

Thermally activated persulfate oxidation of NAPL chlorinated organic compounds: effect of soil composition on oxidant demand in different soil-persulfate systems

Jialu Liu, Zehua Liu, Fengjun Zhang, Xiaosi Su and Cong Lyu

ABSTRACT

This study investigates the interaction of persulfate with soil components and chlorinated volatile organic compounds (CVOCs), using thermally activated persulfate oxidation in three soil types: high sand content; high clay content; and paddy field soil. The effect of soil composition on the available oxidant demand and CVOc removal rate was evaluated. Results suggest that the treatment efficiency of CVOcs in soil can be ranked as follows: *cis*-1,2-dichloroethene > trichloroethylene > 1,2-dichloroethane > 1,1,1-trichloroethane. The reactions of soil components with persulfate, shown by the reduction in soil phase natural organics and mineral content, occurred in parallel with persulfate oxidation of CVOcs. Natural oxidant demand from the reaction of soil components with persulfate exerted a large relative contribution to the total oxidant demand. The main influencing factor in oxidant demand in paddy-soil-persulfate systems was natural organics, rather than mineral content as seen with sand and clay soil types exposed to the persulfate system. The competition between CVOcs and soil components for oxidation by persulfate indicates that soil composition exhibits a considerable influence on the available oxidant demand and CVOc removal efficiency. Therefore, soil composition of natural organics and mineral content is a critical factor in estimating the oxidation efficiency of in-situ remediation systems.

Key words | chlorinated volatile organic compounds, oxidant demand, soil composition, thermally activated persulfate

Jialu Liu
Zehua Liu
Fengjun Zhang
Cong Lyu (corresponding author)
Key Lab of Groundwater Resources and
Environment, Ministry of Education,
Jilin University,
No. 2519, Jiefang Road,
Changchun 130026,
China
E-mail: lvcong0611@163.com

Xiaosi Su
Cong Lyu
Institute of Water Resources and Environment,
Jilin University,
Changchun 130026,
China

INTRODUCTION

Chlorinated organic compounds such as trichloroethylene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA) can be commonly detected in contaminated field sites, posing a serious threat to ecological and human health due to their toxicity and carcinogenicity (Liang *et al.* 2003, 2007; Ko *et al.* 2012). Due to their high density and low water solubility, these substances tend to sink down through soils into the water table, potentially causing free non-aqueous phase liquid (NAPL) contamination. Once the subsurface media is contaminated by NAPL chlorinated organic compounds, it can be difficult to reduce concentrations back to a safe level using natural attenuation.

In-situ chemical oxidation (ISCO) exhibits great potential for the remediation of contaminated sites, a process that involves the insertion of strong oxidants into the subsurface media (Yan & Lo 2013; Hu *et al.* 2015; Peluffo *et al.*

2016). Recently, persulfate ($S_2O_8^{2-}$, PS) has emerged as a useful strong oxidant ($E_0 = 2.01$ V) for in-situ soil remediation (An *et al.* 2015; Girit *et al.* 2015; Hilles *et al.* 2016). Persulfate can be activated by heat, metal or UV irradiation to generate sulfate radicals ($SO_4^{\cdot-}$) with a stronger oxidation potential ($E_0 = 2.6$ V) than $S_2O_8^{2-}$ (Le *et al.* 2011; Ko *et al.* 2012; Yan & Lo 2013; Ahmadi *et al.* 2015; Zhou *et al.* 2016). Thermal activation has been established as a highly effective method to activate persulfate for the degradation of organic contaminants such as methyl *tert*-butyl ether, TCE, tetracycline and polycyclic aromatic hydrocarbons (Huang *et al.* 2002; Liang *et al.* 2003; Eslami *et al.* 2016; Peluffo *et al.* 2016).

The removal of organic contaminants from soil using thermally activated persulfate oxidation has been investigated in previous literature (Haselow *et al.* 2003; Liang *et al.* 2003,

2008b; Deng et al. 2013), although many of these studies focus on the treatment of single contaminants despite a high percentage of contaminated sites being characterized as complex mixtures, sometimes with the presence of NAPL contamination. The presence of contaminant mixtures in soils makes remediation more complex, as processes involve not only interactions between oxidants and the subsurface material, but also competition between contaminants for oxidants. Some previous studies have reported that removal rates for target contaminants were often remarkably reduced using activated persulfate in soil systems, compared to liquid based systems (Liang et al. 2003; Crimi & Taylor 2007). These studies suggest that the removal of target contaminants might be limited by oxidant consumption by a variety of non-target substances associated with subsurface matter, such as natural minerals (e.g., iron and manganese) or organic substances (soil organic carbon, f_{oc}) (Huang et al. 2002; Haselow et al. 2003; Liang et al. 2007, 2008b; Deng et al. 2013). Therefore, the consumption of oxidants in oxidation reactions with soil components must be fully characterized and quantified to understand the impact on oxidant availability for target contaminants, as well as to establish the limitations of in-situ remediation systems.

Much previous literature focusses on the levels of oxidant consumed by contaminants rather than the contribution of soil composition when designing field scale remediation, therefore this study investigates the interaction of persulfate with target contaminants as well as soil components. The purpose of this study is to establish the influence of soil composition on the consumption of persulfate and the removal of NAPL chlorinated organic compounds by thermally activated persulfate oxidation (e.g. 30 °C and 50 °C), in different soil types with varying mineral and f_{oc} content (sand soil, paddy soil and clay soil). The main objectives are: (1) to determine the rates of chlorinated organic compound oxidation and persulfate consumption in the varying soil-water systems; (2) to evaluate the competition between chlorinated organic compounds and soil components for oxidation and hence persulfate consumption; (3) to quantify the level of persulfate consumption by soil components to determine the relative importance of mineral and f_{oc} content on the rate of persulfate consumption.

