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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 (H_2O_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: H_2O_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.

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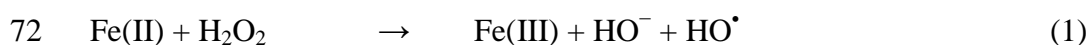
45 **Keywords:** Oil hydrocarbons; Harbor sediments; Remediation; Fenton-like; Persulfate;

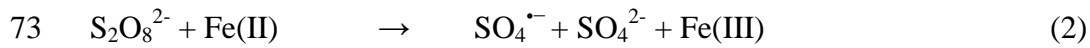
46 Magnetite

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)₂O₄] 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 (H₂O₂) and
93 persulfate (Na₂S₂O₈) 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 (H₂O₂ or Na₂S₂O₈ 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 ₂ O ₂	Magnetite (Commercial) Screened through 0.3 mm sieve.	Petroleum hydrocarbons 1 g Kg ⁻¹	Spiked sand/ Batch	pH = 3, magnetite = 5 wt%, H ₂ O ₂ = 15 wt%	50% hydrocarbon removal after 8 days	(Kong et al., 1998)
H ₂ O ₂	Soluble Fe(II)	Diesel 10-12 g Kg ⁻¹	Spiked sand and peat soil/ Batch	pH = 3, H ₂ O ₂ :Fe(II) molar ratio = 10:1 liquid/solid = 1 and 20 mL g ⁻¹ for sand and peat	>80% removal of hydrocarbons after 72 h in sand	(Goi et al., 2006)
H ₂ O ₂	Basic oxygen furnace slag	Fuel oil or diesel TPH = 10 g kg ⁻¹	Spiked sand and sandy loam/ Batch	pH = 6.7, H ₂ O ₂ = 15% Slag = 100 g kg ⁻¹	TPH removal of 96% and 76% in diesel and fuel oil tests after 40 h	(Tsai and Kao, 2009)
H ₂ O ₂	Soluble Fe(II) in the presence or absence of natural soil Fe minerals (hematite mainly)	Diesel 5 g Kg ⁻¹	Spiked loam soil/ Batch	pH = 2.5 – 3, Fe(II) = 12 mM H ₂ O ₂ = 0.045 g g ⁻¹ 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 ₂ O ₂	Soluble Fe(III) with EDTA	Petroleum hydrocarbons Dichloromethane- extractable organics 14.8 g Kg ⁻¹	Soil samples collected from areas adjacent to oil wells/ Batch	pH = 7, H ₂ O ₂ = 2.45 mol Kg ⁻¹ soil, H ₂ O ₂ :Fe(III) molar ratio = 200:1.	>80% removal of hydrocarbons	(Lu et al., 2010)
Na ₂ S ₂ O ₈	Soluble Fe(II)	Diesel 5 g Kg ⁻¹	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 ₂ S ₂ O ₈	Soluble Fe(II)	Diesel TPH = 3.5 g Kg ⁻¹	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 ⁻² day ⁻¹	(Yen et al., 2011)
H ₂ O ₂ or Na ₂ S ₂ O ₈	Soluble Fe(II) Or Magnetite (lab synthesized)	Petroleum hydrocarbons 4 g Kg ⁻¹ 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 ₂ O ₂) 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 ² g ⁻¹			(Na ₂ S ₂ O ₈)	pollutant removal with soluble Fe(II) as catalyst	
H ₂ O ₂ or Na ₂ S ₂ O ₈	Magnetite (lab synthesized) 30 nm; 103 m ² g ⁻¹	Petroleum hydrocarbons 4 g Kg ⁻¹ of weathered oil	Spiked sand/ Saturated column	pH = 6.7, 20 – 25 °C, magnetite = 10% w/w, oxidant:Fe molar ratio = 10:1 (H ₂ O ₂) and 1:1 (Na ₂ S ₂ O ₈)	60-70% of hydrocarbon removal by both oxidants	(Usman et al., 2013)
H ₂ O ₂	Soluble Fe(III) with or without chelating agent	Biodiesel blend (20 % biodiesel, 80 % diesel) TPH = 1 g Kg ⁻¹	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 ₂ O ₂ = 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 ₂ O ₂	Magnetite and ZVI	Diesel TPH = 5 g Kg ⁻¹	Spiked soil/ Batch	pH = 6.7–7.4 Catalyst = 4.27 wt% H ₂ O ₂ = 2.17 mol L ⁻¹	TPH removal was 57% (magnetite) and 67% (ZVI)	(Jamialahma di et al., 2015)
H ₂ O ₂	Soluble Fe(II) with chelating agent	Crude oil TPH = 15.2 and 27.7 g Kg ⁻¹	Soils collected from two oil wells / Batch	pH = 7.5, Fe(II) = 5.8 mM, H ₂ O ₂ = 1100 mM Citric acid = 17.9 g L ⁻¹	40-50% of TPH removal	(Xu et al., 2016b)
H ₂ O ₂	Soluble Fe(II) with chelating agent	Crude oil contamination TPH = 23.4 g Kg ⁻¹	Soil collected from an oil well/ Batch	pH = 6.5 – 7, Fe(II) = 2.9 mM, H ₂ O ₂ = 900 mM	>20% removal of hydrocarbons in 10 days	(Xu et al., 2017)
Na ₂ S ₂ O ₈	NaOH	Diesel TPH = 4.9 g Kg ⁻¹	Soil collected from train maintenance facility/Batch	pH = ≥ 12, 20 °C, Na ₂ S ₂ O ₈ = 420 mM, NaOH:Na ₂ S ₂ O ₈ = 4, Liquid/solid = 2 mL g ⁻¹	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.

