**REDUCTIVE MOBILIZATION OF OXIDE-BOUND METALS:
THE ROLE OF REDUCTANT CAPACITY AND REDUCTANT REACTIVITY
IN DETERMINING MOBILIZATION RATES IN SOILS AND SEDIMENTS**

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Reductive Mobilization of Oxide-Bound Metals: The Role of Reductant Capacity and Reductant Reactivity in Determining Mobilization Rates in Soils and Sediments

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Scientific Accomplishments FY 90

1. Toxic Metal Adsorption onto MnO_2 and Subsequent Release by Acidification

Adsorption and incorporation of toxic metals onto synthetic MnO_2 has been measured ($3 < \text{pH} < 7$) and found to decrease in the order $\text{Co}, \text{Pb} > \text{Cu} > \text{Ni}$. Acidification to pH 3 causes a substantial fraction of Ni and Cu to be desorbed within 20 hours. With Co, hysteresis is observed; when suspensions equilibrated at pH 6 are acidified to pH 3, dissolved Co concentrations never reach levels measured in comparable suspensions where Co had been equilibrated at pH 3. Comparable results concerning Pb are not yet available. It has been postulated that adsorbed Co (and possibly Pb) are oxidized under near neutral pH conditions, but not under acidic conditions. As a consequence, the environmental behavior of Co (and Pb) is expected to differ substantially from Ni and Cu, which are not subject to oxidation.

2. Toxic Metal Release from the Addition of Oxalate

A variety of low molecular-weight complexants and reductants are present in contaminated aquatic environments which may bring about the mobilization of toxic metals. Co, Ni, and Cu were allowed to adsorb onto synthetic MnO_2 for a period of 17 hours. When oxalate is added at pH 6.0, it acts as a complexant; solubilization of the adsorbed metal ($\text{Cu} > \text{Ni} > \text{Co}$) occurs without bringing about dissolution of the host MnO_2 phase. When oxalate is added at pH 4.0, it acts as both a complexant and reductant; both the adsorbed metal ($\text{Cu} > \text{Ni}, \text{Co}$) and the host MnO_2 phase (which is reduced to Mn^{2+}) are solubilized. These findings indicate that toxic metal mobilization rates are influenced by prevalent chemical conditions (e.g. pH) and by the complexant and reductant characteristics of available organic compounds.

3. Preliminary Experiments Examining Mobilization by Natural Organic Matter (NOM)

NOM collected from the Great Dismal Swamp (near Suffolk, VA) was equilibrated with toxic metals (Co, Ni, Pb) before addition to MnO_2 suspensions. The extent of toxic metal adsorption was less than in NOM-free suspensions. As reductive dissolution of the host MnO_2 phase took place, the extent of adsorption remained relatively constant. These and future experiments allow us to compare the complexant and reductant characteristics of NOM samples with those of low molecular weight representative organic compounds.

ABSTRACT

Natural and synthetic organic compounds can bring about the solubilization of toxic metals that are otherwise adsorbed or incorporated into ferromanganese oxides. Our objective is to examine how the complexant and reductant characteristics of organic compounds found in contaminated aquatic environments influence this mobilization process. Laboratory experiments begin by allowing toxic metals (Co, Ni, Pb, Cu) to adsorb onto host oxide phases (particulate MnO_2 and FeOOH) for a period of 17 hours. Dissolved metal concentrations are then monitored after the addition of low molecular weight reference compounds (such as oxalate, malonate, and citrate) or natural organic matter.

A variety of phenomena have been observed. Oxalate, for example, acts as a complexant at pH 6, solubilizing adsorbed Cu and Ni while leaving the MnO_2 host phase intact. At pH 4, oxalate acts as both a complexant and reductant, causing solubilization of adsorbed Cu and Ni, and the MnO_2 host phase. When toxic metals are equilibrated with NOM from the Great Dismal Swamp before MnO_2 addition, the extent of adsorption is less than in NOM-free suspensions. As the host MnO_2 phase is dissolved, the extent of toxic metal adsorption changes little.

Through this work, we seek to identify environmental factors that exert a decisive influence on the mobilization of oxide-bound toxic metals in soils, sediments, and aquifers.

