Chemosphere 97 (2014) 64–70

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Impact of organic carbon and nutrients mobilized during chemical oxidation on subsequent bioremediation of a diesel-contaminated soil

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## HIGHLIGHTS

- Chemical oxidation (CO) mobilizes carbon, nitrogen, and phosphorous species.
- Dissolved organic carbon released by CO is preferentially biodegraded over diesel.
- Mobilized nutrients enhance biological activity without supporting bioremediation.
- CO coupled with nutrient-amended bioremediation is the most effective treatment.
- Biodegradation of mobilized C, N, and P species has implications for treatment cost.

## ARTICLE INFO

*Article history:*
Received 28 May 2013
Received in revised form 5 November 2013
Accepted 6 November 2013
Available online 7 December 2013

*Keywords:*
*In situ* chemical oxidation (ISCO)
*In situ* bioremediation (ISB)
Fenton's reagent
Dissolved organic carbon (DOC)
Nutrient amendment
Total petroleum hydrocarbons (TPH)

## ABSTRACT

Remediation with *in situ* chemical oxidation (ISCO) impacts soil organic matter (SOM) and the microbial community, with deleterious effects on the latter being a major hurdle to coupling ISCO with *in situ* bioremediation (ISB). We investigate treatment of a diesel-contaminated soil with Fenton's reagent and modified Fenton's reagent coupled with a subsequent bioremediation phase of 187 d, both with and without nutrient amendment. Chemical oxidation mobilized SOM into the liquid phase, producing dissolved organic carbon (DOC) concentrations 8–16 times higher than the untreated field sample. Higher aqueous concentrations of nitrogen and phosphorous species were also observed following oxidation; $NH_4^+$ increased 14–172 times. During the bioremediation phase, dissolved carbon and nutrient species were utilized for microbial growth-yielding DOC concentrations similar to field sample levels within 56 d of incubation. In the absence of nutrient amendment, the highest microbial respiration rates were correlated with higher availability of nitrogen and phosphorus species mobilized by oxidation. Significant diesel degradation was only observed following nutrient amendment, implying that nutrients mobilized by chemical oxidation can increase microbial activity but are insufficient for bioremediation. While all bioremediation occurred in the first 28 d of incubation in the biotic control microcosm with nutrient amendment, biodegradation continued throughout 187 d of incubation following chemical oxidation, suggesting that chemical treatment also affects the desorption of organic contaminants from SOM. Overall, results indicate that biodegradation of DOC, as an alternative substrate to diesel, and biological utilization of mobilized nutrients have implications for the success of coupled ISCO and ISB treatments.



## 1. Introduction

The application of *in situ* technologies, including *in situ* chemical oxidation (ISCO) and *in situ* bioremediation (ISB), for the remediation of soils contaminated with organic compounds is expanding. ISCO treatments, such as permanganate, persulfate, catalyzed hydrogen peroxide, and ozone have shown success in the oxidation and thus remediation of a variety of contaminants (Siegrist et al., 2011). ISB, whereby microorganisms are used to degrade contaminants, has also proved to be a robust, cost-effective remediation technology. While each of these treatments can stand alone, increasing interest focuses on the development of a biphasic technology, whereby ISCO is followed by an ISB step (Sahl and Munakata-Marr, 2006; Cassidy et al., 2009; Valderrama et al., 2009; Sutton et al., 2011).

The oxidative and pH stress associated with chemical oxidation treatments are known to effect soil microbial activity. Thus, research has investigated the regeneration of biodegradation capacity following chemical oxidation (Jung et al., 2005; Sahl et al., 2007;

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0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.11.005

Liang et al., 2009; Sutton et al., 2011). In general, results indicate that, when properly implemented, chemical oxidation only has a minor impact on the biodegradation capacity of soils, with full regeneration occurring rapidly with minimal lag times of 7–21 d (Jung et al., 2005; Valderrama et al., 2009). This fast regeneration compared to the time frame of *in situ* remediation offers opportunities for cost-effective soil clean-up approaches based on chemical pre-treatment followed by a biological polishing step (Sutton et al., 2011). Once optimized, biphasic treatments are expected to achieve higher remediation efficiencies than approaches based on either chemical or biological methods alone.

Further improvements of these biphasic technologies should focus on tailoring ISCO treatments to biological requirements and ensuring necessary amendments, including nutrients, electron donors, and electron acceptors. In addition to investigating microbial community composition and biodegradation capacity, it is important to assess the impact of oxidation on soil organic matter (SOM) quantity and quality. Non-selective chemical oxidants react with a range of organic compounds and SOM may, depending on the quantity and reactivity, consume more oxidants than the contaminant of interest. Previous investigations have focused on the effect of oxidants on soil structure and quality. A comparison of seed germination and root elongation in soils treated with either Fenton's reagent ($Fe^{2+}$ catalyzed $H_2O_2$) or permanganate showed that Fenton's reagent, although unfavorable, was more compatible with re-vegetation (Sirguey et al., 2008). Ozone treatment also degrades the soil matrix, with a reduction in overall SOM and an increase in dissolved organic carbon (DOC) noted (Ohlenbusch et al., 1998; Wang et al., 2012). Jung and Choi (2003) found an increase in the biodegradability of SOM following ozone treatment due to an increase in the hydrophilic content upon oxidation. Changes in the relative abundance of soil fractions such as humic and fulvic acids (HA and FA, respectively) and the humin fraction have been reported (Ohlenbusch et al., 1998; Jung and Choi, 2003; Wang et al., 2012). Wang et al. (2012) found DOM, HA and FA content increased during short ozonation treatments (4–10 h), but these decreased after 15 h of oxidation. Finally, a reduction in SOM and HA content and an increase in FA was observed following Fenton's reagent treatment (Sun and Yan, 2007).

