

The influence of hydrous Mn–Zn oxides on diel cycling of Zn in an alkaline stream draining abandoned mine lands

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Abstract

Many mining-impacted streams in western Montana with pH near or above neutrality display large (up to 500%) diel cycles in dissolved Zn concentrations. The streams in question typically contain boulders coated with a thin biofilm, as well as black mineral crusts composed of hydrous Mn–Zn oxides. Laboratory mesocosm experiments simulating diel behavior in High Ore Creek (one of the Montana streams with particularly high Zn concentrations) show that the Zn cycles are not caused by 24-h changes in streamflow or hyporheic exchange, but rather to reversible in-stream processes that are driven by the solar cycle and its attendant influence on pH and water temperature (T). Laboratory experiments using natural Mn–Zn precipitates from the creek show that the mobilities of Zn and Mn increase nearly an order of magnitude for each unit decrease in pH, and decrease 2.4-fold for an increase in T from 5 to 20 °C. The response of dissolved metal concentration to small changes in either pH or T was rapid and reversible, and dissolved Zn concentrations were roughly an order of magnitude higher than Mn. These observations are best explained by sorption of Zn^{2+} and Mn^{2+} onto the secondary Mn–Zn oxide surfaces. From the T -dependence of residual metal concentrations in solution, approximate adsorption enthalpies of +50 kJ/mol (Zn) and +46 kJ/mol (Mn) were obtained, which are within the range of enthalpy values reported in the literature for sorption of divalent metal cations onto hydrous metal oxides. Using the derived pH- and T -dependencies from the experiments, good agreement is shown between predicted and observed diel Zn cycles for several historical data sets collected from High Ore Creek.

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1. Introduction

Recent investigations have documented the occurrence of large diel (24-h) fluctuations in the concentrations of dissolved Zn, Mn, other heavy metals and As in streams draining abandoned mine lands in the northern Rocky Mountains (Fuller and Davis, 1989; Brick and Moore, 1996; Nimick et al., 2003, 2005; Jones et al., 2004; Gammons et al., 2005a). As an example, Fig. 1 shows the timing and magnitude of diel Zn cycles during normal

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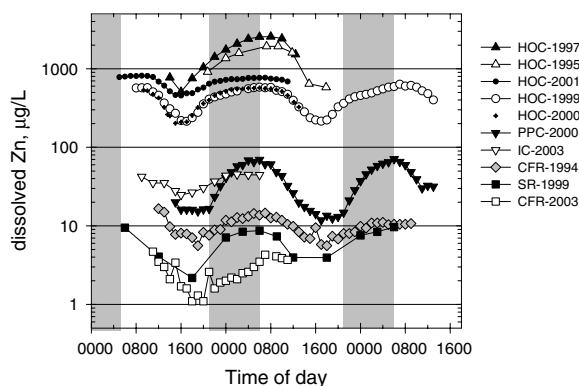


Fig. 1. Diel variations in dissolved Zn concentration from several streams in SW Montana: HOC, High Ore Creek; PPC, Prickly Pear Creek; IC, Indian Creek; CFR, Clark Fork River; SR, Stillwater River. All data are from Nimick et al. (2003) with the exception of CFR-1994 (Brick and Moore, 1996), CFR-2003 and IC-2003 (C. Gammons, unpublished data). Shaded regions denote approximate nighttime hours. All of the data were collected under baseflow conditions in late June, July, August, or early September.

summer baseflow conditions in several Montana streams, all of which have a near-neutral to alkaline pH. Dissolved Zn concentrations in these streams typically reach a maximum shortly after dawn, and a minimum shortly before dusk. The difference between the maximum and minimum Zn concentrations over a 24-h period can be very large (up to a sixfold increase at night). This phenomenon has obvious importance to situations in which the concentration of Zn in a stream is being compared to a regulatory standard. In the State of Montana, the current regulatory standard (MDEQ, 2004) for protection of aquatic health from chronic or acute exposure to Zn is 67 µg/L (at 50 mg/L hardness), which falls roughly in the middle of the data shown in Fig. 1. Recent work by Nimick et al. (2005) has shown that diel cycles in dissolved Zn concentration in streams can occur at all times of the year, and in both low flow and high flow (e.g., spring runoff or summer thunderstorm) conditions. The fact that the Zn concentration maxima and minima are more or less in phase from stream to stream and on different sampling dates suggests that a common mechanism or combination of mechanisms is responsible for the diel patterns.

Possible mechanisms that have been proposed to explain the diel cycling phenomenon in pH-neutral streams include: (1) diel changes in streamflow, or variations in the flux of influent groundwater or hyporheic water (Brick and Moore, 1996; Sullivan

et al., 1998); (2) precipitation and dissolution of a solid phase such as a carbonate or hydrous oxide in which the metal of interest is a major component, or is present in minor amounts as a solid solution (Brick and Moore, 1996; Scott et al., 2002; Haack and Warren, 2003; Nimick et al., 2003); (3) pH and temperature-dependent adsorption and desorption of heavy metals onto organic or inorganic substrates (Fuller and Davis, 1989; Nimick et al., 2003); and (4) daytime uptake of metals by autotrophic biofilms (Morris et al., 2005). Because most of the physical, chemical, and biological variables that could influence metal concentration are changing simultaneously during a 24-h sampling episode, it is virtually impossible to determine reaction mechanisms from examination of a stream in its natural state: eventually, one must perturb the environment by manipulating one variable and holding the others constant, or removing their influence entirely. This can be accomplished in the field by use of in-stream or off-stream chambers that are variously transparent to sunlight or in which pH can be adjusted (Jones et al., 2004; Morris et al., 2005), or in the laboratory under precisely controlled and monitored conditions. To further complicate matters, it is possible that two or more of the above mechanisms may reinforce each other. For example, whereas metal attenuation may fundamentally be an inorganic process, it may be mediated by microbes that create local gradients in pH or redox state near exposed mineral surfaces (e.g., Richardson et al., 1988; Hartley et al., 1996; Olivie-Lauquet et al., 2001; Haack and Warren, 2003).

The objective of this study was to perform a series of laboratory experiments to shed light on the main mechanisms of diel Zn cycling in High Ore Creek, Montana. The hypothesis was that diel cycles in Zn concentration observed in the field could be re-created in the laboratory under conditions in which one or more parameters (e.g., pH, redox state) is varied while holding other parameters constant. High Ore Creek was selected as a focus stream because of its high Zn concentrations (Fig. 1), large amplitude diel cycles, and ease of access. In addition, a large amount of historical water quality data exist for High Ore Creek, including a number of diel investigations spanning 8 a of monitoring by the US Geological Survey, the Montana Bureau of Mines and Geology, and Montana Tech (Tupling, 2001; Shope, 2003; Nimick et al., 2003). High Ore Creek is a small stream, with flows typically in the range of 10–200 L s⁻¹. Peak flows

occur in the Spring (April and May) during melting of the higher elevation snowpack.

The present study employed a mesocosm approach, in which High Ore Creek water was interacted with organic and inorganic substrates (collected from the creek bed) under conditions of variable pH, temperature, illumination, and redox state. The results have important implications to the understanding of heavy metal transport in streams draining abandoned mine lands, and may be useful to agencies conducting pre- or post-reclamation water quality monitoring of mining-impacted watersheds.

2. Methods

The interested reader is referred to Xie (2002) and Shope (2003) for additional details on the methodology of the experiments that are not included in the following summary.

2.1. Characterization of starting materials

Samples of black mineral crust were carefully scraped off boulders collected from High Ore Creek. After drying at 40 °C, a weighed mass of solid was transferred to a 60 mL sampling bottle and 5 mL of Trace Metal grade HCl was added. After a 24 h digestion period, deionized water was added to dilute the sample. The solutions were filtered to 0.45 µm and analyzed for acid-available metals by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in the analytical laboratory of the Montana Bureau of Mines and Geology (Butte, MT). XRD analysis of three mineral crust samples from High Ore Creek was performed at the Department of Metallurgical Engineering (Montana Tech) using a Philips XRG 3100 X-ray diffractometer and Cu K α source. The mineral crusts were also examined by scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX) at the Image and Chemical Analysis Laboratory (ICAL) at Montana State University (Bozeman, MT). A JEOL Model 6100 SEM was operated at 15 kV, with C-coated samples. Samples were characterized by scanning electron imagery (SEI) and backscattered electron (BSE) imagery.

Samples of filamentous green algae and brownish-green biofilm containing abundant diatoms were sampled from 12 different locations along High Ore Creek on May 14, 2002. These samples were rinsed lightly with deionized water to eliminate loosely

bound particulate matter, were dried overnight at 40 °C, and then were digested in 5 mL of concentrated aqua regia for 24 h. The samples were diluted with deionized water, filtered to 0.45 µm, and then analyzed for Zn, Mn, and Fe by flame atomic absorption spectroscopy.

