REDUCTIVE MOBILIZATION OF OXIDE-BOUND METALS
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Progress Report
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Release of MnO₂-Bound Toxic Metals: We have completed a large number of experiments which examine the release of MnO₂-bound Co, Ni, and Cu. Our work has focused upon the following areas: (i) competitive adsorption among the three toxic metals and Mn(II); (ii) toxic metal release upon addition of low MW organic reductants and complexants; and (iii) toxic metal release upon addition of natural organic matter-rich surface waters and IHSS organic matter reference material. A few generalizations can be made based upon this work:

- * Acidification causes [H⁺] to increase. MnO₂ reductive dissolution causes [Mn^{II}] to increase. Both processes are effective at releasing MnO₂-bound toxic metals, through a competitive sorption mechanism.
- * When organic compounds capable of chelating toxic metals are added, release by chelation can equal or exceed release through competitive sorption mechanisms.
- * When MnO₂ reductive dissolution takes place, both the total oxide surface area and surface site concentration (S_T) are decreased. These effects are minor in comparison to other toxic metal release mechanisms until the extent of MnO₂ dissolution reaches approximately 40%.
- * The surfaces of oxides such as MnO₂ may contain high, medium, and low energy sorptive sites. Preferential removal of high energy sorptive sites during the early stages of reductive dissolution would cause a disproportionate release of sorbed toxic metals. Such an effect was not observed.

Experiments have been completed that examine the nature and reactivity of MnO₂-bound toxic metals. Equilibrium experiments provide us with an "adsorption edge" graph of toxic metal sorption as a function of pH. It is important to recall that Ni and Cu remain in the +II oxidation state upon sorption to MnO₂ oxide. Experiments examining how acidification affects toxic metal release provide evidence of this. When suspensions pre-equilibrated for 17 hours at pH 4.0, 5.0, and 6.0 are acidified to pH 3.0, the extent of Ni and Cu release is equal to the amount expected based upon the equilibrium "adsorption edge" graph.

Oxidation of Co(II) to Co(III) upon adsorption to MnO₂ has been demonstrated by others (see Murray and Dillard, 1979; Dillard et al., 1981). Evidence for Co(II) oxidation in our own experiments comes from an observed hysteresis effect. When suspensions pre-equilibrated for 17 hours at pH 4.0, 5.0, and 6.0 are acidified to pH 3.0, the extent of Co release falls short of amount expected based upon the

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equilibrium "adsorption edge" graph (Figure 1). It is likely that the "irreversibly sorbed" Co has been oxidized at the MnO_2 surface. According to this reasoning, the amount of oxidation that has taken place after 17 hours increases as the pre-equilibrium pH is increased.

When the period of pre-equilibration has been extended, the rate and extent of toxic metal release can be changed. Extended pre-equilibration may physically move metals from "accessible" sites which can readily respond to changes in aqueous solution composition to "inaccessible" sites which do not. As shown in Figures 2 and 3, when the duration of Co pre-equilibration has been extended from 17 hours to one month, rates of release caused by acidification and by addition of oxalate are diminished. Conversion of Co(II) to Co(III) during extended pre-equilibration is probably responsible.

We have examined the effects of seven low molecular weight organic reductants and complexants on MnO_2 reductive dissolution and toxic metal release. Pyruvate and hydroquinone reduce and dissolve MnO_2 (forming Mn(II)), without complexing toxic metals to any significant extent. Stoichiometric two-equivalent oxidation of hydroquinone forms p-benzoquinone, which can be measured by HPLC. By measuring concentrations of p-benzoquinone and $\text{Mn}^{2+}(\text{aq})$, it is possible to calculate during the course of a reaction: (i) the remaining amount of MnO_2 , (ii) the total amount of Mn(II) generated by reduction, and (iii) the amount of Mn(II) adsorbed. This information is useful for understanding toxic metal release. In the absence of complexants, toxic metal release occurs primarily because of competition with Mn(II) for available surface sites, and loss of sites arising from oxide dissolution.

Oxalate above pH 6 exhibits complexant characteristics but negligible reductant characteristics. The ability of oxalate to remove sorbed toxic metals is related to trends in complex formation constants. Because of its position in the Irving-Williams Series, Cu has the highest complex formation constant, is released to the greatest extent upon addition of oxalate.

Citrate is another low MW organic compound exhibiting important reductant and complexant characteristics. A dramatic lag period is observed, which diminishes as the pH is decreased and as the concentration of citrate is increased. An important clue concerning the cause of the lag period can be discerned from the experimental results presented in Figure 4. Although addition of Co and Ni causes the lag period to shorten, addition of Cu causes the lag period to lengthen. This behavior sets citrate apart from the other organic compounds that we have examined. Plots of the extent of toxic metal release as a function of the extent of MnO_2 dissolution are presented in Figure 5. Once again, Cu has the highest equilibrium constant for the formation of metal-citrate complexes. For this reason, release by complexation is more important for Cu than for the two other metals, resulting in a steep slope for toxic metal release.

