REDUCTIVE MOBILIZATION OF OXIDE-BOUND METALS
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This project is concerned with the mobilization of MnO_2 - and FeOOH -bound toxic metals in subsurface environments arising from an influx of natural organic matter or organic-containing wastes. Our work to date emphasizes the importance of characterizing the reductant, complexant, and adsorptive characteristics of constituent organic chemicals. Organic chemicals may interact with pollutant metals directly, or may bring about changes in speciation and solubility indirectly by acting upon MnO_2 and FeOOH host phases. The primary application of this work is the understanding of metal sorption and release processes within subsurface environments undergoing changes in redox status.

Release of MnO_2 -Bound Toxic Metals

In September 1991 we reported that a major set of experiments had been completed which examined the release of MnO_2 -bound Co, Ni, and Cu by representative low MW reductants and complexants (hydroquinone, pyruvate, oxalate, citrate, acetoin) and by natural organic matter samples. Oxalate and citrate are especially important, because of their widespread use as nuclear reactor decontamination reagents (Sellers, 1983).

A great deal of work was completed during the past year evaluating the results of these experiments and preparing the work for publication. A Ph.D. thesis based upon this work (Godtfredsen, 1991) was accepted in March. A manuscript entitled "Release of MnO_2 -Bound Copper by Naturally-Occurring Organic Compounds" is ready for submission to the British journal Nature; drafts of two additional manuscripts are nearing completion.

Release of FeOOH -Bound Toxic Metals (I)

Our experimental work now focuses upon the sorption of Fe(II) , Co, Cu, and Pb onto iron(III) oxides, and their subsequent release in response to changes in aqueous phase chemistry. Our work in this area emphasizes the four areas listed below.

(1) Sorption/desorption of toxic metals. Before work on more complex systems can be attempted, metal sorption equilibria must be understood. Quantitative modelling efforts are applied to iron(III) oxide suspensions containing a single metal and to suspensions containing two or more metals.

(2) Simultaneous consideration of sorptive and complexant characteristics of organic compounds. Unlike manganese(IV) oxides, iron(III) oxides sorb significant quantities of carboxylic acids and other organic compounds possessing ligand donor groups. Complexation of metals by dissolved organic compounds provides a driving force for metal release; complexation of metals by sorbed, multidentate organic compounds provides a driving force for increased retention (ternary complex formation).

(3) Evaluating the dual role of organic compounds as complexants and as reductants. Iron(III) oxides are significantly weaker oxidants than manganese(IV) oxides in a

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thermodynamic sense. Despite this fact, several candidate organic complexants (including oxalate and citrate) are known to reduce iron(III) oxides. Under acidic pH conditions, redox reaction is evident from the appearance of Fe(II) in overlying solution. Under neutral and alkaline pH conditions, Fe(II) is retained by the remaining oxide, and may facilitate toxic metal release. Combined reductant/complexant mixtures are much more effective at bringing about the reductive dissolution of iron(III) oxides than reductants alone (dos Santos Afonso et al., 1990).

Contact of Fe(II) with iron(III) oxides generates mixed-valence oxides (Tronc et al., 1992); these surface chemical changes may influence the sorption of toxic metals and complexant organic compounds. Upon the onset of reducing conditions, the surface chemistry of mixed Al(III)-Fe(III) oxides may evolve differently than pure Fe(III) oxides; Al(III) remaining on the surface may armor particles and prevent further dissolution.

(4) Coordination chemistry and toxic metal release. Pb(II) is a classic "soft" metal, while Fe(II), Co(II), and Cu(II) are "borderline" metals. Organic complexants possessing nitrogen- or sulfur-donor substituents are therefore expected to yield greater Pb release than more abundant oxygen-donor complexants.

Release of FeOOH-Bound Toxic Metals (II)

The U.S. Drinking Water Standard (2.4×10^{-8} M for Pb) provides a benchmark for evaluating metal toxicity. We now employ graphite-furnace atomic absorption spectrophotometry (AAS) in order to reach this analytical range, and flame AAS to cover higher concentrations. The BPDS colorimetric method makes it possible for us to reliably distinguish between Fe(II) and Fe(III) in filtered solutions.

FeOOH (type α) has been synthesized and characterized for use in our experiments. In most instances, a loading of 1.0 g/L is employed, which corresponds to a BET area loading of $48 \text{ m}^2/\text{L}$ and a fluoride-binding surface site concentration of 2.3×10^{-4} M.

