



Lowering temperature to increase chemical oxidation efficiency: The effect of temperature on permanganate oxidation rates of five types of well defined organic matter, two natural soils, and three pure phase products



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HIGHLIGHTS

- We tested oxidation of various types of organic matter and pure product DNAPL with permanganate at 5 and 16 °C.
- Oxidation rate of organic matter is influenced by temperature, lower rates are shown at lower temperature.
- Oxidation rate of pure product PCE and TCE is controlled by dissolution rate and this did not show a temperature effect.

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ABSTRACT

In situ chemical oxidation (ISCO) is a soil remediation technique to remove organic pollutants from soil and groundwater with oxidants, like KMnO_4 . However, also natural organic compounds in soils are being oxidized, which makes the technique less efficient. Laboratory experiments were performed to investigate the influence of temperature on this efficiency, through its effect on the relative oxidation rates – by permanganate – of natural organic compounds and organic pollutants at 16 and 15 °C. Specific types of organic matter used were cellulose, oak wood, anthracite, reed – and forest peat, in addition to two natural soils. Dense Non-Aqueous Phase Liquid-tetrachloroethene (DNAPL-PCE), DNAPL trichloroethene (DNAPL-TCE) and a mixture of DNAPL-PCE, -TCE and -hexachlorobutadiene were tested as pollutants.

Compared to 16 °C, oxidation was slower at 5 °C for the specific types of organic matter and the natural soils, with exception of anthracite, which was unreactive. The oxidation rate of DNAPL TCE was lower at 5 °C too. However, at this temperature oxidation was fast, implying that no competitive loss to natural organic compounds will be expected in field applications by lowering temperature. Oxidation of DNAPL-PCE and PCE in the mixture proceeded at equal rates at both temperatures, due to the dissolution rate as limiting factor. These results show that applying permanganate ISCO to DNAPL contamination at lower temperatures will limit the oxidation of natural organic matter, without substantially affecting the oxidation rate of the contaminant. This will make such remediation more effective and sustainable in view of protecting natural soil quality.

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1. Introduction

In situ chemical oxidation (ISCO) is a soil remediation technique that can be used to treat contaminated soils and groundwater.

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With this technique, an oxidant like KMnO_4 , $\text{Na}_2\text{S}_2\text{O}_8$ or Fenton's reagents is injected into the subsurface to oxidize the organic pollutants present. ISCO has been applied to degrade various pollutants like toluene, polycyclic aromatic hydrocarbons and chlorinated hydrocarbons, like tetrachloroethene (perchloroethene or PCE) and trichloroethene (TCE) (EPA, 1998). During the process, oxidant is consumed and numerous previous studies have shown that in general more oxidant is needed for complete degradation of the pollutants than what is calculated based solely on the amount of pollutant present in the soil (Barcelona and Holm,

1991; Schnarr et al., 1998). This implicates that, besides the pollutant, also other soil constituents can act as organic reductants (OR) that consume oxidant. This is known as the natural oxidant demand (NOD). The primary contributor to NOD is usually considered to be the natural organic matter (NOM). This can be present in aquifers in various forms like undecomposed plant matter (biogenic carbon), humic substances, geologically aged organics such as kerogen and bitumen, and black carbon (Gustafsson et al., 2001; Allen-King et al., 2002). Each of these various molecular structures can react in a different way with the oxidant (Mumford et al., 2005).

This paper focuses on oxidation with permanganate. Permanganate is known to be specifically reactive to alkene and alkyne bonds within organic compounds. Alkane structures are more persistent, although substitution of a hydrogen or alkyl group by a functional group like the carboxyl (–COOH) or hydroxyl (–OH) group increases the reactivity. Also aromatic hydrocarbons do not react fast with permanganate, unless alkyl or hydroxyl functional groups are attached to the aromatic ring. Substitution of a hydrogen by a carbonyl (–C=O), carboxyl or nitro (–NO₂) group has the opposite effect and decreases the reactivity (Schnitzer and Desjardins, 1970; Arndt and Lee, 1981; Fatiadi, 1987; Waldemar and Tratnyek, 2006). The differences in reactivity of the various NOM constituents with permanganate have been shown in several recent studies, in which fast and slow oxidizing fractions were observed (Mumford et al., 2005; Xu and Thomson, 2009; Cha et al., 2012).

Oxidation of natural matrices makes ISCO less (cost) efficient, since oxidant is used for other compounds than the pollutant that has to be remediated. It also makes the technique less sustainable since soil structure, and therewith soil function, is damaged. A recent study showed that a decrease in NOM due to chemical oxidation with permanganate resulted in clear loss of fertility of the soil due to loss of organic C and N and other nutrients (Sirguey et al., 2008). ISCO treatment can also change the adsorption capacity of the soil (Woods Pan et al., 2012).

