

Ozone treatment of PAH contaminated soils: Operating variables effect

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ABSTRACT

A three-level full factorial design has been conducted to assess the influence of gas flow-rate, ozone concentration and reaction time on the remediation of soil contaminated with four PAHs (namely acenaphthene, phenanthrene, anthracene and fluoranthene). Under the operating conditions investigated, reaction time and ozone concentration seem to exert a slight positive effect, whereas gas flow-rate does not affect the process efficiency. Average conversions (related to non-ozonated samples) are in the proximity of 50, 70, 60 and 100% for acenaphthene, phenanthrene, anthracene and fluoranthene, respectively. A high conversion percentage is obtained in the first minutes of the process. Ozone decomposition on soil surface can be modelled by its reactions with easily oxidizable organic matter, recalcitrant ozonation intermediates and inorganic active sites.

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1. Introduction

The contamination of subsurface soil all over the world is a serious and challenging problem, particularly in developed countries or highly industrialized areas. For many subsurface geological settings, conventional treatment methods, such as pump-and-treat technology, venting, biological remediation, etc. can be costly and/or inefficient. Emerging *in situ* or *on site* subsurface soil treatment technologies may provide effective, low-cost alternatives. According to the Interstate Technology & Regulatory Council [1], “*in situ* oxidation systems offer two main advantages, i.e. large volumes of waste material are not usually generated and treatment is commonly implemented over a much shorter time frame. Both of these advantages often result in savings on material, monitoring, and maintenance”.

Amongst the technologies that can be applied “*in situ*” or “*on site*”, soil ozone application is catalogued as one of the most promising systems. Molecular ozone (or its primary decomposition radical, HO•) steadily reacts with a high number of organic and inorganic contaminants. Injected ozone gas might directly attack target compounds, or alternatively, it can decompose over metal oxides in the surface soil to generate the non-specific hydroxyl radical which in turn can oxidise/mineralize adjacent sorbed pollutants. The efficiency of ozone in soil treatment has been assessed either at laboratory level [2–5] and field scale [6,7].

Nevertheless, the ozonation efficacy of contaminated soils, *a priori*, does depend on several factors, for instance soil nature (pres-

ence of moisture, organic content, structure, etc.), contaminant speciation and some operating variables such as ozone dose, contact time, flow-rate, etc. Commonly, the effect of operating variables has been visualized by following the “one at a time” change in any of the potential influencing parameters. However this working methodology can lead to erroneous conclusions, especially when assessing the removal of barely soluble pollutants, as it is the case of polycyclic aromatic hydrocarbons (PAHs). Monitorization of these compounds, even when special care is assumed, can involve some analytical errors leading to wrong hypothesis [8]. Following an experimental design cannot minimize the errors associated with PAH manipulation but might help to derive actual trends in operating variables influence. The subject of this manuscript is, therefore, to complete a 27-run experimental design by taking into consideration three main parameters in soil ozonation processes: gas flow-rate, contact time and, ozone concentration. Four PAHs have been selected as model compounds, namely acenaphthene, phenanthrene, anthracene and fluoranthene. In terms of molecular weight, these PAHs cover a range that can be catalogued from light to medium. Toxicity of adsorbed contaminants is a matter of controversy. Thus, some authors claim that strongly adsorbed contaminants do not represent an environmental risk since these substances are not considered as bioavailable. Hence, Sverdrup and co-workers [9] showed that only PAHs with k_{OW} values below 5.2 (i.e. light-medium PAHs) were toxic towards the soil-dwelling springtail *Folsomia fimetaria*. According to this statement, it was decided to consider the four PAHs previously mentioned although a more extensive study should be conducted with heavier PAHs after the conclusions drawn from this work.

In the second part of this investigation a dynamic study of the ozone decomposition process is completed.

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2. Experimental

The soil used was taken from an area in the University of Badajoz (South West of Spain). It was crushed in a mortar (particle size was below 0.5 mm of diameter) and dried for 5 days at 383 K. Moisture elimination and crushing were carried out to obtain a more homogeneous material for further artificial contamination. Although both operations (drying and crushing) are normally applied at laboratory scale, some changes in soil properties may occur. However, this study is aimed at revealing the trends obtained in the soil ozonation process under different operating conditions. No real contaminated soil is used and, accordingly, this manuscript is not a description of the stages that should be followed to scale up the ozone remediation of soils. Results presented in this work should be considered in a relative way rather than in absolute values (for instance the important statement is the positive or negative influence of a specified variable rather than the actual percentage of contaminant removal, the latter value is only applicable to this particular case). Other properties measured after soil conditioning are: pH 6.8 (water soil ratio 2.5), conductivity 201 μS (water soil ratio 2.5), weight loss at 500 °C of 3.23% and oxidability with dichromate of 5.2% (measured as organic carbon).

