

## **Chemical and Biological Reduction of Contaminant Metals by Natural Organic Matter**

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### **ABSTRACT**

Natural organic matter (NOM) contains both electron-rich and electron-deficient sites that are responsible for the electron-donating and electron-accepting properties of NOM. Such redox properties of NOM have recently drawn considerable interest and may play significant roles in the redox transformation of contaminant metals and radionuclides such as chromate ( $\text{CrO}_4^{2-}$ ) and uranyl ( $\text{UO}_2^{2+}$ ). However, because of the heterogeneous nature of NOM, one largely unanswered question is which specific NOM fractions or structural features are involved in transferring electrons to contaminant metals? In this study, we attempted to fractionate the NOM into relatively well-defined subcomponents so that their functionality and structural features can be better characterized and defined. Results to date suggest that different NOM fractions vary greatly in structural features and functional groups with respect to the contents of aromatic moieties, carboxylic and heteroaliphatic hydroxyl functional groups, free radicals as measured by electron spin counts, and molecular weight. Different fractions of NOM were found to be able to directly reduce metals or metal oxides (such as ferric iron oxides and  $\text{CrO}_4^{2-}$ ) although they exhibit varying ability or capacity in reducing these metals. The polyphenolic-rich NOM fraction appeared to be the most reactive in reducing ferric iron or iron oxides, resulting in an increased release of ferrous ions over time. In addition, the reduction of  $\text{CrO}_4^{2-}$  was confirmed by the X-ray near-edge absorption spectroscopy (XNEAS). The present study also suggests that the ability of NOM fractions in reducing metals were correlated with their structural and functional properties, such as the hydroquinone and ketone functional groups.

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Natural organic matter (NOM) contains both electron-rich and electron-deficient sites that are responsible for the electron-donating and electron-accepting properties of NOM (Maximov and Glebko, 1974; Schnitzer and Vendette, 1975; Nash et al. 1981). Such redox properties of NOM have recently drawn considerable interests because NOM may play significant roles in the redox transformation of contaminant metals and radionuclides. Of particular interest is the possibility that NOM-mediated reduction of inorganic contaminants such as chromate ( $\text{CrO}_4^{2-}$ ), uranyl ( $\text{UO}_2^{2+}$ ), and pertechnetate ( $\text{TcO}_4^-$ ) can lead to immobilization and therefore remediation of the contaminated sites. Lovley and his co-workers (Lovley et al., 1996; Coates et al., 1998) have shown that humic substances can act as an electron shuttle by accepting electrons from microbial metabolites and then donating them to redox-sensitive metal or metal oxides such as Fe(III) or Fe(III)-oxides. However, because of the heterogeneous nature of NOM, one largely unanswered question is which specific NOM components or structural features are involved in transferring electrons to contaminant metals? The quinone moieties of NOM have been suggested to be responsible (Tratnyek and Macalady, 1989; Lovley et al., 1996) although other redox-active functional groups or structures in NOM (such as ketones) may also play the role. Additionally, the electron-transfer rate and the mechanisms by which various NOM components transfer electrons from bacteria to metal contaminants are poorly understood. In this study, we attempt to (1) fractionate the NOM into relatively well-defined subcomponents (or fractions) so that their functionality and structural features can be better characterized and defined, and (2) investigate the redox reactions of the fractionated NOM components with contaminant metals or metal oxides.

Figure 1 illustrates some possible interactions and electron transfer pathways between heterogeneous NOM components, microbes, and contaminant metals. The humic acid fraction of NOM isolated from soil is generally considered to be high-molecular weight materials that are rich in aromatic, lignin-like organic derivatives (Stevenson, 1982). It is known to contain substantial quantities of quinone C=O and ketone C=O functional groups (~1.7–4 meq/g) that are capable of accepting or donating electrons. On the other hand, the fulvic acid fraction of NOM generally consists of relatively low-molecular weight organic components and contains low amounts of quinone C=O but relatively high ketone C=O functional groups in comparison with humic acid (Maximov and Glebko, 1974; Schnitzer and Vendette, 1975). The fulvic acid can be further fractionated into the polyphenolic-rich (NOM-PP) and the carbohydrate-rich (NOM-CH) fractions on the basis of their adsorptive behavior on a cross-linked polyvinyl pyrrolidone copolymer under