2.2. Mesocosm experiments

Experiments 1 and 2 were performed in 15 L acrylic aquarium tanks, each with a 5 cm waterfall and pump to circulate and aerate the water. The “complete mesocosm” experiment was assembled with boulders and gravel collected from High Ore Creek (HOC) and arranged in the approximate position that they were found in the stream (e.g., brownish-green biofilms on the top, black mineral crusts on the sides and bottom of the boulders). The tank was filled to near capacity with HOC water from a 38 L Nalgene carboy stored in a walk-in refrigerator. The depth of the water column in the tanks (~20–25 cm) was similar to the average water depth in the stream. A second acrylic tank, labeled “algae only”, was filled with HOC water and a large quantity of filamentous green algae harvested from HOC. The mass of algae per liter of water in the tank was not quantified, but was much higher than in the stream. The algae samples were gently rinsed with deionized water before placing in the tank. A third control tank was filled with HOC water only. All of the tanks were illuminated from the side with a bank of full-spectrum fluorescent lights. The lights were set up on an automatic timer to turn on and off as required. The temperature and pH of the tanks were monitored continuously using either a Hydrolab Datasonde 3 multiprobe, or a Fisher Accumet AR15 pH meter and glass electrode. The pH meters were calibrated at the beginning of each experiment. Samples were withdrawn using a plastic syringe and filtered through 0.45 µm syringe filters into acid washed 60 mL high density polyethylene (HDPE) bottles. The samples were then acidified to 2% v/v with trace metal grade HCl or HNO₃, and stored in a refrigerator until analysis.

Experiment 3 was set up in the same manner as the “complete mesocosm” described above, with the exception that an artificial pH control system was added. In addition, the acrylic tank was wrapped in Al foil to prevent photosynthesis that would otherwise cause pH to fluctuate diurnally. The pH of the tank was adjusted using an LMI Mil-

ton Roy metering pump and pH controller with influent solutions of 0.1 N H₂SO₄ and 0.1 N NaOH. Using this system, it was possible to precisely control the pH of the water in the tank to within ± 0.05 U of a preset value in the pH range 7–8.5. Below pH 7 the system proved awkward to use, and was abandoned in lieu of the CO₂ gas method described below.

2.3. Experiments with HMZO mineral crusts

Experiments 4 and 5 were designed to test the pH-dependence of dissolved metal concentrations in equilibrium with HMZO crusts. In both experiments, 1-L of HOC water was placed in a 3-necked glass vessel with 20 g of HMZO crust. The pH of the system was controlled by bubbling humidified gas of varying CO₂ partial pressure through the reaction vessel. The gases used were compressed air (passed through a filter to remove traces of bacteria and hydrocarbons) and a synthetic CO₂:N₂ gas mixture, roughly 1:10 in composition. By varying the relative amounts of each gas delivered to the solution it was possible to adjust pH between 8.25 and 6.15. The advantage of this procedure over the pH-stat system used for experiment 3 was that no chemical compounds (other than the gases) were introduced to the solution during the experiment. The pH of the experiment was continuously monitored with a Fisher AR15 pH meter and glass electrode. The central flange of the vessel was used for an overhead stirrer, and the vessel was wrapped in Al foil to prevent light-sensitive reactions (e.g., photo-reduction, algal growth). Samples were withdrawn periodically with a syringe and filtered to 0.2 μ m with a disposable PES syringe filter into HDPE bottles. The solutions were preserved with 1% v/v HNO₃ prior to analysis for a suite of major and trace elements by ICP-AES.

Experiments 6 and 7 were set up to test the temperature dependence of dissolved metal concentrations in equilibrium with HMZO crusts. In experiment 6, 1-L of HOC water was reacted with 15 g of HMZO crust in the 3-necked glass vessel with overhead stirrer. The vessel was wrapped in Al foil and immersed in a 19 L water bath whose temperature was regulated within ± 0.1 °C in the range 6–22 °C using a refrigerated circulation system. The pH of the solution was not controlled, but nonetheless remained stable at 8.15 ± 0.05 . In experiment 7, the same conditions were repeated using a wide-neck, opaque 1-L HDPE bottle as a

reaction vessel to see if there was a difference between the trace metal concentrations in plastic vs. glass containers. All water samples were acidified to 1% HNO₃ and analyzed for a suite of trace metals by ICP-MS.

Experiment 8 was set up to test whether the concentrations of dissolved Zn and Mn in equilibrium with HMZO crusts were sensitive to changes in redox state. One liter of HOC water and 0.88 g of HMZO crust were placed on a magnetic stirrer, and humidified O₂ or H₂ gas was bubbled through the flask to adjust the oxidation state of the system. Water samples were periodically withdrawn with a syringe and filtered to 0.2 μ m with a disposable PES syringe filter. Water Eh and pH was monitored with an Orion 1230 multimeter, with Eh standardized to pH 4 and 7 quinhydrone buffers. The solutions were acidified to 2% v/v HNO₃ and analyzed for Zn and Mn by flame AAS.

2.4. Analytical

Water samples from experiments 1, 2, 3, and 8 were analyzed for Zn on a Perkin–Elmer 403 flame atomic absorption spectrometer (AAS). Analytical precision was estimated at 5%, with a detection limit of approximately 0.01 mg/L Zn. Samples from experiments 4 and 5 were analyzed for a suite of major and trace elements by inductively coupled plasma-Ar emission spectroscopy (ICP-AES) at the Murdock Laboratory (University of Montana, Missoula, MT), using EPA Method 200.15. Samples from experiments 6 and 7 were analyzed for a suite of minor and trace elements by inductively coupled plasma mass spectroscopy (ICP-MS) at the KEECO laboratory (Silver Bow, MT). The analytical precision for Zn and Mn on the ICP-AES and ICP-MS was estimated at 5% based on duplicate samples, with a detection limit near 1 μ g/L for both elements.

3. Results

3.1. Characterization of mineral crusts and biofilms

Examination of three hydrous Mn–Zn oxide crust samples by powder XRD revealed each to have a poorly crystalline structure, with two broad peaks at 36.5° and 66.0°2 θ (Fig. 2a). Many Mn-oxyhydroxide and mixed Mn–Zn-oxyhydroxide minerals have a strong peak at 36.5°2 θ (d-spacing of 2.46 Å), including birnessite (δ -MnO₂) and hausmannite (Mn₃O₄), as well as the mixed Mn–Zn

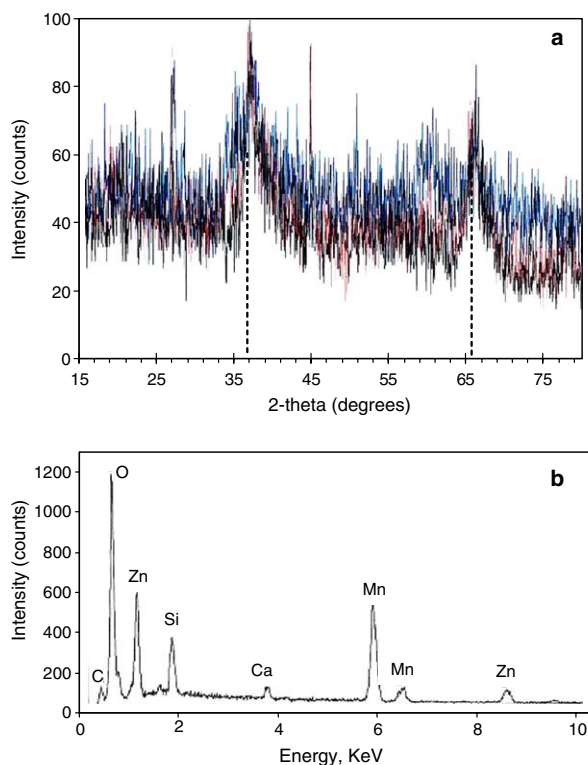


Fig. 2. (a) XRD pattern of three samples of HMZO crust from High Ore Creek (all three scans are superimposed on the same scale); (b) SEM-EDX spectrum of HMZO crust.

minerals hetaerolite ($\text{ZnO} \cdot \text{Mn}_2\text{O}_3$) and hydrohetaerolite ($\text{ZnMn}_2\text{O}_4 \cdot \text{H}_2\text{O}$ or $\text{ZnO} \cdot \text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Work in progress by the US Geological Survey using X-ray absorption fine structure spectroscopy (EXAFS) has indicated the presence of hexagonal birnessite in the coatings on sand grains from a stream sediment sample collected in 2004 from upper High Ore Creek (C.C. Fuller, USGS, pers. commun., 8-05). This is not surprising, as birnessite has been shown to be the most common secondary hydrous oxide of Mn in a wide variety of metal-rich soils, sediments, and ocean floor crusts (Lanson et al., 2002). This phase is renowned for its ability to scavenge trace metals, including Zn (Bendell-Young and Harvey, 1992; Manceau et al., 2000; Power et al., 2005). Although birnessite has the ideal formula of MnO_2 , natural birnessites are characterized by vacancies in the Mn site and substitution of Mn(III) for Mn(IV). The resultant charge imbalance is compensated by uptake of protons, alkali metals, or transition metals in the interlayer spacings between adjacent MnO_x sheets (Manceau et al., 2002). The highest Zn/Mn ratio that is theo-

retically achievable by this mechanism is 0.33, and corresponds to the formula $\text{ZnMn}_3\text{O}_7 \cdot x\text{H}_2\text{O}$ (Manceau et al., 2002).

