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Fenton-like and potassium permanganate oxidations of PAH-contaminated soils: Impact of oxidant doses on PAH and polar PAC (polycyclic aromatic compound) behavior

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HIGHLIGHTS

- KMnO₄ and Fenton-like treatments were applied to PAH contaminated soils.
- The impact of two oxidant doses on PAC contamination were studied.
- Treatments were less efficient on soil with low PAC availability.
- KMnO₄ was more efficient to degrade the PAH than Fenton-like.
- Low dose of KMnO₄ induced the formation of toxic oxygenated by-products.

Keywords: Chemical oxidation; Oxygenated polycyclic aromatic compound (O-PAC); Nitrogen heterocyclic polycyclic aromatic compound (N-PAC); Coking plant soil; Gas plant soil

Abstract

Potassium permanganate and Fenton-like oxidations were applied on two PAH-contaminated soils collected on former coking plant and gas plant sites. The impact of oxidant dose on the polycyclic aromatic compound (PAC) evolution, including 16 US-EPA PAHs, 11 oxygenated- and 4 nitrogen heterocyclic- PACs (O- and N-PACs) was studied for both treatments. The content of extractable organic matter and PACs was determined prior and after oxidation. Overall, permanganate treatment was more efficient than Fenton-like to decrease the PAH content, this latter being limited by the contamination availability. However, permanganate treatment resulted in incomplete PAH degradation, leading to the formation of O-PACs, that was limited with the application of higher dose. It underlines the importance of the dose and the oxidant type in the selection of oxidation parameters for remediation purpose, as improper use of oxidant can lead to the accumulation of oxidation by-products that could be as toxic as the parent compounds.

1. Introduction

The cessation of coal related activities (e.g. coking and gasification) that started in the mid-20th century in Europe left many sites contaminated with polycyclic aromatic hydrocarbons (PAHs). Due to their toxic, carcinogenic and mutagenic properties, 16 of these compounds were included in the priority pollutant list (Keith and Telliard, 1979) and were consequently monitored in the environment since the end of the 70s. Other compounds are encountered alongside PAHs in contaminated sites such as oxygenated and nitrogen heterocyclic- polycyclic aromatic compounds (O- and N-PACs). Some of these compounds exhibit equal or more important toxic, carcinogenic and mutagenic properties than PAHs towards a wide variety of organisms (Chesis et al., 1984; Durant et al., 1996; Knecht et al., 2013; Lemieux et al., 2008; Sverdrup et al., 2003, 2002, 2001), but since they are not regulated, studies considering these compounds remain pretty scarce. These compounds, especially O-PACs, are known to occur in the initial contamination (Biache et al., 2013, 2011; 2008; Lundstedt et al., 2006a) and can also be formed via chemical and biological oxidation of PAHs. Indeed, many O-PACs are intermediate or dead-end products in PAH degradation pathways by microorganisms (Cerniglia, 1997, 1992). They can also be formed by PAH photochemical oxidation (Barbas et al., 1996; Kong and Ferry, 2004; Rivas et al., 2000) or PAH oxidation with singlet oxygen (Kochany and Maguire, 1994), hydroxyl and peroxide radicals (Neilson and Allard, 2008). Therefore they can be generated during natural attenuation and during biological (Andersson et al., 2003; Andersson and Henrysson, 1996; Biache et al., 2017; Lundstedt et al., 2003) and chemical (Lundstedt et al., 2006b) remediation treatments of PAH contaminated soils.

The results exposed in the few studies dealing with O-PAC behavior in contaminated soils are rather concerning. First, they show that O-PACs have the potential to accumulate during PAH degradation in soils (Andersson and Henrysson, 1996; Biache et al., 2017; Lundstedt et al., 2006b, 2003) and can be considered as relatively persistent (Lundstedt et al., 2007). Second, O-PACs have been proven to be more mobile in water than parent compounds (Boulangé et al., 2019; Hanser et al., 2014; Lundstedt et al., 2007) enhancing the risk associated with these compounds.

Considering the data collected so far, it is critical to obtain information on PAC behavior and long-term evolution, especially on their fate during and after remediation treatments.

