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1 **Comparative assessment of a foam-based oxidative**
2 **treatment of hydrocarbon-contaminated unsaturated**
3 **and anisotropic soils**

4

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11

12 Abstract:

13 *In situ* delivery of liquid reagents in vadose zone is limited by soil anisotropy and gravity. The
14 enhanced delivery of persulfate (PS) as oxidant, using a new foam-based method (F-PS) was
15 compared at bench-scale to traditional water-based (W-PS) and surfactant solution-based (S-PS)
16 deliveries. The goal was to distribute PS uniformly in coal tar-contaminated unsaturated and
17 anisotropic soils, both in terms of permeability and contamination. Water was the less efficiently
18 delivered fluid because of the hydrophobicity of the contaminated soils. Surfactant enhanced PS-
19 distribution into contaminated zones by reducing interfacial tension and inverting soil wettability.
20 Regardless of coal tar contamination contrasts (0 vs. 5 and 1 vs. 10 g.kg_{soil}⁻¹) or strong permeability
21 contrasts, PS-solution injection after foam injection led to the most uniform reagents delivery. While
22 PS-concentration varied more than 5-times between zones using W-PS and S-PS methods, it varied
23 less than 1.6-times when the F-PS one was used. Finally, despite unfavorable conditions, the foam-
24 based method did not show any detrimental effect regarding the oxidation of hydrocarbons
25 compared to the W-PS and S-PS methods carried out in ideal conditions. Moreover, hydrocarbon
26 degradation rates were slightly higher when using F-PS than S-PS due to a lower surfactant content in
27 the targeted zone.

28 Keywords :

29 Coal tar contamination ; Vadose zone ; Soil anisotropy ; ISCO ; Surfactant foam

30

31 1. Introduction

32 Persistent organic pollutants (POPs) are hazardous compounds. Their presence in contaminated soils
33 and groundwater often result from spillages. Coal tars are viscous hydrocarbons that contain many
34 POPs such as polycyclic aromatic hydrocarbons (PAHs) [1]. Soils with such contaminations are
35 notoriously difficult to treat because of the contaminants. Indeed, the latter are often tightly bound
36 to soil particles and their release occurs over decades [2]. The *in situ* remediation of contaminated
37 soils is growing, since it reduces the risks associated with contaminants dissemination and hazards
38 [3].

39 *In situ* chemical oxidation (ISCO) is one of the most innovative technologies to remove POPs at
40 residual saturations [3–5]. However, its efficiency is limited by the slow desorption of hydrophobic
41 contaminants. The use of surfactants coupled with chemical oxidation (S-ISCO) revealed the
42 improvement of the availability of hydrocarbons [6–10]. However, the treatment efficiency is often
43 hindered by the poor contact between oxidants and contaminants. This is especially true in the
44 vadose zone, where gravity and anisotropy (permeability and hydrophobicity) limit the isotropic
45 distribution of reactants [11,12]. Indeed, traditional water-based fluids in vadose zone are prone to
46 vertical migration, capillary phenomena, such as capillary suction into small pores, and bypassing of
47 hydrophobic contaminated zones.

48 Currently, there is a growing interest for the use of high viscosity shear-thinning fluids for soil
49 remediation. Among them, surfactant foam has proved to be a promising fluid for *in situ*
50 environmental remediation (ISER) [13–16], especially to deliver remedial amendments [11,17–21].
51 Surfactant foam in porous media appears as trains of gas bubbles separated by thin liquid films
52 (lamellae) stabilized by surfactant molecules. The lamellae rest at pore throats. They have to stretch
53 to go through pores or break, opposing resistance to gas flow. Foam exhibits advantages of high
54 viscosity, shear-thinning behavior and low-density fluid [22], making its propagation in vadose zone
55 less affected by gravity and anisotropy. However, when carrying out foam-enhanced ISCO, the

56 simultaneous presence of surfactant and oxidant, or hydrocarbon may have detrimental effects, both
57 on the selectivity of oxidation and on foam stability [23,24].

58 This work is part of the MOUSTIC project which focuses on the development of innovative
59 technologies for the *in situ* remediation of unsaturated soils contaminated by petroleum
60 hydrocarbons. Previously, we reported an innovative surfactant foam-based technology to improve
61 the control of reagent-delivery in model soils made of monodisperse glass beads [25]. Here, the
62 performance of this new technology was compared with the traditional remedial fluids (water and
63 surfactant solution) first, to distribute PS in 2D-sandboxes filled with real coal tar unsaturated and
64 anisotropic soils having different grain sizes, permeabilities and contamination levels, and second, to
65 remove hydrocarbons. Considering various permeability and wettability contrasts, this study allowed
66 a better understanding of fluids' behaviors in anisotropic contaminated fields. PS-distributions in
67 sandbox were accurately mapped and compared to visual observations. Comparison of hydrocarbons
68 degradation rates and oxidation selectivity was carried out to assess any detrimental effect on the
69 treatment efficiency. Only a few studies compared the use of water, surfactant solution and foam to
70 deliver remedial reagents, namely nano zero-valent iron into porous media made of glass beads
71 [21,26], or calcium polysulfide and phosphate into non-contaminated sediments [11,18]. A
72 comparative study to deliver oxidizing agents using such fluids was never reported in real
73 unsaturated soils contaminated with hydrocarbons in 2D-sandboxes. This represents a challenge
74 regarding detrimental interactions between surfactant and oxidant [24,25]. This work aims to
75 demonstrate the interest of the foam-based method in situations often observed in polluted sites.

