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## Effect of NAPL mixture and alteration on $^{222}\text{Rn}$ partitioning coefficients: Implications for NAPL subsurface contamination quantification

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1 Effect of NAPL mixture and alteration on  $^{222}\text{Rn}$  partitioning  
2 coefficients: implications for NAPL subsurface contamination  
3 quantification

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12  
13 **Abstract**

14 Soils and groundwater are often contaminated by complex organic mixtures also called Non Aqueous  
15 Phase Liquids (NAPLs). Several techniques such as drilling, monitoring of soil gas or injection of tracers  
16 are traditionally used to quantify NAPLs in aquifers but are complex to perform. The use of natural soil  
17 gas such as  $^{222}\text{Rn}$  could be an easy and cheap alternative. This method requires the knowledge of the  
18 radon NAPL-water partitioning coefficients ( $K_{n-w}$ ). Once spilled on soil, NAPL will undergo  
19 degradation (evaporation, effects of sun light among others) and this degradation could impact the  $K_{n-w}$   
20  $w$ . This study aims at investigating the partitioning coefficients of complex NAPLs such as commercial  
21 diesel fuel and gasoline in relation to degradation such as evaporation and UV-degradation. For that  
22 purpose, batch experiments and GCMS investigations were carried out. The results show different  $K_{n-w}$   
23 for the commercial diesel fuel ( $60.7 \pm 6.1$ ) and gasoline ( $37.4 \pm 5.6$ ) The results also show different  
24  $K_{n-w}$  behaviors in relation with degradation. Degraded diesel fuel display opposite  $K_{n-w}$  values ( $74.8 \pm$   
25  $7.5$  and  $25.1 \pm 2.5$  for UV degraded and evaporated diesel fuel, respectively), compared to fresh one.  
26 Degraded gasoline shows no significant variations of the  $K_{n-w}$  compared to fresh one. The molecular  
27 investigation reveals the removal of the most volatile fraction for the evaporation treatment, whereas

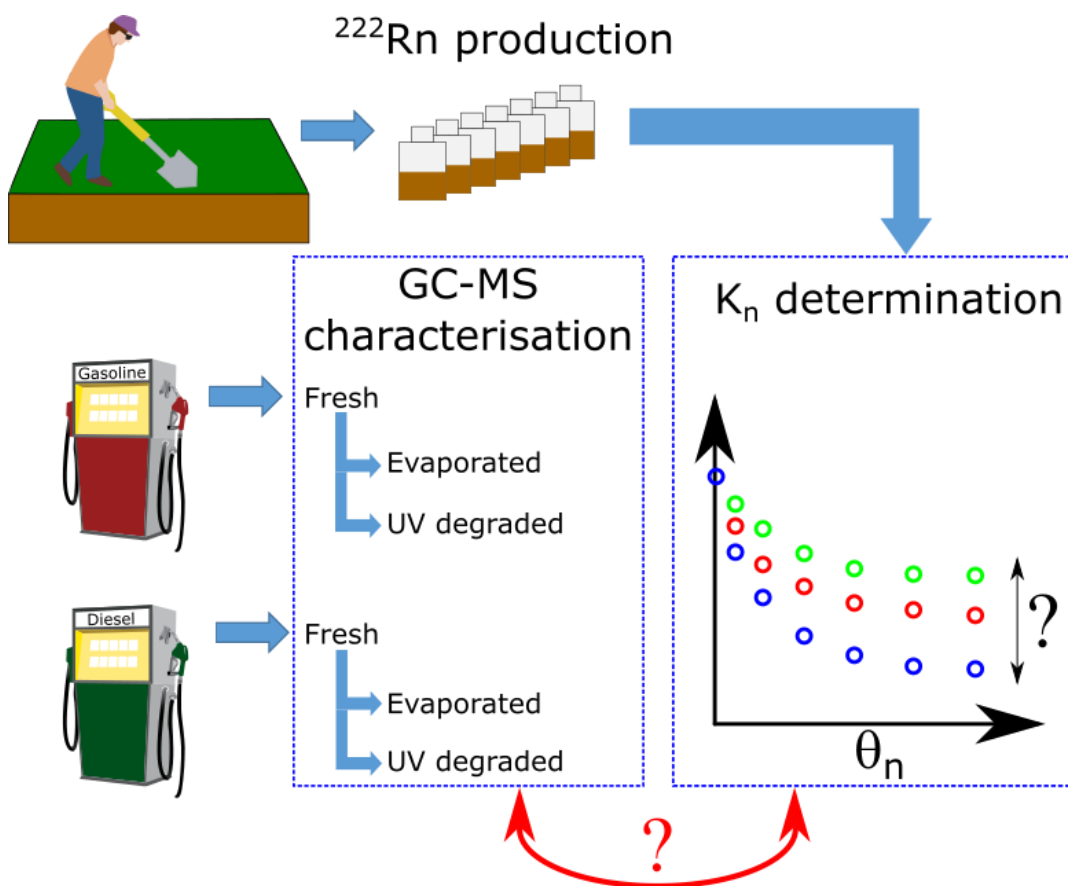
28 UV-degradation do not have pronounced effects on the chromatogram pattern. For the gasoline  
29 molecular investigation, no difference is observed between the treatments excepted a very slight removal  
30 of the lightest compounds under evaporation. These results show that NAPL degradation have effects  
31 on the  $K_{n-w}$  for diesel fuel and no significant effects for gasoline, at least with these degradation paths.  
32 This  $K_{n-w}$  variation will have *in fine* effects on  $^{222}\text{Rn}$  activity interpretation and NAPL subsurface  
33 quantification.

