7 for the corresponding groundwater compositions), for a system buffered by equilibrium with calcite, which is observed at the site. The shaded area shows the typical range of temperature in the saturated and deep vadose zone at the site (see Fig. 5)

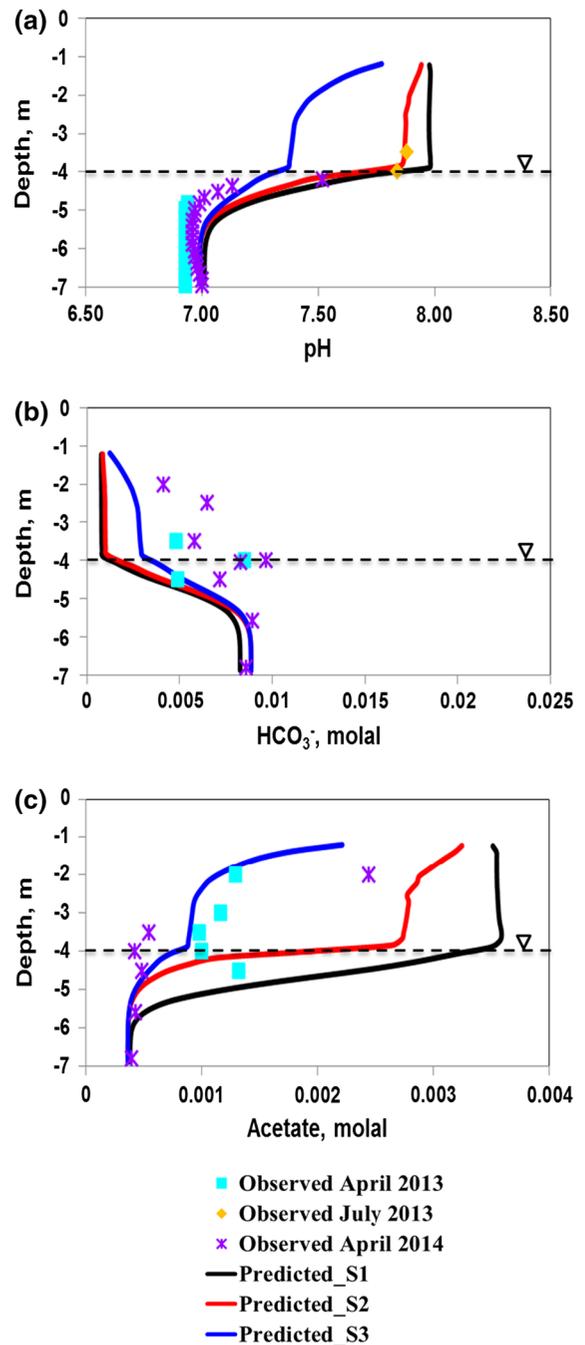
flux of CO<sub>2</sub> in the vadose zone depends not only on microbial activity above the water table, but also on the significant gradient between the elevated CO<sub>2</sub> concentrations at the water table and the low atmospheric values above ground ( $\sim 400$  ppmV). The CO<sub>2</sub> diffusion across this gradient is a function of liquid saturation (through the tortuosity factor, Figure A-1), which in this case lowers the diffusive flux (compared to a fully gas-saturated system) by about 1 order of magnitude at the lowest modeled liquid saturation ( $\sim 0.4$ , Fig. 6), and significantly more so at higher liquid saturations (Figure A-1). Therefore, variations in liquid saturation alone (such as from a rising water table and/or rainfall events) are expected to significantly affect the CO<sub>2</sub> diffusive flux and spatial variability of CO<sub>2</sub> concentrations in the vadose zone.

Figure 9 compares simulated steady state CO<sub>2</sub> concentrations at TT-01, TT-02, and TT-03 wells for the three simulated cases: abiotic (S1), biotic with heterotrophic (S2) and chemolithoautotrophic pathways (S3) with observed profiles. Because water table conditions were stable in the beginning of April 2013, CO<sub>2</sub> measurements from this month were used for comparison. Note that observed CO<sub>2</sub> concentrations for April 2014 are shown for reference only and not used in this analysis because hydrological conditions in 2014 were significantly different from 2013. Figure 9 clearly demonstrates that both simulations S1 and S2 predict relatively low  $P_{\text{CO}_2}$  in the vadose zone that are far from observations. In the saturated zone, simulation S2 results in higher  $P_{\text{CO}_2}$  than S1 as a result of heterotrophic respiration. The inclusion of chemolithoautotrophic processes further increases the predicted CO<sub>2</sub> concentration in the deeper vadose zone (around 3 m), where higher volume fractions of CO<sub>2</sub> are generally observed. Simulation S3 reproduces observed CO<sub>2</sub> profiles better than the other simulated cases in both wells TT-01 and TT-02. However, simulation S3 still underestimates observed CO<sub>2</sub> concentrations particularly at well TT-03 where CO<sub>2</sub> concentrations are elevated and generally higher than those observed at TT-01 or TT-02. As discussed below, temperature has an important effect on CO<sub>2</sub> concentrations and inclusion of the observed temperature gradients in the simulations significantly improves the match of the observations and predictions.