Artificial contamination of the soil was carried out by mixing an acetone solution of acenaphthene (Ac), phenanthrene (Ph), anthracene (An) and fluoranthene (Fl) (Sigma–Aldrich) with the soil to get a theoretical load of 10 mg kg⁻¹ in each PAH after acetone natural evaporation. To allow some extent in sequestration and natural humidification of soil, the latter was stored in the dark in an air opened container. Soil was used after no less than three months from artificial contamination.

Ozonation experiments were carried out in semi-batch mode. The reactor utilized, basically consisted of a column vessel equipped with a porous plate to bubble an oxygen–ozone gas mixture (see Fig. 1). Temperature was not controlled although its value was always in the interval 393 ± 2 K. Gas flow-rate, ozone inlet concentration and reaction time were varied in the interval 30–50 L h⁻¹, 10–30 ppm and 2–15 min, respectively. Ozone was generated in an Erwin Sander 301.7 laboratory ozone generator capable of producing

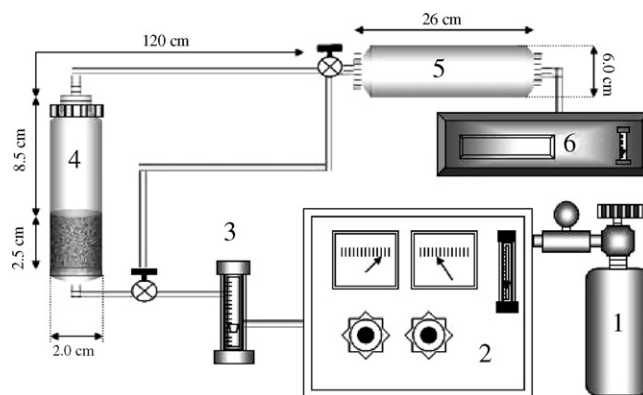


Fig. 1. Experimental setup: 1, oxygen cylinder; 2, ozone generator; 3, flowmeter; 4, reactor; 5, security trap; 6, ozone analyser.

up to 12 g h⁻¹ of ozone from pure oxygen. Once the ozonator was stabilized, O₃ was fed to the reactor containing 10 g of the PAH-contaminated soil. Fig. 1 shows a scheme of the experimental setup used.

Ozone in the gas phase was monitored by means of an Anseros Ozomat ozone analyser. The analysis is based on the absorbance at 254 nm.

Soxhlet extraction of PAHs was completed with 60 mL of HPLC grade methanol for 6 h. Other solvents such as dichloromethane, ethanol, acetone, etc. did not extract PAHs to a higher extent.

Dissolved PAHs were analysed by injecting 25 μL of a sample into a HPLC system (Rheodyne injector, 1050 Hewlett Packard pump, 1046A, Alltech Prevail C18 column (4.6 mm × 150 mm), Hewlett Packard fluorescence detector, Chromjet Spectra Physics integrator) in isocratic mode using an acetonitrile–water mixture 70:30 (v/v) as mobile phase. To assess the reproducibility of results, only the central point of the experimental design was conducted in triplicate. Leverage points are determined by the statistical analysis of results.

Table 1
3³ full factorial design for PAH contaminated soil ozonation.

Flow-rate (L h ⁻¹)	C _{O₃inlet} (ppm)	Time (min)	Ac (%)	Ph (%)	An (%)	F (%)
30.0	10.0	2.0	23.1	60.2	51.0	100.0
30.0	10.0	5.0	38.0	63.8	54.5	100.0
30.0	10.0	15.0	44.9	61.2	57.4	100.0
30.0	20.0	2.0	50.0	52.4	52.0	100.0
30.0	20.0	5.0	55.3	62.0	57.9	100.0
30.0	20.0	15.0	65.0	69.2	61.3	100.0
30.0	30.0	2.0	51.8	70.7	61.3	100.0
30.0	30.0	5.0	59.1	80.0	54.0	100.0
30.0	30.0	15.0	70.0	87.0	64.0	100.0
40.0	10.0	2.0	19.9	54.2	45.0	86.3
40.0	10.0	5.0	30.7	65.6	59.1	82.6
40.0	10.0	15.0	51.7	75.8	62.8	100.0
40.0	20.0	2.0	50.9	60.0	48.9	100.0
40.0	20.0	5.0	47.9	69.7	65.0	100.0
40.0	20.0	15.0	68.1	78.4	65.5	100.0
40.0	30.0	2.0	45.0	71.6	60.3	100.0
40.0	30.0	5.0	51.6	74.7	61.2	100.0
40.0	30.0	15.0	63.2	88.7	66.0	100.0
50.0	10.0	2.0	25.0	37.0	47.0	100.0
50.0	10.0	5.0	56.2	49.0	56.8	100.0
50.0	10.0	15.0	50.5	68.0	67.3	100.0
50.0	20.0	2.0	44.8	65.7	58.4	100.0
50.0	20.0	5.0	46.0	69.1	64.7	100.0
50.0	20.0	15.0	48.9	76.3	72.0	100.0
50.0	30.0	2.0	57.2	78.5	62.9	100.0
50.0	30.0	5.0	58.6	63.5	70.0	100.0
50.0	30.0	15.0	70.0	89.3	84.8	100.0
Average ± (95% confidence)			49.8 ± 5.4	68.2 ± 4.6	60.4 ± 3.1	98.8 ± 1.6

