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Chemical oxidation efficiency for aged, PAH-contaminated sites: an investigation of limiting factors

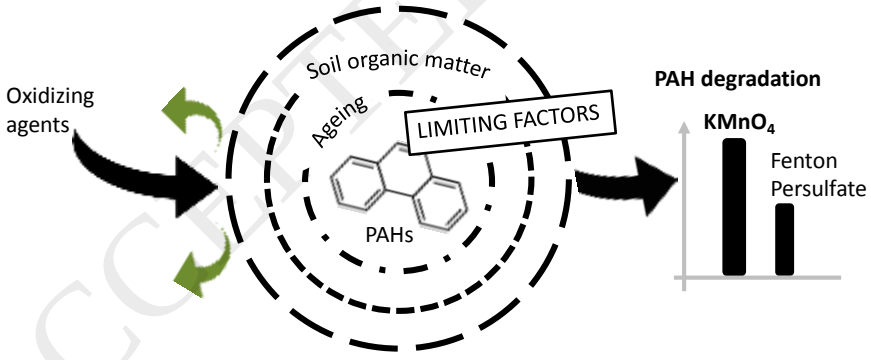
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graphical abstract



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Highlights

- Investigation of the factors limiting PAH degradation in soils during oxidation.
- Permanganate was the most effective oxidant.
- Permanganate oxidation: correlation between PAH degradation and availability.
- Radical oxidation: sequential addition is better than single addition.
- Type/age of soil organic matter and carbonate content influence PAH oxidation.

Abstract

In Situ Chemical Oxidation (ISCO) can be applied to soils contaminated by polyaromatic hydrocarbons (PAHs). PAH degradation yields are often rather low, because of different obstacles not clearly understood. These include the low availability of PAHs, the type and age of soil organic matter and the carbonate content of the soil. The aim of this work was to provide a better understanding of the influence of these limiting factors at a given oxidant dose. Batch experiments were performed on contrasted PAH-contaminated soils or matrices using permanganate, persulfate, modified Fenton's reagent and activated persulfate. PAH availability was estimated by a cyclodextrin-enhanced extraction method. Moderate amounts of oxidant were used in order to lower costs whilst minimizing environmental impacts. Results showed that chemical oxidation efficiency was mainly affected by PAH availability, particularly with low persistent oxidant. With permanganate, a correlation was found between PAH availability and degradation yield. With low persistent oxidants, degradation yields were significantly increased by sequential addition. The negative impacts of a high content of soil organic matter and/or carbonate were highlighted. For the aged contaminated soils, PAH degradation yields remained below 30% after most treatments except with permanganate (40-60%) and sequential addition of Fenton's reagent (40-70%). These results should have useful implications for the design of ISCO treatments.

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Keywords: PAHs; aged contaminated soil; availability; in situ chemical oxidation; limiting factors

1. Introduction

Huge areas of industrial and urban soils are contaminated with polycyclic aromatic hydrocarbons (PAHs), whose content may reach up to a few tens of thousands of mg kg^{-1} in brownfields of ancient steel making or coking plants [1]. These pollutants represent a threat for human health because of their recognized carcinogenic and mutagenic effect [2]. Despite the high PAH diversity encountered in soils, only the 16 PAHs listed by the US Environmental Protection Agency (USEPA) are considered. Most of these neutral, non-polar and hydrophobic molecules are poorly soluble in water, poorly volatile and tend to sorb onto soil organic matter (SOM) [3].

Highly contaminated soils are commonly excavated and treated by thermal desorption, whereas lower contaminated soils (< 1 g_{PAH} $kg^{-1}_{dry\ soil}$) are generally left for natural attenuation or treated by monitored biological treatments [4]. PAH bioremediation is usually quite a long process and can be incomplete because of low PAH availability and recalcitrance especially for higher molecular mass PAHs [5-8].

In situ chemical oxidation (ISCO), widely applied to treat groundwater and saturated zone contaminated by chlorinated organic compounds, has also been investigated to remediate PAH-contaminated soils [9-13]. This method aims at degrading pollutants by injecting an oxidant (e.g. permanganate, Fenton's reagent, ozone, persulfate) into groundwater or soil without excavation. Its efficiency strongly depends on the contact between oxidant and contaminants that can be affected by the low availability of contaminants, the short life of some

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oxidants and the high soil oxidant demand. In the case of aged contaminated soils, PAHs can be strongly sorbed to natural and anthropogenic (coal and coke) soil organic matter and sequestrated in complex soil structures [6, 14-17]. Moreover, high SOM content can consume much oxidant. Consequently, ISCO may not be appropriate in some situations depending on soil characteristics [7, 18]. For this reason, a feasibility study is generally required on a case-by-case basis. Furthermore, ISCO is often integrated with other technologies such as biological treatment to achieve the clean-up objectives [9, 10, 19].

