Published in final edited form as:

Water Res. 2019 February 01; 149: 386–393. doi:10.1016/j.watres.2018.11.028.

The Natural Activation Ability of Subsurface Media to Promote In-Situ Chemical Oxidation of 1,4-Dioxane

Ni Yan^{a,b}, Hua Zhong^b, and Mark L. Brusseau^{*,a,b}

^aHydrology and Atmospheric Sciences Department, School of Earth and Environmental Sciences, University of Arizona, 429 Shantz Building, Tucson, AZ 85721, United States

^bSoil, Water and Environmental Science Department, School of Earth and Environmental Sciences, University of Arizona, 429 Shantz Building, Tucson, AZ 85721, United States

Abstract

The ability of soils and sediments to promote in-situ activation of persulfate and persulfate combined with hydrogen peroxide was investigated for treatment of 1,4- dioxane (dioxane). Experiments were conducted with both batch-reactor and column systems to examine reaction rates and activation mechanisms. Four soils and aquifer sediments were used. ICP-MS and XRD analyses were used to characterize geochemical properties of the solutions and sediments, while EPR spectroscopy was used to characterize radical formation. For the batch experiments, degradation of dioxane was significantly greater in the presence of each of the four subsurface geomedias compared to the controls with no geomedias. This indicates that all four geomedias induced oxidant activation, thereby enhancing dioxane degradation. Dioxane degradation was significantly enhanced by the addition of peroxide to the persulfate solution. It is hypothesized that iron associated with the geomedias is primarily responsible for activation, and that the degree of degradation enhancement relates in part to dissolved- phase iron content. EPR results indicate that manganese oxides and soil organic matter may also have contributed to some degree to persulfate activation, and that manganese oxides enhanced activation of peroxide under the study conditions. Approximately 8% of dioxane was degraded in the miscible-displacement experiments, consistent with the short residence time compared to dioxane's half-life. The pseudo first-order rate coefficients obtained from the batch and column experiments were similar. The results of this study indicate that subsurface geomedias can induce activation of persulfate and peroxide to enhance in-situ chemical oxidation applications.

Graphical Abstract

*Corresponding author. Tel.: +1 520 621 3244; fax: +1 520 621 1647, brusseau@email.arizona.edu (M.L. Brusseau).

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests

Keywords

Natural oxidant activation; Dioxane; Persulfate; hydrogen peroxide

1. Introduction

1,4-Dioxane (dioxane) is a probable carcinogenic compound that commonly co-occurs with chlorinated-solvent compounds in groundwater (IARC, 1999; Anderson et al., 2012; Adamson et al., 2015). Extensive groundwater contaminant plumes of dioxane are readily formed due to its high water solubility and low sorption, and such plumes are present at many sites (Zenker et al., 2003; Isaacson et al., 2006; Mohr et al., 2010; Adamson et al., 2014). The cost-effective management of dioxane plumes is a challenging endeavor, given the physical and chemical properties of dioxane, and is a current focus of research.

Few alternatives to pump and treat exist for remediating large groundwater contaminant plumes (NRC, 2013). Monitored natural attenuation (MNA) is one potential option of great interest. However, its effectiveness is often limited for plumes comprised of dioxane and chlorinated-solvent compounds. Methods to increase the rates of natural attenuation (i.e., enhanced attenuation) and thus improve the effectiveness of MNA are being investigated. One concept of particular interest is the potential for using the capacity of resident soils and sediments to foment abiotic oxidative or reductive transformation of the target contaminants.

It is well known that certain constituents of geomedial media can promote abiotic transformation reactions for some contaminants (Laha and Luthy, 1990; Hofstetter et al., 1999; Li and Lee, 1999; Elsner et al., 2004; Neumann et al., 2009; Ahmad et al., 2010). However, the rates of attenuation associated with these reactions are typically insufficient to effect or maintain plume stasis. Prior research has investigated the use of oxidant/reductant reagents to synergize with geomedial media to enhance attenuation rates. For example, it has been shown that certain minerals can activate persulfate or hydrogen peroxide (H_2O_2) to enhance oxidation of contaminants such as trichloroethene (TCE), pentachlorophenol, and benzene (Ravikumar and Gurol, 1994; Ahmad et al., 2010; Huang et al., 2012; Yan et al., 2013; Liu et al., 2014; Yan et al., 2015). However, the oxidant-catalysis potential of subsurface sediment is likely influenced by many properties and factors given the physical and geochemical complexity of

the media. Hence, results obtained with specific minerals in isolation may not always be representative of the overall catalysis capacity of natural bulk sediment.

The results of recent research indicate that advanced oxidation processes implemented with activated persulfate, particularly in some combination with other oxidants, is effective for degradation of dioxane (e.g., Zhao et al., 2014; Zhong et al., 2015; Eberle et al., 2016; Yan et al., 2016). Very few studies have investigated the effectiveness of persulfate activation by natural aquifer materials (Sra et al., 2010; Liu et al., 2014), and these few studies have focused on oxidant activation and not on the efficacy of contaminant degradation nor on dioxane specifically. The objective of the current study is to investigate the capacity of natural soils and sediments to activate a binary persulfate/peroxide system to specifically enhance insitu degradation of dioxane.

This work is focused on a binary oxidant system as opposed to the traditional Fenton-like reaction (activated hydrogen peroxide) because, while the rates of dioxane degradation are similar, the oxidant decomposition rate is much faster for the peroxide- only system compared to the binary persulfate-peroxide system, which results in excessive waste of oxidant (Figure S1). The addition of persulfate moderates the decomposition rate of hydrogen peroxide (Yan et al., 2013; Yan et al., 2015). Batch and column experiments are conducted with four natural geomedia. X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS) are used to characterize solid and aqueous phase geochemistry, while electron paramagnetic resonance (EPR) spectroscopy is used to characterize radical formation.

