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Spectroscopic Study of Soil Particle Surface Redox Reactions

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The redox reactions of chemicals in soils, sediments, humic substances and natural systems are important to consider whenever we examine site contamination or potential toxic effects of chemicals. The oxidation state of a chemical or element can influence its solubility, mobility and toxicity. Quantitative examination of redox reactions are challenging in soils for a number of reasons, including: a lack of reliable analytical methods to study reactions; the heterogeneity of the mineral components and redox systems occurring in nature; the irreversibility or slow approach to equilibrium of many redox reactions; and the probability that many redox reactions are biologically and/or surface-mediated. Traditionally the redox potential of a soil or sediment sample has been determined and quantified electrochemically. Such a measurement reflects a quasi-steady state electronic snapshot of a weighted sum of those redox pairs present in the system and capable of reversibly interacting with a redox electrode at that point in time. Although we know pure mineral surfaces may contribute to redox activity and assume soil surfaces to be active as well, greater understanding is needed. A review of some important factors operating in the soil redox system has recently been prepared by Bartlett (1986). Recent advances in spectroscopic techniques now suggest the possibility of evaluating *in situ* redox reactions involving a redox center in a mineral and a redox pair member at the solid-liquid interface.

Spectral information in the uv-visible region provides structural and atomic level information that is difficult to obtain from other methods. Karickhoff and Bailey (1973) were able to assign specific electronic transitions (primarily associated with Fe, but also for other constituents of clay minerals) to bands observed in the uv–visible regions of the spectra. Johnston et al. (1990) used uv-visible spectroscopy to follow reversible single electron transfer reactions on the surface of transition-metal-containing clay minerals, and Anderson and Stucki (1979) observed changes in

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the visible absorption spectra of reduced versus oxidized nontronite suspensions. Stucki and Roth (1976, 1977) and Lear and Stucki (1985) have reported other changes that accompany redox changes in nontronite iron. We have reported an *in situ* method to observe mineral surface-solution redox reactions using uv-visible spectroscopy (Risser and Bailey 1992). This approach, which was demonstrated using synthetic MnO_x as the solid phase, allowed the observation of a reaction without resort to phase separations. We now report on an application of this spectroscopic method to a carefully selected, strongly oxidizing soil material and report the fractionation of Cr oxidation and reduction activity with particle (aggregate) size.

MATERIALS AND METHODS

Soil samples known to be active oxidizers of Cr(III) were obtained from Dr. R. J. Bartlett of the University of Vermont. The samples were collected from the A horizon (surface 10 cm) of soils classified as Typic Eutrochrepts, in Franklin County (near Highgate), VT, and were kept moist during storage (Bartlett and James 1988, p. 280). The soil pH was 7.0 in distilled water, organic matter content was 12.8% and the cation exchange capacity was 31.1 cmol(+)/kg. The whole soils, as received, were chemically active in both the oxidation and reduction of Cr when reacted with the appropriate Cr specie. The whole soils, however, were not sufficiently active oxidizers of Cr(III) to allow the progress of the oxidation reactions to be followed spectroscopically. Viewed differently, they were too high in organic and turbid soil materials to allow direct spectroscopic observation of redox reactions.

An aqueous fractionation scheme was employed to select soil size fractions with enhanced Cr oxidation and reduction activity relative to the whole soil. A soil sample that exhibited high Cr redox activity [44.8 μmoles g^{-1} Cr(VI) reduced and 6.0 μmoles g^{-1} Cr(III) oxidized using conditions in this section] was selected for fractionation. The fractionation scheme was based on aggregate size; no efforts were made to chemically disperse the soil or remove organic material. Clay-size particles may have been present as part of the larger aggregate particles. Coarse sieving was the only physical dispersion method employed. The fractionation was first performed using gravity sedimentation, with separated fractions being tested for Cr oxidation and reduction activity. Silt, the most active fraction on a unit weight basis, was selected for further fractionation. Soil aggregates with equivalent diameters less than 10 μm were fractionated using centrifugation. Soil aggregate equivalent diameters were obtained in seven size ranges: 65-30 μm, 30-10 μm, 10-8 μm, 8-6 μm, 6-5 μm, 5-1 μm and less than 1 μm.