34 Key words:  $^{222}\text{Rn}$ , Fresh and altered NAPL, Radon Partitioning Coefficient, NAPL Subsurface Contamination  
35 quantification

36

### 37 Highlights

38 Radon partitioning coefficients were determined for fresh and altered NAPLs  
39 Molecular signatures of fresh and altered NAPL were investigated using GC-MS  
40 Altered and fresh diesel fuel showed different NAPL-water partitioning coefficients  
41 Altered and fresh gasoline showed similar NAPL-water partitioning coefficients  
42 The partition coefficient is of pivotal importance for NAPL delineation  
43



44

45

## 46 **1. Introduction**

47 Soil and groundwater are often contaminated by complex organic mixtures, such as petroleum  
48 products or chlorinated solvents (also known as Non-Aqueous Phase Liquids, or NAPL), and  
49 these liquids are recognized as a critical issue in environmental remediation (Davis et al., 2003).  
50 These NAPL are frequently encountered in industrial or military sites and are releasing toxic  
51 compounds to groundwater. They can persist sometimes for centuries, creating long-term  
52 contamination due to their low solubility in water (Cohen and Mercer, 1993; Zhang et al., 1998).  
53 NAPL can be released to the environment during fueling, maintenance and/or storage  
54 operations. Large volume of spilled NAPL can migrate through unsaturated soil zone to the  
55 water table (Yoon et al., 2013). This migration is complex, following preferential pathways and  
56 forming ganglia and small isolated lenses (Fernandez et al., 2013). The light NAPLs  
57 preferentially float at the top of the water table and dense NAPLs penetrate into the saturated  
58 zone (Castelluccio et al., 2018). During the migration through the vadose zone, a certain amount  
59 of liquid (up to 20%, known as residual saturation) is retained in the pores by capillary forces  
60 forming a source zone (Wiedemeier et al., 1999) where gaseous and aqueous contaminant  
61 plumes are formed (Höhener and Surbeck, 2004). It is then crucial to accurately detect, localize  
62 and quantify residual NAPL sources prior to choose efficient remediation procedures.

63 Traditionally, soil NAPL contamination has been estimated using sampling techniques (drilling  
64 and core-sampling) which are of very high quality but are expensive and time consuming  
65 (Feenstra and Cherry, 1996; Yoon et al., 2013). In addition, without prior information  
66 concerning the contamination pattern, the position of the sampling stations could lead to useless  
67 data (Garcia-Gonzalez et al., 2008). Screening method such as gas monitoring (in particular  
68 Volatile Organic Compounds, VOCs, Wilson et al. 1997) is another non expensive technique  
69 that permits to approximately locate the contamination source zone laterally and vertically  
70 (Robbins et al., 1990). However, NAPL degradation leads to high VOC concentrations that do

71 not reflect the amount of NAPL (Höhener and Surbeck, 2004) in the source zone. This last  
72 technique is thus only suitable for volatile contaminants and hence not suitable for diesel fuel,  
73 fuel, kerosene or hydraulic oil (Schubert et al., 2005). The injection of artificial tracers directly  
74 in soils is another technique cited in the literature (Deeds et al., 1999; Brusseau et al., 2003).  
75 The gas is directly injected in the vadose zone where it can be transported by advection (Mariner  
76 et al., 1999) and/or diffusion (Werner and Hohener, 2002) and the interpretation of the  
77 breakthrough curves permits to obtain the localization and the average volumetric NAPL  
78 content (Dwarakanath et al., 1999). However, this technique is time consuming, expensive  
79 (Höhener and Surbeck, 2004) and can give quite misleading results in heterogeneous  
80 environment (Nelson et al., 1999). Due to the limitations of the different techniques cited above,  
81 alternative options must be proposed. A simpler way to investigate subsurface contaminations  
82 is the use of native soil gas that partitions into NAPLs.

