Chemical Geology 358 (2013) 61–74

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Controls on diel metal cycles in a biologically productive carbonate-dominated river

Marie J. Kurz [a,*], Véronique de Montety [a,1], Jonathan B. Martin [a], Matthew J. Cohen [b], Chad R. Foster [b]

[a] Department of Geological Sciences, University of Florida, 241 Williamson Hall, Gainesville FL 32611-2120, United States
[b] School of Forest Resources and Conservation, University of Florida, 328 Newins Ziegler Hall, Gainesville FL 32611-0410, United States

ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 25 August 2013
Accepted 27 August 2013
Available online 5 September 2013

Editor: Carla M. Koretsky

Keywords:
Diel cycles
Biogeochemical processes
Trace metals
Calcite co-precipitation
Autotrophic assimilation

ABSTRACT

The 24-hour cycle in solar radiation and subsequent primary productivity by submerged vegetation controls the diel cycles of trace metal concentrations in streams directly, via photochemical reactions and autotrophic assimilation, and indirectly through changes in mineral saturation states, redox conditions, and adsorption reactions. Most prior studies have focused on streams with elevated metal concentrations and thus cycling is not as well understood in pristine streams where the effects of submerged plant metabolism may be critical in controlling the availability and diel cycling of metals. To assess controls on diel metal cycling in an alkaline river with naturally low metal concentrations, water samples were collected every 1–2 h for > 24 hours in three seasons between March 2009 and May 2010 in the Ichetucknee River, north-central Florida (USA), a large ($Q > 6$ m^3/s), spring-fed river flowing over a carbonate karst terrain. Ca^{2+}, Ba, Fe, and U concentrations exhibit statistically significant diel cycles regardless of season, while Mn, and possibly Sr, cycles were present only in the spring. Mn, Ba and Ca^{2+} concentrations increased at night, out of phase with the cycles in pH and carbonate saturation state. Daytime precipitation of calcium carbonate could partially control Mn, and to a lesser extent Ba, cycles through co-precipitation. Fe and U concentrations cycled in phase with solar radiation, pH, and DO concentrations, reaching maxima in late afternoon. Adsorption of cationic Mn and Ba species and anionic U and Fe species could explain the opposing cycles of these two sets of metals as could the photo-reduction of Fe, enhanced by the high water clarity. The diel cycles of Mn, Fe and Ba also appear to be directly controlled by autotrophic assimilation based on estimates of net carbon fixation by submerged vegetation and the metal stoichiometry of the dominant submerged macrophyte and algae in the river. These results demonstrate how multiple biogeochemical processes resulting from solar radiation and associated aquatic plant metabolism likely control diel and seasonal cycles of metals and illustrate the importance of these linked processes in mediating the water quality and environmental availability of metals in pristine streams with naturally low metal concentrations.

1. Introduction

The chemical compositions of streams vary with diel (24-hour) periodicity as a result of the solar photo-cycle and associated biogeochemical processes. The most common and best understood of these processes are the photosynthesis and respiration of submerged aquatic vegetation which alternately produce and consume O_2 and CO_2, resulting in diel cycles in dissolved oxygen (DO) concentrations and pH (Odum, 1956; Simonsen and Harremoës, 1978; Desmet et al., 2011). These metabolic processes in turn mediate mineral saturation state, redox conditions, and sorption potential, thereby potentially indirectly controlling the diel cycling of metals. Diel metal cycles may also be directly controlled by metabolism if metals are assimilated as micronutrients by aquatic plants during primary productivity. Consequently, diel cycles of metal concentrations in streams, if present, are likely the result of multiple geochemical and biological processes, which may be out of phase with each other and with solar radiation, thereby complicating our ability to determine the relative control these processes have on in-stream metal concentrations (e.g., Cohen et al., 2013).

Diel metal cycles exhibit the highest variability in streams with elevated metal concentrations, such as those draining abandoned mine lands, and consequently much prior research has focused on this type of system (e.g., Schwartz and Ploethner, 2000; Nimick et al., 2003; Gammons et al., 2005, 2007; Nimick et al., 2011). In these systems abiotic processes, such as variability in metal speciation and solubility controlled by photo-reactions, can be sufficient to explain observed diel metal cycles (e.g. McKnight et al., 2001; Borman et al., 2010), although biofilms and submerged macrophytes have been shown to indirectly enhance or control these inorganic processes (e.g. Jones et al., 2004; Morris et al., 2005; Shope et al., 2006).

