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Effect of pre-heating on the chemical oxidation efficiency: Implications for the PAH availability measurement in contaminated soils

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Highlights

- KMnO₄, H₂O₂ and Fenton-like treatments were applied on PAH-contaminated soils.
- Soils were heated prior the oxidation in order to increase the PAH availability.
- KMnO₄ was efficient to degrade PAHs even in samples presenting low PAH-availability.
- H₂O₂-based treatments were sensitive to PAH availability

Keywords: Hydrogen peroxide; Potassium permanganate; Fenton-like; Polycyclic aromatic hydrocarbon; Contaminant availability

Abstract

Three chemical oxidation treatments (KMnO₄, H₂O₂ and Fenton-like) were applied on three PAH-contaminated soils presenting different properties to determine the potential use of these treatments to evaluate the available PAH fraction. In order to increase the available fraction, a pre-heating (100 °C under N₂ for one week) was also applied on the samples prior oxidant addition. PAH and extractable organic matter contents were determined before and after treatment applications. KMnO₄ was efficient to degrade PAHs in all the soil samples and the pre-heating slightly improved its efficiency. H₂O₂ and Fenton-like treatments presented low efficiency to degrade PAH in the soil presenting poor PAH availability, however, the PAH degradation rates were improved with the pre-heating. Consequently H₂O₂-based treatments (including Fenton-like) are highly sensitive to contaminant availability and seem to be valid methods to estimate the available PAH fraction in contaminated soils.

1. Introduction

The European Environment Agency (EEA) inventoried about 1.5 millions of contaminated sites in Europe including 200,000 sites contaminated by polycyclic aromatic compounds (PACs) comprising polycyclic aromatic hydrocarbons (PAHs) [1]. These sites are mostly former coking plant, gas plant and wood treating facilities. In France these sites account for almost 22% of the inventoried contaminated sites [2]. Due to the PAH recalcitrance and their toxic and carcinogenic properties that place them in the US-EPA pollutant priority list [3], applications of remediation treatments are necessary to rehabilitate these sites. One of the main factors determining the efficiency of these remediation treatments is the contaminant availability [4–6]. Several methods are commonly used to estimate the (bio)available fraction of the contamination. Mild extractions [7,8], cyclodextrine extraction [9,10], Tenax resin extraction [4], passive samplers [11,12], biosensors [13] and microbial incubations [14,15] can be cited. Another method was investigated by Cuypers et al. [16] implying the application of chemical oxidant. Such reagents (e.g., O_3 , $KMnO_4$, H_2O_2 , persulfate) are commonly used to treat contaminated matrixes and they can be activated by catalyst addition [17–25]. The oxidant action will be different according to the type of reagents and their oxidation potentials. For instance hydrogen peroxide is one of the most common oxidant (oxidation potential c.a. 1.8 V; [26]). Its application, associated with ferrous ions, leads to the formation of OH radicals which are strong and non-selective oxidant agents (oxidation potential c.a. 2.7 V; [27,28]). Ferrous ions can be introduced in solution and the mixture with H_2O_2 is called Fenton's reagent. The catalytic potential of iron mineral can also be used, in this case the process is referred to as Fenton-like oxidation [21]. In aqueous system sodium permanganate and potassium permanganate generate MnO_4^- ions presenting an oxidation potential of 1.7 V [17]. Despite this relatively low value, MnO_4^- are able to break organic compounds containing carbon–carbon double bonds, aldehyde and hydroxyl groups and are therefore, considered as strong oxidant agents [29].

Cuypers et al. [16] validated persulfate oxidation as a method for the bioavailability estimation by comparing the PAH fraction of a contaminated soil chemically degraded to the PAHs biodegraded

during batch experiment. Therefore chemical oxidants could be used as alternative ways to determine the available fraction of the contamination. Other studies show the strong connection between chemical oxidation efficiency and contaminant availability. Usman et al. [24] studied the Fenton-like treatment applied on former coking plant soils and on their solvent extractable organic matter (EOM) mixed with sand. The treatment efficiency shows major differences with more than 90% of PAH removal for the EOM/sand mixture whereas oxidation has only negligible effect on the soil PAHs. These results highlight the major constraint of the chemical treatments caused by contamination low availability. The use of solvent extraction to improve PAH availability was explored in another study, where magnetite-activated persulfate treatments were applied on the same soils, with/without a prior solvent extraction [23]. Results demonstrate that the extraction enhances the PAH degradation by magnetite-activated persulfate oxidation by increasing their availability toward the reagents with a modification of the EOM dispersion (including PAHs) on the soil constituents. Although these studies gave new information on chemical oxidation processes and the key role of the contaminant chemo-availability (toward the chemical agent), the field application of solvent extraction to enhance the chemical treatment efficiency seems difficult to implement. Another more practical technique improving the chemo-availability of organic contaminants consists in heating the contaminated matrices at moderate temperatures (60–150 °C) [30]. This technique was applied on the same aged coking plant soil and has proven to be capable to enhance the oxidation efficiency (Fenton-like) for PAH contaminated soils presenting low PAH availability [31,32].

The purpose of the present study was to determine if chemical treatment efficiencies can be used as indicator of contaminant availability and to test the effect of pre-heating on the PAH chemical degradation according to (i) the soil properties and (ii) the type of treatments. In order to fulfill these objectives, three PAH contaminated soils, originating from different industrial activities (coking, gasification and wood treatment) and presenting various characteristics (EOM and total organic carbon (TOC) contents, PAH concentrations and distributions) were selected. Several oxidants (H_2O_2 , Fenton-like, $KMnO_4$) were applied with/without pre-heating used to enhance the PAH chemo-availability.

2. Materials and methods

2.1. Soil samples

The selected soils presented PAH contaminations and originated from the use or transformation of coal or its by-products. Soils were sampled in the former coking plant of Neuves-Maisons (France), in a former gas plant located near Rennes (France) and in an active wood-treating facility located in Midi-Pyrénées (France). After being collected, the samples were stored at $-18\text{ }^{\circ}\text{C}$. They were freeze-dried, sieved at 2 mm and the undersize was crushed at 500 μm .

2.2. Thermal treatment

To modify the PAH availability, fractions of soil samples were placed in 500 mL-Schott bottles which were hermetically closed under N_2 , to prevent air-oxidation, and placed in an oven at $100\text{ }^{\circ}\text{C}$ for one week.

2.3. Chemical oxidations

Each soil (5 g), raw and pre-heated, was placed in 250 mL-Schott bottles. Four reagents were added, (i) 100 mL of deionized (DI) water, as reference; (ii) 14.5 mL of H_2O_2 (30% wt) adjusted to 100 mL with DI water; (iii) Fenton-like reagent with the same procedure as H_2O_2 with addition of magnetite (500 mg); (iv) 100 mL of KMnO_4 solution (16.7 g/L). The bottles were agitated (200 rpm) in the dark for one week. The pre-heated samples were also collected after 1 and 24 h to follow the reaction kinetics.

2.4. Organic matter extraction

OM extractions were carried out on 1.5 g of each sample with an accelerated solvent extractor (Dionex ASE 350). Copper powder (2 g) and sodium sulfate (2 g) were added to the extraction cells to remove the molecular sulfur and the residual water, respectively. The extractions were performed with dichloromethane (DCM) at $100\text{ }^{\circ}\text{C}$ and 100 bars for 10 min. After adjusting the volume at 20 mL, aliquots of the solvent extracts (5 mL) were placed in pre-weighed vials. The EOM content was determined by weighing the vials after solvent evaporation under a gentle N_2 flow.