83 Radon-222 ( $^{222}\text{Rn}$ ) is a good advocacy for the understanding of NAPL behavior in subsurface  
84 (Barrio-Parra et al. 2021).  $^{222}\text{Rn}$  is a natural component, continuously produced in soil matrices  
85 by the alpha-particle decay of  $^{226}\text{Ra}$  in the natural decay of the uranium-238 series (DeWayne-  
86 Cecil and Green, 1999).  $^{222}\text{Rn}$  also decays by alpha-particle decay and has a half-life of 3.82  
87 days (Mason and Moore, 1982). Uranium is ubiquitous in minerals, as a trace element,  
88 permitting almost ubiquity production of radon in the environment. The  $^{222}\text{Rn}$  emanation  
89 coefficient corresponds to the gas fraction released from the host materials which is retained in  
90 the pore space (Andrews and Wood, 1972). The composition and mineralogy of the soil, and  
91 thus especially the particle size contribute to the emanation coefficient. In general, when the  
92 particle size is small, the specific surface area is large and the emanation power of materials  
93 containing  $^{226}\text{Ra}$  is higher (Galhadi and Bonotto, 2012; Thu et al., 2020). Other chemical and  
94 physical parameters can also influence the radon activity such as moisture content and pore size  
95 (Nazaroff, 1992; Galhardi and Bonotto, 2012; Cujic et al., 2020).

96 The use of natural radon to localize and quantify NAPL amount in subsurface is feasible  
97 because its preferential partition into organic phase (Horiuchi and Murakami, 1981; Hunkeler  
98 et al., 1997; Nazaroff, 1992; Sakoda et al., 2011; Semprini et al. 2000; Wong et al., 1992). When  
99 groundwater containing radon migrates towards a residual NAPL contamination area, a local  
100 radon deficit in groundwater is then observed (Hunkeler et al., 1997; Schubert et al., 2007a).  
101 The radon deficit close to a NAPL-contaminated zone depends on (i) the pore space saturated  
102 with residual NAPL and (ii) the radon partitioning coefficient specific for the NAPL present  
103 (Schubert et al., 2007a). If the  $^{222}\text{Rn}$  partitioning coefficient of the NAPL is known, it is possible  
104 to localize and quantify the residual saturation of the organic phase (Schubert et al., 2007a;  
105 Cohen et al., 2019). The knowledge of the partitioning coefficient is therefore of pivotal  
106 importance when dealing with site NAPL contamination delineation. Several partitioning  
107 coefficients have been mainly reported for pure organic compounds (Clever, 1979, Schubert et  
108 al., 2007b) but few authors reported the partitioning coefficient for commercial NAPL mixtures  
109 (Schubert et al., 2002; 2007a). Schubert et al., (2007b) worked on the  $^{222}\text{Rn}$  partitioning  
110 between air, water and three artificial NAPL mixtures. They stated the need of experiments on  
111 NAPL mixtures in order to verify or modify the theoretical framework. Schubert (2015) also  
112 mentioned that NAPL degradation could affect its complex composition, leading in return to a  
113 change of the partitioning coefficient. This change of the partitioning coefficient will affect the  
114 NAPL quantification in soils. However, to our knowledge, no study in the literature deals with  
115 the effect of NAPL alteration on  $^{222}\text{Rn}$  partitioning coefficient.

116 When spilled on the soil, the NAPL will be exposed to wind and heat for a certain time which  
117 might be sufficient to evaporate the light NAPL fraction (Villa et al., 2010). In soils, NAPL  
118 may undergo biodegradation, governed by microorganisms, leading to the loss of contaminants  
119 (Wiedmeier et al., 1999) and the modification of initial NAPL composition. Natural NAPL  
120 biodegradation takes time and depends on different parameters such as soil properties (Jho et

121 al., 2014) and microorganism's ecology in action. These NAPL chemical alterations should  
122 thus lead to a  $^{222}\text{Rn}$  partitioning coefficient modification.