Simulated and observed profiles of pH,  $\text{HCO}_3^-$ , and acetate concentrations at well TT-02 are presented



**Fig. 9** Simulated and observed profiles of  $\text{CO}_2(\text{g})$  volume fraction versus depth at wells **a** TT-01, **b** TT-02, and **c** TT-03 for three modeled cases (S1, abiotic; S2, abiotic + biotic with heterotrophic pathways; and S3, abiotic + biotic with both heterotrophic and chemolithoautotrophic pathways). *Note* that the depth on the *y-axis* corresponds to the modeled domain and not true ground surface. (Color figure online)



**Fig. 10** Simulated and observed profiles of pH, total dissolved carbonate concentration (as  $\text{HCO}_3^-$ ), and acetate concentration versus depth at well TT-02 for three modeled cases (S1, abiotic; S2, abiotic + biotic with heterotrophic pathways; and S3, abiotic + biotic with both heterotrophic and chemolithoautotrophic pathways). *Note* that the depth on the *y-axis* corresponds to the modeled domain, and pH measurements in the vadose zone (orange diamonds) were confined to one sampling event in July 2013. (Color figure online)

in Fig. 10. Again, a comparison between simulated and observed profiles is carried out for April 2013 and observations for April 2014 are shown for reference only. Simulations S2 and S3 predict lower pH values in the vadose zone as compared to S1 (Fig. 10a). This is expected as several biotic pathways including microbially mediated breakdown of acetate cause a decrease in pH ( $R_{O_2}$ ,  $R_{NO_3^-}$ ,  $R_{Fe^{+3}}$ ,  $R_{SO_4^{2-}}$ ,  $R_{NH_3}$ , Table 5). The lower pH by itself would result in a lower bicarbonate concentration. However, in this case the biotic reactions yield an increase in dissolved carbonate concentration (Fig. 10b), and more so for simulation S3 than for S2. Although chemolithoautotrophic reactions ( $R_{O_2-HS}$ ,  $R_{NO_3^-HS}$ ,  $R_{Fe^{+2}}$ ,  $R_{NO_3^-Fe^{+2}}$ , Table 5) do not directly contribute to this increase, the redox cycling of Fe and S and a resulting increase in the breakdown of acetate can lead to higher dissolved carbonate concentrations. A decrease in acetate concentration is clearly visible in the vadose zone for simulation S3 (Fig. 10c). In the saturated zone, the simulated acetate concentration with S3 is also lower than obtained with S1 and S2. These vertical acetate profiles are governed by two controlling processes—one, the microbially mediated breakdown that occurs when its concentration is high and in the presence of TEAs, and two, its release from SOM when its concentration is low.

Figure 9 clearly demonstrates that higher  $CO_2$  concentrations are observed locally at TT-03, which is located within the NRZ. The simulations show an improved agreement with observations when both biotic heterotrophic and chemolithoautotrophic pathways, in addition to abiotic processes, are considered. Thus, simulation S3 will be used for evaluating the  $CO_2$  dynamics under varying water table and temperature conditions at the site.