INTRODUCTION

Both laboratory and field studies have indicated that solids-bound toxic metals in soils, sediments, and aquifers are largely associated with hydrous ferromanganese oxides. This project examines the environmental mobilization of such oxide-bound metals. We seek to identify environmental conditions necessary for mobilization to take place, and to identify the chemical agents responsible for this mobilization.

Specifically, we are interested in how natural and synthetic organic compounds bring about the mobilization of oxide-bound metals. The complexant and reductant characteristics of organic compounds are both relevant in understanding the mobilization of metals. Addition of a dissolved complexant provides a new environmental "compartment" in a mass balance equation for metals that may cause a shift from predominately particle-bound, immobile species (insoluble or adsorbed) towards dissolved, mobile species. A complexant may act on a toxic metal by itself, or may act on both the toxic metal and the hydrous oxide host phase; dissolution of the host phase may lead to toxic metal mobilization by lowering the number of available surface sites. Addition of a reductant may reduce either the particle-bound toxic metal or the hydrous oxide host phase. Changes in oxidation state cause dramatic changes in the solubility and particle-reactive nature of metals; reduction can transform adsorbed toxic metals into more soluble forms, and can bring about the dissolution of the hydrous oxide host phase.

Natural organic matter (NOM) from different environments exhibits a range in physical and chemical characteristics. These characteristics, in turn, affect the nature of interactions with metals. The nature and distribution of complexant and reductant functional groups is of fundamental importance. Highly oxidized NOM from surface waters contains a preponderance of carboxylate groups that are effective complexants but poor reductants. NOM from anoxic (and possibly sulfide-rich) environments may contain such strong reductants as α -hydroxy carbonyls, α -hydroxy-carboxylates and thiols. The partitioning and surface-active behavior of NOM is also important. Moderate- to high- molecular weight humic and fulvic acids may adsorb more strongly to oxide surfaces than low molecular weight NOM molecules, and have a greater effect on surface chemical reactions taking place there.

Our research work is concerned with identifying those factors that exert a decisive influence on the mobilization and attenuation of hydrous oxide-bound toxic metals. On a molecular level, we are interested in mechanisms and rates by which organic compounds react with hydrous oxide-bound toxic metals and their host phases. On an ecosystem level, we are interested in how environmental conditions influence mobilization and attenuation. We are concerned with ways of characterizing the chemical composition of soils, sediments, and aquifers in order to assess toxic metal mobilization and attenuation.

COMPLETED AND ONGOING RESEARCH WORK

Adsorption and Incorporation of Toxic Metals onto MnO_2

During this first phase of research, our efforts were focused upon systems containing manganese(IV) dioxide ($\text{MnO}_2(\text{s})$) as the hydrous oxide host phase. A synthetic MnO_2 has been used, which was prepared by reaction of KMnO_4 with Mn^{2+} (Murray, 1974). A few important characteristics are listed below:

Stoichiometry	$\text{MnO}_{1.92}$
Exchange Capacity	4.7 mmole/g
pH_{zpc}	2.25 (by Coagulation/Subsidence)
Morphology	Indistinct Aggregates (TEM)
Mineralogy	Highly Disordered Burnessite (by EXAFS, A. Manceau)

The measurement of surface area is problematic. In prior research, we have lypholyzed MnO_2 samples before performing B.E.T. measurement, obtaining surface areas in excess of 200 m^2/g . It is not known, however, how this dried surface area relates to the surface area of MnO_2 particles in suspension. In collaboration with other members of the Co-Contaminant group, we would like to investigate potential in situ surface area measurement techniques.

The following transition metals have been chosen for toxic metal adsorption and subsequent release studies: Co, Ni, Cu, and Pb. The nature and extent of adsorption and incorporation into

the host MnO_2 phase depends upon the time allowed for equilibration and upon the aqueous medium composition. Immediately upon addition to a MnO_2 suspension, added metals form complexes with oxide surface sites. Given more time, metals move into inner layer ion exchange sites, and may eventually replace lattice Mn atoms. In the case of Co and Pb, partial or complete oxidation (to Co(III) and Pb(IV)) may take place, increasing the particle-reactive nature of these metals. Thus, processes involved in adsorption and incorporation are quite complex.

