



Identification of persulfate oxidation products of polycyclic aromatic hydrocarbon during remediation of contaminated soil



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HIGHLIGHTS

- Oxy-PAHs such as 9-H-fluoren-9-one existed in coking contaminated soil.
- A variety of oxy-PAHs were produced during persulfate oxidation of PAHs, including 1-H-phenalen-1-one.
- With reaction time extended, oxy-PAHs generated during oxidation were removed.
- Persulfate remediation of PAH-contaminated soil carries low environmental risks.

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ABSTRACT

The extent of PAH transformation, the formation and transformation of reaction byproducts during persulfate oxidation of polycyclic aromatic hydrocarbons (PAHs) in coking plant soil was investigated. Pre-oxidation analyses indicated that oxygen-containing PAHs (oxy-PAHs) existed in the soil. Oxy-PAHs including 1H-phenalen-1-one, 9H-fluoren-9-one, and 1,8-naphthalic anhydride were also produced during persulfate oxidation of PAHs. Concentration of 1,8-naphthalic anhydride at 4 h in thermally activated (50 °C) persulfate oxidation (TAPO) treatment increased 12.7 times relative to the oxidant-free control. Additionally, the oxy-PAHs originally present and those generated during oxidation can be oxidized by unactivated or thermally activated persulfate oxidation. For example, 9H-fluoren-9-one concentration decreased 99% at 4 h in TAPO treatment relative to the control. Thermally activated persulfate resulted in greater oxy-PAHs removal than unactivated persulfate. Overall, both unactivated and thermally activated persulfate oxidation of PAH-contaminated soil reduced PAH mass, and oxidized most of the reaction byproducts. Consequently, this treatment process could limit environmental risk related to the parent compound and associated reaction byproducts.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants, which have carcinogenic, teratogenic, and mutagenic effects [1,2]. PAHs are commonly found in industrial contaminated sites [3,4], can easily adsorb to soil organic matter [5], and some PAHs are resistant to biodegradation [6]. There are 16 of the PAHs identified by the US EPA that are classified as priority-pollutants based on toxicity, potential for human exposure, and frequency of occurrence at hazardous waste

sites [7] (Table S1, Supporting information). Of these PAHs, the US EPA considers seven, i.e., benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene, as probable human carcinogens [8]. As shown in Table S1, generally, PAHs considered to be carcinogenic have higher molecular weight, i.e., number of aromatic rings, and lower vapor pressure and solubility compared to the non-carcinogenic PAHs [9]. The physical-chemical characteristics of PAHs also contribute directly to their recalcitrant nature in the environment [10]. Given the abundance of PAH hazardous waste sites, and the characteristics of PAHs, the development of an efficient, low cost remedial technology with limited risk is an international priority.

In situ chemical oxidation (ISCO) has emerged as an effective remediation technology for the treatment of PAH-contaminated soil and groundwater [11–14]. ISCO involves rapid reactions and

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may therefore lead to shorter cleanup times than other remediation technologies. PAHs were the target pollutants in 6.7% of 223 ISCO remediation cases conducted by Environmental Security Technology Certification Program (ESTCP) in America [15].

Chemical oxidation reaction intermediates and byproducts during PAH oxidation are a key issue in determining the success and overall risk of remediation technology selection. During oxidation of PAHs by Fenton's reagent, ozone, and permanganate, the intermediate products can include quinones, ketones, naphthalic anhydride, aldehydes, carboxylic acids, and short chain compounds [16–21]. Some of the oxygen-containing PAHs (oxy-PAHs) produced during PAH oxidation have toxic and mutagenic effects. Among the bioactive chemical compounds isolated from various environmental samples, oxy-PAHs have the highest mutagenicity [22,23]. The 9,10-anthraquinone and phenanthrene-9,10-dione have been shown to inhibit the growth of duckweed and luminescent bacteria [24,25]. Benzo[a]pyrene quinone and phenanthrene quinone show mutagenic activity [26] requiring no metabolic activation to react with DNA, while some require activation to electrophilic metabolites to exert their mutagenic or carcinogenic effects [27]. Phenanthrenequinone, the major photooxidation product of phenanthrene, was more toxic than phenanthrene for both *Photobacterium phosphoreum* and *Lemna gibba* [24]. Anthraquinone, the photooxidation product of anthracene, and subsequent photooxidation products, were more toxic than the parent compound. 2-hydroxyanthraquinone, which was not subject to further photooxidation, was the most toxic compound [25].

Persulfate can remain active in soils and aquifer material for weeks to months, is not significantly influenced by the pH, and can oxidize a wide range of environmental contaminants [15,28]. Previously, it was confirmed that activated persulfate effectively oxidizes PAHs in contaminated soils [29]. Removal efficiencies were affected by methods of activation (i.e., base, chelated iron, thermal), among which, thermally activation effect was found to be most effective [29]. Few studies have assessed the generation of intermediates and their toxicity from persulfate oxidation of PAHs [30].

In this study, PAH-contaminated soil is treated with persulfate under two conditions, unactivated and thermally activated (50 °C). Here, the objectives were to (1) identify and semi-quantitatively analyze oxy-PAHs in soil before and after persulfate oxidation, (2) assess the extent to which oxy-PAHs are generated and/or removed during the oxidation process, and (3) evaluate the mechanism of generation of oxy-PAHs during persulfate oxidation.

2. Materials and methods

2.1. Experimental design

The PAH-contaminated soil was collected from a coking plant site and mixed fully to ensure uniformity and representativeness. The major pollutants in the soil were PAHs (total concentration 367.1 mg/kg) (Table 1). The soil was freeze-dried (freeze dryer, LGJ-10D, China), mixed thoroughly, passed through a 20-mesh sieve, and kept at –60 °C (freezer, Haier DW-86388V, China).

