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Processes of zinc attenuation by biogenic manganese oxides forming in the hyporheic zone of Pinal Creek, Arizona

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Abstract

The distribution and speciation of Zn sorbed to biogenic Mn oxides forming in the hyporheic zone of Pinal Creek, AZ, was investigated using micro-focused Extended X-ray Absorption Fine Structure (EXAFS) and X-ray fluorescence (μ SXRF) mapping, bulk EXAFS, and chemical extraction. μ SXRF and chemical extractions show that contaminant Zn co-varied with Mn in streambed sediment grain coatings. Bulk and micro-focused EXAFS spectra of Zn in the biogenic Mn oxides coating are indicative of Zn forming triple corner sharing inner-sphere complexes over octahedral vacancies in the Mn oxide sheet structure. Zn desorbed in response to decreasing in pH in batch experiments and resulted in near-equal dissolved Zn at each pH over a 10-fold range in solid to solution ratio. The geometry of sorbed Zn was unchanged after 50% desorption at pH 5, indicating desorption is not controlled by dissolution of secondary Zn phases. In sum, these findings support the idea that Zn attenuation in Pinal Creek is largely controlled by sorption to microbial Mn oxides forming in the streambed during hyporheic exchange. Sorption to biogenic Mn oxides is likely an important process in Zn attenuation in circum-neutral pH reaches of many acid-mine drainage contaminated streams when dissolved Mn is present.

INTRODUCTION

The importance of Mn oxides for sequestration of metals has been widely documented.¹⁻⁴ Formation of Mn oxides in aqueous systems occurs predominantly by microbial oxidation processes at or near zones of transition from reducing to oxidizing conditions.⁵ Bacteriogenic manganese oxides are commonly phyllophanates, such as birnessite, that are highly reactive, and have high affinities for sorption of a wide variety of metal ions including zinc, nickel, lead, and uranium.⁶⁻¹⁰ The strong sorption affinities for metals is in part due to the presence of various types of multidentate binding sites and the need to

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SUPPORTING INFORMATION Details of sediment coating isolation, desorption experiments, synthesis of SG-1 Mn bio-oxide, XAS measurements and analysis, EXAFS fitting approach, tables of stream and groundwater chemistry, sediment metal concentrations, fitting parameters for Zn EXAFS spectra of sediment samples, for Mn K-edge EXAFS of SG-1 bio-oxides and for chalcophanite Zn EXAFS, and figures of μ SXRF map of streambed sediment magnetic fraction, Zn reference compound EXAFS spectra, schematic of Zn tridentate surface complex, and dissolved Mn versus pH in desorption experiments are presented in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

compensate the charge deficit resulting from Mn(IV) octahedral vacancies that comprise about 1 in every 6 octahedral positions.^{6, 11} The reactivity of biogenic Mn oxides has been found to influence the mobility and fate of metal contaminants in natural aquatic environments.^{5, 6, 12, 13} A mechanistic understanding of the processes of metal sorption by naturally occurring biogenic Mn oxides is needed to adequately model reactive transport, attenuation, and bioavailability of metals in contaminated surface and ground waters.

Pinal Creek, Arizona, is a well-studied mine-contaminated stream where microbial activity has been unambiguously demonstrated to produce poorly crystalline layered Mn oxides.¹⁴ Microbial oxidation of Mn(II) during hyporheic exchange of water between surface flow and the streambed has produced extensive coatings of Mn oxides on streambed sediments. The coatings have elevated Co, Ni and Zn concentrations.¹³ Although the Mn oxide coatings are only a few 10s of microns thick¹⁴, hyporheic exchange coupled with ongoing microbial Mn oxidation was found to attenuate 20% of the Mn load and up to 70% of the Co, Ni and Zn contaminant loads over 5 km of stream flow.¹³ This site thus serves as a model for studying terrestrial biological Mn(II) oxidation, its impact on contaminant mobility, and metal-Mn interactions. In addition, the absence of significant input of dissolved Fe to Pinal Creek provides the opportunity to investigate the role of metal sorption by biogenic Mn oxides without having to account for the contribution of sorption by Fe oxides.

Significant advances have been made in characterizing the speciation of metals sorbed to abiotic Mn oxides in laboratory studies.¹⁵⁻¹⁹ Recent studies have employed direct measurement techniques such as Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy to characterize both the structure of biogenic Mn oxides²⁰⁻²³ and the speciation of metals, in particular Zn, sorbed by biogenic Mn oxides produced in the laboratory^{6-8, 10}, and to natural Mn oxides.^{24, 25} These studies show that aqueous Zn^{2+} , in both tetrahedral and octahedral coordination with oxygen, binds to Mn(IV) vacancy sites in hexagonal birnessite forming triple-corner sharing surface complexes with three surface oxygens surrounding the layer vacancy.^{17, 18} Metal sorption processes to natural biogenic Mn oxides from field locations have not been characterized to the extent as laboratory Mn oxides or to other sorbent phases, notably iron oxyhydroxides.¹²