Our last report discussed at length the use of flow-through reaction systems for studying toxic metal retention and release by iron oxides. We discussed our plans extensively with Prof. Donald Sparks (University of Delaware), Prof. Charles O'Melia (Johns Hopkins University) and others. As our ideas matured, we felt that the batch experiments provide the most immediate and straightforward means of obtaining partitioning parameters and kinetic information important for meeting the goals of this project. In the future we would like to collaborate with researchers at PNL and other laboratories to place our work in the context of flow-through environments.

Time studies in our laboratory indicate that Cu and Pb adsorption onto FeOOH reaches quasi-equilibrium within 18 hours of contact time. Adsorption isotherms have been performed at pH 4.9 covering a four order-of-magnitude increase in Cu and Pb concentrations (Figure 1). Linearized forms of the Langmuir Equation can be used to calculate adsorption constants (K^a) and maximum adsorption densities (S_T) from the experimental data. The low concentration data (0.050 to $0.70 \text{ } \mu\text{M}$) yield K^a values that are substantially greater than those obtained from the high concentration data (5.0 to $3000 \text{ } \mu\text{M}$). This is an indication that the FeOOH surface sites are not uniform; a subset of sites exhibits higher affinity for toxic metals. An adsorption "edge" is observed near pH 4.8, as shown in Figure 2.

A major goal of this work is to assess the importance of toxic metal sorption onto iron oxides under conditions of changing redox status. To meet this objective, it is important to establish whether Fe(II) produced by the reduction of FeOOH directly competes with toxic metals for surface sites and whether adsorbed Fe(II) alters the reactivity or adsorptive properties of FeOOH.

The adsorption of Fe(II) onto FeOOH has been measured in our laboratory. Great

care was taken to exclude O_2 from the reactor system, to ensure that autoxidation does not take place; experiments were performed in an inert-atmosphere glove box. S_T for Fe(II) was nearly equal the value obtained for F⁻ adsorption, but approx. 2.5 times higher than S_T obtained for Cu and Pb adsorption. Under comparable conditions (pH 4.9, 18 hours contact time), K^s decreased in the following order: Cu > Pb >> Fe^{II} (See Figure 2).

In our earlier work with MnO_2 , increases in TOTMn(II) brought about significant release of sorbed Co, Ni, and Cu; Mn(II) added to the system as $MnCl_2$ and Mn(II) generated from the reductive dissolution reaction with pyruvate or hydroquinone yielded the same competitive effect. We are interested in whether Fe(II) sorption onto FeOOH can cause sorbed metal release in an analogous manner.

A set of experiments has been performed in which $0.44 \mu M$ Cu(II) and Pb(II) have been equilibrated at pH 4.9 for 18 hours before addition of 50 to $200 \mu M$ Fe(II). $Fe(II)_{ads}$ reached $2.0 \times 10^{-5} M$, which is 8.7 % of S_T and fifty times higher than $[Cu]_{ads}$ and $[Pb]_{ads}$. After 4 hours of reaction time, the extent of metal desorption was negligible; apparently Fe(II) loadings of this magnitude are not high enough to significantly affect metal sorption.

Several low molecular-weight organic reductants have been evaluated with respect to their ability to reduce α -FeOOH. Under the conditions employed (Table I), the maximum extent of reduction dissolution was 0.8 %, obtained with 5.0 mM acetoin. We cannot at present monitor the oxidation of acetoin. We can, however, monitor the oxidation of hydroquinone to p-benzoquinone; we have used this reaction in the past to generate known amounts of Mn(II) from MnO_2 reduction (Godfredsen, 1992).

The sorption behavior of Cu(II) during the reductive dissolution of FeOOH by 5.0 mM acetoin is presented in Figure 3. The reductive dissolution reaction is relatively independent of pH; Fe(II) production at pH 4.9 and 5.8 is nearly the same. As the figure indicates, no measureable release of Cu took place.

Table II presents results of a preliminary experiment examining how the addition of representative low MW organic compounds affects Cu and Pb sorption. Each metal was equilibrated with 1.0 g/L FeOOH for 18 hours prior to organic compound addition. Significant decreases (↓) and increases (↑) in the extent of metal sorption are marked. Two processes are operative here: complexation of metals by dissolved organic compounds decreases sorption, while complexation of metals by FeOOH-bound metals may increase sorption.