A standard set of procedures was used to maintain consistency among solution treatments and to characterize the solid and solution phase after a treatment. Analysis of solution for Mn content was performed by a Perkin Elmer Plasma II[1] inductively coupled argon plasma emission spectrograph (ICP), and test runs were compared with standards prepared in the solution matrix. The Mn content of the 6-8 µm silt size fraction was determined by first dissolving MnO_x with (one drop 10% w/v) $HONH_2.HCl$ (0.1-mL silt suspension containing ≈ 0.01 g dry wt silt to 5 mL final volume) and then measuring the Mn^{2+} concentration by ICP; 215 mg kg^{-1} was found. The redox reactions that are occurring with MnO_x centers and soil organic materials in these soils may be generally written as:

$$Cr(III)_{(soln.)} + MnO_{x}\text{-}soil \rightarrow Cr(VI)_{(soln.)} + MnO_{x}\text{-}soil\text{-}Mn^{2+}{}_{sorbed} + Mn^{2+}{}_{(soln.)}$$

$$Cr(VI)_{(soln.)} + \text{organic material}_{soil}[\text{reduced}] \rightarrow Cr(III)_{(soln.)} + \text{organic material}_{soil}[\text{oxidized}]$$

Chromium oxidizing ability was determined in the following manner. The selected size fraction of soil was reacted with 0.001 *M* $CrCl_3$ (approx. 2.5 g soil + 25 mL solution) and allowed to react for 15 minutes. Thereafter, 0.25 mL 1 *M* KH_2P0_4ŽK_2HP0_4 was added and the mixture was shaken for 30 sec. The solution phase was separated by 0.45 µm membrane filtration (Bartlett 1988). Chromium reducing capacity was determined by shaking approximately 2 g of soil, or lesser amounts of silt size fractions of interest, with 0.005 *M* $K_2Cr_2O_7$ in pH 4.0 ammonium acetate (1.25 *M* with respect to acetate) for 18 hours (Bartlett 1988). The supernatants from the soil-chromium redox reaction suspensions were separated by 0.45 µm membrane filtration. The amount of Cr(VI) in the filtrates was determined by a colorimetric assay which used 1,5-diphenylcarbazide as the indicator reagent (Bartlett 1988). The indicator reagent was prepared by adding 120 mL of 85% phosphoric acid, diluted with 280 mL of deionized water, to 0.4 g of 1,5-diphenylcarbazide dissolved in 100 mL of 95% ethanol. The 1,5-diphenylcarbizide test is both sensitive to and specific for Cr(VI) at micromolar levels, with 0.5 µ*M* often being selected as the low standard.

The oxidation of Cr(III) was monitored by difference spectroscopy. A four-cell sample arrangement in which all components of the system are present in each beam, but in separate cells if no reaction is wanted, produced the most sensitive spectrophotometric results (Risser and Bailey 1992). Appearance of product results in new bands or peaks in the spectra. Absence of a reaction is indicated by a spectra unchanged from the baseline plot.

All uv-visible analyses were performed with a Perkin Elmer Lambda 4c double beam uv-visible spectrophotometer equipped with a scattered transmission accessory and computer-controlled operating parameters and spectral data collection. Light scattering is reduced by juxtiposition of the cells and the photomultiplier to minimize and capture scattered light. Spectral information was transferred to a personal computer for labeling and printing when convenient for data reduction and manipulation or for presentation of spectral scans.

Studies in cuvettes (four-cell arrangement) were conducted under conditions optimized for photometric examination of the reaction and were initiated by rapidly mixing a hanging drop of reactant stock solution into the photometric cell. The conditions used for method development with Cr(III) were: pH about 4.5, 1 m*M* Cr(III) and 2 g L^{-1} soil material. During the course of the experiment the pH drifted down 0.2 units. The samples were scanned over the uv spectrum at different time periods after the reaction was initiated to look for appearance of the hexavalent chromium peaks at 250 and 360 nm. Sometimes several scans taken over a short time period were combined to reduce background noise.

A limitation of the method is the requirement that suspensions be dilute enough to allow scattered light transmission. The amount of transmitted light required is a function of the sample absorption and absorptivity of the bands of interest. Normally the signal should be 1 to 5% of the background absorption before the reference cell is in place, to insure an adequate signal to noise ratio. We used this as a guide for solution preparation.

