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► **To cite this version:**

M Usman, K Hanna, P Faure. Remediation of oil-contaminated harbor sediments by chemical oxidation. *Science of the Total Environment*, 2018, 634, pp.1100-1107. 10.1016/j.scitotenv.2018.04.092 . hal-01807881

**HAL Id: hal-01807881**

**<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01807881>**

Submitted on 28 Aug 2018

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1 Submitted to *Science of The Total Environment*

2 **Remediation of oil-contaminated harbor sediments by chemical oxidation**

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23

24 **Abstract**

25 Oil hydrocarbons are widespread pollutants in sub-surface sediments with serious threats to  
26 terrestrial and aquatic environment. However, very limited data is available about  
27 remediation of historically contaminated sediments. This study reports the use of magnetite-  
28 catalyzed chemical oxidation ( $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{S}_2\text{O}_8$ ) to degrade oil hydrocarbons in aged  
29 contaminated sediments. For this purpose, oil contaminated sediments were sampled from  
30 three different locations in France including two harbors and one petroleum industrial  
31 channel. These sediments were characterized by different hydrocarbon index (HI) values ( $3.7$   
32  $- 9.0 \text{ g kg}^{-1}$ ), total organic carbon contents ( $1.9\% - 8.4\%$ ) and textures (sand, slit loam and  
33 silt). Chemical oxidation was performed in batch system for one week at circumneutral pH  
34 by:  $\text{H}_2\text{O}_2$  alone,  $\text{H}_2\text{O}_2/\text{Fe(II)}$ ,  $\text{H}_2\text{O}_2/\text{magnetite}$ ,  $\text{Na}_2\text{S}_2\text{O}_8$  alone,  $\text{Na}_2\text{S}_2\text{O}_8/\text{Fe(II)}$ , and  
35  $\text{Na}_2\text{S}_2\text{O}_8/\text{magnetite}$ . Results obtained by GC-FID indicated substantial hydrocarbon  
36 degradation ( $40 - 70\%$ ) by  $\text{H}_2\text{O}_2/\text{magnetite}$  and  $\text{Na}_2\text{S}_2\text{O}_8/\text{magnetite}$ . However, oxidants alone  
37 or with soluble Fe(II) caused small degradation ( $< 5\%$ ). In the presence of  $\text{H}_2\text{O}_2/\text{magnetite}$ ,  
38 degradation of extractable organic matter and that of HI were highly correlated. However, no  
39 such correlation was observed for  $\text{Na}_2\text{S}_2\text{O}_8/\text{magnetite}$  which resulted in higher removal of HI  
40 indicating its selective oxidation behavior. Treatment efficiency was negatively influenced by  
41 organic carbon and carbonate contents. For being the first study to report chemical oxidation  
42 of oil hydrocarbons in real contaminated sediments, it may have practical implications to  
43 design a remediation strategy for target contaminants.

44

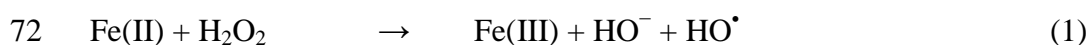
45 **Keywords:** Oil hydrocarbons; Harbor sediments; Remediation; Fenton-like; Persulfate;

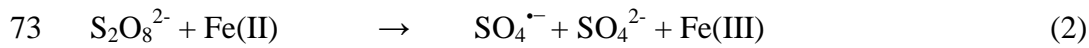
46 Magnetite

47

## 48 **1. Introduction**

49 Oil hydrocarbons are widespread pollutants in sub-surface sediments which pose serious  
50 threats to terrestrial and aquatic environment. Therefore, development of novel and effective  
51 remediation techniques for oil-contaminated sediments is of considerable environmental  
52 interest (Lim et al., 2016). Various remediation techniques have been developed including  
53 biological (Chaîneau et al., 2003; Benyahia et al., 2005), chemical (Usman et al., 2012a;  
54 2013; Chen et al., 2016) and combined approaches (Silva-Castro et al., 2013; Souza et al.,  
55 2014; Agarwal and Liu, 2015; Xu et al., 2016a). Bioremediation is the most commonly used  
56 technique to remediate oil contaminated matrices (soils, sediments and water) primarily  
57 because of its cost-effective and environment friendly nature (Lim et al., 2016). Majority of  
58 molecules in crude oil spills and refined products are biodegradable and thus can largely be  
59 removed by bioremediation (Prince, 1993). However, bioremediation often leaves non-  
60 biodegradable residues due to incomplete mineralization and thus cannot meet the stringent  
61 environmental cleanup standards reported by environmental regulations (Plaza et al., 2005).  
62 Contamination level had reached a plateau for long time in soil subjected to bioremediation  
63 for two years (Lu et al., 2010). Bioremediation or natural attenuation of n-alkanes present in  
64 oil lead to their degradation whereby leaving unresolved complex mixture (UCM) composed  
65 of iso- and cyclo-alkanes, which is totally refractory to microbial attack (Chaillan et al., 2006;  
66 Farrington and Quinn, 2015). However, chemical oxidation has shown strong efficiency to  
67 remove oil hydrocarbons where different oxidants are used to degrade organic pollutants.  
68 Recent studies employing chemical oxidation for the remediation of oil hydrocarbons are  
69 summarized in Table 1. Among chemical oxidation-based treatments, Fenton and persulfate  
70 oxidation are showing great remediation potential to remove oil hydrocarbons. Both oxidants  
71 require ferrous iron Fe(II) to produce stronger radicals through following reactions:





74 Activation by soluble Fe(II) requires an acidic pH (~ 3) to avoid its precipitation which is  
75 harmful for soil quality and microbial population (Laurent et al., 2012). This initial  
76 acidification can be avoided by using chelating agents or iron minerals to perform chemical  
77 oxidation at circumneutral pH (Usman et al., 2016b). Iron oxides especially mixed-valent  
78 Fe(II)-Fe(III) minerals like magnetite [Fe(II)Fe(III)<sub>2</sub>O<sub>4</sub>] and green rust were found more  
79 effective to catalyze chemical oxidation as compared to the ferric minerals or soluble Fe(II)  
80 at circumneutral pH due to the presence of structural Fe(II) (Usman et al., 2018). Previous  
81 batch (Usman et al., 2012a) and column experiments (Usman et al., 2013) showed that  
82 magnetite-catalyzed chemical oxidation (Fenton-like and persulfate) is highly efficient to  
83 remove oil hydrocarbons (90% degradation) in crude oil as well its refractory product after  
84 biodegradation (UCM). However, these findings were based on artificially contaminated sand  
85 where oil hydrocarbons were spiked on sand after extraction from contaminated sediments.  
86 To date, no study has been published on use of chemical oxidation to remediate real oil-  
87 contaminated sediments. It should be noted that chemical oxidation resulted in significant  
88 removal (80%) of polycyclic aromatic hydrocarbons (PAHs) when extracted from aged  
89 contaminated soils and spiked in sand. However, these treatments were ineffective (<5%  
90 degradation) in aged contaminated soils (without any extraction) which has been attributed to  
91 the contaminant unavailability (Usman et al., 2012b; 2012c; 2016a; Biache et al., 2015). In  
92 the present study, we aim to evaluate the efficiency of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and  
93 persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) catalyzed by magnetite to remove oil hydrocarbons in aged  
94 contaminated sediments. Remediation of three kinds of sediments sampled from different  
95 locations in France were investigated. These sediments were subjected to magnetite-catalyzed  
96 chemical oxidation at circumneutral pH under different conditions (H<sub>2</sub>O<sub>2</sub> or Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> with or  
97 without Fe(II) or magnetite as catalyst). Organic analyses were performed by using Gas