Remediation by chemical oxidation has been given interest in the past decade as an interesting alternative for thermal and biological remediation of PAH contaminated soils (Rivas, 2006). Several oxidants, each presenting advantages and drawbacks, can be considered for the treatment (Rivas, 2006) including Fenton (Flotron et al., 2005; Laurent et al., 2012; Pereira et al., 2012; Usman et al., 2012; Yap et al., 2011) and permanganate (Biache et al., 2015; Ferrarese et al., 2008; Forsey et al., 2010; Silva et al., 2009; Sirguy et al., 2008). Fenton treatments are based on the combined application of hydrogen peroxide and ferrous irons in solution (Fenton's reagent) or iron minerals (Fenton-like) leading to the formation of OH[•] radicals which are strong and non-selective oxidant agents (Bacocchi, 2013). Permanganate oxidation is based on the formation of MnO₄⁻ ions from sodium and potassium permanganate in aqueous system. MnO₄⁻ are considered as strong oxidants as they are able to break organic compounds containing carbon-carbon double bonds, aldehyde and hydroxyl groups (Brown et al., 2003). The selection of the oxidant dose for remediation treatment is a critical step in order to avoid the formation of reaction intermediates such as O-PACs (Ranc et al., 2016). However, only few studies integrated these compounds in the post-treatment monitoring of soils treated with chemical oxidation (Lundstedt et al., 2006b) and little is known about the impact of the oxidant dose on their degradation and formation.

The objective of this work was to study PAH, O- and N-PAC behavior in two PAH-contaminated soils from former gas and coking plant sites, treated by chemical oxidations. Two oxidant doses (high and low) of two widely used oxidants (potassium permanganate and Fenton-like with magnetite activation) were tested in order to evaluate the dose impact on degradation/formation of PACs including PAHs, O- and N-PACs. These two treatments were selected as they work according to different modes of action (radical mechanism for Fenton-like and electron transfer for permanganate)

and are among the most reported in the literature for in situ chemical oxidation (ISCO; Ranc et al., 2016 and references therein).

2. Material and Method

2.1. Samples

The studied soils were impacted by PAH contamination inherited from former industrial activities based on the use or transformation of coal. Soils were sampled in the former coking plant of Neuves-Maisons (France) that housed coking and steel plants from 1900 to 1983 and in a former gas plant located in Rennes (France) running from 1884 to 1965 (Tables S1 and S2).

After collection, samples were stored at -18 °C. They were then freeze-dried, sieved at 2mm and the undersize was crushed at 500 mm in order to homogenize the solids.

2.2. Oxidative treatments

Fenton-like and potassium permanganate oxidations were carried out at low dose (D1) and high dose (D2). For each soil, a reference experiment was conducted with deionized (DI) water.

Sixty grams of each soil were placed in 2 L Schott bottles. Three reagents were added. DI water (1200 mL) was used as a reference. Fenton-like reagent was prepared with 1200 mL of hydrogen peroxide (30 wt %) diluted with DI water at 0.975 wt % and 4.35wt % for D1 and D2, respectively; with an addition of 6 g of magnetite. D1 and D2 of potassium permanganate consisted in 1200 mL at 3.34 g/L and 16.7 g/L, respectively.

The bottles were placed at 20 °C, in the dark to avoid photodegradation during the experiment, and the soil/oxidant mixtures were shaken with a magnetic stirrer for one week.

At the end of the chemical treatments, soil samples (soil and magnetite for Fenton-like treatment) were recovered by centrifugation (2700 G), frozen at -18 °C and freeze-dried.

2.3. Organic matter extraction

Isolation of the extractable organic matter (EOM), from initial and oxidized soils, was carried out on 1.5 g of dw sample with an accelerated solvent extractor (Dionex ASE 350). Copper powder (2 g) and anhydride sodium sulfate (2 g) were added to the extraction cells to remove molecular sulfur and residual water, respectively. Extractions were performed with dichloromethane (DCM) at 130 °C and 100 bar for 2 cycles of 10 min. After adjusting the volume at 20 mL, an aliquot of the solvent extract (5 mL) was placed in pre-weighed vials. The EOM content was determined by weighing the vials after solvent evaporation until dryness under a gentle nitrogen flow.

2.4. C,H,N and O quantification in the EOM

Contents of carbon, hydrogen, nitrogen and oxygen in the EOM were determined by elemental analysis with an Elemental vario MICRO cube. Analyses were carried out in the Laboratoire des Mesures Physiques at the University of Montpellier (France) with a thermal conductivity detector (TCD). C, H and N were determined after catalytic combustion of the samples (1150 °C) and reduction of the combustion gas (850 °C). O was determined after sample pyrolysis (1050 °C) and gas conversion into CO for O.

2.5. PAC quantification

Quantification of the 16 regulated PAHs, 11 O-PACs and 4 N-PACs was carried out using internal calibration. An internal standard mixture (20 mL) of 12 deuterated PACs (Table S3; 12mg/mL each) was added to soil EOM (80 mL) before being injected (1 mL) in a gas chromatograph coupled with a mass

spectrometer (GC-MS). For each quantified compound, a calibration curve was drawn with six concentrations (0.3, 0.6, 1.2, 3, 6 and 9.6 mg/mL) injected in split mode with a ratio 1:5. The GC was a Shimadzu GC-2010 plus, equipped with a capillary column in silica glass DB-5MS (60m × 0.25mm i.d. × 0.1 mm film thickness) coupled to a QP2010-Ultra (Shimadzu) MS operated in selected ion monitoring mode (Table S3) with a transfer line heated at 300 °C. The oven temperature program was as follow: 70 °C for 2 min, from 70 to 130 °C at 15°C/min, then from 130 to 315 °C at 3°C/min and a 15 min hold at 315 °C. The carrier gas was helium at 1.2 mL/min constant flow.