2.5. PAH quantification

Quantification of the 16 listed PAHs (Table S1) was carried out using internal calibration. An internal PAH standard mix (20 μL at 16 $\mu\text{g}/\text{mL}$) was added to the EOM (80 μL) before being injected in a gas chromatograph coupled with a mass spectrometer (GC–MS). Analytical conditions and calibration details were reported in the supplementary data file. All results were expressed as a mean value of three experiments and relative standard deviation (RSD) of the three replicates was less than 5%.

2.6. TOC content measurement

The TOC content determination was performed with a total carbon analyzer TOC-V CSH (Shimadzu) associated with a solid sample module SSM-5000A (Shimadzu). The catalytic combustion was performed at 900 °C after carbonate removal with hydrochloric acid (10% wt).

2.7. Radiocarbon analysis

The $\Delta^{14}\text{C}$ activity was measured to determine recent organic carbon proportion in the soil samples [33]. The soils were previously treated with hydrochloric acid (1 M) to remove the mineral carbon (carbonates). Radiocarbon analyses were performed by Poznan radiocarbon laboratory (Poland) and the results were given in percentage of modern carbon (pMC).

2.8. Soil specific areas

The specific area of the different soils and the soils previously extracted with DCM were determined in the dry state using conventional step-by-step volumetric adsorption equipment (B.E.T.) to perform complete nitrogen gas adsorption–desorption cycles at 77 K. The samples were degassed at 110 °C under vacuum prior adsorption.

3. Results

3.1. Initial samples

The soil samples presented various TOC, EOM and PAH contents (Table 1). The TOC varied from 3.3 to 17.2% for the gas plant and the wood-treating facility soils, respectively. The coking plant soil presented an intermediate value (6.5%). The EOM contents were of the same range for the coking and gas plant soils (10.3 and 11.5 mg/g, respectively) whereas it was about eight times higher in the wood-treating facility soil (81.94 mg/g). Similar ranges of PAH content were observed for the coking and gas plant soils (1146 and 1781 $\mu\text{g/g}$, respectively) and the wood-treating facility soil presented much higher value (c.a. 12,000 $\mu\text{g/g}$, Fig. S1). The PAH distribution varied according to the sample origin, the coking plant soil presenting a distribution dominated by 4- and 5-ring PAHs, whereas 2- to 4-ring PAHs dominated the gas plant soil, and pyrene and fluoranthene represented the dominant PAHs in the wood-treating facility soil. These differences were underlined by the low molecular weight over high molecular weight (LMW/HMW) ratio (sum of naphthalene to pyrene concentrations over sum of benz[a]pyrene to benzo[ghi]perylene concentrations; Table 1). This ratio presented a relatively low value for the coking plant soil (0.82) and very high value for the wood-treating facility soil (78) due to high fluoranthene and pyrene concentrations. The soil specific areas varied from 2.1 to 9.8 m^2/g for the wood-treating facility and the coking plant soils, respectively (Table 2). The gas plant soil showed an intermediate value (4.6 m^2/g). The EOM removal induced an increase in the specific area for all samples and reached 5.5, 9.2 and 12.8 m^2/g for the wood-treating facility, the gas plant and the coking plant soils, respectively. Consequently, the EOM occupied 62, 50 and 23% of the specific surface, respectively.

3.2. Effect of the heating pretreatment on the initial samples

The pre-heating used to enhance the PAH availability induced only a slight decrease in the EOM content (Table 1) of the three soils. It did not cause any modification of the PAH content and distribution (Table 1).

Table 1: Total organic carbon (TOC), extractable organic matter (EOM), modern carbon percentage (pMC) and PAH contents of the initial and pre-heated soils (1 week at 100 °C under N₂) (n.d.: not detected).

	Coking plant		Gas plant		Wood treating facility	
	Initial	Preheated	Initial	Preheated	Initial	Preheated
TOC (%)	6.5	/	3.3	/	17.2	/
EOM (mg/g)	10.30	9.42	11.50	10.21	81.94	73.10
pMC (%)	5.6	/	14.7	/	21.8	/
PAH (µg/g)						
Naphthalene	35	40	130	110	4.8	4.9
Acenaphthylene	24	20	59	18	55	39
Acenaphthene	28	28	28	25	320	280
Fluorene	20	18	88	82	130	130
Phenanthrene	87	100	290	300	640	670
Anthracene	28	28	80	72	160	160
Fluoranthene	170	190	310	320	6100	6000
Pyrene	130	150	230	230	4400	4300
Benz[<i>a</i>]anthracene	91	110	110	100	53	53
Chrysene	71	80	81	74	51	51
Benzo[<i>b</i>]fluoranthene	120	140	90	77	26	25
Benzo[<i>k</i>]fluoranthene	53	62	44	43	5.8	7.2
Benz[<i>a</i>]pyrene	87	84	90	82	16	15
Dibenz[<i>a,h</i>]anthracene	19	22	13	11	n.d.	n.d.
Indeno[1,2,3- <i>cd</i>]pyrene	92	100	62	56	n.d.	n.d.
Benzo[<i>ghi</i>]perylene	72	85	52	45	n.d.	n.d.
Σ 16 PAHs ^a	1127	1257	1757	1645	11962	11700
LMW/HMW ^b	0.9	0.9	2.3	2.4	78	76

^a Σ 16 PAHs: Sum of the concentrations of the 16 PAHs listed by the US-EPA as priority pollutants

^b 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)

3.3. Effect of the chemical oxidations

3.3.1. Potassium permanganate (KMnO₄)

Compared to the references (one week in water), KMnO₄ addition induced a decrease in the EOM contents of the three samples (Fig. 1) which was more important for the gas plant soil compared to the other samples. Heating the samples prior KMnO₄ application induced a more important decrease in the EOM contents of the coking and the gas plant soils whereas the pre-heating had minor impact on the wood-treating facility EOM. Overall, KMnO₄ induced a decrease in the PAH content (Table 3, Fig. S2). It decreased by half in the coking plant soil. The pre-heating enhanced this diminution which reached more than 70%. The diminution was more important for the gas plant soil (87%) than for the other samples and it was also enhanced by the pre-heating (96%). The steadiness of the LMW/HMW ratio in both cases indicated no preferential degradation of one fraction or the other. For the wood-

treating facility soil, which showed the highest PAH contents, the pre-heating did not seem to affect the degradation efficiency since the PAH abatement reached 59% and 62% for the unheated and the pre-heated samples, respectively. The LMW/HMW was affected by KMnO_4 due to the diminution of fluoranthene and pyrene concentrations (Table 3), those two compounds being main LMW PAHs; the pre-heating did not affect this ratio any further. The EOM and PAH contents of the pre-heated soils sampled at different times after the treatment application (1 h, 24 h and one week) showed that most of the decrease occurred during the first hour following KMnO_4 addition and kept going until the end of the experiment (Fig. 2). In the gas plant and wood-treating facility soils the EOM proportion decreased more slowly and in a lesser extent than the PAH proportion whereas the opposite was true for the coking plant soil.

Table 2: Soil and of solvent-extracted soil specific areas (\pm SD) and the proportion of area occupied by extractable organic matter (EOM).