98 Chromatography - flame ionization detector (GC-FID). The performance of chemical  
99 oxidation treatment in correlation with the availability of oil hydrocarbons in aged  
100 contaminated sediments was discussed.

101

Oxidant	Catalyst type	Target pollutant and its initial concentration	Medium	Experimental conditions	Extent / rate of pollutant degradation	Ref.
H <sub>2</sub> O <sub>2</sub>	Magnetite (Commercial) Screened through 0.3 mm sieve.	Petroleum hydrocarbons 1 g Kg <sup>-1</sup>	Spiked sand/ Batch	pH = 3, magnetite = 5 wt%, H <sub>2</sub> O <sub>2</sub> = 15 wt%	50% hydrocarbon removal after 8 days	(Kong et al., 1998)
H <sub>2</sub> O <sub>2</sub>	Soluble Fe(II)	Diesel 10-12 g Kg <sup>-1</sup>	Spiked sand and peat soil/ Batch	pH = 3, H <sub>2</sub> O <sub>2</sub> :Fe(II) molar ratio = 10:1 liquid/solid = 1 and 20 mL g <sup>-1</sup> for sand and peat	>80% removal of hydrocarbons after 72 h in sand	(Goi et al., 2006)
H <sub>2</sub> O <sub>2</sub>	Basic oxygen furnace slag	Fuel oil or diesel TPH = 10 g kg <sup>-1</sup>	Spiked sand and sandy loam/ Batch	pH = 6.7, H <sub>2</sub> O <sub>2</sub> = 15% Slag = 100 g kg <sup>-1</sup>	TPH removal of 96% and 76% in diesel and fuel oil tests after 40 h	(Tsai and Kao, 2009)
H <sub>2</sub> O <sub>2</sub>	Soluble Fe(II) in the presence or absence of natural soil Fe minerals (hematite mainly)	Diesel 5 g Kg <sup>-1</sup>	Spiked loam soil/ Batch	pH = 2.5 – 3, Fe(II) = 12 mM H <sub>2</sub> O <sub>2</sub> = 0.045 g g <sup>-1</sup> soil	28% of diesel was degraded with soil minerals (without Fe(II)) while degradation reached 48% in the presence of soluble Fe(II) after 84 h	(Villa et al., 2010)
H <sub>2</sub> O <sub>2</sub>	Soluble Fe(III) with EDTA	Petroleum hydrocarbons Dichloromethane- extractable organics 14.8 g Kg <sup>-1</sup>	Soil samples collected from areas adjacent to oil wells/ Batch	pH = 7, H <sub>2</sub> O <sub>2</sub> = 2.45 mol Kg <sup>-1</sup> soil, H <sub>2</sub> O <sub>2</sub> :Fe(III) molar ratio = 200:1.	>80% removal of hydrocarbons	(Lu et al., 2010)
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Soluble Fe(II)	Diesel 5 g Kg <sup>-1</sup>	Spiked sand and soil/ Batch	pH = 3, Oxidant:Fe molar ratio = 100:1	38% removal but inclusion of metal oxides improved the oxidation efficiency	(Do et al., 2010)
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Soluble Fe(II)	Diesel TPH = 3.5 g Kg <sup>-1</sup>	Soil from an oil refining plant/Batch	Oxidant = 20% Oxidant:Fe = 1:0.01	Total removal 40% after 60 days, Reaction rate constant = 1.47 × 10 <sup>-2</sup> day <sup>-1</sup>	(Yen et al., 2011)
H <sub>2</sub> O <sub>2</sub> or Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Soluble Fe(II) Or Magnetite (lab synthesized)	Petroleum hydrocarbons 4 g Kg <sup>-1</sup> of crude and weathered oil	Spiked sand/ Batch	pH = 6.7, 20 – 25 °C, magnetite = 10% w/w, oxidant:Fe molar ratio = 10:1 (H <sub>2</sub> O <sub>2</sub> ) and 1:1	80-90% of hydrocarbon removal by both oxidants in the presence of magnetite after one week. <10 % of	(Usman et al., 2012a)

	30 nm; 103 m <sup>2</sup> g <sup>-1</sup>			(Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )	pollutant removal with soluble Fe(II) as catalyst	
H <sub>2</sub> O <sub>2</sub> or Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Magnetite (lab synthesized) 30 nm; 103 m <sup>2</sup> g <sup>-1</sup>	Petroleum hydrocarbons 4 g Kg <sup>-1</sup> of weathered oil	Spiked sand/ Saturated column	pH = 6.7, 20 – 25 °C, magnetite = 10% w/w, oxidant:Fe molar ratio = 10:1 (H <sub>2</sub> O <sub>2</sub> ) and 1:1 (Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )	60-70% of hydrocarbon removal by both oxidants	(Usman et al., 2013)
H <sub>2</sub> O <sub>2</sub>	Soluble Fe(III) with or without chelating agent	Biodiesel blend (20 % biodiesel, 80 % diesel) TPH = 1 g Kg <sup>-1</sup>	Spiked sandy clay loam/ Batch	pH = < 3 (without chelating agent) and 4.5 – 6 (with chelating agent) Fe (III) = 20 mM, Citrate = 50 mM, H <sub>2</sub> O <sub>2</sub> = 4000 mM	75% of TPH removal in the absence of chelating agent while 37% of TPH removal in its presence after 300 h	(Pardo et al., 2014)
H <sub>2</sub> O <sub>2</sub>	Magnetite and ZVI	Diesel TPH = 5 g Kg <sup>-1</sup>	Spiked soil/ Batch	pH = 6.7–7.4 Catalyst = 4.27 wt% H <sub>2</sub> O <sub>2</sub> = 2.17 mol L <sup>-1</sup>	TPH removal was 57% (magnetite) and 67% (ZVI)	(Jamialahma di et al., 2015)
H <sub>2</sub> O <sub>2</sub>	Soluble Fe(II) with chelating agent	Crude oil TPH = 15.2 and 27.7 g Kg <sup>-1</sup>	Soils collected from two oil wells / Batch	pH = 7.5, Fe(II) = 5.8 mM, H <sub>2</sub> O <sub>2</sub> = 1100 mM Citric acid = 17.9 g L <sup>-1</sup>	40-50% of TPH removal	(Xu et al., 2016b)
H <sub>2</sub> O <sub>2</sub>	Soluble Fe(II) with chelating agent	Crude oil contamination TPH = 23.4 g Kg <sup>-1</sup>	Soil collected from an oil well/ Batch	pH = 6.5 – 7, Fe(II) = 2.9 mM, H <sub>2</sub> O <sub>2</sub> = 900 mM	>20% removal of hydrocarbons in 10 days	(Xu et al., 2017)
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	NaOH	Diesel TPH = 4.9 g Kg <sup>-1</sup>	Soil collected from train maintenance facility/ Batch	pH = ≥ 12, 20 °C, Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> = 420 mM, NaOH:Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> = 4, Liquid/solid = 2 mL g <sup>-1</sup>	98% removal of TPH after 56 days.	(Lominchar et al., 2018)

