



Oxidation of trichloroethylene, toluene, and ethanol vapors by a partially saturated permeable reactive barrier



Mojtaba G. Mahmoodlu^{a,*}, S.Majid Hassanizadeh^a, Niels Hartog^{a,b}, Amir Raouf^a

^a Utrecht University, Department of Earth Sciences, The Netherlands

^b KWR Watercycle Research Institute, Nieuwegein, The Netherlands

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ABSTRACT

The mitigation of volatile organic compound (VOC) vapors in the unsaturated zone largely relies on the active removal of vapor by ventilation. In this study we considered an alternative method involving the use of solid potassium permanganate to create a horizontal permeable reactive barrier for oxidizing VOC vapors. Column experiments were carried out to investigate the oxidation of trichloroethylene (TCE), toluene, and ethanol vapors using a partially saturated mixture of potassium permanganate and sand grains. Results showed a significant removal of VOC vapors due to the oxidation. We found that water saturation has a major effect on the removal capacity of the permeable reactive layer. We observed a high removal efficiency and reactivity of potassium permanganate for all target compounds at the highest water saturation ($S_w = 0.6$). A change in pH within the reactive layer reduced oxidation rate of VOCs. The use of carbonate minerals increased the reactivity of potassium permanganate during the oxidation of TCE vapor by buffering the pH. Reactive transport of VOC vapors diffusing through the permeable reactive layer was modeled, including the pH effect on the oxidation rates. The model accurately described the observed breakthrough curve of TCE and toluene vapors in the headspace of the column. However, miscibility of ethanol in water in combination with produced water during oxidation made the modeling results less accurate for ethanol. A linear relationship was found between total oxidized mass of VOC vapors per unit volume of permeable reactive layer and initial water saturation. This behavior indicates that pH changes control the overall reactivity and longevity of the permeable reactive layer during oxidation of VOCs. The results suggest that field application of a horizontal permeable reactive barrier can be a viable technology against upward migration of VOC vapors through the unsaturated zone.

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1. Introduction

During the past few decades, the migration of volatile organic compounds (VOCs) by diffusion from contaminated soil or groundwater into overlying buildings has received considerable attention (McHugh et al., 2013; Provoost et al., 2009). Human health risks of VOCs are typically dominated

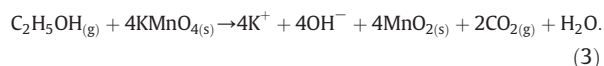
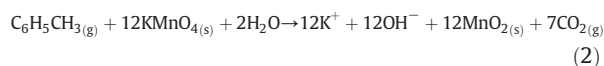
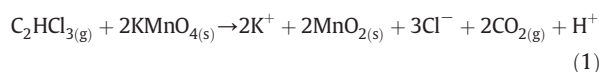
by the extent of exposure through inhalation of indoor air. The health risks from VOC vapor inhalation are much greater than those from drinking comparably contaminated water. Hence, methods to diminish or prevent vapor intrusion into buildings are of great public interest.

A number of techniques exist for treating unsaturated zone contaminated with VOCs. Despite their successful use, they all suffer from several shortcomings. For example, soil vapor extraction requires long-term operation and does not convert the contaminants to less toxic compounds (Cho et al., 2002). Bioventing is an in-situ bioremediation technology

* Corresponding author. Tel.: +31 302535024; fax: +31 30 2534900.

E-mail addresses: m.gharehmahmoodlu@uu.nl,
m.g.mahmoodlu@gmail.com (M.G. Mahmoodlu).

that degrades VOCs. However, the performance of this method can be affected by soil permeability and water content restrictions. Moreover, the method is not effective for aerobic biodegradation of many chlorinated hydrocarbons (Hinchee, 1993; USEPA, 1995). In-situ chemical oxidation (ISCO) of VOCs has been well developed as a remediation technology of dissolved VOCs in groundwater (Heiderscheidt et al., 2008; Li and Schwartz, 2004; Tsitonaki et al., 2010; Yuan et al., 2013). However, only a few studies have applied ISCO to the unsaturated zone using permanganate (Hesemann and Hildebrandt, 2009) or other oxidants (Cronk et al., 2010). In these studies, the oxidant was mostly introduced as an aqueous solution, thus effectively saturating the unsaturated zone. By contrast, our recent study showed that dry solid potassium permanganate granules were able to oxidize TCE, toluene, and ethanol (target compound) vapors, according to the following overall reaction equations (Mahmoodlu et al., 2013):