The focus of this paper is to describe the molecular-scale speciation of sorbed Zn to biogenic hexagonal birnessite forming in the hyporheic zone of Pinal Creek.¹³ We evaluate the distribution and speciation of Zn sequestered by biogenic Mn oxide coatings forming on streambed sediments comprising the hyporheic zone of a mine-contaminated stream, Pinal Creek^{13, 14, 26}, using chemical extraction, bulk and micro-focused EXAFS (μ EXAFS), and micro-focused synchrotron X-ray fluorescence mapping (μ SXRF). The reversibility of Zn sorbed to Mn oxide coatings on streambed sediments was measured as a function of pH and solid-solution ratio to test the response of attenuated Zn to changes in stream water chemistry. This study is the first to our knowledge to characterize the molecular-scale speciation of Zn sorbed to biogenic Mn oxides actively forming in the hyporheic zone of a mine-contaminated stream.

Site Description

Metal contamination in Pinal Creek, Arizona, has resulted from infiltration of acidic water into the alluvial aquifer from Cu mining operations in the watershed 20 km upgradient of the perennial stream.²⁷ The acidic ground water has reacted with minerals in the aquifer to form a neutralized contaminated ground water plume (pH 5.5 -6.5) with elevated dissolved Mn, Co, Ni and Zn of up to 1.5 mM, 20, 25, and 25 μ M, respectively, but very low dissolved iron.²⁸ Discharge of this contaminated groundwater forms the perennial stream where the water table intersects land surface and contributes up to 50% of stream flow at the basin outlet 5 km downstream.²⁶

Previously, we characterized biogenic manganese oxides forming on Pinal Creek streambed sediments. SEM images and μ SXRF maps of sediments from the hyporheic zone indicate extensive grain coatings of Mn oxides of up to 50 μ m thickness.¹⁴ Based on bulk and micro-focused synchrotron-XRD and EXAFS measurements, the Mn coatings are dominated by nanoparticulate Ca-bearing c-disordered hexagonal birnessite (10-Å phyllomanganate) indicative of a biogenic origin. Calculation of Mn(IV) octahedral occupancy in phyllomanganate sheets averaged 85% consistent with 1 vacancy per 6 octahedral positions found in bio-oxides produced in pure cultures.^{21, 22} Weak or absent basal plane (001) reflections in XRD patterns indicate minimal or no stacking of Mn oxide layers. Consistent with this observation, XRD and TEM measurements suggest the oxides consist of nanoparticulate plates averaging 11 nm thick and 35 nm in diameter, with individual particles of very few or single layers.

METHODS

Streambed sediment samples analyzed in this paper are a subset of those described in our previous paper¹⁴ that were collected from the active hyporheic zone of Pinal Creek at two sites (R2B and Z9a) 1 and 1.5 km downstream of the reach where the metal contaminated ground water plume discharges into the stream. Sampling sites, collection, and processing were previously described.^{14, 29} Water chemistry for the overlying stream water and for shallow groundwater (1 m) below the streambed was similar at the two sites (Table SI-1). Stream water at the sampling locations (Table SI-1) was undersaturated with respect to hydrozincite (log SI of -9.5), the Zn solubility limiting phase in this pH range.³⁰ Uncontaminated, background sediment devoid of Mn coatings was collected from the dry bed of the uncontaminated ephemeral stream channel about 1 km upstream of the head of perennial flow and contaminated ground water inflow.

Sediments at the two sites were sampled from the upper 3 cm of streambed and sieved to <1 mm in the field using ambient stream water.²⁹ A streambed push core also was collected at R2B using a push corer.¹³ The 3-6 cm depth interval was used for thin sections in this study. Subsamples of surface sediments were air dried for partial and total chemical extraction, and for preparation of thin sections. The core interval and background sediments were dry sieved to <1 mm. Magnetic minerals were separated from the <1 mm dried sediments and analyzed separately due to their elevated bulk Zn concentration. Mn oxide coatings were recovered from the bulk streambed surface samples by physical abrasion of wet sediments to minimize contribution of non-contaminant Zn contained in the underlying, background minerals (see

Supporting Information). The recovered coatings were used for bulk XAS measurements and for Zn desorption experiments.

Double-polished petrographic thin sections (30 micron thickness) were prepared by Spectrum Petrographics, Inc. from resin mounts (3M Scotchcast) of magnetic and non-magnetic fractions of air-dried streambed sediments (<1 mm).¹⁴

Metal concentrations of streambed sediments (<1 mm) and abraded coatings were determined by partial chemical extraction using 0.1 M hydroxylamine HCl in 0.05 N HNO₃ (HH) at room temperature for 1 hour. This extraction scheme was effective in dissolving Mn oxides from Pinal Creek sediments.¹³ Total metal concentrations were determined following total dissolution of separate sediment samples using HF-HNO₃ digestion. The resulting extraction and total dissolution samples solutions were analyzed by ICP-OES.¹³

The reversibility of Zn sorption to the Pinal Creek biogenic Mn oxides was tested in batch suspensions of the abraded Mn-oxide coatings in artificial stream water, ASW (see Supporting Information), at three solid to solution ratios (solid concentration) to simulate the response of Zn attenuated in the streambed to possible inflow of more acidic water to Pinal Creek from the alluvial aquifer. The pH of the abraded coating suspension was incrementally adjusted downwards from pH 7 to pH 4 (see Supporting Information). After equilibrating at each pH to attain constant dissolved Zn (24 hours), subsamples were collected for dissolved and HH extractable metal content.