3. Results and discussion

3.1. *Is the reference sample representative?*

Differences in PAH and O-PAC behavior were observed in the reference samples of the two studied soils. A decrease in the LMW PAH and an increase in some O-PAC (9H-fluorenone, perinaphtenone, anthraquinone and benzanthrone) concentrations (Table 1) was noticed in the gas plant soil reference compared with the initial sample whereas no major difference was observed between the initial and reference coking plant soil (Table 2). These observations seem to indicate microbial activities in the gas plant soil reference. Indeed, the samples were not sterilized prior experiment and indigenous microorganisms are able to degrade PAHs in this soil under slurry conditions (Biache et al., 2017). Moreover the experiment conditions (20 °C, agitation and slurry with addition of water) can favor microbial degradation of PAHs (Bamforth and Singleton, 2005; Brown, 1997). 9H-fluorenone and anthraquinone, whose concentrations increased, are known to be metabolites of fluorene and anthracene biodegradation, respectively (Bezalel et al., 1996; Boldrin et al., 1993; Van Herwijnen et al., 2003) and the decrease in these PAH concentrations was fairly consistent with the increase in the content of their oxygenated counterparts (Fig. 2). Even if these O-PACs can also be produced by photochemical oxidation (David and Boule, 1993; Mallakin et al., 2000), this hypothesis can be ruled out as samples were kept in the dark throughout the experiment. The fact that this behavior was not observed for the coking plant soil can be explained by a difference in PAH availability. Previous experiments evidenced a low PAH availability in the Neuves-Maisons coking plant soil with very limited PAH degradation by biological or H₂O₂-based oxidative treatments (34% and 0% respectively) (Biache et al., 2015; Cébron et al., 2013; Ouvrard et al., 2011; Pernot et al., 2014, 2013; Usman et al., 2015). On the contrary, microbial incubation (Biache et al., 2017) and chemical oxidation (Biache et al., 2015) remove more than 75% of PAHs in the gas plant soil, indicating high PAH availability.

As microbial degradation of PAHs and subsequent production of O-PACs occurred in the gas plant soil reference sample, the abatement rates will be subsequently given according to the initial sample concentrations. However, as Fenton-like and permanganate treatments affect negatively the microbial communities in term of density and activity (Chen et al., 2016; Laurent et al., 2012; Sercu et al., 2013), the possibility of a PAH biodegradation occurring concomitantly with chemical degradation during the treatments can be excluded.

3.2. *Differences in PAH and O-PAC evolution according to the treatment*

The Fenton-like and permanganate high dose treatments induced about the same decrease in PAH concentrations for the gas plant soil (80% and 84%, respectively - Fig. 1b) whereas permanganate was much more efficient than Fenton-like for the coking plant soil (58% and 14%, respectively - Fig. 1b). These disparities in PAH behavior between both soils can be explained by the treatment selectivity. In a previous study (Biache et al., 2015), Fenton-like treatment was proven to be limited by PAH availability, contrary to permanganate treatment. As already underlined, Neuves- Maisons coking plant soil exhibits low PAH availability unlike the gas plant soil, which explains the difference in Fenton-like treatment efficiency between both soils.

Table 1: Polycyclic aromatic compound concentrations in the initial sample, the reference sample and the sample oxidized with low and high doses of Fenton-like and potassium permanganate of the gas plant soil