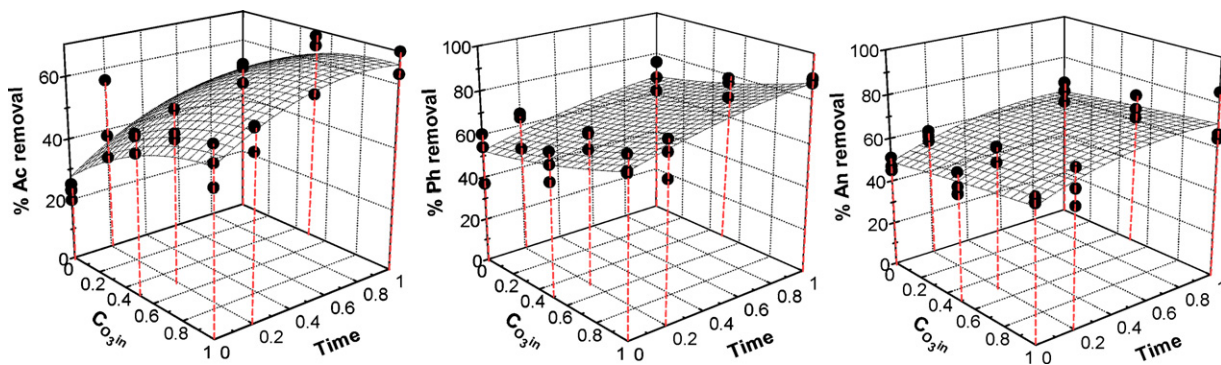
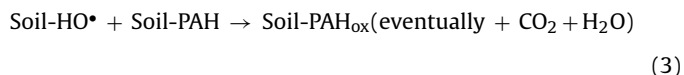


Fig. 2. Ozonation of PAHs adsorbed on soils. Percentage of elimination regarding Soxhlet extraction (coded units used).

3. Results and discussion

3.1. Influence of operating variables: experimental design

To infer the trends that the parameters: ozone flow-rate, ozone concentration and contact time exerted in the removal of PAHs from the soil matrix, a three-level full factorial design with three factors has been considered. Table 1 and Fig. 2 depict the results obtained in terms of individual PAH elimination regarding the amount of Soxhlet-extracted PAH before ozonation. As observed, average values of 50, 70 and 60% of acenaphthene, phenanthrene and anthracene, respectively, are removed under the different experimental conditions used. Additionally, almost all extractable fluoranthene is eliminated from soil. The reactivity of these PAHs towards ozone in methanol [8], follows the order: An > A > Ph > Fl, contrary to results found in this work. Thus, PAHs might present a different reactivity with ozone depending on their physical state (adsorbed or dissolved) and solvent nature. Different authors claim an increasing reactivity of PAHs as the number of rings also increases [5] while others defend a decreasing reactivity as the molecular weight of PAHs increases [4,10]. It seems that, *a priori*, several factors should be taken into account. For instance, gaseous ozone might directly react with sorbed contaminants according to reaction (1). Alternatively, ozone could decompose on soil active surfaces (i.e. metal oxides, soil organic matter, etc.) to generate hydroxyl radicals according to Eq. (2) being the latter species responsible of PAHs degradation. In this case the reactivity should be governed by the radical reaction (3).



Additionally some authors [3] have affirmed that sorbed hydrophobic PAHs (as it is the case of anthracene) react more slowly than would be expected from results found in aqueous matrixes.

In any case, it should be noticed that results displayed in Table 1 are calculated based on the amount of individual PAH extracted by the Soxhlet procedure. Absolute values can be calculated by considering that approximately 45, 70, 18 and 100% of acenaphthene, phenanthrene, anthracene and fluoranthene were extracted in control analysis, respectively.