The experiment was composed of three separate treatment conditions including reaction periods of 4 and 24 h, and each treatment was performed in triplicate. The three treatment conditions were (1) deionized water (DW), (2) non-activated persulfate oxidation (NAPO) (i.e., room temperature 20–22 °C) and (3) thermally activated (50 °C) persulfate oxidation (TAPO). For each treatment, soil (5 g) was mixed with deionized water (7.5 mL) or persulfate solution (1 M, 7.5 mL). The treatments were maintained at room temperature or in a 50 °C water bath and samples were collected at 4- or 24-h reaction time.

After the reaction period, concentrated sulfuric acid (five drops) was added to each treatment reactor for termination of the reaction. The soil particles were allowed to settle for 2 h and separated from the supernatant. The concentrations of PAHs in the soil and solution were determined and the oxidation products were identified followed by a semi-quantitative analysis.

2.2. Sample analysis

2.2.1. Liquid phase PAHs and product analysis

A sample of the liquid phase of the soil slurry (10 mL) was filtered through a 0.45 μm organic filter membrane followed by liquid–liquid extraction with an equal volume of dichloromethane (10 mL; triplicate sequential extractions; mixing oscillation at 250 rpm for 30 min). The extracts were combined in a flask, concentrated to 0.5 mL by rotary evaporation (rotary evaporator, RE-52AA, China), and adjusted to constant volume (1 mL) with *n*-hexane.

To separate liquid phase PAHs and oxy-PAHs, a chromatography column was loaded with cotton, silica gel (5 g), anhydrous sodium sulfate (1 g), and *n*-hexane (20 mL). After the *n*-hexane soaked into the silica gel, samples were loaded and eluted sequentially with *n*-hexane (5 mL), *n*-hexyl/dichloromethane (15 mL), and dichloromethane (30 mL). The second (PAHs) and third (oxy-PAHs) parts of the eluent were collected separately, concentrated by rotary evaporation, and adjusted to constant volume with *n*-hexane (1 mL).

To determine liquid phase PAHs and oxy-PAHs [18], an internal standard (125 μL) was added to each sample and determination of PAHs and oxy-PAHs was performed by gas chromatography–mass spectrometry (GC 7890A-MS 5975C, USA). The products of oxidation reactions were identified by full scan and the major type of each product was determined using the ChemStation library. A selected ion scan was used for quantitative analysis of PAHs and semi-quantitative analysis of oxy-PAHs according to their relative response area compared with the internal standard.

2.2.2. Soil PAHs and product analysis

Soil (2 g) was mixed and ground with anhydrous sodium sulfate (20 g). The ground soil mixture (1 g) was extracted using an 11-mL stainless steel extraction system, sequentially filled from the bottom to the top with a cellulose filter, silica gel (4 g), a cellulose filter, soil sample (1 g), a recovery indicator (50 μL), anhydrous sodium sulfate, and a cellulose filter. PAHs and oxy-PAHs were extracted from the soil by accelerated solvent extraction (ASE 350, USA) using *n*-hexane and *n*-hexane/dichloromethane (1:1), respectively. The extraction conditions were as follows: 140 MPa, 150 °C; two static extraction cycles (5 min each); including one volume for rinsing; and a purging time of 60 s. The extract was concentrated by rotary evaporation and adjusted to constant volume (1 mL) with *n*-hexane.

To determine soil PAHs and oxy-PAHs, samples were diluted and an internal standard (125 μL) was added to the samples prior to GC–MS analysis (full scan). The reaction products were identified using the ChemStation library. A selected ion scan was used for a semi-quantitative analysis according to their relative response area compared with the internal standard.

2.3. Statistical analysis

Statistical analysis of data was performed using the SAS 8.1 statistical software, including significance tests of difference and multiple comparisons.

Table 1
PAH concentrations and mass reduction involving control and chemical oxidation treatment conditions. Oxidant-free control reactors involved de-ionized water (DW); non-activated persulfate oxidation at ambient temperature (20–22 °C) (NAPO); and thermally activated persulfate oxidation (50 °C) (TAPO).

Treatments	[PAH] _{SOIL} ^a (mg/kg)		[PAH] _{AQUEOUS} ^a (mg/L)		[PAH] _{TOTAL} ^b (mg)			PAH mass reduction ^c (%)	
	LMW	HMW	LMW ^d	HMW ^d	LMW	HMW		LMW	HMW
DW (4 h, 20–22 °C)	306.2 ± 66.1a*	292.2 ± 64.6	13.9 ± 1.7	1.8 ± 0.2A*	1.816 ± 0.244	0.002 ± 0.001	1.54 1.475 0.070		
DW (24 h, 20–22 °C)	293.4 ± 220.3a*	281.2 ± 212.6	12.2 ± 7.7	0.1 ± 0.1C*	0.129 ± 0.012	0.001 ± 0.000	1.47 1.407 0.061	4.5	4.6 12.2
Persulfate (4 h, 20–22 °C)	62.3 ± 6.2b*	58.0 ± 5.6	4.3 ± 0.8	0.2 ± 0.0C*	0.186 ± 0.026	0.002 ± 0.001	0.31 0.291 0.022	79.9	80.2 69.0
Persulfate (24 h, 20–22 °C)	57.1 ± 5.2b*	52.0 ± 4.1	5.2 ± 1.3	0.6 ± 0.1B*	0.625 ± 0.144	0.001 ± 0.000	0.29 0.265 0.026	81.2	82.1 62.6
Persulfate (4 h, 50 °C)	49.9 ± 14.0b*	45.3 ± 12.5	4.6 ± 1.9	0.3 ± 0.1C*	0.260 ± 0.100	0.003 ± 0.001	0.25 0.228 0.023	83.8	84.5 66.9
Persulfate (24 h, 50 °C)	40.7 ± 17.0b*	33.4 ± 15.2	7.3 ± 1.8	0.1 ± 0.0C*	0.044 ± 0.017	0.002 ± 0.001	0.20 0.167 0.037	87.0	88.7 47.5

^a Capital and lowercase letters, respectively, indicate significant differences in [PAH]_{SOIL} and [PAH]_{AQUEOUS} between treatments; values with the same letters are not statistically significantly different ($p > 0.05$).