The aim of the present contribution is to bring some understanding of the influences of PAH content, availability and structure (number of cycles) and some soil properties (organic matter content, carbonate content and pH) on oxidation efficiency. To achieve this goal, nine contrasted contaminated matrices were prepared from Fontainebleau white sand and three soil samples of contrasted pH, organic carbon content and carbonate content. The first two soils had been collected from representative former steel-making brownfields contaminated with a classical mixture of PAHs (mainly 2- to 6-ring) and the third one from an uncontaminated agricultural field [17, 20-22]. These contaminated matrices were treated in the laboratory by batch experiments with four of the most commonly used oxidants: permanganate, persulfate, modified Fenton's reagent and persulfate activated with hydrogen peroxide [13]. Moderate amounts of oxidant were used (i) to be suitable with treatment feasibility at field scale, and (ii) to minimize the environmental impacts on soil functions [23, 24] and thus make soil revegetation possible. This work forms part of the OXYSOL project (http://www.oxysol-anr.org), which aims at combining ISCO, bioremediation and soil construction to restore soils at former metallurgical sites.

2. Materials and methods

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2.1. *Chemicals*

Acetonitrile and methylene chloride (99.8% purity) were supplied by Fischer Scientific and the PAHs standard used in HPLC analysis by Dr Ehrenstorfer (16 USEPA PAHs mix, at 100 mg L^{-1} in acetonitrile). Hydroxypropyl-β-Cyclodextrin (HP-β-CD) was purchased from Molekula. Sodium persulfate (>99%) was supplied by Merck, potassium permanganate (>99%) by Fluka Chemika, Fontainebleau sand by Carlo Erba, hydrogen peroxide (50%), ferrous sulfate heptahydrate Rectapur® and hydrochloric acid (37%) by VWR Prolabo.

2.2. *Soil samples*

Two aged industrial soils contaminated by PAHs and metals (soils TNM and TH) and a non-polluted agricultural soil (soil TCh) were selected. TNM was collected from a former steel-making plant (Neuves-Maisons, France) [17, 22, 24-26]. TH was taken from the upper horizon of a former coking plant (Homécourt, France) [23, 25] and TCh from the A_p horizon of an agricultural Cambisol (Chenevières, France) [20, 21, 23]. Soils were sampled, air-dried at 25 °C and sieved at 2 mm from large volumes excavated, and then homogenized by quartering. The main physico-chemical characteristics (Table 1) have been determined by the *Soil Analyses Laboratory* (Arras, France) following French standards (details given in [22]). All concentrations refer to dry soil.

Except for fine texture (sandy loam), both industrial soils TNM and TH exhibit very different characteristics from the agricultural soil TCh. TNM and TH are slightly alkaline (pHs 7.4 and 9.5, respectively) with high carbonate content (35.7 and 369 g kg^{-1} respectively), whereas TCh is an acidic soil (pH 4.7) with a very low carbonate content (< 1 g kg^{-1}). Moreover, TNM and TH have organic carbon contents 10 times higher than TCh. The latter mostly

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contains natural organic matter whereas TNM and TH mainly contain anthropogenic organic particles derived from coal, coke and coal tars [27]. In these two industrial soils, ^{14}C has been measured to determine the percentage of modern carbon pMC; this represents < 6 % of the total carbon in TNM and TH soils [28, 29] confirming the predominance of fossil organic matter. Importantly, TH and especially TNM, were also contaminated by heavy metals, mainly Zn and Pb, but also Cr, Ni, Cu and Hg, unlike TCh whose metal concentrations were comparable to lower values in regional references [30] (Table 1).

2.3. Preparation of PAH-contaminated matrices

In order to investigate the selected limiting factors, eight contrasting matrices were prepared:

- TNM and TH: correspond to TNM and TH raw soils;
- TNM D and TH D: were prepared from TNM and TH soils, respectively as already applied [15, 16, 31]: the extractable organic matter (EOM), including PAHs, was isolated by methylene chloride extraction and re-added into the corresponding soil, in order to increase PAH availability without any other qualitative or quantitative modifications;
- TCh D and SNM: correspond to the TCh soil sample and Fontainebleau white sand, respectively contaminated with the EOM isolated from TNM soil and added at the same concentration;
- TNM-DC and TH-DC: correspond to TNM and TH, respectively after partial decarbonization. TH and TNM soil samples were mixed with ultra-pure water (20% wt ratio) and 37% concentrated HCl in a glass beaker, at a dose of 0.5 equivalent of HCl

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per equivalent of carbonate (13 and 130 g HCl per kg of dry matrix for TNM and TH, respectively).

In a preliminary step, each sample of soil and sand was ground in a vibratory disc mill, until it could be completely sieved at 500 μm in order to produce homogenous samples.

Extractable organic matter (EOM) was isolated from TNM or TH with methylene chloride by Accelerated Solvent Extraction (ASE, Dionex 350). Two extraction cycles were run at 100 °C and 130 bars for 5 min to extract the EOM.

EOMs were both re-added to their native soil TNM and TH at the same concentrations (10 and 15 mg g^{-1} of dry soil respectively) or, in the case of EOM isolated from TNM, introduced into an uncontaminated matrix (TCh or Fontainebleau sand) in a similar proportion as NM (10 mg g^{-1} of dry soil). Mixing was performed in a large glass beaker placed inside a fume hood until complete evaporation of methylene chloride was achieved.

Before treatment, 16 USEPA PAH contents of each contaminated matrix were measured in triplicate (Fig. 1, Fig. S1).