The chemical composition of two HMZO crust samples as determined by ICP-AES analysis is given in Table 1. The Zn:Mn mole ratios from the two samples were 0.48 and 0.43, respectively. Spot analyses of 11 HMZO particles by SEM-EDX gave Zn:Mn atomic ratios that varied from 1.1 to 0.33, with an average value of 0.64 ± 0.24 (error denotes 1 SD). These results imply that birnessite could not have been the only mineral in the sample, and that additional Zn-rich phases (e.g., hetaerolite, hydrozincite, or ZnCO_3) must also be present. As can be seen from the example EDX spectrum (Fig. 2b), the HMZO samples contained a fairly large proportion of silica. This was not apparent from the ICP-AES analyses, because silica did not dissolve in the acid used to digest the samples. Inspection of the crust samples by SEI showed the existence of diatoms imbedded in the HMZO matrix (Fig. 3a and b). The diatoms, which secrete an amorphous silica cell wall (fustule), are probably the main source of Si in the EDX analyses. Examination of boulders in HOC showed a variably thick layer of diatom-rich biofilm which was pale brownish on the surface, but when scraped off the rocks revealed an undercoating of black HMZO crust. In addition, the bottom surfaces of most boulders in the creek bed contained a layer of HMZO. Recent work by Morris et al. (2005) has suggested an intimate associa-

Table 1
Composition (acid-available metals) of HMZO crusts from High Ore creek

Element	HMZO crust 1		HMZO crust 2	
	wt%	at%	wt%	at%
As	0.18	0.4	0.21	0.4
Ca	1.98	7.2	3.91	14.2
Cd	0.04	0.1	0.04	0.1
Cu	0.02	0.0	0.01	0.0
Fe	1.17	3.1	1.33	3.5
K	0.08	0.3	0	0.0
Mg	0.22	1.3	0.22	1.3
Mn	22.7	60.2	21.3	56.5
Na	0.03	0.2	0.04	0.3
P	0.11	0.5	0	0.0
Pb	0.07	0.0	0.06	0.0
Se	0.05	0.1	0.04	0.1
Sr	0.05	0.1	0.04	0.1
Zn	11.9	26.5	12	26.8
Total	38.6	100.0	39.2	100.0
Zn/Mn	0.52	0.44	0.56	0.47

wt%, weight%; at%, atomic%, normalized to 100.

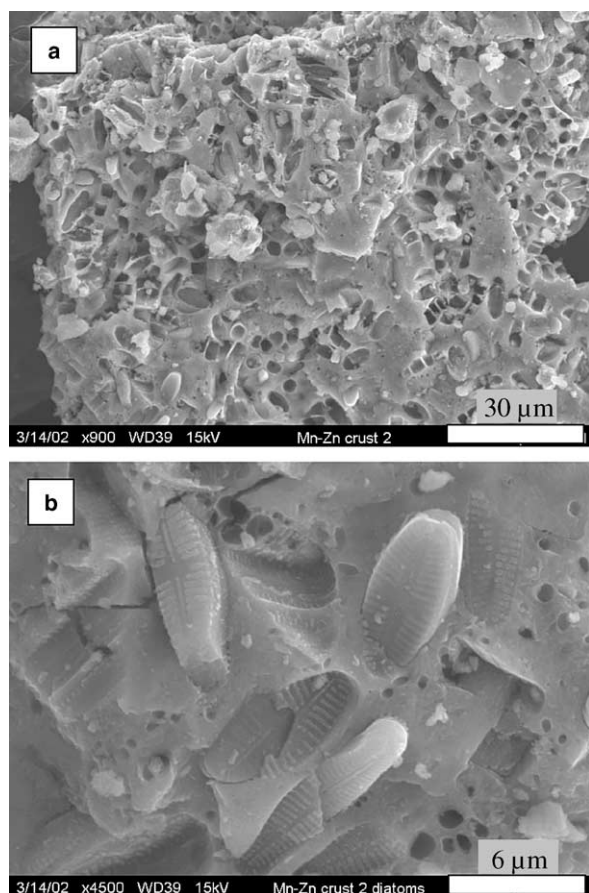


Fig. 3. (a) Scanning electron image of an HMZO crust from High Ore Creek; (b) a closeup image, showing diatom fustules imbedded in HMZO matrix.

tion between biofilm and metalliferous crust in HOC. This is discussed in more detail below.

A suite of 11 samples of filamentous green algae and diatom-rich biofilm collected at nine different locations along HOC was analyzed for acid-available Zn, Mn, and Fe by AAS. Both the filamentous algae and surface biofilms were extremely rich in metals, ranging from 1.2 to 2.7 wt% Zn, 0.3 to 1.1 wt% Mn, and 1.9 to 3.7 wt% Fe. However, it is important to point out that an unknown and possibly dominant percentage of metal in the biological samples was present as admixed particles of hydrous metal oxide. Overall, the Fe concentrations and Zn:Mn ratios of the biological samples were higher than those of the HMZO crusts. SEM-EDX examination showed the existence of loosely bound HFO and HMZO particles in the algae samples, and the SEI images of Fig. 3 suggest a gradation between dominantly biological material (e.g.,

diatoms and bacterial films) at the exterior surface of the biofilms, to dominantly inorganic material at the interior of the biofilms. Although no detailed taxonomic work was done on the microorganisms in HOC, a cursory investigation by an algae specialist (Grant Mitman, pers. commun.) revealed one of the dominant forms of filamentous green algae to be *Stigeoclonium*, a genus that is known to have a high Zn tolerance, and to inhabit Zn-contaminated streams (Armitage, 1980; Kelly and Whitton, 1989).

3.2. Results of mesocosm experiments

The purpose of the mesocosm experiments was to see if diel cycling of Zn could be reproduced in the laboratory using samples of water, periphyton, and boulders from HOC. In the Series 1 and 2 experiments no artificial controls on pH or temperature were imparted: diurnal changes in pH were entirely due to biological reactions that consumed or produced CO₂ depending on the supply of light and whether photosynthesis or respiration was the dominant process. In the Series 3 experiment, the pH of the mesocosm was adjusted over a wider range using a pH-stat system.

Results of the Series 1 experiments (Fig. 4) showed that it was possible to induce substantial diel cycles in dissolved Zn concentration in the laboratory mesocosm by simply switching a light on and off. One tank contained a complete mesocosm (i.e., HOC water and boulders coated with biofilm), while a second tank contained water and filamentous green algae only. A third control tank contained HOC water only. Each tank was subjected to 11 h of light and 13 h of darkness over a 60 h period. Small but reproducible diel changes in pH (~0.2 U) and temperature (~4 °C) were noted for the complete mesocosm (Fig. 4a) and the algae-only tanks (Fig. 4b), whereas the control tank had no discernable change in pH (Fig. 4c). These results are consistent with the hypothesis that pH changes in HOC are mainly driven by biological cycling of CO₂. The temperature changes were due to changes in room temperature during the day, coupled with warming from the artificial lights that were placed next to the tanks. The complete mesocosm tank showed a clear diel fluctuation in dissolved Zn concentration, with roughly a twofold decrease each day between the time that the light was turned on in the morning, and when it was turned off in the evening. Significantly, the algae-only tank showed similar Zn cycles, indicating that the rocky substrate

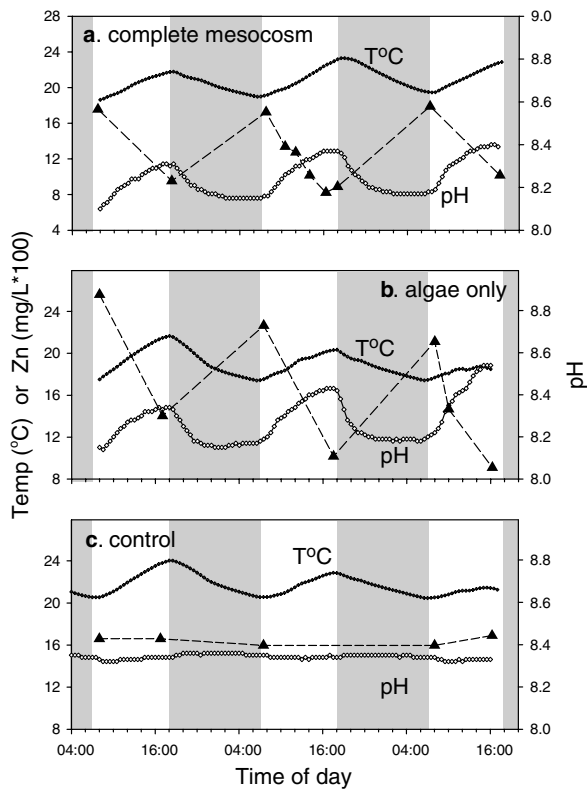


Fig. 4. Results of the Series 1 mesocosm experiments: (a) complete mesocosm, including water, boulders, and biofilms from High Ore Creek; (b) HOC water with filamentous green algae; (c) control tank with HOC water only. Shaded regions denote times when the artificial lights in the laboratory were off.

of HOC is not an essential ingredient for diel Zn cycling to occur. However, it must be kept in mind that filamentous green algae is typically not abundant in the lower reaches of HOC, and the mass ratio of green algae to water in this tank was much greater than what was observed in the field. No variation in Zn concentration was noted for the control tank, ruling out the possibility that the diel Zn cycles could be related to temperature-dependent adsorption onto the plastic tank walls.