An extensive set of experiments has examined MnO_2 reductive dissolution and toxic metal release upon addition of natural organic matter (NOM). Five samples derived from three sources have been used (see Table I). As shown in Figure 6, rates of MnO_2 reductive dissolution by the five samples at equal organic carbon content (12 mgC/L) differ by only a factor of three. This finding can be explained by the similar ecosystem characteristics of the five freshwater swamps from which the samples were

derived. This finding highlights the importance of examining NOM samples from more varied environments.

When the extent of toxic metal release is plotted as a function of MnO_2 reductive dissolution, a steep slope indicates that chelation by NOM is contributing to release. When the slope is shallow, competitive adsorption by Mn^{II} (generated by MnO_2 reductive dissolution) is playing a greater role in toxic metal release. At pH 5.0, the five NOM samples exhibited a similar effect on toxic metal release, as shown in Figure 7. These plots are steepest for Cu, reflecting the greater affinity of Cu for organic complexation in comparison to the two other metals (in agreement with the Irving-Williams Series). The curve with Suwannee River humic acid rises more steeply than with the other samples, indicating slightly more complexant reactivity.

Ni release as a function of MnO_2 dissolution is slightly higher for NOM samples that reduce and dissolve MnO_2 more slowly (such as the raw water samples) than for NOM samples that reduce and dissolve MnO_2 more quickly (such as the IHSS samples). A similar effect was observed with the low MW reductants considered earlier.

Adsorption and Release of FeOOH-Bound Toxic Metals We began our experiments by examining the adsorption and subsequent release of toxic metals bound to FeOOH (goethite). Approximately 200 grams of goethite have been prepared according to the method of Atkinson et al. 1967) and washed repeatedly. Toxic metals are equilibrated overnight with FeOOH before any change in aqueous medium composition is made. Because the surface area (in m^2/g) of FeOOH is approximately four times lower than that of MnO_2 , we have chosen to work under a different "basis set" of chemical conditions: 1.0×10^{-3} moles FeOOH/L, 1.0×10^{-5} M MeCl_2 , 5.0×10^{-3} M Acetate, and 1.0×10^{-2} M NaCl. The adsorption "edge" for FeOOH occurs at a higher pH than was observed for MnO_2 . Adsorption of Cu, for example, rises steeply near pH 6.0.

We have begun experiments examining release of FeOOH-bound toxic metals upon addition of low molecular-weight organic compounds. At pH 6.0, addition of 5.0×10^{-6} M pyruvate had no discernable effect on Cu adsorption. Addition of 5.0×10^{-6} M citrate, in contrast, actually lead to an increase in the extent of Cu adsorption (from approx. 65% to approx. 87%). Many experimental and conceptual details need to be worked out, especially regarding the reactivity of FeOOH towards the low molecular-weight reductants and complexants included in our study.

In our future work with goethite and other iron oxide phases, it is important to follow the sorption and subsequent release of Pb. We have developed a Differential Pulse Method using the PAR 264A Polarographic Analyzer which was purchased with funds provided by this grant. We can now routinely measure Pb^{2+} concentrations as low as 40 nanomolar. Using similar procedures, it should be possible to measure comparable concentrations of Cu, Zn, and Cd.

Modelling Efforts We are interested in comparing data that can be obtained using closed, batch systems with data that can be obtained using open, flow-through systems. Numerical simulation provides an opportunity for sensitivity analysis; reaction steps that have the greatest effect on toxic metal release can be identified by making

systematic changes to model input parameters. Such information can be used to help optimize the experimental design to provide the most meaningful experimental data.

Our modelling effort has focused upon toxic metal adsorption and release in a simple continuously-stirred tank reactor (CSTR). The "characteristic time" for physical dilution is related to the ratio of reactor volume V (in units of m^3) to outflow q (in units of $m^3/min.$). Each model begins by listing the elementary reactions for the chemical processes taking place. The set of differential equations obtained using the Principle of Mass Action can then be solved numerically. We have used the Forward Euler Method. A program developed previously for modelling reductive dissolution reactions in batch systems (see Stone and Ulrich, 1989) has been modified to handle open systems. Model #1, shown in Figure 8, considers toxic metal adsorption to the host oxide without any other chemical reaction taking place. By keeping the adsorption rate constant k_1 fixed and increasing the desorption k_2 , speciation within the reactor shifts towards increased dissolved toxic metal concentrations. As a consequence, toxic metal is lost from the reactor more quickly. Model #3, shown in Figure 9, considers toxic metal release arises from: (i) direct loss of adsorptive surface sites via dissolution, and (ii) competitive adsorption of $Mn(II)$ generated by the reductive dissolution of MnO_2 .

