Natural acid rock drainage in the Judith Mountains, Central Montana, USA

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Abstract This paper is a summary of an ongoing investigation of acid rock drainage in the Judith Mountains, Montana. Three streams draining the central peaks of the range are acidic (pH < 4) in their headwaters and become pH-neutral with distance downstream. The acidic drainage is attributed to natural weathering of pyrite-rich, hydrothermally-altered igneous rock that outcrops on the crest of the mountain range. Concentrations of copper, zinc, and thallium in the stream waters are locally well above regulatory standards. The study area provides a useful comparison to nearby watersheds that have been heavily disturbed by mining.

Keywords Geochemistry, zinc, copper, ferricrete, stream tracer, monitoring

Introduction

The Judith Mountains, one of the classic "island" mountain ranges that rise from the Great Plains of central Montana, consist of a number of late Cretaceous to early Tertiary alkaline plutons that have intruded into Paleozoic and Mesozoic sedimentary rock (Wallace 1953; Porter and Wilde 1999). Near the center of the Judith Mountains, three small streams – Collar Gulch, Chicago Gulch, and Armells Creek – form a radial drainage pattern around a zone of pyrite-rich, hydrothermally-altered porphyry termed Red Mountain (Fig. 1; described in Lindsey and Fisher 1985). Each of these streams transitions from acidic to near-neutral pH with distance downstream, is actively forming hydrous iron and aluminum oxide precipitates, and has abundant ferricrete deposits that have been incised by each active stream channel (Fig. 2). Although historic mining of precious metals has occurred elsewhere in the Judith Mountains (Robertson 1950;

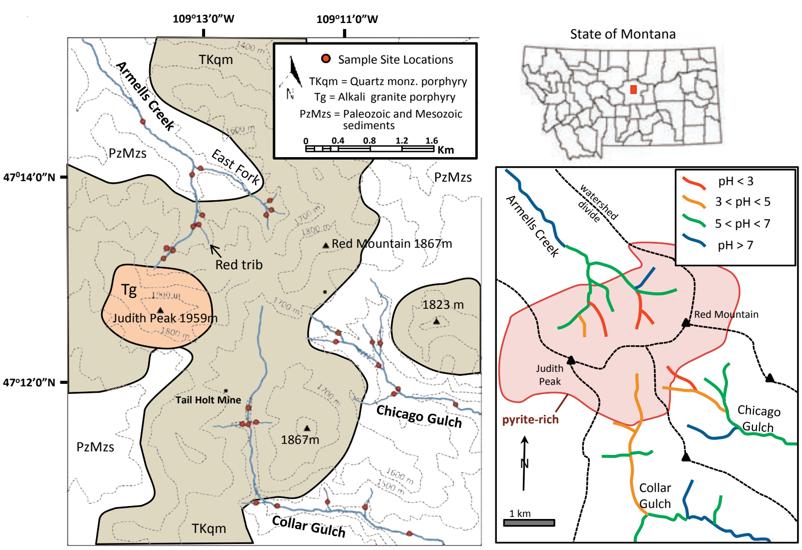

Fig. 1 Location map and geology of the study area. Inset at lower right shows pH values measured at baseflow conditions and border of pyrite-rich alteration. Geology is from Goddard (1998).

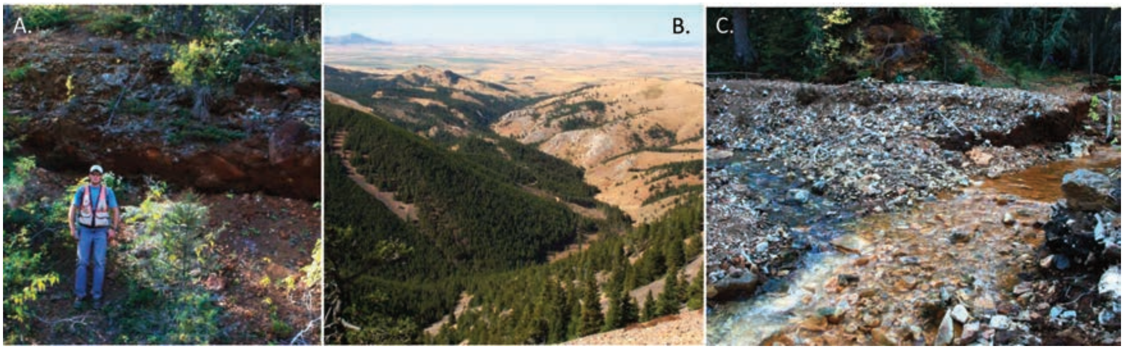

***Fig. 2** Photographs of Armells Creek. A) Ferricrete deposit, approximately 5 m above modern channel; B) View of Armells Creek from Red Mountain, looking NW (North Moccasin Range in background); C) Junction of east and west forks of Armells Creek, with Al-hydroxide forming in mixing zone.*