76

77 2. Materials and methods

78 2.1. Chemicals

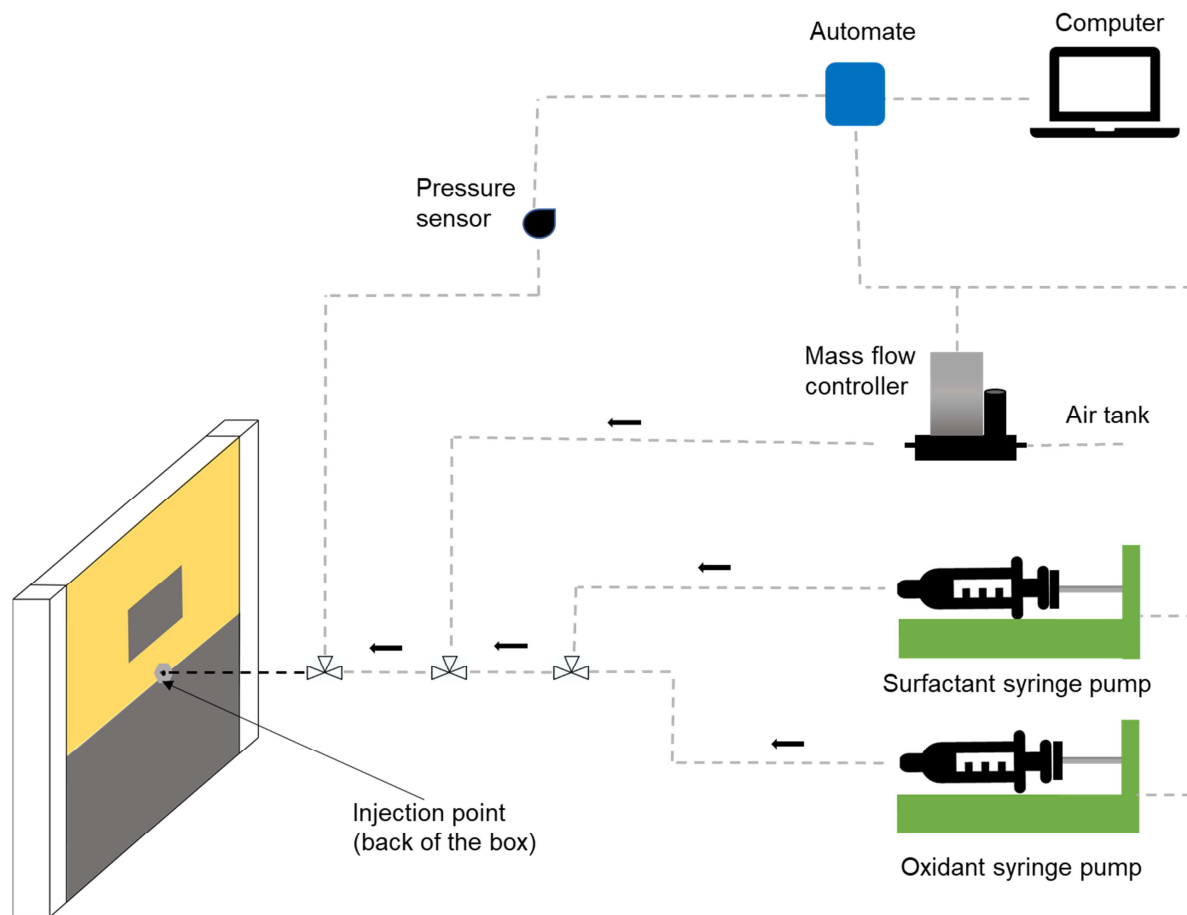
79 Zwitterionic surfactant Lauryl betaine (LB) was used either directly for S-PS or to generate foams for
80 F-PS [24,25]. The contaminant was a liquid coal tar (density 1.15) collected from a former steelwork
81 industrial site, whose composition is provided in Table SM.1. Briefly, the measured fraction of
82 hydrocarbons in coal tar were 56.4 and 42.3%w for C5-C9 (volatile) and C10-C40 (semi-volatile),
83 respectively. Sodium persulfate (>96%, Fisher Scientific) was used as oxidant, because of its higher
84 selectivity towards aromatic hydrocarbons when surfactant is present [24]. Analytical reagents were
85 dichloromethane (>99%, Fisher), n-hexane (99%, VWR), iodide and potassium iodide (99.9%, Fisher),
86 barium chloride dihydrate (>99%, VWR), elementary iron (Prolabo). All solutions were prepared with
87 deionized water.

88 2.2. Soils

89 Two mostly quartzic soils with low carbonate content were used in this study: a silty (ST) and a sandy
90 soil (SD), both locally sourced. The raw sandy soil was sieved under running water to collect a fine
91 (FSD) and coarse fraction (CSD). These two soils were then artificially contaminated by coal tar
92 according to [25]. Four levels of tar contamination were prepared (0.2, 1, 5 and 10 g.kg_{soil}⁻¹) and the
93 soils were aged for five months in sealed glass flasks stored upside-down to avoid hydrocarbon
94 volatilization. The soils' surface areas were estimated by calculation using the particle size
95 distribution, assuming spherical particles. Pore radii were estimated to be equal to $D_{10}/2$ (10th
96 percentile of grain size distribution) for each material assuming that, permeability is mostly affected
97 by smaller grains [27]. Main characteristics of the soils used in this study are summarized in Table
98 SM.2.

99 2.3. Experimental set-up

100 The experimental set-up used for fluids injection experiments is presented in Figure 1.



101 **Figure 1.** Scheme of the experimental set-up for fluids injection in packed sandbox.

102 Soils were packed in a PMMA 2D-sandbox (internal dimensions: 25 cm wide, 2 cm thick, 18 cm high).

103 The front face was removable thanks to screws and gasket. Soil was compacted using a rubber stick

104 while filling. Top lid and gasket were then tightly held using clamps to ensure perfect sealing. All

105 experiments were conducted under unsaturated conditions.

106 Four anisotropic models were studied: two contamination contrasts, where soil permeability was set

107 at $90 \mu\text{m}^2$ and two permeability contrasts with tar-contamination set to 5 g.kg^{-1} . As shown in Fig. 1,

108 the materials were set as two horizontal layers (9 cm high). A rectangular lens (6 cm wide x 3 cm

109 high) of the bottom layer material was embedded within the upper layer. The selected configurations

110 are summarized in Table 1.

111 Table 1: Summary of the sandbox experiments for persulfate delivery.

Contrast	Upper layer soil	Bottom layer soil	Embedded lens soil
C1: contamination 1 st case: clean and moderately contaminated soil	FSD0 90 μm^2 0 g.kg ⁻¹	FSD5 90 μm^2 5 g.kg ⁻¹	FSD5 90 μm^2 5 g.kg ⁻¹
C2: contamination 2 nd case: contrast of 1:10	FSD1 90 μm^2 1 g.kg ⁻¹	FSD10 90 μm^2 10 g.kg ⁻¹	FSD10 90 μm^2 10 g.kg ⁻¹
P1: permeability 1 st case: contrast of 1:18	FSD5 90 μm^2 5 g.kg ⁻¹	CSD5 1362 μm^2 5 g.kg ⁻¹	CSD5 1362 μm^2 5 g.kg ⁻¹
P2: permeability 2 nd case: contrast of 1:23	FSD5 90 μm^2 5 g.kg ⁻¹	ST5 4 μm^2 5 g.kg ⁻¹	ST5 4 μm^2 5 g.kg ⁻¹

112 All fluids were injected at the center of the sandbox by an opening at the back (i.d. 0.8 mm, Fig. 1).

113 Syringe pumps, flow-meter and pressure sensor were as in [25].

114 2.4. Injection procedures

115 2.4.1. Foam injection

116 Prior to PS-injection, foam was formed into the soil [25]. For C1, C2 and P2, foam was injected using
 117 the solution alternating gas (SAG) method, since it requires the lowest pressure for injection in soils
 118 with such permeability [15,28]. Slugs of air and surfactant (1%w) were injected in alternation. Flow
 119 rates and volumes per cycle were 70 and 2 mL.min⁻¹ and 5 and 0.2 mL for gas and surfactant,
 120 respectively. For P1 experiment, due to the presence of the highly permeable CSD5, foam was pre-

121 generated by co-injecting surfactant and gas through a pre-column (9 cm) filled with FSD0. For pre-
122 generated foam, flow rates were 700 mL.min⁻¹ and 8 mL.min⁻¹ for gas and surfactant solution,
123 respectively (foam quality (FQ) = 99%). A pressure limit at 100 kPa.m⁻¹ was set for injection in each
124 experiment to avoid soil fracturing or heaving [29].

125 2.4.2 Persulfate injection

126 Non-activated PS (10 g.L⁻¹) was delivered in three forms with increasing complexity: solubilized in
127 water (W-PS), in LB (1%w) surfactant solution (S-PS), or as solution in water delivered after foam
128 injection (F-PS). The injected PS-concentration was chosen mainly to limit dilutions for soil analyses
129 used to map PS-delivery. This was acceptable, since PS-concentration does not affect foamability of
130 the surfactant even at high concentrations close to its solubility limit [24].