Taking measures before or during the ISCO treatment that decrease the (rate of) oxidation of NOM – without negatively influencing the oxidation of the pollutant – can help to protect the natural soil structure and function and at the same time make treatment more cost efficient. One of the parameters that influence oxidation rates of both NOM and pollutants is temperature. Previous studies showed that increasing temperature increases the oxidation rate of dissolved TCE and PCE following the Arrhenius equation (Huang et al., 1999; Yan and Schwartz, 2000; Huang et al., 2002). Knowledge on the temperature dependence of oxidation rates of NOM or chlorinated hydrocarbons present as pure phase product (so-called Dense Non-Aqueous Phase Liquid or DNAPL) is limited. It is unclear if, and to what extent, changes in temperature have a relevant influence on the relative oxidation rates of NOM.

Here we test the hypothesis that application of ISCO at a relatively low temperature may limit NOM oxidation and thereby increase ISCO cost-efficiency and its sustainability with respect to preserving natural soil characteristics and functions. Since organic matter in soils and aquifers is comprised of various nonwell-defined components, we tested specific types of NOM in this study, consisting of oak wood, anthracite and two types of dried peat. Cellulose as a very-well defined organic substance was also included. Natural soil material, the specific types of NOM and cellulose were oxidized by KMnO₄ at two different temperatures to gain insight in the range of oxidation rates and the effect of temperature. The effect of temperature was also tested for chlorinated hydrocarbon DNAPL to see if lowering the temperature could indeed affect ISCO efficiency and sustainability in a positive way.

2. Materials and methods

2.1. Specific NOM, cellulose and soil samples used

For the natural compounds oxidation experiments, four specific types of NOM were used as OR (Table 1). The selection was based on their expected reactivity, with anthracite as the least reactive compound and peat as the most reactive. Cellulose was included as a well-defined organic substance that bears similarities to NOM constituents. The cellulose consists of α-cellulose fibers with a grain size <2 μm and was obtained from Sigma–Aldrich, Steinheim (Germany). Oak wood, anthracite, and two types of dried peat were obtained from field samples as dried grinded material with grain size <2 μm, and were characterized by CS-analyzer (LECO, St. Joseph, Michigan, USA) on C, N, H and S before oxidation. Oxygen content was calculated by difference (Table 1). Also, two different natural soil samples were used. The soil samples, W3C and W5B were collected at a railway refueling station in Węgliniec (Poland) and are characterized for total organic carbon (TOC) contents by thermogravimetric analysis (TGA, Table 1), without detailed C, H, O, N and S analysis. These samples were also dried and grained before analysis.

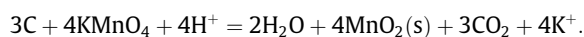
2.2. Chlorinated hydrocarbon DNAPL

Both pure TCE and PCE and a mixed DNAPL from a polluted site in Brückl, Austria were used as contaminant OR for oxidation experiments with KMnO₄. The pure product was collected from the active carbon remediation tanks at the site and consists of a mixture of chlorinated organic pollutants, the main three being: TCE, PCE and hexachlorobutadiene HCBd (Table 2).

2.3. Experimental conditions

Permanganate oxidation experiments were performed at two different temperatures: 16 and 5 °C, more or less within the range of natural groundwater temperature in moderate climate (Collins, 1925; Bense and Kooi, 2004). Various stoichiometric ratios of oxidant to OR were applied, based on the assumption of complete oxidation to CO₂. In addition, the effect of KMnO₄-concentration was studied by doubling the amounts of both KMnO₄ and sample material for some stoichiometric ratios (Table 3).

For the specific NOM types, stoichiometric calculations were based on the measured C, H, O, N and S contents (Table 1). The TOC values were used to calculate the amount of KMnO₄ needed for the soil samples. The assumption was made that C in TOC was zero-valence, the reaction occurred at intermediate pH, and the permanganate reacted to solid MnO₂, given the following:



The calculated amounts of the different specific types of organic matter (OM) or soil were weighted into dark colored glass bottles with screw cap and Teflon inlayer. Thereafter, the bottles were filled with 65 mL of KMnO₄-solution prepared at the desired concentration. For the DNAPL experiments, stoichiometric amounts were calculated based on the known chemical formula for pure PCE and the measured composition of the sampled mixed pure product (Table 2). Crimp cap vials of 100 mL were filled with 65 mL of the required KMnO₄-solution. After addition of the oxidant, the bottles were closed with a viton stopper and sealed with a crimp cap. Using a syringe, the calculated amounts of DNAPL PCE or mixed pure product were added. Control bottles, with only KMnO₄-solution, were also prepared (Table 3). Bottles for 5 °C were constantly put on ice during preparation and all solutions

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