Gas plant soil	Initial	Reference	Fenton-like - low dose	Fenton-like - high dose	KMnO ₄ - low dose	KMnO ₄ - high dose
HAP (µg/g of soil)						
<i>Naphthalene</i>	31	0	14	5	11	7
<i>Acenaphthylene</i>	51	33	23	12	23	5
<i>Acenaphthene</i>	18	14	9	0	3	1
<i>Fluorene</i>	63	41	43	0	5	0
<i>Phenanthrene</i>	218	183	164	35	99	34
<i>Anthracene</i>	67	46	23	7	20	4
<i>Fluoranthene</i>	217	204	155	45	200	47
<i>Pyrene</i>	159	142	111	29	82	24
<i>Benz[a]anthracene</i>	82	78	62	18	46	9
<i>Chrysene</i>	49	58	49	14	52	11
<i>Benzo[b]fluoranthene</i>	44	56	67	26	79	22
<i>Benzo[k]fluoranthene</i>	34	31	24	9	26	8
<i>Benzo[a]pyrene</i>	69	59	40	13	34	6
<i>Indeno[1,2,3-c,d]pyrene</i>	54	46	38	15	37	12
<i>Dibenzo[a,h]anthracene</i>	12	10	9	3	8	0
<i>Benzo[ghi]perylene</i>	41	42	31	12	32	7
Σ 16 PAHs	1210	1043	861	243	758	197
Σ 16 PAH/Σ 31 PAC	0.9	0.9	0.9	1	0.8	0.8
LMW/HMW^a	2.1	1.7	1.7	1.2	1.4	1.6
O-PAC (µg/g of soil)						
<i>Dibenzofuran</i>	43	33	27	3	39	17
<i>9H-fluorenone</i>	6	12	6	0	49	17
<i>Perinaphthenone</i>	4	10	0	0	0	0
<i>Anthraquinone</i>	7	13	23	0	71	21
<i>Cyclopenta[def]phenanthrone</i>	4	0	0	0	6	0
<i>Methylanthracene-9,10-dione</i>	4	0	5	0	16	3
<i>Benzo[a]fluorenone</i>	8	0	9	0	30	3
<i>Benzanthrone</i>	6	10	2	0	8	1
<i>Benzanthracenedione</i>	3	0	4	0	23	3
<i>Naphthacene-5,12-dione</i>	6	0	0	0	4	0
<i>Benzo[cd]pyrenone</i>	1	0	0	0	0	0
Σ 11 O-PACs	92	78	77	3	246	64
Σ 11 O-PAC/Σ 31 PAC	0.07	0.07	0.08	0.01	0.24	0.24
N-PAC (µg/g of soil)						
<i>Quinoline</i>	0	0	0	0	0	0
<i>Benzo[h]quinoline</i>	0	0	0	0	0	0
<i>Acridine</i>	2	0	0	0	0	0
<i>Carbazole</i>	15	11	3	0	2	0
Σ 4 N-PACs	17	11	3	0	2	0
Σ 4 N-PAC/Σ 31 PAC	0.013	0.009	0.003	0.000	0.002	0.000
Sum of the PAC (µg/g of soil)	1319	1131	940	246	1005	261

^a LMW/HMW: Sum of low molecular weight PAH concentrations (naphthalene to pyrene) over sum of high molecular weight PAH concentrations (benz[a]anthracene to benzo[ghi]perylene)

Despite lower oxidation potential, KMnO₄ was more efficient than Fenton-like to degrade PAHs with 58% and 84% decrease rate for the first and 14% and 80% decrease rate for the latter, with the high oxidant dose applied on the coking and the gas plant soil, respectively (Fig. 1b, Tables 1 and 2). It can be explained by the persistence of MnO₄⁻ in the soil after treatment application (Lemaire et al., 2013), resulting in longer action duration and better efficiency. Indeed, permanganate is a stable oxidant and can persist in the soil for months (The Interstate Technology and Regulatory Council, 2016) which contributes to diffusive transport of the oxidant into low-permeability materials. It permits deeper penetration of the oxidant into soil particles (Huling and Pivetz, 2006) and a better access to sequestered PAHs, explaining the absence of availability limitation with KMnO₄. On the contrary, for

Fenton-like treatment, hydroxyl radicals exhibit fast reaction rate (Huling and Pivetz, 2006) and fast consumption of these radicals can occur, especially through radical scavenging (Huling and Pivetz, 2006), limiting their action through time. Our previous study (Biache et al., 2015) confirmed this hypothesis as it showed different PAH degradation kinetic between both treatments and evidenced a longer action duration of KMnO₄ than Fenton-like and an overall better efficiency of KMnO₄ to degrade PAHs.

Table 2: Polycyclic aromatic compound concentrations in the initial sample, the reference coking sample and the sample oxidized with low and high doses of Fenton-like and potassium permanganate of the coking plant soil