Samples	Specific area (m^2/g)
Coking plant soil	9.8 ± 0.2
Extracted coking plant soil	12.8 ± 0.2
EOM surface ^a	23%
Gas plant soil	4.6 ± 0.3
Extracted gas plant soil	9.2 ± 0.2
EOM surface ^a	50%
Wood treating facility soil	2.1 ± 0.4
Extracted wood treating facility soil	5.5 ± 0.3
EOM surface ^a	62%

^a Proportion of the specific area occupied by the EOM calculated by difference in the specific area between the non extracted and the extracted samples

3.3.2. Hydrogen peroxide (H_2O_2)

The coking plant soil EOM remained stable after H_2O_2 application (Fig. 1) whereas the pre-heating induced a 25% decrease. The gas plant soil exhibited the highest EOM decrease with 67% and 87% for the unheated and the pre-heated samples, respectively. In the wood-treating facility soil H_2O_2 caused only a minor decrease in the EOM contents (7%) which was slightly enhanced by the pre-heating (9%). The evolution of the PAH content in the coking plant soil showed the same pattern as the EOM (Table 4, Fig. S3). It remained steady after the H_2O_2 application and the pre-heating allowed 18% of PAH degradation with no discrimination between LMW and HMW PAHs, as attested by the steady LMW/HMW ratio (Table 4). The PAH evolution was also similar to the EOM in the gas plant soil after

H₂O₂ application with 89% and 92% of PAH decrease in the unheated and the pre-heated soil, respectively. For the wood-treating facility soil, the PAH diminution was much higher than the EOM and was about the same range for the unheated and the pre-heated samples (53% and 49%, respectively). Most of the PAH and EOM decrease occurred during the first hour following the H₂O₂ addition (Fig. 3) in the coking plant and the wood-treating facility pre-heated soils. On the contrary, the decrease in EOM and PAH proportions continued until the end of the experiment for the gas plant soil. As with the KMnO₄, the diminution of the PAH proportion was faster and more extended than the decrease in EOM proportions in both gas plant and wood-treating facility soils, unlike the coking plant soil where the decrease in PAH proportion was slower and less extended than the EOM diminution.

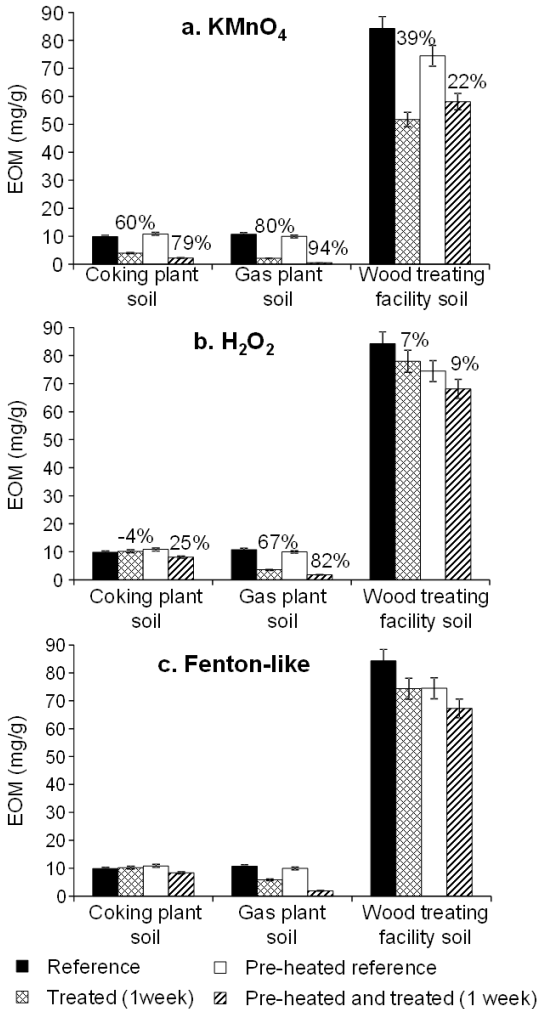


Figure 1: Extractable organic matter (EOM) content for the references (one week in water) and samples treated with (a) KMnO₄, (b) H₂O₂ and (c) Fenton-like (one week), with/without pre-heating (±SD; percentages correspond to the EOM decrease rate after the treatments compared to the reference counterparts)

Table 3: Soil PAH concentrations in the reference (H₂O for one week) and one week after KMnO₄ application, with (PH)/without pre-heating (n.d.: not detected).

(µg/g)	Coking plant soil				Gas plant soil				Wood treating facility			
	Reference	KMnO ₄	PH reference	PH KMnO ₄	Reference	KMnO ₄	PH reference	PH KMnO ₄	Reference	KMnO ₄	PH reference	PH KMnO ₄
Naphthalene	24	21	21	17	11	5.4	19	5.7	4.6	6.3	3.4	5.0
Acenaphthylene	23	7.8	17	4.0	37	4.7	17	1.6	58	30	31	28
Acenaphthene	21	9.4	22	5.4	9.8	n.d.	11	n.d.	110	n.d.	46	0.8
Fluorene	15	5.5	13	3.5	11	0.4	50	0.7	100	0.9	58	4.7
Phenanthrene	61	47	85	33	31	25	320	8.7	640	390	310	220
Anthracene	24	10	23	6.8	57	7.0	69	5.0	170	100	150	100
Fluoranthene	150	85	170	59	390	47	330	13	6300	3200	6400	2900
Pyrene	120	56	120	34	310	24	240	6.2	4600	1100	4400	1000
Benz[<i>a</i>]anthracene	85	33	91	18	150	11	110	4.1	51	35	51	34
Chrysene	70	34	71	26	99	15	84	3.9	51	47	43	50
Benzo[<i>b</i>]fluoranthene	110	59	130	35	100	20	97	4.4	27	27	23	29
Benzo[<i>k</i>]fluoranthene	47	28	56	18	64	9.2	45	1.0	6.5	4.6	5.8	4.9
Benzo[<i>a</i>]pyrene	79	19	72	7.4	110	7.2	87	3.4	16	n.d.	16	17
Dibenz[<i>a,h</i>]anthracene	18	8.5	21	4.6	16	2.6	13	0.6	n.d.	n.d.	n.d.	n.d.
Indeno[1,2,3- <i>cd</i>]pyrene	94	39	98	24	79	11	65	2.1	n.d.	n.d.	n.d.	n.d.
Benzo[<i>ghi</i>]perylene	71	30	74	20	68	8.9	56	1.7	n.d.	n.d.	n.d.	n.d.
Σ 16 PAHs ^a	1012	492	1084	316	1543	198	1613	62	12134	4940	11537	4393
LMW/HMW ^b	0.8	1.0	0.8	1.1	1.2	1.3	1.9	1.9	79	42	82	32
PAH decrease (%)		51		71		87		96		59		62

^a Σ 16 PAHs: Sum of the concentrations of the 16 PAHs listed by the US-EPA as priority pollutants

^b 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)

Table 4: Soil PAH concentrations in the reference (H₂O for one week) and one week after H₂O₂ application, with (PH)/without pre-heating (n.d.: not detected).