2.4. Oxidation experiments

Batch oxidation experiments were performed in triplicate at room temperature (20 °C) in 250 mL glass flasks covered with aluminum foil and stirred at 250 rpm. Fifteen g of soil or sand were mixed with 30 mL of ultra-pure water and the appropriate amount of oxidant for 5 d (Table 2).

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Four chemical oxidation treatments were chosen according to a previous investigation and our background information [17, 20-22]:

- PM: potassium permanganate,
- PS: sodium persulfate,
- APS: activated sodium persulfate, molar ratio $[H_2O_2]:[Na_2S_2O_8]$ = 5:1,
- F: modified Fenton's reagent, molar ratio $[H_2O_2]:[FeSO_4]$ = 20:1 (without modifying soil pH).

A control treatment (C) with only ultra-pure water was performed for each contaminated matrix.

The same oxidant amount was used for each soil (Table 2). It corresponded to a medium amount of oxidant: molar ratio [oxidant]:[16 USEPA PAHs] between 3:1 and 8:1, depending on the treated matrix. Molar ratios lower than 10:1 were chosen in order to: (i) prevent radical self-consumption or scavenging effects (for F and APS), (ii) limit the impacts on soil properties [23, 24] and also (iii) keep a moderate treatment cost.

Sequential addition was tested with F and APS at the same molar ratio as for single addition. Oxidants were added 4 times a day with intervals of 2 h over 5 d. These treatments are called Fseq for 'sequential Fenton' and APSseq for 'sequential activated persulfate'.

At the end of the batch experiments, supernatant pHs were measured, the mixtures were freeze-dried (Christ Alpha 1-2 LD freeze-dryer) and the concentrations of the 16 USEPA PAHs analyzed by HPLC. Before chemical treatment, the proportion of available PAHs (among the 16 USEPA PAHs) was evaluated by an extraction using a concentrated solution of hydroxypropyl-β-cyclodextrin (CD) (in triplicate) [32].

The total extractable organic matter (EOM) degradation was measured to estimate the oxidant selectivity towards PAHs (competition with others organic compounds).

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2.5. *Analytical methods*

2.5.1. *Extractable organic matter (EOM) isolation and quantification of the 16 USEPA PAHs*

Ten g of dry contaminated matrix were ground in a ball mill for 10 min at 25 Hz to obtain homogenous samples. EOMs were extracted from 1 g sub-samples using Accelerated Solvent Extraction (ASE Dionex 350). One g of anhydrous sodium sulfate and 1 g of Florisil® were added to a sub-sample in the extraction cell to purify the extract and trap potential traces of water. Extraction, using a mixture of acetone and methylene chloride (v/v 50/50), was performed at 100 °C and 100 bars for 5 min. After re-concentration of the solution to 1 mL under gentle nitrogen flow (TurboVap® Evaporation Workstation), a solvent exchange was carried out, in order to replace acetone and methylene chloride by acetonitrile for HPLC analysis. The vials containing these solutions were previously weighed before/after to estimate the volumes of the final extracts.

PAHs were quantified with a HPLC (Shimadzu system) equipped with a UV diode array detector, a Prosphere® column C-18 (Alltech, 250 mm x 46 mm, particle size 5 μm) and a pre-column (Alltech, 150 mm x 4.6 mm). The mobile phase was 85% acetonitrile and 15% ultrapure water (flow rate: 0.4 mL min^{-1}). External calibrations were made with a standard mixture of 16 USEPA PAHs in acetonitrile in the 1-100 mg L^{-1} range (Dr Ehrenstorfer PAH-Mix 9) with 5 calibration levels [20, 21].

2.5.2. *PAH extractability with a cyclodextrin solution*

PAH availability was evaluated by extraction using a concentrated solution of hydroxypropyl-β-cyclodextrin (CD) [17, 32]. Two g of each contaminated matrix were placed in Teflon (Nalgene®) tubes with 25 mL CD solution (69.5 g L^{-1}) and stirred for 12 h in a rotating

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stirrer at 24 °C. The CD solution containing the available PAHs was isolated from the solid matrix by centrifugation (10 min at 10000 g, Sorvall RC 5B). A sequence of 3 liquid-liquid extractions was performed with 10 mL methylene chloride each time (3 min stirring and 3 min settling). The organic phase was collected and the solvent almost totally evaporated (TurboVap® Evaporation Workstation) in order to carry out a solvent exchange (methylene chloride to acetonitrile) before HPLC analyses.

2.6. Statistical analysis

Analytical triplicates and treatment triplicates were needed in order to take into account possible contamination heterogeneity. Statistical analyses were performed to compare oxidant efficiency appropriately. In the case of PAH measurements, a reference standard deviation was defined for each contaminated matrix as the average standard deviation of different triplicates. Fischer's tests proved that each standard deviation of different triplicates was not significantly higher than the reference value with a 5% alpha risk.

For each contaminated matrix, normal z-tests were run to compare mean values of PAHs contents before and after control treatment. The reference standard deviation was used as previously defined. As expected, they demonstrated that the control treatment did not change significantly PAHs (p < 5%). The mean values after control treatment were used as the references to calculate PAH degradation yields. The degradation percentage corresponds to the PAH content difference between the initial (t0) and the oxidized sample normalized by the PAH content of the initial (t0) sample. Pearson's correlation coefficient r-tests were performed to assess the correlation between PAHs degradation yields and the percentage of PAHs extracted with cyclodextrin solution.