Zhang and Spry 1994), the three watersheds of interest have not been heavily impacted by mining. Therefore, the study area provides an excellent opportunity to examine the geochemistry of trace metals and metalloids in acidic streams in a natural setting. In addition, the study area could be utilized as a reference site for pre-mining water quality conditions for mining-impacted streams elsewhere in the Judith Mountains, or in nearby mining districts that have similar geology, such as the closed Zortman-Landusky Au mines in the Little Rocky Mountains (Wilson and Kyser 1988; Kill Eagle *et al.* 2009) or the closed Kendall Au mine in the North Moccasin Mountains (Lindsey 1985).

The main objective of the current study, funded by the U.S. Bureau of Land Management, is to collect seasonal data on streamflow and water chemistry for the three drainages of interest, with a focus on documenting concentrations and loads of trace metals and metalloids. To augment routine water quality monitoring, three types of field experiments are being conducted: 1) Continuous tracer injection studies (Kimball *et al.* 2002) to quantify longitudinal changes in the concentrations and loads of contaminants of concern, including Al, Cu, Fe, Mn, Pb, Zn, F, sulfate, and thallium (Tl); 2) Diel (24-h) sampling to examine short-term changes in the concentrations of trace metals (Gammons *et al.* 2005; Parker *et al.* 2007; Nimick *et al.* 2011); and 3) Collection of a longitudinal transect of natural ferricrete samples for trace metal analysis, to compare with modern Fe- and Al-hydroxide precipitates. The latter method was recently proposed (Nimick *et al.* 2009) as an assessment technique to compare pre-mining *vs.* post mining water quality in streams where no pre-mining baseline exists. Although the above activities are being performed in all three drainages of interest, this paper will focus on the results of the synoptic tracer study in Armells Creek.

Methods

Field activities in the Judith Mountains for this project began in Sept. of 2011, and will continue through the Fall of 2013. Water quality samples are being collected approximately every two months (except winter) from selected monitoring sites (Fig. 1). Streamflow measurements are being measured at a number of these sites, with continuous water level recorders at the mouth of each stream. During June of 2012, a continuous tracer injection study was performed in Armells Creek, following the method of Kimball *et al.* (2002). In addition, a synoptic set of water samples, in-stream precipitates, and near-stream ferricrete deposits was collected from Armells Creek in July of 2012. Similar tracer tests and ferricrete samplings are scheduled for Collar Gulch and Chicago Gulch in 2013. The discussion which follows mainly deals with the results of the June 2012 tracer study in Armells Creek.

A concentrated KBr stock solution was injected into the headwaters of Armells Creek for over 24 hours at a constant rate of 11 mL/min. Tracer breakthrough and time-to-saturation were monitored at two downstream locations using automated samplers. Water samples collected from the samplers were also used to test for diel (24-h) changes in trace metal concentration. After KBr saturation was achieved, a set of filtered (0.2 µm) and non-filtered water samples was collected along the main channel of Armells Creek and its tributaries at predetermined locations spaced approximately 100 m apart. At each location, field parameters (pH, temperature, conductivity, dissolved oxygen) were measured using a datasonde, and alkalinity was measured in the field by potentiometric titration. Streamflow at each main stem location was calculated based on the measured dilution of the KBr tracer (Kimball *et al.* 2002). All water samples were preserved with 1 % HNO_3 (except samples used for ion chromatography) and later analyzed by ICP-AES for major and trace metals and by IC for anions, including bromide. The synoptic samples were later reanalyzed by ICP-MS for improved detection limits. Solute loads were calculated as the product of concentration and streamflow.

Results

Synoptic changes in the concentrations of iron (Fe), aluminum (Al), manganese (Mn), zinc (Zn), copper (Cu) and thallium (Tl) collected during the Armells Creek tracer test are shown in Fig. 3. Metal loads for the same sampling stations are shown in Fig. 4. The combined data can be used to infer hydrogeochemical processes occurring in Armells Creek. Although a significant amount of dissolved Fe and Al exists in the upper reaches of the stream, both of these elements are mainly present as suspended solids below the confluence of the east and west forks of Armells Creek (Fig. 3A, 3B). Precipitation of Fe(III)- and Al-hydrous-oxides is consistent with the observed increases in pH (Fig. 1), and was confirmed visually by the presence of orange and white precipitates in the stream (Fig. 2C). Examination of the trends in Fe and Al loads (Fig. 4A, 4B) shows significant inputs of these metals from the so-called "red tributary" and the east fork of Armells. The "red tributary" is a small flow of highly acidic ($pH < 3$), Fe-stained water that enters Armells Creek from the east, high on the flanks of Red Mountain (Fig. 1). Upstream, this tributary has flows that emanate from the ground as a series of springs, with extensive ferricrete deposits covered with moss carpeting the forest floor. Diffuse groundwater seepage also enters Armells Creek below the "red tributary", explaining the increases in loads and concentrations of most of the metals (excepting Cu) at distances of 500 m to 750 m below the tracer injection site. These groundwater seeps may be from hillslope drainage re-mobilizing Fe from ferricrete deposits on banks above the existing stream course. The east fork is the main source of additional metal loading in lower Armells Creek (Fig. 4). The drainage areas and flows of the east and west forks are approximately similar, and although the mouth of the east fork typically has slightly higher pH than the west fork, it also contains highly acidic springs in its headwaters along the flanks of Red Mountain (Fig. 1).