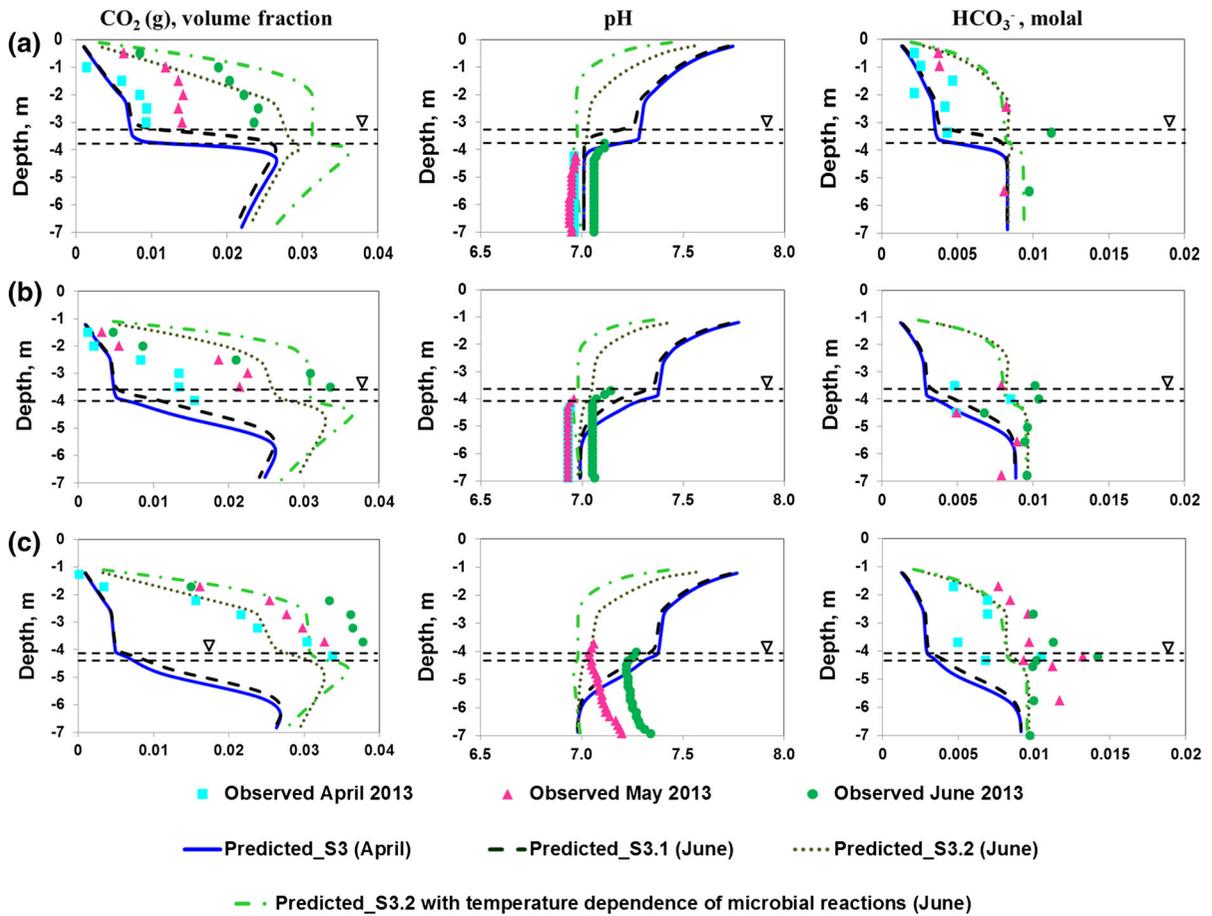
#### $CO_2$ concentrations under seasonal water table and temperature variations

Figure 11 shows simulated and observed profiles of  $CO_2(g)$  volume fraction, pH, and  $HCO_3^-$  concentration between April and June 2013. Note that the water table rises and temperature increases during this time period (Figs. 4, 5). The observations show a consistent increase in  $CO_2$  volume fractions in the vadose zone from April (blue squares) to May (pink triangles) to June 2013 (green circles) at all three wells. A slight

increase in pH from May to June is also observed at all wells. Note that the trend of increasing pH with depth below the water table is observed only in well TT-03. The total dissolved carbonate concentration shows a slight increase below the water table at wells TT-01 and TT-02, but decreases from May to June at TT-03.

Evolving from the simulated steady water table conditions of S3 (blue solid lines) that are representative of April 2013, S3.1 predicts  $CO_2$  production under rising water table conditions (green dashed lines) for June 2013. The simulations shown in Figs. 11a, c estimate a higher partial pressure of  $CO_2$  at TT-01 than TT-03 below the water table (at matching depths), which seems to be related to the difference in water table rise at these two locations (a 0.6 m rise at TT-01 compared to only 0.1 m rise at TT-03; Fig. 4b, c). As discussed above, gas diffusivity decreases sharply with increasing liquid saturations (through the effect of tortuosity, Figure A-1), thus allowing more retention of  $CO_2$  as the water table rises. Although simulation S3.1 is a realistic representation of the up-gradient recharge at the site, the simulated  $CO_2$  profiles are not able to capture the observed increase in volume fraction of  $CO_2$  between April and June 2013 for any of the wells.