Experimental Work for the Remaining Project Period

Additional experiments are currently underway which examine how increases in TOTFe(II) influence the extent of Co, Cu, and Pb sorption. Introduction of $Fe(NO_3)_2$ leads to the creation of "sorbed" Fe(II). We are interested in whether Fe(II) added in this manner sorbs like other transition metals, or whether it becomes somehow irreversibly sorbed. Addition of organic reductants generates "lattice-bound" Fe(II), which may be more difficult to displace from the oxide surface. Timescales of sorption/desorption processes are of importance here, and have important consequences for the sorption/desorption of toxic metals present in these systems.

It is critical that we determine the extent of oxalate, citrate, salicylate, ethylenediamine, and glycine sorption during toxic metal sorption and release. Chemical derivatization/HPLC for measuring environmental levels of carbonyl compounds and amines has been demonstrated by Mopper (1983) and others, and will be employed. One advantage of this approach over conventional radiotracer techniques is that parent organic compounds can be distinguished from partial oxidation products generated by reaction with the FeOOH surface. We plan to examine how the uptake or release of metals from the surface depend upon the surface coverage by representative organic compounds. We also

plan to examine how the uptake or release of organic compounds is affected by the presence of metals.

Our group has exchanged ideas and information with Liyuan Liang of Oak Ridge National Laboratories, who is studying the solubilization of subsurface iron by natural organic matter; Don Girvin at PNL, who is studying redox reactions between EDTA-complexed Co and manganese oxides; Bill Fish of the Oregon Graduate Institute of Science and Technology, who is studying the adsorption and reaction of chromate; and John Zachara, who is studying how various mineral surfaces and NOM influence metal sorption and redox reactions.

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TABLE I. Reductive dissolution of 1.0 g/L α -FeOOH (goethite) by low molecular-weight organic reductants (5.0 mM acetate, 10.0 mM NaNO_3).

Reductant	pH	Reaction Time	$[\text{Fe}^{II}(\text{aq})]$
10.0 μM Thiosalicylate	4.6	18.00 Hours	2.11 μM
2.5 μM Hydroquinone	4.6	8.25	3.22
5.0 mM Acetoin	4.6	49.0	91.5
5.0 mM 2,5-dihydroxyphenylacetate	4.0	49.0	49.1
5.0 mM 3,4-Dihydroxyphenylacetate	4.0	20.0	11.7
5.0 mM Mandelic Acid	3.6	49.0	7.8
1.0 mM Mandelic Acid	4.6	49.0	4.2

Note: 1.0 g/L FeOOH corresponds to 1.13×10^{-2} M TOTFe

TABLE II. Release of FeOOH-bound Cu and Pb following addition of representative low MW organic compounds. Each metal was pre-equilibrated with 1.0 g/L FeOOH for 18 hours; the extent of metal sorption was determined 4 hours after organic compound addition. Conditions: pH 4.9 (5 mM acetate, 1.0×10^{-2} M NaNO_3).

	Fraction Adsorbed			
	0.50 μM TOTCu	0.50 μM TOTCu	0.50 μM TOTPb	0.50 μM TOTPb
Complexant-Free	0.88	0.88	0.67	0.67
Oxalic Acid	0.53 $\uparrow$	0.98 $\uparrow$	0.30 $\uparrow$	0.77 $\uparrow$
Citric Acid	0.78 $\uparrow$	0.97	0.79 $\uparrow$	0.78 $\uparrow$
Salicylic Acid	0.89	-	-	-
EN	0.42 $\uparrow$	0.86	-	0.72
EDTA	0.50 $\uparrow$	0.94	0.20 $\uparrow$	-
Glycine	0.94	0.98 $\uparrow$	0.55 $\uparrow$	0.69

FIGURE 1. Adsorption isotherms for Fe(II), Cu, and Pb onto 1.0 g/L FeOOH. The concentration range for Cu and Pb covers almost four orders of magnitude. (1.0×10^{-2} M NaNO_3 , 5.0×10^{-3} M acetate, pH 4.9).

FIGURE 2. Adsorption of Fe(II), Cu, and Pb in 1.0 g/L FeOOH suspensions as a function of pH. ($1.0 \times 10^{-2} \text{ M NaNO}_3$).

FIGURE 3. Reductive dissolution of 0.5 g/L α -FeOOH by 5.0 mM acetoin. Cu was equilibrated with the FeOOH sample for 18 hours before addition of reductant. After 75 hours of reaction with acetoin, no Cu(II) desorption was detected (5.0 mM acetate buffer, 10.0 mM NaNO₃).

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