The speciation of Zn sorbed to Pinal Creek Mn oxides was compared to Zn sorbed to biogenic Mn oxides produced using spores of *Bacillus sp.*, strain SG-1. The Mn oxides were produced by culturing spores from *Bacillus sp.* strain SG-1²⁰ but with the addition of dissolved Zn as ZnCl₂ to yield Zn:Mn molar ratio of 1:100 and 1:10 (see Supporting information).

Bulk EXAFS, μ SXRF and μ EXAFS measurements

Bulk Zn K-edge EXAFS spectra of the isolated sediment coatings, the Zn-bearing SG1 bio-oxide, Zn mineral specimens and aqueous Zn(II) species were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline 11-2 with a Si 220 monochromator crystal. μ SXRF elemental maps (10 KeV) and Zn K-edge μ EXAFS spectra of streambed sediment thin sections were collected at the Advanced Light Source beamline 10.3.2 X-ray microprobe.³¹ Zn K-edge EXAFS fluorescence spectra were collected at points with elevated Mn and Zn concentration identified in μ SXRF maps. Details of XAS data collection and data analysis are presented in the Supporting Information.

RESULTS and DISCUSSION

Sediment Chemistry

Mn-oxide-coated sediments were black, in contrast to background sediments, ranged from buff to brown depending on mineralogy. The <1 mm fraction of streambed sediment samples is predominantly sand-size material with less than 1 wt% of particles of <125 μ m diameter. Sediments consist primarily of quartz, feldspar, illite, mica and chlorite along with

magnetic minerals, primarily magnetite and illmenite.³² The magnetic fraction comprised 7 and 15 wt % of the Z9a and R2B streambed sediment samples, respectively. The total Fe content of the magnetic fraction accounts for nearly all (~98%) of the total Fe in the sediment (Table SI-2).

Comparison of partial chemical extraction (HH) of streambed sediments from the contaminated stream reach with the background sediment shows a 5- to 25-fold increase in Mn, Zn, Co and Ni concentration (Table SI-2). In particular, the easily extractable component defined by the HH extraction accounts for a majority of the increase in these metals in the contaminated sediments relative to the uncontaminated, background sediment. The HH extraction of contaminated bulk sediment accounts for more than 80% of the total Mn content determined by total dissolution compared to 7% of the uncontaminated sediment. Zn in HH extractions is 15% (R2B) and 24% (Z9a) of the total Zn but only 3% for the uncontaminated sediment. Assuming the HH primarily dissolves Zn associated with the coatings, the remainder of the Zn is contained within more resistant mineral components. For example, the HH-insoluble magnetic mineral fraction of Z9a sediments contains 28% of the total Zn.

HH extraction of the isolated coatings dissolved all of the Mn and >95% of other the contaminant metals (Zn, Co, Cu, Ni) (Table SI-2). Assuming the HH extractable Mn concentration of the bulk sand is from the coatings, the coatings are estimated to comprise 2.8 and 3.0% of the bulk R2b and Z9a sediment mass, respectively. The Zn:Mn molar ratio in the coatings agrees well with the ratio in HH extraction of the bulk sediment suggesting that the material removed by abrading is the same as the material removed by HH extraction. The Mn oxide content of the coatings is about 20 wt % assuming a stoichiometry of MnO₂. Organic material such as microbial cell material comprised 3% of the mass.¹⁴ The remainder of the material is comprised of clays¹⁴ and other fine grained sediment particles entrained within the coating, and water. Using secondary ion mass spectrometry, Best et al determined that Fe in Pinal Creek sediment coatings was not spatially correlated with Mn but, instead, existed as discrete particles.³² An upper limit of 3% of the total Zn in the coatings was estimated for the fine-grained magnetic minerals by multiplying the total Fe measured in coatings by the ratio of Zn:Fe measured in magnetic sand fraction. Similarly, the upper limit of 10% Zn in the coatings from aluminosilicate minerals was estimated by multiplying the coating Al content by the Zn:Al ratio of uncontaminated bulk sediment. Thus, Zn measured in coatings is largely associated with the Mn oxide phases.

Contaminant Metal Distribution

μSXRF maps illustrate the distribution of metals in and on streambed sediment grains. Mn primarily occurs as coatings on sand grains of the nonmagnetic mineral fraction (Figure 1) consistent with the HH extraction. Zn co-varies with Mn in the coatings, but is also present in the interiors of some grains (Figure 1C). The close association of Zn with Mn is further illustrated by the high correlation of Zn and Mn in grain coatings that have little Zn or Mn within the underlying mineralogy such as quartz grains (Figure 1B). Zn is also present in Mn oxide coatings on the magnetic mineral fraction although high Zn concentrations are evident within magnetic mineral grains (Figure SI-1).