Concentrations of Cu and Zn in upper Armells Creek are well above chronic regulatory standards (MDEQ 2010) for protection of aquatic life. Because these standards – shown as red lines in Fig. 3 – are dependent on hardness, they need to be computed for each individual sample based on the measured Ca and Mg concentrations. Also, it should be noted that aquatic standards in Montana are currently based on "total recoverable" metal concentrations (MDEQ 2010). Although concentrations of dissolved Zn, total Zn, and dissolved Cu dropped below aquatic standards downstream of the confluence of the east and west forks, concentrations of total Cu (acid recoverable) remained close to the standard. The de-

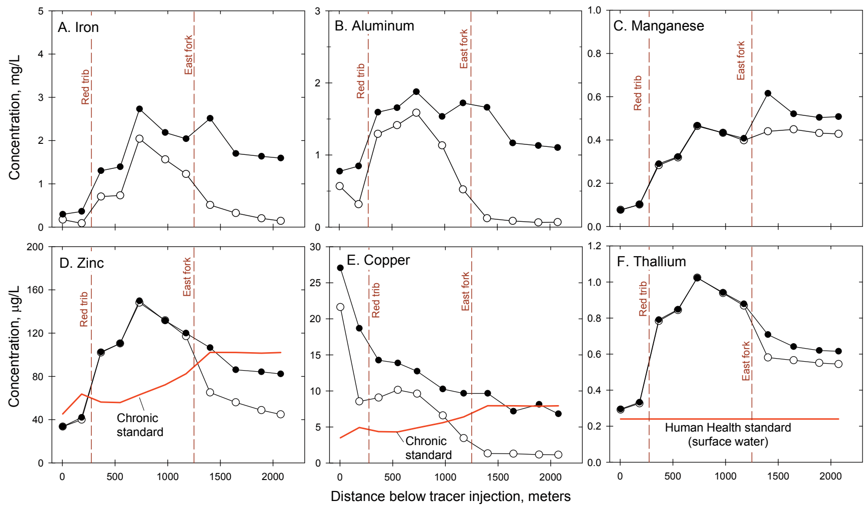

Fig. 3 *Synoptic changes in the concentrations of total (filled symbols) and dissolved (open symbols) iron (A), aluminum (B), manganese (C), zinc (D), copper (E), and thallium (F) in Armells Creek. Also shown are regulatory standards for protection of aquatic life (chronic-Zn, -Cu) and human health (Tl). Locations of major tributary streams are shown with dashed lines. Note: top row of diagrams is in mg/L; bottom row is in µg/L.*

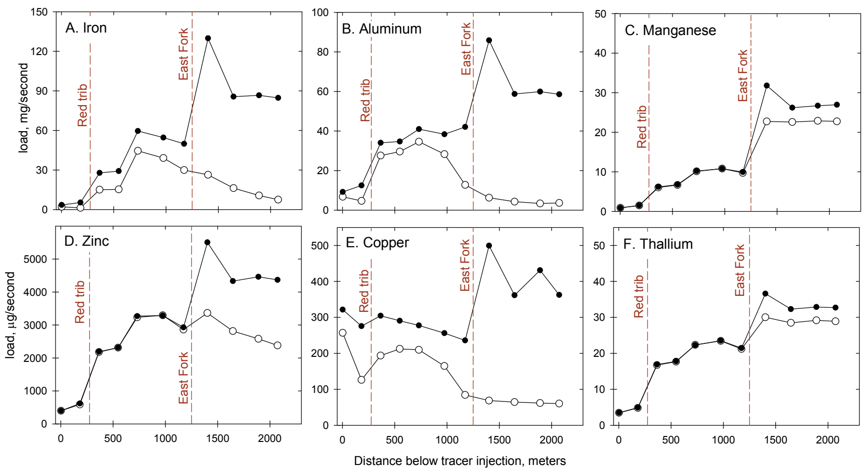

Fig. 4 *Synoptic changes in the loads of total (filled symbols) and dissolved (open symbols) iron, aluminum, manganese, zinc, copper, and thallium in Armells Creek. Locations of major tributary streams are shown with dashed lines. Note: top row (A-C) of diagrams is in mg/second; bottom row (D-F) is in µg/second.*