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3. Results

3.1. Distribution of the 16 PAHs before oxidation

The initial abundances and distributions of the 16 PAHs in the original soil samples TH and TNM, in the same soils previously extracted and then spiked with their corresponding EOM (THD, TNMD), and in the matrices spiked with the EOM of TNM soil (TChD and SNM) are similar for TH-t0, THD-t0 on the one hand, and TNM-t0, TNMD-t0, TChD-t0 and SNM-t0 on the other hand (Fig. 1, Fig. S1, Table S1). Therefore, the stages of extraction and spiking have not modified PAH contamination. In contrast, the results for CD extraction reveal that EOM extraction and incorporation into soil matrices (THD, TNMD and TCh) caused an increase in PAH availability, from 8 to 39% (Table 3).

3.2. Control experiments (C)

After the control experiments, no significant difference was recorded in PAH distribution before/after treatment (Table S1) and so the differences observed after oxidation are due to oxidation.

3.3. Oxidation experiments

The results of the oxidation experiments are all plotted in Fig. 1, which gives the concentrations of the sum of the 16 PAHs in each soil sample before/after oxidation. The degradation yields of the 16 PAHs have been calculated as follows:

$$\boldsymbol{degradation\ yield} = \frac{\sum_{16PAHs}(C)_{fin} - \sum_{16PAHs}(C)_{in}}{\sum_{16PAHs}(C)_{in}} \boldsymbol{x100} \quad (1)$$

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where $\sum_{16HAP}(C)_{fin}$ and $\sum_{16HAP}(C)_{in}$ are the total concentrations of the 16 PAHs in a soil sample after and before oxidation (mg kg^{-1})

3.3.1 Oxidation with permanganate (PM)

Permanganate was the most efficient oxidant for all the soil samples since degradation yields ranged from 40.2 to 98.6% (Fig. 1, Table S1). The highest degradation yield was obtained with the contaminated sand (SNM), followed by the freshly contaminated soil samples (TH D, TNM D and TCh D), whereas aged contaminated soils were the most recalcitrant. These results clearly show that oxidation depends on PAH availability, which is consistent with previous data [29, 33]. Indeed, a positive correlation has been established between degradation yields and availability, measured by the fractions of PAHs extractable by CD (not measured for SNM) (confidence levels > 95%) (Fig. 2). Moreover, the LMW/HMW ratio remained constant, showing that PM was effective whatever the number of aromatic rings (Table 4). This result could not be checked for SNM because of the very high degradation yield (98.6%), preventing accurate calculation of the LMW/HMW ratio.

After treatment, pHs were very close for TH and TNM (6.86 and 7.25) and lower than the reference soils without influence of the extraction/re-incorportion steps (Fig. S2). The pH of TChD-PM remained stable whereas it increased from 6.77 to 8.70 for soil SNM .

3.3.2 Oxidation with persulfate (PS)

Overall, PS was less efficient than PM with degradation yields from 10.6 to 43.5% (Fig. 1, Table S1). A similar oxidation efficiency was recorded for the freshly contaminated soil samples (THD and TNMD) and for aged ones (TH and TNM). No significant correlation was found between PAH degradation yield and PAH extraction yield with CD. As with PM, the

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LMW/HMW ratio was not modified after oxidation with PS, showing no preferential degradation (Table 4).

After treatment, pHs were close for each matrix (7.13 to 7.38) except for Chenevière soil (TChD-PS – pH = 5.05) and Fontainebleau sand (SNM-PS – pH = 1.50) (Fig. S2). This decrease is explained by the low buffering effect due to the low carbonate content.

3.3.3 Oxidation with activated persulfate (APS)

With APS, degradation yields ranged from 1.9 to 39.2%, comparable to PS (Fig. 1, Table S1). No obvious effect of PAH availability and no selective degradation was observed linked to the molecular weight of the PAHs (Table 4). The effect of APS treatment on pH was similar to PS treatments (Fig. S2), with a low pH for TChD-APS and especially so for SNM-APS.

3.3.2 Oxidation with modified Fenton's reagent (F)

Modified Fenton oxidation led to the lowest degradation yields whichever the soil; no degradation was recorded for TNM-F and THD-F and the highest was 45.2% for SNM-F. No significant correlation could be found between degradation yields and extraction yield with CD. The LMW/HMW ratios remained stable for each soil (Table 4).

After oxidation, soil suspension pHs were close to those attained after PS or APS treatment, except for TCh-F, with a pH drop to *ca* 2.7 and SNM-F, with a pH value of 2 (Fig. S2).

4. Discussion

The different oxidation treatments led to a very wide range of effectiveness, partly due to the differences in soil characteristics. PAH availability and distribution, pH, carbonate content, nature of the soil and the amount of organic carbon all can drastically affect oxidation

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efficiency [7, 17, 20, 21, 34-36]. Furthermore, these potential limiting factors can interact and their effects also depend on the nature of the oxidant and its method of addition.

4.1. Influence of PAH availability

The low availability of PAHs has been identified as one the main limiting factors for soil clean-up by chemical oxidation [15-17]. Its effect strongly depends on oxidant type [29]. With PM, a positive correlation has been found between the degradation yields of the 16 PAHs and their availability measured by CD extraction rate (Fig. 2). The treatment effectiveness was clearly governed by PAH availability; the highest oxidation rate (98.6%) obtained with Fontainebleau sand is explained by the very weak interaction between PAHs and the mineral matrix.