Mn oxide coatings are absent from the background sediments consistent with the small fraction of the total Mn and Zn that was HH extractable. Instead, Zn and Mn are only observed within the minerals of the sand sized grains, in particular, in the magnetic fraction.

Combined, the μ SXRF maps and chemical extraction results support the hypothesis that ongoing Mn oxide formation in the hyporheic zone enhances attenuation of Zn in Pinal Creek.¹³ The co-distribution of Zn and Mn in the streambed sediment coatings from the contaminated reach of the stream likely is the result of microbial Mn oxidation and sequestration of contaminant Zn from stream water during hyporheic exchange. The presence of Zn within the underlying minerals of the sediment from the contaminated stream reach represents the background or non-contaminant Zn and accounts for about 80% of the total Zn in bulk sediment.

Local molecular structure of sorbed Zn

Zn EXAFS spectra for Pinal Creek samples are generally similar to one another, to the Zn-sorbed SG-1 bio-oxide, and to chalcophanite (Figure 2). The chalcophanite FT peak positions are somewhat shifted compared to the samples due to a greater abundance of tetrahedral Zn (Zn_{TET}) in the samples (*vide infra*). The sample spectra are different from those of hydrozincite, zincite, smithsonite, and hetaerolite (Figure SI-2), Zn phases not found in Pinal Creek sediments.³² Zn spectra of coatings also differ from Zn sorbed to hydrated alumina or iron oxides.^{33, 34} All Pinal Creek Zn EXAFS spectra, as well as that for Zn sorbed SG-1 Mn bio-oxides, are dominated by a Zn-O pair correlation in the Fourier Transforms (FTs) at *ca* 1.5 Å uncorrected for phase shift (R+dR), which corresponds to a real-space Zn-O distance of *ca* 1.97 Å. This distance is characteristic of tetrahedral Zn coordination.^{6, 15} In contrast, the longer Zn-O distance present in the FT for chalcophanite (*ca* 1.7 Å R+dR, Figure 2) indicates an octahedral environment (Zn_{OCT}). This qualitative comparison suggests that Zn exhibits dominantly tetrahedral coordination in Pinal Creek Mn oxides.

The Zn EXAFS spectra also show strong pair correlations between 2.8 and 3 Å, R+dR and at *ca* 4.8 Å R+dR (Figure 2). The exact position and shape of these frequencies vary from sample to sample, indicating the presence of variations in the local structure around Zn. It is likely that these pair correlations contain contributions from Mn and O atoms within the hexagonal birnessite substrates. Pinal Creek Mn oxides grow in biofilms produced by Mn(II) oxidizing bacteria for surface attachment.¹⁴ Thus, Zn also may be bound to biopolymers, *i.e.*, the 2.8 to 3 Å correlations (Figure 2) could contain contributions from organic ligands. Toner et al showed that Zn added to biofilms containing Mn oxides was sorbed onto the Mn oxide component at ratios of Zn:Mn < 0.37 with no evidence of Zn binding to organic matter.⁶ In comparison, Zn:Mn ratios in Pinal Creek coatings are 0.01 (R2B and Z9a) and 0.06 in the SG-1 biooxide, suggesting that complexation by organic matter should be negligible. Indeed, adequate fits were obtained using only O and Mn shells. Organic ligands subsequently were neglected in EXAFS fitting. Zn-Mn frequencies in the observed distance range suggest that ZnO_4 and MnO_6 polyhedra share corners and are qualitatively consistent with a high degree of order resulting from binding of Zn as tridentate complexes over Mn octahedral vacancies observed in previous studies (Figure SI-3).^{6, 15, 16}