viation between the dissolved and total lines below the east and west fork confluence (Figs. 3, 4) indicates partitioning of trace metals into freshly formed Fe and Al hydrous oxide precipitates in the approximate order Cu > Zn > Mn > Tl. Although the concentrations of thallium in Armells Creek are very low (around 1 µg/L or less), Tl is highly toxic to most living organisms (Peter and Viraraghavan 2005). Montana DEQ does not list an aquatic life standard for Tl, but the current human health standard for Tl in surface water in Montana is 0.24 µg/L (MDEQ 2010). Concentrations of Tl are well above this standard for all of Armells Creek (Fig. 3F), and the element apparently exists primarily in the dissolved phase. In this study, the hydrogeochemical behavior thallium is very similar to that of zinc, as has been reported from flooded mines in Sardinia (Cidu *et al.* 2007).

Water samples collected hourly near the mouth of Armells Gulch during the June 2012 tracer test were analyzed by ICP-AES to test for diel fluctuations in trace metal concentration. Concentrations of total Zn decreased during the day from an early morning high of 63 µg/L to a late afternoon low of 44 µg/L. This type of diel fluctuation in Zn concentration is typical of small, pH-neutral streams draining abandoned mine lands, and is thought to be caused by 24-h changes in pH and water temperature coupled with adsorption to metal oxide and biotic surfaces (Nimick *et al.* 2011). Among the other metals of interest, a weak diel pattern with large scatter was noted for total Al and total Fe, with higher concentrations at night and lower concentrations during the day. Nighttime increases in the concentrations of particulate metals have also been noted from many streams draining abandoned mine lands (Nimick *et al.* 2011). Although interesting, the diel cycles noted in Armells Creek are relatively small in magnitude, and should not be too much of a concern in the interpretation of synoptic or long term monitoring data.

Discussion

The geology of upper Armells Creek is dominated by hydrothermally-altered and pyrite-rich intrusive rocks that underlie Red Mountain and Judith Peak, whereas lower Armell Creek flows through outcrops of Paleozoic limestone and younger sediments (Fig. 1). This geological transition explains the overall evolution of the stream from acidic and metal-rich in its headwaters, to pH-neutral and relatively metal-poor near its mouth. The abundance of ferricrete in the headwaters of Armells Creek, Collar Gulch and Chicago Gulch, all of which drain different sides of Red Mountain, suggests that the acidic drainage is natural, and has been occurring for millennia. No large mines occur in the study area, although some surface disturbances exist, including road construction and installation of radio and radar towers on the summits of Red Mountain and Judith Peak. Chemical analysis of the ferricrete deposits are in progress, following the methods of Nimick *et al.* (2009), to see if hydrogeochemical conditions present today in upper Armells Creek are similar to what was present during ferricrete formation. Findings will be reported at the 2013 IMWA meeting.

The hydrothermally-altered porphyry rocks at the headwaters of Armells Creek resemble similar rocks exposed 90 km to the north in the Little Rocky Mountains. Here, the Zortman-Landusky open pits were mined for gold at a large scale by cyanide heap-leach methods between 1979 and 1998, and left behind a legacy of serious acid rock drainage in Swift Gulch (Kill Eagle *et al.* 2009). The Judith Mountains also share geologic similarities to the closed Kendall gold mine in the North Moccasin Mountains, located just 20 km west of the study area. At Kendall, gold occurs in brecciated limestone and dolomite cut by numerous subvolcanic intrusions (Lindsey 1985; Lindsey and Fisher 1985). Due to the abundance of carbonate rock, acid mine drainage is not a problem at Kendall. However, groundwater that has contacted waste rock is elevated in dissolved thallium, and Tl removal technologies are being evaluated (*e.g.* Mueller 2001). The geologic source of thallium at Kendall and in the Judith Mountain drainages has not been determined.

Conclusions

Three small streams located in the central Judith Mountains, Montana, are highly acidic in their headwaters and transition to near-neutral pH over a distance of several km. Judging from the abundance of ferricrete in the headwaters, this acidic drainage has been occurring for millennia. Concentrations of Cu and Zn are well above chronic standards for aquatic life in upper Armell Creek, and concentrations of thallium (Tl), although very low (around 1 μg/L), are still well above human health standards for surface water. Concentrations of total Al, Fe, and Zn in lower Armells Creek increased at night and decreased during the day, following the diel pattern shown by many pH-neutral streams draining abandoned mine lands. Overall, the study area is a good example of acid rock drainage in a natural setting, although some acceleration of pyrite-weathering rates due to road construction along the crest of the mountain range cannot be discounted.

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