



Links between climate change, water-table depth, and water chemistry in a mineralized mountain watershed



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ARTICLE INFO

Article history:

Received 7 February 2013

Accepted 2 July 2013

Available online 19 July 2013

Editorial handling by M. Kersten

ABSTRACT

Recent studies suggest that climate change is causing rising solute concentrations in mountain lakes and streams. These changes may be more pronounced in mineralized watersheds due to the sensitivity of sulfide weathering to changes in subsurface oxygen transport. Specific causal mechanisms linking climate change and accelerated weathering rates have been proposed, but in general remain entirely hypothetical. For mineralized watersheds, a favored hypothesis is that falling water tables caused by declining recharge rates allow an increasing volume of sulfide-bearing rock to become exposed to air, thus oxygen. Here, we test the hypothesis that falling water tables are the primary cause of an increase in metals and SO₄ (100–400%) observed since 1980 in the Upper Snake River (USR), Colorado. The USR drains an alpine watershed geologically and climatologically representative of many others in mineralized areas of the western U.S. Hydrologic and chemical data collected from 2005 to 2011 in a deep monitoring well (WP1) at the top of the USR watershed are utilized. During this period, both water table depths and groundwater SO₄ concentrations have generally increased in the well. A numerical model was constructed using TOUGHREACT that simulates pyrite oxidation near WP1, including groundwater flow and oxygen transport in both saturated and unsaturated zones. The modeling suggests that a falling water table could produce an increase in metals and SO₄ of a magnitude similar to that observed in the USR (up to 300%). Future water table declines may produce limited increases in sulfide weathering high in the watershed because of the water table dropping below the depth of oxygen penetration, but may continue to enhance sulfide weathering lower in the watershed where water tables are shallower. Advective air (oxygen) transport in the unsaturated zone caused by seasonally variable recharge and associated water table fluctuations was found to have little influence on pyrite oxidation rates near WP1. However, this mechanism could be important in the case of a shallow dynamic water table and more abundant/reactive sulfides in the shallow subsurface. Data from WP1 and numerical modeling results are thus consistent with the falling water table hypothesis, and illustrate fundamental processes linking climate and sulfide weathering in mineralized watersheds.

Published by Elsevier Ltd.

1. Introduction

Climate change is significantly altering mountain hydrologic systems through changes in the distribution and volume of snowpack, shifts in the timing of spring snowmelt runoff, and the melting of alpine glaciers (e.g., Pederson et al., 2004; Mote et al., 2005; Barnett et al., 2008; Clow, 2010). A growing number of studies suggest that climate change is also impacting the chemistry of mountain lakes and streams in many regions (Wögrath and Psenner, 1995; Sommaruga-Wögrath et al., 1997; Rogora et al., 2003; Thies et al., 2007; Baron et al., 2009; Lami et al., 2010; Mast et al., 2011; Todd et al., 2012). These studies report rising concentrations of multiple dissolved constituents over the past three decades (SO₄

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reases of 1–10 mg/L, or 50–150%, are typical), and attribute these changes to factors ultimately driven by climate warming. Proposed causal mechanisms include: (1) less dilution of solutes due to declining snowpack and a lower volume of dilute stream inflows; (2) increased weathering reaction rates due to warmer air and ground temperatures; (3) reduction in the extent and duration of snow and ice cover resulting in warmer summer ground temperatures, further enhancing mechanism 2; (4) melting of glaciers, rock glaciers, and permafrost contributing solute-rich meltwater to lakes and streams; (5) a decline in the extent of permafrost and seasonally frozen ground enhancing weathering in parts of the shallow subsurface previously shielded from the flow of water and oxygen; and (6) water tables dropping due to decreased groundwater recharge, resulting in more rock exposed to air and enhanced mineral oxidation. Though all of these mechanisms appear plausible, they remain speculative (except, perhaps, dilution

glacial melt-water influences); studies that directly examine these mechanisms and test whether they are indeed capable of producing observed changes in surface water chemistry are lacking.

Weathering rates in mineralized watersheds containing abundant pyrite (the most common sulfide mineral) and other sulfides may be particularly sensitive to climate change given the sensitivity of sulfide weathering rates to oxygen availability in the subsurface. Mast et al. (2011) examined changes in the chemistry of lakes in three high-elevation wilderness areas in Colorado, USA, from 1985 to 2008. They observed the largest solute concentration increases (up to 250% for SO_4) in lakes having contributing areas with hydrothermally altered bedrock, and attributed the upward trends to enhanced pyrite weathering. Todd et al. (2012) presented a 30-year streamwater chemistry data set from the Upper Snake River (USR) in the Front Range of Colorado, which drains a mineralized alpine watershed with widespread hydrothermal alteration and abundant sulfides, and is naturally acidic and metal-rich (natural acid-rock drainage, or NARD). Dissolved concentrations of Zn and other metals increased by 100–400% (400–2000 $\mu\text{g/L}$) during low-flow months, when metal concentrations were highest. Concentrations of SO_4 and other major ions showed similar relative increases. Both studies examined the likelihood of various possible climate-change-related causes for these trends, taking into account local climate and streamflow records and other available information, and concluded that falling water tables and/or melting of frozen ground were most likely responsible. The potential importance of climate in NARD production has been discussed in review papers (e.g., Plumlee and Logsdon, 1999; Nordstrom, 2011), but studies of specific processes linking climate and sulfide weathering on a watershed scale are few (Nordstrom, 2009).