(µg/g)	Coking plant soil				Gas plant soil				Wood treating facility			
	Reference	H ₂ O ₂	PH	PH	Reference	H ₂ O ₂	PH	PH	Reference	H ₂ O ₂	PH	PH
			reference	H ₂ O ₂			reference	H ₂ O ₂			reference	H ₂ O ₂
Naphthalene	24	31	21	21	11	2.4	19	7.3	4.6	4.7	3.4	3.4
Acenaphthylene	23	26	17	15	37	8.0	17	3.3	58	46	31	29
Acenaphthene	21	24	22	15	9.8	n.d.	11	0.5	110	21	46	20
Fluorene	15	19	13	11	11	2.1	50	4.2	100	39	58	30
Phenanthrene	61	87	85	80	31	19	320	24	640	550	310	520
Anthracene	24	25	23	18	57	5.8	69	7.1	170	120	150	100
Fluoranthene	150	160	170	140	390	32	330	21	6300	3000	6400	3100
Pyrene	120	140	120	110	310	19	240	15	4600	1800	4400	1900
Benz[<i>a</i>]anthracene	85	89	91	69	150	13	110	7.6	51	46	51	42
Chrysene	70	70	71	59	99	11	84	6.2	51	46	43	45
Benzo[<i>b</i>]fluoranthene	110	86	130	98	100	16	97	7.9	27	24	23	26
Benzo[<i>k</i>]fluoranthene	47	54	56	46	64	6.6	45	3.0	6.5	4.7	5.8	5.9
Benzo[<i>a</i>]pyrene	79	78	72	55	110	11	87	6.1	16	14	16	14
Dibenz[<i>a,h</i>]anthracene	18	19	21	16	16	2.3	13	1.1	n.d.	n.d.	n.d.	n.d.
Indeno[1,2,3- <i>cd</i>]pyrene	94	86	98	73	79	12	65	5.1	n.d.	n.d.	n.d.	n.d.
Benzo[<i>ghi</i>]perylene	71	73	74	59	68	9.8	56	4.3	n.d.	n.d.	n.d.	n.d.
Σ 16 PAHs ^a	1012	1067	1084	885	1543	170	1613	124	12134	5715	11537	5835
LMW/HMW ^b	0.8	0.9	0.8	0.8	1.2	1.1	1.9	2.0	79	41	82	43
PAH decrease (%)		0		18		89		92		53		49

^a Σ 16 PAHs: Sum of the concentrations of the 16 PAHs listed by the US-EPA as priority pollutants

^b 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*]pérylène)

Table 5: Soil PAH concentrations in the reference (H₂O for one week) and one week after Fenton-like treatment, with (PH)/without pre-heating (n.d.: not detected).

(µg/g)	Coking plant soil				Gas plant soil				Wood treating facility			
	Reference	Fenton-like	PH		Reference	Fenton-like	PH		Reference	Fenton-like	PH	
			reference	Fenton-like			reference	Fenton-like			reference	Fenton-like
Naphthalene	24	28	21	25	11	5.9	19	7.4	4.6	5.3	3.4	4.3
Acenaphthylene	23	27	17	16	37	16	17	3.6	58	48	31	31
Acenaphthene	21	25	22	18	9.8	1.5	11	0.8	110	36	46	30
Fluorene	15	19	13	11	11	5.0	50	4.1	100	53	58	38
Phenanthrene	61	86	85	77	31	45	320	24	640	600	310	550
Anthracene	24	27	23	19	57	10	69	7.0	170	120	150	100
Fluoranthene	150	160	170	140	390	65	330	21	6300	3200	6400	3000
Pyrene	120	130	120	110	310	38	240	15	4600	2100	4400	1900
Benz[<i>a</i>]anthracene	85	86	91	71	150	24	110	7.3	51	45	51	44
Chrysene	70	69	71	64	99	23	84	6.1	51	46	43	48
Benzo[<i>b</i>]fluoranthene	110	100	130	91	100	30	97	7.7	27	27	23	25
Benzo[<i>k</i>]fluoranthene	47	51	56	41	64	13	45	2.8	6.5	5.2	5.8	5.6
Benzo[<i>a</i>]pyrene	79	78	72	48	110	18	87	6.2	16	16	16	15
Dibenz[<i>a,h</i>]anthracene	18	18	21	15	16	4.1	13	1.1	n.d.	n.d.	n.d.	n.d.
Indeno[1,2,3- <i>cd</i>]pyrene	94	82	98	69	79	21	65	5.1	n.d.	n.d.	n.d.	n.d.
Benzo[<i>ghi</i>]perylene	71	67	74	54	68	17	56	4.2	n.d.	n.d.	n.d.	n.d.
Σ 16 PAHs ^a	1012	1053	1084	869	1543	337	1613	123	12134	6302	11537	5791
LMW/HMW ^b	0.8	0.9	0.8	0.9	1.2	1.2	1.9	2.0	79	44	82	41
PAH decrease (%)		0		20		78		92		48		50

^a Σ 16 PAHs: Sum of the concentrations of the 16 PAHs listed by the US-EPA as priority pollutants

^b 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)

3.3.3. Fenton-like (H_2O_2 + magnetite)

The EOM evolution after the Fenton-like treatment was very similar to the one observed with H_2O_2 (Fig. 1). The coking plant soil EOM content did not decrease except when the sample was pre-heated. Overall, the EOM diminution was always higher when the soils were pre-heated. The gas plant soil was the most affected by the Fenton-like treatment (<80% of EOM decrease). The evolution of the PAH content and distribution was also similar to the one observed after H_2O_2 addition (Table 5, Fig.S4). No decrease in PAH content was observed for the coking plant soil, unless the sample was pre-heated (20% decrease). The unheated and pre-heated gas plant soils showed the highest degradation rates (78% and 92%, respectively). The PAH degradation rates reached 49% and 50%, for the unheated and pre-heated wood-treating facility soils, respectively. A decrease in the LMW/HMW ratio of this sample indicated a preferential degradation of LMW compounds (i.e. pyrene and fluoranthene; Table 5). The evolution of EOM and PAH proportions during the Fenton-like treatment of the pre-heated soils were similar to those observed during H_2O_2 treatment (Fig. 4). For the coking and gas plant soils, most of the degradation occurred during the first hour following the reagent addition. For the gas plant soil, the proportion of remaining PAHs was lower than the EOM proportion whereas, for the coking plant soil, both were about the same range. The gas plant soil, who showed the highest EOM and PAH degradation rates, exhibited a more important and faster PAH decrease compared to EOM, and the diminution of the EOM and PAH contents kept occurring until the end of the experiment (Fig. 4).

4. Discussion

4.1. Chemical oxidation treatment and evaluation of PAH availability

4.1.1. Differences in contamination distribution

As mentioned previously, three soils presenting various properties (EOM and PAH contents and distributions) were selected because they represented various sites highly impacted by PAH contamination. The coking and gas plant soils presented similar values for the PAH and EOM contents but different PAH distributions, the PAH coking plant soil being dominated by higher molecular weight

compounds than the gas plant soil. These disparities could be an indication of different soil histories. First, the composition of the original contamination could be responsible for the difference in PAH distribution. Second, the presence of higher molecular weight PAHs in the coking plant soil than in the gas plant soil may be explained by a more advanced level of weathering. Indeed, due to differences in their physicochemical properties, LMW compounds are known to be preferentially affected by evaporation, water-washing and biodegradation compared to HMW PAHs [34–36]. The difference in LMW/HMW PAH ratios between the coking and the gas plant soils (0.9 and 2.3, respectively) support this hypothesis. The contamination of the wood-treating facility soil was much higher than for the other soils as the PAH contents were 7 and 10 higher than in the gas and the coking plant soils, respectively. This contamination can be considered as fresh since the wood-treating site is still on activity.