123 In the frame of the above discussion, the objectives of this article are (i) to determine the  
124 partitioning coefficient of mixed commercial NAPLs, (ii) to investigate the effects of NAPL  
125 degradation on  $^{222}\text{Rn}$  partitioning coefficient and (iii) to investigate the relationship between  
126 the partitioning coefficient modification and NAPL chemical composition. To reach these  
127 goals, batch experiments were conducted to determine  $^{222}\text{Rn}$  soil production and water-NAPL  
128 partitioning coefficient ( $K_{n-w}$ ) in fresh and degraded complex NAPL mixtures. These  
129 experiments aim at better characterizing the ability of  $^{222}\text{Rn}$  method to delineate NAPL  
130 pollution at contaminated sites.

## 131 **2. Material and methods**

### 132 **2.1. Porous media**

133 The porous media used in this study is an alluvial sand from the Aquitaine basin (France). It  
134 was sampled in a natural soil and sieved in order to only retain the fine fraction (710 – 250  $\mu\text{m}$ )  
135 which presents higher  $^{222}\text{Rn}$  emanation coefficient (Chitra et al., 2018). The density of this soil  
136 fraction was measured using a pycnometer (Rodier et al., 2009).

### 137 **2.2. Reagents**

138 Six NAPLs were used in this study. Two of them are commercial “fresh” gasoline (SP98) and  
139 diesel fuel, both obtained from a pump at a road fuel station (Casino supermarket, France). Four  
140 were obtained from the degradation of both “fresh” NAPLs following two degradation paths  
141 (described below). For NAPLs dilution prior liquid GC-MS injections, n-heptane solvent (n-  
142 Heptane, 99+%, residues analysis, ACROS Organic, UK) was used.

### 143 **2.3. NAPL characterization and degradation**

#### 144 **2.3.1. NAPLs density**

145 As for the porous media, NAPLs densities were characterized using a pycnometer (Rodier et  
146 al., 2009).

### 147 **2.3.2. GC-MS analysis**

148 In order to characterize chemical compositions of fresh and altered NAPLs, GC-MS analyses  
149 were conducted. These analyses were performed using two devices to increase the separation  
150 and thus identification ability of this study, the first and second one performing liquid and Head-  
151 Space (HS) injections, respectively. Indeed, HS-GC-MS technique permits the detection of the  
152 most volatile compounds, and has a low detection limit, suitable for diesel fuel compounds  
153 identification (D'Auria et al., 2008; Safarova et al., 2004). The liquid GC-MS is also suitable  
154 for NAPL investigation as they contain heavy hydrocarbons with long chain, easily detectable  
155 using this technique (D'Auria et al., 2008). For both analytical systems, ultra-high purity He  
156 (Alphagaz 2, Air Liquide, France) was used as carrier gas.

157 Liquid injections were performed on a GC (7820A, Agilent, USA) equipped with a low polarity  
158 HP-5ms (30 m × 250 μm × 0.25 μm, Agilent, USA) column and coupled with a mass  
159 spectrometer (5977E, Agilent, USA) operated with an electron ionization (EI) source. The GC  
160 operating parameters for the liquid injections were: splitless mode injection of 1 μl (NAPLs  
161 diluted at 2 mg. L<sup>-1</sup>) at 280°C with a constant flow rate of 1 mL min<sup>-1</sup>. The primary oven  
162 temperature was programmed at 50°C during 5 min then ramping at 5°C min<sup>-1</sup> to 300°C and  
163 hold for 20 min.

164 Head-Space (HS) injections were performed on a GC (8860, Agilent, USA) equipped with an  
165 intermediate polarity Rxi-624 Sil MS (30 m x 250 μm x 1.4 μm, Restek, USA) column, which  
166 is more appropriate for volatile compounds separation, coupled to a mass spectrometer (5977B,  
167 Agilent, USA) containing a EI-Xtr source. The GC operating parameters for the HS injections  
168 were: split ratio (20:1) mode injection of 0.5 mL at 280°C with a constant flow rate of  
169 1.5 mL min<sup>-1</sup>. The primary oven temperature was 35°C during 1 min, then ramping at 5°C min<sup>-1</sup>



170 <sup>1</sup> to 300 °C and hold for 20 min. Prior HS injections, each vial was incubated at 60°C for 30  
171 min and head-space phase sampled with a syringe heated at 60°C.

172 The MS parameters were the same for both devices: electron ionization mode with an electron  
173 energy of 70 eV. The ion source and quad temperatures were 230 and 150°C, respectively. MS  
174 acquisition was done in SCAN mode, analyzing m/z between 25 and 300 amu and included a 5  
175 min solvent delay for liquid injections. Chromatograms were interpreted with Masshunter Qual  
176 software (Agilent, USA) and mass spectrum compared to the literature (Turner and Goodpaster,  
177 2012; Naggar et al., 2017) and to the NIST MS 2.2 2017 database.

