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Soil organic matter–hydrogen peroxide dynamics in the treatment of contaminated soils and groundwater using catalyzed H_2O_2 propagations (modified Fenton's reagent)

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ABSTRACT

The interactions between catalyzed H_2O_2 propagations (CHP—i.e. modified Fenton's reagent) and soil organic matter (SOM) during the treatment of contaminated soils and groundwater was studied in a well-characterized surface soil. The fate of two fractions of SOM, particulate organic matter (POM) and nonparticulate organic matter (NPOM), during CHP reactions was evaluated using concentrations of hydrogen peroxide from 0.5 to 3 M catalyzed by soluble iron (III), an iron (III)-ethylenediamine tetraacetic acid (EDTA) chelate, or naturally-occurring soil minerals. The destruction of total SOM in CHP systems was directly proportional to the hydrogen peroxide dosage, and was significantly greater at pH 3 than at neutral pH; furthermore, SOM destruction occurred predominantly in the NPOM fraction. At pH 3, SOM did not affect hydrogen peroxide decomposition rates or hydroxyl radical activity in CHP reactions. However, at neutral pH, increasing the mass of SOM decreased the hydrogen peroxide decomposition rate and increased the rate of hydroxyl radical generation in CHP systems. These results show that, while CHP reactions destroy some of the organic carbon pools, SOM does not have a significant effect on the CHP treatment of soils and groundwater.

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1. Introduction

In situ chemical oxidation (ISCO) is an increasingly popular method for the remediation of contaminated soils and groundwater (Watts et al., 1990; Tyre et al., 1991; Watts, 1998; Siegrist et al., 2001). Along with ozone, persulfate, and permanganate, catalyzed H_2O_2 propagations (CHP) systems are widely used for ISCO remediation (Watts and Teel, 2006). CHP is based on the standard Fenton's reaction, in which dilute hydrogen peroxide is slowly added to a degassed solution of excess iron (II), resulting in the production of hydroxyl radicals (OH·) in near stoichiometric yields:

$$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + OH^- + Fe^{3+}. \quad (1)$$

Hydroxyl radical is a short-lived, relatively nonspecific reactive oxygen species that oxidizes most contaminants of concern at near diffusion-controlled rates (Haag and Yao, 1992). Most organic priority pollutants react rapidly with hydroxyl radical when dissolved in water; however, sorbed contaminants and nonaqueous phase liquids (NAPLs) exhibit minimal reactivity with hydroxyl radical (Sedlak and Andren, 1994; Watts et al., 1999).

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The standard Fenton's reaction is usually modified for CHP ISCO applications through the use of higher hydrogen peroxide concentrations and the use of different catalysts, such as naturally occurring iron oxides and chelated iron. The higher concentrations of hydrogen peroxide promote a series of propagation reactions that produce perhydoxyl radical ($HO_2\cdot$), superoxide anion ($O_2^-\cdot$), and hydroperoxide anion (HO_2^-) in addition to hydroxyl radical (Walling, 1975). Although superoxide radical and perhydroxyl radical have traditionally been considered unreactive in aqueous systems, superoxide radical has recently been shown to have significant reactivity in aqueous systems in which cosolvents are present (Smith et al., 2004). The mix of reactive oxygen species provides a highly reactive matrix that has the potential to transform a wide range of organic contaminants.

CHP remediation has been implemented at hundreds of sites throughout the world over the past decade, and the results have been highly varied. Contaminants have been treated to undetectable concentrations at some sites, while minimal cleanup has been accomplished at other sites. Possible reasons for the mixed results of CHP ISCO include an ineffective mixture of reactive oxygen species, ineffective catalysis, minimal contact of reactive oxygen species with pollutants, and inhibitory effects of soil organic matter (SOM).

The most common conceptual model for the role of naturally occurring SOM in ISCO processes is that its oxidation by ISCO reagents is rapid and occurs preferentially to contaminant oxidation. Oxidation of SOM by permanganate has been studied most extensively. A parameter developed for use in permanganate ISCO is natural oxidant demand (NOD), which is defined as the mass of permanganate consumed through the oxidation of a mass of SOM, reduced inorganic compounds, and reduced metals (Siegrist et al., 2001). For example, in batch experiments containing humic acids as model SOM, a significant NOD was found using permanganate (Siegrist, 1999). NOD in permanganate systems is usually evaluated using treatability studies to ensure sufficient permanganate is delivered to the subsurface to compensate for the mass of organic matter or other reduced species that consume the oxidant source. The concept of NOD has not been applied to CHP because, unlike permanganate, numerous other pathways of hydrogen peroxide decomposition exist (e.g. its catalytic decomposition by iron and manganese oxides), and many reactive species are generated. Therefore, the complicated relationships between SOM and CHP are not well understood, and many studies have demonstrated conflicting results. For example, some studies have concluded that the effectiveness of CHP treatment of polycyclic aromatic hydrocarbons (PAHs) decreases with increasing SOM (Bogan and Trbovic, 2003). In contrast, Huling et al. (2001) documented that an increase in the demand of hydroxyl radical by peat is insignificant compared to the scavenging of hydroxyl radical by hydrogen peroxide.