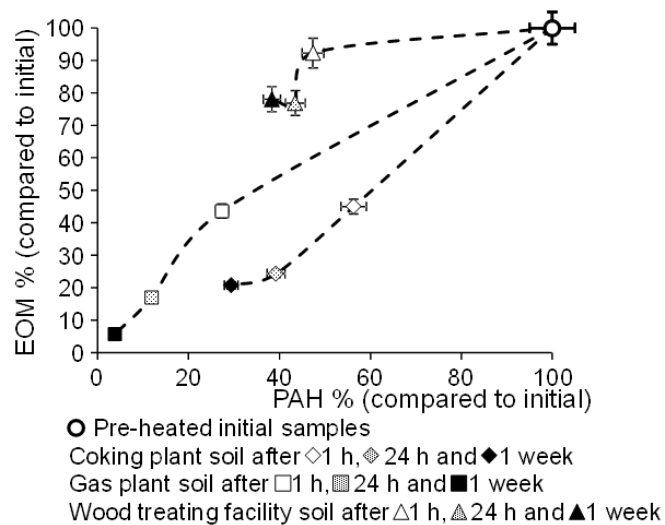


Figure 2: Extractable organic matter (EOM) and PAH proportions related to the initial samples 1, 24 h and one week after KMnO_4 addition in the pre-heated soils (\pm SD)

4.1.2. Responses to H_2O_2 and Fenton-like treatments

Due to the higher oxidation potential of OH compared to H_2O_2 (2.7 V and 1.8 V, respectively), the Fenton-like treatment was expected to induce higher degradation rate than the H_2O_2 . However, the soil responses to both treatments were very similar. Several studies aiming to compare the efficiency

of H₂O and Fenton or Fenton-like treatments to degrade PAHs [18,37] point out similar observation i.e. ferrous iron addition has no significant impact on the PAH degradation with H₂O₂. In addition to H₂O₂, magnetite was used in the Fenton-like treatment as a catalyst to generate the radicals involved in the oxidation reaction and to increase the reaction kinetic [17,20,38]. It is known that other minerals occurring naturally in soil (e.g., magnetite, hematite, goethite, and ferrihydrite) are able to catalyze radical formation [39] and therefore initiate Fenton-like reactions. Indeed Petigara et al. [40] studied O₂ and OH production after H₂O₂ application in soils and suggest that organic constituent oxidation with H₂O₂ in soils primarily involves OH reaction rather than peroxidic reactions. Indigenous iron oxides or other metal oxides could participate to initiate Fenton-like reaction in the studied soils explaining why the H₂O₂ alone was as efficient as the Fenton-like treatment to degrade EOM and PAHs.

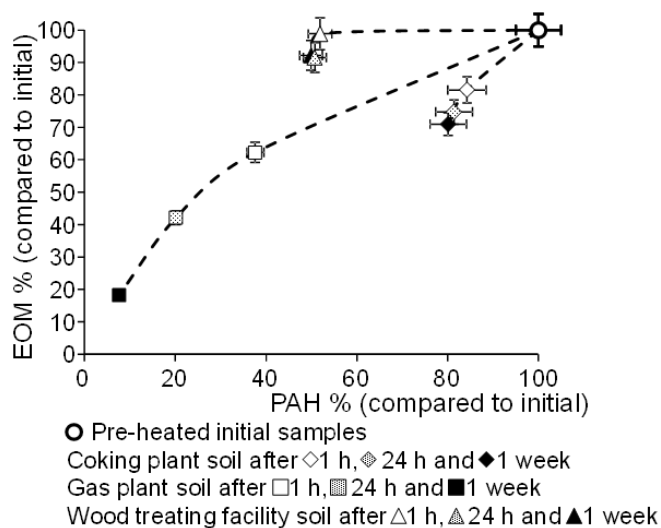


Figure 3: Extractable organic matter (EOM) and PAH proportions related to the initial samples 1, 24 h and one week after H₂O₂ application in the pre-heated soils (\pm SD)

Both H₂O₂ and Fenton-like treatments were very efficient to decrease the PAH concentrations in the gas plant soil but showed less efficiency for the other samples, especially for the coking plant soil. One explanation could be differences in soil structure and contamination repartition. Indeed, the coking plant soil presented higher specific area than the gas plant and the wood-treating facility soils. However, the EOM containing the contamination occupied 23% of this area which is lower than the

gas plant soil (50%). These proportions give indications on the contaminant repartition in soils, impacting the contaminant accessibility toward the oxidant. The higher the surface occupied by the contamination, the higher the surface contact between the oxidant and the contaminant and the higher the probability for the oxidant to react with it. These differences can then explain the higher treatment efficiency for the gas plant soil than for the coking plant soil and be directly related to the contamination (chemo)availability. The poor PAH availability in the coking plant soil was underlined in several studies [23,24,41–43]. It has been shown that Fenton treatment efficiency is correlated to the matrix characteristics but also to the PAH availability, in regard to the age and level of contamination [37,44]. Indeed, artificially spiked PAHs are more easily oxidized than PAHs from historically contaminated sites [24] due to increasing sorption strength and binding over time [45]. The difference in degradation rate during Fenton-like and H₂O₂ treatments between the coking and the gas plant soils was likely due to a decrease in extractability and availability of contaminants with increasing sequestration into the soil during aging.

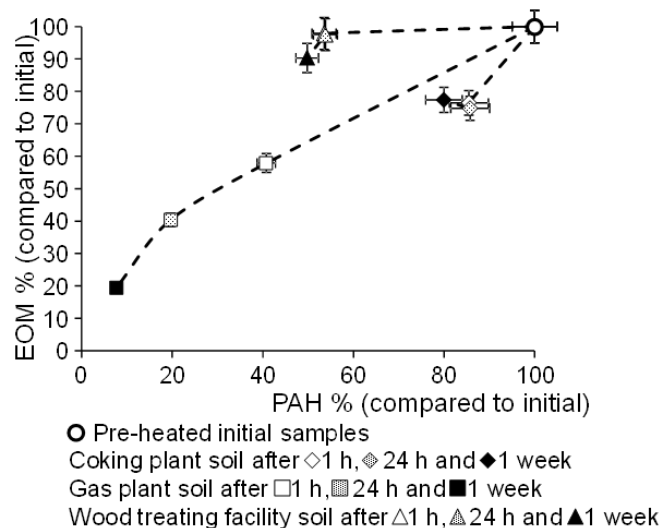


Figure 4: Extractable organic matter (EOM) and PAH proportions related to the initial samples 1, 24 h and one week after Fenton-like treatment of the pre-heated soils (\pm SD)

The wood-treating facility soil showed about 50% of PAH degradation after H₂O₂ and Fenton-like oxidations. However, in this case the treatment efficiency was not related to PAH availability since the

contamination was fresh and biodegradation experiments were proven to effectively reduce PAH concentration of about 96% [46]. The PAH concentrations in the wood-treating soil being much higher than in the other soils, it seems that the PAH degradation limitation was rather related to the oxidant dose. Indeed, from calculations based on Lemaire et al. [47] the H₂O₂ amount added to the wood-treating facility soil corresponded to 11.73 times the stoichiometric oxidant demand (SOD) based only on the PAH concentrations. This value did not take into account the presence and concentrations of other organic compounds that could possibly react with the oxidant. This value was much higher for the other soil samples (158 and 249 for the gas and coking plant soils, respectively) due to lower PAH contents and same oxidant doses.

The PAH and EOM decrease rates in the coking plant soil after H₂O₂ and Fenton-like treatments were similar whereas the PAH decrease rates were much higher than the diminution of the EOM proportion in the gas plant and wood-treating facility soils. These observations underlined a selectivity in compound degradation after H₂O₂ and Fenton-like treatments in the latter soils. The published results concerning the influence of OM on H₂O₂ and Fenton-like treatment efficiency are opposing. Overall, the OM content is negatively correlated with the treatment efficiency to degrade PAHs due to a competition between PAHs and other organics [18,20,40]. However, Bogan and Trbovic [48] studied the effect of Fenton oxidation on soils spiked with coal tar and presenting various OM and TOC contents. They show that the oxidation efficiency for PAH removal was limited for soils presenting low OM content (TOC < 5%) but PAH degradation was much higher in soils rich in OM. The type of OM seems to be a more relevant factor than its content to explain these contradictions [48]. The coking plant soil presented a much lower pMC (Table 1) than the other samples and consequently a higher proportion of fossil carbon [33] i.e. that underwent diagenesis process. Bogan and Trbovic [48] underlined that contamination associated with OM exposed to diagenesis alteration is more refractory than contamination associated with recent OM. The fact that the gas plant and the wood-treating facility soils presented higher pMC than the coking plant soil, and consequently more recent OM, could then explain the selectivity in PAH degradation observed for the former soils.

