



## Technical Note

# Ozonation of diesel–fuel contaminated sand and the implications for remediation end-points



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## HIGHLIGHTS

- Ozonation of light alkanes was 1.1-fold higher than heavy alkanes.
- Diesel ozonation in fine sands was 1.2-fold higher than that in coarse sands.
- Soil moisture below 18% had insignificant influence on diesel ozonation efficiency.
- Ozonation resulted in significant soil acidification as pH declined from 6 to 3.
- Aldehydes and carboxylic acids should be monitored for assessing end-points.

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## ABSTRACT

In this study, we investigate specifically the influence of soil grain size and water content on the degradation of n-alkane fractions and the formation of aldehydes and carboxylic acid during ozonation. 15 g of quartz sand spiked with diesel (25 g kg<sup>-1</sup>) were exposed to ozone for 20 h at concentrations of 10, 30 and 50 mg L<sup>-1</sup>, respectively. Results indicated that ozonation of the n-alkanes in fine grain size sand (0.15–0.25 mm) was 1.2 times faster than coarse sand due to higher surface contact area between O<sub>3</sub> and sand particles. Soil moisture below 18% w/w did not influence the ozonation efficiency. In contrast the ozonation led to an increase of acidity of the sand samples (pH = 3.0) after 20 h treatment. This was due to the formation of carboxylic acid. Formaldehyde, one of the key by-products of ozonation, was always <13 mg kg<sup>-1</sup> after the treatment which is below the industrial soil clean-up target level. While the aldehydes and carboxylic acid further reacted with O<sub>3</sub> and their ozonation rate were slower than those of the alkanes suggesting that the hydroxylated by-products accumulated in the sand during the process. Overall the findings demonstrated that not only the alkanes but also aldehydes and carboxylic acid should be considered when defining remediation end-points.

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## 1. Introduction

Ozonation is an effective and rapid method for removing petroleum hydrocarbons including linear alkanes and polycyclic aromatic hydrocarbons (PAHs) from contaminated soils (Masten and

Davies, 1997; Lee and Kim, 2002; Jonsson et al., 2006; O'Mahony et al., 2006; Yu et al., 2007; Rivas et al., 2009). The hydrocarbons are either oxidised through direct reaction with O<sub>3</sub> molecules or by indirect reaction with the hydroxyl free radicals. Promotion of the free radical formation occurs in the presence of key organic compounds such as alcohols, carboxylic acid, and humics which are all fairly common constituents of most soil matrices (ITRC, 2005).

Among the major ozonation by-products identified in previous studies, aldehydes and carboxylic acid are the two main organic compound groups (Nawrocki et al., 2003). Aldehydes especially constitute a group of relatively reactive organic compounds which can be oxidised into carboxylic acid and subsequently converted to

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CO<sub>2</sub> by microorganisms. However, there are some drawbacks to the application of ozonation in contaminated soils such as the potential exposure to aldehydes especially formaldehyde at site; this is of concern as inhalation of formaldehyde even at low doses has the potential to irritate the eyes and the air passage to humans (Stavridis, 2008). Meanwhile carboxylic acid, such as butyric (C4:0), valeric (C5:0) and caprylic (C6:0) acids have an offensive odour and therefore pose a nuisance at site.

Jung et al. (2005) also showed that the abundance of indigenous microbes in a contaminated soil with diesel decreased significantly during ozonation treatment while the microbial population recovered 9 wk after the treatment completion. However, it is important to note that the polar by-products are more bioassimilable and potentially more toxic than the non-polar hydrocarbons which may pose potential risk to the receptors (Stavridis, 2008).

While efforts have been devoted to diesel ozonation, there are still only a few studies that have investigated the influences of multiple environmental factors such as soil grain size, water content, soil pH, composition of the oil source fractions (precursor compounds) and the formation of aldehydes and carboxylic acid on the ozonation efficiency. It is also commonly acknowledged that PAHs are more reactive than aliphatic hydrocarbons to ozonation (Wang et al., 2013). However the hydroxylation of the petroleum hydrocarbon fractions based on the Equivalent Carbon (EC) numbers, especially the aliphatic fractions, has not yet been investigated. Instead, only the total petroleum hydrocarbons were considered which could be misleading when defining the remediation target end-point. The formation of by-products such as aldehydes and carboxylic acid, especially formaldehyde, has also been largely ignored.

The main objectives of this study were to (1) investigate the relationship between the O<sub>3</sub> dose and the hydroxylation rate of the different n-alkane fractions; (2) characterise the influence of grain size and water content on the n-alkanes hydroxylation; and (3) quantify the formation of aldehydes and carboxylic acid and the implication for remediation end-points.