2. Materials and methods

2.1. Materials

Four natural soils and aquifer sediments were used, AFP44, Florence MR, Camp Gruber, and BR1. AFP44 was collected from the Tucson International Airport Area (TIAA) Superfund site in Tucson, AZ. It is used to represent a standard sandy alluvial aquifer sediment. Florence MR was collected from Florence Military Reservation, AZ. Camp Gruber was collected from Camp Gruber, OK. Florence MR and Camp Gruber were chosen due to their higher clay and lower organic carbon (OC) contents. The BR1 soil was collected from a site in Brazil, and has high iron and organic carbon contents. Commercially available natural silica sand (40/50 mesh Accusand, Unimin Corporation) was used to represent a model low-reactivity porous medium for both the batch and column experiments. The physical and chemical properties of these subsurface media are reported in Table 1.

AFP44 is a sandy medium composed primarily of quartz, with smectite, mica, and kaolinite. Florence MR and Camp Gruber are loam and clay loam media, respectively, composed of quartz, with smectite, mica, kaolinite, and biotite. BR1 is a clayey medium, consisting primarily of hematite, gibbsite, goethite, magnetite, and quartz.

All solutions used in this study were prepared using ultrapure (filtered, distilled) water (Barnstead NANOpure ultrapure water system). No buffer or other pH modification was used. All of the reagents are reagent grade or higher. 1,4-Dioxane ($C_4H_8O_2$, class 1B) was

obtained from Fisher Scientific Inc., NJ; hydrogen peroxide (H_2O_2 , ~35 wt. % in water), potassium iodide (KI, > 99.4%) and sodium bicarbonate (NaHCO_3 , powder), were obtained from Sigma-Aldrich Corp., St. Louis, MO; sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >98%) was obtained from Acros Organics, NJ; ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, granular) was obtained from J.T.Baker Inc., Phillipsburg, NJ; sulfate reagent powder pillows were obtained from Hach Corp., Loveland, CO, USA. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO, 98%) was purchased from Matrix Scientific (Columbia, SC).

The concentration of dioxane was 0.57 mM (50 mg/L) for all experiments, which is representative of the upper range of groundwater concentrations reported for contaminated sites (Mohr et al., 2010). Concentrations of persulfate and peroxide were 6.3 mM and 150 mM (1190 mg/L and 5100 mg/L), respectively, for most experiments, based on results of our prior work that showed that these concentrations produced significant contaminant degradation while maintaining moderate oxidant utilization (Yan et al., 2013). While these oxidant concentrations are significantly greater than the concentration of dioxane, they are much lower than the concentrations typically used for standard field ISCO applications (ITRC, 2005). These lower concentrations are employed to enhance cost effectiveness of projected field-scale applications.

2.2. Batch Experiments

The degradation of dioxane by persulfate alone and by a persulfate-peroxide binary solution was measured using batch reactors. Batch experiments (in duplicate) were conducted at a room temperature of 25 ± 1 °C with borosilicate vials fitted with PTFE septum caps. Each vial contained 5 g of the selected subsurface media. For the persulfate system, solutions of 21 mM $\text{Na}_2\text{S}_2\text{O}_8$ and 11.3 mM dioxane were mixed 6:1 (v:v) in the vial. For the persulfate- H_2O_2 binary oxidant system, solutions of 21 mM $\text{Na}_2\text{S}_2\text{O}_8$, 300 mM H_2O_2 , and 11.3 mM dioxane were mixed 6:10:1 (v:v:v) in the vial. Ultrapure water was added to a final volume of 40 mL. Subsamples (0.5 mL) were collected over the course of the batch experiment, extracted with 0.5 mL hexane, and centrifuged for 5 minutes to separate solid and liquid phases. The samples (10 μL) were then analyzed using gas chromatography immediately.

A preliminary experiment was conducted for 192 hours using persulfate and peroxide in the presence of Florence soil to characterize temporal dioxane-degradation behavior (Figure S2). There was minimal degradation after 36 h and 98 h under persulfate-alone and persulfate-peroxide-combined conditions, respectively. Therefore, the experiments were conducted for a maximum of 98 h.

Several control treatments were conducted during the experiments. The first control contained only ultrapure water and dioxane, which was used to monitor non-oxidative mass loss of dioxane during the experiment. The purpose of the second control (dioxane + oxidant, with no sediment) was to determine dioxane degradation by oxidant in the absence of porous media. The third control, dioxane solution with porous media but no oxidant, tested for sorption and native sediment-associated degradation potential of dioxane. The fourth control was conducted to provide a comparison to the standard ISCO approach of using dissolved iron (FeSO_4) to activate the binary persulfate/hydrogen-peroxide system.

For this control, the same dioxane, persulfate, and peroxide concentrations were used, and no sediment was added. The concentration of FeSO_4 was 0.8 mM (121.6 mg/L).

A set of experiments was conducted to characterize the formation of radicals for the different treatments described above, to support delineation of operative activation-oxidation mechanisms. Radical generation was detected by EPR spectroscopy using DMPO as a spin trap agent (Fang et al., 2013; Yan et al., 2015; Zhong et al., 2015). BR1 soil and two differentially treated fractions of the BR1 soil were used for this test. BR1 soil (“bulk soil”) was pre-treated by adding hydrogen peroxide and heating in the aqua bath until no bubbles evolved to remove soil organic matter, providing a mineral-only fraction (“mineral fraction”) (Robinson, 1927; Ahmad et al., 2010). A portion of the mineral fraction was further treated with hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in nitric acid (HNO_3) to remove manganese oxides, providing an iron-only fraction (“iron fraction”) (Chao, 1972; Ahmad et al., 2010). Four mL of the reaction solution was mixed with DMPO to a final DMPO concentration of ~0.4 M. The mixed solution was transferred to a 1 mm ID capillary tube, and analyzed with EPR spectroscopy.