MATERIALS AND METHODS

Materials

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >99.7%) and methanol (CH_3OH , >99.5%) were purchased from Sinopharm

Chemical Reagent Co. Ltd (Shanghai, China). TCE ($\geq 97\%$), *cis*-1,2-dichloroethene (*cis*-DCE, $\geq 97\%$), 1,1,1-trichloroethane (1,1,1-TCA, $\geq 97\%$) and 1,2-dichloroethane (1,2-DCA, $\geq 98\%$) were purchased from Sigma-Aldrich Chemical Co. Ltd (USA). Water was purified using a Millipore reverse osmosis purification system.

Three types of soils: high sand content, paddy field and high clay content soil were applied in this study. The sand soil-type and paddy field soil-type were obtained from a depth of 10 cm, from local farmland in southern Changchun, China. The clay soil-type was obtained from a depth of 3 m below the ground surface (Changchun, China). The soil samples were air-dried, then ground by hand and sieved through sieve #35 (0.5 mm) prior to use. The characteristics of the various soil materials used in this study are presented in Table 1.

Experimental procedures

All experiments were performed in triplicate in a series of 35 mL brown glass bottles equipped with Agilent caps and polytetrafluoroethylene liners. The solid-water ratio (m/v) of 1:2 was used with 15 g of dry soil and 30 mL of aqueous solution. 90 μL of mixed NAPLs containing TCE, 1,1,1-TCA, *cis*-DCE and 1,2-DCA (volume ratio, 1/1/1/1) were syringe injected into the test reactors, filling up reaction bottles completely to allow for no air bubbles. All the reaction bottles were shaken continuously, using a ZWY-240 thermostatic reciprocating shaker at 100 rpm at either 30 °C or 50 °C. Residual contaminants present in the soil slurry system were determined following methanol extraction. The extraction vials were shaken for 48 h using a reciprocating shaker, as specified previously. Following extraction, the mixtures were centrifuged (2,000 rpm, 5 min), with the supernatant

Table 1 | Characteristics and properties of soil types used in assessment

Type of materials	Sand soil	Paddy soil	Clay soil
pH	6.93	7.64	7.38
TOC, f_{oc} (%)	0.2907 ± 0.0572	0.9446 ± 0.0575	0.4671 ± 0.0635
SSA (m^2/g)	0.065 ± 0.0115	0.139 ± 0.0044	0.242 ± 0.0025
Median particle diameter, D50 (μm)	241.3	82.32	25.14
Iron (Fe) (g kg^{-1})	22.16	26.81	51.28
Manganese (Mn) (g kg^{-1})	0.76	0.65	0.91

collected for the quantification of the concentrations of four chlorinated volatile organic compounds (CVOCs), TCE; 1,1,1-TCA; *cis*-DCE; and 1,2-DCA. Control tests were performed in triplicate, assessing CVOC concentrations in the absence of persulfate.

Analytical methods

Persulfate concentration was determined using UV spectrophotometry with potassium iodide (Liang et al. 2008a). The four representative CVOCs were quantified using an Agilent 7890A gas chromatograph equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm), using a micro-electron capture detector. Nitrogen was used as the carrier gas with a constant flow rate of 50 mL min⁻¹, with column, injector and detector temperatures of 40 °C (isothermal), 150 °C and 250 °C, respectively. The pH of soil samples was determined using a PHS-25C pH meter (NY-T 1377-2007, China). Soil organic matter mass was established based on the weight fraction of organic carbon in the soil (f_{oc} : with the units g^C per g^S, where g^C is the number of grams of carbon and g^S is the number of grams of soil). Total organic carbon (TOC, f_{oc}) of soil samples was measured using a TOC analyzer (Shimadzu SSM-5000A). Mineral content was quantified using X-ray fluorescence spectrometry (Shimadzu XRF-1800). Particle size distribution and specific surface area (SSA) of soil samples were characterized using a laser particle size distribution analyzer (Bettersize 2000).

Date analysis

The percentage of removal of each contaminant (Equation (1)) and the percent removal of each of the four CVOCs (Equation (2)) were calculated according to Equations (1) and (2):

$$\% \text{ removal}_i = \left\{ \frac{C_{i,\text{control}} - C_{i,\text{ox}}}{C_{i,\text{control}}} \right\} \times 100 \quad (1)$$

$$\% \text{ removal}_{4\text{CVOCs}} = \left\{ \frac{\sum C_{i,\text{control}} - \sum C_{i,\text{ox}}}{\sum C_{i,\text{control}}} \right\} \times 100 \quad (2)$$

where $C_{i,\text{ox}}$ and $C_{i,\text{control}}$ (mg L⁻¹) represent concentrations of individual CVOCs within the soil systems, with and without the presence of oxidants respectively; $\sum C_{i,\text{ox}}$ and $\sum C_{i,\text{control}}$ represent the sum of individual CVOC concentrations within the soil systems with and without the presence of oxidants, respectively.

The level of oxidant consumption was defined as the difference between the initial and final oxidant concentrations, as shown in Equation (3).

$$\% \text{ oxidant consumption} = \left\{ \frac{Ox_i - Ox_f}{Ox_i} \right\} \times 100 \quad (3)$$

where Ox_i is the initial oxidant concentration (g L⁻¹) and Ox_f is the final oxidant concentration (g L⁻¹).