^b [PAH]_{TOTAL} (mg) = M_{SOIL} × [PAH]_{SOIL} + V_{AQUEOUS} × [PAH]_{AQUEOUS}, where M_{SOIL} = 5 g and V_{AQUEOUS} = 7.5 mL.

^c PAH mass reduction (%) = $\frac{([PAH]_{TOTAL,INITIAL} - [PAH]_{TOTAL,FINAL})}{([PAH]_{TOTAL,INITIAL})} \times 100$.

^d The values of [LMW PAHs]_{AQUEOUS} and [HMW PAHs]_{AQUEOUS} are with more significant figures, for they are too small.

3. Results and discussion

3.1. PAHs removal in persulfate oxidation treatments

The changes in PAH concentration and reaction system equilibrium of each treatment are shown in Table 1. The amount of total PAHs decreased according to the following order: TAPO > NAPO > DW. The overall mass removal of total PAHs (i.e., aqueous+soil PAH) by non-activated persulfate reached 81.2% and thermal activation of persulfate further improved the removal of PAHs to 87.0%. Ferrarese et al. reported that the removal of PAHs from sediments with catechol-chelated ferrous ion activated persulfate was 76–88% [11]. Nadim et al. reported that the removal of seven PAHs (phenanthrene, pyrene, fluoranthene, benzo(a)anthracene, benzo(a)pyrene, chrysene, and benzo(a)fluoranthene) in soil by EDTA-chelated iron activated persulfate reached 75–100% [32]. Clearly, activated persulfate can oxidize PAHs in contaminated soils, however, PAHs that are aged in soil can affect the efficiency of oxidation. It was reported that magnetite-activated persulfate effectively removed PAHs from an artificially contaminated sandy soil (removal rate 70–80%), however, the efficiency of PAH removal was limited in a naturally contaminated soil representing aged conditions [30].

In all treatments, only a small amount of PAHs were soluble and measured in solution, with the majority of PAHs adsorbed to the soil. In the DW treatment, [PAH]_{SOIL} at 24 h showed no significant difference relative to that at 4 h, while [PAH]_{AQUEOUS} declined from 4 to 24 h contact time. Addition of the DW resulted in a new dynamic system, and the [PAH]_{AQUEOUS} was relatively high at 4 h due to the time dependency of equilibrium sorption. Then over time, PAHs were removed from the aqueous phase through adsorption and partitioning mechanisms. Approximately 24 h was considered sufficient time for equilibrium of non-ionic organic compounds to be adsorbed [31]. In comparison with DW treatments, [PAH]_{SOIL} declined significantly at 4 h and 24 h in the NAPO treatments. After TAPO treatment for 4 h and 24 h, [PAH]_{SOIL} declined significantly compared with the DW but did not result in a significant difference compared with the NAPO treatment. From 4 to 24 h, [PAH]_{SOIL} decreased in both NAPO and TAPO treatment due to the oxidative decomposition. Although [PAH]_{AQUEOUS} differed slightly between treatments and changed slightly with time, it did not affect the total PAHs removal for the small proportion of [PAH]_{AQUEOUS}.

The 24 h pre- and post-oxidation concentrations of the 16 PAHs in soil are illustrated in Fig. 1. Similar data for the 4 h results are illustrated in the Supporting information (Fig. S1). It can be seen that before and after the oxidation treatment, soil PAHs were dominated by low-molecular-weight (LMW, 2–3-ring) PAHs whose

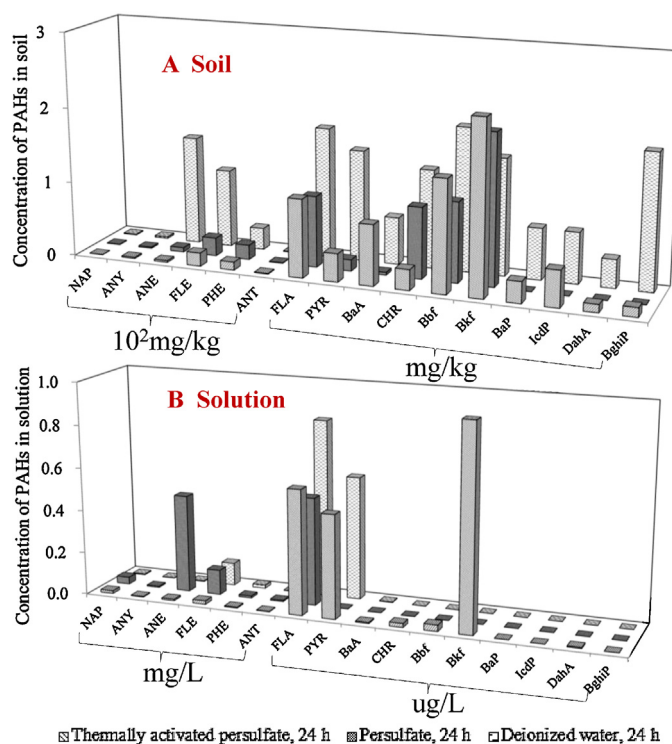


Fig. 1. Compositions of 16 PAHs in soil and solution after 24 h DW, NAPO and TAPO treatment. The “mg/kg” and “10² mg/kg”, the “mg/L” and “μg/L” indicate that they are on different scales. The full name of each abbreviation are as follows: “NAP”: naphthalene, “ANY”: acenaphthylene, “ANE”: acenaphthene, “FLE”: fluorene, “PHE”: phenanthrene, “ANT”: anthracene, “FLA”: fluoranthene, “PYR”: pyrene, “BaA”: benzo(a)anthracene, “CHR”: chrysene, “BbF”: benzo(b)fluoranthene, “BkF”: benzo(k)fluoranthene, “BaP”: benzo(a)pyrene, “IcdP”: indeno(1,2,3-cd)pyrene, “DahA”: dibenzo(a,h)anthracene, “BghiP”: benzo(g,h,i)perylene.