4.1.3. Response to the KMnO₄ treatment

Unlike H₂O₂ and Fenton-like, the KMnO₄ treatment was very efficient to decrease the PAH concentrations in both gas and coking plant soils. As previously underlined, both soils presented very similar EOM and PAH contents but differences in PAH availability explaining the disparities in the H₂O₂ treatment efficiency. However, this parameter did not affect the KMnO₄ treatment efficiency in removing PAHs. A previous study [47] has already underlined the high efficiency of KMnO₄ to degrade PAHs in aged contaminated soils. When comparing PAH and EOM degradation rates after the KMnO₄ treatment, it appeared that the degradation rates were about the same for the coking and the gas plant soils whereas the proportion of degraded PAHs was much higher than the degraded EOM in the wood-treating facility soil, showing a selectivity of the oxidant for the contamination.

4.2. Effect of the pre-heating on the treatment efficiency

4.2.1. Dose limitation

According to the soil specificities and whatever the chemical treatment applied, two different behaviors in response to the pre-heating can be distinguished. The pre-heating induced an increase in the PAH and EOM abatements for the coking and gas plant soils whereas the effect of the pre-heating was very limited for the wood-treating facility soil. As previously mentioned, the treatment efficiency for this sample was related to dose limitation rather than accessibility constrain (cf. 4.1.2). The pre-heating did not induce any improvement in the treatment efficiency since the oxidant doses were too low to degrade all the accessible fraction of the contamination. This dose constrain was also visible on the PAH and EOM degradation kinetics as most of the decrease occurred during the first hour following the treatment application on the wood-treating facility soil, whatever the chemical oxidant used.

4.2.2. H₂O₂ and Fenton-like treatments: influence of the chemo-availability

For the coking and gas plant soils, differences in the H₂O₂ and Fenton-like treatment efficiency were already pointed out. The pre-heating treatment had a marked effect for both soils with an increase in PAH and EOM removal. Differences between these soils can be observed on the degradation kinetics,

PAHs and EOM being degraded until the end of the experiment (one week) for the gas plant soil whereas most of the degradation occurred during the first hour following the treatment application for the coking plant soil. For the latter, the limited accessibility of the contamination for the H₂O₂-based treatment was already underlined [37,44] since the PAH availability was extremely low. The pre-heating allowed degrading about 20% of PAHs with H₂O₂ and Fenton-like treatments whereas no degradation was observed without it. The pre-heating induced a remobilization of the contamination, likely through a change in the PAH sorption sites. However, even if improved, the availability remained limited. For the gas plant soil there was much less limitation in the PAH availability however, the pre-heating also improved the degradation.

4.2.3. KMnO₄ treatment

For all the soils, KMnO₄ showed the highest efficiency compared to the other treatments. As shown by the degradation kinetics and contrary to the other treatments, the PAH degradation in the coking plant soil continued until the end of the experiment. As under-lined by Lemaire et al. [47], MnO₄⁻ tend to persist in the soil after the treatment application explaining the better efficiency and the longer action duration. The pre-heating also induced better treatment efficiencies even if they seemed less constrained by the PAH availability, as shown by the high degradation rate in the coking plant soil.

5. Conclusion

In this study, several oxidation treatments were investigated as way to determine PAH availability in contaminated soils presenting various specificities. A pre-heating was applied to the soils, prior chemical oxidations, to improve the PAH availability. H₂O₂-based treatment (including Fenton-like) efficiency happened to be more sensitive to the PAH accessibility and availability. Therefore H₂O₂ and Fenton-like treatments seemed to be valid methods to estimate the PAH availability, unlike the KMnO₄ treatment which was very efficient to degrade PAHs even in samples presenting low contamination availability.

The pre-heating has proven to be efficient to increase the contamination availability as the treatment efficiencies were enhanced by heating the sample at 100°C for one week under N₂ prior the oxidant application.

In this study, only the listed PAHs were taken into account, however, it is known that chemical oxidation leads to the formation of oxygenated species [22,28] presenting the same toxic and carcinogenic properties than parent-PAHs [49] but higher solubility, hence an increased mobility, due to the presence of oxygenated moieties [50,51]. Since these treatments are commonly used to remediate contaminated matrixes, this statement underlines the importance of dealing with this aspect inherent to the application of chemical oxidation treatments. This question is currently investigated and will be addressed as another part of this project.

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Supplementary Data

Effect of pre-heating on the chemical oxidation efficiency: implications for the PAH availability measurement in contaminated soils

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GC-MS analyses for PAH quantification	S2
Table S1: PAH names and corresponding abbreviations used in the following Figures	S3
Figure S1: PAH content for the references (one week in water) and samples treated with (a) KMnO ₄ , (b) H ₂ O ₂ and (c) Fenton-like (one week), with/without pre-heating (±SD; percentages correspond to the EOM decrease rate after the treatments compared to the reference counterparts).....	S4
Figure S2: 16 PAH concentrations in (a.) the coking plant, (b.) the gas plant and (c.) the wood-treating facility soils, for the references and the KMnO ₄ treated, unheated and pre-heated samples (± STD). S5	
Figure S3: 16 PAH concentrations in (a.) the coking plant, (b.) the gas plant and (c.) the wood-treating facility soils, for the references and the H ₂ O ₂ treated, unheated and pre-heated samples (± STD)	S6
Figure S4: 16 PAH concentrations in (a.) the coking plant, (b.) the gas plant and (c.) the wood-treating facility soils, for the references and the Fenton-like treated, unheated and pre-heated samples (± STD)	S7

GC-MS analyses for PAH quantification

Quantification of the 16 listed PAHs (Table S1) was carried out using internal calibration. An internal PAH standard mix of [²H₈]naphthalene, [²H₁₀]acenaphthene, [²H₁₀]phenanthrene, [²H₁₂]chrysene, [²H₁₂]perylene, supplied by Cluzeau® (20 µL at 16 µg/mL) was added to the EOM (80 µL) before being injected in a gas chromatograph coupled with a mass spectrometer (GC-MS). For each quantified compound (Table S1), calibration curve was drawn with six concentrations (0.3, 0.9, 1.5, 3, 6 and 9 µg/mL). The gas chromatograph was a Shimadzu GC-2010 plus, equipped with a capillary column in silica glass DB-5MS (60 m × 0.25 mm i.d. × 0.1 µm film thickness) coupled to a QP2010-Ultra (Shimadzu) MS in fullscan mode 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 then a 15 min hold at 315 °C. The carrier gas was helium at 1.4 mL/min constant flow.