102 **Table 1:** Summary of studies using chemical oxidation to remove oil hydrocarbons in contaminated soils.

103



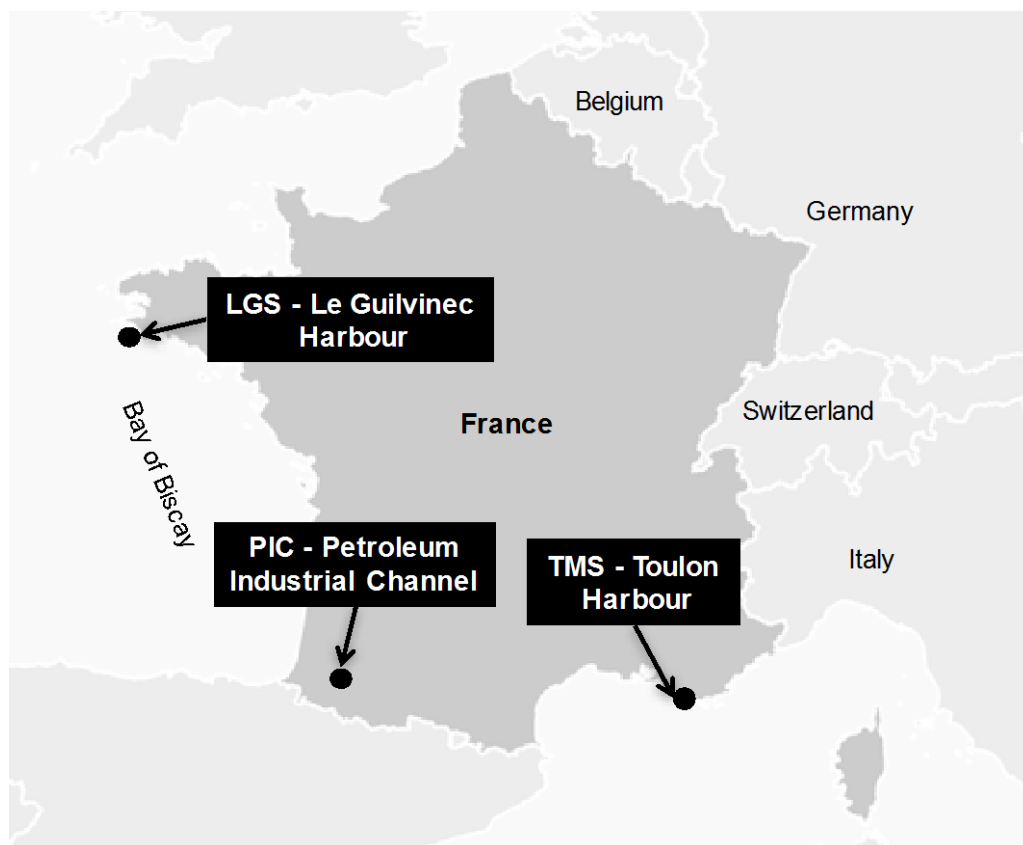
## 104 **2. Experimental section**

### 105 **2.1. Chemical reagents and materials**

106 Following reagents were used: FeSO<sub>4</sub>·7H<sub>2</sub>O with purity greater than 98% obtained from  
107 VWR, sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and hydrogen peroxide 35% (H<sub>2</sub>O<sub>2</sub>) of Acros Organics.  
108 Dichloromethane and chloroform, both purchased from VWR were used as received.  
109 Deionized water was produced with a Milli-Q system from Millipore.  
110 Magnetite used in the present study was synthesized and characterized in the context of  
111 previous study (Usman et al., 2012a). This magnetite is characterized as nano-magnetite  
112 (particle size range of 30 – 50 nm) with BET surface area of  $103 \pm 2 \text{ m}^2 \text{ g}^{-1}$ , PZC of 7.9 and  
113 Fe(II)/Fe(III) ratio of 0.46.

### 114 **2.2. Sediment samples**

115 This study concerned three contaminated sediments from two different harbors, and one  
116 petroleum industrial channel. The locations of these three sites are shown in the Figure 1 and  
117 are detailed below: LGH Sediments were sampled in February 2007 by dredging in Le  
118 Guilvinec harbor (north-western of France), TMH Sediments were dredged in Toulon  
119 military harbor (southern France) in April 2008, PIC sediments were sampled in 2011 in a  
120 petroleum industrial channel located in the south of France. These samples were freeze-dried,  
121 sieved at 2 mm, placed in glass bottles, and stored at 5 °C before analysis and/or treatment.  
122 Properties of the tested sediments are reported in Table 2.  
123 These three locations are affected by petroleum by-product contamination for several decades  
124 and polluted sediments have already undergone natural biological alteration.