Unlike PM, oxidation by F and PS or APS resulted in lower degradation yields, without any relationship between availability and degradation; degradation yields were no higher with freshly contaminated soil samples (THD and TNMD) than to the equivalent aged ones (TH and TNM) (Fig. 1 and Table S1).

The low PAH availability in aged contaminated soils can be due to sequestration (transfer in micropores, possibly clogged) and to the strong sorption onto soil organic matter. It depends on organic carbon content and the nature of organic compounds [14]. Both industrial soils had a high content of organic carbon (close to 10 wt % - Table 1). Moreover, their nature is very different from organic matter of natural soils (as for example in soil TCh). Indeed, in industrial residues from former steel-making and coking plants, most of the organic compounds generally derive from coal tar and their aromaticity and hydrophobicity enhance PAH sorption [23, 28, 37]. This absence of correlation suggests that other parameters are involved.

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4.2. Oxidant persistence – successive additions

APS and Fenton's reagent involve highly reactive and very short half-life radicals with many possible radical scavenging reactions [10, 22, 38-40]. The chemical availability of catalyst 'activators' plays a major part in these activated systems [15, 16]. With these oxidants, sequential addition may lead to higher PAH degradation yields [41, 42].

Activated persulfate (APS vs. APSseq): sequential addition of APS considerably improved its efficiency for most soil samples (11.0 to 96.3% degradation yields) (Fig. 3, Table S2). Degradation yields increased particularly for freshly contaminated matrices (THD, TNMD, TChD and SNM). No significant correlation could be found between degradation yields resulting from Fseq and APSseq treatments and PAH availability.

Fenton treatments (F vs. Fseq): as for APS, sequential addition of Fenton's reagent improved its efficiency for most of soil samples (10 to 70% degradation yields) (Fig. 3 and Table S2). However, unlike APS, the highest degradation yields were obtained with aged contaminated matrices (TH and TNM). When soil samples are spiked with EOM, not only PAHs but also other organic compounds become more available. Given that oxidation with radicals is non-selective, they may react with many other compounds. Therefore the increase in availability resulting from spiking does not only enhance PAH degradation and the degradation yields are not higher. This effect could be more pronounced with PS acting as a detergent likely to solubilize organic matter.

4.3. Influence of content and nature of organic matter

Oxidants are not selective; the competition between PAHs and other organic constituents therefore plays a significant role in treatment efficiency [10, 14, 17, 22, 24, 43]. Its effect has

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been described earlier for Fenton's reagent and APS. The influence of the competition with organic matter was also recorded with PM but to a lesser extent; degradation yields decreased as organic content increased with SNM-PM, TChD-PM and TNMD-PM, the PAH concentration being the same. The same trend was observed with APS by comparing results obtained with TNMD-APS and TChD-APS.

The nature of organic matter also plays a role. TH and TNM contained organic matter derived from industrial activities, mainly composed of persistent aromatic compounds [28, 29] whereas TCh contained natural organic matter which was easier to oxidize.

4.4. Influence of carbonate content and pH

Among the different parameters which can induce contrasting behaviors between soils, carbonate content can play a major role. TH and THD contain especially high amounts of carbonate (369.0 $g_{CaCO3}\,kg^{-1}$), ten times more than TNM and TNMD (35.7 $g_{CaCO3}\,kg^{-1}$), whilst TChD and SNM did not contain any carbonate (Table 1). In order to evaluate the specific effect of carbonate on oxidation effectiveness, TH and TNM were partially decarbonized before further oxidation experiments (see 2.4). TH-DC and TNM-DC were oxidized with PM, PS in one addition and with F and APS sequentially.

The influence of carbonate content was estimated by comparing results with partially decarbonized soil samples TH-DC and TNM-DC with results obtained with the original TH and TNM (Fig. 4). High carbonate content did not have an impact on PM efficiency (similar results for TH and TH-DC and for TNM and TNM-DC), whereas partial decarbonization increased APS performance, especially in the case of the most carbonated soil sample TH (Fig. 4). It was consistent with previous published reports since unlike PM, APS involving radical species can be inhibited by carbonate anions [9, 10, 36, 39]. However, partial decarbonization

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of TH and TNM soil samples drastically decreased the efficiency of Fenton's reagent (hydroxyl radical pathway) [11, 17, 21, 22]. A release of trapped organic matter or an enhancement of its availability during decarbonization could explain this decrease. Indeed, Fenton's reagent seemed less selective and more affected by competition between PAHs and other organic compounds (see section 4.2).

Our data revealed that the pH reached during chemical oxidation could have an impact on PAH degradation. Fenton's reaction is known to be favored at low pH and persulfate at alkaline pH (with or without activation) but permanganate remained efficient over a large range of pHs [10, 17, 22, 38]. During our experiments (Fig. S2), no severe pH decrease occurred with soil samples TNM and TH and their derivatives (TNMD, THD) because of their high carbonate content being responsible for a buffering effect (pH between 5 and 7), even in partial decarbonized ones (TNM DC and TH DC). This pH range could explain the low efficiency of Fenton's reagent with these matrices, in addition to other limiting factors, compared to other oxidants not particularly hindered at a pH around 6. However, with contaminated sands (SNM) the severe pH decrease observed with Fenton's reagent was an advantage but a great drawback for persulfate, especially without any activation.