Simulation S3.2, which considers a gradient of decreasing temperatures with depth (Fig. 5b), estimates  $CO_2$  concentrations (green dotted lines) that are significantly higher than those obtained with simulation S3.1 and are closer to observed concentrations in June (green circles) at both TT-01 and TT-02 wells. However, this simulation considers temperature dependence on only abiotic reactions and still underestimates observed concentrations of  $CO_2$  at well TT-03. The inclusion of temperature effects on microbially mediated reaction rates (green dash-dot lines) leads to a significant improvement in the estimation of  $CO_2$  concentrations, particularly at TT-03 where a field survey of the microbial populations has confirmed the presence and activity of chemolithoautotrophic bacteria. Both observed and simulated  $CO_2$  concentrations suggest that abiotic processes alone may be important drivers of seasonal  $CO_2$  variability at wells TT-01 and TT-02, with temperature playing an important role on abiotic reaction rates but also on the solubility of  $CO_2$ . As noted above, the partial pressure of  $CO_2$  derived from total dissolved (inorganic) carbon in



**Fig. 11** Simulated and observed profiles of CO<sub>2</sub>(g) volume fraction, pH, and total dissolved carbonate concentration (as HCO<sub>3</sub><sup>-</sup>) versus depth at wells **a** TT-01, **b** TT-02, and **c** TT-03 for three modeled cases all considering abiotic + biotic with both heterotrophic and chemolithoautotrophic pathways and S3, constant water levels and temperature; S3.1, adding water

table fluctuations; and S3.2 adding temperature gradients. Observations for May 2013 are shown for reference only. *Note* that the depth on the *y*-axis corresponds to the modeled domain, and pH measurements in the vadose zone were not available during this time frame

groundwater at the water table is by itself a significant contributor of CO<sub>2</sub> to the vadose zone and is significantly impacted by temperature (Fig. 8). Figure 11 further suggests that the observed total dissolved carbonate concentrations and pH profiles are captured reasonably well by simulation S3.2 (green dash-dot lines) at all wells.

These results suggest that seasonal variability in CO<sub>2</sub> efflux at up-gradient locations within the site (TT-01, TT-02) is governed by abiotic processes, while a large efflux from the down-gradient location is a function of both microbially mediated processes and temperature controls. These results highlight the fact

that CO<sub>2</sub> fluxes at a relatively small flood plain site (~90,000 m<sup>2</sup>) can show significant spatiotemporal variations. Capturing these variations in a model requires adequate process representation including site-specific microbial reactions and reactive transport in both aqueous and gas phases under non-isothermal and variably saturated conditions.

#### Annual carbon fluxes

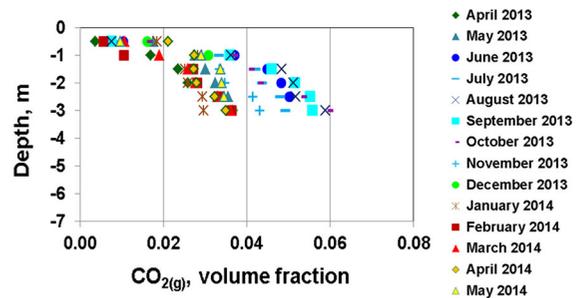
Here we focus on subsurface CO<sub>2</sub> fluxes because these are typically neglected in carbon cycling studies on the basis that they are much lower than atmospheric fluxes

**Table 9** Annual groundwater carbon exports to the river

Simulation	Dissolved inorganic carbon export, (g m <sup>-2</sup> d <sup>-1</sup> )	Dissolved organic carbon export, (g m <sup>-2</sup> d <sup>-1</sup> )
S1	1.208	0.048
S2	1.210	0.042
S3	1.212	0.042
S3.1'	1.210	0.041
S3.2' (with temperature dependence of only abiotic processes)	3.265	0.121
S3.2' (with temperature dependence of abiotic and biotic processes)	3.303	0.342

(Pulliam 1992; Raymond et al. 2000; Richey et al. 2002). Table 9 shows computed groundwater exports of inorganic and organic carbon to the river from the site along the TT transect based on the modeling described here (Simulations S1, S2, S3, S3.1', and S3.2'). Note that for these calculations, simulations S3.1' and S3.2' were run for an entire year to capture the effect of annual water table and temperature variations. Again, a distinction between temperature impacts on abiotic and biotic processes is made in the table. These subsurface exports were computed as the product of the groundwater flow velocity and acetate or bicarbonate concentration at the down-gradient model boundary. For comparison, diffusive fluxes of CO<sub>2</sub> into the atmosphere at the top model boundary were also derived from the modeled CO<sub>2</sub> concentrations in the vadose zone. However, it should be noted that these fluxes do not include effects of plant respiration and transpiration, which for simplicity are not modeled here. These computed CO<sub>2</sub> fluxes to the atmosphere are significantly greater (8.24 kg m<sup>-2</sup> d<sup>-1</sup> using S3.2') than subsurface carbon exports (Table 9) and within the ranges reported for other flood plain sites (Billings et al. 1998; Batson et al. 2015).