In the Series 2 experiments, samples were collected at more closely spaced time intervals over a single 24-h period. The results (Fig. 5) again showed distinct cycles in pH, temperature, and dissolved Zn concentration in both the complete mesocosm and the algae-only tanks. Based on the shape of the various diel curves, it appears that Zn concentration was more strongly influenced by pH than by temperature. This is backed up by linear regression of Zn vs. pH ($r^2 = 0.78$ and 0.64 for the complete and algae-only tanks) as compared to Zn vs.

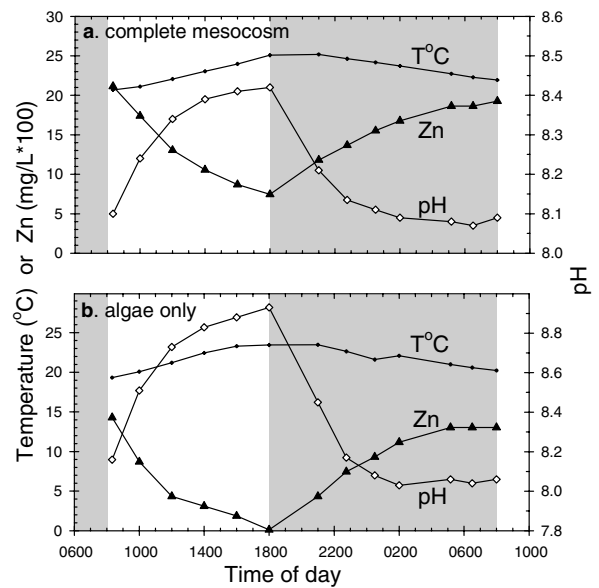


Fig. 5. Results of the Series 2 mesocosm experiments: (a) complete mesocosm, including water, boulders, and biofilms from High Ore Creek; (b) HOC water with filamentous green algae. The shaded regions denote times when the artificial lights in the laboratory were off.

temperature ($r^2 = 0.46$ and 0.45 , respectively). However, because both variables were changing simultaneously, it is not possible to isolate the effect of one from the other based on these experiments. It is important to note the rapidity in the response of both pH and Zn concentration to the changing conditions of illumination, as well as the symmetry in shape of the curves for the light and dark cycles. This underscores the reversibility of whatever mechanism is controlling pH and Zn concentration in the laboratory system. Fig. 6 compares data from the

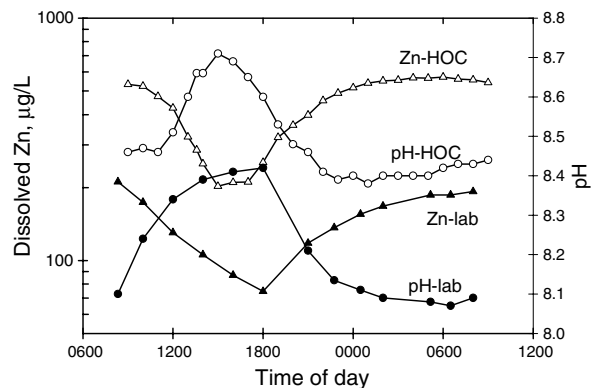


Fig. 6. Comparison of pH and dissolved Zn concentrations from the Series 2a experiment of this study vs. field data from High Ore Creek. The latter were collected by the US Geological Survey in July, 2000, and were reported in Nimick et al. (2003).

Series 2 mesocosm experiment to field data from HOC collected in July-2000 (Nimick et al., 2003). The timing and magnitude of the diel cycles of Zn concentration and pH are remarkably similar. Differences in the shape of the curves are mainly due to the fact that the lights were turned on and off abruptly in the experiments, whereas in the field the transition from light to dark is gradual.

In the Series 3 experiment, a pH-stat system was used to lower the ambient pH of a complete mesocosm tank from ~ 8.2 to 7.0 in 0.5 U increments. The results (Fig. 7) confirmed the strong dependence of Zn concentration on pH, but also showed that it took >24 h for the tank to come to an equilibrium Zn concentration at each pH step. Linear regression of the data collected after 36 h at each pH showed an inverse relationship between log Zn and pH, with a slope of -0.89 ($r^2 = 1.00$).

3.3. Results of experiments with HMZO crusts

Separate experiments were performed in which HOC water was interacted with HMZO crusts under conditions of controlled pH, temperature, and redox state.

3.3.1. pH variation

Two long term experiments (Series 4 and 5) were performed in which pH was varied by bubbling gas of differing CO_2 partial pressure through the experimental system. Both the Series 4 and 5 results showed a strong inverse relationship between pH and dissolved Zn (Fig. 8). Dissolved Mn tracked nearly identically with Zn, and the Zn:Mn mass

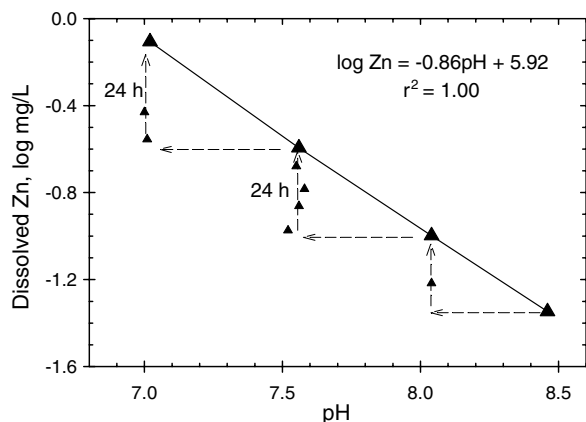


Fig. 7. Results of the Series 3 mesocosm experiments with artificial pH control. Arrows show the sequence in which the samples were collected.

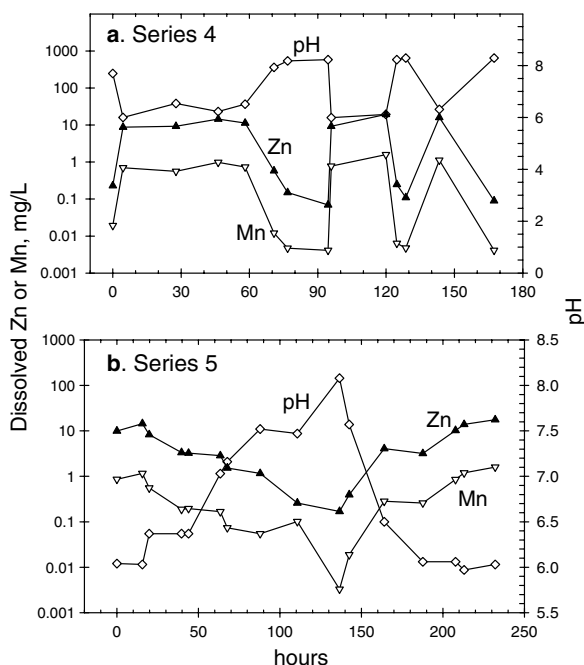


Fig. 8. Results of the Series 4 and 5 experiments with HMZO crusts and pH control.

ratio was nearly constant at $\sim 20:1$. Unlike the mesocosm experiments, metal concentrations in the HMZO experiments appeared to equilibrate within a few hours of any change in pH. This most likely reflects the relative simplicity of the abiotic Series 4 and 5 experiments vs. the biotic Series 3 experiment. The Zn concentrations in Series 4 and 5 were in excellent agreement, and linear regression of the combined data (Fig. 9) yielded slopes of -0.90 for

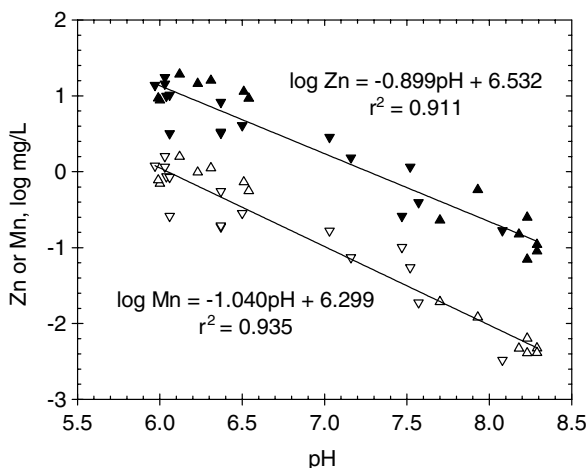


Fig. 9. The dependence of dissolved Zn and Mn concentration on pH from the Series 4 and Series 5 experiments with HMZO crusts.

Zn ($r^2 = 0.91$) and -1.04 for Mn ($r^2 = 0.94$). These results concur with the data in Fig. 7, indicating that the pH-dependence of Zn mobility in the complete HOC mesocosm is similar to water interacted with HMZO crusts alone. Although samples from Series 4 and 5 were analyzed for a complete set of metals by ICP-AES, no other solutes (e.g., Ca, Fe, K, Mg, Na, Sr) were found to vary significantly in concentration. This indicates that whatever mechanism influenced Zn and Mn mobility in the experiments was highly specific to these metals.