131 For each situation, the volume of PS solution injected was the same for the three delivery fluids to
132 allow comparison. The injected volume of PS solution was the volume that filled the foam occupied
133 area and moved surfactant from the network of lamellae. It was estimated according to F-PS
134 experiments [25]. This was achieved by calculating the porous volume of soil occupied by foam using
135 the ImageJ software [30]. Injected volumes of PS solution were 80, 120, 90 and 50 mL for C1, C2, P1
136 and P2, respectively.

137 2.5. PS-analysis in sandboxes

138 2.5.1. PS-distribution in contaminated anisotropic sandboxes

139 For all injection experiments, with the three fluids in the four configurations (C1, C2, P1, P2), pictures
140 of the sandbox were taken periodically (see Fig. SM.1 and SM.2). However, evaluating the oxidant
141 distribution only visually may be inaccurate. To overcome this limitation, PS-concentrations were
142 locally measured across the sandbox. Soil was thoroughly sampled after the removal of the sandbox's
143 front face. Mapping of PS-concentrations (g.kg_{soil}⁻¹) was done for every experiment after PS-injection
144 according to [31,32]. Details can be found in the supplementary material.

145 To quantify PS-distribution efficiency, an isotropic distribution factor, (I_f , dimensionless) was
 146 calculated according to Eq.1. The I_f is the PS concentration-weighted ratio of its propagation
 147 distances in the vertical and horizontal directions from the injection point, which allows the
 148 comparison of delivery and sweeping efficiency between experiments.

$$149 \quad I_f = \frac{\sum d v^- C v^- / \sum d v^+ C v^+}{\sum |d h| C h / \sum |d v| C v} \quad (1)$$

150 where d and C are the propagation distance and the PS-concentration at a given distance from the
 151 injection point, respectively. The indexes v and h represent the vertical and horizontal directions,
 152 respectively and the + or – signs indicate the upper and lower or right and left direction for the
 153 vertical and horizontal distances, respectively. Herein, the optimal value for I_f would be 1,
 154 representing an isotropic reagents distribution and meaning that the horizontal and vertical
 155 distribution of PS are equal. In contrast, high or low I_f -values indicate an anisotropic distribution of
 156 reagents around the injection point.

157 The capillary number (N_c , dimensionless) is defined as the ratio of viscous forces to capillary forces. It
 158 is defined by Eq.2 and was calculated for each PS-delivery fluid [33].

$$159 \quad N_c = \frac{\mu u}{\gamma} \quad (2)$$

160 where μ is the injected fluid apparent viscosity (Pa.s), u is the fluid velocity ($m.s^{-1}$), and γ is the
 161 interfacial tension (IFT) at the air/solution interface ($N.m^{-1}$). It allows a quantitative assessment of
 162 forces controlling the remedial fluid propagation. Here, flow rates for W-PS, S-PS and surfactant
 163 solution when injecting foam were unchanged ($Q = 2 \text{ mL.min}^{-1}$). The effective viscosity of the foam
 164 was estimated for C1 and C2 experiments from the Darcy Law:

$$165 \quad \eta_{foam} = \frac{k.A}{Q} \cdot \nabla P \quad (3)$$

166 where A is the cross-section used by foam to propagate, ∇P is the pressure gradient, and k is the soil
 167 permeability ($m.s^{-1}$).

168 2.6. Contact angles and interfacial tension measurements

169 The contact angle θ at which an air–water interface meets a solid surface [34] (Fig. SM.1), is an
170 important measurement directly linked to surface wettability. It controls the rate and amount of
171 spontaneous imbibition of water by soil [35]. It can be calculated using the Young equation [36]:

172
$$\cos\theta = \frac{\gamma_{nw-s} - \gamma_{w-s}}{\gamma_{nw-w}} \quad (4)$$

173 where w, nw and s are the liquid wetting and non-wetting phases, and the solid phase, respectively.
174 Solid phases in this study were the different soils presented in Table SM.2. The wetting and non-
175 wetting phases were air and/or water-based solutions depending on the experimental conditions
176 (see §2.7 for details). θ -values less than 90° indicates a water-wet solid phase, or an oil-wet solid if
177 higher; The latter impeding the spontaneous infiltration of the aqueous phase into the porous
178 medium.

179 θ were measured using the modified sessile drop method for all soils using PS-solution in water or
180 aqueous surfactant [37].

181 The IFT at the air/solution interface was measured for PS solution in water or surfactant, using the
182 pendant drop method [14].

183 2.7. Liquids entry pressure calculations

184 Capillary forces play an important role in fluids circulation in porous media [38]. The entry capillary
185 pressure in pores P_{ce} (Pa), is given by the Young–Laplace equation [39]:

186
$$P_{ce} = \frac{2\gamma}{R} \cos\theta_w \quad (5)$$

187 where θ_w is the contact angle of the wetting phase and R is the pore radius (m).

188 The non-wetting phase flows into the porous medium when the capillary pressure ($P_c = P_{nw} - P_w$)
189 exceeds P_{ce} .

190 For $\theta < 90^\circ$, the wetting phase is the liquid, the non-wetting phase is the air and $\theta_w = \theta_{liquid}$. Air
191 replacement by water occurs when P_c remains lower than P_{ce} .

$$P_c < P_{ce} P_{nw} - P_w < P_{ce}$$

192 $P_{air} - P_{liquid} < \frac{2\gamma}{R} \cos\theta \leftrightarrow P_{liquid} - P_{air} > \frac{-2\gamma}{R} \cos\theta$ (6)

193 which gives the excess of pressure that should be applied to liquid (compared to air) in order it
194 propagates into the soil.

195 For $\theta > 90^\circ$, the wetting phase is the air and the non-wetting phase is the liquid, so $\theta_w = \theta_{air} =$
196 $180 - \theta_{liquid}$ and then $\cos\theta_{liquid} = -\cos\theta_{air}$ which explains the change of sign in the right side of
197 Eq.6.

198 2.8. Hydrocarbons degradation experiments

199 To compare the oxidation efficiency of hydrocarbons by PS delivered with the three methods, the
200 fine sandy soil (FSD0) was contaminated at $200 \pm 14 \text{ mg.kg}_{soil}^{-1}$ (FSD02). The latter was hydrophilic
201 and water-wet. This lower contamination level was chosen to not penalize the efficiency of
202 traditional water-based delivery methods and to avoid high oxidant doses in the media. W-PS and S-
203 PS experiments were performed in stirred glass batch reactors to ensure good contact between
204 contaminated soil and PS. In these experiments, 101 mL of oxidant solution was mixed with 290 g of
205 contaminated soil. F-PS experiments were carried out, in vertical glass columns (length: 18 cm high,
206 i.d.:3.6 cm). In those experiments, foam was injected first, then PS-solution. PS was injected until all
207 surfactant solution was pushed away from the foam zone. This PS-volume was estimated to be about
208 30.4 mL, considering that water saturation after foam injection is 30%. Injection flow rates were the
209 same as in § 2.4. Two PS doses were assessed and calculated from the stoichiometric molar ratio
210 (SMR) between PS and benzene. The latter was assumed as a model organic compound to represent
211 the entire coal-tar mass, as previously reported [40]. Those doses corresponded to 1 and 3 SMR and
212 were equal to 9.1 and $27.4 \text{ g}_{PS} \cdot \text{kg}_{soil}^{-1}$, respectively. In all cases, after PS was injected, the