The prospect of rising background metal concentrations in mineralized areas is concerning because of potential negative impacts on downstream ecosystems and water resources. Rising background concentrations could also significantly complicate the process of establishing attainable remediation objectives at mine sites. Critical questions regarding the extent of this phenomenon and how high metal concentrations may rise in the future cannot be answered without an improved understanding of controlling processes. Chemical and hydrologic data collected since 2005 from the U.S. Geological Survey's Handcart Gulch Research Watershed (HCG), located adjacent to the USR watershed, provide a unique opportunity to investigate processes controlling the increasing metal concentrations reported by Todd et al. (2012).

In this study, we utilize data from a deep monitoring well (WP1) located at 3687 masl on the ridge dividing HCG and USR watersheds to test the hypothesis that falling water tables, specifically, are a primary cause of rising metal concentrations in the USR. First, we examine trends and interrelationships in groundwater chemistry and water table elevation data to determine if they are consistent with this hypothesis. We then use these data along with drill core mineralogy and measured oxygen profiles to construct a 1-D reactive solute transport model that includes both diffusive and advective oxygen transport in the unsaturated zone (UZ). The model is used to simulate possible past and future water table drops in the vicinity of WP1 and compute resulting changes in groundwater chemistry, addressing the question of whether falling water tables may be capable of producing the substantial increases in metal concentrations observed in the USR. The model is also used to explore fundamental relationships between water table depth/dynamics and sulfide weathering rates in mineralized watersheds, such as the effects of large seasonal water table oscillations (due to seasonal recharge) on pyrite oxidation. The objective of the modeling is therefore to utilize unique subsurface data from an unmined mineralized area to test the sensitivity of local groundwater chemistry to water table elevation. These data are too few to develop a definitive model of the site and confidently

identify the most likely cause of rising metal concentrations in the USR. However, the data are sufficient for constructing a model that can be used to test the viability of the falling water table hypothesis, and to investigate possible links between climate, water table depth, and sulfide weathering in a mountain setting.

2. Site description

The USR drainage and HCG are small alpine watersheds (12 and 6 km^2 , respectively) located in the Colorado Front Range in the southern Rocky Mountains (Fig. 1). Surface elevations range from 3200 to 4000 masl. Mean annual air temperature is in the range of -1.0 to 0.5 $^\circ\text{C}$ based on data from the meteorological station in HCG and nearby snowpack telemetry (SNOTEL) sites at elevations >3300 masl. Mean annual total precipitation at these SNOTEL sites is 75–85 cm, with 55–80% falling as snow. The USR and Handcart Creek (HC) are perennial snowmelt-dominated streams. Springtime high flows are typically 0.8 and 0.15 m^3/s , respectively, and low flows in autumn and winter are typically 0.05 and 0.02 m^3/s , respectively, (Kahn et al., 2008; Todd et al., 2012). No glaciers are present, but upper HCG hosts a large, multi-lobed rock glacier that may be active (Cuddus and Caine, 2012). No significant land disturbances have occurred in the area shown in Fig. 1 (site area) during the past 30 years.

The USR watershed and HCG are located on the periphery of the Montezuma Mining District within the Colorado Mineral Belt. Although extensive historical mining occurred within the district from the 1860s to the 1940s, only a few relatively small abandoned mines are present in the USR watershed and these have little or no influence on streamwater chemistry (Belanger, 2002; Neubert et al., 2011; Crouch, 2011). The watersheds are underlain by fractured Precambrian metamorphic rocks consisting of gneiss, schist, and amphibolite that have been intruded by small Proterozoic granitic bodies and Tertiary-age, felsic-porphyry stocks (Lovering, 1935). Ferricrete deposits (iron-hydroxide-cemented alluvium and colluvium) and/or iron fens exist near the USR and HC along most of their course. Disseminated and veinlet-hosted pyrite occurs in large zones of hydrothermal alteration related to the Tertiary intrusions (Caine et al., 2008). Veins and veinlets may contain other sulfide minerals including sphalerite, galena, chalcopyrite, and enargite (Lovering, 1935).

Natural weathering of pyrite and associated sulfides results in USR and HC water having low pH (typically 3.0–4.5) and elevated concentrations of SO_4 (typically 50–300 mg/L) and dissolved metals. In the USR, elevated metals (commonly >0.1 mg/L) include: Al, 3–10 mg/L ; Fe, 0.5–2.0 mg/L ; Zn, 0.4–1.4 mg/L ; and Mn 0.7–3.0 mg/L (Todd et al., 2012). In HC, elevated metals include: Al, 2–25 mg/L ; Fe, 0.5–20 mg/L ; Zn, 0.03–0.20 mg/L ; Mn 0.06–0.35 mg/L ; and Cu, 0.03–0.20 mg/L (Verplanck et al., 2008). Over the past 30 yr, concentrations of dissolved metals and other constituents in USR samples collected at site SW-044 (Fig. 1) have displayed statistically significant upward trends in all seasons, with the largest increases observed during low-flow months when concentrations are the highest (Todd et al., 2012). For example, in September, Zn and SO_4 concentrations have increased from roughly 0.4 and 50 mg/L , respectively, to roughly 1.4 and 150 mg/L , respectively, between 1980 and 2011 (Fig. 2). Todd et al. (2012) performed a trend analysis on several climate indices computed from temperature and precipitation data from the three closest SNOTEL sites, and on streamflow indices computed from flows measured at a gage on the Snake River about 10 km downstream from SW-044. Mean annual air temperature (MAAT) and mean summer air temperature (June–September, MSAT) displayed statistically significant upward trends having median magnitudes of 0.34 and 0.33 $^\circ\text{C}/\text{decade}$, respectively. No other indices displayed

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