If absolute values are taken into consideration, anthracene is the most recalcitrant PAHs towards ozonation, however, as stated before, a significant fraction of this compound is not extracted under vigorous extraction conditions, and likely adsorbed anthracene does not show a high ecotoxicity level.

Direct effects of investigated variables are displayed in Fig. 3. Although far away from linearity, with the exception of gas flow-rate, a general positive influence of considered factors on PAHs removal is envisaged. Nevertheless, this positive effect is not excessively pronounced. It seems that under the conditions investigated, the amount of ozone fed is in large excess so no significant differences between runs can be expected. Thus, outlet ozone gas immediately reaches steady-state conditions suggesting that PAHs oxidation proceeds at the beginning of the ozone feeding. Such behaviour has also been reported for the elimination of phenanthrene under less drastic conditions (flow-rate 3 L h^{-1}) than those used in this work [2] or phenanthrene and benzo(a)pyrene in slurry reactors [11].

An attempt to model the influence of the three factors investigated was conducted by assuming a second order model plus interactions (interaction means that the effect of one factor depends on the levels of one or more other factors). Only significant terms have been considered. Table 2 shows the results obtained while Fig. 4 depicts the direct comparison between calculated and experimental PAH removal. Calculated *p* values for the coefficients (not shown) suggest that the factors containing ozone concentration and reaction time are the most influencing terms in the regression, in fact the linear term corresponding to gas flow-rate, although kept

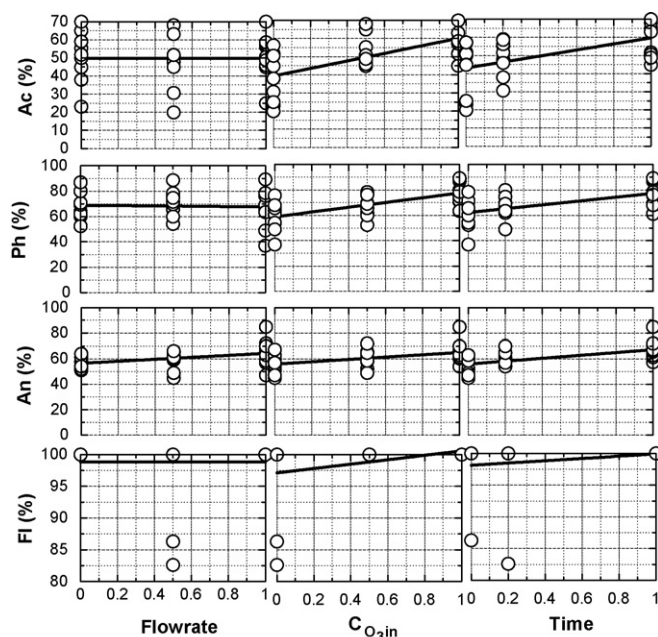


Fig. 3. Ozonation of PAHs adsorbed on soils. Percentage of elimination regarding Soxhlet extraction. Direct effects of investigated variables (coded units used).

Table 2
Second order + interaction model for the removal of PAHs from soil by ozone (variables in coded units).

	β_0	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_8	β_9	β_{10}	β_{11}
% Ac removal = $\beta_0 + \beta_1 \times C_{O_3 \text{ inlet}} + \beta_2 \times t + \beta_3 \times Q^2 + \beta_4 \times Q \times C_{O_3 \text{ inlet}} + \beta_5 \times C_{O_3 \text{ inlet}} \times C_{O_3 \text{ inlet}} + \beta_6 \times C_{O_3 \text{ inlet}} \times t + \beta_7 \times t^2 + \beta_8 \times Q \times C_{O_3 \text{ inlet}} \times t^2 + \beta_9 \times C_{O_3 \text{ inlet}} \times t^2 + \beta_{10} \times Q$	21.6	82.2	79.4	12.5	-68.3	-50.1	-74.9	-56.1	61.3	65.0	-3.9	-2.6
% Ph removal = $\beta_0 + \beta_1 \times C_{O_3 \text{ inlet}} + \beta_2 \times t + \beta_3 \times Q^2 + \beta_4 \times Q \times C_{O_3 \text{ inlet}} + \beta_5 \times C_{O_3 \text{ inlet}} \times C_{O_3 \text{ inlet}} + \beta_6 \times C_{O_3 \text{ inlet}} \times t + \beta_7 \times t^2 + \beta_8 \times Q \times C_{O_3 \text{ inlet}} \times t^2 + \beta_9 \times C_{O_3 \text{ inlet}} \times t^2 + \beta_{10} \times Q$	60.1	-29.3	33.0	-16.6	83.5	38.1	-29.6	-61.6	-33.4	25.0	16.7	-2.6
% An removal = $\beta_0 + \beta_1 \times C_{O_3 \text{ inlet}} + \beta_2 \times t + \beta_3 \times Q^2 + \beta_4 \times Q \times C_{O_3 \text{ inlet}} + \beta_5 \times C_{O_3 \text{ inlet}} \times C_{O_3 \text{ inlet}} + \beta_6 \times C_{O_3 \text{ inlet}} \times t + \beta_7 \times t^2 + \beta_8 \times Q \times C_{O_3 \text{ inlet}} \times t^2 + \beta_9 \times C_{O_3 \text{ inlet}} \times t^2 + \beta_{10} \times Q$	48.2	9.4	50.2	11.1	-48.6	-40.7	10.6	43.9	-2.0			