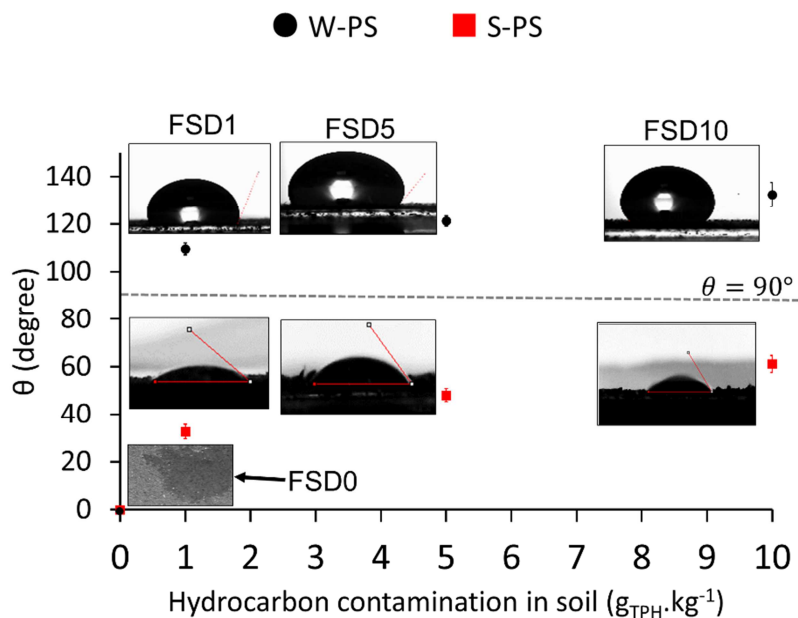
213 contaminated soil was quickly transferred in glass bottles and placed at 60°C in a thermostated water
214 bath for PS-activation. Four control experiments without oxidant, using the 3 compared methods
215 were also carried out. After 70h-contact, total petroleum hydrocarbon (TPH) indexes measurements
216 for semi-volatile fractions were obtained according to the NF EN ISO 9377-2 method, after 25 g of
217 soil were extracted three-times at room temperature using n-hexane.

218 2.9. Selectivity calculation

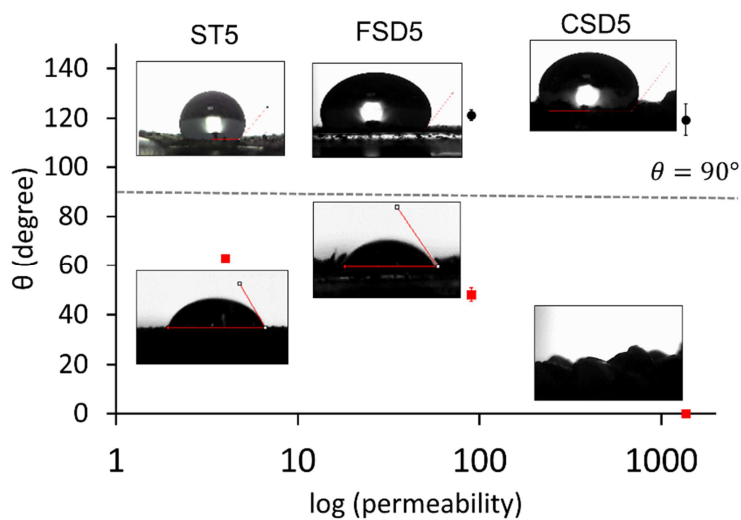
219 The selectivity of hydrocarbons degradation illustrates the preferential degradation of hydrocarbons
220 over the surfactant. It was calculated as follows:

$$221 \textit{Selectivity} = \frac{k_{\text{obs,hydrocabons}}}{k_{\text{obs,Surfactant}}} \quad (7)$$

222 Where $k_{\text{obs,hydrocabons}}$ and $k_{\text{obs,Surfactant}}$ are the pseudo first-order oxidation rate constants for
223 hydrocarbons and surfactant, respectively, obtained by linear fitting of concentrations vs. time.



A



B

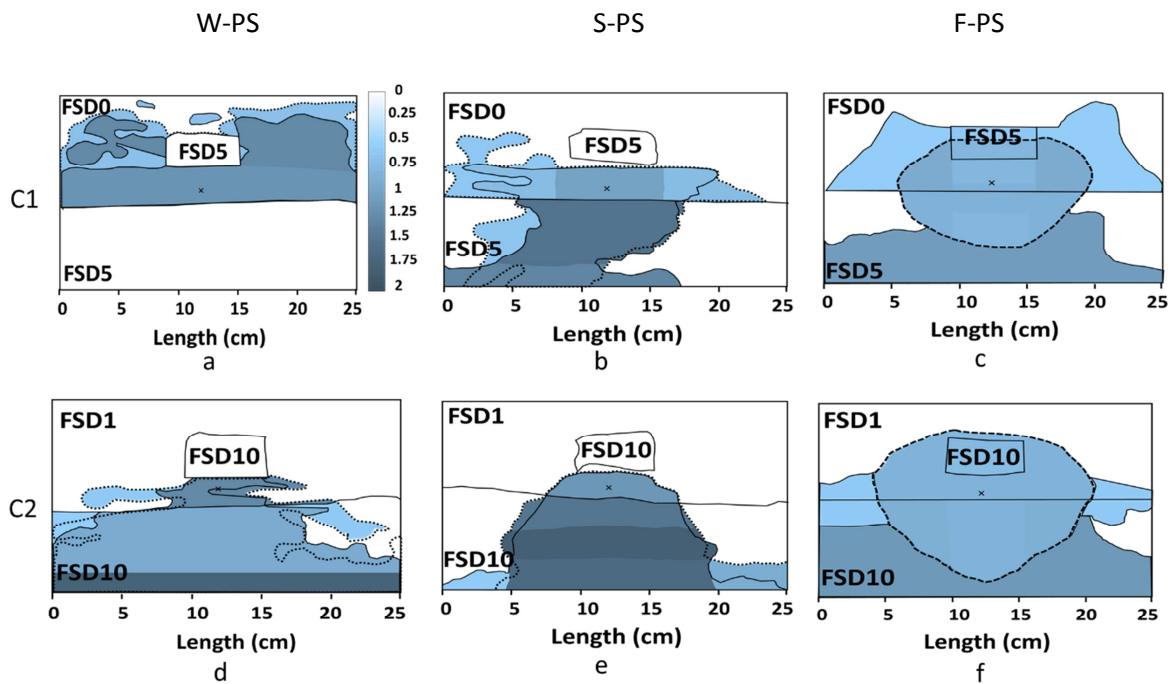
226 Figure 2. Contact angles (θ) measured for the soils used in this study: a) $90 \mu\text{m}^2$ permeability FSD soils
 227 with different hydrocarbon contamination levels (FSD0 – FSD10) and b) $5 \text{ g}_{\text{TPH}}\cdot\text{kg}^{-1}$ contaminated soils
 228 with different permeabilities (ST5 – CSD5). PS in water (W-PS, ●) and in 1% surfactant solution (S-PS,
 229 ■).