A shell by shell fitting approach was used to model the EXAFS spectra. Details are described in the Supporting Information. Both tetrahedral and octahedral Zn environments were assumed to be present.^{6, 16, 35} The coordination number (CN) for each complex was fixed to a value of 4 for Zn_{TET} and 6 for Zn_{OCT}. In order to decrease the number of varied parameters and to increase the robustness of the fit, the relative proportion of each type of Zn complex was floated with the Zn_{OCT} coordination number scaled by a floated parameter f_{OCT} , and the Zn_{TET} coordination was scaled by $[1 - f_{OCT}]$. This procedure ensured that the total effective coordination number for the Zn-O shell would remain between 4 and 6 and accounted for amplitude reduction from destructive interference by oxygens in the two subshells.²² Best fits (Figure 2 and Table SI-3) indicate that streambed sediment bulk coatings and the SG1 bio-oxides contain on average 80% Zn_{TET} and 20% Zn_{OCT} despite a 6-fold variation in Zn:Mn ratio, equivalent to an effective overall Zn-O CN of 4.4 (3.2 for Zn_{TET} and 1.2 for Zn_{OCT}). A similar proportion of Zn_{TET} (70%) and Zn_{OCT} (30%) was found for a Zn sorbed abiotic, synthetic hexagonal birnessite with similar Zn loading (Zn/Mn = 0.008).¹⁶ Our results contrast, however, the finding of 100% Zn_{TET} for a biogenic Mn oxide with Zn/Mn molar ratio of 0.07.⁶ The average Zn-O tetrahedral distance at 1.97 ± 0.03 Å and the octahedral Zn-O distance of 2.17 ± 0.03 Å are in good agreement with those for Zn sorbed on abiotic birnessite¹⁶ and a biogenic hexagonal birnessite derived in the laboratory from *Pseudomonas Putida*.⁶ Density functional theory shows that the Zn_{TET} forms stronger bonds with O atoms surrounding the vacancy but that both Zn_{TET} and Zn_{OCT} are stable interlayer species.¹⁸ The best fits also yield second and third shell Mn atoms at distances of 3.36 ± 0.03 and 5.39 ± 0.03 Å for Zn_{TET} and 3.53 ± 0.03 and 5.60 ± 0.03 Å Zn_{OCT}, respectively, as expected for binding over the octahedral vacancy. Overall, the spectra provide strong evidence that sorbed Zn occurs primarily as tridentate complexes above Mn octahedral vacancies (Figure SI-3).

μ-EXAFS spectra for discrete points on sediment grain coatings of both the nonmagnetic and magnetic sediment fractions all have the general features present in the bulk coating and SG1 bio-oxide spectra (Figure 2). The higher frequency features are not as well resolved as the bulk spectra, in part because of the limited data range of the μ-EXAFS. Fits yield the same Zn geometries observed in the bulk coatings samples (Table SI-3). Individual points within the coatings exhibit a wider range of %Zn_{TET} (72 to 90%) but a similar average (78%) as observed in the bulk coatings and SG-1 bio-oxide (80%). The wider range of Zn_{TET} in the discrete points measured by μEXAFS also may be related to local variations Zn/Mn ratios or to the hydration state of the sample. An important difference between the thin section samples used to collect μEXAFS spectra and the bulk samples was that drying of sediments was required for preparation of resin casts used for making thin sections. In support of this statement, we note that the dried R2B bulk coatings had a lower component of Zn_{TET} (75 ± 4 %) than in the wet sample (80 ± 5 %) (Table SI-3).

Zn desorption

In desorption experiments with abraded coatings, dissolved Zn concentration, [Zn], increased with decreasing pH from pH 7 to 5 and was independent of solid concentration over a factor of 10 range in solid concentration (Figure 3A). The slope of log [Zn] vs pH ranged from 0.73 to 0.88 for the three conditions, yielding an average macroscopic proton

stoichiometry of 1.3 H⁺ per mole Zn desorbed. A decrease in slope was observed below pH 5. About 50% of the total Zn desorbed from the Mn oxides by pH 5 in the lowest solid concentration system (Figure 3B). At the pH (>6.5) of the stream where Mn oxidation and Zn attenuation occur, very little Zn desorbed (0.3 μM). The observed pH dependence of Zn desorption is consistent with the pH dependence of Zn uptake by Mn oxide in lab studies.¹² Previous studies have found that Zn is reversibly sorbed to synthetic δ-MnO₂³⁶ and to biogenic Mn oxides produced Mn-oxidizing fungus.³⁷

The release of Mn also increased with decreasing pH with the greatest release observed for the lowest solid concentration (Figure SI-4) with about 6% of the total Mn released at pH 4.3. By comparison, this material contains 9% Mn(II) as determined by fits Mn K-edge XANES.¹⁴ It is unknown if Mn release is the result of dissolution or desorption of Mn(II) or Mn(III) bound by the hexagonal birnessite. Less than 2% of the total measured Zn desorption in each of experimental systems can be attributed to Mn oxide dissolution assuming congruent dissolution where Zn released is proportional to Mn release and controlled by the total Zn to Mn ratio of the solid.

The near-equal concentrations of dissolved Zn resulting from desorption in the experiments spanning a factor 10 range in solid concentration could be interpreted as a solubility control for Zn. However, because Mn⁴⁺ is not soluble in water, birnessite dissolution as such is not possible. In the absence of reduction, mineralogic transformation of hexagonal birnessite was not observed between pH 7 and 5.5³⁸ suggesting Zn sorption likely is not affected by structural changes to the Mn oxide in response to the pH decrease. Furthermore, Zn-Mn distances indicative of incorporation into the Mn oxide layer are not observed, consistent with density functional theory simulations that show Zn is unstable in the octahedral layer vacancy, and instead is repelled out of sheet to the more stable tridentate corner sharing complex over vacancy.¹⁹ Hence, Zn is not incorporated into the 3-dimensional structure of the hexagonal birnessite.