Concentrations of hydrogen peroxide similar to those used in CHP ISCO are commonly used in laboratory procedures to oxidize SOM prior to mineralogical analysis (Kunze and Dixon, 1986). Griffith and Schnitzer (1977) provided detailed analyses of oxidation products of SOM treated with hydrogen peroxide. They documented the formation of hundreds of degradation products, most of which were organic acids, aldehydes, and ketones. However, the nature of SOM is inherently variable and complex, and its dynamics in various fate and remediation processes remain in question. To aid in elucidating SOM dynamics in environmental processes, size fractionation has been developed for investigating the fate of labile and recalcitrant carbon in soils (Cambardella and Elliott, 1992, 1993; Kelly et al., 1996; Gill et al., 1999). Organic matter $>53\,\mu m$ is classified as particulate organic matter (POM), and organic matter smaller $<53\,\mu m$ is classified as nonparticulate organic matter (NPOM). The POM fraction is composed predominantly of biologically labile carbon fragments in various stages of decomposition; the NPOM fraction consists of biologically recalcitrant carbon usually sorbed to minerals (Cambardella and Elliott, 1992). Such fractionation techniques provide an effective method for evaluating (1) the effect of CHP on SOM pools and (2) the effect of SOM on CHP dynamics. The purpose of this research was to determine the effects of a range of CHP conditions on different pools of SOM, and to evaluate the effects of SOM on hydrogen peroxide stability and hydroxyl radical activity in CHP reactions in a well-characterized surface soil.

2. Experimental section

2.1. *Materials*

1-Hexanol and ethylene diaminetetraacetic acid disodium salt (EDTA) were purchased from Sigma-Aldrich (Milwaukee, WI), 2-propanol was obtained from J.T. Baker (Phillipsburg, NJ), and iron (III) sulfate was purchased from Sigma Chemical Co. (St. Louis, MO). Sodium hexametaphosphate was purchased from VWR International (West Chester, PA). Hydrogen peroxide (50%) was provided gratis by Solvay Interox (Deer Park, TX). All soil slurry and aqueous solutions were prepared with $>18\,M\Omega\,cm$ deionized water purified using a Barnstead Nanopure II deionizing system.

2.1.1. *Soil sampling, preparation, and analysis*

The soil used was a silt loam sampled from the Palouse silt loam soil series located near Johnson, WA. Three soil horizons were sampled and used in CHP reactions. Soil depth *A* was collected from a depth of 0–75 cm; it was placed in a soil splitter to provide homogeneity during CHP reactions. Soil depth *B* was sampled from a depth of 45 to 60 cm, and soil depth C was sampled from a depth of 105 to 120. Samples were collected using a hand auger and were stored in 4-L polyethylene bags. Each soil horizon was characterized for particle size distribution by the pipette method (Gee and Bauder, 1986). Organic carbon was determined by combustion at 900 °C with evolved CO_2 trapped in KOH and measured by back-titration of unreacted KOH (Nelson and Sommers, 1982). Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 (SCS, 1986). Crystalline and amorphous iron and manganese oxyhydroxides were determined by citrate–bicarbonate–dithionite extraction (Jackson et al., 1986). Characteristics of the soil horizons are listed in Table 1.

2.1.2. *Catalyzed hydrogen peroxide propagations (CHP)*

Soil depth A was treated with six different CHP process conditions in which the catalyst and the pH were varied. Reaction conditions consisted of 5 and 10 mM soluble iron (III)