230 Contact angles measured for PS in water and surfactant solution with the soils are presented in Fig.
 231 2. The non-contaminated sand was totally water-wet ($\theta = 0^\circ$). For all the contaminated materials, in
 232 absence of surfactant, θ were above 90° because of their hydrophobicity. For the $90 \mu\text{m}^2$
 233 contaminated soil, θ , and, as a result, the hydrophobicity of the soil, increased from 115 to 130° for
 234 hydrocarbon concentrations ranging from 1 to 10 g.kg^{-1} (Fig. 2a), showing that higher contaminated
 235 soils are more hydrophobic.

236 As shown in Fig. 2, the presence of surfactant decreased θ below 90° for all contaminated soils,
 237 showing the alteration of wettability from oil-wet to water-wet [41]. However, θ still increased from
 238 35 to 61° for hydrocarbon concentrations ranging from 1 to 10 g.kg^{-1} , respectively, because of the
 239 higher soil hydrophobicity.

240 3.2. Contamination-contrasted sandboxes

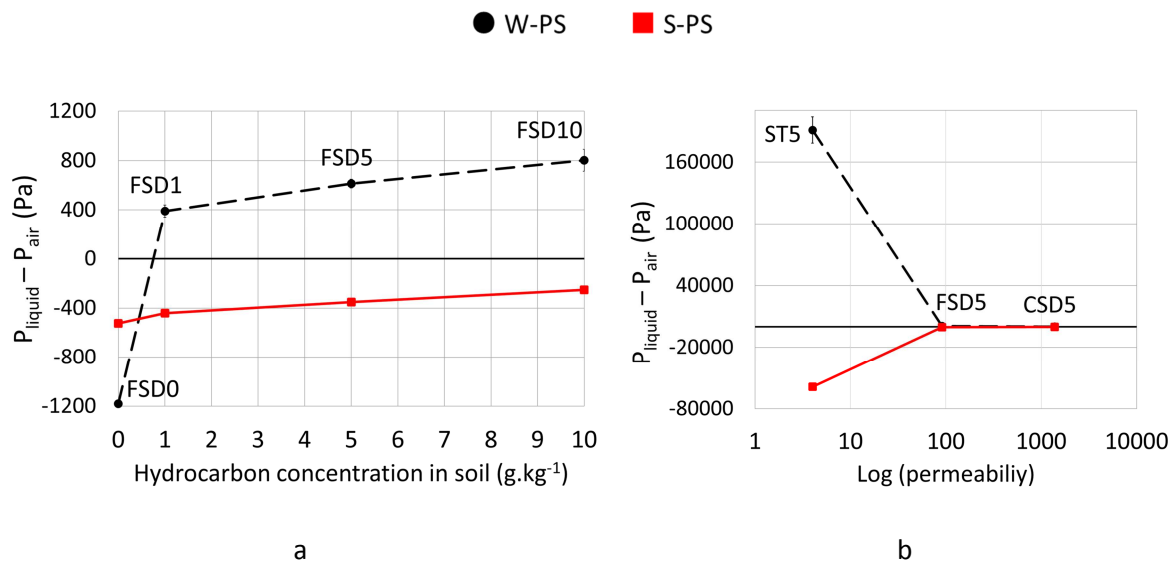
241 Concentration maps for PS delivery using the three compared methods of injection are plotted in
 242 Figure 3 for the contrast contamination models C1 and C2.



243 Figure 3. PS-concentration maps ($\text{g}\cdot\text{kg}_{\text{soil}}^{-1}$) in contamination contrasted sandboxes. Black cross
244 indicates the injection point. Solid, and dotted lines represent the wet areas at front and back sides,
245 respectively. For F-PS experiments, dashed lines represent the foam limit. PS-concentrations varied
246 from 0 (white) to $2 \text{ g}_{\text{PS}}\cdot\text{kg}_{\text{soil}}^{-1}$ (dark blue).

247 Considering C1, when W-PS was used as a delivery fluid, it propagated only in the non-contaminated
248 area (Fig. 3a). No entrance into the contaminated zones was observed. Two mechanisms occurred:
249 on the one hand, in the clean zone, the soil was strongly water-wet and capillary suction attracted
250 water within the pore spaces. Comparing the evolution of $P_{\text{liquid}} - P_{\text{air}}$ using W-PS and S-PS in the
251 studied soils (Fig. 4), the negative value of $P_{\text{liquid}} - P_{\text{air}}$ confirms capillary suction. On the other
252 hand, the hindered water flow into the contaminated soil was emphasized because of its strong
253 hydrophobicity (Fig. 2a) and the higher capillary pressure required for the liquid to flow into it. For C2
254 using W-PS, a different behavior was observed, since the strong hydrophobicity of soils caused an
255 important edge effect and water did not propagate into the soil. Indeed, when using water, the edge
256 effect altered the visual observations that were no longer representative of actual PS-concentrations.
257 Water propagated preferentially along the cell walls which were more water-wet than the soil. Fig.
258 SM.2 compares the visual propagation of PS and its actual concentrations (see Figs. SM.3 and SM.4
259 for the rest of the experiments). Visually, it seems that water propagated in the whole contaminated
260 bottom layer uniformly, saturating it. However, this visual observation was inaccurate since
261 measured PS-concentration in this area was low (Fig. SM.2b). Thus, experimenters should beware of
262 edge effects, especially occurring for solutions with high interfacial tensions, that might not be
263 always representative of reality. In this case, calculated $P_{\text{liquid}} - P_{\text{air}}$ were high for both soils and
264 increased about 2-times with contamination for FSD1 and FSD10, respectively (Fig. 4a). It explains the
265 difficulty for water to flow into hydrophobic zones and its inefficiency to deliver PS. PS-distribution
266 within the swept area was heterogeneous, and its concentration varied 2.3 and 6.8-times between
267 lowest and highest PS-concentrations for C1 and C2, respectively. This could be explained by local soil
268 heterogeneity, affecting water saturation. For water-delivered PS in C1 and C2, the I_f -value obtained

269 from visual observations is wrong, since the water propagated only within the clean layer (C1) and
 270 only along the cell walls (C2).