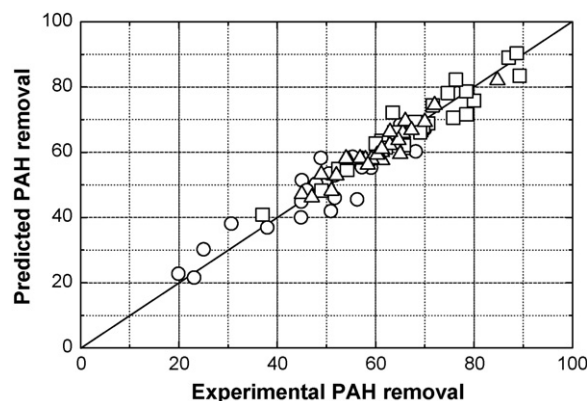


Fig. 4. Ozonation of PAHs adsorbed on soils. Modelling of elimination percentage regarding Soxhlet extraction. (○) acenaphthene; (□) phenanthrene; (△) anthracene.

in the model, shows a p value above 0.05, indicating the negligible role played by this variable.

A summary of the regressions obtained is shown in Table 3. The parameters displayed include the coefficient of determination (R^2) or fraction of total variability explained by the model. As observed, regardless of the considered PAH, around 90% of data can be well explained by the model. Moreover, R^2 adjusted values are slightly lower than the coefficient of determination, indicating that the terms included in the model are significant enough to make acceptable predictions. The Durbin Watson autocorrelation test suggests no time dependency of errors. Additionally, the low values of F_{signif} confirm the significance of the models used.

3.2. Dynamic study

As stated previously (see Fig. 3), direct variable effects are not excessively pronounced. It seems that the decontamination process is too fast to accurately follow the influence of variables. Accordingly it was decided to conduct a dynamic study by using less severe conditions. For instance the gas flow-rate was lowered to values in the range 7.5–15 L h⁻¹ and ozone inlet concentrations in the interval 6–25 mg L⁻¹.

3.2.1. Ozone decomposition dynamics

A key factor in the technology considered is the decomposition of ozone through reactions with soil organic and inorganic material, accordingly, in preliminary experiments the capacity of the soil to decompose ozone was investigated. Thus, non-contaminated soil was ozonated and the ozone outlet concentration monitored. Fig. 5 shows the results obtained. As inferred from this figure, three different regions can be visualized. In the first region (initial period) it seems that ozone is not decomposed by soil, however, this behaviour is just due to the experimental setup conformation.

Table 3
ANOVA calculations for the second order + interaction model in the removal of PAHs from soil by ozone.

	Ac	Ph	An
R^2	0.868	0.906	0.914
R^2 adjusted	0.785	0.837	0.875
Standard error	6.218	4.893	2.946
Durbin-Watson d	2.417	2.615	2.619
Sum of squares (regression)	4065.3	3455.4	1651.6
Sum of squares (residual)	618.55	359.07	156.18
Mean square (regression)	406.53	314.13	206.45
Mean square (residual)	38.659	23.938	8.677
F	10.52	13.12	23.79
F_{signif}	2.8×10^{-5}	8.9×10^{-6}	4.6×10^{-8}