Coking plant soil	Initial	Reference	Fenton like - low dose	Fenton like- high dose	KMnO ₄ - low dose	KMnO ₄ - high dose
HAP (µg/g of soil)						
<i>Naphthalene</i>	38	36	32	31	28	23
<i>Acenaphthylene</i>	46	38	36	28	22	14
<i>Acenaphthene</i>	24	24	19	19	10	8
<i>Fluorene</i>	20	19	16	14	5	2
<i>Phenanthrene</i>	85	90	75	77	51	44
<i>Anthracene</i>	37	35	28	27	16	10
<i>Fluoranthene</i>	160	135	141	139	104	71
<i>Pyrene</i>	122	116	118	110	62	50
<i>Benz[a]anthracene</i>	91	108	96	89	50	37
<i>Chrysene</i>	51	76	63	62	42	30
<i>Benzo[b]fluoranthene</i>	130	131	117	86	96	61
<i>Benzo[k]fluoranthene</i>	53	54	44	47	35	22
<i>Benzo[a]pyrene</i>	83	97	85	75	43	28
<i>Indeno[1,2,3-c,d]pyrene</i>	98	102	88	86	51	37
<i>Dibenzo[a,h]anthracene</i>	25	26	25	20	15	9
<i>Benzo[ghi]perylene</i>	74	79	74	65	37	27
Σ 16 PAHs	1136	1167	1057	974	668	475
Σ 16 PAH/Σ 31 PAC	0.9	0.9	0.9	0.9	0.8	0.8
LMW/HMW^a	0.9	0.7	0.8	0.8	0.8	0.9
O-PAC (µg/g of soil)						
<i>Dibenzofuran</i>	19	18	17	17	20	11
<i>9H-fluorenone</i>	26	27	22	23	56	43
<i>Perinaphthenone</i>	3	0	0	0	0	0
<i>Anthraquinone</i>	17	18	17	17	31	21
<i>Cyclopenta[def]phenanthrone</i>	20	15	10	9	4	2
<i>Methylantracene-9,10-dione</i>	2	2	0	2	2	0
<i>Benzo[a]fluorenone</i>	13	19	15	13	12	6
<i>Benzanthrone</i>	11	12	9	9	8	5
<i>Benzoanthracenedione</i>	3	5	4	4	11	5
<i>Naphthacene-5,12-dione</i>	5	4	3	3	3	2
<i>Benzo[cd]pyrenone</i>	11	0	0	0	0	0
Σ 11 O-PAC	129	119	97	97	147	96
Σ 11 O-PAC/Σ 31 PAC	0.1	0.1	0.1	0.1	0.2	0.2
N-PAC (µg/g of soil)						
<i>Quinoline</i>	0	0	0	0	0	0
<i>Benzo[h]quinoline</i>	0	0	0	0	0	0
<i>Acridine</i>	0	0	0	0	0	0
<i>Carbazole</i>	7	5	5	4	3	0
Σ 4 N-PAC	8	5	5	4	3	0
Σ N-PAC/Σ 31 PAC	0.006	0.004	0.004	0.004	0.003	0.000
PAC (µg/g of soil)	1274	1292	1159	1075	818	571

^a LMW/HMW: Sum of low molecular weight PAH concentrations (naphthalene to pyrene) over sum of high molecular weight PAH concentrations (benz[a]anthracene to benzo[ghi]perylene)

However, permanganate treatment seemed to favor the production of O-PACs, compared to Fenton-like. Indeed most of the OPAC concentrations increased after the application of low KMnO₄

dose on gas plant soil (Table 1) and it caused an increased in 9H-fluorenone, anthraquinone and benzantracenedione for the coking plant soil (Table 2). This O-PAC formation was not observed when using high oxidant dose (Fig. 1c). The dissimilarities in O-PAC evolution can be attributed to difference in the degradation kinetic but also to difference in the oxidant strength, leading to variable step of completion in PAH degradation. Indeed, the oxidation potential of the hydroxyl radical generated during the Fenton-like treatment is higher than the permanganate oxidation potential (2.8 and 1.7 eV, respectively (Ray et al., 2006)), leading to a more complete degradation, unlike permanganate which caused the accumulation of degradation by-products when applied at insufficient dose.

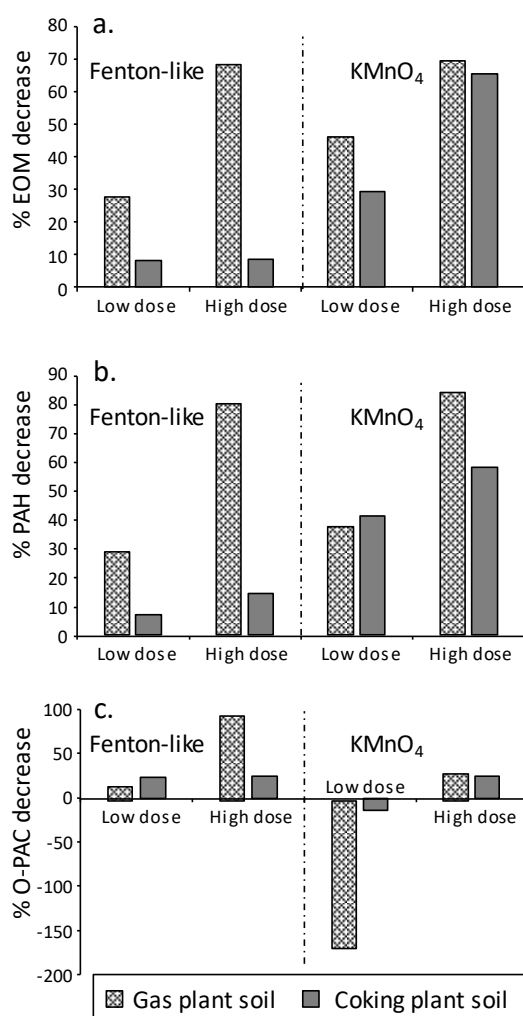


Fig. 1: Decrease rate of (a.) extractable organic matter (EOM), (b.) 16 regulated PAHs and (c.) 11 quantified oxygenated polycyclic aromatic compounds (O-PACs) after low and high doses of Fenton-like and KMnO₄ treatments for the gas and coking plant soils, compared to the initial samples