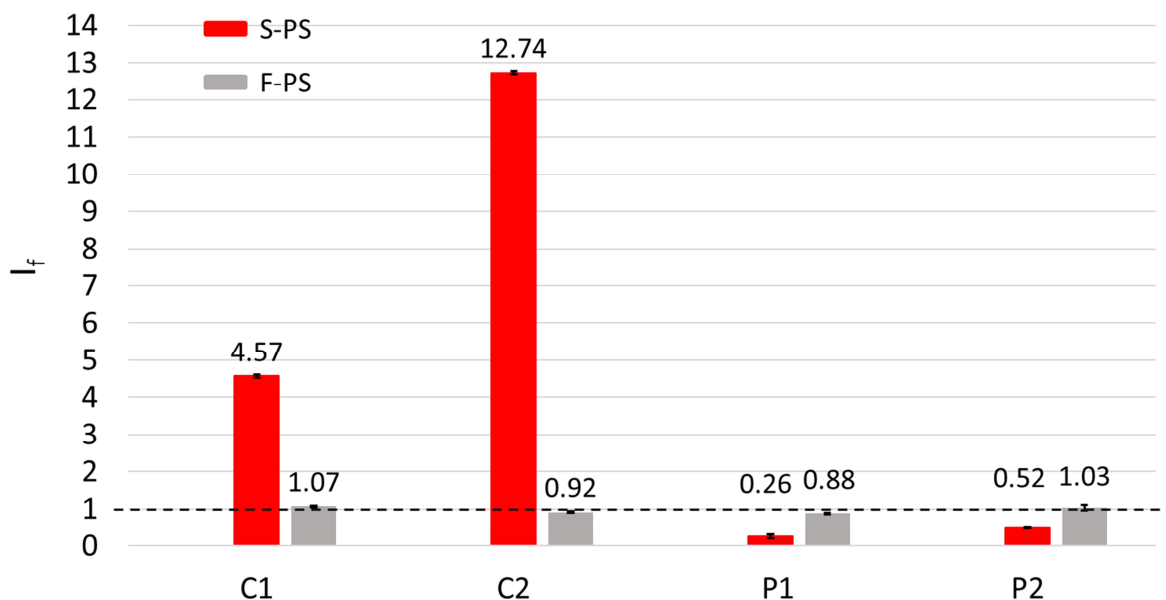


271 Figure 4. Evolution of $P_{liquid} - P_{air}$ with hydrocarbon concentration for W-PS (●) and S-PS (■)
 272 calculated from eq. 6: a) $90 \mu m^2$ permeability FSD soils with different contaminations levels (FSD0 –
 273 FSD 10) and b) $5 g.kg^{-1}$ contaminated soils with different permeabilities (ST5 – CSD5).

274 When surfactant was added (S-PS), PS-distribution was enhanced, compared to W-PS, both for C1
 275 and C2 (Figs 3b and 3e), thanks to two mechanisms: first, the reduction in the air–water IFT from 72
 276 to $32 mN.m^{-1}$, which yielded a slight increase in N_c from 3.68 to 8.28×10^{-5} for W-PS and S-PS,
 277 respectively (Table SM.3); The effect of capillary forces was reduced twice. Second, surfactant
 278 adsorption reversed soil wettability, from oil-wet to water-wet (Fig. 2) [41,42]. This change to water-
 279 wet behavior promoted the spontaneous imbibition of the contaminated zone, as confirmed by
 280 negative $P_{liquid} - P_{air}$ values in Fig.4a. Hence, surfactants proved to be beneficial for enhancing PS-
 281 delivery in hydrocarbon-wet contaminated soils, as previously reported [20]. However, within the
 282 wet zone, as observed for W-PS, PS-concentrations remained heterogeneous and varied 2.8 and 3.6-
 283 times for C1 and C2, respectively. As reported in Fig. 5 which summarizes I_f -values, the latter was
 284 quite high and equal to 4.57 and 12.74 for S-PS in C1 and C2, respectively. Despite a great
 285 enhancement compared to W-PS, the PS-distribution was still anisotropic, and its vertical distribution

286 was more important than its horizontal one. Besides, both for W-PS and S-PS, the contaminated lens
 287 embedded in the upper layer was not swept by the oxidant.

288



289 Figure 5. Isotropic delivery factor (I_f) values for contamination contrasts (C1 and C2) and permeability
 290 contrasts (P1 and P2) experiments, using S-PS and F-PS delivery methods. Horizontal dashed line at I_f
 291 = 1 represents an ideally isotropic PS-distribution. Error bars are shown for each experiment.

292 Contamination contrasted media only slightly affected the propagation of foam, which flowed in
 293 every direction around the injection point without any viscous fingering (Fig. 3c,f), as previously
 294 reported [11,12,21,25,43]. In contrast to solutions, foam propagation was mainly controlled by its
 295 high viscosity ($168 \cdot 10^{-3}$ Pa.s) and its shear-thinning behavior, that overcame gravitational effects and
 296 fingering [44]. As for S-PS, the use of foam decreased the air–water IFT from 72 to 32 mN.m⁻¹. In
 297 order to maximize the selectivity of the oxidation, PS was injected only once foam was set in place, as
 298 previously described [25]. PS-delivery around the injection point was much more isotropic when the
 299 F-PS method was used. The PS solution efficiently swept the contaminated lens situated above the
 300 injection point. Horizontal and vertical PS-distributions were roughly equal as demonstrated by the
 301 I_f -values amounting to 1.07 and 0.92 for C1 and C2, respectively (Fig. 5). In the meantime, N_c ,

302 increased at least by 150-times from S-PS to F-PS, as shown in Table SM.3, improving the sweeping
303 efficiency of the foam in contamination contrasted media [45]. Surfactant drainage was observed
304 due to the unsaturated conditions and destabilizing effect of hydrocarbons on foam lamellae, as
305 explained previously [25]. In addition, the PS-concentration was very homogeneous within the foam
306 network and varied less than 1.3-times for C1 and C2 (Fig. 3c). The maximal PS-concentration that
307 can be delivered was $1.03 \text{ g}_{\text{PS}} \cdot \text{kg}_{\text{soil}}^{-1}$, considering both the injected PS solution ($10 \text{ g} \cdot \text{l}^{-1}$) and a typical
308 water saturation of 30% within the foam network. To deliver higher PS-concentrations in soil using
309 foam, larger PS-concentrations in solution have to be used, with the aim of overcoming the lower
310 water saturation when using the foam-based method. PS-concentrations in soil were higher in the
311 liquid drainage zone outside the foam than inside, because of the higher water saturation.
312 Nevertheless, the injection of an excessive volume of PS may be avoided by better evaluating the
313 volume of liquid to replace in the foam zone. PS remains trapped in place for months despite foam
314 decay with time, because water is trapped by capillary forces.