RESULTS AND DISCUSSION

The capacity of the silt to oxidize Cr(III) on a weight of Mn basis was three-fold greater than for pure synthetic Mn oxides (birnessite) (Risser and Bailey 1992). The greater relative activity of the soil Mn suggests that Mn oxides exist and function as a surface coating. The aggregate size fractionation employed to obtain a component with enhanced Cr(III) oxidation capacity resulted in the size fraction and quantity of material distribution shown in Figure 1. The redox activity of each size fraction and the whole soil on a unit weight basis is shown on Figures 2 and 3. The 6 to 8 μm size fraction was both the most active oxidizer of Cr(III) and the most effective reducer of Cr(VI) . The enhanced activity of the 6 to 8-μm size fraction allowed the spectroscopic observation of redox reactions in suspension.

The general spectroscopic features of the reaction components employed in this study allowed surface redox reactions to be observed *in situ* in a spectrophotometer cell (i.e., without phase separation via filtration or centrifugation). Spectral examination of the soil material suspension showed broad featureless absorbance in the visible wavelength region. The model inorganic reactant, Cr(III), does not have uv absorbance bands that are strong enough to interfere with the 255 and 363 nm bands of Cr(VI), the oxidized product (Fig. 4).

The reaction of soil material with Cr(III) can be followed by observing the change of absorbance intensity of the Cr(VI) band, which is the oxidation reaction product. Spectral band positions of the various reactants and products can be seen in Figure 4.

Figure 1.

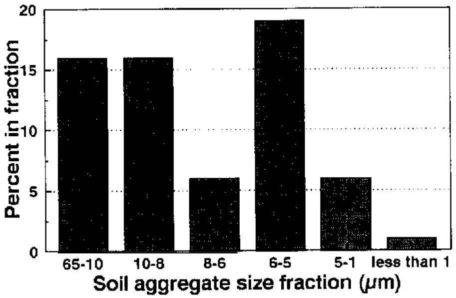

Figure 2.

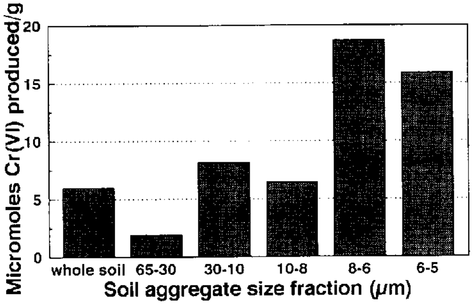

Figure 3.

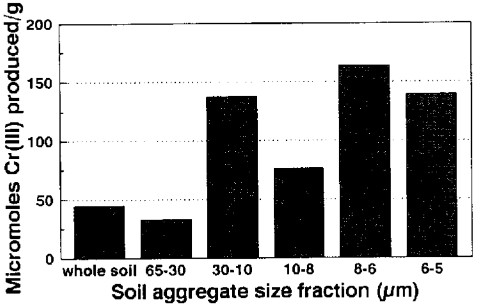

Figure 4.

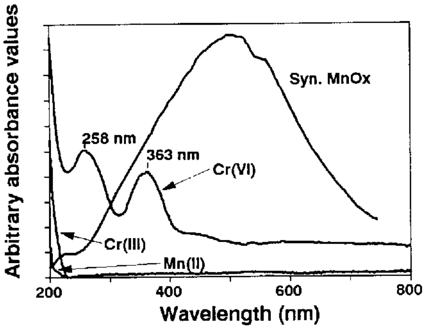

Figure 5.

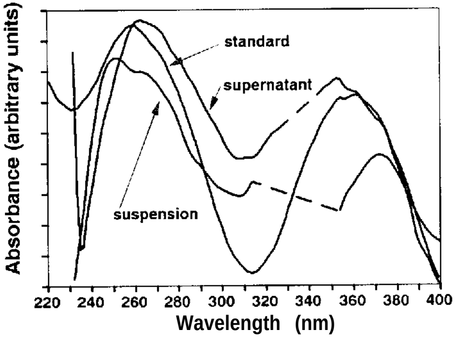

Figure 1. Soil aggregate size distribution.

Figure 2. Distribution of Cr oxidation activity among soil fractions.

Figure 3. Distribution of Cr(VI) reduction activity among soil fractions

Figure 4. UV-visible spectra of individual reaction components and products from oxidation of Cr(III) by MnOx.

Figure 5. UV-Visible sectra of Cr(VI) in a standard soution in soil suspension and in soil supernatant.

Figure 5 displays the spectra for the reaction mixture of Cr(III) and soil material at two time intervals after redox production of Cr(VI) was initiated, first (after ~five min) in the stirred suspension and later (after ~ ten min) in the unstirred supernatant. Increased absorbency at 256 and 353 nm is indicative of Cr(VI) production. The broken line in the spectra replaces discontinuous curves where the instrument light source changed.