3.3.2. Temperature variation

Two sets of experiments (Series 6 and 7) were performed to determine the dependence of Zn and Mn concentration on temperature for HOC water in equilibrium with HMZO crusts. Results for Series 6 (Fig. 10) show an inverse relationship between Zn mobility and temperature, with rapid equilibration and good reversibility. Manganese again tracked in a similar fashion as Zn, and was roughly 20× less soluble. In Series 7, the temperature-stat experiment was repeated, but using an opaque HDPE plastic bottle as a reaction vessel instead of the three-necked glass flask. The results for Zn from the two sets of experiments were in good agreement (Fig. 11), minor offsets being partly explained by slightly different pH values. A decrease in temperature from 22 to 6 °C caused roughly a 2.5-fold increase in the concentration of both dissolved Zn and Mn. Results from a control experiment using an HDPE bottle without any HMZO solids showed no change in Zn concentration with temperature.

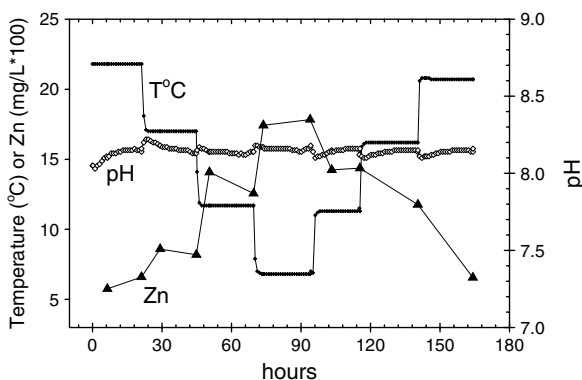


Fig. 10. Results of the Series 6 experiments with HMZO crusts and temperature control.

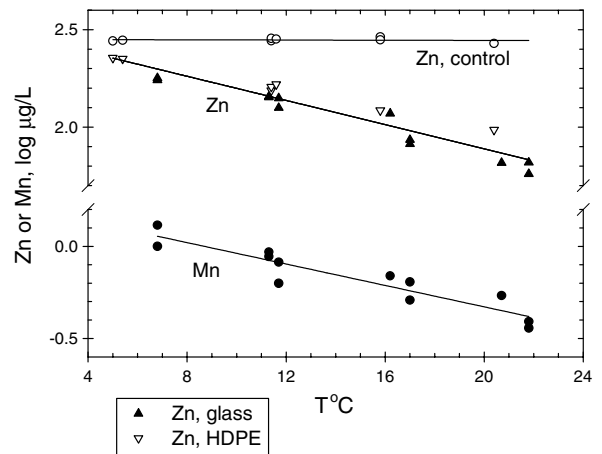


Fig. 11. The dependence of dissolved Zn and Mn concentration on temperature ($1000 \times$ reciprocal T , in Kelvin) from the Series 6 and Series 7 experiments with HMZO crusts.

3.3.3. Redox variation

The Series 8 experiments were designed to test the hypothesis that aqueous Zn and Mn concentrations may be influenced by the oxidation state of the water. In this case, redox state was varied by bubbling either H_2 or O_2 through the reaction vessel containing HOC water and HMZO crusts. In so doing, the experimental Eh of the system alternated between +420 mV (with O_2) and -320 mV (with H_2). However, no systematic change in the dissolved concentration of Zn or Mn was found (Fig. 12), other than a decline in metal concentration at the beginning of the experiment that is most likely explained by sorption. The significance of this experiment is discussed in more detail below.

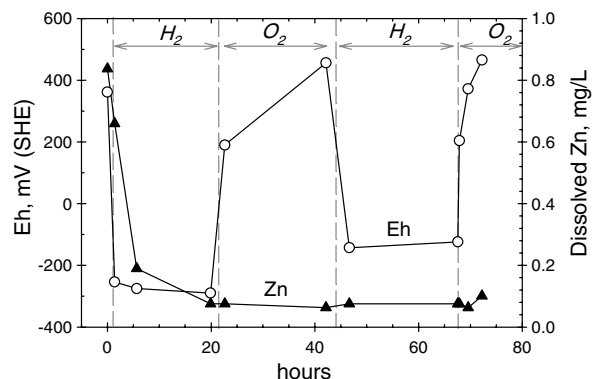


Fig. 12. Results of the Series 8 experiments with HMZO crusts and artificial Eh control. Dashed lines separate periods of time in which either O_2 gas or H_2 gas was bubbled through the reaction vessel.

4. Discussion

4.1. Reaction mechanisms

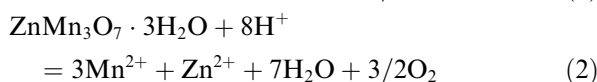
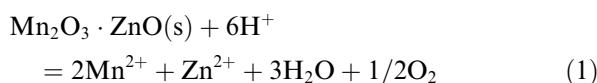
In this section, each of the possible mechanisms that could control diel cycling of Zn briefly listed in the Introduction are discussed in light of the experimental results of this study, and in combination with previously reported field investigations.

4.1.1. Changes in flux of groundwater or hyporheic water

Diel changes in the mass contribution of water to a stream from different sources can result in diel cycles in metal concentration. In the summer months, day-time loss of shallow groundwater and hyporheic water to evapo-transpiration often results in a decrease in streamflow during the afternoon (Bond et al., 2002). If the subsurface water is enriched in metals relative to the surface water, this will result in afternoon decreases in metal concentrations in the stream. However, previous field studies have shown a consistently poor correlation between streamflow and diel Zn concentration patterns (Nimick et al., 2003, 2005). Recent hydrogeological work (Shope, 2003) has shown that High Ore Creek is perched or losing groundwater over most of its length, and therefore would have received very little subsurface water for several kilometers upstream of the locations where past diel investigations (Fig. 1) have been performed. Furthermore, the fact that diel cycles in Zn concentration were reproduced in the closed system mesocosm experiments of this study is strong evidence that the fundamental mechanism controlling Zn mobility in HOC is an in-stream chemical or biological process.

4.1.2. Mineral dissolution and precipitation

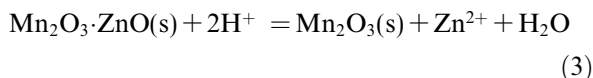
It is possible that diel metal cycles are caused by cyclic precipitation and/or dissolution of a solid phase on the streambed. In the case of HOC, it has already been shown that HMZO crusts are ubiquitous, and have the approximate composition of hetaerolite and/or Zn-substituted hexagonal birnessite (i.e., chalcophanite). Dissolution of these phases can be written as follows:



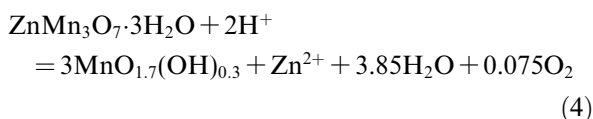
Note that both of the above reactions involve redox, and therefore would be expected to be kinetically slow, especially for the reverse reaction where Mn(II) is oxidized to Mn(IV). However, a growing body of research has shown that redox reactions involving Mn species are microbially catalyzed, and can impart a major control on the concentration of metals in solution (Richardson et al., 1988; Scott et al., 2002 Haack and Warren, 2003). Reductive dissolution of HMO and/or HFO has been proposed as a potential mechanism to explain diel cycling of metals in streams (Brick and Moore, 1996; Scott et al., 2002).

The Series 8 experiments of this study showed that dissolved Zn and Mn concentrations in contact with HMZO crusts were unresponsive to large changes in the ambient redox state of the water (Fig. 12). However, this does not discount the hypothesis that Mn redox reactions could play an important role in HOC since the experimental system was essentially abiotic. In natural aquatic environments the requisite electron transfer reactions involving Mn species are catalyzed by bacteria that likely would have been present in scarce numbers in the prepared HMZO samples compared to biofilms coating the natural stream bed. However, any mechanism involving stoichiometric dissolution of HMZO or pure hydrous Mn-oxide is incompatible with the observation that dissolved Zn:Mn mole ratios were $\gg 1$ in the experiments of this study, as well as in HOC itself (Zn:Mn mole ratios in HOC ranged from 4 to 17 for samples collected in 1999, 2000, 2001, and 2004, Nimick et al., 2003, and USGS, unpublished data).