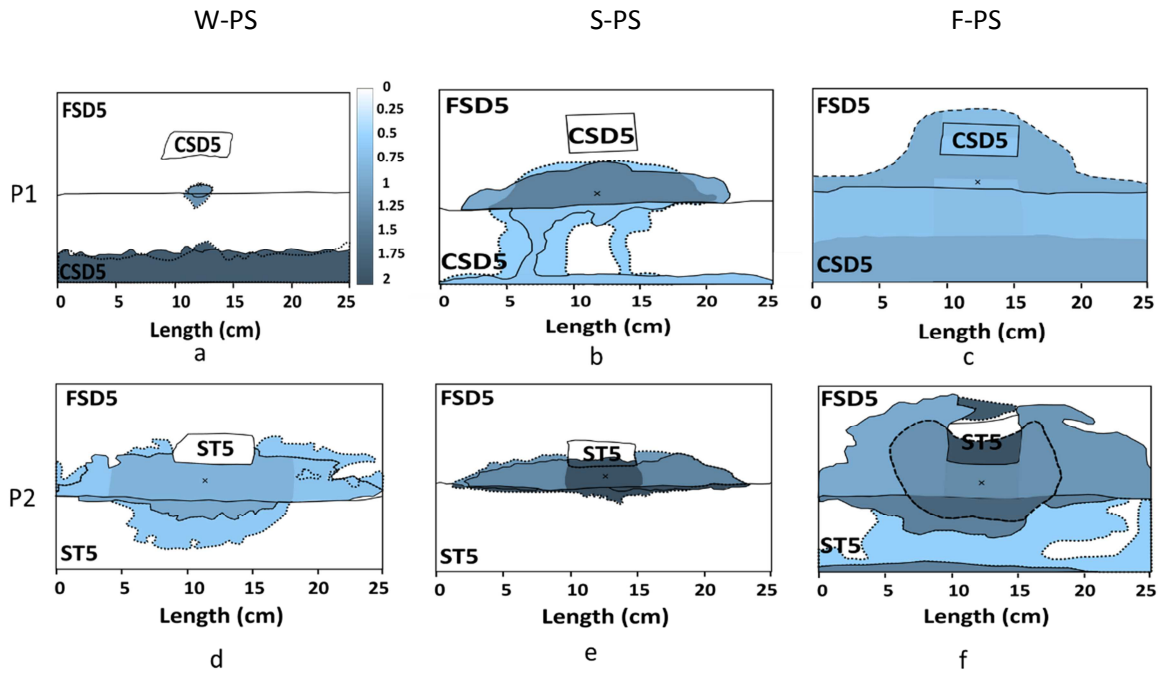
315

316 3.3. Permeability-contrasted contaminated soils

317 Considering strong permeability contrasts in contaminated soils, two situations were studied. In the
318 former (P1), the medium was built using a high and a moderate permeability soil, whereas in the
319 latter (P2), moderate and low permeability soils were used. PS-concentration maps using the
320 compared methods of oxidant delivery are plotted in Figure 6.

321

322



324 Figure 6. PS-concentration maps ($\text{g.kg}_{\text{soil}}^{-1}$) for permeability-contrasted sandboxes using the three
 325 delivery methods. Black cross indicates the injection point. Solid, and dotted lines represent the wet
 326 areas at the front and back sides, respectively. For F-PS experiments, dashed lines represent the
 327 foam limit. PS-concentrations varied from 0 (white) to $2 \text{ g.kg}_{\text{soil}}^{-1}$ (dark blue).

328 3.3.1. Permeability contrast in a moderate to high permeability medium (P1)

329 For P1, using the W-PS method of injection, the solution accumulated in the most permeable bottom
 330 layer where PS-concentration was maximal (Fig. 6a). Downward water flow resulted from the low
 331 capillary retention caused by the large pore throats of the soil and the transport was only controlled
 332 by gravity. Since no horizontal PS-distribution was observed, the I_f -value was set to zero. Despite
 333 smaller pore size, the upper layer was avoided because its high hydrophobicity and higher
 334 $P_{\text{liquid}} - P_{\text{air}}$. Besides, important edge effects were observed when using W-PS in P2, like for C2,
 335 due to the hydrophobicity of the soils and the low permeability of ST5. In this case, $P_{\text{liquid}} - P_{\text{air}}$
 336 were 613 and 1.9×10^6 Pa for FSD5 and ST5, respectively (Fig. 4b). The huge contrast of $P_{\text{liquid}} - P_{\text{air}}$
 337 values between FSD5 and ST5 led to the complete avoidance of ST5 layer by water and to 2.8-times
 338 variability in PS-concentration between the zones.

339 The addition of surfactant had similar effects as presented in §3.2, causing the inversion of soils
340 wettability for P1 (Fig. 2) and the elimination of the edge effect for P2, as confirmed by the PS-
341 concentration map (Fig. 6e). For P1, the value of $P_{liquid} - P_{air}$ dropped significantly when the
342 surfactant was used for both contamination levels (5 and 10 g.kg⁻¹, Fig. 4b). This led to a higher
343 suction of the solution in both layers and a better horizontal oxidant distribution compared to water
344 alone (Fig. 6b). However, in the CSD5 layer, gravity forces still had strong effects and altered the
345 migration of the surfactant solution, since preferential pathways were observed in the bottom layer.
346 Conversely, in the case of P2, the solution only propagated 2 cm vertically in ST5 and spread
347 horizontally into the most permeable layer (FSD5). In fact, adding surfactant did not seem to inverse
348 wettability of the low permeability soil as expected from θ -values (Fig. 2b). Indeed, $P_{liquid} - P_{air}$
349 value should have, theoretically, decreased from 3207 to -5.9×10^4 Pa and the solution should have
350 been sucked preferentially in this zone. However, the oxidant only accumulated in the most
351 permeable upper layer. In fact, the surface area of the silt, which was 3-times higher than the sand,
352 caused a bigger surfactant adsorption [46,47]. Hence, the wettability inversion was probably slower
353 in this zone, compared to the high permeability layer. For permeability contrast experiments using S-
354 PS, the I_f -values were very low (Fig. 5) and PS-concentrations remained very heterogeneous since
355 they varied more than 5-times. Using a direct injection of PS solutions, the contaminated lens above
356 the injection point was never swept, following the example of C1 and C2.

357 When using the F-PS method, the PS-solution propagated within all the contaminated zones,
358 regardless of the permeability contrasts, especially for P1 (Fig. 6c). In both cases, a slight effect of the
359 permeability contrast on the foam propagation rate was noticed, since it propagated faster into the
360 high permeability soil [28,46,47]. For P2, the foam propagation in the low permeability zone was
361 slowed down by a higher destabilization rate caused both by the higher surface area and the
362 hydraulic resistance of the material. Drainage was observed in both layers, like for C1 and C2.

363 Once the PS solution was injected, it distributed in the area occupied by foam and beyond. For P1,
364 the PS-concentration was quite homogeneous inside the foam zone and varied only 1.6-times. For
365 P2, in contrast to previous observations with foam, the PS-distribution was not so homogeneous
366 inside the foam network; a variability of 2.9-times was observed in PS-concentrations (Fig. 8f).
367 However, it is still satisfying, since PS successfully distributed into the ST5 zone too. In this zone, the
368 PS-concentration was $2 \text{ g.kg}_{\text{soil}}^{-1}$. It is beyond the maximal value expected within the foam, and it
369 shows the destabilization of the latter, since such concentrations can only be obtained when the
370 solution saturates the pores. Moreover, the F-PS method successfully delivered the oxidant into the
371 low permeability zones. For both permeability contrast experiments using F-PS, the I_f -values were
372 closer to one, despite the complex behavior of foam and the PS-distribution in P2 (Fig. 5). This
373 observation confirmed that, the PS-distribution was rather homogeneous in the case of the whole
374 sandbox, for P2.

375

376 3.4. Comparative oxidation of hydrocarbons

377 Considering the removal of hydrocarbons in comparative degradation experiments, controls were
378 performed in order to better amount what is related to oxidation. Hydrocarbons removal rates in
379 control experiments increased in the following order: foam ($0.11 \pm 0.03\%$) < surfactant (2.70 ± 2.02
380 %) < water ($5.50 \pm 2.00\%$). Naphthalene and phenanthrene were identified as major components of
381 the removed fraction, and the volatilization was assumed to be the main phenomenon for non-
382 specific removal. Thus, the previous order is explained by the micelles stabilizing effects towards
383 hydrocarbons and by the bubbles, which hindered the volatilization of the contaminant by trapping it
384 into the soil.