Table 1 – Soil characteristics of Palouse silt loam soils A, B, and C

	Soil A	Soil B	Soil C
Depth (cm)	0–75	45–60	105–120
pH	6.9	7.0	7.1
Organic carbon (%)	1.6	1.6	0.2
Amorphous oxides			
Fe (μg/g)	1800	1600	830
Mn (μg/g)	410	650	410
Crystalline oxides			
Fe (μg/g)	7100	7200	6800
Mn (μg/g)	400	410	340
Cation exchange capacity (cmol(+)/kg)	22	22	22
Particle size distribution			
Sand (%)	21.2	21.2	19.2
Clay (%)	14.8	14.8	10.8
Silt (%)	64.0	64.0	70.0
Texture (USDA 1950)	Silt loam	Silt loam	Silt loam

at pH 3, 5 and 10 mM iron (III)-EDTA chelate at neutral pH, and no iron amendment at pH 3 and neutral soil pH with catalysis by naturally-occurring soil minerals. Sulfuric acid (25% H_2SO_4) was used to adjust the pH to 3; the slurries were then allowed to equilibrate for 1 h. In each CHP system, hydrogen peroxide concentrations ranged from 0.5 to 3 M. CHP reactions were conducted in 250 mL borosilicate glass batch reactors with 20 g of soil and 20 mL of reactant solution at 20 °C. After addition of the hydrogen peroxide, catalyst, and acid for pH adjustment, the suspensions were mixed for 1 min on a vortex. Reactions proceeded until the hydrogen peroxide decomposed to undetectable concentrations. All reactions were conducted in triplicate, and control reactions were conducted in parallel using deionized water in place of hydrogen peroxide.

2.1.3. *Soil fractionation and carbon analysis*

After the CHP reactions proceeded to completion, the soils were dried at 40 °C; 5 g of the dried soil were then ground and analyzed for total organic carbon on a LECO CNS-2000 carbon analyzer. The remaining 15 g of soil were fractionated using the methodology described by Cambardella and Elliott (1992) and Gill et al. (1999). A 0.5 M sodium hexametaphosphate solution (150 mL) was added to the remaining 15 g of soil, which was then placed on an orbital shaker at 120 rpm for 18 h. The soil slurry was then passed through a 53 μm sieve and rinsed with deionized water until the rinse water from the sieve was clear. Particles caught in the sieve were dried at 40 °C, ground, and analyzed for organic carbon content. The organic carbon of the soil fraction >53 μm is classified as particulate organic matter (POM), and the organic carbon of the soil fraction <53 μm (obtained by the difference of total carbon and POM) is classified as NPOM.

2.1.4. *Hydrogen peroxide stability*

Hydrogen peroxide concentrations were monitored during CHP reactions in two different horizons of the Palouse silt loam (soil depths *B* and *C*) to evaluate the effect of SOM content on hydrogen peroxide stability. CHP reactions with 5 mL total liquid volume and 5 g soil were conducted in 40 mL borosilicate glass vials containing 3 M hydrogen peroxide at pH 3 catalyzed by naturally occurring soil minerals. Hydrogen peroxide was analyzed by iodometric titration in triplicate at eight time points over the course of the reactions.

2.1.5. *Relative rates of hydroxyl radical activity*

1-Hexanol was used as a hydroxyl radical probe in two horizons of the Palouse silt loam (soil depths *B* and *C*) to evaluate potential scavenging of hydroxyl radical by SOM. 1-Hexanol is rapidly oxidized by hydroxyl radicals ($k_{OH^\cdot} = 3 \times 10^9\,M^{-1}\,s^{-1}$) but is not reactive with superoxide, perhydroxyl, or hydroperoxide anion (Watts et al., 2005). CHP reactions were conducted with 5 g of soil and 5 mL liquid volume in 40 mL vials closed to the atmosphere and fitted with ORBO-32© gas adsorbent tubes to capture any hexanol that could potentially escape through volatilization. The reactions consisted of 2 mM hexanol and 3 M hydrogen peroxide at pH 3 and were catalyzed by naturally occurring soil minerals. Triplicate sets of reactions were shake extracted with hexane at eight time points over the course of the reaction. Triplicate control systems were performed in parallel using deionized water in place of hydrogen peroxide.

2.1.6. *Analysis*

The organic carbon content of the soils and of the POM and NPOM fractions was quantified using a LECO-CNS 2000 carbon analyzer with oxygen combustion at 1350 °C and an infrared (IR) cell detector. 1-Hexanol concentrations were quantified using a Hewlett-Packard 5890A gas chromatograph fitted with a 15 m × 0.53 mm DB-1 capillary column with a flame ionization detector. Gas chromatographic conditions included an injection temperature of 240 °C, detector temperature of 260 °C, initial oven temperature of 80 °C, program rate of 20 °C/min, and final temperature of 240 °C. Hydrogen peroxide concentrations were determined by iodometric titration with 0.1 N sodium thiosulfate (Schumb et al., 1955).