The oxidant efficiency (OE, Equation (6)) of each oxidative treatment was defined as the ratio of the sum of the total CVOCs removed (Equation (4)) and the amount of oxidant consumed (Equation (5)). The related equations are expressed as follows:

$$M_{4\text{CVOCs,removed}} = \left(\sum C_{i,\text{control}} - \sum C_{i,\text{ox}} \right) \times V_{\text{sol}} \quad (4)$$

$$M_{\text{ox,consumed}} = (Ox_i - Ox_f) \times V_{\text{sol}} \quad (5)$$

$$OE = \frac{M_{4\text{CVOCs,removed}}}{M_{\text{ox,consumed}}} \quad (6)$$

where V_{sol} is the total volume of solution in the test reactor (L); $M_{4\text{CVOCs, removed}}$ is the mass of total CVOCs removed (mmol); and $M_{\text{ox, consumed}}$ is the mass of oxidant consumed (g).

RESULTS AND DISCUSSION

Oxidation of CVOCs

In the natural environment, polluting substances do not occur in isolation, instead existing simultaneously in complex mixtures in contaminated soils. Therefore investigation of the dynamics of contaminant mixtures present in different soil-persulfate systems are of vital importance. The removal rates of individual CVOCs by activated persulfate oxidation at 30 °C and 50 °C are shown in Figure 1, where at both 30 °C and 50 °C, following 11-days of treatment by persulfate oxidation, the mass removal of the CVOCs showed the decreasing order: *cis*-DCE > TCE > 1,2-DCA > 1,1,1-TCA (Figure 1). Electrophilic SO₄⁻ molecules attack organic compounds via electron transfer, hydrogen abstraction or addition. As increasing levels of chlorine is substituted on carbon, C–H bonding increases in strength due to more electrons being withdrawn from carbon to chlorine species, making it more difficult for

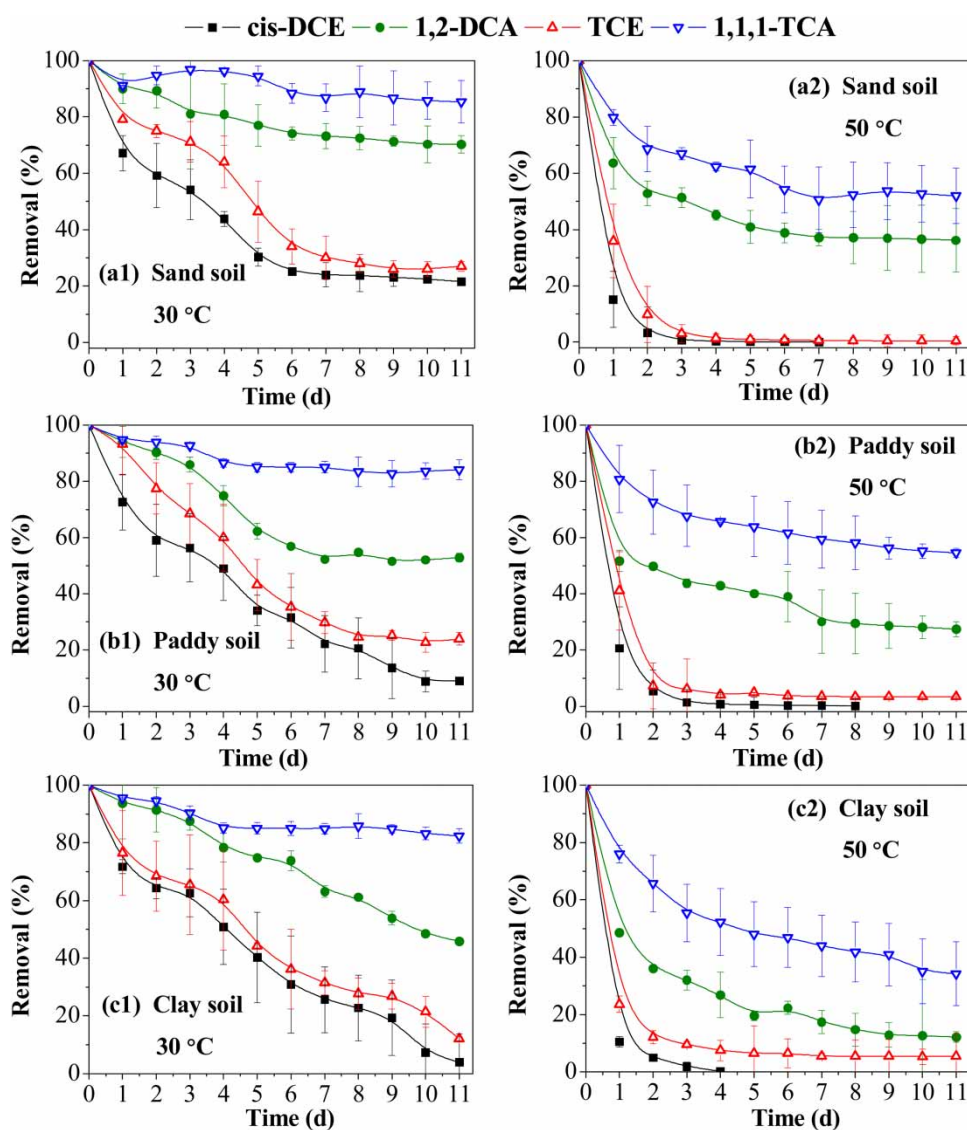


Figure 1 | The removal of the four assessed CVOCs, using activated persulfate oxidation at 30 °C and 50 °C in (a) sand-, (b) paddy- and (c) clay-soil-persulfate systems, respectively. [*cis*-DCE]₀: 963 mg L⁻¹. [1,2-DCA]₀: 942 mg L⁻¹. [TCE]₀: 1095 mg L⁻¹. [1,1,1-TCA]₀: 1004 mg L⁻¹. [Na₂S₂O₈]₀: 30 g L⁻¹.