The concentrations of metals in aqueous and solid phases of all the soils and for the different soil fractions of BR1 soil were measured for parallel batch experiments. Aqueous samples were collected at 1 h and 192 h after the reaction began. Solids were rinsed more than 10 times with de-ionized water after separation from the aqueous phase, and then dried with pure N_2 . The dried solids were then subjected to acid digestion. X-ray diffraction was used to identify surface element composition and mineral formation for the geomeidia. The concentrations of dissolved organic carbon (DOC) in aqueous solution was also measured for all media. Samples were collected after 98 h of contact of geomeidia with ultrapure water. Samples were filtered with a 0.45 μm filter, and measured by a TOC analyzer.

2.3. Miscible-Displacement Experiments

The BR1 soil was selected as the representative porous medium for the subsequent miscible-displacement experiments due to its relatively poorer performance in the batch experiments, thus providing a conservative representation of column-based performance. The miscible-displacement experiments were conducted using a stainless steel column (7.5-cm long by 2.2-cm inner diameter). Stainless-steel distribution plates were placed on each end of the column to promote uniform flow and retain the porous media. All tubing and connectors were constructed of stainless steel. After packing, the column was vertically positioned and flushed with CO_2 to displace air. It was then saturated with de-aired water using a single-piston precision-flow HPLC pump (Gilson, Acuflo Series II). Once complete saturation of the column was obtained (a constant mass was attained), the column was then oriented horizontally for the experiments.

Four sets of tests were conducted. For the first set, a solution of 5 mM persulfate was injected into the column to test for activation/decomposition of persulfate. A solution of 5 mM persulfate and 0.5 mM dioxane was injected for the second set to test for dioxane degradation by persulfate alone. The third set was conducted using a mixed solution of 6.3 mM persulfate, 150 mM peroxide, and 0.57 mM dioxane to test for dioxane degradation by the binary oxidant. The final set was designed to determine the impact of a higher oxidant

concentration, by injecting a mixed solution of 21 mM persulfate, 300 mM peroxide, and 0.57 mM dioxane. Control experiments were conducted to examine the transport and degradation of persulfate and peroxide in silica sand. Tracer tests were also conducted using bromide (Br^-) as conservative tracer to characterize the hydrodynamic properties of the packed porous media.

A constant flow rate of ~ 0.1 ml/min, equivalent to pore-water velocity of ~ 3 cm/h, was used for the experiments. After 5–6 pore volumes of injection, the influent was switched to water to begin elution. Effluent samples were collected in glass tubes and placed in an ice-water bath to quench the reaction. The fluid discharge (determined by the mass of the sample collected), concentrations of dioxane/oxidant/sulfate, and pH were analyzed immediately. The concentrations of dioxane/oxidant/sulfate in the reservoir were measured before, during, and after each experiment to monitor for potential loss.

2.4. Chemical Analysis

Dioxane was analyzed using gas chromatography (Shimadu GC-14A, Columbia, MD) equipped with a $30 \text{ m} \times 0.53 \text{ mm}$ SPB^{TM}-624 capillary column (film thickness was $3 \mu\text{m}$), and a flame ionization detector (FID). Splitless direct injection was used. External standards were used for quantification. The temperatures of the injection port and detector were 200 and 250 °C, respectively. The initial oven temperature was 50 °C, maintained for 2 minutes, and then heated at a rate of 10 °C/min to a final temperature of 110 °C.

Concentrations of persulfate and peroxide were measured with a modified iodide spectrophotometry method (Liang et al., 2008). This method was also applied to the persulfate-peroxide system, and the concentrations of the oxidants were determined as the sum of the two oxidants (Figure S3). 100 g/L KI stock solution was made in a 5 g/L NaHCO_3 solution. Samples were measuring after 20 min mixing with the KI- NaHCO_3 solution at a ratio of 1:19 (v:v) using spectrophotometry (Hach DR2800, Loveland, CO) at a wavelength of 400 nm. Sulfate was monitored by spectrophotometry using the Ba^{2+} - based USEPA SulfaVer4 method (HACH module No.8051). Bromide was measured by UV-Vis spectrophotometry (Shimazu, Model 5150) at wavelength of 212 nm. The pH of the samples was measured with a Beckman 510 pH meter (Brea, CA).

Concentrations of metals were analyzed using inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC-II, Perkin Elmer, Shelton, CT), with detection limits for different elements ranging from 10^{-3} - 10^{-1} $\mu\text{g/L}$ for the aqueous phase and 10^{-3} - 10^{-1} $\mu\text{g/g}$ for the solid phase. X-ray diffraction was conducted using a Bruker model D8 Advance (Madison, WI).

Formation of radicals were analyzed using an X-band EPR spectrometer (Elexsys E500, Bruker, Woodlands, TX) equipped with the rectangular resonator operating in TE102 mode. The instrument settings were as follows: microwave frequency, 9.340 GHz; microwave power, 2 mW; magnetic field modulation amplitude of 1 G.

3. Results and discussion

3.1. Batch experiments

The degradation of dioxane by persulfate in the absence/presence of subsurface media is presented in Figure 1A. The control tests for dioxane in water (Figure 1) and water + solids (Figure S4) show minimal loss of dioxane during the experiment. The loss of dioxane in persulfate solution with no solids was minimal after 36 hours. However, dioxane underwent slight degradation in the presence of persulfate and solids for all four media, with concentration decreases ranging from 10–15% (Figure 1A). The results indicate that all four subsurface media used in the experiment have the ability to enhance persulfate-induced oxidation of dioxane.

A first-order rate equation was applied to the data, and pseudo-first-order reaction rate constants for dioxane degradation by persulfate alone in the presence of the soil ranged from 0.003 to 0.009 h⁻¹ (Table 2). The capacity of the four media to enhance persulfate-induced oxidation of dioxane followed the order Camp Gruber > Florence MR ~ BR1 > AFP44. Dioxane degradation by persulfate in the presence of iron filings has been reported, with a rate constant of 0.016 h⁻¹ obtained from a batch experiment (Zhong et al., 2015). The smaller rate constants observed for the soils are expected based on the higher iron content and surface area of the ironfiling particles compared to the soils.