3. Results and discussion

3.1. *Destruction of SOM by CHP reactions.*

Reactions were conducted in systems containing soil depth *A* and six different CHP process conditions; when the reactions were complete, the remaining SOM was fractionated to evaluate the effect of CHP reactions on the different pools of organic carbon. Destruction of organic carbon associated with the total SOM, the POM fraction, and the NPOM fraction of soil depth *A* by CHP treatment using 0.5–3 M hydrogen peroxide catalyzed by 5 and 10 mM soluble iron (III) at pH 3 is shown in Figs. 1a and b. Destruction of all organic carbon fractions was directly proportional to the hydrogen peroxide dosage for both iron (III) catalyst concentrations. Results from linear regression analyses of carbon destruction as a function

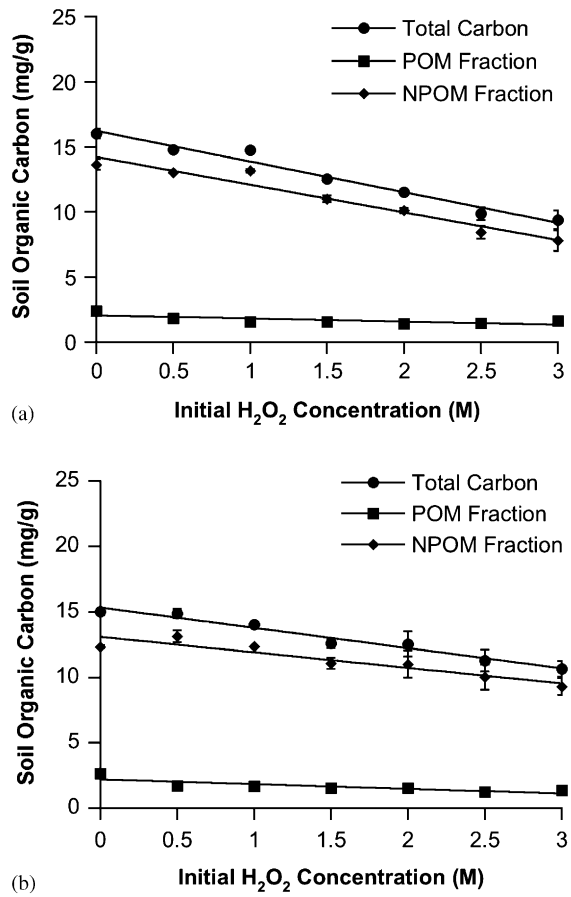

Fig. 1 – Mass of carbon remaining in soil depth A fractions after reaction completion with (a) 5 mM soluble iron (III) catalyst at pH 3 and (b) with 10 mM soluble iron (III) catalyst at pH 3.

of hydrogen peroxide dosages are listed in Table 2. Reactions conducted at pH 3 resulted in a significant destruction of organic carbon mass (30–60%) as the hydrogen peroxide dosage increased. Statistical analysis of the data using completely randomized design analysis of variance (ANOVA) showed no significant difference ($\alpha = 0.05$) for the destruction of each organic carbon fraction between the 5 and 10 mM soluble iron (III) CHP catalysts at pH 3. Approximately 90% of the organic carbon in soil depths *A*, *B*, and *C* exists in the NPOM fraction therefore, on a mass basis, the loss of carbon in the NPOM fraction was greater than the loss of carbon in the POM fraction. A greater loss of organic carbon in the NPOM fraction is expected because (1) this pool of organic carbon is more abundant, and (2) water soluble organic carbon is included in the NPOM fraction and therefore more available for oxidant attack.

To evaluate potential differences in SOM destruction between the use of added soluble iron and natural soil minerals as catalysts, subsequent reactions were conducted using soil minerals as the only CHP catalyst. Destruction of organic carbon associated with the total SOM, the POM fraction, and the NPOM fraction by CHP reactions using 0.5–3 M hydrogen peroxide catalyzed by naturally occurring soil minerals at pH 3 and at neutral pH is shown in Figs. 2a and b. The loss of organic carbon in each fraction using naturally occurring mineral catalysts at pH 3 was not significantly different ($\alpha = 0.05$) from that in reactions catalyzed by soluble iron (III) at pH 3 (Figs. 1a and b). In contrast, no measurable organic carbon loss occurred when naturally-occurring minerals catalyzed CHP reactions at the neutral soil pH. These results suggest that SOM destruction in CHP reactions is pH-dependant.