electrophilic SO₄⁻ to attack the C-H bond (Ko et al. 2012), resulting in a decrease in the reaction rate of chlorinated organic molecules with SO₄⁻ due to the lower electron density of carbon (Anipsitakis et al. 2006; Ko et al. 2012). For chlorinated ethane compounds, as the number of chlorine species substituting ethane increased, lower treatment efficiency was observed (e.g., 1,1,1-TCA < 1,2-DCA in Figure 1), also for chlorinated ethene substitution with chlorine (e.g., TCE < *cis*-DCE in Figure 1). Compared to 1,2-DCA and 1,1,1-TCA, SO₄⁻ preferably reacts with *cis*-DCE and TCE due to their specific molecular structure, where the unsaturated C=C bond present in *cis*-DCE and TCE molecules is surrounded by a high-density electron

cloud, resulting in a highly reactive substance in the presence of electrophilic SO₄⁻. Thus, *cis*-DCE and TCE were almost completely removed (>95% removal) within a reaction period of 11 days at 50 °C (Figure 1). While 1,1,1-TCA and 1,2-DCA had a lower removal efficiency, of 45–66% and 64–88%, respectively, within 11 days of treatment at 50 °C (Figure 1). Chlorinated ethene species exhibited a higher level of treatment effectiveness, relative to chlorinated ethane species, with a general trend established by Huang et al. (2005), which classified chlorinated ethene species as highly degradable compounds but chlorinated ethane species as relatively persistent in terms of persulfate reactivity.

Thermal activation temperature is a critical factor in the removal of all CVOCs investigated, as their removal in all cases was significantly improved by an increase of reaction temperature from 30 °C to 50 °C (Figure 1). In the case of 1,2-DCA, levels of removal of 30%, 48% and 55% were achieved at 30 °C in sand-, paddy- and clay-soil-persulfate systems, respectively. A significantly higher level of removal was achieved at 50 °C with 64%, 72% and 88% removed from sand-, paddy- and clay-soil-persulfate systems, respectively. It is of note that this increase in reaction rate in association with a rise in reaction temperature is an established standard Arrhenius behavior. The overall removal of all four CVOC species studied within the 11-day treatment of sand-, paddy- and clay-soil-persulfate systems, is shown in Figure 2, indicating that all CVOCs had the highest removal efficiency in clay-soil-persulfate system, followed by the paddy-soil-persulfate system, with lastly the sand-soil-persulfate system showing the lowest removal efficiency. One potential explanation for this phenomenon may be that the clay-based soil had the largest SSA ($0.242 \pm 0.0025 \text{ m}^2/\text{g}$, Table 1), assisting the reaction of soil minerals with persulfate. The high mineral content in the clay soil sample (Table 1) appears to contribute to an improved rate of removal of soil contaminants (e.g., *cis*-DCE, Figure 1), which may be due to soil minerals activating persulfate to generate more sulfate radicals, resulting in further contaminant oxidization (Deng *et al.* 2013).

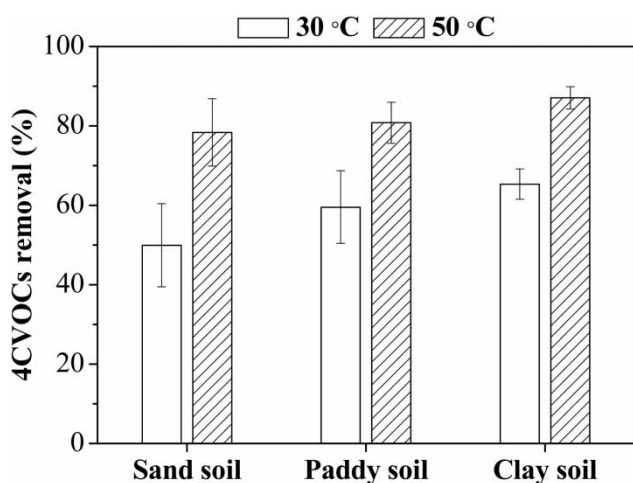


Figure 2 | The overall removal of the combined CVOC loading, using activated persulfate oxidation at 30 °C and 50 °C in sand-, paddy- and clay-soil-persulfate systems, respectively. [*cis*-DCE]₀: 963 mg L⁻¹. [1,2-DCA]₀: 942 mg L⁻¹. [TCE]₀: 1095 mg L⁻¹. [1,1,1-TCA]₀: 1004 mg L⁻¹. [Na₂S₂O₈]₀: 30 g L⁻¹. Time: 11 d.

Persulfate consumption

In persulfate ISCO systems, oxidant dosage is closely related to the level of contaminant removal efficiency and effectiveness (Tsitonaki *et al.* 2010). Therefore, an investigation of the performance of persulfate consumption in soil-persulfate systems was carried out, with the results shown in Figure 3. Persulfate was consumed gradually throughout the treatment period in the soil system (Figure 3), contributing to the effectiveness of persulfate in soil media, due to the short oxidant transport distances caused by persulfate being rapidly consumed. Figure 3 shows the significant effect that reaction temperature has on persulfate consumption, which notably increases from 30 °C to 50 °C, resulting in more persulfate being consumed at 50 °C than 30 °C, supported by the findings of the present study, where in sand-, paddy-, and clay-soil-persulfate systems, 35, 35 and 36% was consumed at 30 °C, whilst 82, 84 and 76% was consumed at 50 °C, for each soil type, respectively.