Table S1: PAH names and corresponding abbreviations used in the following Figures

Name	Abbreviation
Naphthalene	Na
Acenaphthylene	Acy
Acenaphthene	Ace
Fluorene	Fl
Phenanthrene	Phe
Anthracene	An
Fluoranthene	Fluo
Pyrene	Py
Benz[<i>a</i>]anthracene	BaA
Chrysene	Chry
Benzo[<i>b</i>]fluoranthene	BbF
Benzo[<i>k</i>]fluoranthene	BkF
Benz[<i>a</i>]pyrene	BaP
Indeno[1,2,3- <i>cd</i>]pyrene	IP
Benzo[<i>ghi</i>]perylene	BghiP
Dibenzo[<i>a,h</i>]anthracene	DBahA

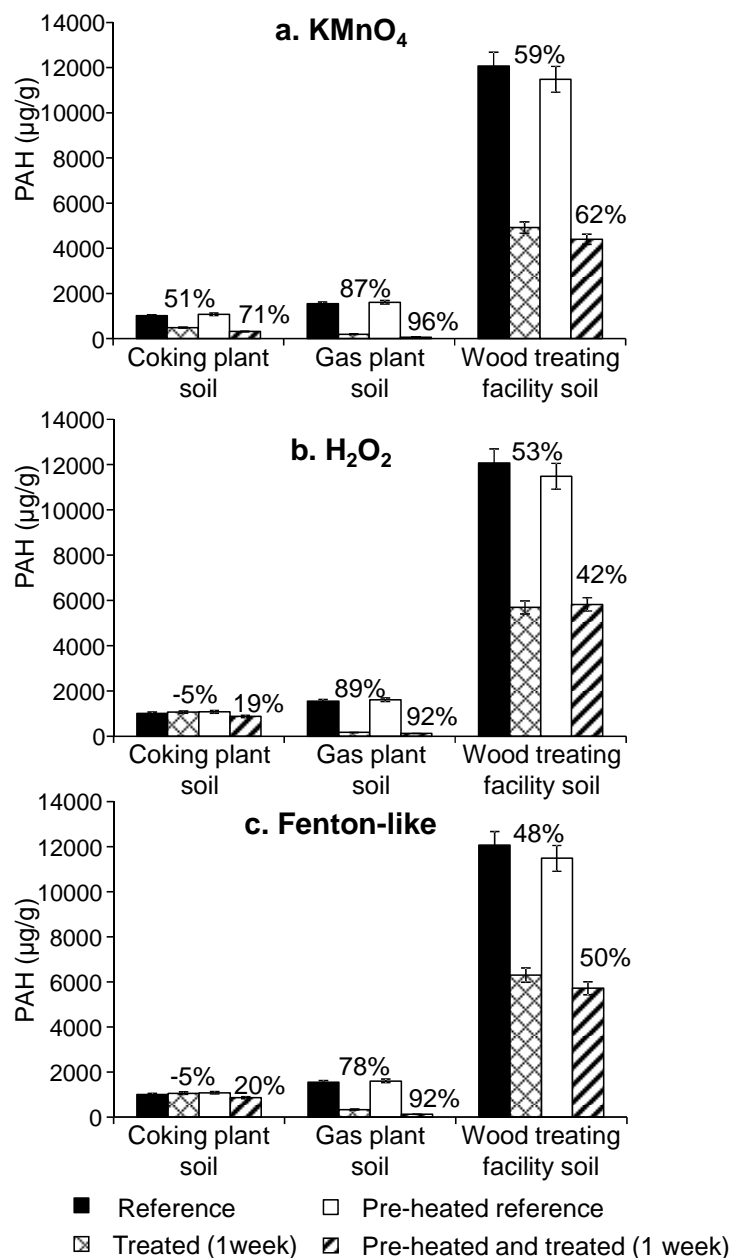


Figure S1: PAH content for the references (one week in water) and samples treated with (a) KMnO_4 , (b) H_2O_2 and (c) Fenton-like (one week), with/without pre-heating (\pm SD; percentages correspond to the EOM decrease rate after the treatments compared to the reference counterparts)

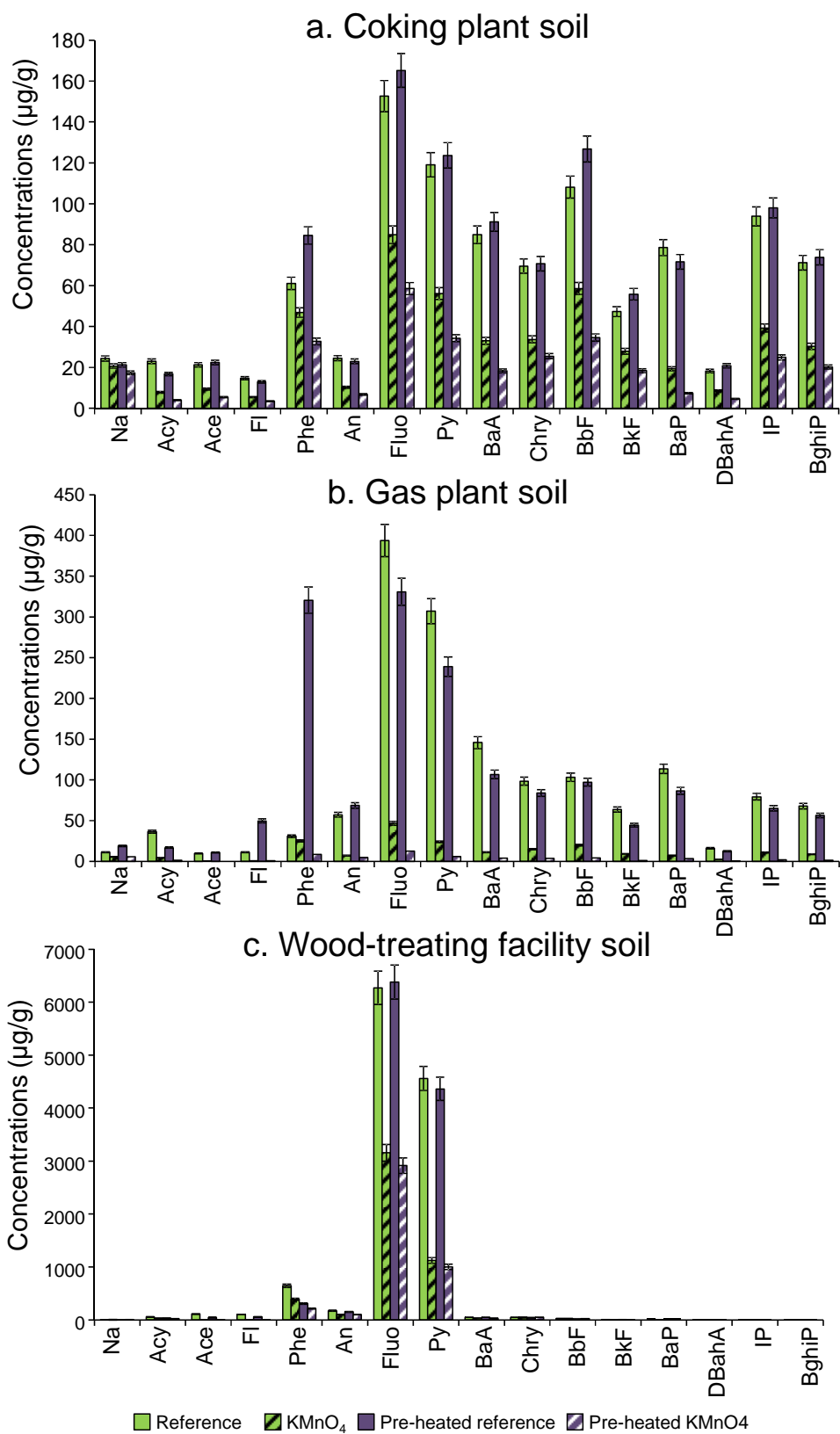


Figure S2: 16 PAH concentrations in (a.) the coking plant, (b.) the gas plant and (c.) the wood-treating facility soils, for the references and the KMnO₄ treated, unheated and pre-heated samples (\pm STD)