Table 9 shows that inorganic carbon exports are at least an order of magnitude greater than organic carbon exports to the river for both steady and transient conditions. Ignoring the biotic pathways (S2 or S3 versus S1) leads to an overestimation of only 12 % in dissolved organic carbon exports to the river; however, the contribution of biotic pathways to atmospheric CO<sub>2</sub> fluxes is almost 230 %. Table 9 further demonstrates a decrease in inorganic carbon export and no change in organic carbon export when annual water table fluctuations are considered (S3.1')

**Fig. 12** Observed profiles of CO<sub>2</sub>(g) concentrations versus depth in the vadose zone at TT-03

as compared to steady water table conditions (S3). Thus, the annual wetting and drying events can have a cyclic effect and even decrease annual carbon fluxes from a given site. Certain studies also corroborate this decrease in groundwater carbon export due to water table fluctuations (Kim et al. 2012, and references therein). On the other hand, incorporation of annual temperature variations greatly increased groundwater carbon exports to the river. An increase of almost 150 % in both inorganic and organic carbon fluxes was obtained when considering temperature fluctuations and their impact on abiotic processes only (e.g., CO<sub>2</sub> solubility) as compared to the base case simulation (S1) in which a constant temperature was assumed. A three-fold increase in organic carbon was further obtained when temperature dependence on microbially mediated reactions was included. Figure 12 shows observed annual CO<sub>2</sub> concentration in the vadose zone at TT-03. It is clearly evident that the highest CO<sub>2</sub> concentrations are obtained between June and November 2013, which is strongly correlated with warming temperature months rather than sporadic

precipitation events or the growing season (April–October). This monthly rise in CO<sub>2</sub> concentration between June and November 2013 is also observed at TT-01 and TT-02 (not shown here). These results clearly highlight that temperature variations exert an outsized control on subsurface carbon fluxes at the Rifle site.

## Conclusions

This study demonstrates that the decoupling of different biogeochemical processes (abiotic, heterotrophic, chemolithoautotrophic) in model simulations can reveal the underlying controls on the distribution and release of CO<sub>2</sub> from a flood plain environment, a critical need within research on subsurface carbon fluxes. The biogeochemical processes affecting carbon dynamics at the site were evaluated using a 2-D, non-isothermal, unsaturated–saturated flow and reactive transport model. Different model simulations highlighted the role of abiotic processes as a major contributor to carbon fluxes in up-gradient locations, while microbial respiration and chemolithoautotrophic oxidation of reduced minerals played a major role in controlling soil CO<sub>2</sub> efflux at a down-gradient location (TT-03) close to the flood plain–Colorado River interface.

We also found significant spatial and temporal heterogeneity in subsurface carbon fluxes at the site. For example, locally high CO<sub>2</sub> concentrations were observed at an NRZ location (TT-03) within the site. The flow and reactive transport modeling suggested that these spatially-variable field observations could not be reproduced without incorporating microbial contributions from chemolithoautotrophic processes (e.g., sulfur and iron oxidation). Results further indicated that temporal variations in modeled CO<sub>2</sub>

concentrations were strongly related to soil temperature. Therefore, adequate process representation (abiotic and biotic reactive processes; variably saturated, non-isothermal flow; reactive gas phase) was required to match observed CO<sub>2</sub> concentrations at the site. Including or excluding these processes also yielded large differences in predicted carbon fluxes from the site. Groundwater exports of organic carbon decreased by only 12 % when biotic pathways were included in the simulations; however, atmospheric CO<sub>2</sub> fluxes showed a difference of up to 230 % when these chemolithoautotrophic pathways were included. Results indicated lower overall carbon exports in groundwater when annual water table fluctuations were considered and almost a three-fold increase when annual temperature gradient variations were considered compared to steady water table and temperature simulations. Overall the simulated subsurface carbon exports (DIC flux of 3.3 and DOC flux of 0.3 g m<sup>-2</sup> d<sup>-1</sup>) from the site to the river were well within the ranges reported for other flood plain sites (Robertson et al. 1999; Richey et al. 2002; Aufdenkampe et al. 2011). In comparison, the annual atmospheric CO<sub>2</sub> fluxes from the site (8.2 kg m<sup>-2</sup> d<sup>-1</sup>) estimated with the model were three orders of magnitude greater than subsurface carbon exports to the river.

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## Appendix 1

See Tables 10, 11 and Fig. A1.