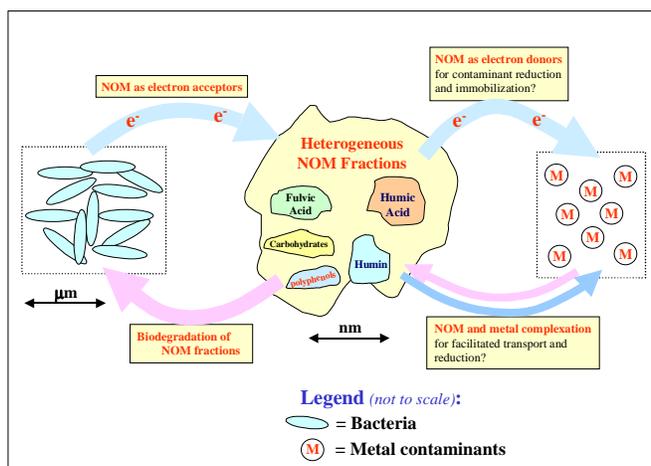


Figure 1. Illustration of various NOM fractions and NOM-mediated transfer of electrons from microbes to redox-active metals.

acidic conditions. Previous studies have shown that the NOM-PP fraction generally contains low-molecular weight polyphenolic materials, whereas the NOM-CH fraction consists of primarily carbohydrates and uronic acids with low amounts of either quinone or ketone functional groups (Stevenson, 1982; Gu and Lowe, 1992). The NOM-CH fraction is thus anticipated to be less important in mediating the electron transfer from bacteria to redox-sensitive metals. However, this fraction is expected to be more readily metabolized (as electron donors) by microorganisms than the NOM-PP and humic acid fractions (Cheshire, 1979; Schnitzer and Khan, 1972).

Two fractions of an aquatic NOM (Gu et al., 1994; 1995) and a reference soil HA (from International Humic Substances Society) were obtained and characterized in this study by means of ultraviolet-visible (UV/Vis),  $^{13}\text{C}$  nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR), fluorescence, and electron spin resonance (ESR) spectroscopy (Chen et al., 2000). Results confirmed that different components or fractions of NOM each possess different structural and functional properties. Both the soil HA and NOM-PP fractions exhibited a high degree of aromaticity, but the NOM-PP fraction showed a high content of carboxylic functional groups, high free-radical concentrations, and strong fluorescence intensity in comparison with the Soil HA and the NOM-CH fractions. On the other hand, the NOM-CH fraction displayed the lowest aromaticity, ESR spin counts, and fluorescence intensity, but possessed a relatively high aliphatic carboxyl and hydroxyl functional group content. These NOM fractions are therefore anticipated to display widely varying reactivities with environmental contaminants such as the reduction of metal oxides or some redox-sensitive contaminant metals.

As shown in Figure 2, different fractions of NOM exhibited varying reaction kinetics with ferric ions and reducing capacity in homogeneous solution at pH ~3. All three NOM fractions were capable of reducing ferric ions although the initial reduction rate was faster in the soil HA and NOM-PP fractions than in the NOM-CH fraction. However, reduction of  $\text{Fe}^{3+}$  by soil HA appeared to reach a steady state quickly (within ~2 h), but the rate increased consistently in both the NOM-PP and NOM-CH systems. Among the three NOM fractions studied, the NOM-PP fraction appeared to be the most reactive with  $\text{Fe}^{3+}$  under the given experimental conditions. This observation can be well correlated to its high UV absorption, high electron spin counts (by ESR analysis), and strong fluorescence intensity of the NOM-PP fraction (Chen et al., 2000). In a similar study with chromate, we found that the NOM-PP fraction effectively reduced Cr(VI) to Cr(III) species on iron oxide surfaces. The reduction of chromate increased with an increased addition of the NOM-PP and was confirmed by the X-ray near-edge absorption spectroscopy (Figure 3).

Results (Figure 2) also suggested that a high aromaticity of the soil HA by  $^{13}\text{C}$ -NMR analysis (Chen et al., 2000) did not appear to correlate with its ability in reducing  $\text{Fe}^{3+}$  in the homogeneous solution at a low pH. Similarly, studies of the reductive dissolution of iron oxyhydroxides by these NOM fractions revealed that the NOM-PP fraction was about 2–4 times more effective than the soil HA in reducing ferrihydrite and hematite after an extended equilibration (up to ~3 weeks) (Choi et al., 2000). These results are partially attributed to its high molecular size and condensed polyaromatic structure of the soil HA which make it less reactive in dissolving and reducing Fe(III) species. A low pH