3.3. Impact of the treatment at a molecular scale

Among the quantified O-PACs, 9H-fluorenone, anthraquinone and benzantracenedione are known to be oxidation products of fluorene, anthracene and benz[*a*]anthracene, respectively (David and Boule, 1993; Lee et al., 2001; Mallakin et al., 2000; Perraudin et al., 2007; Yao et al., 1998). The decrease in fluorene and anthracene concentrations was about the same extent as the increase in 9H-fluorenone and anthraquinone concentrations, respectively, with low KMnO₄ dose indicating an accumulation of degradation products which was not observed, or to a lesser extent, with low dose of Fenton-like reagent (Figs. 2 and 3). These observations are consistent with the higher oxidation potential of

hydroxyl radicals in the Fenton-like treatment compared to permanganate. High KMnO_4 dose led to a higher decrease in fluorene and anthracene concentrations and to a lesser increase in their O-PAC equivalents compared to low-dose treatment, indicating that a higher amount of KMnO_4 was able to reach a higher level of degradation completion and also started to degrade the generated oxidation by-products. The same observation can be made with the high dose of Fenton-like treatment as the concentrations of both PAH and O-PAC counterparts decreased.

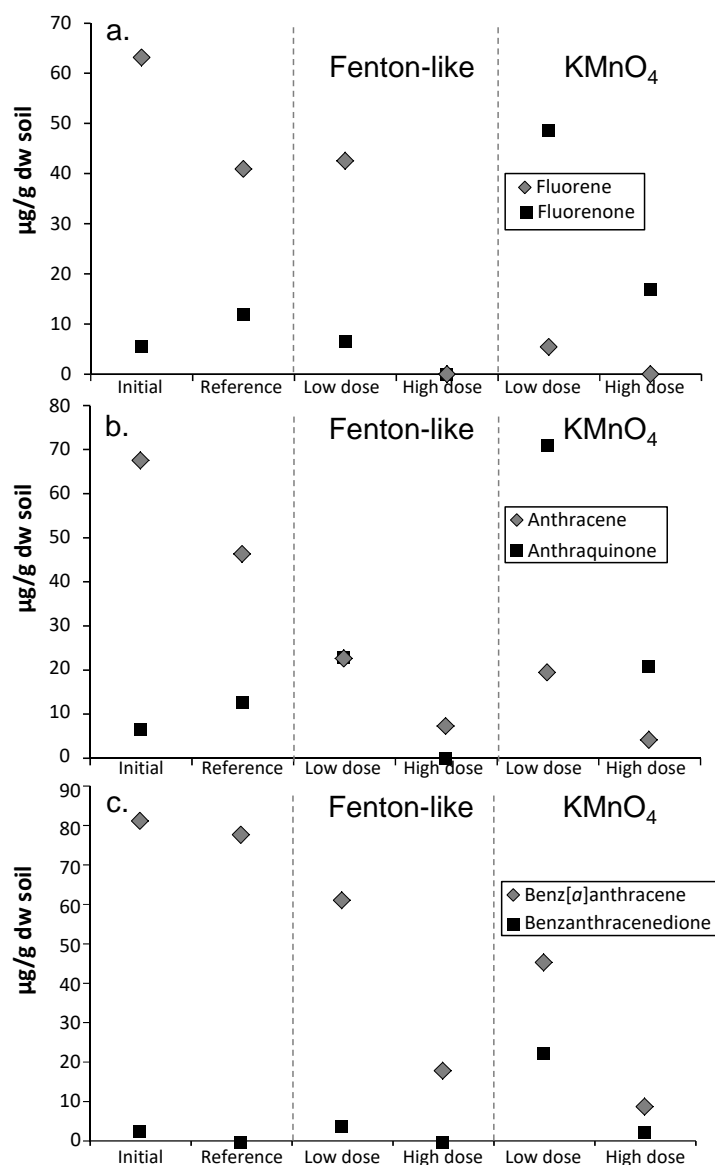


Fig. 2: Concentrations of (a.) fluorene, (b.) anthracene and (c.) benz[a]anthracene and of some of their possible oxidation by-products in the gas plant soil before and after the Fenton-like and permanganate oxidations and in the reference sample