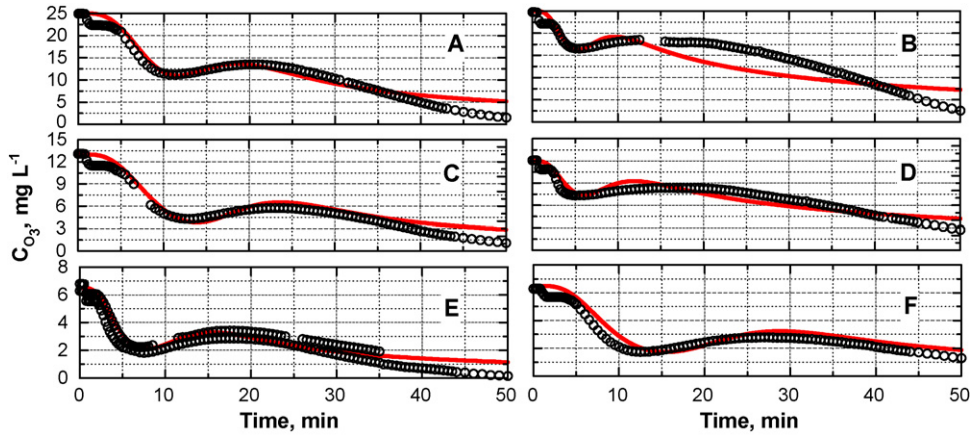
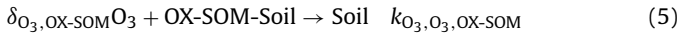
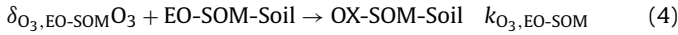


Fig. 5. Ozonation of soils. Evolution of outlet ozone concentration. Lines correspond to model results. (A) $Q = 7.5 \text{ L h}^{-1}$, $C_{O_3 \text{ inlet}} = 25 \text{ ppm}$; (B) $Q = 15 \text{ L h}^{-1}$, $C_{O_3 \text{ inlet}} = 25 \text{ ppm}$; (C) $Q = 7.5 \text{ L h}^{-1}$, $C_{O_3 \text{ inlet}} = 13 \text{ ppm}$; (D) $Q = 15 \text{ L h}^{-1}$, $C_{O_3 \text{ inlet}} = 13 \text{ ppm}$; (E) $Q = 15 \text{ L h}^{-1}$, $C_{O_3 \text{ inlet}} = 6.5 \text{ ppm}$; (F) $Q = 7.5 \text{ L h}^{-1}$, $C_{O_3 \text{ inlet}} = 6.5 \text{ ppm}$.

Thus, the detected ozone corresponds to the ozone accumulated in the pipes and trap of the installation before introducing O_3 through the soil bed (see Fig. 1). Although not appreciated in the figure, in this stage, easily oxidizable soil organic matter (EO-SOM) is oxidized by ozone to likely more refractory substances (OX-SOM). In the second period, the oxidized soil organic matter (OX-SOM) is slowly attacked by ozone. As a consequence, ozone outlet concentration slightly increases. In the final period, OX-SOM is gradually being removed leading to the appearance of likely active inorganic sites capable of efficiently decompose ozone [12]:



where $\delta_{O_3,EO-SOM}$, $\delta_{O_3,OX-SOM}$ and $\delta_{O_3,Soil}$ are the apparent stoichiometric coefficients of the proposed mechanism. In an attempt to model the process, the following considerations were assumed:

- The gas flow through the reactor was considered to be plug-flow, both through the soil bed and the empty space above it.
- Soil was a non-porous material so diffusion limitations are not applicable.
- Plug-flow is also assumed in system pipes.
- Flow through the trap was modelled by a series of perfectly mixed tanks in series.

Accordingly, the following expressions can be applied:
Ozone concentration through the soil bed:

$$\frac{\partial C_{O_3}}{\partial t} = v_{BED} \frac{\partial C_{O_3}}{\partial z} - k_{O_3,EO-SOM} \frac{\rho}{\varepsilon} C_{O_3} C_{EO-SOM} - k_{O_3,OX-SOM} \frac{\rho}{\varepsilon} C_{O_3} C_{OX-SOM} - k_{O_3,Soil} \frac{\rho}{\varepsilon} C_{O_3} C_{Soil} \quad (7)$$

with boundary conditions:

$$\begin{cases} C_{O_3} = C_{O_3 \text{ inlet}} & z = 0, \forall t \\ C_{O_3} = 0 & t = 0, \forall z > 0 \end{cases}$$

where ε stands for porosity, ρ is the soil bed bulk density and v_{BED} is the gas velocity according to $v_{BED} = \text{gas flow-rate}/(\text{sectional area} \times \varepsilon)$. Units used in this expression were mg L^{-1} for ozone concentration, seconds for time, cm s^{-1} for velocity and mass percentage for the rest of concentrations.