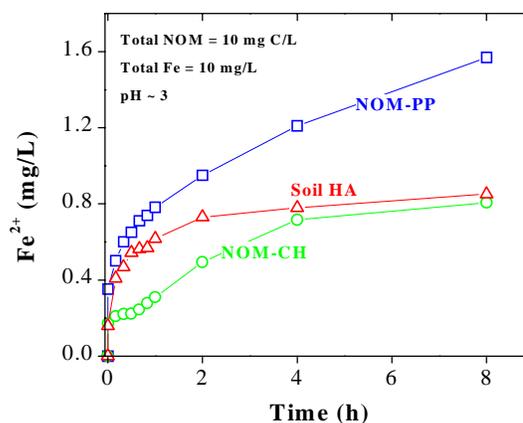


Figure 2. Reaction kinetics of  $\text{Fe}^{3+}$  with NOM fractions at pH ~3 and an initial NOM concentration of 10 mg C/L.

condition is another contributing factor which could result in a coiled structure of the soil HA macromolecules and sterically less reactive with  $\text{Fe}^{3+}$  or iron oxides.

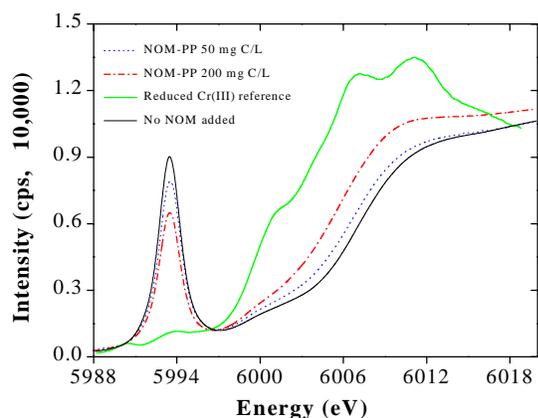


Figure 3. X-ray near-edge absorption spectroscopic analysis of  $\text{CrO}_4^{2-}$  reduction (sorbed on iron oxide surfaces) by NOM-PP fraction at pH ~5.

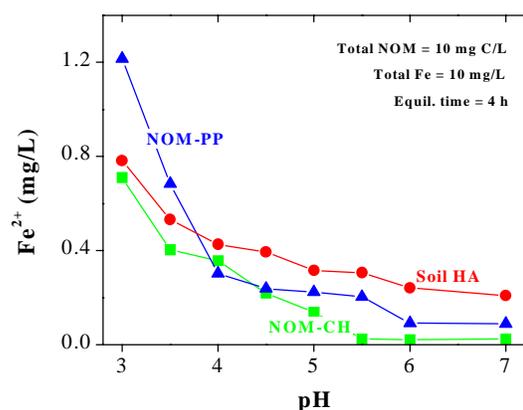


Figure 4. Effect of pH on the reduction of  $\text{Fe}^{3+}$  by NOM fractions in a homogeneous solution.

The reduction of  $\text{Fe}^{3+}$  or iron oxyhydroxides by NOM fractions is strongly pH dependent (Figure 4), as has been reported previously (Deiana et al., 1995). Ferrous ion concentration in solution decreased rapidly as pH increased, particularly with the NOM-PP fraction with a short equilibrium time (4 h). However, reduction of  $\text{Fe}^{3+}$  by the soil HA appeared to be less pH dependent. Although it was less reactive at a low pH (< 4), the soil HA exhibited a more reducing power (or produced more ferrous ions) than the NOM-PP and NOM-CH fractions at a relatively high pH range. These results are thus consistent with previous observations that soil humic acids possess a high aromaticity and quinone functional groups and are effective in mediating the electron transfer reactions in the environmental media (Lovley et al. 1996). In summary, the present study demonstrates that different fractions of NOM are able to directly or abiotically reduce metals or metal oxides (such as  $\text{Fe}^{3+}$  and  $\text{CrO}_4^{2-}$ ). However, the ability of these NOM fractions in reducing metals depends on their structural and functional properties as well as the specific experimental conditions such as pH and reaction time. Although the effects of microbial activity on the reduction of  $\text{Fe}^{3+}$  and  $\text{CrO}_4^{2-}$  were not evaluated in the present study, they were expected to be negligible because of a low pH (<4) and a short reaction time period used for the experiment. Future studies will determine the microbial reduction of contaminant metals and metal oxides as mediated by various NOM components.

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