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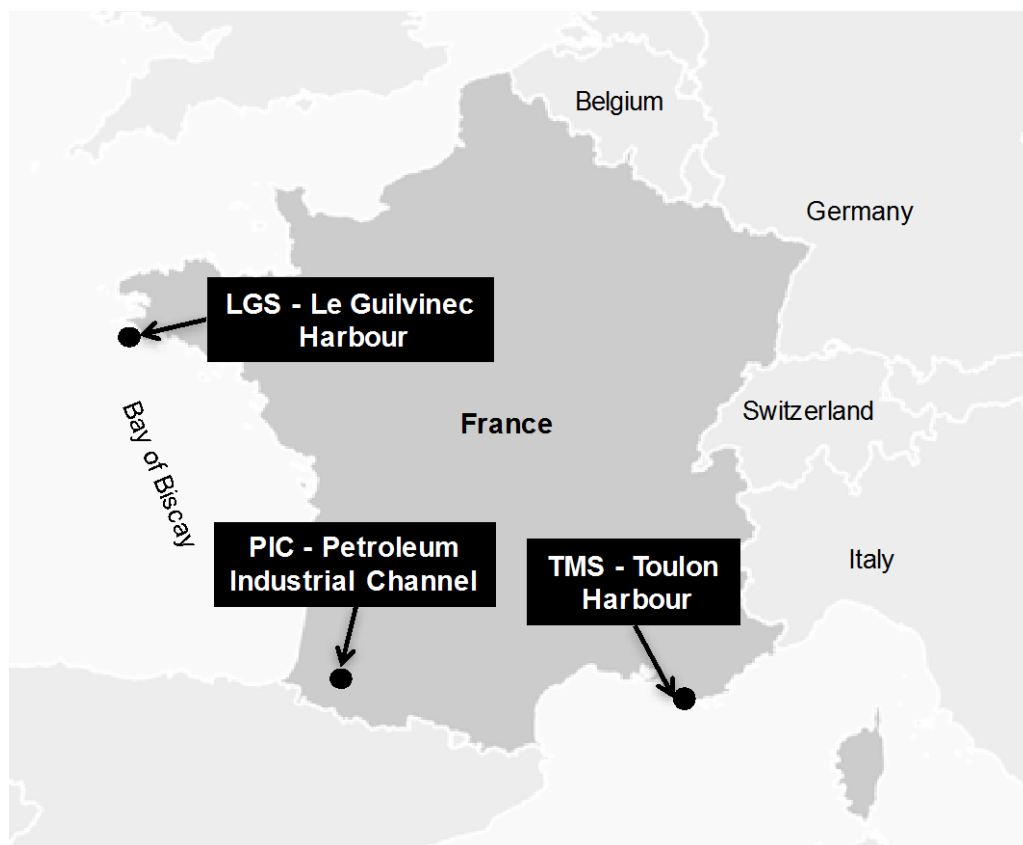
104 **2. Experimental section**