3.4. Dose effect

The oxidant doses used in this experiment were selected according to previous studies (Bache et al., 2015) and were based on the stoichiometric oxidant demand (SOD). SOD is calculated to estimate the oxidant requested to degrade the contamination (Lemaire et al., 2013; Ranc et al., 2016). It is based on the concentrations of the contaminants to be degraded and the stoichiometric molar ratio (SMR) of the oxidant over the contaminants. The SOD_{PAC} - based on the quantified PAC contents - calculated

for both oxidants were similar for both soils (Table 3) which is not surprising since their PAC contents were very close. The chosen hydrogen peroxide doses in Fenton-like treatment were much higher (c.a. $24 \times \text{SOD}_{\text{PAC}}$ and $120 \times \text{SOD}_{\text{PAC}}$ for low and high doses, respectively; Table 3) compared to potassium permanganate (c.a. $2.7 \times \text{SOD}_{\text{PAC}}$ and $13.5 \times \text{SOD}_{\text{PAC}}$ for low and high doses, respectively, Table 3). It was so as, contrary to the permanganate, the Fenton-like reaction is very fast, the hydroxyl radical are not persistent and they can be consumed by radical scavenging (Huling and Pivetz, 2006).

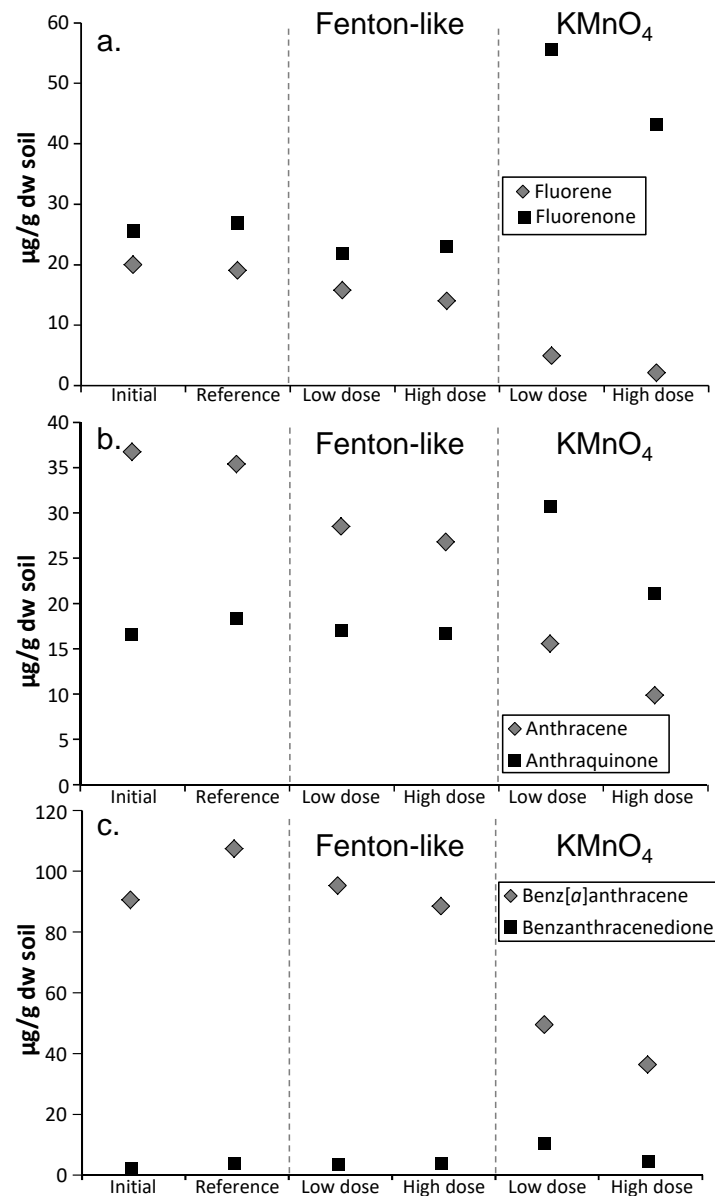


Fig. 3: Concentrations of (a.) fluorene, (b.) anthracene and (c.) benz[a]anthracene and of some of their possible oxidation by-products in the coking plant soil before and after Fenton-like and permanganate oxidations and in the reference sample

Considering these values, the low oxidant dose should have been sufficient to degrade all the PACs, which was not the case. As the SOD_{PAC} was calculated based only on the quantified PAC concentrations it was not representative of the oxidant consumption in the soil. Indeed, oxidants are not selective and they are consumed by reacting with other constituent of the soil OM. It was clearly shown by the strong decrease in the EOM content that reached up to 70% and 66% with the application of high dose of KMnO_4 for the gas and the coking plant soils, respectively (Fig. 1a.) which, in this case,

is mostly anthropogenic (Table S1). As suggested by Ranc et al. (2016) the SOD was also calculated based on the EOM from its elemental composition (Table S4), according to Eq. (1), which is more accurate than the one based on the PAC content (Table 3).