To further investigate the role of pH in organic carbon destruction, CHP reactions were conducted using an iron (III)-EDTA catalyst at pH 7. Destruction of organic carbon associated with the total SOM, the POM fraction, and the NPOM fraction by CHP reactions using 0.5–3 M hydrogen peroxide catalyzed by 510 mM iron (III)-EDTA at pH 7 is shown in Figs. 3a and b. Similar to the reactions catalyzed by naturally-occurring minerals at neutral pH, minimal destruction of the SOM and NPOM fractions was found in CHP reactions catalyzed by 5 mM EDTA-iron (III) at pH 7, and no measurable organic carbon destruction occurred in the reactions catalyzed by 10 mM iron (III)-EDTA. Statistical analysis of the data of Figs. 3a and b using completely randomized design ANOVA demonstrated no significant difference ($\alpha = 0.05$) between the loss of organic carbon using 5 mM iron (III)-EDTA and 10 mM iron (III)-EDTA as catalysts. These results are consistent with the data shown in Figs. 1 and 2 that neither SOM nor its fractions were destroyed by any CHP conditions at pH 7. Using hexanol ($k_{OH\cdot} = 3 \times 10^9\,M^{-1}\,s^{-1}$) as a hydroxyl radical probe, hydroxyl radical activity was confirmed in the iron (III)-EDTA catalyzed reactions at neutral pH (Fig. 4). The results shown in Figs. 3a,b and 4 confirm that neither hydroxyl radical nor any other reactive oxygen species destroy SOM in the soil at neutral pH regimes.

Soluble iron (III)-catalyzed CHP reactions at pH 3 (Figs. 1a and b) and EDTA-iron (III)-catalyzed CHP reactions at pH 7 (Fig. 3) were conducted with equal concentrations of iron (III) and hydrogen peroxide. The reactions conducted at pH 7 resulted in minimal SOM loss compared to those conducted at pH 3, suggesting that organic carbon destruction through CHP reactions is greater at acidic pH regimes. Cationic organic matter is bound to negatively charged clay minerals by hydrogen bonds in soil systems (Mortland, 1986). Furthermore, the SOM can occlude iron and manganese oxides, decreasing the available surface area and corresponding catalytic activity (Tate, 1987). The disruption of hydrogen bonds between SOM and soil minerals at acidic pH regimes and the corresponding release of SOM has been well documented (Troeh and Thompson, 1993); this release of SOM at acidic pH regimes likely makes it more accessible for oxidation by CHP reactions. The data of Figs. 1–4 demonstrate that system pH of CHP reactions has a significant effect on the destruction of SOM, and may also influence other aspects of CHP dynamics.

3.2. *Effect of SOM on hydrogen peroxide stability*

Hydrogen peroxide stability is the primary limitation of the use of CHP for ISCO (Kakarla and Watts, 1997; Watts and Teel, 2005). In order to investigate the effect of SOM on hydrogen

Table 2 – Slopes of the lines created by the change in carbon (y-axis) with increasing hydrogen peroxide concentrations using various CHP conditions

CHP conditions	Total carbon			POM			NPOM		
	Slope	Intercept	R^2	Slope	Intercept	R^2	Slope	Intercept	R^2
5 mM Iron (III) pH 3	−2.35	16.2	0.97	−0.236	2.04	0.55	−2.13	14.2	0.947
10 mM Iron (III) pH 3	−1.55	15.6	0.967	−0.359	2.22	0.695	−1.19	13.1	0.878
Naturally-occurring mineral catalyst pH 3	−2.31	16.5	0.99	−0.485	2.31	0.921	−1.83	14.2	0.969
Naturally-occurring mineral catalyst pH 7	−0.0905	15.7	0.017	−0.0903	2.54	0.0982	−0.000217	13.2	6.7E−08
5 mM EDTA-iron (III) pH 7	−0.847	18.1	0.32	−0.125	2.23	0.715	−0.723	15.9	0.252
10 mM EDTA-iron (III) pH 7	0.0662	19.2	0.014	−0.124	2.15	0.464	0.186	17.1	0.081