Increased temperature conditions from 30 °C to 50 °C resulted in an increased overall treatment efficiency for all CVOCs assessed (Figure 2), as well as a greater level of consumption of persulfate (Figure 3). Treatment at 30 °C resulted in effective yet incomplete removal of the four CVOCs (50–66% removal, as shown in Figure 2), with lower levels of persulfate consumption (35–36% consumed, as shown in Figure 3). In the case of sand-soil-persulfate systems, when temperature conditions increased from 30 °C to 50 °C, an increase in persulfate consumption was also observed from 35% to 82%, resulting in an increased level of removal of total CVOCs from 50% to 78%, consistent with the findings of previous studies, establishing that higher levels of persulfate consumption result in a higher degree of chlorinated organic removal in aqueous systems (Gu *et al.* 2012; Deng *et al.* 2013). In comparison to the sandy-soil-persulfate system, the paddy-soil-persulfate system consumed almost equal amounts of persulfate (ranging from 35% to 84% depending upon other conditions), but achieved a lower degree of CVOC removal (from 60% to 80%) with an increase in operational temperature from 30 °C to 50 °C. The same case was found for clay-soil-persulfate systems, with persulfate consumption of between 36–76% and total CVOC removal of 66–87% at 30 °C–50 °C. The occurrence of significantly increased persulfate consumption with only limited removal of CVOC species, was observed with elevated reaction temperatures in paddy- or clay-soil-persulfate system, showing that the consumption of persulfate was not only due to CVOC oxidation.

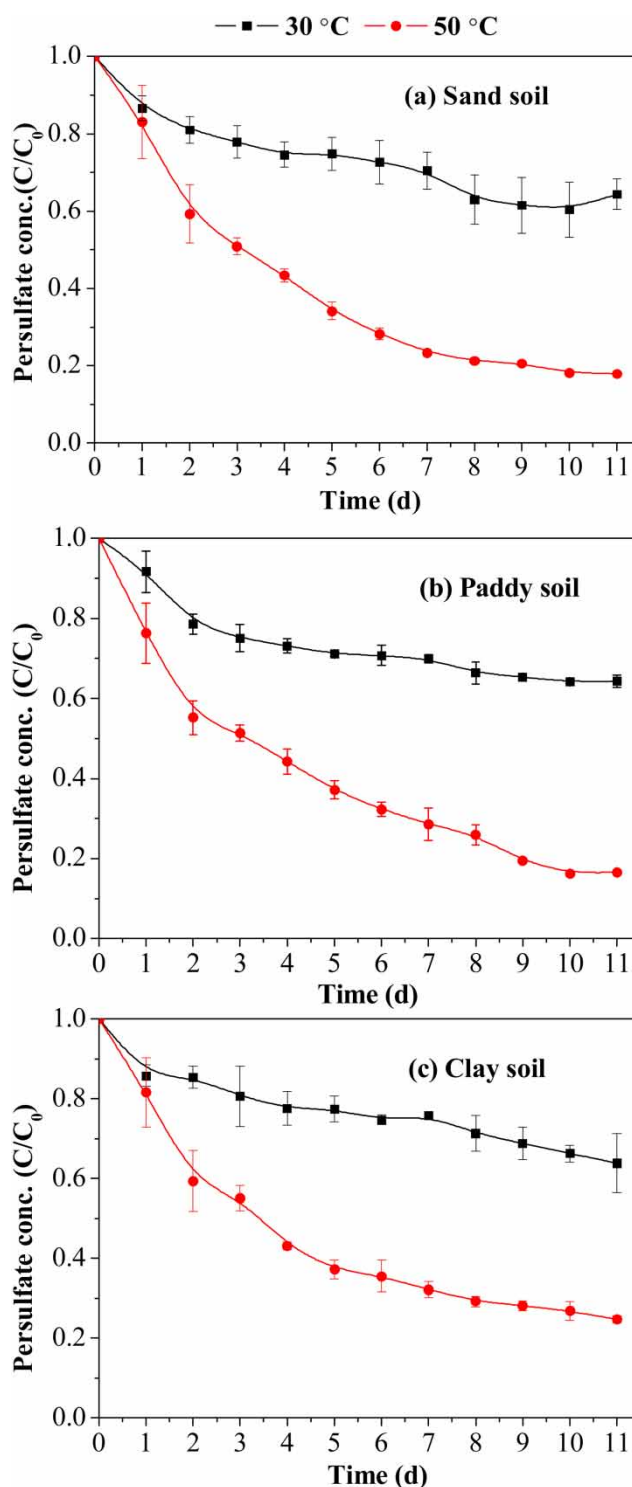


Figure 3 | Persulfate consumption during total CVOC oxidation at 30 °C and 50 °C in (a) sand-, (b) paddy- and (c) clay-soil-persulfate systems, respectively. [Na₂S₂O₈]₀: 30 g L⁻¹.