125

126 **Figure 1:** Location of tested sediments in France

127

### 128 **2.3. Oxidation procedures**

129 Following experiments were performed to evaluate the chemical oxidation of contaminated  
 130 sediments:  $H_2O_2$  alone,  $H_2O_2/Fe(II)$ ,  $H_2O_2/magnetite$ ,  $Na_2S_2O_8$  alone,  $Na_2S_2O_8/Fe(II)$ , and  
 131  $Na_2S_2O_8/magnetite$ . Experiments were performed in batch slurry without pH adjustment  
 132 (circumneutral), room temperature (20 – 25 °C), in the absence of light (by aluminum foil  
 133 coverings). Oxidant dose was adjusted according to the oxidant:Fe molar ratio equal to 20:1  
 134 ( $H_2O_2$ ) and 2:1 ( $Na_2S_2O_8$ ) in slurry on the basis of our previous studies (Usman et al., 2012a;  
 135 2012b). Because the parasite reactions including nonproductive oxidant demand and  
 136 hydroxyl radical scavenging are more important for  $H_2O_2$  (Liang et al., 2004; Xue et al.,  
 137 2009b; Usman et al., 2012a; 2012b), we used higher dose of  $H_2O_2$  than persulfate. Blank  
 138 experiments were performed by using magnetite alone without any oxidant but no pollutant  
 139 degradation was observed (data not shown). Magnetite was added in concerned sediments to

140 achieve 10% w/w as final contents (0.1 g of magnetite for 1 g of sediment). Equivalent molar  
141 amount of Fe was used to compare the efficiency of both catalysts (soluble Fe(II) and  
142 magnetite) to activate the tested oxidants. Standard procedure is detailed in our previous  
143 study by Usman et al. (2012a). Sediments (2 g) were stirred for 15 minutes with suitable  
144 amount of water to have a final volume of 20 mL after oxidant addition. Photocatalytic  
145 degradation was avoided by using aluminum foil coverings. These slurries were reacted for  
146 one week under vigorous magnetic-stirring. Reaction was then stopped by freezing these  
147 batches. After two days, water was removed by freeze drying these samples.

148 One week time point was chosen based on previous studies where no further degradation was  
149 observed after one week (Usman et al., 2012a; 2012b) while oxidants were fully consumed  
150 after this period as confirmed by iodometric titration (Rybnikova et al., 2016). All  
151 experiments were performed in duplicates and results are expressed as a mean value of the 2  
152 experiments and standard deviation of the duplicates was less than 5%.

#### 153 **2.4. Extraction and analysis**

154 *Quantification of extractable organic matter (EOM)*: Freeze-dried sediments were extracted  
155 with chloroform at 60 °C for 45 min as detailed previously (Usman et al., 2016a). This was  
156 performed in a glass vessel which was connected to a water-cooled reflux condenser to let  
157 reflux the evaporated solvent. Temperature of extraction medium was homogenized by  
158 magnetic stirring. After extraction, the vessel was allowed to cool at room temperature before  
159 opening it. The supernatant was filtered through a pre-washed glass microfiber filter (d = 45  
160 mm, porosity = 0.7 mm; Whatman). Volume of organic extract was reduced to 20 mL under  
161 N<sub>2</sub> and 5 mL of this solution was transferred in a pre-weighed vial. The amount of extractable  
162 organic matter (EOM) was determined by weighing the vial after evaporation of the solvent.  
163 This method resulted in complete recovery of EOM in previous studies (Usman et al., 2012a;  
164 2012c).

165 *Hydrocarbon Index (HI) quantification:* The HI was measured according to the ISO  
166 16703:2004 procedure using a GC-FID 7890 Agilent technologies. Briefly, a standard  
167 mixture (ASTM D5307) is used to define the integration limits of the chromatogram area.  
168 These limits correspond to the *n*-decane (C<sub>10</sub>H<sub>22</sub>) and *n*-tetracontane (C<sub>40</sub>H<sub>82</sub>) retention time.  
169 An ISO 11046 standardized oil is used as standard solution (external calibration). Seven  
170 solutions of different concentrations (0.5, 1, 2, 4, 6, 8 and 10 mg mL<sup>-1</sup>) are prepared from this  
171 standardized oil solution and injected into the chromatograph in order to obtain calibration  
172 curves. The integration of the area under each chromatogram is corrected by the background  
173 noise (by integrating the area chromatogram obtained with a sample of pure dichloromethane  
174 that serves as a control).

### 175 3. Results and discussion

#### 176 3.1. Characterization of sampled sediments

177 The main properties of tested sediments are reported in Table 2. These sediments were  
178 characterized by different mineral fractions including sand (LGH, 98% sand), silt loam  
179 (TMH, 35% sand, 57% silt), and silt (PIC, 9% sand, 81% silt, 10% clay) with different pH  
180 values: 8.60 (LGH), 8.28 (TMH) and 7.67 (PIC). Total organic carbon (TOC) contents were  
181 in order of 1.85%, 4.96% and 8.39% in LGS, TMH and PIC sediments, respectively.  
182 Observed order of TOC contents could be correlated to increasing silt contents and  
183 decreasing sand contents as reported by Augustin and Cihacek (2016). Indeed, total silt was  
184 positively correlated ( $P \leq 0.01$ ) to the TOC while sand was negatively correlated ( $P \leq 0.10$ )  
185 to it. An order similar to TOC was observed for HI values: LGH ( $3.7 \text{ g kg}^{-1}$ ) < TMH ( $5.5 \text{ g}$   
186  $\text{kg}^{-1}$ ) < PIC ( $9.0 \text{ g kg}^{-1}$ ). These sediments contained higher  $\text{CaCO}_3$  amounts of 18.63%  
187 (LGH), 28.43 (TMH) and 23.1 (PIC). Higher content of Cu, Pb and Zn were also detected in  
188 these sediments (Table 2).

189 The molecular distributions of initial sediments (Figure 2) are dominated by UCM which  
190 comprise a mixture of iso- and cyclo-alkanes (Tolosa et al., 2004) and cannot be resolved by  
191 classical chromatographic column. The main identified products correspond to pentacyclic  
192 triterpanes. Such signatures are typical of biodegraded and weathered oil containing  
193 compounds which are resistant to biodegradation (Tolosa et al., 2004; Farrington and Quinn,  
194 2015). Sampled areas were under natural attenuation for years which eliminated the easily  
195 biodegradable *n*-alkanes leaving UCM as the sole contamination in three sediments. GC-FID  
196 chromatograms (Fig. 2) provide a visual representation of efficiency of chemical oxidation to  
197 degrade UCM as observed previously in spiked sand (Usman et al., 2012a).

