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Bank storage in karst aquifers: The impact of temporary intrusion of river water on carbonate dissolution and trace metal mobility

Amy L. Brown [a,*], Jonathan B. Martin [a], Elizabeth J. Screaton [a], John E. Ezell [a], Patricia Spellman [b], Jason Gulley [c]

[a] Department of Geological Sciences, University of Florida, 241 Williamson Hall, Gainesville, FL 32611-2120, United States
[b] Department of Civil and Environmental Engineering, Michigan Technological University, 870 Dow Environmental Sciences, 1400 Townsend Drive, Houghton, MI 49931, United States
[c] Geological and Mining Engineering and Sciences, Michigan Technological University, 630 Dow Environmental Sciences, 1400 Townsend Drive, Houghton, MI 49931, United States

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ABSTRACT

Storms can trigger changes in river stage that alter the hydraulic gradients between rivers and adjacent aquifers. In eogenetic carbonate karst aquifer systems, storms enable river water to intrude >1 km into the adjacent aquifer systems for days to weeks. This process is similar to bank storage of streams in siliciclastic sediments but can have longer temporal and larger spatial scales. River intrusion triggers changes in mineral saturation states and redox conditions in the aquifer due to the input of low pH, low specific conductivity (SpC), and high dissolved organic carbon (DOC) flood water. To assess the effects of river intrusion into karst aquifers, we measured SpC, temperature, pH, redox state, and concentrations of dissolved major and trace elements through an intrusion event at Madison Blue Spring in northern Florida, USA. River water displaced groundwater in the conduit at least 1 km into the aquifer and flowed into the pores of the unconfined aquifer matrix. Distinct Cl^- concentrations between river water and groundwater provide estimates for mixing fractions. The location and magnitude of oxidation of organic matter in the subsurface controlled trace metal concentration, redox state and saturation state of the water with respect to calcite (SIcal). Organic matter oxidation in the phreatic conduits was limited by the terminal electron acceptors (TEAs) present in the conduit water. Calcite dissolution and trace metal sorption were limited by the lower surface area to porosity ratios in the conduits than the matrix. Organic matter oxidation was enhanced in the matrix by mixing with matrix waters with available DO and NO_3^-, resulting in greater CO_2 production and calcite dissolution than in the conduit. After the intruded river water discharged, conditions remained more reducing in the aquifer than baseflow conditions due to the reduction of DO and NO_3^- in the matrix water. The organic matter transported into the aquifer during river intrusion drives carbonate dissolution, alters redox state, and impacts trace metal mobility, impacting groundwater and surface water quality.

1. Introduction

Carbonate karst systems represent an extreme end-member of groundwater–surface water interactions due to the reactive nature and heterogeneous permeability of the aquifer materials. The heterogeneous permeability of karst aquifers is characterized by the formation of conduits and the presence of springs, which provide baseflow to rivers. When rivers flood in karst settings, the springs can also serve as point sources of recharge to the preferential flow paths within the aquifers, focusing reactive surface water into conduits (Hess et al., 1989; Alberic, 2004; Gulley et al., 2011). This focused intrusion of river water could trigger reactions that impact water quality in aquifers as well as in rivers as spring discharge resumes.

River intrusion into springs has similarities to bank storage in siliciclastic systems, where the temporary storage of surface water in riverbanks can trigger periods of increased biogeochemical reactivity (McClain et al., 2003; Gu et al., 2012). River intrusion into karst aquifers differs from bank storage in siliciclastic aquifers due to the presence of conduits in karst aquifers, the composition of the groundwater, and the location of the potential reactive zone. Bank storage is generally restricted to permeable sediments adjacent to river channels (e.g. Gu et al., 2012). In karst systems conduits allow river water to flow hundreds to thousands of meters into the aquifer at depths tens of meters below the water table (Alberic, 2004; Gulley et al., 2011). In limestone that has low matrix permeability, storage of intruded water occurs predominantly in air-filled portions of conduits (Hess et al., 1989). In limestone that has high matrix permeability, river intrusion can occur on an even larger scale because changes in hydraulic gradient between the conduits and the matrix can trigger water flow and storage in the aquifer matrix adjacent to the conduits (Martin et al., 2006; Wong et al., 2012).

The magnitude of the reactions resulting from temporary river intrusion and storage will be controlled by the chemical composition of the interacting waters, the hydrology of the system, the composition of the aquifer materials, and the length of time that water is stored in

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* Corresponding author. Tel.: +1 352 392 2231; fax: +1 352 392 9294.
E-mail address: amy.brown@ufl.edu (A.L. Brown).

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the aquifer, but the relationship between river intrusion and the types and magnitudes of reactions has not been investigated. Reactions resulting from surface water intrusion have been studied in environments where river water is continuously lost to the adjacent aquifer, such as bank filtration settings and sinking rivers (Bourg and Bertin, 1993; Alberic and Lepiller, 1998). In these settings the intruding DOC is oxidized along a redox gradient (Table 1, Reactions 1–3) (Jacobs et al., 1988; Farnsworth and Hering, 2011). Similar reactions occur at sinking rivers entering carbonate aquifers, but in addition, the CO_2 produced by DOC oxidation will hydrate to carbonic acid and enhance calcite dissolution (Table 1, Reaction 4) (Alberic and Lepiller, 1998; Katz et al., 1998). Similar studies of reactions resulting from temporary transient storage of river water in carbonate aquifers are lacking.