## 2. Materials and methods

### 2.1. Sample preparation

Quartz sand was used in this study as an alternative to natural sand, as it often contains metal oxidants and natural organic carbon which may have increased the complexity of multi-factor interactions on ozonation. The coarse sand (0.5–2.0 mm), medium sand (0.25–0.5 mm) and fine sand (0.15–0.25 mm) fractions were obtained by passing the quartz sand through a series of mesh sieves. The diesel fuel used in this study was obtained from commercial fuel (density: 0.81 g mL<sup>-1</sup>; sulphur content: <3.5 × 10<sup>-4</sup>; viscosity at 20 °C: 2.43 cP). The n-alkanes of the diesel fuel were divided based on their EC numbers, which is either related to the BP normalized to the BP of the n-alkanes, or determined via the retention time of the compounds in gas chromatography columns (Twerdok, 1999). This approach has been recognised as a more appropriate differentiation technique than the actual carbon number of the chemical (Brown et al., 1999; Twerdok, 1999). The n-alkanes consisted of EC<sub>10–12</sub>, EC<sub>12–16</sub>, and EC<sub>16–35</sub> and their relative mass contribution were 1%, 4% and 4%, respectively. Water was added to the quartz sand and then diesel was added to create a range of moisture levels of 6%, 12% and 18%. The diesel spiked contaminated sand was prepared by adding 2.5 mL diesel to 80 g quartz sand in a 2 L glass beaker. The sand and water was manually mixed using a glass rod at least 5 min. This process was repeated for five times and thus a total of 10 g of diesel was spiked to 400 g quartz sand. In order to mimic the weathering process, the samples were stored in darkness at room temperature for 3 wk before use.

### 2.2. Experimental setup

The ozonation reactor was made from a glass column (0.02 m id × 0.25 m length) with a perforated Teflon plate at the bottom. O<sub>3</sub> was generated by an Anseros ozone generator COM-AD-01-OEM. O<sub>3</sub> in the gas phase was monitored via ultra violet absorbance at 253.7 nm using an Anseros ozone monitor GM-6000-OEM. In order to prevent the samples from drying out in the column, a phosphoric acid with pH of 2 was used to humidify O<sub>3</sub>. This process also helped to prevent the slow decomposition of O<sub>3</sub> when the pH dropped below 4 during the experiments (Hsu and Masten, 1997).

The diesel spiked quartz sands (15 g) was packed in the soil column, which was then exposed to O<sub>3</sub> at concentration levels 10, 30 and 50 mg L<sup>-1</sup>, respectively. The O<sub>3</sub> flux was controlled at 180 mL min<sup>-1</sup> and samples (4 g) were collected for alkanes analysis at 20, 40 min and thereafter 1, 3, 5, 7, 9 and 20 h, respectively. All experiments were carried out in triplicate at 20 ± 2 °C.

### 2.3. Sample extraction and analysis

The concentration of alkanes in the quartz sands was determined by solvent extraction previously described by Risdon et al. (2008). The concentration of aldehydes in the quartz sands were analysed after O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride derivatisation (Dai et al., 2008). The carboxylic acid in the quartz sands were prepared by N,O-Bis(trimethylsilyl)trifluoroacetamide: trimethylchlorosilane (99:1) derivatisation (Dai et al., 2008). Alkanes, aldehydes and carboxylic acid were identified and quantified by GC-MS. Details of the sample preparation and GC-MS operation conditions are available in the [Supplementary Material \(SM\)](#).

After ozonation, the pH of the samples was measured in a 1:2.5 soil water solution by pH meter.

### 2.4. Statistical analysis

Principal Component Analysis (PCA) using Primer version 6 and Pearson Correlation analysis using SPSS version 20 were conducted to investigate the statistical significance of the relationships between the formation of aldehydes and carboxylic acid, the chemical by-products of ozonation, the degradation of n-alkane fractions and time.

## 3. Results and discussion

### 3.1. Effect of ozone concentration on n-alkanes removal

The highest n-alkanes removal rate was observed when the O<sub>3</sub> concentration was 30 mg L<sup>-1</sup>. The increase in O<sub>3</sub> concentration to 50 mg L<sup>-1</sup> did not result in higher ozonation efficiency (Fig. 1). Therefore the influence of the particle grain size and water content was investigated using an O<sub>3</sub> concentration of 30 mg L<sup>-1</sup>. After 20 h of ozonation, the EC<sub>10–12</sub>, EC<sub>12–16</sub> fractions were almost completely hydroxylated while 22% of the initial EC<sub>16–35</sub> fraction was remaining (Fig. 1). This result suggests that the relatively low molecular weight of the alkanes are hydroxylated more easily than the heavier alkanes, which is consistent with Goi et al. (2006). Fig. 1 also shows that the removal rate of total alkanes during the first 9 h was 8 times higher than that in the last 11 h when the sands were exposed to 30 mg L<sup>-1</sup> O<sub>3</sub>. The low degradation rate at the end of ozonation was expected because of the lack of alkanes, the increased consumption of O<sub>3</sub> from the resulted by-products, and the decreased contact area between O<sub>3</sub> and the residual alkanes due to the increased amount of by-products. Additionally, the

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