Considerably less work has focused on non-polluted streams with naturally low concentrations of metals. In these systems the direct and indirect effects of submerged plant metabolism may be critical in

---

* Corresponding author. Tel.: +1 352 392 2231; fax: +1 352 392 9294.
E-mail address: mjkurz@ufl.edu (M.J. Kurz).

[1] Present address: Hydrosciences Montpellier UMR 5569, Université Montpellier 2, CC MSE, Montpellier, 34095 cedex 5, France.

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.08.042

controlling the availability and diel cycling of metals. The primary production of aquatic vegetation responds to, and in turn alters, environmental availability of elements (Sterner and Elser, 2002). Plants require certain elements, both macro- and micro-nutrients, in particular and generally constrained proportions during growth for metabolic functions (Elser et al., 2003) and to maintain compositionally homeostatic biomass (Frost et al., 2005; Kerkhoff et al., 2005). However, biomass stoichiometry (commonly assessed as elemental/C ratios) may also adjust in response to changes in element availability and light (Sterner et al., 1998; Persson et al., 2010), as may the relative abundance of plant species with varying elemental requirements (Hall, 2004). A better understanding of the reciprocal interactions between biological and geochemical processes controlling the cycling and availability of metals is therefore critical not only for managing water quality and assessing trace metal mobility, but also to evaluating the structure and health of stream ecosystems, particularly in systems where low concentrations may create micronutrient limitation.

Previous work has identified a number of inorganic processes which can control diel cycling of metals in streams, many of which are regulated by metabolism. Precipitation and dissolution of carbonate minerals may control diel metal cycling, particularly in high pH systems at or near carbonate mineral saturation. Ecosystem metabolism regulates the saturation state of carbonate minerals, by increasing pH during the day in response to autotophic assimilation of bicarbonate, and decreasing pH at night due to respiration (Spiro and Pentecost, 1991; Liu et al., 2006, 2008; de Montety et al., 2011). Carbonate precipitation should decrease, and dissolution increase, Ca^{2+} concentrations, although these changes are not always observed in supersaturated streams (Usdowski et al., 1979; Neal et al., 2002; Parker et al., 2007). Nonetheless, precipitation and dissolution of calcite could influence concentrations of divalent metals that partition strongly with calcite, such as Cd, Mn, Fe, and Zn (Lorens, 1981; Dromgoole and Walter, 1990; Tesoriero and Pankow, 1996; Nimick et al., 2003; Parker et al., 2007). This co-precipitation has been observed to remove Cd, Cu, Mn, Pb and Zn with distance downstream (Schwartz and Ploethner, 2000) and to create simultaneous cycles of Cd concentrations and carbonate precipitation and dissolution in a eutrophic lake (Cicerone et al., 1999). At low concentrations, adsorption of divalent metals to calcite surfaces may also affect dissolved metal concentrations (Zachara et al., 1991; Mettler et al., 2009). Diel cycles of some dissolved metals may therefore be linked to variations in saturation state and resulting precipitation or dissolution of calcite, caused by photosynthesis and respiration.

In systems with elevated metal concentrations, redox state has been shown to control diel cycles in dissolved Fe and Mn through both photochemical reactions and metabolically enhanced oxidation processes. Daytime increases in Fe and Mn concentrations have been attributed to photo-reduction of Fe- and Mn-oxides (McKnight et al., 1988; Sunda and Huntsman, 1994; Sullivan et al., 1998; Gammons et al., 2005). However, these reaction rates are pH controlled and photoreduction is not expected to be a major control on diel Fe cycles in pH-neutral to basic streams (McKnight et al., 2001; Parker et al., 2008; Borman et al., 2010). Instead, dissolved Fe and Mn concentrations typically decrease during the day in streams with high pH, suggesting the diel cycles of these metals may be primarily controlled by increased daytime oxidation as a result of photosynthesis or microbially mediated oxidation (Brick and Moore, 1996; Scott et al., 2002; Parker et al., 2007), the rate of which is further enhanced by daytime increases in pH (Stumm and Morgan, 1996).