To meet the goals of our research, it is only necessary that the extent of adsorption and incorporation at the onset of our experiments be known and reproducible. We have chosen to work with suspensions containing 1.0×10^{-4} M TOTMn (as MnO_2) and 1×10^{-5} M TOTMe (Co, Ni, Cu, or Pb) equilibrated in the presence of air for 17 hours. Oxidation of Co(II) to Co(III) or Pb(II) to Pb(IV) may take place, either through reaction with molecular oxygen (O_2) or with Mn(IV). The extent of Co, Ni, Mn, and Cu adsorption as a function of pH is shown in Figure 1; sorption onto MnO_2 decreases in the order Co, Pb > Cu, Mn(II) > Ni. The extent of adsorption decreases in suspensions equilibrated at lower pH. Because of the low pH_{zpc} (2.25) and ion exchange properties of MnO_2 , the slope is more gradual than the "adsorption edge" behavior seen with iron(III) oxides.

This data can be used for calculating adsorption constants, based upon the following relationships:

$$\begin{aligned} >\text{S} + \text{Me}^{2+} &= >\text{S}-\text{Me}^{2+} & K_{\text{ads}} &= \frac{[>\text{S}-\text{Me}]}{[>\text{S}][\text{Me}]} \\ S_T &= [>\text{S}] + [>\text{S}-\text{Me}] \end{aligned}$$

These calculations are largely empirical, because the nature of adsorption and ion exchange reactions involving MnO_2 is difficult to characterize. Partial or complete oxidation of adsorbed Co and Pb adds an additional level of complexity.

Metal Release Arising from Acidification

To continue the discussion of metal ion adsorption onto hydrous oxides, we must consider possible hysteresis effects. Consider the following example: If Ni(II) is equilibrated with MnO_2 at pH 6.0 and then acidified to pH 3.0, how much Ni^{2+} is released into overlying solution, and how fast does the release take place? An experiment of this nature is shown in Figure 2. Following acidification, a substantial fraction of Ni and Cu is desorbed within the first 20 hours. More gradual desorption continues to take place during the next five days.

Solubilization of Co upon acidification is slight in comparison with solubilization of Ni and Cu (Figure 2). In one experiment, Co was equilibrated with MnO_2 at pH 6.0 for 17 hours then acidified to pH 3.0. Upon acidification, dissolved Co concentrations rose only slightly, never reaching the level measured in comparable suspensions where Co had been added at pH 3.0. Adsorbed Co equilibrated with MnO_2 at pH 4.0, in contrast,

is readily desorbed when acidified to pH 3.0. Our hypothesis is that oxidation of Co(II) to Co(III) takes place in neutral and alkaline solutions, but not in acidic solutions. Once formed, Co(III) remains adsorbed, even when suspensions are acidified.

Metal Release Arising from the Addition of Organic Compounds

There are several accounts in the literature of the ligand-assisted (non-reductive) and reductive dissolution of oxide host phases. Relatively little work has been done on the solubilization of secondary metals adsorbed onto the host phase.

Many organic compounds relevant to contaminated aquatic environments have both complexant and reductant characteristics which are difficult to distinguish from one another. To aid in our studies, we have performed equilibrium calculations to predict the magnitude of complexant effects on metal release. As shown in Figure 3, a substantial fraction of total dissolved Ni is present as Ni-organic complexes under the medium conditions examined. For the three strongest ligands, the extent of complex formation decreases in the order citrate > oxalate > malonate. Complex formation lessens as the pH is decreased. Using experimentally-derived adsorption constants, we have also made preliminary equilibrium calculations concerning the ability of organic ligands to compete with MnO_2 surface sites for metal complexation.

We would now like to consider experimental measurements of metal release (Co, Ni, Pb, Cu) from MnO_2 upon addition of organic compounds. In an experiment, both thermodynamic and kinetic aspects of complexant reactivity are involved; a particular ligand may complex a large fraction of nickel at equilibrium, but may require an extended period of time for these complexes to form. Reductant reactivity must also be considered. For all the organic compounds under consideration, complete oxidation by MnO_2 to carbon dioxide is thermodynamically favorable. In most cases, however, only partial oxidation is achieved. Reductant reactivity depends upon whether a suitable mechanism is available, and upon how fast the reaction takes place.