**Table 10** Aqueous complexes considered in the simulations

Reaction	log K (25 °C)	Source
$\text{AlO}^+ \leftrightarrow \text{Al}^{+3} + \text{H}_2\text{O} - 2\text{H}^+$	10.342	1
$\text{AlO}_2^- \leftrightarrow \text{Al}^{+3} + 2\text{H}_2\text{O} - 4\text{H}^+$	22.204	1
$\text{AlOH}^{+2} \leftrightarrow \text{Al}^{+3} + \text{H}_2\text{O} - \text{H}^+$	5.0004	1
$\text{HAIO}_2(\text{aq}) \leftrightarrow \text{Al}^{+3} + \text{H}_2\text{O} - 3\text{H}^+$	15.602	1
$\text{AlSO}_4^+ \leftrightarrow \text{Al}^{+3} + \text{SO}_4^{-2}$	-3.010	1
$\text{Al}(\text{Acetate})^{+2} \leftrightarrow \text{Acetate}^- + \text{Al}^{+3}$	-2.75	3
$\text{Al}(\text{Acetate})_2^+ \leftrightarrow 2\text{Acetate}^- + \text{Al}^{+3}$	-4.600	3

Table 10 continued

Reaction	log K (25 °C)	Source
$\text{CaCl}^+ \leftrightarrow \text{Ca}^{+2} + \text{Cl}^-$	0.293	1
$\text{CaCl}_2(\text{aq}) \leftrightarrow \text{Ca}^{+2} + 2\text{Cl}^-$	0.644	1
$\text{CaSO}_4(\text{aq}) \leftrightarrow \text{Ca}^{+2} + \text{SO}_4^{-2}$	-2.111	1
$\text{CaOH}^+ \leftrightarrow \text{Ca}^{+2} + \text{H}_2\text{O} - \text{H}^+$	12.833	1
$\text{CaNO}_3^+ \leftrightarrow \text{Ca}^{+2} + \text{NO}_3^-$	-0.700	1
$\text{CaCO}_3(\text{aq}) + \text{H}^+ \leftrightarrow \text{Ca}^{+2} + \text{HCO}_3^-$	7.002	1
$\text{CaHCO}_3^+ \leftrightarrow \text{Ca}^{+2} + \text{HCO}_3^-$	-1.047	1
$\text{Ca}(\text{Acetate})^+ \leftrightarrow \text{Acetate}^- + \text{Ca}^{+2}$	-0.930	3
$\text{Ca}(\text{Acetate})_2(\text{aq}) \leftrightarrow 2\text{Acetate}^- + \text{Ca}^{+2}$	-1.900	3
$\text{CO}_3^{-2} \leftrightarrow \text{HCO}_3^- - \text{H}^+$	-10.329	1
$\text{CO}_2(\text{aq}) \leftrightarrow \text{H}^+ + \text{HCO}_3^- - \text{H}_2\text{O}$	-6.345	1
$\text{FeO}(\text{aq}) \leftrightarrow \text{Fe}^{+2} + \text{H}_2\text{O} - 2\text{H}^+$	20.405	1
$\text{FeO}^+ \leftrightarrow \text{Fe}^{+3} + \text{H}_2\text{O} - 2\text{H}^+$	5.650	1
$\text{FeO}_2^- \leftrightarrow \text{Fe}^{+3} + 2\text{H}_2\text{O} - 4\text{H}^+$	21.620	1
$\text{FeOH}^+ \leftrightarrow \text{Fe}^{+2} + \text{H}_2\text{O} - \text{H}^+$	9.315	1
$\text{Fe}(\text{OH})_3^- \leftrightarrow \text{Fe}^{+2} + 3\text{H}_2\text{O} - 3\text{H}^+$	31.000	1