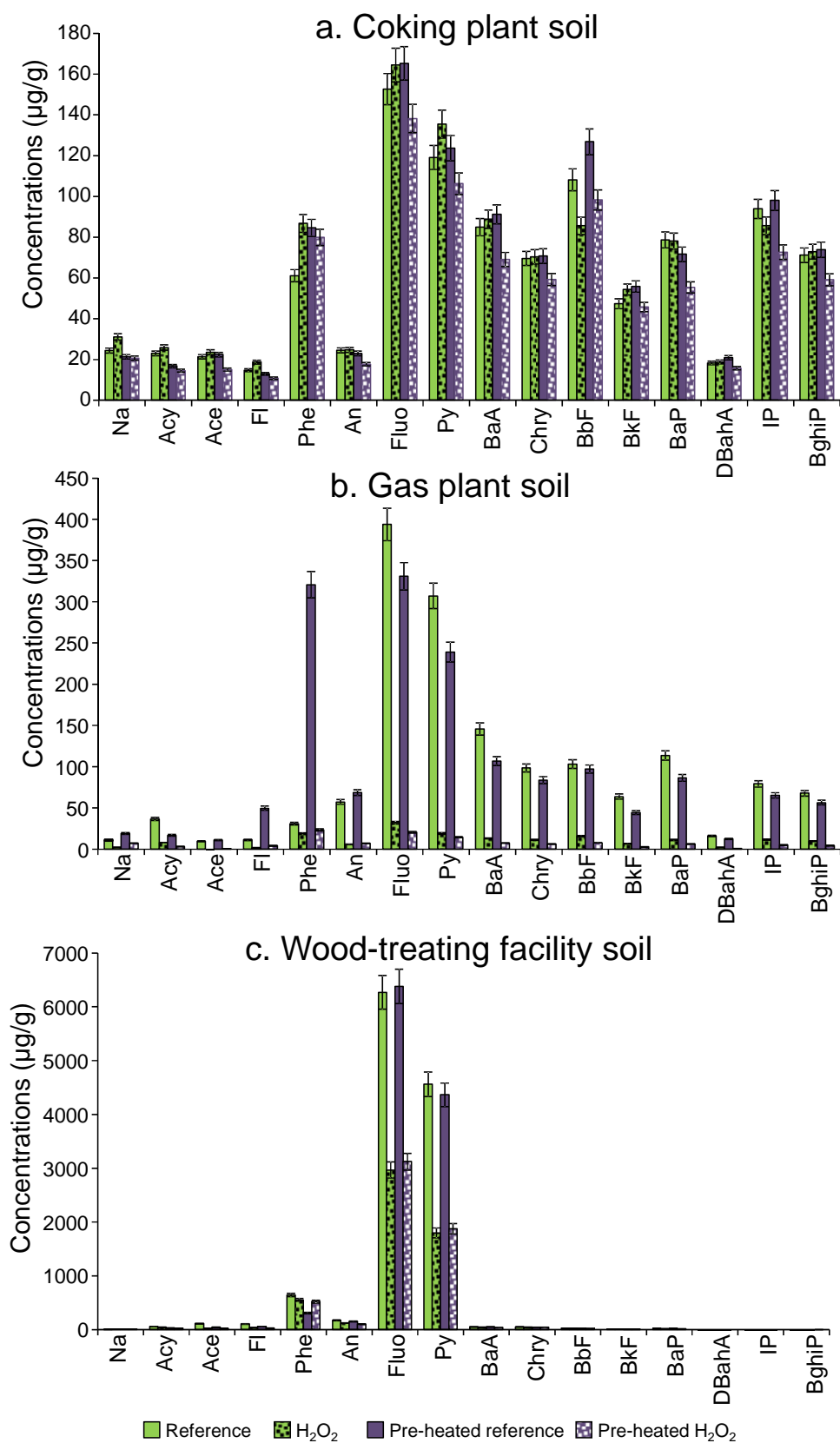


Figure S3: 16 PAH concentrations in (a.) the coking plant, (b.) the gas plant and (c.) the wood-treating facility soils, for the references and the H₂O₂ treated, unheated and pre-heated samples (\pm STD)

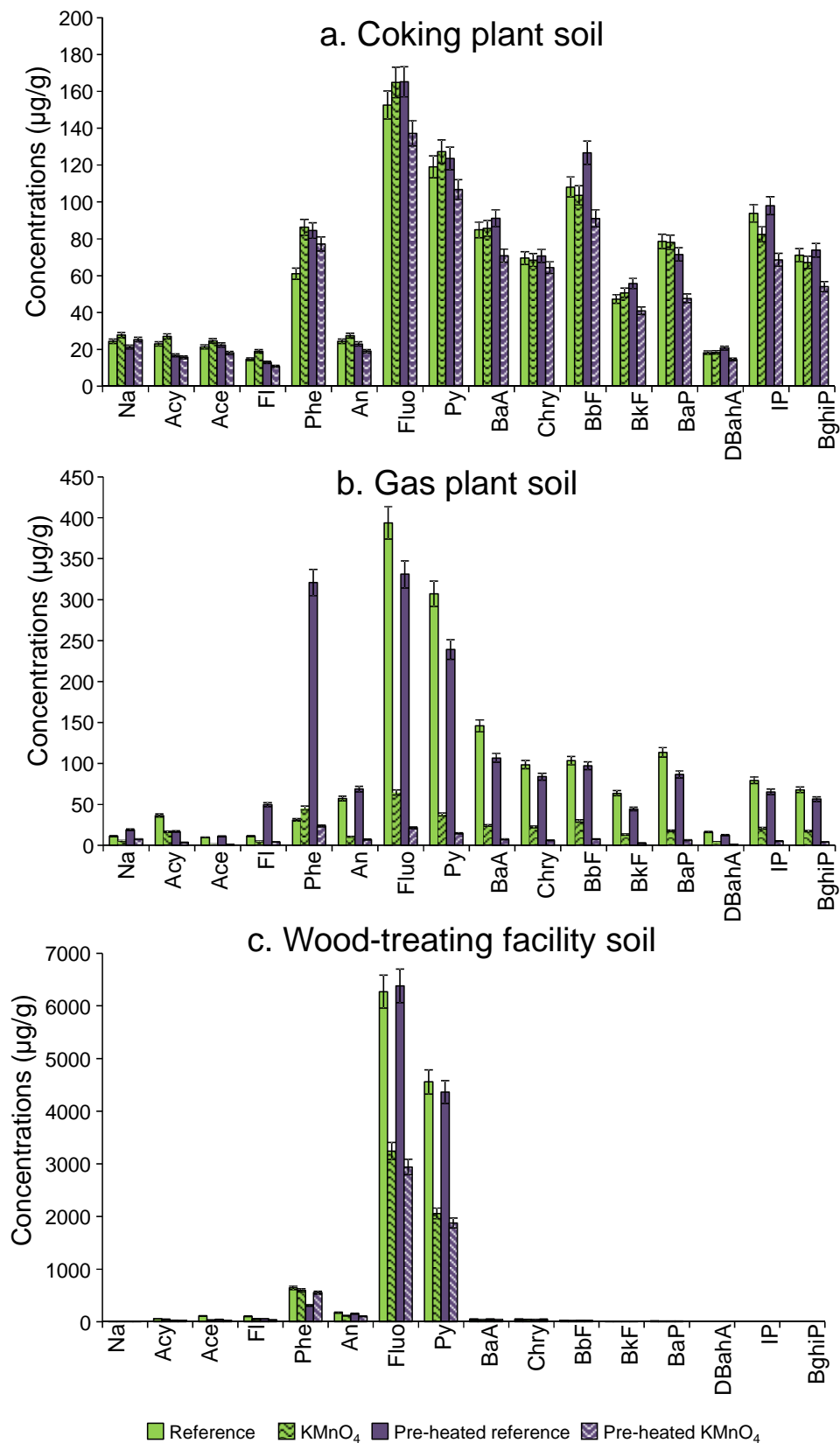


Figure S4: 16 PAH concentrations in (a.) the coking plant, (b.) the gas plant and (c.) the wood-treating facility soils, for the references and the Fenton-like treated, unheated and pre-heated samples (\pm STD)