Rates of MnO_2 reduction upon addition of organic substrate are used as a measure of reductant reactivity. The ability of several organic compounds (and Fe(II)) to solubilize manganese has been tested in a series of experiments (Table 1). For most organic compounds, MnO_2 reduction rates increase with decreasing pH. Malonate and oxalate reduce significant amounts of MnO_2 only when the pH is below 6; at pH values above 6, malonate and oxalate act as complexants without appreciable reductant reactivity. Citrate reductant reactivity is significant at all pH values examined.

In Figure 4, 1.00×10^{-5} M Co, Ni, and Cu were equilibrated separately with 1.00×10^{-4} M MnO_2 for 17 hours at pH 6.0 before addition of 1.00×10^{-4} M oxalate. The amount of Mn^{2+} released (by reduction) was less than 5 % in all the experiments. From this work, it is quite apparent that oxalate acting as a complexant solubilizes Cu more quickly and more completely than Ni or Co.

At pH 4.0, oxalate is both a complexant and a reductant. As shown in Figure 5, addition of 1.00×10^{-4} M oxalate causes both adsorbed metal (Co, Ni, and Cu) and the host phase (MnO_2 reduction to Mn^{2+}) to be solubilized. Once again, Cu is solubilized more quickly and completely than Ni or Co.

Reactions Involving Natural Organic Matter (NOM)

Natural Organic Matter (NOM) is a collection of low, intermediate, and high molecular-weight organic compounds which display a range of complexant and reductant characteristics. Experiments have been performed that examine (1) NOM reductant reactivity, as evidenced by MnO_2 reduction to Mn^{2+} , and (2) NOM mobilization of metals, as evidenced by Co, Ni, Cu, and Pb solubilization.

NOM was collected from the Great Dismal Swamp near Suffolk, Virginia. Our sample of Dismal Swamp Water (DSW) contained 77.5 mgC/L TOC, 72.2 mgC/L DOC (as defined by a 0.2 micron filter), approximately 3×10^{-5} M TOTFe, 4×10^{-6} M TOTMn, and less than 1×10^{-7} M TOTCo, TOTNi, and TOTPb. As shown in Figure 6, dissolved Mn^{2+} concentrations after 200 minutes of reaction became higher as the pH was decreased. At equimolar ionic strength, reaction was faster in CaCl_2 than in NaCl solutions, because Ca^{2+} increased NOM adsorption onto MnO_2 (Dempsey, 1981). Normal laboratory lighting caused noticeable increases in dissolution rate. To prevent such photochemical reactions from occurring, reactors were wrapped with aluminum foil.

A series of experiments were performed in which toxic metals (Co, Ni, and Pb) were equilibrated with NOM (Dismal Swamp Water) prior to addition to MnO_2 suspensions. The adsorption of toxic metals in these suspensions always occurred to a lesser extent when compared to NOM-free suspensions. As shown in Figure 7, formation of Mn^{2+} by reductive dissolution began after addition of 62 mgC/L NOM. Added toxic metals (Co, Ni, and Pb) had little effect on Mn^{2+} release. As reductive dissolution of the host MnO_2 phase took place, changes in the extent of Co, Ni, and Pb adsorption were quite small. This finding was surprising at first glance, since the number of available MnO_2 surface sites is decreasing as reductive dissolution takes place. One possible explanation is that toxic metals may be associated with adsorbed NOM molecules, rather than underlying MnO_2 surface sites.

In separate experiments, it was found that 1.0×10^{-4} M oxalate reduces MnO_2 much more quickly than 62 mgC/L Dismal Swamp NOM. We were interested in examining whether NOM added to oxalate solutions would enhance or inhibit the surface chemical reaction. The experimental findings are presented in Figure 8; Dismal Swamp NOM inhibits reaction with oxalate. Adsorption of humic and fulvic acids can take place despite unfavorable electrostatic interactions (Dempsey, 1981), causing the negative charge on the MnO_2 surface to increase. As a consequence, oxalate adsorption is blocked by adsorbed NOM molecules and inhibited by unfavorable electrostatic interactions with the negatively-charged surface.