Although the desorption experiments were well below saturation with respect to hydrozincite across the experimental pH range, the presence of a secondary Zn phase that might result in the observed desorption behavior was evaluated. The local structure of the remaining sorbed Zn was determined by analysis of the Zn EXAFS spectrum of the biogenic oxide coatings following 50% desorption at pH 5 in the lowest solids concentration system. Fitting of this spectrum yielded the same overall geometry of Zn bound to octahedral layer vacancies as measured in the coatings prior to desorption (Figure 2 and Table SI-3) and did not require inclusion of other Zn-bearing phases. These data are consistent with the absence of a secondary Zn phase that could control Zn by a solubility process. Interestingly, increases in Zn_{OCT} from 20 to 30%, and in Zn-Mn1 distance of about 0.08 Å for both Zn_{TET} and Zn_{OCT} were observed at pH 5. We hypothesize that vacancy protonation by two H⁺ replacing Zn¹⁸ as pH decreases causes expansion of the vacancy from steric effects of two charge compensating protons bound over a single vacancy. Adjacent vacancies capped with Zn_{TET} or Zn_{OCT} complexes may contract in response to the resulting stress created by protonation of the octahedral sheet. Vacancy contraction would in turn cause the Zn tetrahedra and octahedra to move away from the vacancy. The increase in % Zn_{OCT} in response to the 50% decrease in sorbed Zn is contrary to previously reported decrease in

Zn_{OCT} with decreased loading and to the negligible effect of pH on the fraction of Zn_{OCT}.¹⁷ The presence of other metals and major cations (e.g. Ca²⁺) in the biogenic Mn oxides formed in the field may account for the difference in % Zn_{OCT} observed in simpler laboratory systems.

The absence of secondary Zn phases together with the lack of a direct Mn oxide solubility control during desorption and the instability of Zn for incorporation into the birnessite structure¹⁹ are inconsistent with a solubility process controlling Zn desorption that the constant dissolved Zn over the range of solids concentration suggests (Figure 3A). Instead, the observed release of Zn may be the result of a surface complexation process in which the Zn triple corner sharing complex desorbs from the octahedral vacancy sites in exchange for protons or other cations to compensate the -2 charge on the octahedral vacancy. The observed macroscopic proton stoichiometry of 1.3 indicates other cations in addition to protons, such as Ca²⁺, also contribute to the charge compensation required by Zn desorption. The strong correlation between Ca and Mn observed in Pinal Creek Mn oxide coatings¹⁴ indicates that interlayer Ca²⁺ in addition to Mn²⁺ likely accounts for a majority of charge compensation of the vacancies. Sorption data spanning a wider range of conditions (e.g. Zn:Mn ratio, pH, solid concentration, electrolyte composition) are needed to test if Zn desorption is controlled by surface complexation or dissolution processes. These data would enable developing a surface complexation model that is consistent with the observed tridentate corner sharing Zn complexes over the octahedral vacancies and the resulting charge compensation required for release of Zn such as proposed by Appelo and Postma.³⁹ Additionally, the effect of other sorbed metals and cations present in stream water (e.g. Ca²⁺ ~10 mM) and associated with the biogenic Mn oxide needs to be incorporated into the surface complexation model.