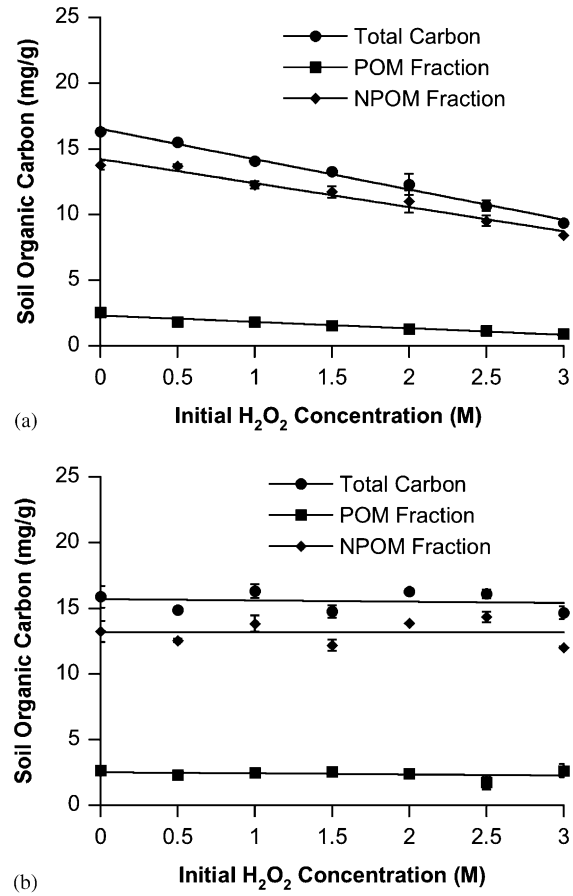

Fig. 2 – Mass of carbon remaining in soil depth A fractions after reaction completion with (a) naturally-occurring soil minerals as the catalyst at pH 3 and (b) with naturally-occurring soil minerals as the catalyst at neutral pH.

peroxide consumption rates, hydrogen peroxide concentrations were measured over time in two soil horizons of varied organic carbon contents under acidic conditions at the natural pH of the soil. Hydrogen peroxide decomposition as a function of time using natural soil mineral catalysts and 3 M hydrogen peroxide at pH 3 or at the neutral soil pH in two soils of similar mineralogical content, but different organic carbon content, is shown in Figs. 5a and b. Hydrogen peroxide decomposed at equal rates in both soil depth B (organic carbon content = 1.6%) and soil depth C (organic carbon content = 0.2%) at pH 3. These results are in agreement with the results of Tyre et al. (1991), who also found no significant difference ($\alpha = 0.05$) in hydrogen peroxide decomposition rates as a function of soil organic carbon content at pH 3 when CHP reactions were catalyzed by naturally occurring minerals. Huling et al. (2001) proposed that the minimal influence of SOM on hydrogen peroxide decomposition results from the predominant catalytic decomposition of hydrogen peroxide by iron and manganese oxides, rather than SOM.

Under neutral pH conditions, hydrogen peroxide decomposed more slowly in soil depth B (organic carbon = 1.6%) than in soil depth C (organic carbon = 0.2%), which may be due to SOM coating the iron and manganese minerals and

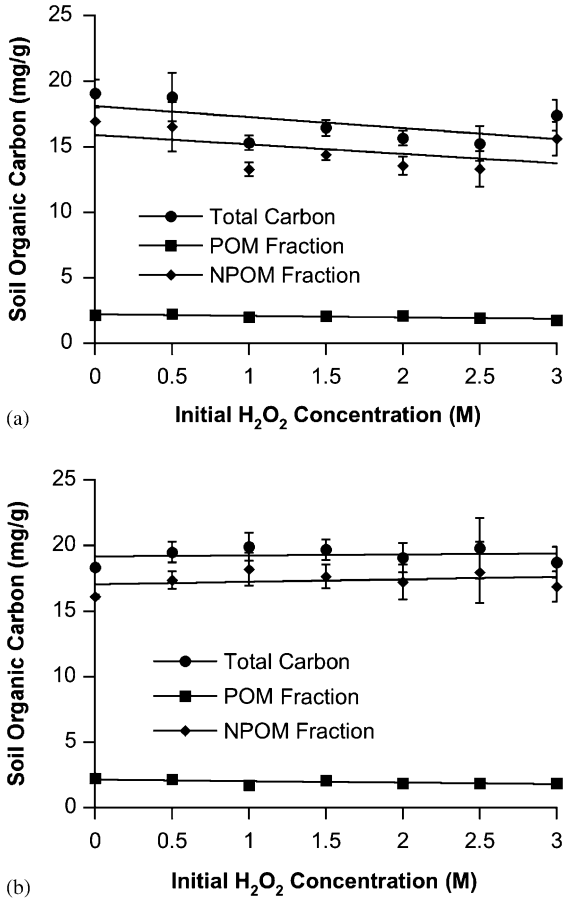

Fig. 3 – Mass of carbon remaining in soil depth A fractions after reaction completion with (a) 5 mM EDTA-iron(III) as the catalyst at pH 7 and (b) with 10 mM EDTA-iron (III) as the catalyst at pH 7.