Plans for the Upcoming Year

At the recent "Mineral-Water Interface Geochemistry" MSA Short Course, Kathy Godtfredsen discussed our research effort with John Zachara, the coordinator for Co-Contaminant Chemistry projects. In late November or early December, Alan Stone plans to meet with John Zachara and other members of the Chemistry group to discuss further integration of our effort.

We plan to investigate further how the toxic metal-host phase association affects subsequent mobilization. Most of our experiments to date have been performed with MnO_2 as the host phase and allowing 17 hours of contact time. Experiments are planned where the contact time has been extended to 1 month. We also plan to incorporate various iron(III) oxide phases into our experimental work. Iron(III) oxides are weaker (in a thermodynamic sense) and less reactive (in a kinetic sense) oxidants than manganese dioxides, but are still important host phases for toxic metal adsorption. We expect to see important differences in the mobilization of metals adsorbed onto the two host phases.

Our work to date has shown us that the complexant and reductant characteristics of relevant organic compounds are of critical importance in determining the nature and extent of toxic metal release and host oxide dissolution. We will continue to develop this conceptual approach towards understanding the mobilization of toxic metals.

Mobilization by low molecular-weight compounds is an important aspect of our study. Since metal mobilization is a surface chemical reaction, it is important that methods be developed for measuring the surface coverage by these low molecular weight compounds. Prior research has indicated that adsorption of organic compounds with complexant characteristics can result in what has been called "ligand-promoted" dissolution of host oxide phases (see Stumm and Wieland, 1990). We will investigate the use of HPLC to measure concentrations of potential organic complexants in solution. From such measurements and from mass balance considerations, amounts of adsorbed ligand can be calculated.

With respect to redox processes, it would be useful to know how much electron transfer has taken place, by measuring concentrations of reduced organic substrate and oxidized organic product. Our work in this area will focus on organic compounds that undergo stoichiometric conversion to a single reaction product. Hydroquinone/p-benzoquinone, catechol/o-benzoquinone, and acetoin/2,3-butanedione half reactions may be suitable for this purpose.

We will continue to examine complexant and reductant characteristics of NOM samples. We would like to discuss sources of dissolved and particulate NOM samples with other members of the Co-Contaminant Chemistry group. The adsorptive characteristics of NOM are an important aspect of their reactivity which must be addressed. The recent work by Murphy et al. (1990) provides a useful approach for measuring and characterizing NOM adsorption onto oxide surfaces, which can help guide in our research.

REFERENCES

Dempsey, B.A. (1981) "The Protonation, Calcium Complexation, and Adsorption of a Fractionated Aquatic Fulvic Acid", Ph.D. Thesis, University of North Carolina at Chapel Hill.

Murphy, E.M.; Zachara, J.M.; Smith, S.C. (1990) "Influence of Mineral-Bound Humic Substances on the Sorption of Hydrophobic Organic Compounds" Environ. Sci. Technol. 24:1507-1516.

Murray, J.W. (1974) "The surface chemistry of hydrous manganese dioxide". J. Colloid Interface Sci. 46:357-371.

Stumm, W.; Wieland, E. (1990) "Dissolution of Oxide and Silicate Minerals: Rates Depend on Surface Speciation", Chapter 13 In: "Aquatic Chemical Kinetics", W. Stumm, Edit., Wiley-Interscience, NY.

TABLE 1. Reduction of MnO_2 by Various Organic Compounds.