$\text{Fe}(\text{OH})_4^{-2} \leftrightarrow \text{Fe}^{+2} + 4\text{H}_2\text{O} - 4\text{H}^+$	46.000	1
$\text{FeOH}^{+2} \leftrightarrow \text{Fe}^{+3} + \text{H}_2\text{O} - \text{H}^+$	2.205	1
$\text{HFeO}_2^- \leftrightarrow \text{Fe}^{+2} + 2\text{H}_2\text{O} - 3\text{H}^+$	29.207	1
$\text{HFeO}_2(\text{aq}) \leftrightarrow \text{Fe}^{+3} + 2\text{H}_2\text{O} - 3\text{H}^+$	12.018	1
$\text{FeCl}^+ \leftrightarrow \text{Fe}^{+2} + \text{Cl}^-$	0.161	1
$\text{FeCl}^{+2} \leftrightarrow \text{Fe}^{+3} + \text{Cl}^-$	-1.480	1
$\text{FeCl}_2(\text{aq}) \leftrightarrow \text{Fe}^{+2} + 2\text{Cl}^-$	8.172	1
$\text{FeS}(\text{aq}) \leftrightarrow \text{Fe}^{+2} + \text{HS}^-$	2.200	7
$\text{FeSO}_4(\text{aq}) \leftrightarrow \text{Fe}^{+2} + \text{SO}_4^{-2}$	-2.200	1
$\text{FeSO}_4^+ \leftrightarrow \text{Fe}^{+3} + \text{SO}_4^{-2}$	-1.928	1
$\text{FeNO}_2^{+2} \leftrightarrow \text{Fe}^{+3} + \text{NO}_2^-$	-3.150	1
$\text{FeNO}_3^{+2} \leftrightarrow \text{Fe}^{+3} + \text{NO}_3^-$	-1.000	1
$\text{Fe}(\text{CO}_3)_2^{-2} \leftrightarrow \text{Fe}^{+2} + 2\text{HCO}_3^- - 2\text{H}^+$	-13.498	1
$\text{FeCO}_3(\text{aq}) \leftrightarrow \text{Fe}^{+2} + \text{HCO}_3^- - \text{H}^+$	4.879	1
$\text{FeHCO}_3^+ \leftrightarrow \text{Fe}^{+2} + \text{HCO}_3^-$	-1.470	1
$\text{Fe}(\text{Acetate})^+ \leftrightarrow \text{Acetate}^- + \text{Fe}^{+2}$	-1.290	3
$\text{Fe}(\text{Acetate})_2 \leftrightarrow 2\text{Acetate}^- + \text{Fe}^{+2}$	-2.485	3
$\text{H}(\text{Acetate})(\text{aq}) \leftrightarrow \text{Acetate}^- + \text{H}^+$	-4.76	3
$\text{KOH}(\text{aq}) \leftrightarrow \text{K}^+ + \text{H}_2\text{O} - \text{H}^+$	14.437	1
$\text{KCl}(\text{aq}) \leftrightarrow \text{K}^+ + \text{Cl}^-$	2.536	1
$\text{KSO}_4^- \leftrightarrow \text{K}^+ + \text{SO}_4^{-2}$	-0.880	1
$\text{KHSO}_4(\text{aq}) \leftrightarrow \text{K}^+ + \text{SO}_4^{-2} + \text{H}^+$	1.495	1
$\text{K}(\text{Acetate})(\text{aq}) \leftrightarrow \text{Acetate}^- + \text{K}^+$	0.260	3
$\text{MgOH}^+ \leftrightarrow \text{Mg}^{+2} + \text{H}_2\text{O} - \text{H}^+$	11.683	1
$\text{Mg}_4(\text{OH})_4^{+4} \leftrightarrow 4\text{Mg}^{+2} + 4\text{H}_2\text{O} - 4\text{H}^+$	39.750	1
$\text{MgCl}^+ \leftrightarrow \text{Mg}^{+2} + \text{Cl}^-$	0.135	1