$$SOD_{EOM} = \frac{SMR \times m \times 10^{-3} \times (w_C + w_H + w_O)}{M_C \times c + M_H \times h + M_O \times o} \quad (1) \text{ from Ranc et al. (2016).}$$

With:

- SOD_{EOM} : stoichiometric oxidant demand of the EOM (mol)
- SMR: stoichiometric molar ratio oxidant/the equivalent molecular formula of the EOM $C_cH_hO_o$ (mol/mol)
- m: soil mass to be treated (g)
- EOM: extractable organic matter content in the soil (mg/g)
- w_C , w_H and w_O : mass fraction of carbon, hydrogen and oxygen, respectively, in the EOM (g/g - Table S4)
- M_C , M_H and M_O : molar mass of carbon, hydrogen and oxygen, respectively (g/mol)
- c, h and o: number of atoms of carbon, hydrogen and oxygen, respectively, in $C_cH_hO_o$ (equivalent molecular formula of the EOM)

As the EOM contents of both soils were similar, the same trends were observed as for the SOD_{PAC} but the SOD_{EOM} was about 8 times higher than the SOD_{PAC} . Consequently, the applied doses in term of SOD_{EOM} were much lower. The low dose of $KMnO_4$ did not allow to reach the SOD_{EOM} ($0.31 \times SOD_{EOM}$ and $0.36 \times SOD_{EOM}$ for the gas and the coking plant soil, respectively), explaining the low level of oxidation completion and the formation of O-PAC by-products occurring for this oxidant dose. The high oxidant doses allowed reaching the SOD_{EOM} for both soils and both oxidants (Table 3).

Table 3: Stoichiometric oxidant demand (SOD) of the coking plant and gas plant soils calculated for the 31 quantified PACs for $KMnO_4$ and Fenton-like and the SOD equivalent of the applied doses.

	Gas plant soil		Coking plant soil	
	$KMnO_4$	Fenton-like (H_2O_2)	$KMnO_4$	Fenton-like (H_2O_2)
SOD_{PAC} (g of oxidant/batch) ¹	1.52	0.49	1.46	0.47
SOD_{EOM} (g of oxidant/batch) ²	12.75	4.12	11.06	3.57
Low dose	$2.64 \times SOD_{PAC}$ $0.31 \times SOD_{EOM}$	$23.81 \times SOD_{PAC}$ $2.83 \times SOD_{EOM}$	$2.75 \times SOD_{PAC}$ $0.36 \times SOD_{EOM}$	$24.82 \times SOD_{PAC}$ $3.26 \times SOD_{EOM}$
High dose	$13.21 \times SOD_{PAC}$ $1.57 \times SOD_{EOM}$	$118.35 \times SOD_{PAC}$ $14.08 \times SOD_{EOM}$	$13.77 \times SOD_{PAC}$ $1.81 \times SOD_{EOM}$	$123.39 \times SOD_{PAC}$ $16.23 \times SOD_{EOM}$

¹ stoichiometric oxidant demand calculated for the 31 quantified polycyclic aromatic compounds

² stoichiometric oxidant demand calculated for the soil extractable organic matter (EOM) based on its C, H and O content

4. Conclusion

Low and high doses of $KMnO_4$ and Fenton-like treatments were applied on two aged PAH-contaminated soils. Fenton-like efficiency was proven to be limited by the contaminant availability, as its efficiency to degrade PAHs was low for the coking plant soil, which presents low PAH availability. $KMnO_4$ led to a better PAH decrease rate than Fenton-like, probably due to longer action duration and a better diffusion of the MnO_4^- in the soil pores allowing the degradation of sequestered PAHs. However, $KMnO_4$ led to an incomplete PAH degradation causing the production of O-PACs which can be explained by the fact that oxidation potential was lower than for Fenton-like and that the applied $KMnO_4$ doses - in term of SOD - were much lower than the Fenton-like doses and did not reach the SOD_{EOM} in the case of the low $KMnO_4$ dose. The production of O-PACs was avoided by the application

of higher dose of oxidant. Fenton-like oxidation led to a higher decrease in the O-PACs content than KMnO_4 for the gas plant soil, where the contamination was available. The results obtained in this study underline the importance in the choice of the dose and the oxidant for contaminated soil remediation. The soil properties that can impact the treatment efficiency (e.g. contamination availability, EOM content) should be taken into account (calculation of the SOD_{EOM}) and the compounds monitored throughout the treatment should include potential by-products, i.e. O-PACs, as they are known to be equally toxic and can potentially accumulate in soil. Another aspect to explore - which we are currently investigating - is the risk associated to these treatments for aqueous mobilization of polar-PACs since they are more water-soluble due to the presence of polar functioning groups.

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Appendix A. Supplementary data

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