concentrations were 1–2 orders of magnitude higher than the high-molecular-weight (HMW, 4–6-ring) PAHs present. PAHs in original contaminated soil were dominated by LMW PAHs such as acenaphthene, fluorene, and phenanthrene (>93% of total PAHs). After unactivated and thermally activated persulfate oxidative treatment, soil acenaphthene, fluorene, and phenanthrene concentrations decreased significantly. The concentrations of all HMW PAHs also declined in both NAPO and TAPO treatments compared with those in DW treatment. The composition of 16 PAHs in solution before and after the oxidative treatments are also shown in Figs. 1 (24 h) and S1 (4 h) (Supporting information). Compared with DW-4 treatment, LMW and HMW PAHs in solution declined significantly in the NAPO and TAPO treatments (except

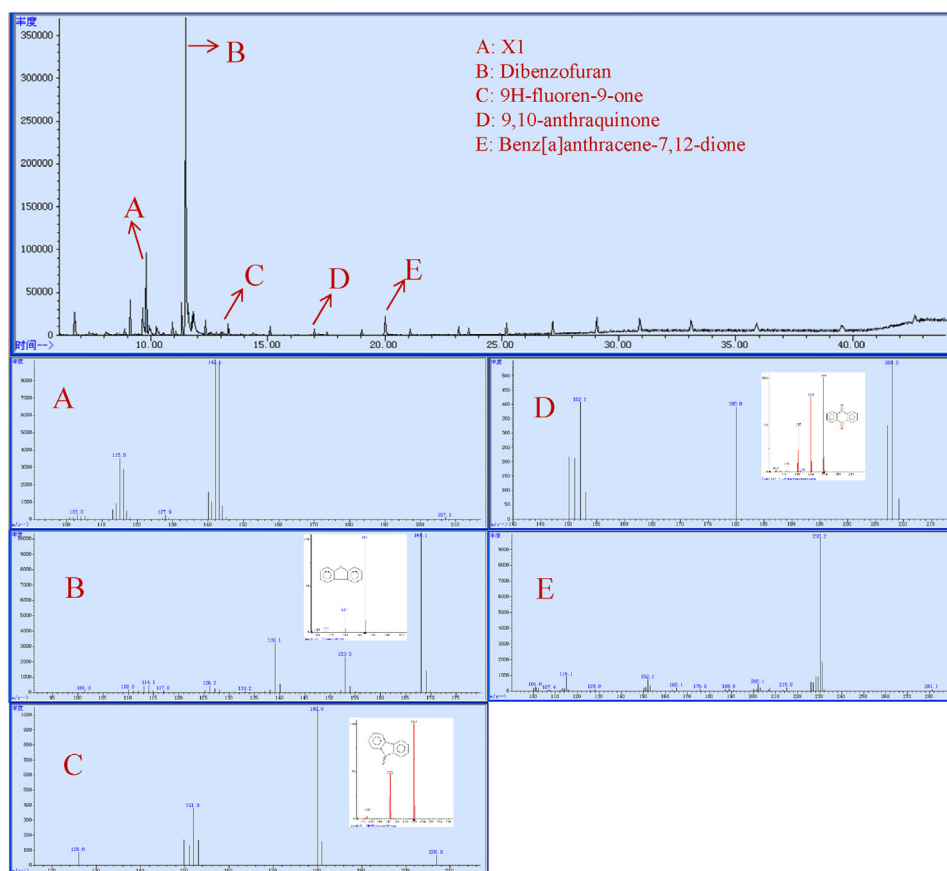


Fig. 2. GC–MS full scan of the products in solution after non-activated persulfate oxidation of PAH-contaminated soil.

benzo(k)fluoranthene). In general, the more benzene rings contained in PAHs, the more difficult is to oxidize [33]. Fenton's reagent has a relatively low efficiency for the removal of HMW PAHs [12,18], while its removal rates of anthracene, benzo[a]pyrene, and pyrene are relatively high compared with other PAHs with similar structure [34]. Liao et al. demonstrated that potassium permanganate has a lower efficiency for the removal of HMW PAHs compared with LMW PAHs [14]. In addition, magnetite activated persulfate has certain selectivity for the removal of PAHs with a relatively low removal rate of HMW PAHs [30]. However, Kulik et al. reported that ozone has better efficiency for the removal of HMW PAHs than LMW PAHs [35]. It is noteworthy that in this study, thermally activated persulfate showed good removal of HMW PAHs as well as LMW PAHs.

3.2. Product identification and semi-quantification during persulfate oxidation of PAHs

Figs. 2 and 3 indicate the oxy-PAHs in solution and soil, respectively, in NAPO treatment identified using GC–MS. Similar results were obtained in TAPO treatment (data not included). A few oxy-PAHs were present in the solution in NAPO and TAPO treatments, including dibenzofuran, 9H-fluoren-9-one, 9,10-anthraquinone, benz[a]anthracene-7,12-dione, and X₁ (an unidentified product) (Fig. 2). The products of PAH oxidation in the soil were relatively more diverse (Fig. 3) including naphthalene 1-(2-hydroxypropyl), 1H-phenalen-1-one, dibenzofuran, 1(2H)-acenaphthylene, 9H-fluoren-9-one, 9,10-anthraquinone, and 1,8-naphthalic anhydride, as well as Y₁ and Y₂ (unidentified products). Among these compounds, dibenzofuran, 9H-fluoren-9-one, 9,10-anthraquinone, naphthalene 1-(2-hydroxypropyl), 1H-phenalen-1-one, 1(2H)-acenaphthylene, and 1,8-naphthalic anhydride were identified

according to their characteristic ions in the ChemStation library. The MS spectra of each compound identified and the matching oxy-PAHs are provided (Figs. 2 and 3). In addition, benz[a]anthracene-7,12-dione was identified by comparing with the existing substance in terms of *m/z* [36].