Adsorption reactions are also pH- as well as temperature-dependent and can be influenced by the pH metabolically produced by submerged macrophytes and biofilms (e.g. Jones et al., 2004; Shope et al., 2006; Carling et al., 2011). Cationic adsorption to substrates such as metal oxides and biofilms generally increases with pH and, to a lesser extent, temperature (Nimick et al., 2003 and references therein) and thus the concentrations of adsorbing cationic species in solution should decrease during the day. Conversely, anionic absorption generally decreases with pH and temperature producing increased daytime concentrations in anionic species in solution (e.g. Carling et al., 2011). Adsorption and sequestration of metals into biofilms has even been shown to control instream diel metal cycles in the absence of diel pH changes in the bulk water column by providing microenvironments unique from the bulk stream chemistry (e.g. Morris et al., 2005, 2006; Kamennaya et al., 2012).

The phase and amplitude of diel cycles as well as seasonal changes in these cycles are critical to assess overlapping geochemical and biological processes that may be controlling diel metal cycling (e.g., Cohen et al., 2013). The connection that diel cycling has to solar radiation, both indirectly through the co-precipitation with carbonate minerals and productivity of submerged vegetation and directly through photic-reactions, suggests that seasonal changes in solar radiation could affect both the timing and magnitude of diel metal cycles. Variations in seasonal frequencies may help distinguish relative controls on diel cycling through comparison with changes in solar radiation and plant metabolism at annual periodicities. Such an evaluation requires observing a model system with little seasonal changes in flow to minimize complications caused by changes in hydrologic characteristics including variations in discharge and water compositions (e.g. Sullivan and Drever, 2001; Nimick et al., 2005).

In this study, we assess the presence of and potential controls on diel metal cycles across a range of seasons in the Ichetucknee River, an entirely spring-fed river in north-central Florida characterized by neutral to basic pH, low metal concentrations, and high primary productivity. Florida's karstic, spring-fed rivers, including the Ichetucknee River, have stable chemical compositions and discharge, extreme water clarity and thus high productivity, which make them ideal for this study. We hypothesized that diel cycles of metals in the Ichetucknee River may be controlled by metabolism of the submerged vegetation; indirectly, via co-precipitation with calcium-carbonate (e.g., de Montety et al., 2011); and directly by autotrophic assimilation (e.g., Roberts and Mulholland, 2007; Heffernan and Cohen, 2010; Cohen et al., 2013). To test this hypothesis, we compare observations of the magnitude and phase of metal cycles with calculations of predicted removal due to co-precipitation and assimilation, as well as changes in redox chemistry and adsorption. Because multiple processes may control metal concentrations, we are unable to uniquely identify the magnitude of each process, but we are able to show which processes are likely to have primary or secondary affects, or have no effect, over diel metal cycles. This improved understanding of the controls on metal cycling in pristine streams will be important for monitoring of water quality and assessing the potential effects of metals as micro-nutrients on primary production in streams with abundant submerged vegetation.

2. Methods

2.1. Study site

The Ichetucknee River is fed by eight named springs and numerous small unnamed springs. The river flows approximately eight kilometers before discharging into the Santa Fe River, a tributary of the Suwannee River. The springs feeding the river are sourced from the Floridan Aquifer, an eogenetic carbonate karst aquifer (Vacher and Mylroie, 2002) characterized by high matrix storage (Budd and Vacher, 2004; Florea and Vacher, 2006) and active conduit-matrix exchange (e.g., Martin and Dean, 2001; Bailly-Comte et al., 2010). The springs drain an estimated 960 km^2 springshed (Champion and Upchurch, 2006) that includes both confined and unconfined areas of the Floridan Aquifer (Fig. 1a & b). The Ichetucknee River in the southern, unconfined portion of the springshed flows directly on top of the Ocala Limestone, which comprises the Floridan Aquifer. The gradient along the entire river is less than 1 m/km and, although there is little evidence for physical erosion, bedrock is increasingly exposed downstream in and along the channel. The entire study area is within the boundaries of Ichetucknee Springs State Park and thus land use immediately surrounding the