The addition of peroxide to the system, creating a binary oxidant, greatly increased the rate of dioxane degradation (Figure 1B). Specifically, dioxane degradation in the presence of persulfate and peroxide but without soil was approximately 17% after 36 hours and 25% after 98 hours. Comparison of the single and binary oxidant results in the absence of soil reveals that the addition of peroxide produced a significant (factor of ~6) increase in dioxane degradation (3% vs 17% in 36 h).

The interactions between persulfate and peroxide, and the advantages of employing a binary oxidant system, have been discussed in our prior work (Yan et al., 2013; Yan et al., 2015). Persulfate moderates the decomposition of peroxide, producing a more sustainable release of HO·. In addition, the heat released by the decomposition of peroxide helps promote the activation of persulfate. The results of molecular probe and EPR tests indicated that hydroxyl, sulfate, hydroperoxyl, and superoxide radicals were present in the binary oxidant system.

The addition of soil to the binary oxidant system increased dioxane degradation to approximately 30–56% after 36 hours and 41–100% in 98 hours. The addition of peroxide to the systems containing soil increased dioxane degradation greatly compared to the persulfate-only treatment. In addition, the presence of soil increased dioxane degradation by factors of 3–4 for the binary system, suggesting that the soils used in the experiment can promote peroxide-induced oxidation of dioxane in addition to enhancing persulfate-induced oxidation.

Similar magnitudes of dioxane degradation were attained within the first 24 hours in the presence of Camp Gruber, Florence MR, and BR1. After 24 hours, however, the rate of

degradation slowed for Florence MR and BR1, compared to Camp Gruber. Dioxane degradation exhibited a multi-stage reaction pattern for the latter medium, with an extremely high rate of degradation in the first hour followed by a steady state stage (concentration plateau) for several hours and a final stage with a relatively slow rate of degradation. Conversely, dioxane degradation exhibited a two-stage reaction pattern for the other three porous media. Pseudofirst-order reaction rate constants for dioxane degradation by the binary oxidant in the presence of the porous media ranged from 0.09 to 0.45 h⁻¹ for the initial degradation stage, and from 0.004 to 0.013 h⁻¹ for the later stage (Table 2). The capacity of the four soils to enhance peroxide-persulfate-induced oxidation of dioxane follows the same order as the persulfate-induced reaction, which is Camp Gruber > Florence MR ~ BR1 > AFP44.

Complete degradation of dioxane was attained within 4 hours for the persulfate/peroxide system activated with dissolved Fe²⁺ (Figure S5). The pseudo-first-order reaction rate constant for dioxane degradation for this system is 3.5 h⁻¹. The k for dissolved-Fe²⁺ activation is approximately 10 times larger than the fast-stage values for the porous-media activation. The initial concentration of dissolved Fe²⁺ used for the standard FeSO₄ activation was 0.8 mM, approximately 30 to 1000 times larger than the dissolved iron generated from the soils (Table 4). The significantly smaller rate coefficients obtained for the porous-media activation are consistent with the much lower iron availability.

It is well known that the oxidation effectiveness of persulfate and peroxide can vary as a function of pH. In this study, the AFP44 and Florence MR systems had identical solution pH ~7, but the degree of degradation enhancement was much greater for Florence MR than for AFP44 (Table S1). Similarly, degradation enhancement was much great for Camp Gruber compared to BR1, even though they have similar solution pH ~4.5 (Table S1). These results indicate that factors other than pH are primarily responsible for the differences in degradation enhancement observed among the soils.

3.2. Constituents Contributing to Oxidant Activation

Several components of geomedia have been identified as having the potential to activate persulfate and peroxide. These include iron, other transition metals (i.e., Mn²⁺, Ag⁺ (under acidic conditions), Co²⁺, Ni²⁺), and soil organic carbon (Anipsitakis and Dionysiou, 2004; Liang et al., 2004; Ahmad et al., 2010; Ahmad et al., 2013; Liu et al., 2014). The ICP-MS analysis for the four porous media shows that the BR1 soil has a much greater iron content compared to the other three porous media (Table 3). Florence MR and Camp Gruber have comparable iron contents, while AFP44 has the lowest iron content. However, the degree of degradation enhancement was much greater for Camp Gruber than for BR1. This indicates that total sediment-phase iron is not the determinant factor for magnitude of activation.

Iron concentrations in the aqueous phase after 1 and 192 h of contact between soil and ultrapure water were measured by ICP-MS (Table 4). The iron concentrations for AFP44 and Florence MR after 192 h were smaller than after 1 h contact, indicating precipitation of dissolved iron. Although ICP-MS gives total ion concentrations (Fe²⁺ and Fe³⁺), Fe³⁺ can convert to Fe²⁺ in the presence of peroxide. The results show that the dissolved iron concentrations decreased in the order Camp Gruber > Florence MR > BR1 > AFP44. This

order is consistent with the observed degree of dioxane-degradation enhancement. The results indicate the crucial role of available iron from the porous media on the activation of oxidant. Inspection of Table 3 and Table 4 shows that the magnitudes of dissolved iron do not correlate directly to the respective solid-phase iron contents. This likely reflects differences in iron mineralogy and surface distribution.

Dissolved Mn, Co, and Ni are also present in solution, with Mn the only one at significant levels (Table S2). Dissolved Mn concentrations are much lower than dissolved iron concentrations for all of the geomedias except the BR1 soil. Other elements and their concentrations in the aqueous phase measured by ICP-MS are also presented in Table S2.

As discussed above, the Florence MR and the BR1 soils had similar degrees of enhancement of dioxane degradation. However, the Florence MR soil has almost a factor of 10 higher dissolved iron concentration than the BR1 soil. Table S2 shows that the BR1 soil has considerably more dissolved Mn compared to the Florence soil. This suggests that dissolved Mn may have contributed to the enhanced activation of oxidant for the BR1 soil.