The relative concentrations of oxy-PAHs in soil before and after different treatments are shown in Table 2. The original soil from the coking plant also contained oxy-PAHs such as 9H-fluoren-9-one, 1H-phenalen-1-one, 1(2H)-acenaphthylene, 1,8-naphthalic anhydride and others. The probable cause of this is that they were present in the raw coking material or were formed as a result of natural attenuation during the long-term aging process. Given the time dependency and relative concentrations of oxy-PAHs under the different oxidative treatment conditions, increased concentrations of naphthalene 1-(2-hydroxypropyl), Y₁, 1H-phenalen-1-one, dibenzofuran, 9H-fluoren-9-one, Y₂ and 1,8-naphthalic anhydride indicated that these oxy-PAHs are produced as a result of the oxidation of PAHs. Further, given the relative GC/MS responses to oxy-PAHs in NAPO and TAPO treatments, all oxy-PAHs showed declining concentrations with time indicating that all oxy-PAHs can be transformed by persulfate oxidation.

Using the DW-4 as baseline, the concentration of naphthalene 1-(2-hydroxypropyl) at 4 h in the NAPO treatment and TAPO treatment increased by factors of 1.9 and 28.7, respectively. Similarly, relative to the DW-4 baseline, the concentration of 1,8-naphthalic anhydride at 4 h in the NAPO treatment and TAPO treatment increased by factors of 1.9 and 12.7, respectively. Similar increasing trends were measured at 24 h for naphthalene 1-(2-hydroxypropyl) and 1,8-naphthalic anhydride compared with the DW-24 baseline. Accumulation of naphthalene 1-(2-hydroxypropyl) and 1,8-naphthalic anhydride suggested that these compounds were produced in large quantities resulting from

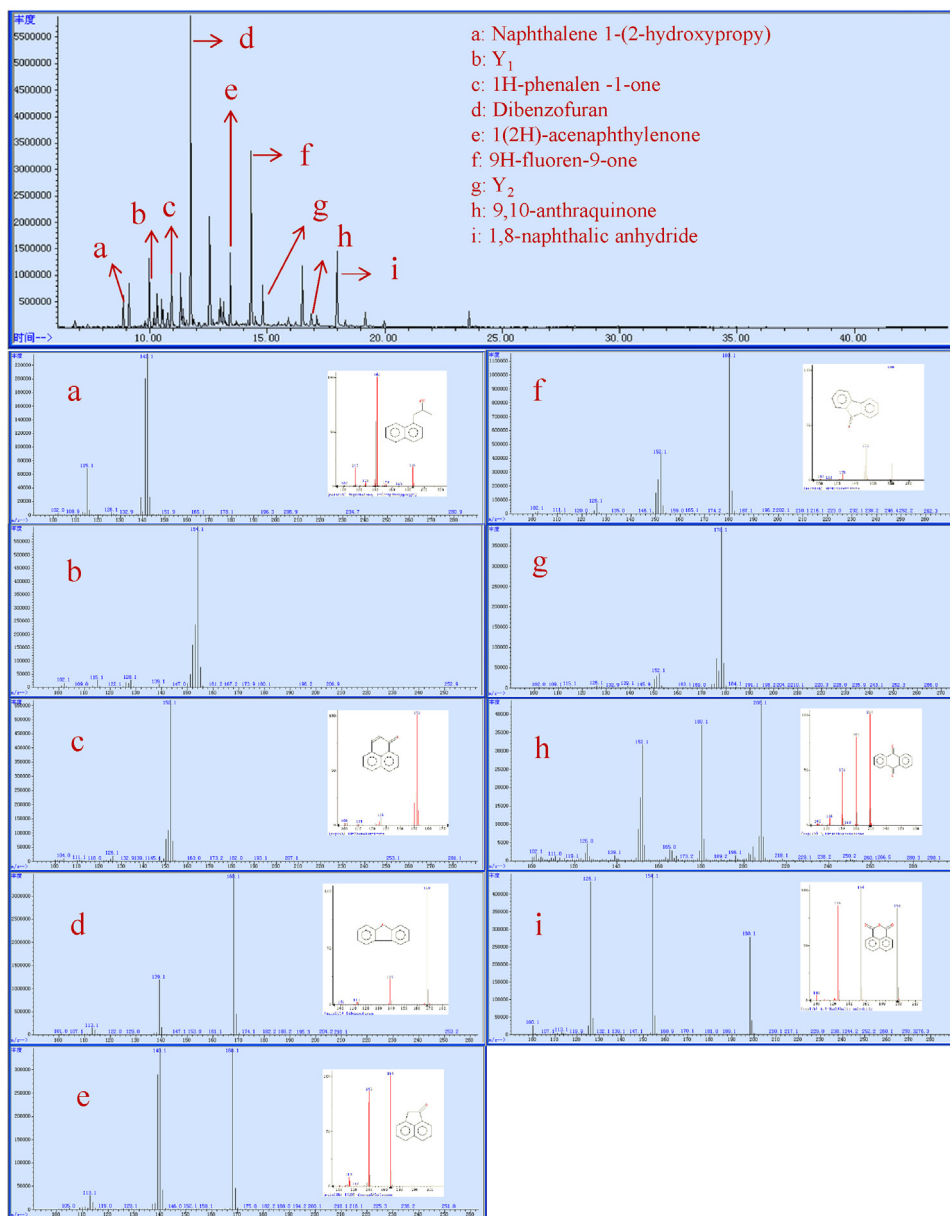


Fig. 3. GC-MS full scan of the products in soil after non-activated persulfate oxidation of PAH-contaminated soil.

the oxidation and decomposition of the parent PAHs during the oxidation process. Further, contrasting the concentrations of naphthalene 1-(2-hydroxypropyl) at 24 h to that at 4 h in TAPO treatment and 1,8-naphthalic anhydride at 24 h to those at 4 h in NAPO and TAPO treatments, decline in concentrations was measured indicating that the oxidation products could also be transformed by persulfate or thermally activated persulfate.