The OE in each treatment is defined as the ratio of the total CVOCs removed ($M_{4\text{CVOCs, removed}}$, Equation (4)) and the amount of oxidant consumed ($M_{\text{Ox, consumed}}$, Equation

(5)), and Figure 4 shows the OE values in sand-, paddy-, clay-soil-persulfate systems (0.050, 0.061, 0.066 at 30 °C; 0.034, 0.034, 0.041 at 50 °C; respectively). The increasing reaction temperature resulted in a significant increase in persulfate consumption (Figure 3) but slightly improved the overall CVOC removal efficiency (Figure 2), resulting in an overall reduction in OE as the temperature increased from 30 °C to 50 °C. As shown in Figure 4, elevated reaction temperature resulted in no improvement in OE in the persulfate-soil system, further supporting the theory that components and contaminants in soil matter, other than the four CVOC species investigated in this study, also competitively consume persulfate. The reaction of organic matter in the soil with persulfate, was accelerated at higher temperatures (50 °C), thus increasing the relative contribution to persulfate consumption caused by organic matter within the soil. Conversely, the relative contribution to persulfate consumption from contaminant oxidation was decreased with increasing reaction temperature. Therefore, the slight reduction in OE with increasing temperature from 30 °C to 50 °C may be partly apportioned to the increased reaction of various soil components with persulfate. Three of the types of soil material investigated in the present study (Table 1) contained components such as natural organic substances and minerals, which may consume extra oxidants present in the system (Haselow *et al.* 2003; Deng *et al.* 2013). As shown in Table 1, paddy soil material had a high f_{oc} content, which itself requires high amounts of persulfate, therefore affecting the demand for available persulfate, a factor which may be responsible for the significant decrease in OE occurring in the paddy-soil-persulfate

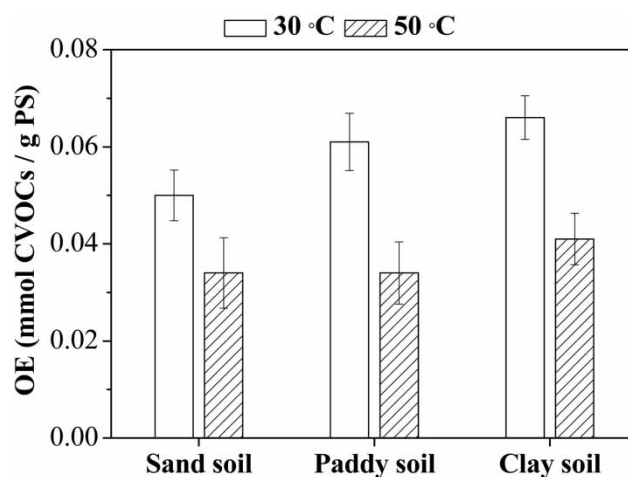


Figure 4 | Oxidation efficiency (OE, mmol of the total combined CVOC species removed per g of persulfate consumed) at 30 °C and 50 °C in sand-, paddy- and clay-soil-persulfate systems, respectively. [Na₂S₂O₈]₀: 30 g L⁻¹. Time: 11 d.

system. Therefore, soil composition, such as natural mineral and organic species content, exerts a considerable effect on OE and thereby contaminant removal in soil-persulfate systems.

Influence of soil composition on the persulfate consumption and CVOC removal

To further understand the influence of soil composition on persulfate consumption, studies were performed in the absence of any CVOC contaminants, but with the same oxidant concentration ($30 \text{ g L}^{-1} \text{ Na}_2\text{S}_2\text{O}_8$). As shown in Figure 5, a significant amount of persulfate was consumed in the soil-persulfate system in the absence of CVOCs, highlighting the importance of interactions of soil components with persulfate (Cuypers *et al.* 2002). As outlined in Figure 6 and Table 1, a high percentage of natural minerals and organic species (f_{oc}) in soil samples caused notable persulfate consumption in soil-persulfate systems containing no CVOCs, with a loss of natural soil minerals or f_{oc} content after the 11 d treatment period. This is supported by various studies showing that the active chemistry in soil-persulfate systems involves a combination of the reactions of persulfate with soil organics, minerals and other soil components (Haselow *et al.* 2003; Liang *et al.* 2008b; Deng *et al.* 2013). Comparison of persulfate consumption in soil-persulfate systems with and without CVOCs (Figure 3 and Figure 5) shows differences in the overall level of persulfate consumption after 11 d reaction, demonstrating the degree of competition between CVOCs and soil components for persulfate oxidation.

The consumption of persulfate during the reaction with soil components is referred to as the natural oxidant demand (NOD) and is expressed in $\text{g Na}_2\text{S}_2\text{O}_8/\text{kg}$ dry weight soil (dw). In situations where contaminants are present, the term TOD (total oxidant demand) is used, which is composed of NOD combined with contaminant demand (Haselow *et al.* 2003). Comparison of TOD values and NOD values shown in Table 2 highlights that the reactions which drive NOD occur in parallel with the reaction between soil contaminants and persulfate. The loss of natural soil minerals or f_{oc} content after an 11 d period in the soil-persulfate system in the absence of CVOCs, suggests that the NOD is composed of several reactions, including the reactions of persulfate with soil organics, minerals and other components. There is only a minor difference between the TOD and NOD values in sand-, paddy- or clay-soil-persulfate systems, suggesting that the reaction of soil components with persulfate (NOD), exerted a large relative