It has been suggested that soil organic matter has the potential to enhance oxidant activation (Ahmad et al., 2010). In this prior research, persulfate decomposition was compared for a bulk soil and a mineral-only fraction of the soil (OC removed). The results were similar for both treatments at $\text{pH} < 7$, with a small magnitude of decomposition. Conversely, decomposition was much greater for the bulk soil compared to the mineral-only fraction at $\text{pH} > 12$. Fang et al. (2013) reported that persulfate could be activated by humic acids at neutral pH. Bissey et al. (2006) concluded that soil organic matter had no influence on peroxide decomposition and radical generation at pH 3, whereas it could promote radical generation at neutral pH. These results indicate that activation of persulfate and peroxide by soil organic matter is pH dependent, with greatest effect at neutral to alkaline pHs.

Among the porous media used in the present study, BR1 has the highest solid-phase organic carbon content (Table 1) and dissolved organic carbon (Table S3), but it exhibited relatively lower degradation enhancement. The solution pH of all of the systems before and after the reactions are presented in Table S1. Inspection shows that all reaction systems maintained pH less than 8, with most under acidic condition. These results suggest that soil organic matter was not a significant source of oxidant activation for the tested systems.

It should also be noted that soil organic matter (and dissolved organic matter) are sources of natural oxidant demand, and that the presence of substantial quantities of SOM and DOC may reduce the magnitude of dioxane degradation. The solid and carbon contents of BR1 soil are several times larger than the other geomedias. The substantial amount of organic carbon present for the BR1 soil may partially explain the lower magnitude of dioxane degradation obtained. The concentration of DOC measured for the BR1 soil was 87032 $\mu\text{g/L}$ (Table S3). This converts to a molar concentration of ~ 0.1 mM, using a molecular weight of 900 g/mol (Hendry et al., 2003). The relatively considerable amount of DOC for the BR1 soil may be sufficient to affect the magnitude of dioxane degradation (initial concentration of 0.57 mM), depending upon the relative lability of the two. The concentrations of DOC for the other porous media are much lower, and unlikely to have a significant impact.

3.3. Activation Mechanisms

To further investigate the role of the various soil constituents (organic matter, Fe, and Mn) in oxidant activation, BR1 soil was pre-treated to generate a fraction containing minerals but devoid of soil organic matter, and a fraction containing iron oxides but no soil organic matter or manganese oxides. EPR spectroscopy was used to examine radical generation among the soil fractions, using DMPO as the spin trap. DMPO-OH, DMPO-SO₄^{•-}, and DMPO-H/DMPO-R signals were observed in the EPR spectrum for both persulfate and persulfate-peroxide systems (Figure 2), indicating the presence of HO[•], SO₄^{•-}, and a spin adduct with a H/carbon-centered radical. In addition, the signal of DMPO-OH is the strongest. That is because DMPO-SO₄ is short-lived, and can easily decay into DMPO-OH (Davies et al., 1992; Zalibera et al., 2009; Yan et al., 2015). Therefore, HO[•] was used to indicate the activation ability of different treatments of BR1.

In the persulfate-only system, the HO[•] concentrations decreased in the order of bulk soil > mineral fraction > iron fraction (Figure 2A). This indicates that soil organic matter and manganese oxides, as well as iron oxides, contributed to the activation of persulfate. Conversely, the generation of HO[•] in the persulfate-peroxide system was similar for the bulk soil and the mineral fraction (Figure 2B). This indicates that soil organic matter was not a significant activator for the binary system. Less HO[•] was generated for the iron fraction compared to the bulk soil and mineral fraction, indicating that manganese oxides may have contributed to the activation of the binary oxidants. As shown in Table S4, the dissolved iron concentration in the bulk soil system is higher than for the mineral and iron fraction treatments (for which soil organic matter was removed). This indicates that soil organic matter in the bulk soil system facilitated the dissolution of iron, which thereby facilitated the generation of HO[•].

Assuming that dissolved iron is the primary activator, the amount of dioxane degraded should be proportional to the amount of dissolved iron present. On this basis, the dissolved iron data were normalized by the concentration reported for BR1 (29.3 µg/L), the medium with the lowest value. The normalized dioxane degradation for the persulfate-peroxide system was then calculated for each soil system using the normalized dissolved iron present. Details of the calculations are provided in SI Text S1. Inspection of Table S5 shows that the normalized dioxane degraded values are similar for AFP44, Florence MR, and Camp Gruber. These results illustrate the significant corresponding relationship between the magnitude of dioxane degradation and the amount of dissolved iron, indicating the essential role of dissolved iron in the activation process. However, the normalized degraded dioxane in the BR1 system was significantly larger than for the other soils, which illustrates the existence of other sources of activation for this soil. In total, the above results indicate that dissolved iron was the primary source of oxidant activation, with additional contributions from Mn and soil organic matter particularly for the BR1 soil.

3.4. Miscible-Displacement Experiments

Persulfate exhibited slight mass loss for the miscible-displacement experiments conducted with the BR1 soil. Mass loss of ~5% was observed at the 3 cm/h pore water velocity (hydraulic residence time (t_r) = 2.5 h) (Figure 3). The generation of sulfate was also

identified, consistent with the observed persulfate mass loss. Mass balance on sulfur (sum of persulfate and sulfate) was complete.

Persulfate breakthrough (pore volume at which $C/C_0 = 0.5$) was observed at approximately 1.4 pore volumes, and the breakthrough of sulfate was observed at approximately 1.6 pore volumes (Figure S6). The transport of a standard non-reactive tracer, bromide, also exhibited retardation (breakthrough at approximately 1.4 pore volumes, Figure 3). These results indicate that the transport of the anionic solutes is influenced by adsorption, which is consistent with the fact that the BR1 soil has a measurable anion exchange capacity (AEC). The BR1 is an acidic soil (pH ~4.2) (Table 1). The points of zero charge (PZC) of the primary iron minerals of the soil (hematite ~8, gibbsite ~5, goethite ~8, and magnetite ~7) are higher than the soil pH, which provides measurable AEC to produce the observed anion retardation.

An experiment was also conducted with a pore-water velocity of 30 cm/h ($t_r = 0.25$ h) to test the influence of hydraulic residence time (t_r) on persulfate transport (Figure S7). The results indicate that the impact of hydraulic residence time (t_r) on persulfate transport was minimal (persulfate breakthrough showed at approximately 1.4 pore volumes, and mass loss during transport was ~6%). The lower pore water velocity (3 cm/h) was used for the subsequent experiments.