Easily oxidizable soil organic matter:

$$\frac{\partial C_{EO-SOM}}{\partial t} = - \frac{k_{O_3,EO-SOM}}{\delta_{O_3,EO-SOM}} C_{O_3} C_{EO-SOM} \quad (8)$$

Oxidized soil organic matter:

$$\frac{\partial C_{OX-SOM}}{\partial t} = \frac{k_{O_3,EO-SOM}}{\delta_{O_3,EO-SOM}} C_{O_3} C_{EO-SOM} - \frac{k_{O_3,OX-SOM}}{\delta_{O_3,OX-SOM}} C_{O_3} C_{OX-SOM} \quad (9)$$

Soil active sites:

$$\frac{\partial C_{Soil}}{\partial t} = \frac{k_{O_3,OX-SOM}}{\delta_{O_3,OX-SOM}} C_{O_3} C_{OX-SOM} \quad (10)$$

Ozone concentration through the pipes:

$$\frac{\partial C_{O_3}}{\partial t} = \nu \frac{\partial C_{O_3}}{\partial z} \quad (11)$$

where ν is the gas velocity according to $\nu = \text{gas flow-rate}/\text{sectional area}$ (cm s^{-1}).

Ozone concentration through the trap:

$$\left\{ V \frac{\partial C_{O_3}}{\partial t} = Q [C_{O_3 \text{ IN}} - C_{O_3}] \right\}_i \quad (12)$$

where i denotes the i th tank in series considered, Q the gas flow-rate ($\text{cm}^3 \text{ s}^{-1}$) and V is the trap volume (cm^3).

The set of PDE (7–12) was numerically solved by the finite difference method implemented in EXCEL. Fig. 5 illustrates the outlet ozone curves calculated by optimization

Table 4
Kinetic modelling of ozone decomposition in soils. Adjusted parameters.

$Q (\text{L h}^{-1})$	$C_{O_3 \text{ inlet}} (\text{mg L}^{-1})$	$k_{O_3,EO-SOM} (\rho/\varepsilon)$	$k_{O_3,OX-SOM} (\rho/\varepsilon)$	$k_{O_3,Soil} (\rho/\varepsilon)$	$k_{O_3,EO-SOM}/\delta_{O_3,EO-SOM}$	$k_{O_3,OX-SOM}/\delta_{O_3,OX-SOM}$
7.5	25	35	5×10^{-3}	140	8.75×10^{-2}	3.33×10^{-4}
7.5	13	30	1×10^{-2}	140	7.50×10^{-2}	6.66×10^{-4}
7.5	6.5	25	2×10^{-2}	140	6.25×10^{-2}	1.33×10^{-3}
15	25	30	5×10^{-3}	140	7.50×10^{-2}	3.33×10^{-4}
15	13	25	1×10^{-2}	140	6.25×10^{-2}	6.66×10^{-4}
15	6.5	35	5×10^{-2}	140	8.75×10^{-2}	3.33×10^{-3}