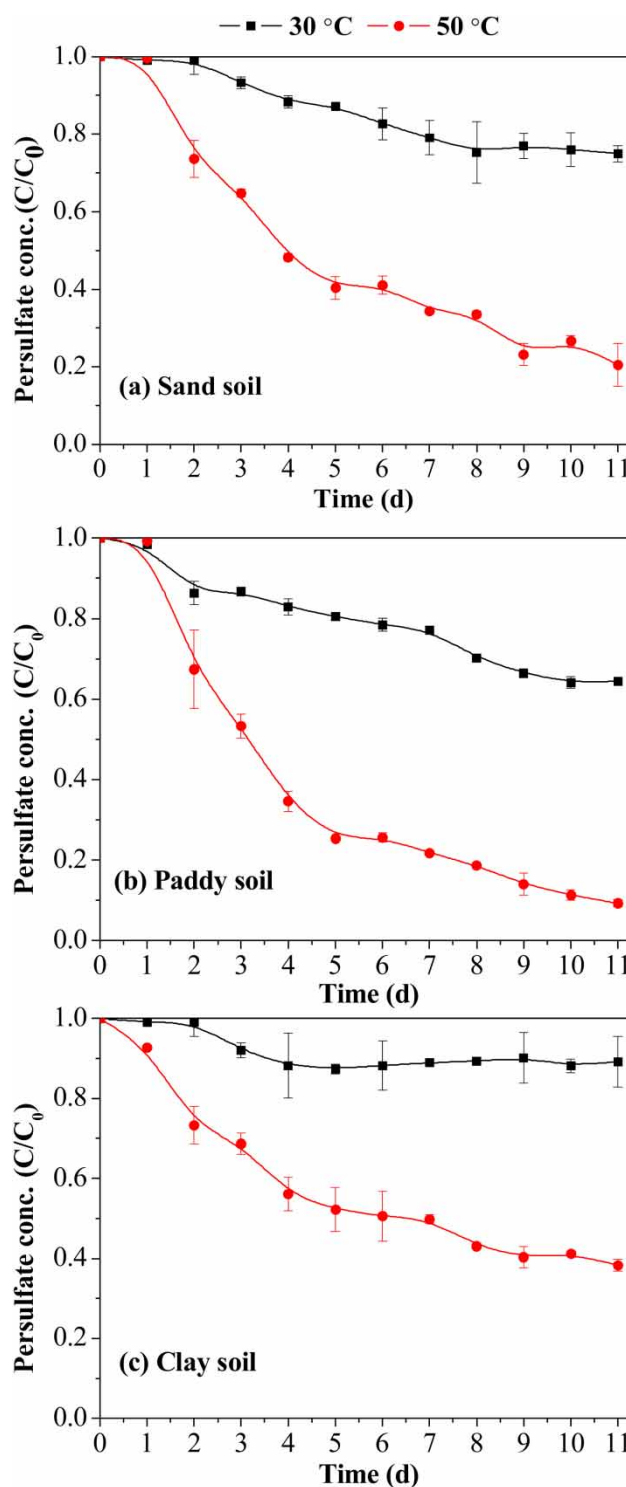


Figure 5 | Persulfate consumption with no CVOC addition at 30 °C and 50 °C in (a) sand-, (b) paddy- and (c) clay-soil-persulfate systems, respectively. $[\text{Na}_2\text{S}_2\text{O}_8]_0: 30 \text{ g L}^{-1}$.

contribution to the TOD. Therefore, the reactions of soil components with persulfate had a significant impact on the available oxidant demand and must be taken into

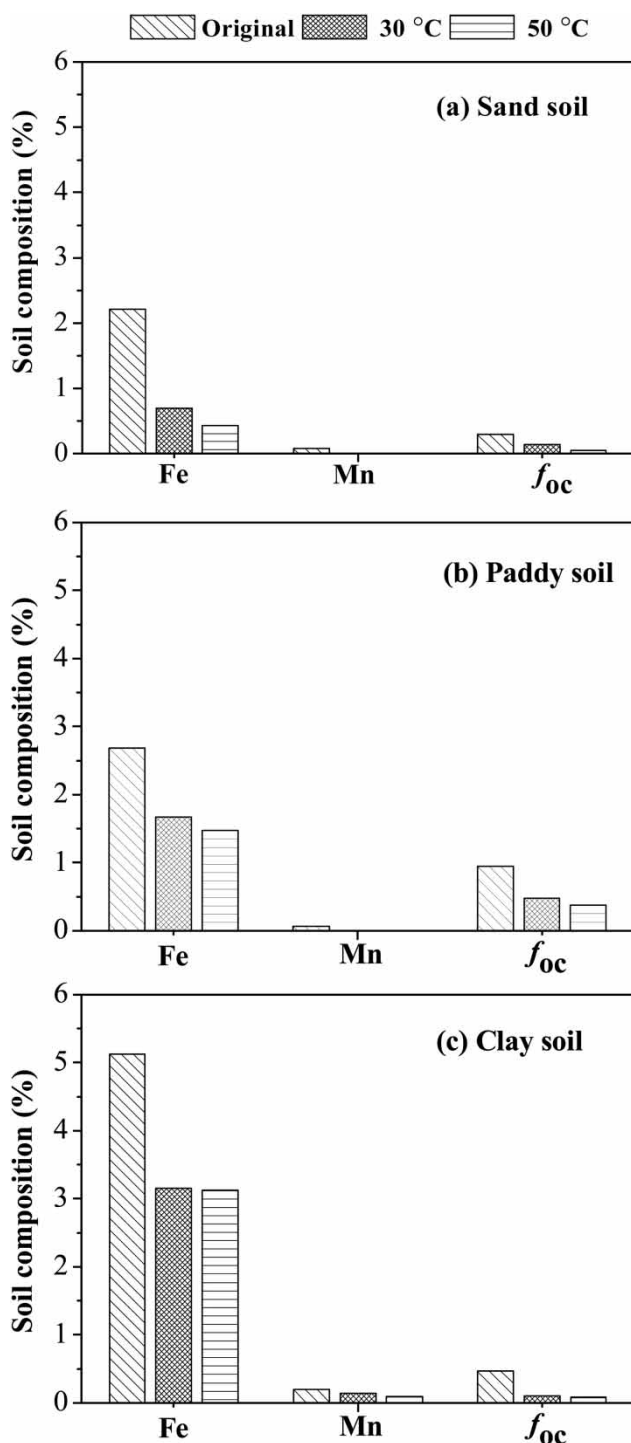


Figure 6 | Variation of mineral and f_{oc} content in soil materials during persulfate oxidation in the absence of CVOC contaminants at 30 °C and 50 °C in (a) sand-, (b) paddy- and (c) clay-soil-persulfate systems, respectively. Time: 11 d.

account when estimating the oxidation efficiency of in-situ oxidation remediation systems.