198

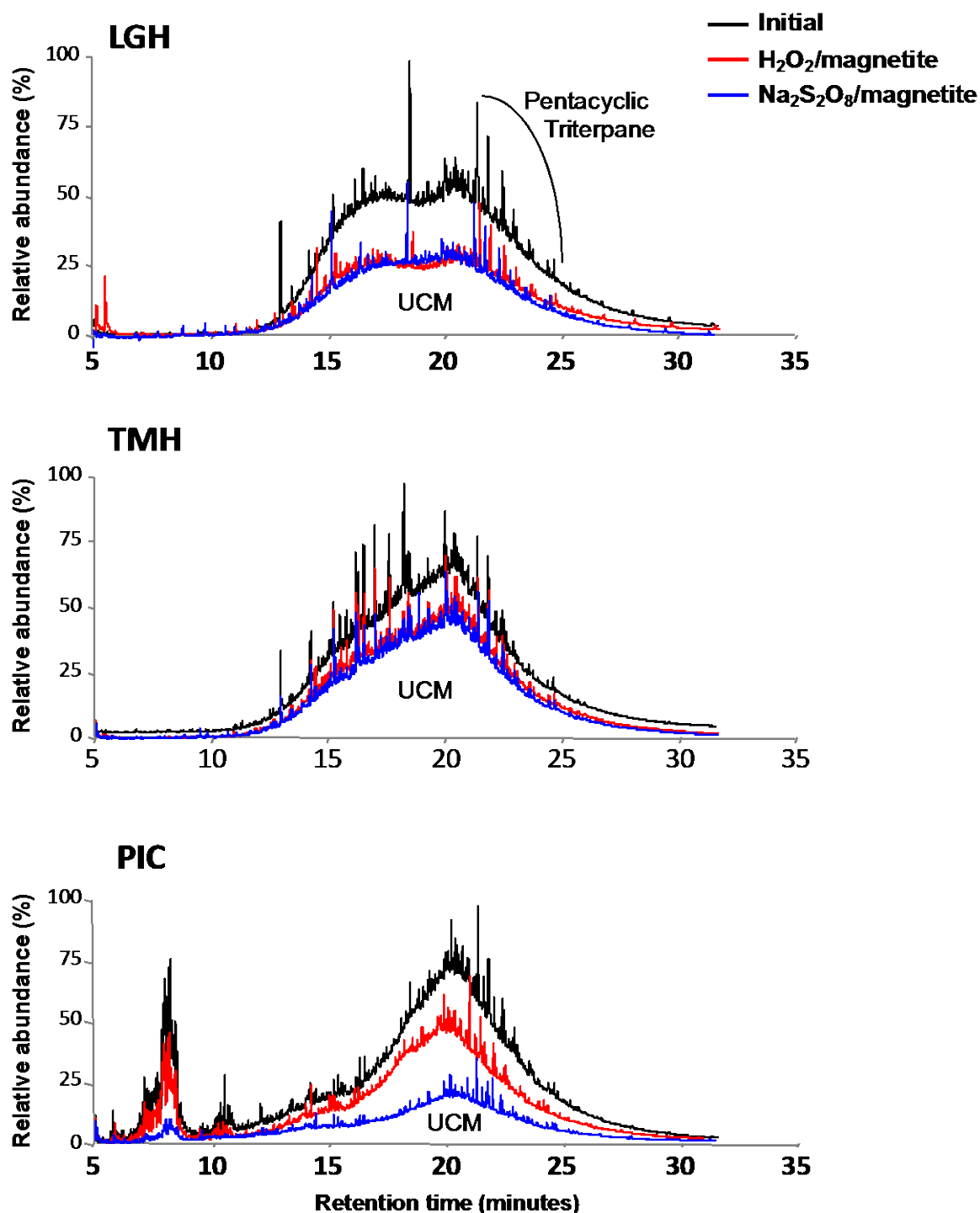
199

	<b>LGH</b>	<b>TMH</b>	<b>PIC</b>
Origin of sediments	Le Guilvinec harbor	Toulon military harbor	Petroleum industrial channel
Granulometric fraction	0-1 mm	0-1 mm	0-2 mm
Clay (<2 $\mu\text{m}$ ) (g $\text{kg}^{-1}$ )	15*	75	100
Fine silt (2–20 $\mu\text{m}$ ) (g $\text{kg}^{-1}$ )		376	440
Coarse silt (20–50 $\mu\text{m}$ ) (g $\text{kg}^{-1}$ )		196	370
Fine sand (50–200 $\mu\text{m}$ ) (g $\text{kg}^{-1}$ )	215	266	90
Coarse sand (200–2000 $\mu\text{m}$ ) (g $\text{kg}^{-1}$ )	772	87	0
pH (water)	8.60	8.28	7.67
Total $\text{CaCO}_3$ (%)	18.63	28.43	23.1
TOC (%)	1.85	4.96	8.39
HI (g $\text{kg}^{-1}$ )	3.7	5.5	9.0
<b>Total element contents</b>			
Fe (g $\text{kg}^{-1}$ )	15.39	30.00	110.29
P (g $\text{kg}^{-1}$ )	2.12	0.56	9.4
K (g $\text{kg}^{-1}$ )	5.87	7.69	1
Mg (g $\text{kg}^{-1}$ )	7.22	14.36	8.9
Ca (g $\text{kg}^{-1}$ )	67.15	109.77	144.9
Na (g $\text{kg}^{-1}$ )	2.37	17.08	5.3
As (mg $\text{kg}^{-1}$ )	N.D.	125.95	46.9
Cd (mg $\text{kg}^{-1}$ )	N.D.	N.D.	1.9
Cr (mg $\text{kg}^{-1}$ )	82.36	71.08	135
Cu (mg $\text{kg}^{-1}$ )	659.65	1498.76	83.7
Hg (mg $\text{kg}^{-1}$ )	N.D.	59.31	0.5
Ni (mg $\text{kg}^{-1}$ )	26.13	29.27	43.4
Pb (mg $\text{kg}^{-1}$ )	364.94	597.52	66.7
Zn (mg $\text{kg}^{-1}$ )	588.28	1760.74	802

201 **Table 2:** Salient characteristics of tested sediments

202 \* represents the sum of clay, fine silt and coarse silt.