Transport and degradation of dioxane in the BR1 column in the presence of persulfate is shown in Figure 4. Ideal transport of dioxane was observed, with no retardation or degradation. Persulfate breakthrough in the presence of dioxane was approximately 1.6 pore volumes. The residence time for the column experiment is 2.5 h, significantly shorter than dioxane's half-life ($t_{1/2}$, ~108 h) obtained from the batch experiments, hence no dioxane degradation was anticipated. Persulfate decomposition (~6%) had minimal difference with and without dioxane during transport. Sulfate generation was also observed, and the calculated total sulfur recovery was complete.

The dioxane breakthrough curve for transport in the presence of persulfate and peroxide in the BR1 column is presented in Figure 5. A small (~8%) loss of dioxane in the presence of peroxide and persulfate was observed (Figure 5A). The pseudo-first-order reaction rate constant for dioxane degradation obtained from the column experiment is $0.035 \pm 0.002 \text{ h}^{-1}$ (Text S2). This value is intermediate to the k values calculated for the fast and slow degradation stages of the batch experiment, and is essentially identical to the geometric mean of the two (0.032 h^{-1}). Increasing the oxidant (both persulfate and peroxide) concentration resulted in a slight increase in the degradation of dioxane to ~11% (Figure 5B).

4. Conclusion

The batch and column experiments demonstrated that the selected subsurface media successfully induced activation of oxidant, which led to enhanced dioxane degradation. The oxidation-enhancement potential of the four geomedia used herein varied, and was

demonstrated to depend primarily upon the magnitude of available sediment-phase iron. Mn and soil organic matter possibly provided additional contributions to activation.

The magnitude of dioxane degradation in the column experiments was relatively small due to the short residence time (2.5 h) compared to dioxane's half-life ($t_{1/2}$, ~100 h). Approximate transport distances required to achieve a targeted degree of dioxane degradation can be estimated using the measured rate coefficients and assumed values for groundwater velocity. For example, transport distances of 3 and 10 meters are estimated to be required to achieve 99% reduction of dioxane for the Camp Gruber and AFP44 media, respectively (with a velocity of 0.2 m/d). These calculations suggest that geomedia-promoted oxidation has the potential to achieve effective in-situ degradation of dioxane and other contaminants.

Employing in-situ activation of oxidants by natural soils and sediments may reduce or obviate the need for addition of catalysts such as dissolved iron to the oxidant solutions. This would in turn have the potential to reduce premature activation and increase the transport distance of oxidant from the injection points, which would reduce application costs. The effectiveness of employing in-situ activated ISCO will depend on numerous site-specific factors including groundwater hydraulics and contaminant concentrations in addition to geochemical properties of the geomedia and groundwater. For smaller-scale sites, it may be cost effective to apply oxidant solution to the entire plume. An alternative strategy for larger-scale sites could involve application at the leading edge of the plume to prevent further migration.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Paul Wallace in the University Spectroscopy & Imaging Facility (USIF), Prakash Dhakal in the Center for Environmental Physics and Mineralogy, and Mary Kay Amistadi in the Arizona Laboratory for Emerging Contaminants (ALEC), University of Arizona, for their assistance with XRD and ICP-MS analyses, respectively. We thank the reviewers for their constructive comments. This research was supported by the National Institute of Environmental Health Sciences Superfund Research Program (P42 ES04940), and the Strategic Environmental Research and Development Program (ER-2302). The first author acknowledges support by the China Scholarship Council.

References

- Adamson DT, Anderson RH, Mahendra S, Newell C, 2015 Evidence of 1, 4 Dioxane Attenuation at groundwater sites contaminated with chlorinated solvents and 1, 4-dioxane. *Environ. Sci. Technol* 49 (11), 6510–6518. [PubMed: 25970261]
- Adamson DT, Mahendra S, Walker K, Rauch S, Sengupta S, Newell C, 2014 A multi-site survey to identify the scale of the 1,4- dioxane problem at contaminated groundwater sites. *Environ. Sci. Technol. Lett* 1 (5), 254–258.
- Ahmad M, Teel AL, Watts RJ, 2010 Persulfate activation by subsurface minerals. *J. Contam. Hydrol* 115 (1–4), 34–45. [PubMed: 20439128]
- Ahmad M, Teel AL, Watts RJ, 2013 Mechanism of persulfate activation by phenols. *Environ. Sci. Technol* 47 (11), 5864–5871. [PubMed: 23663058]