Plans for the Upcoming Year Our most immediate task during the upcoming year is to complete the analysis and interpretation of our experiments with MnO_2 -bound toxic metals. During the next 6 months, Kathy Godtfredsen will complete her thesis in this area and work on three manuscripts for publication.

Most of our experimental work will be devoted to studying the release of iron oxide-bound toxic metals. We will follow a research plan very similar to the one taken with MnO_2 . We have already begun our work on the sorption and release of toxic metals onto synthetic iron oxide phases as a function of pH, and in the presence of low molecular-weight organic compounds. Completion of this work will take a great deal of time and effort, because our present understanding of the reductive dissolution reactions of iron oxides is poor relative to our understanding of comparable reactions of MnO_2 . Major differences between the behavior of manganese oxides and iron oxides are expected.

Once this work has made sufficient progress, we will then examine reactions of NOM samples derived from the field. The need for new sources of representative natural organic matter has already been mentioned. In collaboration with John Zachara, we are investigating whether soil, aquifer solids, or groundwater samples can be collected that can serve as NOM reference material. John Zachara has also offered to provide iron oxide samples from relevant field sites for inclusion in our study.

We are actively investigating the use of flow-through reactor systems for studying toxic metal retention and release by iron oxides. We plan to visit Prof. Donald Sparks at the University of Delaware in October to learn more about experimental designs and analytical approaches used in his laboratory. Maintaining a constant surface loading of iron oxide within the reactor represents a formidable challenge; we hope that Prof. Sparks and others can assist us in developing a flow-through system that is able to accomplish this.

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TABLE I Natural Organic Matter Samples Used in the Toxic Metal Release Experiments

IHSS Reference Material:	Abbrev.	Characteristics				
Suwannee River Fulvic Acid	SRFA	Lower MW, Less Surface-Active				
Suwannee River Humic Acid	SRHA	Higher MW, More Surface-Active				
Raw Water Samples:	Abbrev.	TOC	pH	Fe _T	Mn _T	
Suwannee River Raw Water	SRNOM	64 mgC/L	3.9	19 μ M	0.24 μ M	
DOE Georgetown Site Water	GTW	64	7.4	20	0.11	
Dismal Swamp Water	DSW	72	3.5	9.1	0.11

FIGURE 1. Acidification experiments examine the nature of Co sorption onto MnO_2 . Total column height represents the fraction of 1.0×10^{-5} M Co sorbed after 17 hours pre-equilibration with 1.0×10^{-4} M MnO_2 . Half-shade areas represent the fraction of Co desorbed during five days of acidification at pH 3.0. White areas represent Co that cannot be desorbed by acidification.

FIGURE 2 1.0×10^{-5} M Co was pre-equilibrated with 1.0×10^{-4} M MnO_2 for 17 hours and for one month. Release takes place upon acidification to pH 3.0.

FIGURE 3 1.0×10^{-5} M Co and Cu were pre-equilibrated with 1.0×10^{-4} M MnO_2 for 17 hours and for one month. Release takes place upon addition of 1.0×10^{-4} M oxalate. (pH 5.0 throughout the experiment).

FIGURE 4 Reductive dissolution of 1.0×10^{-4} M MnO_2 by 1.0×10^{-4} M citrate in the presence and absence of added 1.0×10^{-5} M Co, Ni, and Cu.

FIGURE 5 Extent of toxic metal release as a function of the extent of MnO_2 reductive dissolution by citrate.

Conditions: 1.0×10^{-4} M MnO_2 , 1.0×10^{-4} M citrate,
 1.0×10^{-5} M TOTMe.

FIGURE 6 Reductive dissolution of 1.0×10^{-4} M MnO_2 by 12 mgC/L natural organic matter samples (pH 5.0).

FIGURE 7 Toxic metal release relative to MnO₂ reductive dissolution by 12 mgC/L natural organic matter samples (pH 5.0).

FIGURE 8 CSTR Model #1: Toxic Metal Retention by Adsorption. In this model, the half-life for water renewal in the reactor is 100 days. The adsorption rate constant k_1 is fixed at $1.0 \times 10^2 \text{ M}^{-1} \text{ Day}^{-1}$. As desorption rate constant k_2 is increased the fraction of Cu sorbed to the oxide surface is decreased.

FIGURE 9 CSTR Model #3: Addition of Reductant that Generates Mn(II) Through the Reduction of MnO_2 . As the reductant concentration is increased, production and competitive adsorption of Mn(II) causes Cu desorption and loss from the reactor.

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