105 **2.1. Chemical reagents and materials**

106 Following reagents were used: FeSO₄·7H₂O with purity greater than 98% obtained from
107 VWR, sodium persulfate (Na₂S₂O₈) and hydrogen peroxide 35% (H₂O₂) 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 N₂ 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 (C₁₀H₂₂) and *n*-tetracontane (C₄₀H₈₂) 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⁻¹) 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 g kg^{-1}) < TMH (5.5 g
186 kg^{-1}) < PIC (9.0 g kg^{-1}). These sediments contained higher 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).

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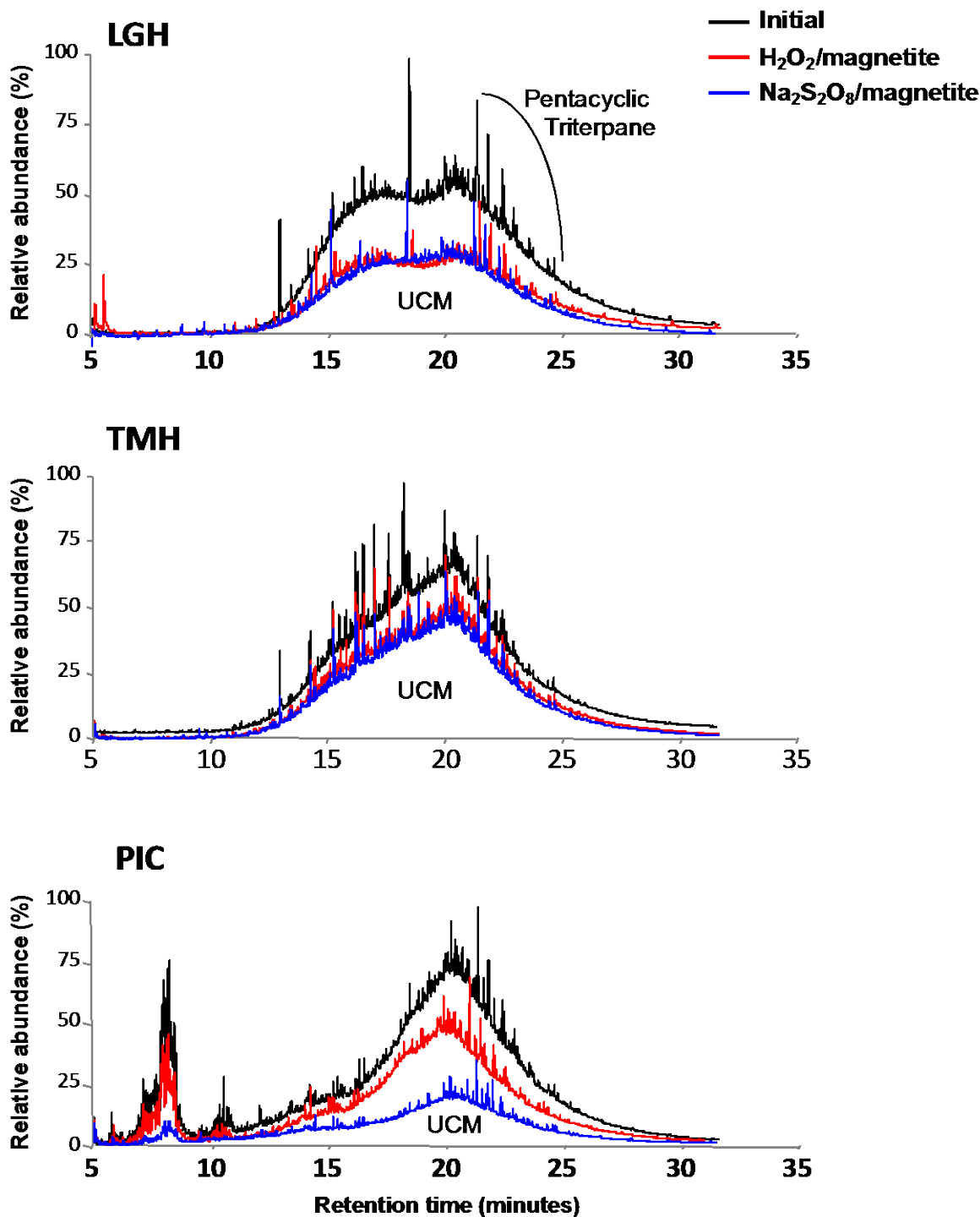
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	LGH	TMH	PIC
Origin of sediments	Le Guilvinec harbor	Toulon military harbor	Petroleum industrial channel
Granulometric fraction	0-1 mm	0-1 mm	0-2 mm
Clay (<2 μm) (g kg^{-1})	15*	75	100
Fine silt (2–20 μm) (g kg^{-1})		376	440
Coarse silt (20–50 μm) (g kg^{-1})		196	370
Fine sand (50–200 μm) (g kg^{-1})	215	266	90
Coarse sand (200–2000 μm) (g kg^{-1})	772	87	0
pH (water)	8.60	8.28	7.67
Total CaCO_3 (%)	18.63	28.43	23.1
TOC (%)	1.85	4.96	8.39
HI (g kg^{-1})	3.7	5.5	9.0
Total element contents			
Fe (g kg^{-1})	15.39	30.00	110.29
P (g kg^{-1})	2.12	0.56	9.4
K (g kg^{-1})	5.87	7.69	1
Mg (g kg^{-1})	7.22	14.36	8.9
Ca (g kg^{-1})	67.15	109.77	144.9
Na (g kg^{-1})	2.37	17.08	5.3
As (mg kg^{-1})	N.D.	125.95	46.9
Cd (mg kg^{-1})	N.D.	N.D.	1.9
Cr (mg kg^{-1})	82.36	71.08	135
Cu (mg kg^{-1})	659.65	1498.76	83.7
Hg (mg kg^{-1})	N.D.	59.31	0.5
Ni (mg kg^{-1})	26.13	29.27	43.4
Pb (mg kg^{-1})	364.94	597.52	66.7
Zn (mg 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