VOC vapor oxidation presented in our earlier study occurred through the exposure of VOC vapor to excess amounts of solid potassium permanganate. As a result, any potential long-term effects on the reactivity of potassium permanganate through the accumulation of reaction products, such as manganese dioxide (MnO_2) and pH changes, could not be assessed. Also, the experiments were performed at low moisture conditions with only ambient air providing initial humidity. While the study confirmed the potential of using permanganate for permeable reactive barriers in the unsaturated zone, it remained unclear how water content and chemical evolution would affect the reactivity of a permeable reactive barrier. In this study we therefore performed a series of column experiments to (1) evaluate the ability of solid potassium permanganate as a horizontal permeable reactive layer to oxidize the vapor of three VOCs under various degrees of water saturation, (2) investigate the impact of the accumulations of by-products on the long-term reactivity of potassium permanganate, and (3) numerically simulate the migration and oxidation process of each target compound diffusing through the permeable reactive layer.

2. Materials and methods

2.1. Materials

The contaminants (target compounds) used in this study were pure TCE, toluene, and ethanol (from Sigma-Aldrich, Merck, and ACROS, respectively). Solid potassium permanganate of 99% purity was obtained from Sigma-Aldrich and well mixed with sand to create a permeable reactive layer. The sand used in this study originated from a river bed in Papendrecht (Filcom Company, The Netherlands) and was

sieved to retain sizes of 0.5–1 mm. The porosity of sand was estimated to be approximately 0.35. Since the mean size of potassium permanganate grains was almost equal to the sand mean grain size, we assumed the same porosity for potassium permanganate.

Two additional TCE experiments were conducted to test the effect of pH buffering by adding sodium bicarbonate (NaHCO_3) ($\geq 99.0\%$, Merck) and calcium carbonate (CaCO_3) ($\geq 99.0\%$, Merck). Deionized (DI) water was used to adjust the required initial water saturation in the permeable reactive layer, and to investigate the effect of adding water on the reactivity of permeable reactive layer.

A glass cylinder of 5.0 cm length and 4.0 cm internal diameter, capped by a steel stainless lid, was used to construct the experimental columns. The columns were divided into two parts by means of a glass filter (P0, $\phi = 0.3$, Robu & Schott, ISO 4793), which was fused to the inner wall of the columns. Horizontal permeable reactive layers consisting of a combination of solid potassium permanganate, sand, and DI water, were placed on top of the glass filters, through which VOC vapor could diffuse from below (Fig. 1).

2.2. Sampling and measurements

During the experiments, gas samples of 1.5 ml were periodically taken from the headspace of the reactive and control columns using a 2.5 ml gas-tight syringe (SGE Analytical Science, Australia). To eliminate the effect of a pressure drop due to sampling, the same volume of air (1.5 ml) was simultaneously injected in the upper part of the column through a separate valve. The gas sample subsequently was injected into a 10-ml transparent glass vial which was capped with a magnetic cap and hard septum (Magnetic Bitemall; red lacquered, 8 mm center hole; Pharma-Fix-Septa, silicone blue/PTFE gray; Grace Alltech). Sampling vials were immediately placed into the tray of a gas chromatograph (GC). Gas samples of 2.0 ml were taken by an autosampler using the headspace syringe of the GC from each vial. Samples were next injected into the GC. The GC (Agilent 6850) was equipped with a flame ionization detector (FID). Separation was done on an Agilent HP-1 capillary column (stationary phase: 100% dimethylpolysiloxane, length: 30 m, ID: 0.32 mm, film thickness: 0.25 μm). A temperature programmed run was used to analyze the samples. VOC concentrations were determined using a headspace method as employed in previous studies (e.g. Almeida and Boas, 2004; Przyjazny and Kokosa, 2002; Sieg et al., 2008; Snow, 2002). The limits of quantification (LOQ) were calculated by using a signal-to-noise ratio of 10:1 (Kubinec et al., 2005).

To measure the total organic carbon (TOC) content, the sand ($D_0 = 0.5\text{--}1\text{ mm}$) was grained before the experiment and sieved to a particle size fraction of $<250\ \mu\text{m}$. Measurements were next carried out using Fisons Instruments analyzer (NA 1500 NCS) with a cycle time of 180 s and a source temperature of 190 °C.

2.3. Experimental procedure

Mixtures of potassium permanganate grains (20 g) and sand (10 g) with different water saturation (0.0, 0.2, 0.4, and 0.6) were used to create the permeable reactive layers. First, potassium permanganate and the sand grains were placed

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