For soil-persulfate systems in the absence of CVOCs, NOD values in paddy-field soil were the closest to TOD at

30 °C, further increasing at 50 °C (Table 2), suggesting the available oxidant demand in paddy-field soil was affected significantly by NOD, followed by sand soil types and finally clay soil types. The most significant decrease in OE values with increased temperature from 30 °C to 50 °C occurred in the paddy-soil-persulfate system (Figure 4), which also indicates that soil composition had the most significant effect on treatment efficiency in the paddy-soil-persulfate system. In comparison with the sand and clay-soil-persulfate systems, the paddy-soil-persulfate system had the most notable loss of f_{oc} and the lowest reduction in natural minerals at either 30 °C or 50 °C (Table 2). This phenomenon suggests that the most important factor affecting the available oxidant demand in paddy-field soil was natural organic species (f_{oc}) rather than natural mineral content. Moreover, as the temperature increased from 30 °C to 50 °C, the greatest increase in NOD (34.2 g $\text{Na}_2\text{S}_2\text{O}_8/\text{kg dw}$) and Δf_{oc} (1.03 g/kg dw) was observed, along with the lowest measured increase in CVOC species removal (21%) in paddy-field soil. These results suggest that natural organic species contribute to the additional consumption of persulfate, without any increase in the rate of CVOC species removal in paddy-field soil. Conversely, for the clay-soil-persulfate system, the maximal loss of natural minerals (20.40 g/kg dw at 30 °C and 21.17 g/kg dw at 50 °C, Table 2), in combination with the lowest observed NOD values (11.4 g $\text{Na}_2\text{S}_2\text{O}_8/\text{kg dw}$ at 30 °C and 40.2 g $\text{Na}_2\text{S}_2\text{O}_8/\text{kg dw}$ at 50 °C, Table 2) resulted in a highly efficient removal rate for the CVOC species assessed (65% at 30 °C and 87% at 50 °C, Table 2) with also the highest OE values observed (0.066 at 30 °C and 0.041 at 50 °C, Figure 4). These results show that the natural mineral content contributed significantly to CVOC removal in clay soil types. For the sand-soil-persulfate system, as the temperature increased from 30 °C to 50 °C, the significant increase in mineral content (2.66 g/kg dw, Table 2) and CVOC species removal (28%, Table 2) suggests that the changes in mineral content had a positive effect on the removal efficiency of CVOCs in sand soil types.

CONCLUSION

The mass removal of four individual CVOCs, using thermally activated persulfate oxidation, decreased in efficiency in the order: *cis*-DCE > TCE > 1,2-DCA > 1,1,1-TCA. Persulfate was consumed gradually over time in all soils and elevated reaction temperature resulted in an increase of persulfate consumption and CVOC removal,

Table 2 | The removal rate of total CVOCs and the consumption of persulfate, natural minerals and organic substances (f_{oc}) at 30 °C and 50 °C in sand-, paddy- and clay-soil-persulfate systems, respectively

Test conditions	Persulfate dosage (g L ⁻¹)	Persulfate oxidation with CVOC addition		Persulfate oxidation with no CVOC addition		
		CVOC removal (%)	TOD (g Na ₂ S ₂ O ₈ /kg dw) ^a	NOD (g Na ₂ S ₂ O ₈ /kg dw) ^b	Δf_{oc} (g/kg dw) ^c	Δ Minerals (g/kg dw) ^d
30 °C, Sand soil	30	50	21.0	16.8	1.50	15.93
30 °C, Paddy soil	30	60	21.0	20.4	4.69	10.74
30 °C, Clay soil	30	66	21.6	11.4	3.63	20.40
50 °C, Sand soil	30	78	47.8	48.6	2.41	18.59
50 °C, Paddy soil	30	80	49.2	54.6	5.72	12.78
50 °C, Clay soil	30	87	41.9	40.2	3.87	21.17

^aTotal oxidant demand, g of Na₂S₂O₈ consumed per kg of dry weight of soil.

^bNatural oxidant demand, g of Na₂S₂O₈ consumed per kg of dry weight of soil.

^cTotal consumption of natural organic substances in the soil phase, g of organics consumed per kg of dry weight of soil.

^dTotal consumption of natural mineral substances (e.g., Fe and Mn), g of mineral substances per kg of dry weight of soil.

but no improvement of oxidation efficiency. The degree of persulfate consumption was found to not only be driven by CVOC species oxidation in soils, but also by various interactions between persulfate and soil components, leading to an increased NOD. The reaction of persulfate with soil components had varying effects on the available oxidant demand and rate of CVOC removal, depending on specific soil type composition of minerals and f_{oc} content. NOD exerted a large relative contribution to the TOD; therefore, the reactions of soil composition with persulfate must be taken into account when estimating the oxidation efficiency of in-situ oxidation remediation systems.

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