**Table 10** continued

Reaction	log K (25 °C)	Source
$\text{MgSO}_4(\text{aq}) \leftrightarrow \text{Mg}^{+2} + \text{SO}_4^{-2}$	-2.300	1
$\text{Mg}(\text{Acetate})^+ \leftrightarrow \text{Acetate}^- + \text{Mg}^{+2}$	-1.280	3
$\text{MgCO}_3(\text{aq}) + \text{H}^+ \leftrightarrow \text{Mg}^{+2} + \text{HCO}_3^-$	7.350	1
$\text{MgHCO}_3^+ \leftrightarrow \text{Mg}^{+2} + \text{HCO}_3^-$	-1.036	1
$\text{NH}_4\text{SO}_4^- \leftrightarrow \text{NH}_3(\text{aq}) + \text{SO}_4^{-2} + \text{H}^+$	-0.940	1
$\text{HNO}_2(\text{aq}) \leftrightarrow \text{H}^+ + \text{NO}_2^-$	-3.225	1
$\text{HNO}_3(\text{aq}) \leftrightarrow \text{H}^+ + \text{NO}_3^-$	1.303	1
$\text{NH}_4^+ \leftrightarrow \text{H}^+ + \text{NH}_3(\text{aq})$	-9.241	1
$\text{NaOH}(\text{aq}) \leftrightarrow \text{Na}^+ + \text{H}_2\text{O} - \text{H}^+$	14.205	1
$\text{NaCl}(\text{aq}) \leftrightarrow \text{Na}^+ + \text{Cl}^-$	0.777	1
$\text{NaSO}_4^- \leftrightarrow \text{Na}^+ + \text{SO}_4^{-2}$	-0.700	1
$\text{NaCO}_3^- + \text{H}^+ \leftrightarrow \text{Na}^+ + \text{HCO}_3^-$	9.815	1
$\text{NaHCO}_3(\text{aq}) \leftrightarrow \text{Na}^+ + \text{HCO}_3^-$	-0.154	1
$\text{Na}(\text{Acetate})(\text{aq}) \leftrightarrow \text{Acetate}^- + \text{Na}^+$	0.100	3
$\text{OH}^- \leftrightarrow \text{H}_2\text{O} - \text{H}^+$	13.995	1
$\text{S}^{-2} \leftrightarrow \text{HS}^- - \text{H}^+$	12.935	1
$\text{H}_2\text{S}(\text{aq}) \leftrightarrow \text{H}^+ + \text{HS}^-$	-6.988	1
$\text{HSO}_4^- \leftrightarrow \text{H}^+ + \text{SO}_4^{-2}$	-1.979	1
$\text{H}_2\text{SO}_4(\text{aq}) \leftrightarrow 2\text{H}^+ + \text{SO}_4^{-2}$	1.021	1
$\text{HSiO}_3^- \leftrightarrow \text{SiO}_2(\text{aq}) + \text{H}_2\text{O} - \text{H}^+$	9.585	1
$\text{CaHSiO}_3^+ \leftrightarrow \text{Ca}^{+2} + \text{SiO}_2(\text{aq}) + \text{H}_2\text{O} - \text{H}^+$	8.575	1
$\text{MgHSiO}_3^+ \leftrightarrow \text{Mg}^{+2} + \text{SiO}_2(\text{aq}) + \text{H}_2\text{O} - \text{H}^+$	8.325	1
$\text{NaHSiO}_3(\text{aq}) \leftrightarrow \text{Na}^+ + \text{SiO}_2(\text{aq}) + \text{H}_2\text{O} - \text{H}^+$	7.754	1

<sup>1</sup> SNL (2007), mostly from Shock et al. (1997)

<sup>2</sup> Rickard (2006)

<sup>3</sup> Reed and Palandri (2006), mostly from Shock and Koretsky (1993) and (Shock et al. 1997)

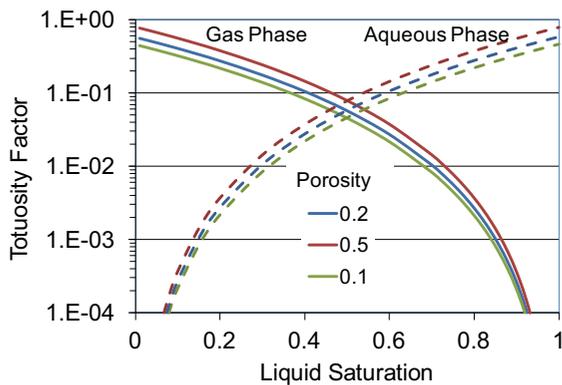
**Table 11** Mineral dissolution/precipitation reactions considered in the simulations

Reaction	log K (25 °C)	Source
$\text{Calcite} \leftrightarrow \text{Ca}^{+2} + \text{H}_2\text{O} + \text{HCO}_3^- - \text{H}^+$	1.849	1
$\text{Goethite} \leftrightarrow \text{Fe}^{+3} + 2\text{H}_2\text{O} - 3\text{H}^+$	0.176	2
$\text{Siderite} \leftrightarrow \text{Fe}^{+2} + \text{HCO}_3^- - \text{H}^+$	-0.192	1
$\text{Pyrite} \leftrightarrow \text{Fe}^{+2} + 1.75\text{HS}^- + 0.25\text{H}^+ + 0.25\text{SO}_4^{-2} - \text{H}_2\text{O}$	-24.653	1
$\text{C}_6\text{H}_{10}\text{O}_5(\text{cellulose}) \leftrightarrow 3\text{Acetate}^- + 3\text{H}^+ - \text{H}_2\text{O}$	-34.647	3

<sup>1</sup> SNL (2007), from Shock et al. (1997) and Helgeson et al. (1978)

<sup>2</sup> Adjusted from SNL (2007) for consistency with Majzlan et al. (2004)

<sup>3</sup> Calculated to yield observed background acetate concentrations at the measured field pH near 7



**Fig. A1** The tortuosity factor  $\tau$  is computed as a function of liquid saturation ( $S_1$ ) and porosity ( $\phi$ ) as  $\tau_l = S_1^{10/3} \phi^{1/3}$  and  $\tau_g = (1 - S_1)^{10/3} \phi^{1/3}$  (Millington and Quirk 1961)

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