<u>Reductant</u>	<u>pH studied</u>	<u>[Reductant]</u>	<u>[MnO_2]</u>	Amount of diss. after 4 hours
acetoin	pH 4.0, 5.0, 6.0	1×10^{-4} M	1×10^{-4} M	pH 4.0: 0.2% pH 5.0: no rxn pH 6.0: no rxn
citrate	pH 4.7, 5.7	1×10^{-4} M	5×10^{-4} M	pH 4.7: 29% pH 5.7: 7%
malonate	pH 4.0, 5.0, 5.8, 7.2	1×10^{-4} M	1×10^{-4} M	pH 4.0: 49% pH 5.0: 20% pH 5.8: 6% pH 7.2: no rxn
oxalate	pH 4.2, 5.0, 6.0, 7.0	1×10^{-4} M	1×10^{-4} M	pH 4.2: 100% pH 5.0: 51% pH 6.0: 1% pH 7.0: no rxn
phthalate	pH 4.0, 5.0, 6.0, 7.2	1×10^{-4} M	1×10^{-4} M	pH 4, 5, 6, 7.2: no rxn
pyruvate	pH 4.0, 5.0	1×10^{-4} M	1×10^{-4} M	pH 4.0: 45% pH 5.0: 20%
salicylate	pH 4.0, 5.0	1×10^{-4} M	1×10^{-4} M	pH 4.0: 23% pH 5.0: no rxn
HQ	pH 5.1	1×10^{-4} M	1×10^{-4} M	pH 5.1: 100%
Cl-HQ	pH 6.6	1×10^{-4} M	1×10^{-4} M	pH 6.5: 100%
Aceto-HQ	pH 6.5	1×10^{-4} M	1×10^{-4} M	pH 6.5: 100%
Fe(II)	pH 5.0	TOTFe= 8.6×10^{-6} M	1×10^{-4} M	pH 5.0: no rxn

HQ Hydroquinone
Cl-HQ Chlorohydroquinone
Aceto-HQ Acetohydroquinone

FIGURE 1. Adsorption of 1.00×10^{-5} M Co, Ni, Mn, and Cu onto 1.0×10^{-4} moles/L MnO_2 (as oxide particles) as a function of pH. Added metals were allowed 17 hours (under air) for equilibration. The aqueous medium contains 5.0×10^{-4} M NaClO_4 and 5.0×10^{-3} acetate buffer.

FIGURE 2. 1.00×10^{-5} M Co, Cu, and Ni are equilibrated with 1.0×10^{-4} moles/L MnO_2 at pH 6.0 for 17 hours. Upon addition of strong acid, the pH drops to 2.9 and metal desorption takes place. Reaction conditions: 5.0×10^{-3} M acetate buffer, 5.0×10^{-2} M NaClO_4 .

FIGURE 3. Complexation of Ni in the presence of various organic ligands. Equilibrium calculations were performed for the following conditions: 1.00×10^{-5} M TOTNi , 1.00×10^{-4} M total ligand, 5.0×10^{-2} M ionic strength.

FIGURE 4. Oxalate as a complexant. Release of MnO_2 -bound Co, Ni, and Cu upon addition of 1.00×10^{-4} M oxalate at pH 6.0. Reaction Conditions: 1.00×10^{-4} M MnO_2 , 1.00×10^{-5} M metal, (5.00×10^{-3}) M Acetate Buffer, 1.00×10^{-2} M NaClO_4 .

FIGURE 5. Oxalate as both a complexant and reductant.
Release of MnO_2 -bound Co, Ni, and Cu upon addition of 1.00×10^{-4} M oxalate at pH 4.0. Oxalate was added at $t = 0$.
Reaction Conditions: 1.00×10^{-4} M MnO_2 , 1.00×10^{-5} M metal, (5.00×10^{-3}) M Acetate Buffer, 1.00×10^{-2} M NaClO_4 .

FIGURE 6. Dissolution of 1.00×10^{-4} M MnO_2 dissolution upon addition of 62 mgC/L Dismal Swamp Water as a function of pH. Supporting Electrolyte: 5.00×10^{-2} M NaClO_4 or 1.67×10^{-2} M CaCl_2 . (pH 4 and 5 used 5.0×10^{-3} M acetate buffer; pH 6 and 6 used 5.0×10^{-3} M p-nitrophenol buffer).

FIGURE 7. Effect of NOM (from Dismal Swamp Water) on MnO_2 dissolution and adsorbed metal release. Co, Ni, and Pb were separately equilibrated NOM before addition to with MnO_2 suspensions. Reaction Conditions: 1.00×10^{-4} M MnO_2 , 1.00×10^{-5} M

FIGURE 8. The Effect of NOM (from Dismal Swamp Water) on the reaction between 1.00×10^{-4} M oxalate and MnO_2 . Reaction Conditions: 1.00×10^{-4} M MnO_2 , pH 5.0 (5.0×10^{-3} M acetate), 5.0×10^{-2} M NaClO_4 .

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