203



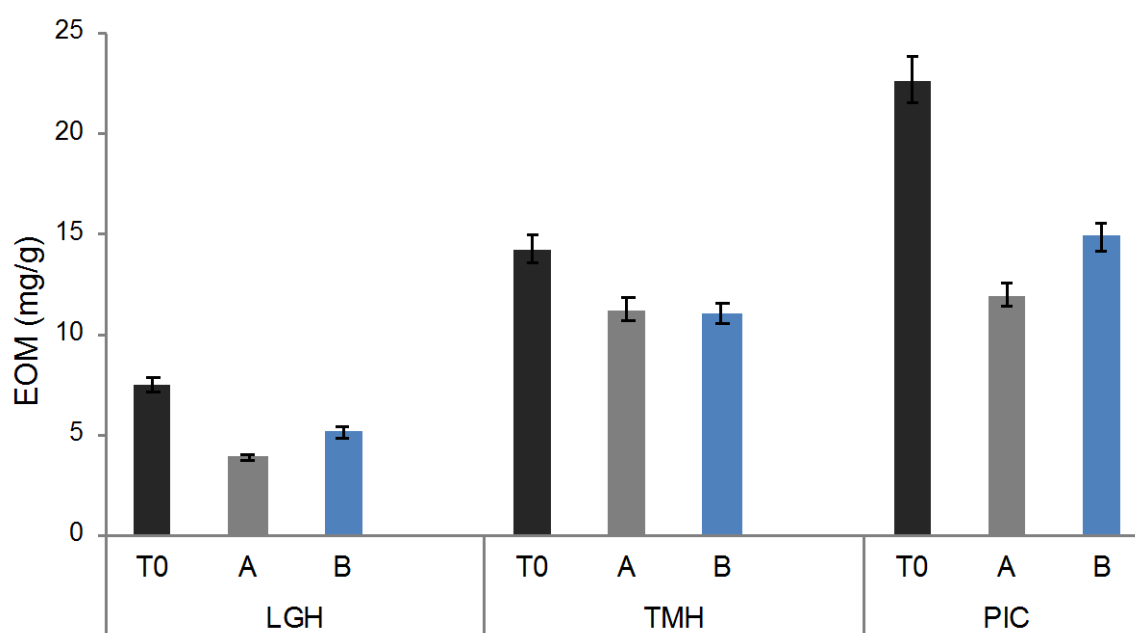
UCM : Unresolved Complex Mixture

204

205 **Figure 2:** GC-FID spectra of tested sediments before (initial) and after chemical oxidation by  
 206 H<sub>2</sub>O<sub>2</sub>/magnetite and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite. Tested sediments were obtained from Le Guilvinec  
 207 harbor (LGH), Toulon military harbor (TMH) and petroleum industrial channel (PIC). Each  
 208 organic extract was analyzed by GC-FID using the same procedure (same initial amount of  
 209 soil before treatment, same amount of solvent for the extraction of sediment after treatment  
 210 and same volume injected in the GC-FID).

### 211 3.2 Chemical oxidation of contaminated sediments

212 Contaminated sediments were subjected to chemical oxidation in batch experiments.  
213 Efficiency of various oxidation treatments was tested at circumneutral pH including H<sub>2</sub>O<sub>2</sub>  
214 alone, H<sub>2</sub>O<sub>2</sub>/Fe(II), H<sub>2</sub>O<sub>2</sub>/magnetite, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> alone, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Fe(II), and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite.  
215 Evolution of extractable organic matter (EOM) was obtained by measuring the weight of  
216 organic extract before and after chemical oxidation (Figure 3).



217

218 **Figure 3:** Extractable organic matter (EOM) before (T0) and after chemical oxidation by  
219 H<sub>2</sub>O<sub>2</sub>/magnetite (A) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite (B) in contaminated sediments obtained from Le  
220 Guilvinec harbor (LGH), Toulon military harbor (TMH) and petroleum industrial channel  
221 (PIC). Experimental conditions were sediment = 2 g, volume of solution = 20 mL, oxidant  
222 doses were used according to the oxidant:Fe molar ratio equal to 20:1 (H<sub>2</sub>O<sub>2</sub>) and 2:1  
223 (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) with 10% w/w magnetite.

224

225 Obtained results (Figure 3) indicated a significant decrease in EOM (25 – 50%) when  
226 magnetite was used as a catalyst. In TMH, EOM removal extent was lowest (~25% by both  
227 oxidants) that might be correlated to its higher carbonate contents (28.43% in TMH  
228 sediments as compare to the 18.63% and 23.1% in LGH and PIC sediments, respectively).

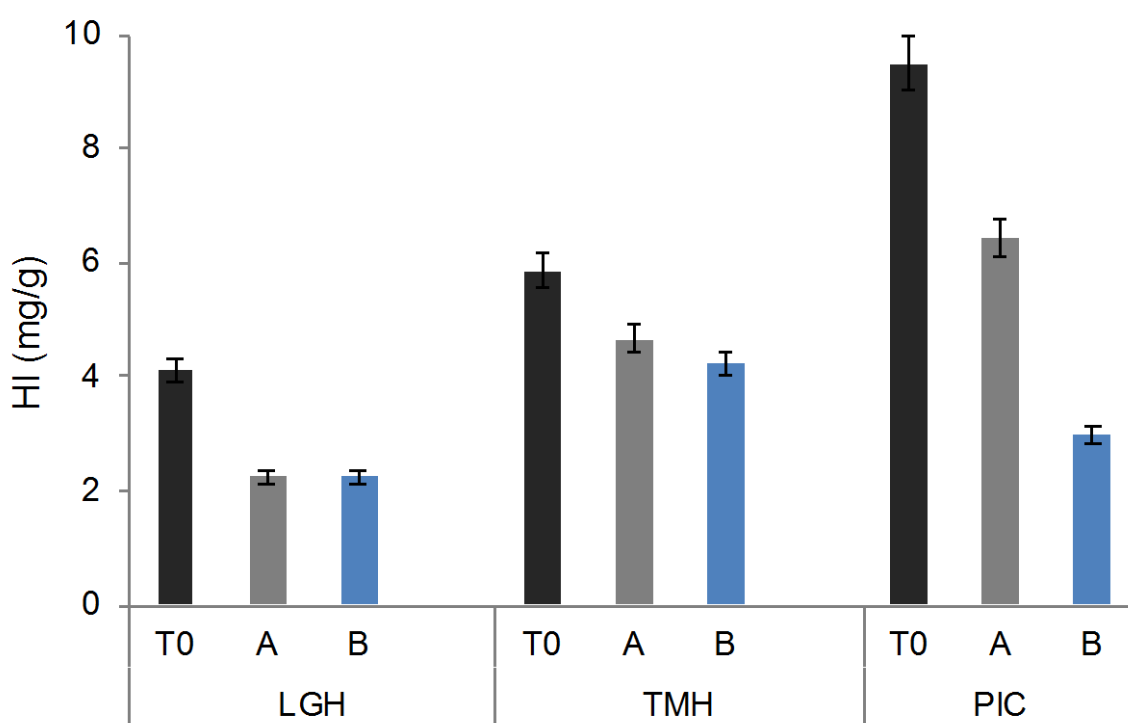
229 Carbonates were shown to have scavenging effects for radicals and thus resulting in



230 decreased oxidation efficiency (Liang et al., 2006; Grebel et al., 2010). Loss of EOM was  
231 50% and 32% in LGH sediments and 48% and 35% in PIC sediment by H<sub>2</sub>O<sub>2</sub>/magnetite and  
232 Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite, respectively. However, use of both oxidants alone or with soluble Fe(II)  
233 resulted in lower removal of EOM (< 5 %, data not shown) that can be associated to the  
234 inability of Fe(II) to catalyze chemical oxidation at circumneutral pH (Xue et al., 2009b;  
235 Usman et al., 2012a). Soluble Fe(II) precipitates at circumneutral pH which obstructed its  
236 catalytic ability. Reaction pH is very important factor controlling the remediation efficiency.  
237 Owing to its strong stability, magnetite was found effective at a wide range of pH (Usman et  
238 al., 2016b).