The possibility of *non-stoichiometric* dissolution of HMZO particles should also be considered. One possible end member reaction with hetaerolite as a reactant and bixbyite as a product can be written:

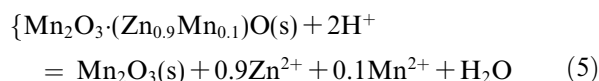


A second possible reaction using Zn-substituted birnessite as a reactant and hexagonal birnessite as a product can be written:



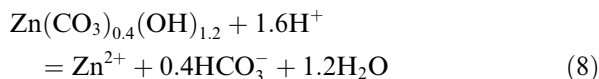
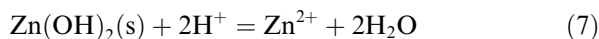
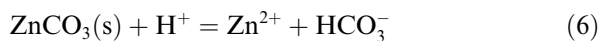
Note that reaction (3) is independent of redox, yet still provides a mechanism for HMZO to be the

primary source of available Zn for interaction with creek water. It is likely that mixing of Zn and Mn would take place in the divalent metal site of the hetaerolite–hausmannite solid solution, as shown by the following hypothetical reaction:



In reaction (5), the Zn:Mn ratio in the divalent metal site of the HMZO crusts would be influenced by the Zn:Mn ratio of the aqueous phase (and vice versa). This would explain the observation that dissolved Zn and Mn show a very strong co-variation in the experiments of this study. The main problem with this hypothesis (as well as reaction (4)) is that Zn concentration would vary with the *square* of the proton concentration, which is inconsistent with the observed field and laboratory data that show an inverse *linear* relationship between log Zn concentration and pH (Figs. 7 and 9).

It is also possible that pure Zn phases, such as $\text{Zn}(\text{OH})_2$, ZnCO_3 , or hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) are present in the HMZO crusts, or as particles admixed with surface biofilms. Although geochemical modeling (e.g., PHREEQC, Parkhurst and Appelo, 1999) predicts that the saturation indices of these Zn minerals are negative in HOC water (as well as in the experimental solutions used in this study), it is still possible that such phases could precipitate in actively metabolizing biofilm, due to pH gradients developed at the biofilm-bulk water interface (e.g., Hartley et al., 1996). Solubility reactions for each of these minerals are given as follows:

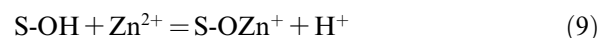


The main problem with reaction (7) is that the concentration of dissolved Zn in equilibrium with $\text{Zn}(\text{OH})_2(s)$ again increases as the square of the proton concentration, whereas for hydrozincite it increases as $\{\text{H}^+\}^{1.6}$. Of the three minerals listed, only ZnCO_3 (smithsonite, or its poorly crystalline, hydrous variety) shows a 1:1 correlation between Zn concentration and proton concentration. However, arguments against the possibility that Zn-carbonate could be a controlling factor include: (1) the dissolution and precipitation of most carbonate minerals is kinetically slow (Stumm and Morgan, 1996), and therefore one would not expect to see ra-

pid and reversible changes in Zn concentration for small pH or temperature changes; and (2) previous workers (Nimick et al., 2003) have shown that the phenomenon of diel Zn cycling in pH-neutral streams is independent of Zn concentration; near-pristine streams with very low Zn concentrations display diel Zn cycles that can be as big or bigger than highly polluted streams with very high Zn concentrations (Fig. 1). Clearly, saturation with ZnCO_3 cannot be a prerequisite for Zn cycling in all of the streams previously investigated. Applying Occum's Razor, it is therefore unlikely that it is the dominant control in High Ore Creek.

4.1.3. Adsorption

It is well known that adsorption of trace metals onto hydrous metal oxide is strongly pH-dependent (Dzombak and Morel, 1990). The sorption reaction of a divalent metal ion such as Zn^{2+} onto a metal oxide surface (S) is often written as follows:



In this example reaction, adsorption of a Zn^{2+} ion involves displacement of a proton from a surface hydroxyl group attached to the hydrous oxide solid. Reaction (9) would therefore predict roughly a 1:1 relationship between dissolved Zn concentration and proton concentration, which is consistent with the experiments of this study. Adsorption of metal cations onto hydrous oxides is also endothermic, being favored by an increase in temperature (Machesky, 1990; Trivedi and Axe, 2000, 2001). Machesky (1990) derived the following equation that describes the temperature dependence of the residual concentration of a dissolved solute in equilibrium with a solid surface on which it is actively adsorbing:

$$H_{\text{ads}} = 2.303R [\log(C_2) - \log(C_1)] / (1/T_2 - 1/T_1) \quad (10)$$

where ΔH_{ads} is the adsorption enthalpy (J mol^{-1}), R is the gas constant ($8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$), and C_1 and C_2 are the dissolved metal concentrations at T_1 and T_2 , where T is in Kelvin. Following eq. (10), the slope of a line plotting $\log(C)$ versus $1/T$ can be used to derive the value of ΔH_{ads} . The results of Series 6 and 7 experiments were used to derive the slopes and sorption enthalpies for Zn^{2+} and Mn^{2+} onto HMZO (Fig. 13). The dissolved metal concentrations plotted in Fig. 13 were corrected for small changes in pH between sampling times, by applying the previously determined correction factors ($\log \text{Zn}^* = \log \text{Zn} - 0.9[\Delta \text{pH}]$, and $\log \text{Mn}^* = \log \text{Mn}$

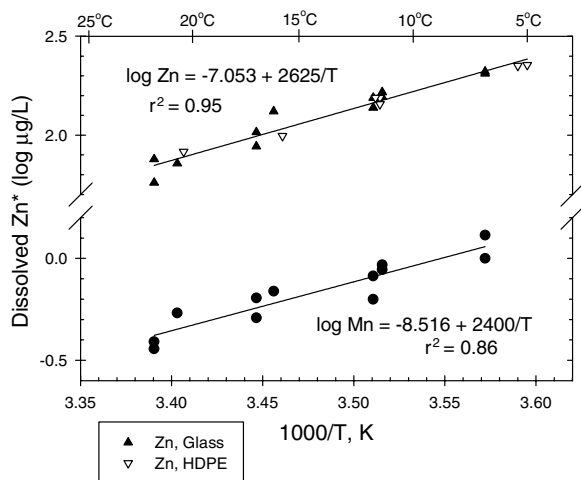


Fig. 13. The dependence of dissolved Zn and Mn concentration on temperature ($1000 \times$ reciprocal T , in Kelvin) from all experiments with HMZO crusts. The data were adjusted for minor differences in pH between samples. The slopes of the linear regressions were used to derive enthalpies for the adsorption of Zn^{2+} and Mn^{2+} onto HMZO.

$-1.0[\Delta pH]$). The adsorption enthalpies obtained were $+50.3$ kJ/mol (Zn) and $+46.0$ kJ/mol (Mn). These strongly endothermic enthalpies for adsorption of Zn^{2+} and Mn^{2+} onto HMZO are consistent with enthalpies reported in the literature for sorption of divalent metals onto other hydrous oxides (Machesky, 1990; Johnson, 1990; Rodda et al., 1996; Trivedi and Axe, 2000, 2001).

As discussed by Nimick et al. (2003), a sorption model has the advantage of being able to explain the fact that diel Zn cycles occur in rivers with similar pH ranges, but greatly differing Zn concentrations (Fig. 1). The sorption hypothesis also explains the antithetic behavior of As and divalent metals in the streams previously investigated. Dissolved As in pH neutral or alkaline rivers exists mainly in anionic form as $HAsO_4^-$, and therefore its sorption behavior with respect to changes in pH and temperature is the opposite of what is predicted for divalent metal cations (Fuller and Davis, 1989; Nimick et al., 2003). If the adsorption hypothesis is correct, the similarity in diel behavior of Zn^{2+} in streams of Western Montana with similar average pH values suggests that a common mineral or biological sorbate is present in all of the systems investigated. Reconnaissance field work has shown that black Mn-oxide crusts are ubiquitous within the streams in question, and that a correlation exists between the Zn:Mn ratio of the oxide crusts and

the dissolved Zn:Mn ratio of the stream (Gammons et al., 2005b). Although it is tempting to use a detailed surface complexation model (SCM) to predict diel Zn and Mn cycles in HOC, this cannot be undertaken at the present time for several reasons. First, more information is needed on the mineralogy and availability (e.g., specific surface area) of the HMZO surfaces in the natural stream environment. Second, the requisite SCM parameters needed to model the proton condition and binding constants of metals onto HMZO crusts as a function of pH and temperature are lacking. Finally, although this study has shown that interaction of HOC water with HMZO crusts is a plausible mechanism to explain diel metal cycles, it is equally plausible that Zn^{2+} and Mn^{2+} are simultaneously adsorbing onto surface sites in biofilms coating the mineral and boulder surfaces. This is discussed in greater detail in the following section.

4.1.4. Biological uptake

There are several ways in which microorganisms may play an important role in diel metal cycling in High Ore Creek. At a minimum, it is known that microbial reactions that sequester or release CO_2 change the pH of the water column on a diel basis (Odum, 1956). Furthermore, it has been demonstrated (e.g., Hartley et al., 1996) that the pH at the surface of an active autotrophic biofilm can be very different from that of the bulk solution, due to the slow kinetics of diffusion of CO_2 into and out of the biological matrix. Although the timing of pH maxima and minima within the biofilm is likely to follow that of the bulk water column, the amplitude of the diel pH cycles will be much greater in the former. For this reason, the tendency for a pH-dependent reaction to occur will be amplified within the immediate environment of the biofilm. In addition to their role in generating spatial and temporal gradients in pH, biofilms are also well known for their ability to bind with Zn and other metals (Whitton et al., 1981; Bender et al., 1994), due to an abundance of functional groups that deprotonate within the pH range of natural waters (Fein et al., 2001). Finally, it is possible that metals can be absorbed into the interior of living cells. This type of “active” metal attenuation contrasts to “passive” processes that occur whether or not the cells are actively metabolizing.