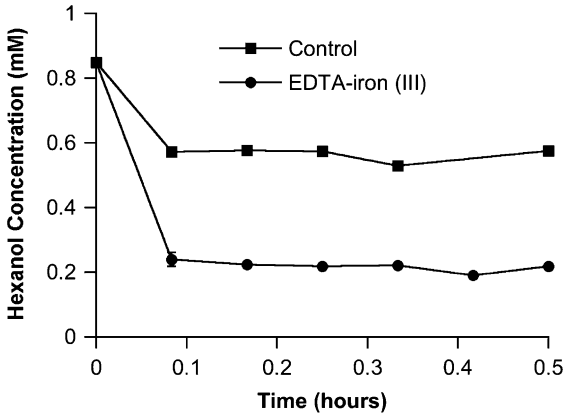

Fig. 4 – Confirmation of hydroxyl radical generation in iron(III)-EDTA-chelated CHP systems using hexanol as a probe molecule using soil depth B (1.6% C) and soil depth C (0.2% C).

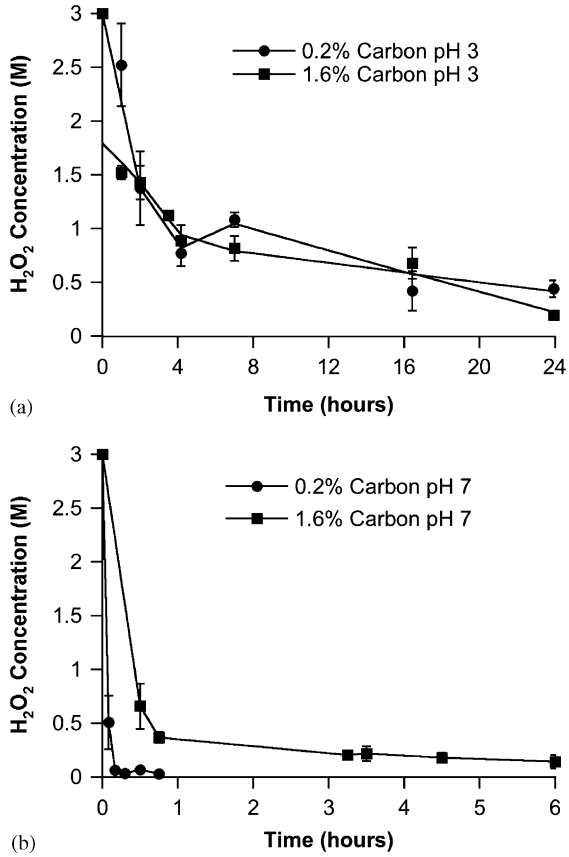

Fig. 5 – Hydrogen peroxide decomposition over time in soils of similar mineralogical content and different carbon content (soil depth B (1.6% C) and soil depth C (0.2% C)) for CHP reactions using (a) 3 M hydrogen peroxide and naturally occurring mineral catalysts at pH 3 and (b) 3 M hydrogen peroxide and naturally occurring mineral catalysts at neutral pH.

inhibiting their catalytic decomposition of hydrogen peroxide. The data of Figs. 5a and b are in agreement with the dynamics of SOM destruction at neutral vs. acidic pH regimes (Figs. 1–3); at neutral pH regimes, SOM may occlude iron and manganese oxides, which are the primary catalysts for hydrogen peroxide decomposition and SOM destruction.

3.3. *Effect of SOM on hydroxyl radical activity*

If SOM competes with hydroxyl radical in a manner similar to NOD in permanganate ISCO, then SOM would represent a significant limitation to contaminant treatment in CHP ISCO systems containing high SOM. In order to investigate the effect of SOM on the ability of CHP reactions to generate hydroxyl radical, hexanol ($k_{OH\cdot} = 3 \times 10^9\,M^{-1}\,s^{-1}$) was used as a hydroxyl radical probe in CHP reactions in two soil horizons of different organic carbon contents, but similar mineralogical characteristics (Soils *B* and *C*). The oxidation of hexanol during CHP reactions using naturally occurring soil mineral catalysts with the addition of 3 M hydrogen peroxide at pH 3 and at neutral pH is shown in Figs. 6a and b. In the reactions conducted at pH 3 (Fig. 6a), hexanol was oxidized to undetectable concentrations at the same rate in both soil horizons. In reactions conducted at neutral pH, approximately 60% of the hexanol was oxidized in soil depth *B* (1.6% soil organic carbon) while approximately 40% of the hexanol