All other oxy-PAHs including unidentified compounds Y₁ and Y₂ decreased in concentration when comparing NAPO-4 and TAPO-4 with DW-4, and NAPO-24 and TAPO-24 with DW-24 (except one outlier 1H-phenalen-1-one). For example, the 9H-fluoren-9-one concentration decreased 99% at 4 h both in the NAPO and TAPO treatment. 9,10-anthraquinone concentrations decreased 80% and 85%, respectively, at 24 h in the NAPO and TAPO treatment. These changes suggest that the oxy-PAH compounds present initially can be oxidized and transformed by persulfate and thermally activated persulfate. Comparing the oxy-PAHs at 24 h to those at 4 h in NAPO and TAPO treatments, concentration of dibenzofuran, 9H-fluoren-9-one, Y₁ and Y₂ showed increasing tendency, which means they

were simultaneously produced during the oxidation process and could not be completely degraded in 24 h. Additional oxidative treatment would be required to further reduce the concentrations of this compound.

Concentrations of naphthalene 1-(2-hydroxypropyl) and 1,8-naphthalic anhydride in TAPO treatment were higher than those in NAPO treatment. That thermally activated persulfate increased the removal of PAHs and insufficient persulfate was added to fully oxidize the products may account for this result, which need further investigation. The relative concentration of some oxy-PAHs including 1H-phenalen-1-one, 1(2H)-acenaphthylene, 9H-fluoren-9-one, 9,10-anthraquinone, Y₁ and Y₂ in TAPO treatment were lower than that in NAPO treatment (except one outlier 1(2H)-acenaphthylene). Overall, given these results, thermal activation can promote persulfate oxidation of PAHs and most of the oxy-PAHs.

Compared with DW-4, concentrations of oxy-PAHs in solution decreased or stayed the same in NAPO-4 (Table 3). Conversely, compared with NAPO-4, concentrations of oxy-PAHs increased in

Table 2
Retention time and relative response area of oxy-PAH products in soil after different treatments.

Oxy-PAHs	Retention time	Characteristic ions	Relative response area (A/AI) ^a					
			Deionized water, 4 h	Deionized water, 24 h	Persulfate, 4 h	Persulfate, 24 h	Thermally activated persulfate, 4 h	Thermally activated persulfate, 24 h
<i>Oxy-PAHs increased after NAPO and TAPO for 24 h</i>								
Naphthalene 1-(2-hydroxypropyl)	8.67	142.1, 115.1	0.71 ± 0.01	0.38 ± 0.37	2.09 ± 1.34	5.32 ± 2.77	21.08 ± 5.51	20.00 ± 4.9
1,8-Naphthalic anhydride	17.97	126.1, 154.1, 198.1	0.83 ± 0.58	0.24 ± 0.09	2.99 ± 3.19	0.86 ± 0.26	11.37 ± 5.48	1.33 ± 0.45
<i>Oxy-PAHs decreased after NAPO and TAPO for 24 h</i>								
Y ₁	9.99	154.1, 128	0.48 ± 0.02	0.25 ± 0.14	0.11 ± 0.03	0.13 ± 0.04	0.08 ± 0.01	0.08 ± 0.03
1H-phenalen-1-one	10.94	152.1, 126, 111	0.74 ± 0.09	0.50 ± 0.40	0.91 ± 1.47	0.11 ± 0.02	0.12 ± 0.01	0.04 ± 0.01
Dibenzofuran	11.82	168.1, 139.1, 153.0	4.56 ± 1.81	2.56 ± 1.82	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.43 ± 0.06
1(2H)-acenaphthyleneone	13.44	140.1, 168.1, 113.1	0.53 ± 0.19	0.31 ± 0.23	0.30 ± 0.36	0.09 ± 0.02	0.12 ± 0.01	0.11 ± 0.01
9H-fluorene-9-one	14.33	180.1, 152.1, 126	45.78 ± 48.39	32.64 ± 39.41	0.63 ± 4.65	1.24 ± 1.08	0.53 ± 0.16	0.97 ± 0.09
Y ₂	14.92	178.1, 152.1	3.57 ± 1.33	2.86 ± 1.84	0.35 ± 0.45	0.39 ± 0.05	0.32 ± 0.02	0.03 ± 0.01
9,10-Anthraquinone	17.12	208, 180, 152	9.01 ± 9.00	0.46 ± 0.31	0.12 ± 0.05	0.09 ± 0.03	0.07 ± 0.02	0.07 ± 0.01

^a A/AI: the area response of each compound relative to an internal standard.

Table 3
Retention time and relative response area of oxy-PAH products in solution after different treatments.