The reaction of Cr(III) with synthetic MnO_x results in rapid initial formation of Cr(VI) followed by an attenuation in the rate of the Cr(VI) formation (Risser and Bailey 1992). McBride (1989) has calculated that reactions with MnO_x may become surface-limited due to complete reaction of Mn(IV) on particle surfaces and slow diffusion of Mn(II) from the particle surface. This may contribute to the decreased rate of Cr(VI) formation with time. In soil systems very significant reformation of Cr(III) is expected due to reaction with organic materials, so the Cr(VI) produced represents a net effect of Cr oxidation and subsequent reduction in soil systems. That the reaction represents a net effect may be emphasized by using lower initial levels of Cr(III) (0.1 m*M*) thereby showing net Cr(VI) formation in only the most oxidizing, least reducing soils (Bartlett and James 1988). Reformation of MnO_x surfaces to allow the continued production of Cr^{+3} is expected to occur slowly. However, under field conditions we expect either oxide surface or microbially mediated oxidation of Mn(II) by O_2 to occur.

Among the many mechanisms that may contribute to, and affect, the net or observed rate and extent of reaction are: amount of MnO_x coated and available on soil particle surfaces, spatial proximity of soil oxidizers and reducers, and amount of active reduced organic material that can readily interact with Cr(VI). The presence of certain organic acids has been shown to enhance Cr(VI) reduction. Among these are citric, oxalic, and lactic acids, all having an O on a C adjacent to a COOH group (Bartlett 1988). Other possible factors complicating our understanding of the reaction include complexation and sorption competition and surface Mn^{2+} reactions such as oxidation by free radicals, dissolved o_2 or lattice Mn(IV).

Manganese oxides are a very important and reactive surface in soils (Bartlett 1988). Organic materials and manganese constitute the most important abiotic redox active components in many sediments and soils. The reactions of MnO_x residing on soil particle surfaces are sure to be of environmental consequence in soils and geologic materials (Amacher 1981; Stone 1987; Stone and Ulrich 1989). Manganese oxides are constantly being formed and dissolved in soil systems, and one should not be surprised to find active MnO_x in soils and sediments. In a similar fashion, the existence of both Cr(III) and Cr(VI) may be demonstrated in soils and sediments as well as the capacity to produce both the oxidized and reduced forms when the soil is reacted with the complimentary form (Bartlett 1988). We conclude that there is active biogeochemical cycling of these and presumably other redox components in soils and sediments.

Hydrogen ion activity is an important influence on the redox reactions of MnO_x on soil particle surfaces. Under acidic conditions, the dissolution of MnO_x is promoted. High pH values encourage the precipitation of Cr oxides-hydroxides. **Lower pH may** increase the effectiveness of H^+ competition with Cr(III) and Mn^{2+} for surface sites on MnO_x. A series of computer simulations using the MINTEQA2 model (Allison et al. 1991) was used to help define experimental conditions by adjusting pH and initial concentrations so that solutions were no more than marginally oversaturated. Based on stability data and first and second hydrolysis constants for Cr(III) (log K_1=-4.0, log K_2=-9.7 (Garrels and Christ 1965)) and initial reaction conditions, solutions were calculated to be oversaturated with respect to Cr_2O_3 and marginally oversaturated with respect to $Cr(OH)_3$ (amorphous) and at a pH of 4.5 or less, we find that a maximum of 5% Cr(III) exists as the $Cr(OH)_2^+$ species. The Cr^{3+} species ranges from 25% of the total Cr(III) at pH 4.5 to about 75% at pH 3.5. Over this pH range, the remainder of the Cr(III) species exists as $CrOH^{2+}$. Other pH effects modify the degree of metal complexation to solution ligands and to the mineral surface and consequently influence the activity of the Cr(III) species.

By using uv–visible spectroscopic observation of suspensions of soil material in a spectrophotometer equipped with a scattered transmission accessory, investigators can observe distinct bands characteristic of redox reactions. Depending upon the solution component of the redox reaction under study, bands characteristic of the solution redox reactant or its oxidized product may be more sensitive in the uv-visible spectral region, and thus more useful for a specific redox reaction pair. The ability to directly observe products spectroscopically suggests the use of fast flow experiments to allow both the direct determination of reaction rates and the ready modification of reaction conditions.

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