5. Conclusion

In this work, oxidation has been investigated as a method to degrade PAHs from different soil samples in diverse conditions, in order to bring an understanding on the role of the type of oxidant and injection method, the type and age of organic matter, of PAH availability and of carbonate content. It was clearly shown that permanganate was the most effective oxidant, whatever the conditions, even if low PAH availability limited its action. Indeed, a positive correlation has been revealed between PAH availability and the PAH degradation yield by

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permanganate. To the best of our knowledge, no clear correlation has ever been proposed before to explain the impact of PAH availability on oxidation effectiveness.

The other oxidants employed (modified Fenton's reagent, persulfate, activated persulfate) were less effective under all conditions. Different obstacles limited their action; the type and age of organic matter, injection method and/or high carbonate content. Persulfate led to low PAH degradation in all cases. Moving from single to sequential addition of oxidant improved the action of low persistent oxidants (modified Fenton's reagent and activated persulfate). The decrease in carbonate content also improved the action of activated persulfate.

This work provides additional evidence that oxidation requires a systematic feasibility study at the laboratory scale before being applied at field scale. Furthermore, it clearly shows the role of the limiting factors that must be taken into account. In addition to the degradation performance, other factors should also be considered, namely the influence of oxidant on later remediation operations, such as bioremediation or soil revegetation. Therefore, the impact of chemical oxidation on soil physical, chemical and biological properties should be limited, and the oxidant type and dose as well as of the operating conditions must be carefully selected with this in mind.

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Figure captions

Fig 1. 16 US EPA PAH content in soil samples (TH THD, TNM, TNMD, TChD and SNM) before and after different oxidative treatments (C, PM, PS, PS, F).

Fig. 2. Degradation yields of the 16 PAHs after permanganate oxidation as a function of PAH availability measured by cyclodextrin extraction.

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Fig. 3. PAH concentrations before (t0), after single or sequential addition of Fenton's reagent (F and Fseq) or activated persulfate (APS and APSseq) for initial soils (TH and TNM) and modified soils (THD, TNMD, TChD and SNM).

Fig. 4. PAH concentrations before (t0) and after oxidation (C, PM, PS, APS, Fseq, APSseq) of partial decarbonatation of TH (TH-DC) and TNM (TNM-DC) soil samples.

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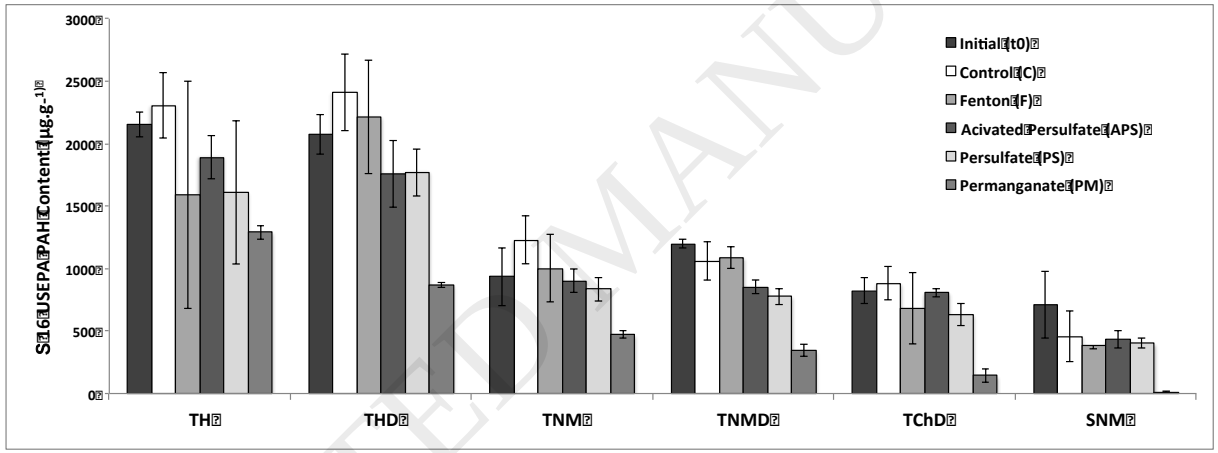


Fig. 1.