Morris et al. (2005) recently published a series of laboratory and field experiments which quantified the rate of uptake of Zn from HOC water by biofilm.

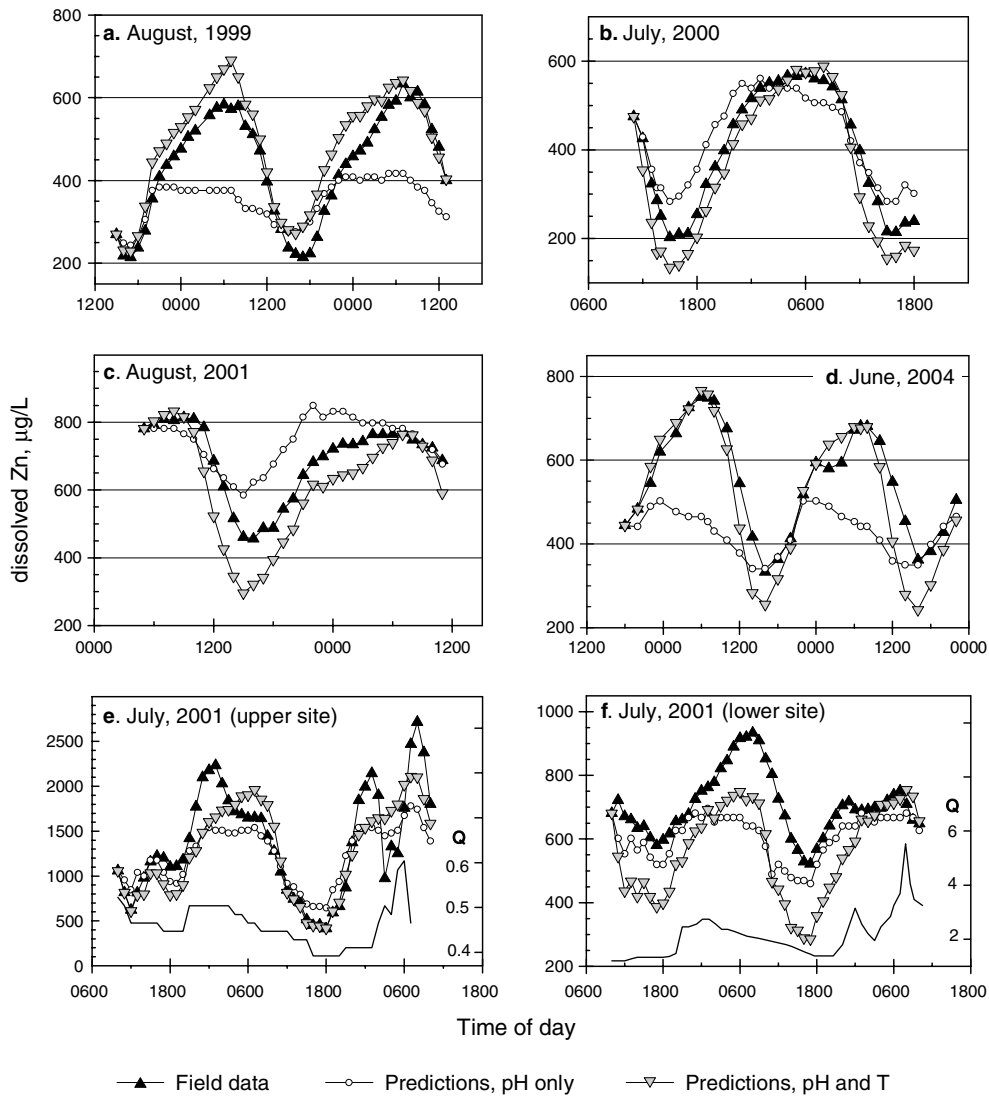


Fig. 14. A comparison of observed and predicted Zn concentrations for six different diel investigations conducted at High Ore Creek by the US Geological Survey (Nimick et al., 2003, and unpublished data). Streamflow (Q , $\text{ft}^3 \text{s}^{-1} = 0.0283 \text{ m}^3 \text{ s}^{-1}$) is shown on the right y-axis for Fig. 14e and f. The predictions are based on a model that takes into account pH changes only, or a combination of pH and temperature changes (see text).

The field site used in their study was located ~ 5 km upstream of the site where most of the data for HOC in Fig. 1 were collected, in a reach of the stream with unusually thick biofilm and abundant hydrous oxide of Fe, Mn, and Zn. Morris et al. (2005) demonstrated that biofilm cultured in the laboratory sequestered Zn from solution in the presence of light, and released a portion of this Zn during dark periods. This result is similar to what we observed in the Series 1 and 2 experiments performed with algae only (Figs. 4 and 5). Morris et al. (2005) proposed a “two-compartment” model in which dissolved Zn is first sequestered from the water column by the bio-

film but then is eventually transferred to the underlying mineral surface where it accumulates as hydrous oxide. The precise nature of the bonding of the metal in the biofilms studied by Morris et al. (2005) could not be determined from their experiments. This would appear to be an important direction for future research.

4.2. Comparison of experimental results to field data

The results of the laboratory experiments were used to model 6 sets of diel field data from High Ore Creek, spanning the period of time from 1999

to 2004 (Fig. 14). All field data were collected by the US Geological Survey (Nimick et al., 2003, and D. Nimick, unpublished data) and employed continuous in-stream monitoring of pH and temperature. The field investigations shown in Fig. 14a–d were conducted during summer baseflow conditions on the lower reach of HOC (roughly 0.5 km from its mouth). The data shown in Fig. 14e and f were collected during a rain event in July of 2001 at an upper and lower location, the latter being the same as for the other data sets. In the modeled data sets, the initial dissolved Zn concentration was fixed to the measured Zn concentration of the first water sample collected during each diel investigation. The Zn concentrations of subsequent samples were then predicted from a spreadsheet, based on the observed hourly changes in pH and temperature. One set of predictions considered changes in pH only (assuming a -0.9 slope between \log Zn and pH, as determined previously), whereas a second set considered changes in both pH and temperature (using the slope for the temperature regression shown in Fig. 13). The calculations assumed equilibrium between the water column and the HMZO crusts of High Ore Creek, and were insensitive to changes in streamflow. It should be stressed that this modeling approach, although based on the results of laboratory experiments, is essentially empirical in nature, and may not be valid for other streams.

The results in Fig. 14 show a general agreement between the shape, timing, and amplitude of the diel Zn cycles for the predicted curves and the field data. In most of the data sets, better agreement was obtained when both pH and temperature were considered in the modeling than when only pH was used. This is somewhat different from the conclusion of Jones et al. (2004), who found that pH exerted a much greater control than temperature on Zn cycling in nearby Prickly Pear Creek based on the results of in-stream chamber experiments. The ease with which the simple empirical model simulated field observations lends credence to the validity of the experiments of this study, and also implies that both pH and temperature are important controlling factors for Zn concentration in High Ore Creek.

Although most of the previous diel investigations of High Ore Creek have been conducted in the summer, a set of diel samples was collected on May 16–17, 2002, during Spring runoff, and again on October 11–12, 2002, when cold weather had set in and ice was starting to form on the creek

(Shope, 2003). In both cases, significant diel fluctuations were noted in total (unfiltered) Zn concentration, despite cold water temperatures. This agrees with the findings of Nimick et al. (2005), who observed large diel changes in dissolved and total Zn concentration in Prickly Pear Creek (the neighboring watershed to the north of High Ore Creek) at all times of the year, and during all types of hydrological conditions (high flow, low flow, etc.). In contrast to filamentous algae and biofilm, which may be periodically flushed out of the watershed during high water events, the HMZO crusts adhere strongly to the boulder and stream sediment substrates, and are therefore unlikely to be swept downstream. For this reason, it may take many decades or centuries before the large mass of Zn and Mn in the hydrous oxide that accumulated along the course of the stream in the period prior to reclamation is removed by natural processes. Indeed, ample evidence exists that new HMZO crusts are still forming in the upper reaches of High Ore Creek (Shope, 2003; Morris et al., 2005), thus providing fresh substrate for trace element adsorption and diel metal cycling.

5. Conclusions

This study has documented the existence of hydrous Mn–Zn oxide (HMZO) in High Ore Creek, an alkaline stream draining abandoned mine lands in Montana, and has elaborated on the role of HMZO on diel cycling of Zn in this stream. Diel cycles in dissolved Zn concentration were reproducible in laboratory mesocosm experiments containing site water and boulders from the stream (with mineral crusts and surface biofilm) by simply turning a light on and off. This supports the hypothesis that diel Zn cycles observed in the field are not due to mixing of waters from different sources, but rather to in-stream bio-geochemical processes. Additional experiments focused on the inorganic interactions between creek water and HMZO crusts, and showed that: (1) dissolved Zn and Mn concentrations increased linearly with proton concentration; (2) Zn and Mn concentrations decreased with increase in temperature; (3) Zn and Mn concentrations were unaffected by change in Eh of the experimental solutions; and (4) Zn was consistently 10–20 times more soluble than Mn in all experiments. These observations are best explained by sorption of Zn and Mn onto HMZO crusts. Sorption enthalpies determined from the temperature dependence of residual

dissolved metal concentrations were +50 and +46 kJ/mol for Zn and Mn, respectively, and are consistent with literature values for sorption of divalent cations onto hydrous metal oxide. The empirical relationships between pH, temperature, and dissolved Zn concentration derived from the experiments were used to predict hourly Zn concentrations for several recent diel investigations in High Ore Creek conducted in summer baseflow and wet weather flow conditions. The results showed good agreement between the predicted and observed Zn values.