239 Hydrocarbon index (HI) measured by GC-FID is presented in Figure 4. Use of magnetite-  
240 catalyzed chemical oxidation resulted in approximately 30 – 70% removal of oil  
241 hydrocarbons in tested sediments. On the other hand, negligible degradation (< 5%) was  
242 observed when both oxidants were applied alone or with soluble Fe(II) (data not shown). Xu  
243 et al. (2017) also reported a comparable oxidation efficiency by H<sub>2</sub>O<sub>2</sub> in the presence or  
244 absence of Fe(II) at circumneutral pH (6.5 – 7) in loamy soil highlighting the inability of  
245 Fe(II) to act as a catalyst. They observed that use of H<sub>2</sub>O<sub>2</sub> (225, 450 and 900 mM) with  
246 soluble Fe(II) (2.9 mM) resulted in total petroleum hydrocarbon removal of 2, 15, and 25%,  
247 respectively whereas a comparable oxidation efficiency was noted by H<sub>2</sub>O<sub>2</sub> without Fe(II) of  
248 1, 17, and 22%, respectively (Xu et al., 2017). It should, however, be noted that total  
249 concentration of native Fe(II) in their soil was 4.8 g kg<sup>-1</sup> which could explain the reported  
250 oxidation efficiency without any added Fe(II) by Xu et al (2017). Native Fe in contaminated  
251 soils has been found to catalyze Fenton-like oxidation with no Fe addition for the removal of  
252 PAHs in contaminated soils with 57.5 g kg<sup>-1</sup> endogenous Fe oxides (amorphous + crystalline)  
253 (Watts et al., 2002). Similarly, Flotron et al. (2005) reported an equivalent PAH degradation  
254 by H<sub>2</sub>O<sub>2</sub>/soluble Fe(II) and H<sub>2</sub>O<sub>2</sub> in contaminated sludge (pH 8.8) and sediments (pH 4.4)

255 bearing 94 and 30 g kg<sup>-1</sup> as total native Fe, respectively. Owing to the presence of native Fe  
 256 (16.4 g kg<sup>-1</sup>), 52% of PAHs were degraded by H<sub>2</sub>O<sub>2</sub> (0.4 g g<sup>-1</sup> soil) under saturated  
 257 conditions without any Fe(II) addition (Palmroth et al., 2006). Role of endogenous Fe (18.2 g  
 258 kg<sup>-1</sup>) was also highlighted by Pardo et al. (2016) when they observed similar degradation of  
 259 PAHs by Fenton oxidation (882 mM H<sub>2</sub>O<sub>2</sub> without pH adjustment) by adding  
 260 1 mM Fe(III) or without external addition of Fe. However, Usman et al. (2012b; 2012c)  
 261 reported that native iron (25 g kg<sup>-1</sup> Fe<sub>2</sub>O<sub>3</sub>) was unable to catalyze H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to  
 262 remediate PAH contaminated soils at circumneutral pH. Similarly, Ahmad et al. (2010)  
 263 observed that native iron oxides (8.8 g kg<sup>-1</sup> amorphous + crystalline) in soil did not promote  
 264 measureable activation of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in natural soils. They suggested that quantities of native  
 265 iron oxides are not sufficient to catalyze persulfate oxidation in soils. However, even at  
 266 varying concentrations of native iron (15 – 110 g kg<sup>-1</sup>) in tested sediments, it was found  
 267 ineffective in promoting the oxidation reaction for harbor sediments. Thus, catalytic role of  
 268 native Fe oxides is variable depending on many factors including their nature, total content  
 269 and availability of Fe oxides.



270

271 **Figure 4:** Hydrocarbon index (HI) before (T0) and after chemical oxidation by  
272 H<sub>2</sub>O<sub>2</sub>/magnetite (A) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite (B) in contaminated sediments obtained from Le  
273 Guilvinec harbor (LGH), Toulon military harbor (TMH) and petroleum industrial channel  
274 (PIC). Experimental conditions were sediment = 2 g, volume of solution = 20 mL, oxidant  
275 doses were used according to the oxidant:Fe molar ratio equal to 20:1 (H<sub>2</sub>O<sub>2</sub>) and 2:1  
276 (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) with 10% w/w magnetite.  
277

278 A good correlation was observed between hydrocarbon index and extractable organic matter  
279 for H<sub>2</sub>O<sub>2</sub>/magnetite highlighting the non-specific nature of chemical oxidation to degrade the  
280 non-target compounds. However, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite resulted in lower removal of EOM  
281 while higher loss of HI especially in the PIC sediments. It should be noted that HI quantifies  
282 only low molecular weight compounds (less than 40 carbons), whereas EOM quantifies low  
283 as well as high molecular weight compounds. This observed difference in degradation of  
284 EOM and HI by Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite could be caused by selective behavior of persulfate  
285 oxidation as observed previously where it showed less efficiency towards high molecular  
286 weight PAHs while Fenton oxidation was equally efficient for all PAHs (Usman et al.,  
287 2012b; 2012c). Similarly, when crude oil rich in *n*-alkanes with pristane and phytane spiked  
288 on sand was subjected to magnetite-catalyzed chemical oxidation (Usman et al., 2012a),  
289 H<sub>2</sub>O<sub>2</sub>/magnetite showed non-selective oxidation with equal efficiency towards all *n*-alkanes  
290 (C<sub>21</sub> – C<sub>36</sub>). On the other hand, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite was less reactive towards high molecular  
291 weight *n*-alkanes (C<sub>31</sub> – C<sub>36</sub>). However, it is difficult to point out such selectivity in studied  
292 sediments because they are contaminated with UCM whereby individual components of this  
293 complex mixture are difficult to resolve (Farrington and Quinn, 2015). Observed difference  
294 in term of degradation of EOM and HI for persulfate for PIC sediments could also be  
295 correlated to the lower affinity of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> towards natural organic compounds leading to  
296 higher removal of target pollutants (Lim et al., 2016). Very recently, non-productive  
297 consumption of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was lower than 10% after 56 days of reaction in non-polluted soil  
298 (despite 6.5% CaCO<sub>3</sub>) highlighting the low reactivity of oxidant with different soil

299 components (Lominchar et al., 2018). Rather, persulfate was also found to be activated at  
300 basic pH by organic compounds similar to those present in soil organic matter (Ahmad et al.,  
301 2010). Similarly, the impact of soil matrix was less pronounced on the efficiency of  
302 persulfate oxidation to remove PAHs from historically contaminated soil as compared to the  
303 Fenton oxidation system (Usman et al., 2012b; 2012c).