Along with the major solutes, intruding surface waters also carry trace metals into karst aquifers, where they accumulate (Vesper and White, 2003, 2004). These trace metals may be either micronutrients or toxins depending on their concentration and speciation and thus are critical for both surface water and groundwater quality. Trace metals such as Fe, Mn, Cu, Ni, and Pb occur in many different forms in surface water, including dissolved and colloidal phases, and chelated with particulate organic matter (Gibbs, 1973; Tipping et al., 1998; Allard et al., 2004; Hartland et al., 2012; Karlsson and Persson, 2012). Much of the Fe occurs as suspended floc particles, defined as conglomerates of multiple inorganic and organic particles held together by a biologic framework (Droppo et al., 1997; Aiken et al., 2011; Plach et al., 2011). Floc particles could be particularly important for metal concentrations because turbulence during surface water intrusion can transport suspended matter deep into the subsurface (Atteia et al., 1998b; Mahler and Lynch, 1999; Vesper and White, 2003; Hartland et al., 2012).

The fate of these trace metals may vary during and following surface water intrusion. Experiments examining infiltration of surface water into the subsurface found that Fe concentration in water decreased due to sorption and aggradation, but other trace metals such as Cu and Pb, may be mobilized by the oxidation of organic matter (Jacobs et al., 1988; Atteia et al., 1998a, 2001). Trace metal precipitates also frequently occur at redox boundaries in air-filled and partially submerged caves (White et al., 2009; Florea et al., 2011; Frierdich et al., 2011; Frierdich and Catalano, 2012). These precipitates are Fe/Mn oxides that contain elevated concentrations of Cu, Ni, and Pb (White et al., 2009; Frierdich et al., 2011; Frierdich and Catalano, 2012). Similar Fe/Mn oxide precipitates have been reported in phreatic cave systems that are subject to periodic river intrusion (Martin, 1990), but the timing and mechanism of formation are not known. Whether surface water intrusion into phreatic cave systems mobilizes or sequesters trace metals, or switches between mobilization and sequestration through time is also unknown. Understanding how trace metal concentration is altered during and after surface water intrusion is critical to predict the impact river intrusion and storage will have on water quality.

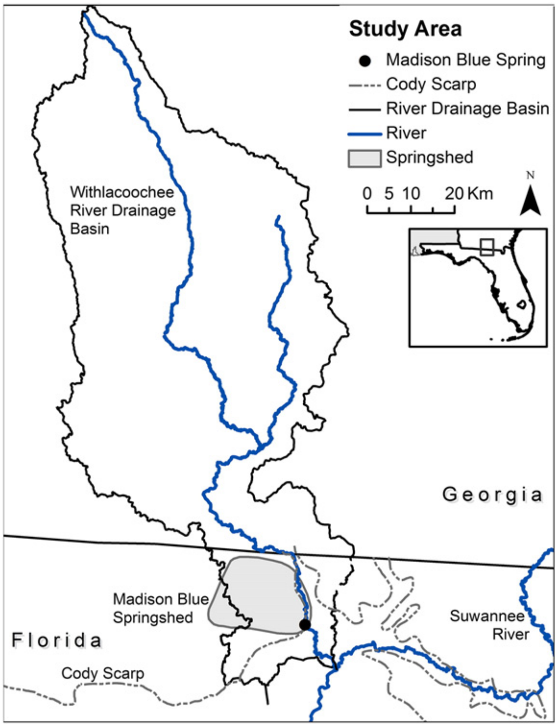

Fig. 1. Location map. Madison Blue Spring is in north-central Florida. The spring discharges to the Withlacoochee River. The drainage area for the river, the recharge area for the spring, and the Cody Scarp are shown on the map.
Source: Suwannee River Water Management District (SRWMD), Florida Department of Environmental Protection (FDEP).

In this study we investigate the timing and magnitude of organic carbon oxidation, calcite dissolution, and mobilization and sequestration of trace metals triggered by intrusion and temporary storage of river water in karst aquifers during spring reversals. We investigate these reactions using chemical sensors and chemical compositions of grab samples collected during baseflow and through a river intrusion event at Madison Blue Spring in north-central Florida. We refer to dissolved components as those that pass through a 0.45 μm filter and use the term organic matter to refer to the total (dissolved and particulate) organic carbon pool. We assume two end-member mixing between river water and groundwater and use Cl^- as a conservative tracer to establish relative amounts of river water and groundwater entering and leaving the spring. This mixing model allows us to estimate the amounts of dissolution of calcite, the consumption of oxygen, the oxidation of DOC, and the sequestration and mobilization of trace metals during and after river water intrusion. Our results show changes in net mobilization and sequestration of major and trace elements per liter through time and demonstrate how intrusion of high-DOC river water into a carbonate karst aquifer affects water quality.

2. Site description

Madison Blue Spring discharges from an unconfined portion of the upper Floridan aquifer (Fig. 1). The spring vent is connected to the aquifer by a network of phreatic conduits, over 7 km of which have been mapped, in the Suwannee Limestone and the underlying Ocala Limestone (Fig. 2). All conduits are completely submerged. Both the

Table 1
Reactions.

Organic carbon oxidation	
Oxygen respiration	(*1*)
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow 106CO_2 + 16NO_3^- + HPO_4^{2-} + 122\ H_2O + 18H^+$	
Denitrification	(*2*)
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94.4\ NO_3^- + 92.4\ H^+ \rightarrow 106\ CO_2 + 55.2\ N_2 + HPO_4^{2-} + 177.2\ H_2O$	
Manganese reduction	(*3*)
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212MnO_2 + 438\ H^+ \rightarrow 106\ CO_2 + 16\ NH_4^+ + HPO_4^{2-} + 318\ H_2O + 212\ Mn^{2+}$	
Calcite dissolution	(*4*)
$CO_2 + H_2O + CaCO_3 \rightarrow 2HCO_3^- + Ca^{2+}$	