- Anderson RH, Anderson JK, Bower PA, 2012 Co-occurrence of 1,4-dioxane with trichloroethylene in chlorinated solvent groundwater plumes at US Air Force installations: Fact or fiction. *Integr. Environ. Assess. Manage* 8 (4), 731–737.
- Anipsitakis GP and Dionysiou DD, 2004 Radical generation by the interaction of transition metals with common oxidants. *Environ. Sci. Technol* 38 (13), 3705–3712. [PubMed: 15296324]
- Bissey LL, Smith JL, Watts RJ, 2006 Soil organic matter–hydrogen peroxide dynamics in the treatment of contaminated soils and groundwater using catalyzed H₂O₂ propagations (modified Fenton's reagent). *Water Res* 40 (13), 2477–2484. [PubMed: 16815526]
- Davies MJ, Gilbert BC, Stell JK, Whitwood AC, 1992 Nucleophilic substitution reactions of spin adducts. Implications for the correct identification of reaction intermediates by EPR/spin trapping. *J. Chem. Soc., Perkin Trans 2* (3), 333–335.
- Elsner M, Schwarzenbach RP, Haderlein SB, 2004 Reactivity of Fe (II)-bearing minerals toward reductive transformation of organic contaminants. *Environ. Sci. Technol* 38 (3), 799–807. [PubMed: 14968867]
- Eberle D, Ball R, Boving TB, 2016 Peroxone activated persulfate treatment of 1,4-dioxane in the presence of chlorinated solvent co-contaminants. *Chemosphere* 144, 728–735. [PubMed: 26408980]
- Fang G, Gao J, Dionysiou DD, Liu C, Zhou D, 2013 Activation of persulfate by quinones: free radical reactions and implication for the degradation of PCBs. *Environ. Sci. Technol* 47(9), 4605–4611. [PubMed: 23586773]
- Hendry MJ, Ranville JR, Boldt-Leppin BEJ, Wassenaar LI, 2003 Geochemical and transport properties of dissolved organic carbon in a clay-rich aquitard. *Water Resour. Res* 39 (7), 1194.
- Hofstetter TB, Heijman CG, Haderlein SB, Holliger C, Schwarzenbach RP, 1999 Complete reduction of TNT and other (poly) nitroaromatic compounds under iron-reducing subsurface conditions. *Environ. Sci. Technol* 33 (9), 1479–1487.
- Huang W, Liu F, Yan N, Lu A, Chen H, Chen L, Wang F, 2012 Removal of trichloroethylene in groundwater with two oxidants: siderite catalyzed hydrogen peroxide and sodium persulfate. *Water Sci. Technol.: Water Supply* 13 (1), 36–43.
- IARC, 1999 Monograph on 1,4-Dioxane; International Agency for Research on Cancer: Lyon, France.
- ITRC, 2005 Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd ed.; Interstate Technology and Regulatory Council: Washington, DC.
- Isaacson C, Mohr TK, Field JA, 2006 Quantitative determination of 1, 4-dioxane and tetrahydrofuran in groundwater by solid phase extraction GC/MS/MS. *Environ. Sci. Technol* 40 (23), 7305–7311. [PubMed: 17180982]
- Laha S and Luthy RG, 1990 Oxidation of aniline and other primary aromatic amines by manganese dioxide. *Environ. Sci. Technol* 24 (3), 363–373.
- Li H and Lee LS, 1999 Sorption and abiotic transformation of aniline and α -naphthylamine by surface soils. *Environ. Sci. Technol* 33 (11), 1864–1870.
- Liang C, Bruell CJ, Marley MC, Sperry KL, 2004 Persulfate oxidation for in situ remediation of TCE. II. Activated by chelated ferrous ion. *Chemosphere* 55 (9), 1225–1233. [PubMed: 15081763]
- Liang C, Huang CF, Mohanty N, Kurakalva RM, 2008 A rapid spectrophotometric determination of persulfate anion in ISCO. *Chemosphere* 73 (9), 1540–1543. [PubMed: 18922560]
- Liu H, Bruton TA, Doyle FM, Sedlak DL, 2014 In situ chemical oxidation of contaminated groundwater by persulfate: decomposition by Fe (III)- and Mn (IV)-containing oxides and aquifer materials. *Environ. Sci. Technol* 48 (17), 10330–10336. [PubMed: 25133603]
- Mohr T, Stickney J, DiGiuseppi W, 2010 Environmental Investigation and Remediation: 1,4-Dioxane and other Solvent Stabilizers; CRC Press.
- Neumann A, Hofstetter TB, Skarpeli-Liati M, Schwarzenbach RP, 2009 Reduction of polychlorinated ethanes and carbon tetrachloride by structural Fe (II) in smectites. *Environ. Sci. Technol* 43 (11), 4082–4089. [PubMed: 19569334]
- NRC, 2013 Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites Natl. Res. Council, Wash., DC.
- Ravikumar JX and Gurol MD, 1994 Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand. *Environ. Sci. Technol* 28 (3), 394–400. [PubMed: 22165872]

- Sra KS, Thomson NR, Barker JF, 2010 Persistence of persulfate in uncontaminated aquifer materials. *Environ. Sci. Technol* 44 (8), 3098–3104. [PubMed: 20205387]
- Teel AL, Ahmad M, Watts RJ, 2011 Persulfate activation by naturally occurring trace minerals. *J. Hazard. Mater* 196, 153–159. [PubMed: 21968122]
- Teel AL, Finn DD, Schmidt JT, Cutler LM, Watts RJ, 2007 Rates of trace mineral-catalyzed decomposition of hydrogen peroxide. *J. Environ. Eng* 133, 853–858.
- Yan N, Liu F, Huang W, 2013 Interaction of oxidants in siderite catalyzed hydrogen peroxide and persulfate system using trichloroethylene as a target contaminant. *Chem. Eng. J* 219, 149–154.
- Yan N, Liu F, Xue Q, Brusseau ML, Liu Y, 2015 Wang J Degradation of trichloroethene by siderite-catalyzed hydrogen peroxide and persulfate: Investigation of reaction mechanisms and degradation products. *Chem. Eng. J* 274, 61–68. [PubMed: 26236152]
- Yan N, Liu F, Chen Y and Brusseau ML, 2016 Influence of Groundwater Constituents on 1, 4-Dioxane Degradation by a Binary Oxidant System. *Water, Air, Soil Pollut* 227 (12), p.436. [PubMed: 28943674]
- Zalibera M, Raptá P, Staško A, Brindzova L, Brezova V, 2009 Thermal generation of stable spin trap adducts with super-hyperfine structure in their EPR spectra: An alternative EPR spin trapping assay for radical scavenging capacity determination in dimethylsulphoxide. *Free Radic. Res* 43 (5), 457–469. [PubMed: 19353392]
- Zenker MJ, Borden RC, Barlaz MA, 2003 Occurrence and treatment of 1, 4-dioxane in aqueous environments. *Environ. Eng. Sci* 20, 423–432.
- Zhao L, Hou H, Fujii A, Hosomi M and Li F, 2014 Degradation of 1, 4-dioxane in water with heat-and Fe^{2+} -activated persulfate oxidation. *Environ. Sci. Pollut. Res* 21 (12), 7457–7465.
- Zhong H, Brusseau ML, Wang Y, Yan N, Quig L, Johnson GR, 2015 In-situ activation of persulfate by iron filings and degradation of 1, 4-dioxane. *Water Res* 83, 104–111. [PubMed: 26141426]

Highlights

- ▶ subsurface-media induced oxidation of dioxane by persulfate-peroxide was investigated.
- ▶ all geomeia tested induced oxidative degradation of dioxane.
- ▶ dissolved iron appears to be the primary contributor to activation.
- ▶ calculations based on the transport experiments indicate dioxane attenuation in reasonable distances.