To date, research has focused on the impact of ISCO on either biodegradation or SOM characteristics, with the goal of understanding the deleterious effect of chemical oxidants on microbial communities or soil structure. However, SOM oxidation during chemical oxidation can also have consequences for a subsequent bioremediation phase once microbial biomass has regenerated, thus impacting the overall remediation efficiency. We investigated how changes in aqueous constituents due to oxidation of SOM with Fenton's reagent and modified Fenton's reagent impact the remediation of diesel-contaminated soils. By identifying changes in the quantity of biodegradable organic carbon and nutrients upon chemical treatment, and linking these changes to biodegradation activity under different nutrient conditions, this research seeks to improve the application of coupled ISCO and ISB.

## 2. Materials and methods

### 2.1. Soil sampling

A field-contaminated soil was sampled at a railroad station in Węgliniec, Poland in March 2010. Refueling activities between 1970 and 2000 caused diesel contamination with up to 70 cm of non-aqueous phase liquids present in some areas. Sampling was performed directly adjacent to the refueling location in the vadose zone of an anthropogenic fill layer at a depth of up to 100 cm (Table 1). Soil, collected with hand-augers, was immediately placed in clean HDPE vessels (CurTec, The Netherlands) and stored at 4 °C upon arrival in our laboratory in The Netherlands. The soil was sieved at 2 mm to homogenize the sample prior to use.

**Table 1**
Properties of field-collected soil. Values and standard errors are given for triplicate analyses.

| Parameter | Value |
|---|---|
| Sample depth (cm bgl[a]) | 0–100 |
| Total TPH (g TPH[b] $kg^{-1}$) | 5.24 ± 0.14 |
| Bioavailable TPH (g TPH $kg^{-1}$) | 1.75 ± 0.00 |
| TOC[c] (%) | 10.49 ± 0.32 |
| pH | 7.1 |

[a] Below ground level.
[b] Total petroleum hydrocarbons.
[c] Total organic carbon.

### 2.2. Experimental setup

Chemical oxidation was performed with catalyzed hydrogen peroxide as either traditional Fenton's reagent or modified Fenton's reagent. In each case, $H_2O_2$ was added either at once (1×), or was portioned into three aliquots added sequentially over 3 d (3×). In the four chemical oxidation treatments, the same dosage of $Fe^{2+}$ and $H_2O_2$ was used. Additionally, biotic and abiotic control treatments were included. In the biotic control without chemical oxidation, all constituents of Fenton's reagent were added; however $H_2O_2$ was replaced with water. Abiotic control microcosms underwent 1× modified Fenton's reagent treatment; thereafter, $NaN_3$ (Merck, Germany) was added to a final concentration of 2 mM after chemical oxidation and at days 56 and 124 of incubation.

Microcosms in 125 mL serum bottles contained 4 g of sieved soil and a final volume of 10 mL of liquid. The liquid contained a total concentration of 150 mg $L^{-1}$ $Fe^{2+}$ as $Fe_2SO_4{\cdot}7H_2O$ (Merck, Germany), 5% $H_2O_2$ (30%; Merck, Germany), de-ionized-$H_2O$, and either 23 mM of $H_2SO_4$ (for Fenton's Reagent; pH of less than 3) or 1.2 g $L^{-1}$ citrate (monohydrate; Merck, Germany) as a chelator (for modified Fenton's reagent; pH between 6.5 and 7). For sequential addition microcosms, one third of the $H_2O_2$ was added each day for 3 d. The reaction was performed in open bottles until no residual hydrogen peroxide was measured with testing strips (Quantofix, Germany).

After chemical oxidation, bioremediation was stimulated under oxic conditions. No bioaugmentation was performed in order to understand the natural regeneration of microbial communities that had been exposed to chemical oxidation. Microcosms that did not receive nutrient amendment were immediately closed with Viton stoppers (Rubber bv, The Netherlands) and crimped. For nutrient amendment, 1 mL of a concentrated mineral medium in 100 mM phosphate buffer was added prior to stoppering. The mineral media contained 10.2 g $L^{-1}$ $NH_4Cl$, 0.48 g $L^{-1}$ $CaCl_2$, 0.54 g $L^{-1}$ $MgSO_4{\cdot}7H_2O$, 12 mg $L^{-1}$ $FeCl_3{\cdot}4H_2O$, 12 mg $L^{-1}$ $CoCl_2{\cdot}6H_2O$, 3 mg $L^{-1}$ $MnCl_2{\cdot}4H_2O$, 0.18 mg $L^{-1}$ $CuCl_2{\cdot}2H_2O$, 0.3 mg $L^{-1}$ $ZnCl_2$, 0.3 mg $HBO_3$, 0.5 mg $L^{-1}$ $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0.6 mg $L^{-1}$ $Na_2SeO_3{\cdot}5H_2O$, 0.3 mg $L^{-1}$ $NiCl_2{\cdot}6H_2O$, 6 mg $L^{-1}$ EDTA, and 1 mL $L^{-1}$ 36% HCl. Prepared microcosms were incubated at 20 °C on a shaker at 120 rpm in the dark.

A number of parameters were monitored throughout the experiment (Table SM-1 in Supplementary Material (SM)). pH measurements indicated that the soil buffering capacity was not significantly impacted by treatment and that soil pH remained near neutral. Total petroleum hydrocarbons (TPH) were measured in all microcosms before and after chemical oxidation, and on days 28, 56, 124, and 187 of incubation; microcosms with nutrient amendment were also measured on day 14. Remediation efficiency