Whereas the experiments in this study focused on the interaction between stream water and hydrous Mn–Zn oxides, it is stressed that biological reactions may also play an important role in sequestering metals in the natural stream environment, as shown by the recent study of Morris et al. (2005). On the other hand, although biofilms clearly influence the fate and transport of Zn in the natural setting of High Ore Creek, the results of our abiotic laboratory experiments with HMZO crusts indicate that diel cycling of dissolved Zn concentrations can take place in the absence of biofilms. The relative importance of biological vs. inorganic reactions in controlling diel Zn cycles in streams is an important area for future research, as is illumination of the precise mechanisms by which HMZO crusts form, and their range in composition and mineralogy.

Acknowledgments

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References

- Armitage, P.D., 1980. The effects of mine drainage and organic enrichment on benthos in the River Nent system, northern Pennines, England, UK. *Hydrobiology* 74, 119–128.
- Bendell-Young, L.I., Harvey, H.H., 1992. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. *Geochim. Cosmochim. Acta* 56, 1175–1186.
- Bender, J., Washington, J.R., Graves, B., Phillips, P., Abotsi, G., 1994. Deposit of zinc and manganese in an aqueous environment mediated by microbial mats. *Water Air Soil Poll.* 75, 95–204.
- Bond, B.J., Jones, J.A., Moore, G., Phillips, N., Post, D., McDonnell, J.J., 2002. The zone of vegetation influence on baseflow revealed by diel patterns of streamflow and vegetation water use in a headwater basin. *Hydrol. Proc.* 16, 1671–1677.
- Brick, C.M., Moore, J.N., 1996. Diel variation of trace metals in the upper Clark Fork River, Montana. *Environ. Sci. Technol.* 30, 1953–1960.
- Dzombak, D.A., Morel, F.M.M., 1990. *Surface Complexation Modeling*. Wiley, New York.
- Fein, J.B., Martin, A.M., Wightman, P.G., 2001. Metal adsorption onto bacterial surfaces: development of a predictive approach. *Geochim. Cosmochim. Acta* 65, 4267–4273.
- Fuller, C.C., Davis, J.A., 1989. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters. *Nature* 340, 52–54.
- Gammons, C.H., Nimick, D.A., Parker, S.R., Cleasby, T.E., McCleskey, C.B., 2005a. Diel behavior of Fe and other heavy metals in a mountain stream with acidic to neutral pH: Fisher Creek, Montana, USA. *Geochim. Cosmochim. Acta* 69, 2505–2516.
- Gammons, C.H., Shope, C.L., Xie, Y., 2005b. Causes of diel cycling of Zn in streams with near-neutral pH draining abandoned mine lands. *Geochim. Cosmochim. Acta* 69 (Suppl. 1), A770.
- Haack, E.A., Warren, L.A., 2003. Biofilm hydrous manganese oxyhydroxides and metal dynamics in acid rock drainage. *Environ. Sci. Technol.* 37, 4138–4147.
- Hartley, A.M., House, W.A., Leadbeater, B.S.C., Callow, M.E., 1996. The use of microelectrodes to study precipitation of calcite upon algal biofilms. *J. Colloid Interface Sci.* 183, 498–505.
- Johnson, B.B., 1990. Effect of temperature and concentration on the adsorption of cadmium on goethite. *Environ. Sci. Technol.* 24, 112–118.
- Jones, C.A., Nimick, D.A., McCleskey, R.B., 2004. Relative effect of temperature and pH on diel cycling of dissolved trace elements in Prickly Pear Creek, Montana. *Water Air Soil Poll.* 153, 95–113.
- Kelly, M.G., Whitton, B.A., 1989. Relationship between accumulation and toxicity of zinc in *Stigeoclonium* (Chaetophorales, Chlorophyta). *Phycologia* 28, 512–517.
- Lanson, B., Drits, V.A., Gaillot, A.-C., Silverster, E., Plançon, A., Manceau, A., 2002. Structure of heavy-metal sorbed birnessite: Part I. Results from X-ray diffraction. *Am. Mineral.* 87, 1631–1645.
- Machesky, M.L., 1990. Influence of temperature on ion adsorption by hydrous metal oxides. In: Melchior, D.C., Bassett, R.L. (Eds.), *Chemical Modeling of Aqueous Systems II*, ACS Symposium Series 416. American Chemical Society, Washington DC, pp. 282–292.
- Manceau, A., Lanson, B., Schlegel, M.L., Hargé, J.C., Musso, M., Eybert-Bérard, L., Hazemann, J.L., Chateigner, D., Lamble, G.M., 2000. Quantitative Zn speciation in smelter-contaminated soils by EXAFS spectroscopy. *Am. J. Sci.* 300, 289–343.
- Manceau, A., Lanson, B., Drits, V.A., 2002. Structure of heavy metal sorbed birnessite Part III: results from powder and polarized extended X-ray absorption fine structure spectroscopy. *Geochim. Cosmochim. Acta* 66, 2639–2663.

- MDEQ, 2004. Montana Numeric Water Quality Standards. Montana Department of Environmental Quality, Circular WQB-7, January, 2004.
- Morris, J.M., Nimick, D.A., Farag, A.M, Meyer, J.S., 2005. Does biofilm contribute to diel cycling of Zn in High Ore Creek, Montana? *Biogeochemistry* 76, 233–259.
- Nimick, D.A., Gammons, C.H., Cleasby, T.E, Madison, J.P., Skaar, D., Brick, C.M., 2003. Diel cycles in dissolved metal concentrations in streams: occurrence and possible causes. *Water Resour. Res.*, 39. doi:10.1029/WR001571, citation no. 1247.
- Nimick, D.A., Cleasby, T.E., McCleskey, R.B., 2005. Seasonality of diel cycles of dissolved metal concentrations in a Rocky Mountain stream. *Environ. Geol.* 47, 603–614.
- Odum, H.T., 1956. Primary production in flowing waters. *Limnol. Oceanogr.* 1, 102–117.
- Olivie-Lauquet, G., Gruau, G., Aline, D., Riou, C., Jaffrezic, A., Henin, O., 2001. Release of trace elements in wetlands: role of seasonal variability. *Water Res.* 35, 943–952.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geol. Surv. Water-Resour. Invest. Rep. 99-4259.
- Power, L.E., Arai, Y., Sparks, D.L., 2005. Zinc adsorption effects on arsenic oxidation kinetics at the birnessite–water interface. *Environ. Sci. Technol.* 39, 181–187.
- Richardson, L.L., Aguilar, C., Neelson, K.H., 1988. Manganese oxidation in pH and O₂ microenvironments produced by phytoplankton. *Limnol. Oceanogr.* 33, 352–363.
- Rodda, D.P., Johnson, B.B., Wells, J.D., 1996. Modeling the effect of temperature on adsorption of lead(II) and zinc(II) onto goethite at constant pH. *J. Colloid Interface Sci.* 184, 365–377.
- Scott, D.T., McKnight, D.M., Voelker, B.M., Hrnir, D.C., 2002. Redox processes controlling manganese fate and transport in a mountain stream. *Environ. Sci. Technol.* 36, 453–459.
- Shope, C.L., 2003. Field and Laboratory Investigation of the Hydrogeochemistry of High Ore Creek, Basin, Montana. M.S. thesis, Montana Tech University of Montana.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry*, third ed. Wiley, New York.
- Sullivan, A.B., Drever, J.I., McKnight, D.M., 1998. Diel variation in element concentrations, Peru Creek, Summit County, Colorado. *J. Geochem. Explor.* 64, 141–145.
- Trivedi, P., Axe, L., 2000. Modeling Cd and Zn sorption to hydrous metal oxides. *Environ. Sci. Technol.* 34, 2215–2223.
- Trivedi, P., Axe, L., 2001. Predicting divalent metal sorption to hydrous Al, Fe, and Mn oxides. *Environ. Sci. Technol.* 35, 1779–1784.
- Tupling, R., 2001. Reclamation of the High Ore Creek Watershed. M.S. thesis, Montana Tech University of Montana.
- Whitton, B.A., Gale, N.L., Wixson, B.G., 1981. Chemistry and plant ecology of zinc-rich wastes dominated by blue-green algae. *Hydrobiology* 83, 331–342.
- Xie, Y., 2002. Experimental Investigation of the Causes of Diurnal Cycling of Zinc in a Stream Impacted by Acid Mine Drainage. M.S. thesis, Montana Tech University of Montana.