385 After 70 h of contact with the oxidant, hydrocarbons removal rates were very high for all of the PS-
386 concentrations and methods, showing that the SMR estimation was correct. Hydrocarbons removal
387 rates followed the order W-PS > F-PS > S-PS. Increasing PS-concentration slightly increased

388 hydrocarbons removal rates, because it promoted the generation of more free radicals in solution
389 (*i.e.* $S_2O_8^{2-}$, $SO_4^{\bullet-}$ and HO^{\bullet}) as reported [24,48–51]. For 1 and 3-SMR, hydrocarbon removal rates were:
390 95.6 (0.5)% and 99.2 (0.8)% for W-PS; 92.2 (1.2)% and 97.0 (1.3)% for S-PS; and 95.0 (1.1)% and 98.6
391 (1.8)% for F-PS, respectively.

392 The contaminated soil used here was initially water-wet and mixed before activation in W-PS and S-
393 PS experiments; Therefore the contact between PS and contamination was optimal, leading to high
394 oxidation efficiencies even for W-PS. However, with hydrophobic soils (*coal tar* $\geq 1 \text{ g.kg}_{\text{soil}}^{-1}$), as
395 seen in §3.1 and 3.2, the conditions would not be so favorable [25,26] and the oxidation using the W-
396 PS method is expected to be low. The slightly higher degradation of hydrocarbons using F-PS
397 compared to S-PS was explained by the lower content of surfactant in the soil after the PS-injection,
398 since the latter pushed away about 80% of the initial surfactant used to generate foam. Considering
399 the calculated selectivity of hydrocarbons oxidation, the increasing of the PS-concentration had no
400 significant effect (0.33 ± 0.02 and 12.31 ± 0.19) for S-PS and F-PS methods, respectively, in agreement
401 with previous report [13]. However, the sequential delivery of PS using the F-PS method improved
402 the selectivity of the oxidation by 38-times, as expected, since it removed the 80% of the surfactant
403 from the soil pores. Thus, non-productive oxidant consumption by surfactant was lowered when
404 using the F-PS method. Consequently, even though hydrocarbons degradation rates were similar
405 between F-PS and W-PS methods in the tested conditions, gains are expected to be higher when
406 injections occur in more hydrophobic media (Figs 3 and 6). The most important aspect is that despite
407 the adverse comparative conditions used in this study, the foam-based method did not show any
408 detrimental effect regarding the oxidation of hydrocarbons. Even more, it showed a better
409 degradation efficiency and a more uniform oxidant distribution than usual S-ISCO, carried out using
410 full mixing of soil and oxidizing solutions.

411

412 4. Conclusion

413 Three PS-delivery methods, with increasing complexity, were compared to distribute PS in
414 unsaturated coal tar-contaminated soils with high permeability or contamination contrasts. Pure
415 water proved to be the less favorable method to deliver PS in such contaminated soils, since the
416 hydrophobicity of the latter had a strong impact on oxidant-distribution. The addition of surfactant
417 lowered IFT and inverted the wettability of the contaminated materials. It resulted in enhanced PS
418 propagation into the contaminated zones. However, gravity forces still led to preferential circulation
419 pathways. The most isotropic PS-distributions were obtained when this oxidant was delivered within
420 a foam network, which is much more viscous than traditional fluids. The oxidizing solution exhibited
421 the best sweeping efficiency when it was delivered using the foam-based method and its propagation
422 was only slightly affected by gravity. Moreover, despite unfavorable comparative conditions to the
423 usual methods, the sequential injection of foam and PS solution did not show any detrimental effect
424 regarding the removal of hydrocarbons. The latter was very high for the tested PS-concentrations.
425 The foam-based method proved to be more selective than the usual S-ISCO, due to the lower
426 surfactant content in the oxidized zone. To deliver higher PS-concentrations in soil using the foam-
427 based method, larger PS-concentrations of the injected solution have to be used, in order to
428 overcome the lower water saturation in the soil, by using this foam-based method.

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432

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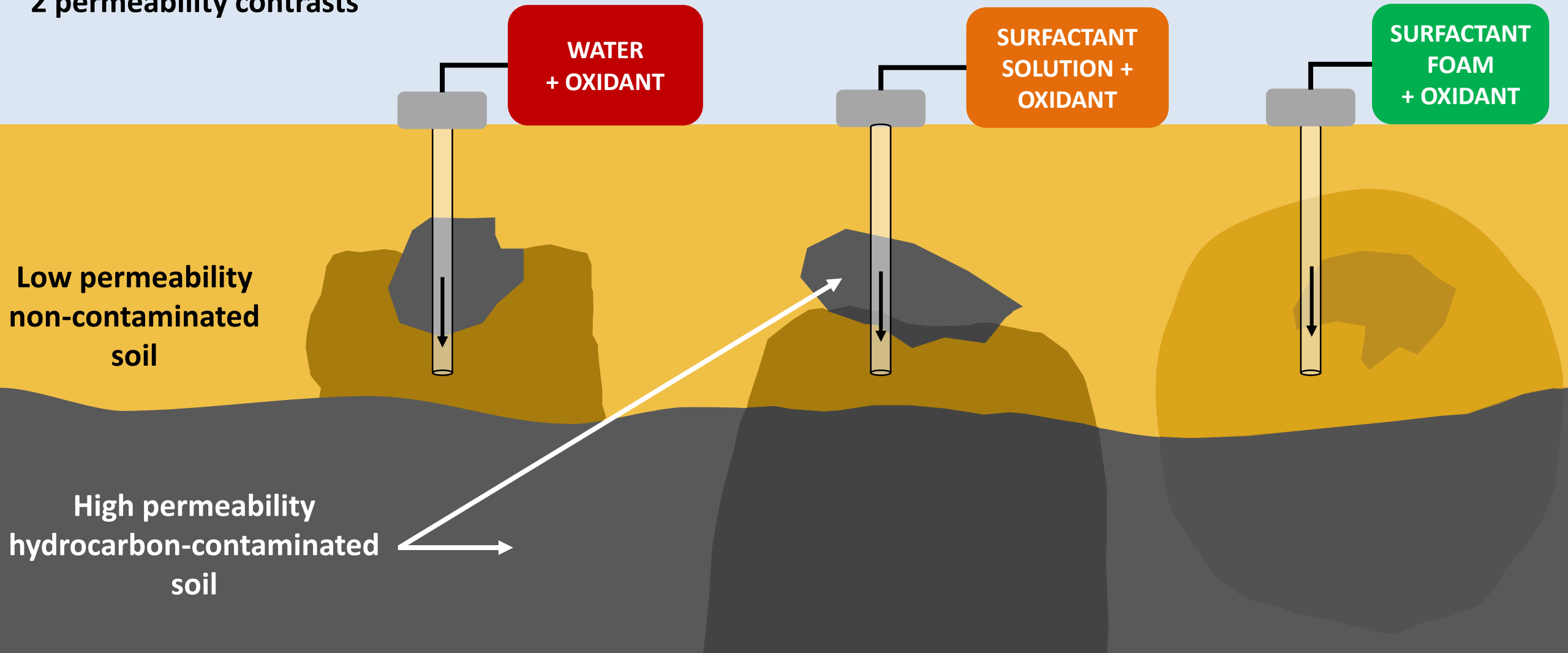
12 injection experiments:

3 oxidant delivery fluids

2 contamination contrasts

2 permeability contrasts

Enhancement of remediation efficiency



WATER
+ OXIDANT

SURFACTANT
SOLUTION +
OXIDANT

SURFACTANT
FOAM
+ OXIDANT

Low permeability
non-contaminated
soil

High permeability
hydrocarbon-contaminated
soil