Products	Retention time	Characteristic ions	Relative response area (A/AI) ^a					
			Deionized water, 4 h	Deionized water, 24 h	Persulfate, 4 h	Persulfate, 24 h	Thermally activated persulfate, 4 h	Thermally activated persulfate, 24 h
X ₁	9.65	143.1, 115.1	0.66 ± 0.56	0.37 ± 0.18	0.02 ± 0.00	0.38 ± 0.20	0.30 ± 0.02	0 ± 0.00
Dibenzofuran	11.82	168.1, 139.1, 153.0	0.85 ± 0.09	0.98 ± 0.62	0.05 ± 0.04	0.47 ± 0.04	0.88 ± 0.02	0.04 ± 0.04
9H-Fluorene-9-one	14.38	180.1, 152.0, 126	2.24 ± 0.74	1.58 ± 0.97	1.47 ± 0.13	1.50 ± 0.13	2.44 ± 0.56	0.23 ± 0.13
9,10-Anthraquinone	17.23	180.1, 208, 152	0.10 ± 0.02	0.12 ± 0.02	0.11 ± 0.01	0.04 ± 0.01	0.13 ± 0.01	0.12 ± 0.12
Benz[a]anthracene-7,12-dione	20.03	230.2, 202, 115	0.50 ± 0.11	0.48 ± 0.04	0.43 ± 0.05	0.38 ± 0.05	0.46 ± 0.02	0.66 ± 0.25

^a A/AI: the area response of each compound relative to an internal standard.

Table 4
Comparison of PAH oxidation products with different oxidants.

PAH compound	Oxidant				
	Fenton's reagent	Potassium permanganate	Ozone	Hydroxyl radical	Persulfate ^j
Acenaphthylene	1,8-Naphthalic anhydride ^{c,d}		Secondary ozonide ^e	10-C ring-opened product and dialdehydes ^e	1,8-Naphthalic anhydride ^j
Acenaphthene		Acenaphthenone ^a			1(2H)-acenaphthylene ^j
Fluorene	9-Fluorenone or hydroxyl-9-fluorenone ^{c,d}	9-Fluorenone ^a			9H-fluoren-9-one ^j
Phenanthrene		Biphenyl dicarboxylic acid ^a			
Anthracene	9,10-Anthraquinone ^{c,d}	9,10-Anthraquinone ^a			9,10-Anthraquinone ^j
Pyrene			Phenanthrene dialdehyde, biphenyl tetracarboxylic aldehyde, benzene carboxylic acid (1,2-phthalic acid), diisooctyl, long-chain aliphatic compounds ⁱ		
			14 types, aldehyde- and carboxylic acid-substituted phenanthrene and biphenyl-type oxidation products ^g		
Benzanthracene	Benz[a]anthracene-7,12-dione ^(b,c,d)		15 types, quinone or hydroxyl functional groups, phenyl/naphthyl group-containing products ^f		Benz[a]anthracene-7,12-dione ^j
Benzopyrene	Benzo[a]pyrene-1,6-dione, benzo[a]pyrene-3,6-dione, benzo[a]pyrene-6,12-dione ^c	Benzo[a]pyrene 1,6-quinone ^b			
Others	1-Methyl anthraquinone, 2-methyl-anthraquinone, 1-indanone and hydroxy-9-fluorenone isomer ^d				Naphthalene 1-(2-hydroxypropyl), dibenzofuran, 1H-phenalen-1-one ^j

^a Forsey et al. (2010) [21].

^b Lee and Hosomi (2001) [36].

^c Lee et al. (2001) [16].

^d Lundstedt et al. (2006) [18].

^e Reisen and Arey (2002) [17].

^f Yao et al. (1998) [37].

^g Yao et al. (1998) [39].

^h Zang et al. (2007) [19].

ⁱ Zeng et al. (2000) [38].

^j The present study.

TAPO-4. This suggests that significant oxy-PAH mass may have been transformed but that the sorbed phase still support dissolved phase concentrations. Assuming the DW-24 as baseline, all of the compounds either declined or stayed the same in NAPO and TAPO treatments at 24 h except for Benz[a]anthracene-7,12-dione. The persistence of some oxy-PAH in the aqueous phase was attributed to incomplete oxidation of the oxy-PAH and sufficient time for equilibrium conditions to occur (i.e., desorption).

3.3. The formation mechanism and potential risk of PAH oxidation products

Chemical oxidation of PAHs generally involves two mechanisms, hydrogen substitution and addition reaction of the double bond, namely, side-chain oxidation and ring oxidation. The products of PAHs oxidation by various oxidants are different for the differences in reaction mechanism (Table 4). Fenton's reagent can produce hydroxyl radicals, and PAHs oxidation products by this mechanism are often a mixture of ketones, quinones, aldehydes, and carboxylic acids [16]. Potassium permanganate mainly oxidizes PAHs through permanganate ions, generating three types of products,

i.e., aromatic ketones, aromatic quinones, and aliphatic or aromatic acids [21]. Ozone achieves PAH oxidation through direct ozone oxidation and formation of hydroxyl radicals which also oxidize PAHs as discussed for Fenton's mechanism above. This mechanism generates a large number of short-chain alkanes, aldehydes, and monocarboxylic acids [20,37–39]. While in this study, oxy-PAHs generated in the unactivated and thermally activated persulfate oxidation process included naphthalene 1-(2-hydroxypropyl), 1H-phenalen-1-one, dibenzofuran, 1(2H)-acenaphthylene, 9H-fluoren-9-one, 9,10-anthraquinone, 1,8-naphthalic anhydride and benz[a]anthracene-7,12-dione. Persulfate oxidation acts through persulfate ions, whereas the TAPO system acts through persulfate ions and hydroxyl radicals simultaneously.