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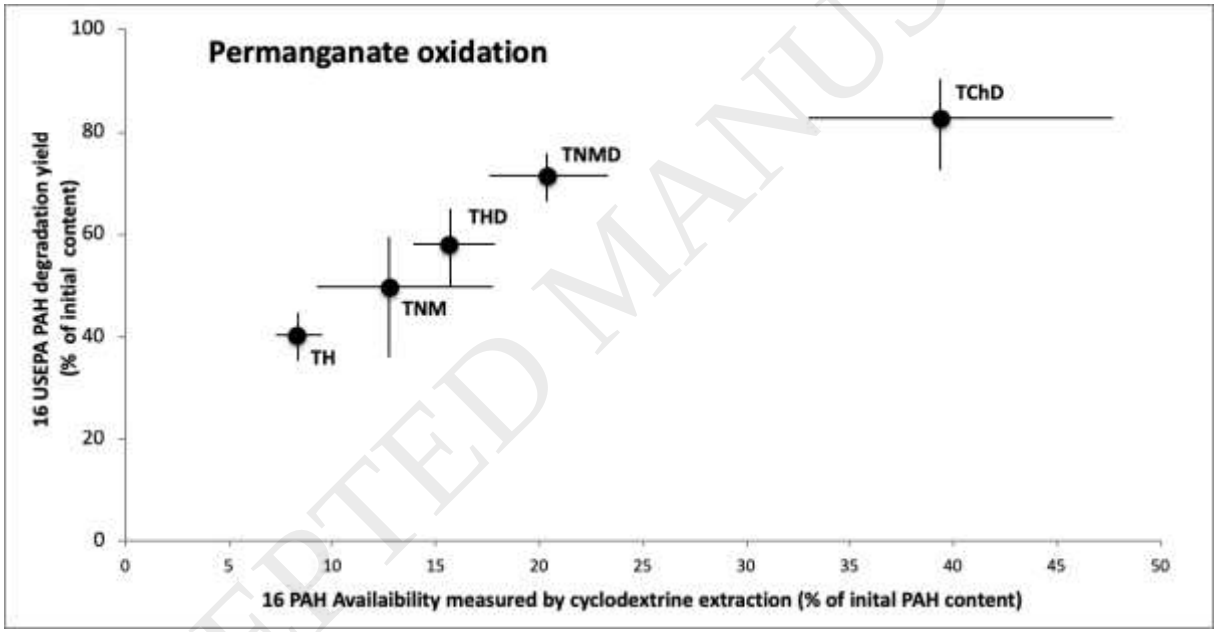


Fig. 2.
(the title of the vertical axis was corrected)

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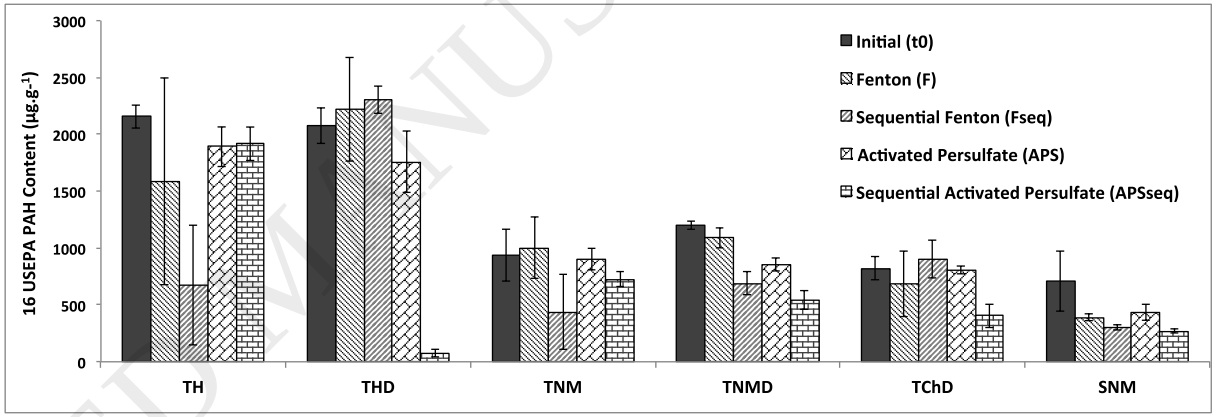


Fig. 3.

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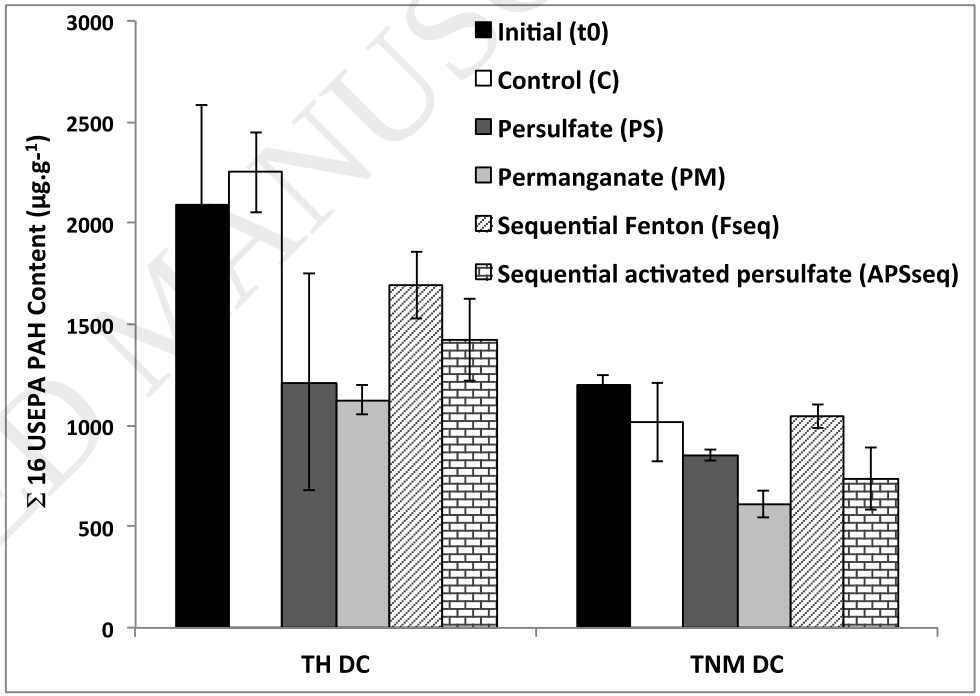


Fig. 4.