304

### 305 **3.3 Magnetite-catalyzed chemical oxidation vs. common oxidation systems**

306 As mentioned above, the available literature severely lacks investigations on the chemical  
307 oxidation of oil hydrocarbons in real contaminated sediments (Table 1) and thus a fair  
308 comparison of present findings with the literature is not straightforward. Previous studies  
309 were either performed on artificially contaminated sand/soil or soil obtained from  
310 contaminated site (Table 1) and present study is the first report of using magnetite-catalyzed  
311 chemical oxidation in real sediments.

312 Most of the remediation studies to degrade oil hydrocarbons employing  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{S}_2\text{O}_8$   
313 were performed at acidic pH ( $\leq 3$ ) by Fe-catalyzed chemical oxidation (Kong et al., 1998;  
314 Goi et al., 2006; Do et al., 2010; Villa et al., 2010; Pardo et al., 2014) (Table 1). Due to  
315 detrimental effects of this initial acidification, efforts were made to perform chemical  
316 oxidation of oil hydrocarbons at circumneutral pH by using catalytic ability of basic oxygen  
317 furnace slag (Tsai and Kao, 2009), soluble Fe(III) or Fe(II) with chelating agents (CAs) like  
318 EDTA or trisodium citrate or citric acid (Lu et al., 2010; Pardo et al., 2014; Xu et al., 2016b;  
319 Xu et al., 2017), magnetite (Usman et al., 2012a; 2013; Jamialahmadi et al., 2015) and zero-  
320 valent Fe (Jamialahmadi et al., 2015). Very high pH ( $>12$ ) also resulted in strong activation  
321 of  $\text{Na}_2\text{S}_2\text{O}_8$  for the removal of diesel. Use of chelating agents resulted in effective removal of  
322 oil hydrocarbons (Table 1). However, these CAs being organic in nature will act as oxidant  
323 scavenger by competing with the target pollutants (Pardo et al., 2014; Usman, 2016). For

324 example, Pardo et al. (2014) applied Fenton oxidation to treat biodiesel contaminated soil  
325 with or without trisodium citrate as CA (for details of experimental conditions, see Table 1).  
326 Obtained oil hydrocarbon removal reached 75% in the absence of CA (at pH <3). Use of CA  
327 allowed them to perform chemical oxidation at higher pH (5-6) but degradation efficiency  
328 decreased to 37% which was associated to the consumption of oxidant by CA at higher pH.  
329 Use of CA can also be pH sensitive as reported by Lu et al. (2010). H<sub>2</sub>O<sub>2</sub> catalyzed by Fe(III)  
330 in the presence of a CA (EDTA) was more efficient to degrade petroleum hydrocarbons at pH  
331 7 while oxidation efficiency decreased at pH 6 which was associated to quick degradation of  
332 EDTA leading to the precipitation of Fe(III). However as reported in literature, magnetite has  
333 shown strong stability and catalytic capacity over a wide range of pH and thus, it offers  
334 control over drawbacks associated to initial acidification or CAs. Moreover owing to its  
335 ferromagnetic nature, it can be easily recovered after reaction by magnetic separation and can  
336 be used for further oxidation cycles without any significant decline in catalytic ability (Xue et  
337 al., 2009a; Jia et al., 2018). Other reusability studies indicated a decline in oxidation  
338 efficiency of 20% after 8 oxidation cycles for the removal of phenol in aqueous solutions  
339 (Zhang et al., 2009). However, reusability and/or fate of magnetite has rarely been  
340 investigated in soils or sediments.

341 Regarding efficiency of magnetite-catalyzed chemical oxidation in present study, degradation  
342 of hydrocarbons varied between 40 – 70% when tested sediments were subjected to chemical  
343 oxidation at circumneutral pH with oxidant:Fe molar ratio equal to 20:1 (H<sub>2</sub>O<sub>2</sub>) and 2:1  
344 (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) with 10% w/w magnetite. This would be economically relevant by avoiding initial  
345 acidification and/or use of chelating agents.

346 It is worth noting that efficiency of chemical oxidation is strongly limited by the availability  
347 of polycyclic aromatic hydrocarbons (PAHs) in aged contaminated soils and sediments  
348 (Flotron et al., 2005; Choi et al., 2014; Usman et al., 2016b). As a matter of fact,

349 H<sub>2</sub>O<sub>2</sub>/magnetite or Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/magnetite did not cause any PAH degradation unless tested soils  
350 were subjected to chemical (Usman et al., 2012c) or thermal pretreatment (Biache et al.,  
351 2015; Usman et al., 2016a). However, no such pollutant unavailability was observed for oil  
352 hydrocarbons in tested sediments. It might be correlated to difference between the nature of  
353 both matrices (soils vs. sediments), history of contamination and type of pollutants (aliphatic  
354 vs. aromatic) (Flotron et al., 2005; Trellu et al., 2017; Lominchar et al., 2018). The specific  
355 deposition, the preservation in water can probably explain the difference in term of  
356 availability between soils and sediments. Moreover, in our case, the contamination originated  
357 from petroleum source (a liquid) compared to coal-tar (source of PAHs) which becomes solid  
358 with aging while losing the low molecular compounds which leads to enrichment of heavy  
359 compounds in coal-tar particles (Trellu et al., 2017). Coal-tar can be observed in historically  
360 contaminated soil as a small ball-like aggregate with low specific area as compared to the  
361 petroleum pollution which exists as a thin film on minerals in sediments (Trellu et al., 2017).  
362 In addition to the *in-situ* application, magnetite-catalyzed chemical oxidation could offer a  
363 quick and cost-effective alternative to conventional remediation strategies (landfilling,  
364 stabilization etc.) for dredged sediments (Akcil et al., 2015) ensuring safe reuse of dredged  
365 sediments.

#### 366 **4. Conclusion**

367 This is the premier study reporting the use of magnetite-catalyzed chemical oxidation to  
368 remove biorefractory oil residues (remaining of natural attenuation) in different historically  
369 contaminated sediments. Magnetite showed strong efficiency to catalyze chemical oxidation  
370 at circumneutral pH. Oxidation efficiency was, however, limited by the nature and properties  
371 of sediments. No issue related to pollutant availability was observed as was the case for PAH  
372 aged contaminated soils which might be correlated to the difference of contaminant type  
373 (aliphatic hydrocarbons and PAHs) and mediums (soils and sediments). Due to the strong

374 efficiency of magnetite to degrade biorefractory oil residues without any initial acidification  
375 (circumneutral pH), this study may have strong implications to design an innovative stand-  
376 alone technology for *in-situ* and ex-situ remediation of contaminated sediments.

377 **Acknowledgments:**

378 Authors thank the GISFI (French Scientific Interest Group - Industrial Wasteland,  
379 [www.gisfi.univ-lorraine.fr](http://www.gisfi.univ-lorraine.fr)).

380

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