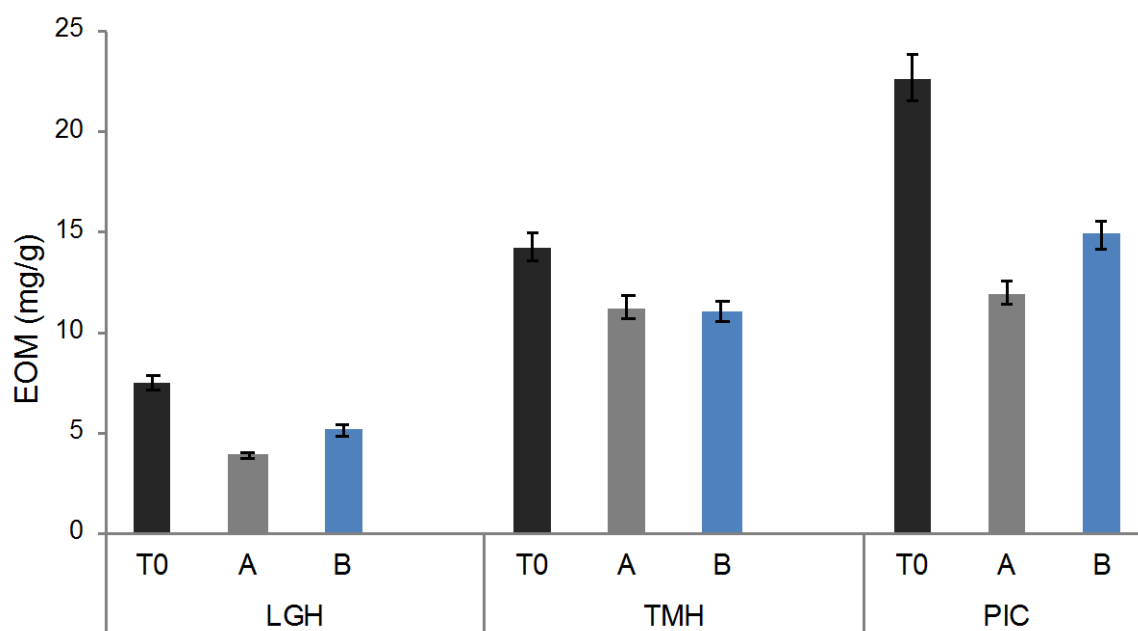
UCM : Unresolved Complex Mixture

204

205 **Figure 2:** GC-FID spectra of tested sediments before (initial) and after chemical oxidation by
 206 H₂O₂/magnetite and Na₂S₂O₈/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 H₂O₂
214 alone, H₂O₂/Fe(II), H₂O₂/magnetite, Na₂S₂O₈ alone, Na₂S₂O₈/Fe(II), and Na₂S₂O₈/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).



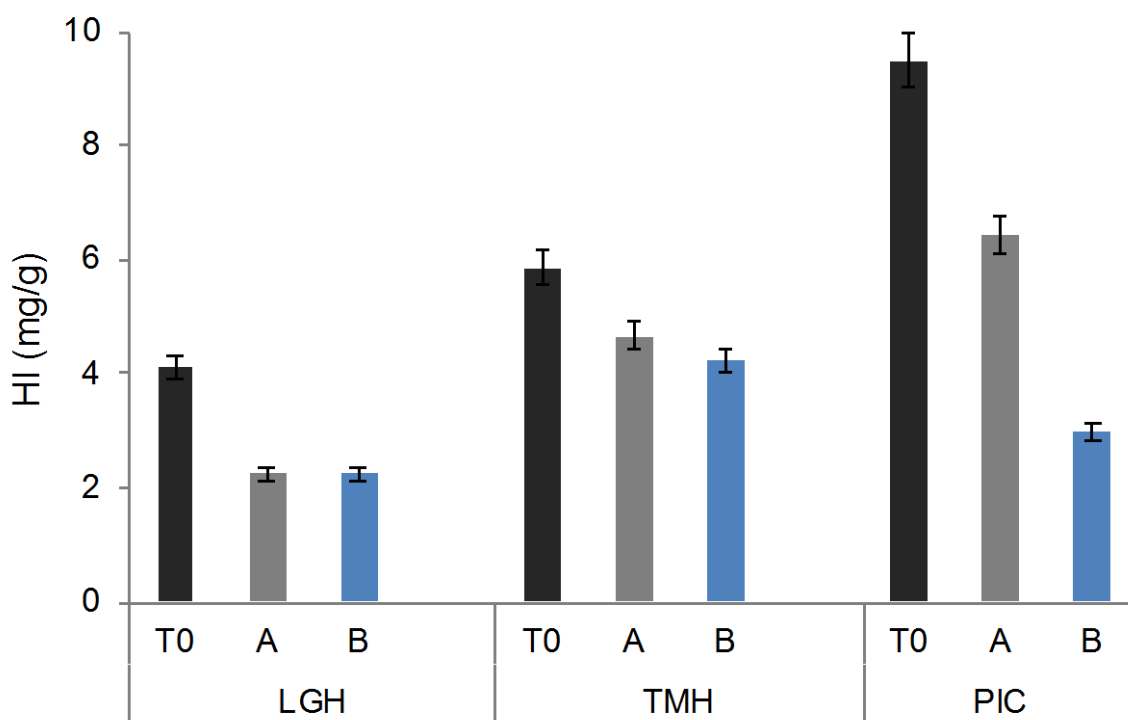
217 **Figure 3:** Extractable organic matter (EOM) before (T0) and after chemical oxidation by
218 H₂O₂/magnetite (A) and Na₂S₂O₈/magnetite (B) in contaminated sediments obtained from Le
219 Guilvinec harbor (LGH), Toulon military harbor (TMH) and petroleum industrial channel
220 (PIC). Experimental conditions were sediment = 2 g, volume of solution = 20 mL, oxidant
221 doses were used according to the oxidant:Fe molar ratio equal to 20:1 (H₂O₂) and 2:1
222 (Na₂S₂O₈) with 10% w/w magnetite.
223
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 H₂O₂/magnetite and
232 Na₂S₂O₈/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 H₂O₂ 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 H₂O₂ (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 H₂O₂ 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⁻¹ 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⁻¹ endogenous Fe oxides (amorphous + crystalline)
253 (Watts et al., 2002). Similary, Flotron et al. (2005) reported an equivalent PAH degradation
254 by H₂O₂/soluble Fe(II) and H₂O₂ in contaminated sludge (pH 8.8) and sediments (pH 4.4)