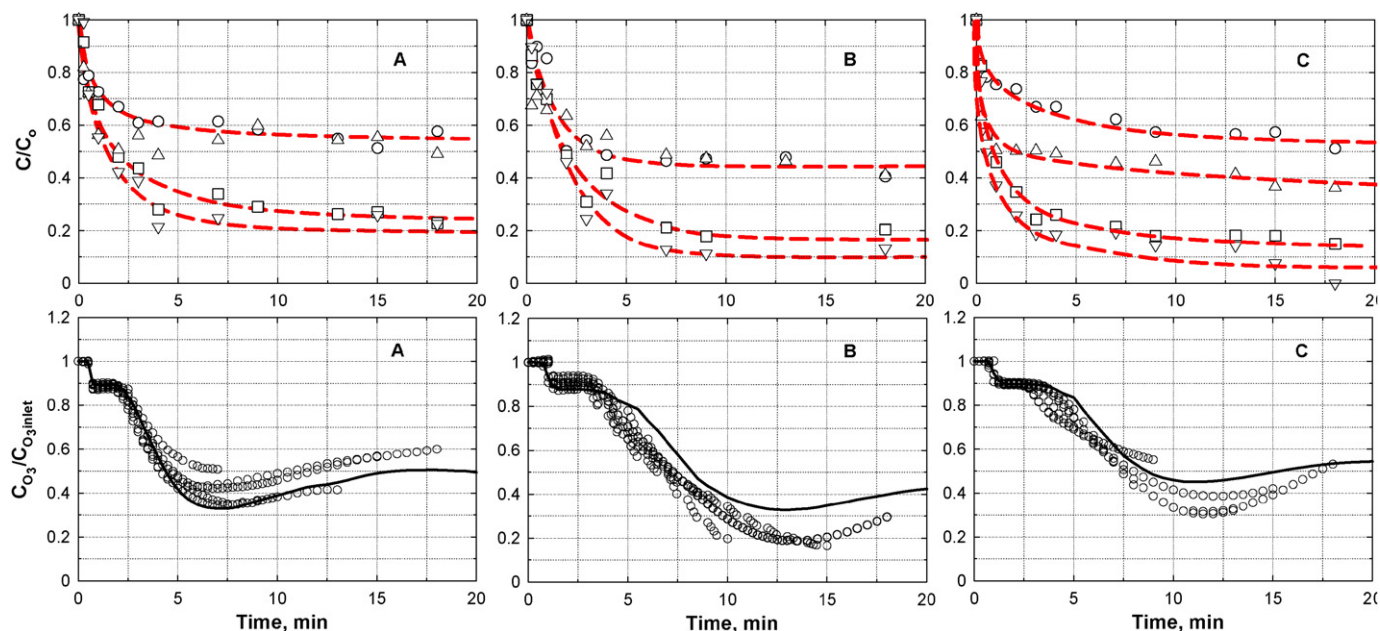


Fig. 6. Ozonation of PAHs adsorbed on soils. Normalized elimination percentage regarding Soxhlet extraction versus time. (○) acenaphthene; (□) phenanthrene; (△) anthracene; (▽) fluoranthene. (A) $Q=15 \text{ Lh}^{-1}$, $C_{O_3 \text{ inlet}} = 6.5 \text{ ppm}$. (B) $Q=7.5 \text{ Lh}^{-1}$, $C_{O_3 \text{ inlet}} = 13 \text{ ppm}$. (C) $Q=7.5 \text{ Lh}^{-1}$, $C_{O_3 \text{ inlet}} = 25 \text{ ppm}$. Bottom figures show outlet ozone concentration (lines correspond to blank runs).

of the unknown parameters: $k_{O_3,EO-SOM}(\rho/\varepsilon)$, $k_{O_3,OX-SOM}(\rho/\varepsilon)$, $k_{O_3,SOIL}(\rho/\varepsilon)$, $k_{O_3,EO-SOM}/\delta_{O_3,EO-SOM}$ and $k_{O_3,OX-SOM}/\delta_{O_3,OX-SOM}$. The optimization process was carried out by means of the SOLVER adding included in EXCEL. The procedure was to adjust the five parameters for a single experiment, thereafter, with the values obtained the other runs were simulated trying to modify the lowest number of parameters initially obtained.

The optimization results led to split the trap into 5 perfectly mixed tanks of equal volume. Fig. 5 shows the model curves obtained. Table 4 depicts the adjustable parameter values. As observed from Fig. 5, the model acceptably simulates the ozone decomposition profiles with minor changes in the parameters with the exception of the rate constants related to oxidation of oxidized SOM. It should be pointed out that the model is quite sensitive to changes in porosity, organic content and/or gas flow-rate. From Table 4 it is inferred that $k_{O_3,OX-SOM}(\rho/\varepsilon)$ decreases as the ozone concentration fed to the reactor increases. Obviously, the model used is an oversimplification of the actual mechanism taking place, however it can be hypothesized that as the ozone concentration is raised, the amount of intermediate oxidized material formed is likely lowered leading, therefore, to the generation of final products that do not consume ozone.

3.2.2. PAHs depletion dynamics

Next, three series of experiments were repeated under similar conditions than those used in blank experiments but different reaction times. Accordingly, the evolution of PAHs with time was obtained for the three series. Some important issues are derived from Fig. 6:

- By comparison of the run conducted with 6 ppm of inlet ozone and the rest of experiments completed at higher concentrations, a slight positive effect of ozone concentration can be envisaged.
- Experiments carried out with 13 and 25 ppm of ozone inlet concentration are similar (with the exception of the abnormally low depletion rate of acenaphthene for the 25 ppm run). It seems that ozone concentration does not significantly influence the process above a minimum value.

- Reactivity of PAHs is confirmed under the less stringent operating conditions, $Ac \approx An < Ph < F$.
- The highest fraction of PAHs removal is obtained in the first 5 min after ozone injection. From an economic point of view, time for ozone feeding can be significantly shortened.
- Broadly speaking, the presence of PAHs involves ozone outlet profiles similar to those obtained in the absence of the hydrocarbons. PAHs used in this work can be catalogued as easily oxidizable organic matter.

4. Conclusions

From this work, the following conclusions apply:

- Gas ozone can be used as a soil remediation process when the latter is contaminated with PAHs.
- Reactivity of PAHs might differ in soils and liquid solvents. Nature and soil composition are key factors influencing reactivity.
- Ozone concentration exerts a slight positive effect, difficult to appreciate when high ozone concentrations are used. Flow-rate seems to have no influence on the process efficiency.
- A high percentage of PAHs removal occurs at the beginning of the process
- Ozone decomposition on soil surface can be modelled by assuming a series of reactions involving easily oxidizable material, recalcitrant oxidized intermediates and inorganic active sites.

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