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Table 1
Agronomic properties, organic parameters and metal contents of the two industrial soils (TNM and TH) and the agricultural soil (TCh)

		TNM	TH	TCh	Regional reference[a]	
					mean	max
Agronomic parameters[b]						
Sand	wt %	62.9	63.7	88.7		
Silt	wt %	24.1	25.5	6.3		
Clay	wt %	13.0	10.8	5.0		
pH water		7.4	9.5	4.7		
Total $CaCO_3$	g kg^{-1}	35.7	369.0	<1.0		
Total N	g kg^{-1}	2.69	2.14	1.19		
Organic parameters						
Organic carbon[b]	g kg^{-1}	71.5	99.7	12.4		
pMC (percentage of modern carbon)	%	5.6	4.5	-		
Metals[b]						
Zn	mg kg^{-1}	2.68	361	33.1	120	500
Pb	mg kg^{-1}	684	121	27.2	25	100
Cr	mg kg^{-1}	325	55.5	19.4	80	500
Ni	mg kg^{-1}	260	24.3	7.4	30	100
Cu	mg kg^{-1}	110	28.5	8.6	15	50
Hg	mg kg^{-1}	3.9	12.0	< d.l.	0.5	2.0

[a] values taken from (30); [b] values taken from (17); < d.l.: below the detection limit

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Table 2
Oxidant amount used in batch experiments to treat 15 g of the different contaminated matrices

		Fenton's reagent		**Activated persulfate**		**Sodium persulfate**	**Potassium permanganate**
		H_2O_2	$FeSO_4,7H_2O$	H_2O_2	$Na_2S_2O_8$		
Amount	g	0.75	0.306	0.625	0.875	5.25	2.32
	g kg^{-1}	50	20.4	41.7	58.3	350	155

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Table 3
Sum of the 16 USEPA PAH concentration in initial soils (t0) and sum of the 16 USEPA PAH concentration mobilized by cyclodextrine extraction (CD) for TH, THD, TNM, TNMD, TChD soils. Individual PAH concentrations are supplied in Table S2.

		∑ 16 HAP (mg kg^{-1})
TH-t0	mean	**2155.4**
	Std.-Dev.	*100.4*
TH-CD	mean	**179.8**
	Std.-Dev	*25.5*
% available		**8.3**
THD-t0	mean	**2074.2**
	Std.-Dev	*159.2*
THD-CD	mean	325.5
	Std.-Dev	*18.5*
% available		**15.7**
TNM-t0	mean	**933.9**
	Std.-Dev	*230.5*
TNM-CD	mean	**119.0**
	Std.-Dev	*18.0*
% available		**12.7**
TNMD-t0	mean	**1198.5**
	Std.-Dev	*34.1*
TNMD-CD	mean	244.2
	Std.-Dev	*38.8*
% available		**20.4**
TChD-t0	mean	821.4
	Std.-Dev	*104,1*
TChD-CD	mean	323.7
	Std.-Dev	*23.9*
% available		**39.4**

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Table 4
Values of the ratio of the concentration of low molecular weight (LMW) PAHs (from Naphtalene to Pyrene) to the concentration of the high molecular weight (HMW) PAHs (from Benzo(a)anthracene to Dibenzo(a.h)anthracene) before (t0) and after the different oxidation treatments (C, F, APS, PS, PM) for the different matrices (TH, TNM, TChD, THD, TNMD and SNM)

	LMW/HMW*		LMW/HMW*		LMW/HMW*
TH-t0	**0.81**	TNM-t0	**0.84**	TChD-t0	**0.83**
TH-C	**0.79**	TNM-C	**0.80**	TChD-C	**0.74**
TH-S	**0.79**	TNM-S	**0.84**	TChD-F	**0.61**
TH-APS	**0.78**	TNM-APS	**0.79**	TChD-APS	**0.80**
TH-PS	**0.78**	TNM-PS	**0.81**	TChD-PS	**0.77**
TH-PM	**0.86**	TNM-PM	**1.17**	TChD-PM	**0.85**
THD-t0	**0.82**	TNMD-t0	**0.78**	SNM-t0	**0.93**
THD-C	**0.80**	TNMD-C	**0.78**	SNM-C	**0.75**
THD-F	**0.79**	TNMD-F	**0.73**	SNM-F	**0.78**
THD-APS	**0.76**	TNMD-APS	**0.82**	SNM-APS	**1.03**
THD-PS	**0.80**	TNMD-PS	**0.84**	SNM-PS	**0.64**
THD-PM	**0.77**	TNMD-PM	**0.66**	SNM-PM	**4.59**

* LMW: sum of the 16 USEPA PAH from Naphthalene to Pyrene
HMW: sum of the 16 USEPA PAH from Benzo(a)anthracene to Dibenzo(a,h)anthracene

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