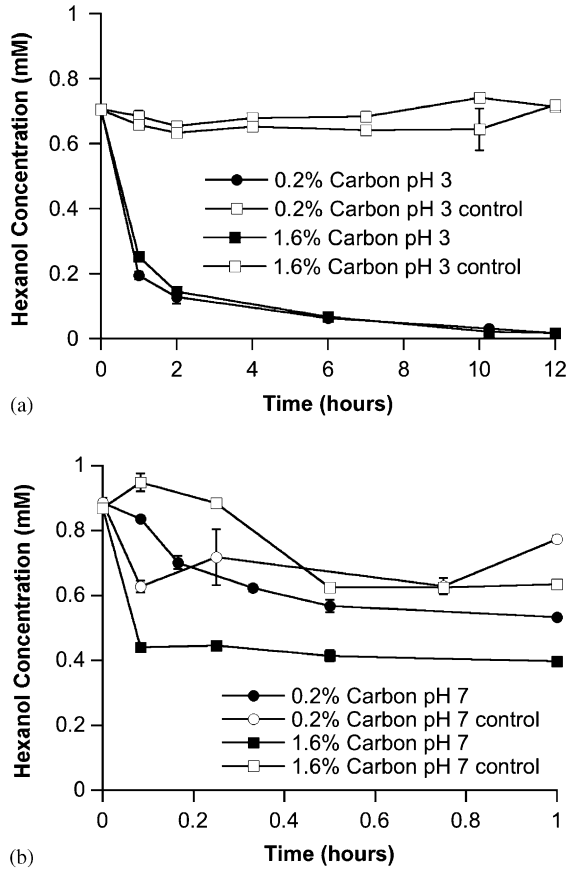

Fig. 6 – Hexanol degradation over time in soils of similar mineralogical content but different SOM contents (soil depth B (1.6% C) and soil depth C (0.2% C)). CHP reactions consisted of (a) 3 M hydrogen peroxide with naturally-occurring minerals as the catalyst at pH 3 and (b) naturally-occurring minerals as the catalyst at neutral pH.

was oxidized in soil depth C (0.2% organic carbon). Minimal hexanol loss was observed in control reactions conducted in parallel to each of the CHP treatments.

The results shown in Figs. 6a and b demonstrate that hydroxyl radical activity was not affected by the SOM content when CHP reactions were conducted at pH 3. In contrast, at neutral pH, hydroxyl radical activity was higher in soil depth B with higher SOM than in soil depth C with lower SOM. These data are similar to the results described by Huling et al. (2001), in which hydroxyl radical activity was enhanced in the presence of peat, possibly by the enhanced catalytic activity of metals chelated by the peat. The results shown in Figs. 4 and 5 suggest that when CHP reactions are conducted at neutral pH regimes, some SOM may enhance CHP reaction effectiveness by providing a decreased hydrogen peroxide decomposition rate as well as an increase in hydroxyl radical generation compared to lower SOM concentrations. The results of this research are in agreement with previous studies by Tyre et al. (1991) and Huling et al. (2001) showing that contaminant destruction by CHP is not affected by the SOM content of the soil. However, the data shown in Figs. 1–4 differ from the most common conceptual model for the destruction of SOM by chemical oxidants; although permanganate rapidly oxidizes SOM, CHP systems do not. Larson and Weber (1994) reported a rapid second-order rate constant of 5×10^4 mg/L s for the oxidation of dissolved organic matter by hydroxyl radical. However, the slower oxidation of SOM shown in this study suggests that the sorbed and colloidal nature of SOM likely lowers its reactivity with oxidants.

4. Conclusions

The destruction of SOM in CHP systems was directly proportional to the applied hydrogen peroxide dosage, and was significantly greater at pH 3 than at neutral pH regimes; furthermore, SOM destruction occurred predominantly in the NPOM fraction. SOM destruction at pH 3 was likely due to disruption of hydrogen bonds in these acidic systems, resulting in the release of exchanged SOM and its resulting increased reactivity in the aqueous phase. At pH 3, SOM did not affect hydrogen peroxide decomposition rates or hydroxyl radical activity. However, at neutral pH, larger masses of SOM decreased the hydrogen peroxide decomposition rate and increased the rate of hydroxyl radical generation in CHP systems. The results of this research demonstrate that SOM does not significantly affect the remediation of contaminated soils and groundwater when CHP ISCO reactions are conducted at pH 3 because SOM does not affect hydroxyl radical activity nor prevents its generation. However, when CHP reactions are conducted at neutral pH regimes, some SOM may enhance CHP reaction effectiveness by providing a decreased hydrogen peroxide decomposition rate as well as an increase in hydroxyl radical generation compared lower SOM concentrations.

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