Environmental Implications

The co-variation of Zn with Mn in coatings combined with the observed triple corner sharing Zn complexes over octahedral vacancies in the biogenic Mn oxide sheet structure are consistent with the observed attenuation of Zn contamination in Pinal Creek occurring largely by sorption to microbial Mn oxides forming during hyporheic exchange. The apparent strong binding of the Zn suggests little desorption would occur in response to a decrease in dissolved Zn inputs to the stream, such as resulting from the ongoing remediation strategy of interception and lime-treatment of contaminated ground water plume and discharge of neutral pH treated water with low metal concentrations to the stream.¹⁴ However, if the acidic plume reached the perennial stream flow and caused a substantial decrease in stream water pH, then desorption of the attenuated Zn from the biogenic Mn oxides would occur, resulting in large increases in dissolved Zn concentration in response to the lower pH. In acidic mine drainages, significant attenuation of Zn and Mn often does not occur until pH increases to near neutral in response to reaction and mixing with uncontaminated water.⁴⁰ The strong binding of Zn to octahedral vacancies of biogenic Mn oxides found at Pinal Creek is likely to be an important process in Zn attenuation in the circum-neutral pH reaches of many mine contaminated streams.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- McKenzie RM. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Aust. J. Soil Sci.* 1980; 18:61–73.
- Balistreri LS, Murray JW. The surface chemistry of sediments from the Panama Basin: The influence of Mn oxides on metal adsorption. *Geochim. Cosmochim. Acta.* 1986; 50:2235–2243.
- Catts JG, Langmuir D. Adsorption of Cu, Pb and Zn by δ MnO₂: applicability of the site binding-surface complexation model. *Appl. Geochem.* 1986; 1:255–264.
- Shope CL, Xie Y, Gammons CH. The influence of hydrous Mn-Zn oxides on diel cycling of Zn in an alkaline stream draining abandoned mine lands. *Appl. Geochem.* 2006; 21:476–491.
- Tebo BM, Bargar JR, Clement BG, Dick GJ, Murray KJ, Parker D, Verity R, Webb SM. Biogenic manganese oxides: Properties and mechanisms of formation. *Ann. Rev. Earth Planet. Sci.* 2004; 32:287–328.
- Toner B, Manceau A, Webb SM, Sposito G. Zinc sorption to biogenic hexagonal-birnessite particles within a hydrated bacterial biofilm. *Geochim. Cosmochim. Acta.* 2006; 70:27–43.
- Webb SM, Fuller CC, Tebo BM, Bargar JR. Determination of uranyl incorporation into biogenic manganese oxides using X-ray absorption spectroscopy and scattering. *Environ. Sci. Technol.* 2006; 40:771–777. [PubMed: 16509317]
- Villalobos M, Bargar J, Sposito G. Mechanisms of Pb(II) sorption on a biogenic manganese oxide. *Environ. Sci. Technol.* 2005; 39:569–576. [PubMed: 15707057]
- O'Reilly SE, Hochella MF Jr. Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides. *Geochim. Cosmochim. Acta.* 2003; 67:4471–4487.
- Peña J, Kwon KD, Refson K, Bargar JR, Sposito G. Mechanisms of nickel sorption by a bacteriogenic birnessite. *Geochim. Cosmochim. Acta.* 2010; 74:3076–3089.
- Lanson B, Drits VA, Silvester E, Manceau A. Structure of H-exchanged hexagonal birnessite and its mechanism of formation from Na-rich monoclinic buserite at low pH. *Am. Mineral.* 2000; 85:826–838.
- Tonkin JW, Balistreri LS, Murray JW. Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. *Appl. Geochem.* 2004; 19:29–53.
- Fuller CC, Harvey JW. Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona. *Environ. Sci. Technol.* 2000; 34:1150–1155.
- Bargar JR, Fuller CC, Marcus MA, Brearley AJ, Perez De la Rosa M, Webb SM, Caldwell WA. Structural characterization of terrestrial microbial Mn oxides from Pinal Creek, AZ. *Geochim. Cosmochim. Acta.* 2009; 73:889–910.

15. Lanson B, Drits VA, Gaillot A- Silvester E, Plançon A, Manceau A. Structure of heavy-metal sorbed birnessite: Part 1. Results from X-ray diffraction. *Am. Mineral.* 2002; 87:1631–1645.
16. Manceau A, Lanson B, Drits VA. Structure of heavy metal sorbed birnessite. Part III: Results from powder and polarized extended X-ray absorption fine structure spectroscopy. *Geochim. Cosmochim. Acta.* 2002; 66:2639–2663.
17. Grangeon S, Manceau A, Guilhermet J, Gaillot A- Lanson M, Lanson B. Zn sorption modifies dynamically the layer and interlayer structure of vernadite. *Geochim. Cosmochim. Acta.* 2012; 85:302–313.
18. Kwon KD, Refson K, Sposito G. Zinc surface complexes on birnessite: A density functional theory study. *Geochim. Cosmochim. Acta.* 2009; 73:1273–1284.
19. Kwon KD, Refson K, Sposito G. Understanding the trends in transition metal sorption by vacancy sites in birnessite. *Geochim. Cosmochim. Acta.* 2013; 101:222–232.
20. Bargar JR, Tebo BM, Bergmann U, Webb SM, Glatzel P, Chiu VQ, Villalobos M. Biotic and abiotic products of Mn(II) oxidation by spores of the marine *Bacillus sp.* strain SG-1. *Am. Mineral.* 2005; 90:143–154.
21. Villalobos M, Lanson B, Manceau A, Toner B, Sposito G. Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *Am. Mineral.* 2006; 91:489–502.
22. Webb SM, Tebo BM, Bargar JR. Structural characterization of biogenic Mn oxides produced in seawater by the marine bacillus sp. strain SG-1. *Am. Mineral.* 2005; 90:1342–1357.
23. Santelli CM, Webb SM, Dohnalkova AC, Hansel CM. Diversity of Mn oxides produced by Mn(II)-oxidizing fungi. *Geochim. Cosmochim. Acta.* 2011; 75:2762–2776.
24. Lanson B, Marcus MA, Fakra S, Panfili F, Geoffroy N, Manceau A. Formation of Zn-Ca phyllomanganate nanoparticles in grass roots. *Geochim. Cosmochim. Acta.* 2008; 72:2478–2490.
25. Marcus MA, Manceau A, Kersten M. Mn, Fe, Zn and As speciation in a fast-growing ferromanganese marine nodule. *Geochim. Cosmochim. Acta.* 2004; 68:3125–3136.
26. Harvey JW, Fuller CC. Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance. *Water Resour. Res.* 1998; 34:623–636.
27. Eychaner, JH. Solute transport in perennial streamflow at Pinal Creek, Arizona. U.S. Geological Survey; 1991. p. 481-485. USGS Water Resources Investigations Report 91-4034
28. Stollenwerk KG. Geochemical interactions between constituents in acidic groundwater and alluvium in an aquifer near Globe, Arizona. *Appl. Geochem.* 1994; 9:353–369.
29. Kay JT, Conklin MH, Fuller CC, O'Day PA. Processes of nickel and cobalt uptake by a manganese oxide forming sediment in Pinal Creek, Globe mining district, Arizona. *Environ. Sci. Technol.* 2001; 35:4719–4725. [PubMed: 11775144]
30. Zachara JM, Kittrick JA, Dake LS, Harsh JB. Solubility and surface spectroscopy of zinc precipitates on calcite. *Geochim. Cosmochim. Acta.* 1989; 53:9–19.
31. Marcus MA, MacDowell AA, Celestre R, Manceau A, Miller T, Padmore HA, Sublett RE. Beamline 10.3.2 at ALS: A hard X-ray microprobe for environmental and materials sciences. *J. Synchrotron Rad.* 2004; 11:239–247.
32. Best, JE.; Geiger, KE.; O'Day, PA. Partitioning of trace metals between contaminated stream waters and manganese oxide minerals, Pinal Creek, Arizona. Vol. 1. U.S. Geological Survey; 1999. p. 227-237. USGS Water Resources Investigations Report 99-4018A
33. Waychunas GA, Fuller CC, Davis JA. Surface complexation and precipitate geometry for aqueous Zn(II) sorption on ferrihydrite I: X-ray absorption extended fine structure spectroscopy analysis. *Geochim. Cosmochim. Acta.* 2002; 66:1119–1137.
34. Trainor TP, Brown GE Jr. Parks GA. Adsorption and precipitation of aqueous Zn(II) on alumina powders. *J. Colloid Interface Sci.* 2000; 231:359–372. [PubMed: 11049686]
35. Bochatay L, Persson P. Metal ion coordination at the water-manganite (γ -MnOOH) interface: II. An EXAFS study of zinc(II). *J. Colloid Interface Sci.* 2000; 229:593–599. [PubMed: 10985840]
36. Li X, Pan G, Qin Y, Hu T, Wu Z, Xie Y. EXAFS studies on adsorption-desorption reversibility at manganese oxide-water interfaces: II. Reversible adsorption of zinc on d-MnO₂. *J. Colloid Interface Sci.* 2004; 271:35–40. [PubMed: 14757074]