Figure 1.

Oxidative degradation of dioxane in the absence/presence of subsurface media in batch reactor systems. (A) Persulfate only. (B) Persulfate combined with peroxide. The “ultrapure water” control contained only ultrapure water and dioxane. The “oxidant only” control contained only dioxane and oxidant, with no sediment. Error bars show mean $\pm$ standard deviation (range may be smaller than the symbol). The initial reaction conditions: subsurface media = 5 g, [persulfate] = 6.3 mM, [peroxide] = 150 mM.

Figure 2.

Electron paramagnetic resonance (EPR) spectra obtained from DMPO trapping experiments after 20 min mixing. (A) EPR spectra for supernatant of persulfate-BR1 and different BR1 fractions. (B) EPR spectra for supernatant of persulfate-peroxide-BR1 and different BR1 fractions. The initial reaction conditions: soil = 5 g, [persulfate] = 6.3 mM, [peroxide] = 150 Mm, [DMPO] = 0.4 M. [■] DMPO-OH; [●] DMPO-SO₄; [▼] DMPO-H or DMPO-R.

Figure 3.

Breakthrough curves of persulfate, sulfate, total sulfur (the elution started from 5.2 pore volumes), and bromide (the elution started from 4.3 pore volumes) in the BR1 column (no dioxane added). Influent persulfate and bromide concentrations are 5 mM and 10 mg/L. Sulfate concentration was calculated by converting sulfate concentration as persulfate. The pore-water velocity is 3 cm/h.

Figure 4. Breakthrough curves of dioxane, persulfate, the subsequent generated sulfate, and total sulfur during the transport of dioxane and persulfate in the BR1 column at the pore-water velocity of 3 cm/h. Influent dioxane and persulfate concentration are 0.5 mM and 5 mM, respectively. The elution started from 5.2 pore volumes.

Figure 5.

Degradation of dioxane by persulfate and peroxide in the BR1 column and the related solution chemistry. “Oxidant” refers to the sum of persulfate and peroxide. (A) Influent dioxane, persulfate, and peroxide concentration are 0.57 mM, 6.3 mM, and 150 mM, respectively. The elution started from 5.2 pore volumes. (B) Influent dioxane, persulfate, and peroxide concentration are 0.57 mM, 21 mM, and 300 mM, respectively. The elution started from 4.9 pore volumes.

Table 1

Physical and chemical properties of the subsurface media

Medium	Texture	Clay (%)	Silt (%)	Sand (%)	OC ^a (%)	EC ^b (mS·cm ⁻¹)	SSA ^c (m ² ·g ⁻¹)	CEC ^d (mS·cm ⁻¹)	pH ^e	Mineralogy ^f
Accusand	Sand			100	0.03		0.14		6.1	Q
AFP44	Sand	2.0	1.8	96.3	0.03				8.1	Q,S,M,K
Florence MR	Loam	26.8	33.5	39.7	0.45	417	33	12.2	8.0	Q,S,M,K,B
Camp Gruber	Clay loam	32.3	44.9	22.8	0.83	74	38.3	14.3	5.4	Q,S,M,K,B
BR1	Clay	71.1	14.7	14.2	9.97	0.7	61.8	3.2	4.2	H,GI,GO,M,Q

^aOC is organic carbon

^bEC is electrical conductivity

^cSSA is specific surface area

^dCEC is cation exchange capacity

^epH was measured in DI water

^fPrimary minerals detected. Mineralogy key listed in order of decreasing content: S = smectite, M = mica, K = kaolinite, Q = quartz, B = biotite, H = hematite, GI = gibbsite, GO = goethite, M = magnetite

Table 2
Pseudo-first-order reaction rate constant (k) and half-life ($t_{1/2}$) for dioxane degradation in batch reactors

Medium	Rate constant k (h^{-1}) ^a			Half-life $t_{1/2}$ (h)		
	Persulfate	Persulfate + Peroxide	Slow ^c	Persulfate	Persulfate + Peroxide	Slow
AFP44	0.003 (0.002–0.004) ^d	0.09 (0.08–0.10)	0.004 (0.002–0.005)	267.6	7.7	187.3
Florence MR	0.006 (0.003–0.009)	0.29 (0.25–0.33)	0.005 (0.004–0.006)	113.6	2.4	133.3
Camp Gruber	0.009 (0.004–0.015)	0.45 (0.44–0.46)	0.014 (0.011–0.016)	73.7	1.5	51.3
BR1	0.006 (0.004–0.008)	0.21 (0.20–0.22)	0.005 (0.003–0.006)	108.3	3.3	147.5

^a All correlation coefficients for rate constants are greater than 0.90, except for slow reaction period of AFP44 which is 0.84.

^b Rate constant k for activated binary oxidant system calculated for fast reaction period

^c Rate constant k for activated binary oxidant system calculated for slow reaction period

^d The data in parentheses are 95% confidence intervals

Table 3

Selected metal contents of solid phase before reaction based on ICP-MS analysis

Medium	Fe (mg/g)	Mn (µg/g)	Co (µg/g)	Ni (µg/g)
AFP44	2.1	79	0.87	1.4
Florence MR	12	36	3.1	4.6
Camp Gruber	9.3	369	7.4	13
BR1	110	122	0.82	11

Table 4

Iron concentrations in aqueous phase after media contact with ultrapure water for 1 h and 192 h.

Medium	1 h (µg/L)	192 h (µg/L)
AFP44	88.8	6.0
Florence MR	265.1	195.9
Camp Gruber	576.8	1721.5
BR1	29.3	32.8