255 bearing 94 and 30 g kg⁻¹ as total native Fe, respectively. Owing to the presence of native Fe
 256 (16.4 g kg⁻¹), 52% of PAHs were degraded by H₂O₂ (0.4 g g⁻¹ soil) under saturated
 257 conditions without any Fe(II) addition (Palmroth et al., 2006). Role of endogenous Fe (18.2 g
 258 kg⁻¹) was also highlighted by Pardo et al. (2016) when they observed similar degradation of
 259 PAHs by Fenton oxidation (882 mM H₂O₂ 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⁻¹ Fe₂O₃) was unable to catalyze H₂O₂ and Na₂S₂O₈ to
 262 remediate PAH contaminated soils at circumneutral pH. Similarly, Ahmad et al. (2010)
 263 observed that native iron oxides (8.8 g kg⁻¹ amorphous + crystalline) in soil did not promote
 264 measureable activation of Na₂S₂O₈ 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⁻¹) 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_2O_2 /magnetite (A) and $\text{Na}_2\text{S}_2\text{O}_8$ /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_2O_2) and 2:1
276 ($\text{Na}_2\text{S}_2\text{O}_8$) with 10% w/w magnetite.
277

278 A good correlation was observed between hydrocarbon index and extractable organic matter
279 for H_2O_2 /magnetite highlighting the non-specific nature of chemical oxidation to degrade the
280 non-target compounds. However, $\text{Na}_2\text{S}_2\text{O}_8$ /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 $\text{Na}_2\text{S}_2\text{O}_8$ /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_2O_2 /magnetite showed non-selective oxidation with equal efficiency towards all *n*-alkanes
290 ($\text{C}_{21} - \text{C}_{36}$). On the other hand, $\text{Na}_2\text{S}_2\text{O}_8$ /magnetite was less reactive towards high molecular
291 weight *n*-alkanes ($\text{C}_{31} - \text{C}_{36}$). 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 $\text{Na}_2\text{S}_2\text{O}_8$ towards natural organic compounds leading to
296 higher removal of target pollutants (Lim et al., 2016). Very recently, non-productive
297 consumption of $\text{Na}_2\text{S}_2\text{O}_8$ was lower than 10% after 56 days of reaction in non-polluted soil
298 (despite 6.5% CaCO_3) 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 H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$
313 were performed at acidic pH (≤ 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). H₂O₂ 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 (H₂O₂) and 2:1
344 (Na₂S₂O₈) 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 H₂O₂/magnetite or Na₂S₂O₈/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; Trelu 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 (Trelu 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 (Trelu 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.

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380

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