37. Tani Y, Ohashi M, Miyata N, Seyama H, Iwahori K, Soma M. Sorption of Co(II), Ni(II), and Zn(II) on biogenic manganese oxides produced by a Mn-oxidizing fungus, strain KR21-2. *J. Environ. Sci. Health., A.* 2004; 39:2641–2660.
38. Lefkowitz JP, Rouff AA, Elzinga EJ. Influence of pH on the Reductive Transformation of Birnessite by Aqueous Mn(II). *Environ. Sci. Technol.* 2013; 47:10364–10371. [PubMed: 23875781]
39. Appelo CAJ, Postma D. A consistent model for surface complexation on birnessite (--MnO_2) and its application to a column experiment. *Geochim. Cosmochim. Acta.* 1999; 63:3039–3048.
40. Kimball, BA.; Walton-Day, K.; Runkel, RL. Quantification of metal loading by tracer injection and synoptic sampling, 1996-2000. In: Church, SE.; von Guerard, P.; Finger, SE., editors. *Integrated investigations of Environmental Effects of Historical Mining in the Animas River Watershed, San Juan, County, Colorado.* U.S. Geological Survey; 2007. p. 423-495. USGS Professional Paper 1651

Figure 1.

Zn and Mn distribution from μ SXRF mapping of thin sections of non-magnetic mineral fractions of hyporheic zone sediments from sites R2B (A and B) and Z9a (C). Brighter areas are higher concentration. Circled grain (R2B grain 1) in A is shown in B as a higher resolution map in which the grain orientation is rotated 90° clockwise from A. White circle in B depicts location of Zn μ EXAFS spectrum R2B grain 1 point 1. Arrow in A points to the location of Zn μ EXAFS spectrum R2B grain 2 point 3.

Figure 2.

Zn EXAFS spectra and Fourier transforms of Pinal Creek samples (solid lines). Fits are represented by circular symbols. Spectrum A is SG-1 bio-oxide; B R2B bulk coatings (wet); C R2B bulk coatings (dried); D Z9a bulk coatings; E Z9a bulk coatings after desorption at pH 5; F R2B non-magnetic grain 1 point 1; G R2B non-magnetic grain 2 point 3; H R2B magnetic grain 1 point 1; and I R2B magnetic grain 3 point 3. Spectrum J is chalcophanite model compound; its shell by shell fit is presented in Supporting Information, Table SI-5.

Figure 3.

A. Dissolved Zn concentration (log moles/L) released from Mn oxide coatings as a function of pH. The solid concentration is expressed as millimoles Mn in solid per liter. B. Fraction remaining Zn sorbed versus pH after desorption from Mn oxide coatings.