Several studies have revealed the mechanism of oxidation and products formation for different PAHs. Wheland indicated that the electron distribution of PAHs determines the energy for separation of π electrons from the system and thus determines the position with the strongest reactivity in the molecule [40]. To date, a number of reaction indices have been used for characterizing the positioning energy, one of which is Dewar's reactivity number (Nu). The smaller the value of Nu , the smaller the activation energy, and

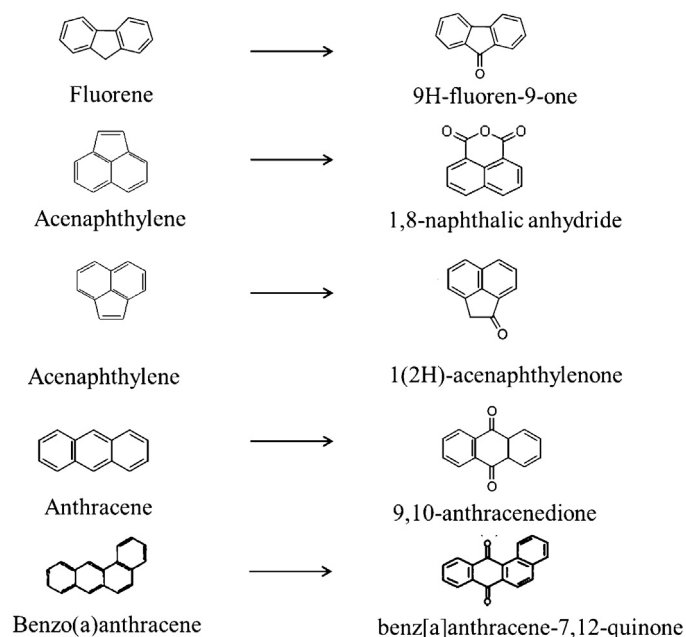


Fig. 4. Oxy-PAHs and their corresponding parent PAHs derived from the information in this study.

the greater the addition reaction rate. For anthracene the reaction activity is higher at positions 9 and 10, and is highest at positions 7 and 12 for benzo(a)anthracene [41]. Lee et al. indicated that the site of Fenton oxidation is related to the front-end electron density in PAHs [16]. That with the maximal frontier electron density (f_r) serves as the site of Fenton oxidation, such as the positions 7 and 12 for benzo[a]anthracene, the position 1 for acenaphthylene, and the positions 9 and 10 for anthracene. Clar's aromatic sextet theory has been used to predict the capability of potassium permanganate for PAHs oxidation [21]. The principles are to form the maximum number of benzene rings, so anthracene has the characteristics of double bonds and the sextet can be present in any ring structure, which also means that oxidation is easy to occur at positions 9 and 10.

As shown in Fig. 4, 9,10-anthraquinone, benz[a]anthracene-7,12-dione and 1(2H)-acenaphthyleneone in the persulfate oxidation system may be the products of anthracene, benzo[a]anthracene and acenaphthylene, respectively. The speculation is consistent with theoretical methods of Nu positioning energy, front-end electronic density, and Clar's aromatic sextet theory as described above. Taking into account the products of PAH oxidation by other oxidants (see Table 4), 9H-fluoren-9-one and 1,8-naphthalic anhydride may be generated from fluorene and acenaphthylene oxidation, respectively (see Fig. 4). As this study provided no direct evidence on the formation pathway of oxy-PAHs, the above speculations need to be demonstrated in subsequent studies.

Although studies have shown that certain oxy-PAH products are toxic [24,25], it has been confirmed that some oxy-PAHs can be further degraded by oxidation. In our study, given sufficient oxidation reaction time, greater removal of PAHs and oxy-PAHs could be achieved, which was consistent with previous studies. The method of coupling *Penicillium chrysogenum* with KMnO_4 was efficient in the degradation of benzo(a)pyrene (BaP) and its metabolites, including benzo[a]pyrene-1,6-quinone (BP 1,6-quinone), trans-7,8-dihydroxy-7,8-dihydrobenzo[a]pyrene (BP 7,8-diol), 3-hydroxybenzo[a]pyrene (3-OHBP) [19]. Rivas et al. also showed that after long-term oxidation (>30 min), some chemical and photochemical degradation intermediates of acenaphthylene with strong

toxicity, such as furans, polychlorinated biphenyls, and pyrans, were completely oxidized to harmless low-molecular-weight organic acids such as acetic and oxalic acids [5]. Consequently, persulfate oxidation would reduce both the PAHs toxicity in soil and other environmental risks these contaminants and reactions byproducts represent given site-specific exposure pathways.

4. Conclusions

Unactivated (20–22 °C) and thermally activated (50 °C) persulfate in coke-contaminated soils was used to successfully transform PAHs and subsequently result in the formation and loss of PAH decomposition products (i.e., oxy-PAHs). Specifically, changes in the concentration of PAHs and oxy-PAHs in soil were measured before and after persulfate oxidation by GC–MS identification and semi-quantitative measurement, respectively. Major conclusions are as follows:

- (1) Oxy-PAHs (i.e., PAH oxidation byproducts) existed in the stock coking soil including 9H-fluoren-9-one, 1H-phenalen-1-one, 1(2H)-acenaphthyleneone and 1,8-naphthalic anhydride.
- (2) Unactivated persulfate at ambient temperature (20–22 °C) and thermally activated persulfate (55 °C) can effectively oxidize and destroy PAHs. Persulfate oxidation resulted in the removal of low molecular weight PAHs (i.e., 2–3 rings) as well as the high molecular weight PAHs (i.e., 4–6 rings).
- (3) In the process of unactivated and thermally activated persulfate oxidation of PAH-contaminated soil, a variety of oxy-PAHs were generated including naphthalene 1-(2-hydroxypropyl), 1H-phenalen-1-one, dibenzofuran, 9H-fluoren-9-one, 1,8-naphthalic anhydride. Based on post-oxidation analysis of the aqueous and soil phases, analytical measurements indicated that the oxy-PAHs naphthalene 1-(2-hydroxypropyl) and 1,8-naphthalic anhydride were the most abundant. These results suggest that they are byproducts involving multiple transformation pathways.
- (4) Persulfate oxidation effectively destroyed oxy-PAHs (except naphthalene 1-(2-hydroxypropyl) and 1,8-naphthalic anhydride) from soil. The thermally activated persulfate resulted in the greatest mass reduction relative to the control and the unactivated persulfate test conditions. It is projected that the application of either unactivated or thermally activated persulfate under the testing conditions used here could reduce PAH contaminant mass and oxidation products in PAH-contaminated soil to reduce their toxicity and limit secondary environmental risks.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2014.05.018>.

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