178 A semi-quantification was applied for the samples. The proportion of different families (linear-  
179 alkanes, ramified-alkanes, monoaromatics, cycloalkanes) was integrated. For that purpose, the  
180 proportion of each family (%) class was calculated by dividing the sum of the area of different  
181 compounds of each family by the sum of the peak areas of all analyzed compounds of fresh  
182 NAPL (TIC) and multiplied by 100.

### 183 **2.3.3. Degradation of commercial NAPLs**

184 As it is difficult to mimic natural biodegradation under laboratory conditions “fresh” NAPLs  
185 were artificially degraded using two different methods: evaporation and UV degradation.

186 Concerning the first one, a simple 50% and 30% weight evaporation of the gasoline and diesel  
187 fuel, respectively, was performed in order to remove the most volatile compounds. For that  
188 purpose, 700 g of fresh NAPLs were placed in a beaker (200 cm<sup>2</sup>) and exposed at open air under  
189 the hood for two weeks and 2 hours for diesel fuel and gasoline, respectively. The  
190 photodegradation experiments were carried out in a photolytic reactor which consists in a 1 L  
191 glass bottle. A UV light (TUV PL-L 95w/4P HO, 250 nm, Philips) was placed close to the  
192 reactor and the set up was wrapped with aluminum foil to avoid radiation release. A mass of  
193 350 g of fresh NAPL was inserted into the reactor and exposed under UV light for two hours at  
194 room temperature with magnetic stirring (110 rpm).

## 195        **2.4. Batch experiments**

196    In order to determine the evolution of  $^{222}\text{Rn}$  partitioning coefficient between gas and NAPL,  
197    depending on NAPL chemical composition, eight sets of batch experiments were conducted in  
198    this study, each set performed with 6 ( $^{222}\text{Rn}$  production) or 6 ( $K_{n-w}$  determination) batches  
199    presenting different fluids contents. The two first sets were dedicated to the measurement of the  
200     $^{222}\text{Rn}$  production of the porous media coming from the same area, but at different depths (20  
201    and 70 cm) in order to investigate the  $^{222}\text{Rn}$  production variability of a large volume of soil.  
202    The third and fourth sets of batch were dedicated to the determination of the partitioning  
203    coefficient of the fresh gasoline and diesel fuel (14 batches). The sets 5-8 permitted this  
204    characterization for artificially degraded commercial NAPL mixtures.

205    All the different sets of experiments were performed using 1 L glass bottles sealed with gas  
206    tight pre-perforated rubber stoppers as they prevent any gas linkage (Cohen et al., 2019). Gas  
207    leakage was checked for every batch by lowering the pressure in the batch and by monitoring  
208    the pressure during 5 min. Then, the atmospheric pressure was restored using a syringe needle.  
209    A mass  $m_s$  (~ 700g) of sieved soil was chosen for each batch. Different water and NAPL (if  
210    applicable) contents were chosen and mixed with the porous media prior insertion of the  
211    mixture in the batch. For batches with NAPL, prior NAPL contamination, the dry porous media  
212    was moistened with a desired volumetric water content ( $\theta_w= 0.02$ ) in order to better mimic  
213    natural conditions. For each set of batches containing the different NAPLs (fresh and degraded),  
214    one batch was dedicated to the measurement of the  $^{222}\text{Rn}$  activity without NAPL at a water  
215    content similar to the batches with NAPL ( $\theta_w=0.02$ ), referred hereafter as “check-batches”.  
216    These check-batches were used in order to verify the  $^{222}\text{Rn}$  production for the amount of soil  
217    used for each set of batches. The batch reactors were left for 25-30 days to reach radioactive  
218    equilibrium before  $^{222}\text{Rn}$  activity measurement (Höhener and Surbeck, 2004).

## 219        **2.5. $^{222}\text{Rn}$ activity measurements**

220 Scintillation flasks of 125 cm<sup>3</sup> (Algade, France) were used for <sup>222</sup>Rn measurements. First, a  
 221 pump (Neuberger 816, KNF, Germany) was used to vacuum the flasks (-850 to -900 mbar).  
 222 Then, the soil-gas from the batch was extracted by suction, using a steel needle linked to a  
 223 valve. The flasks were inserted into the counter chamber of a portable alpha counter (CAPP2,  
 224 Algade France) and kept in the dark for 10 min. After radioactive equilibrium, <sup>222</sup>Rn activity in  
 225 each flask was determined six times with counting times of 20 min. Radon background, referred  
 226 as blank values was measured on the same flask, under the same counting conditions and were  
 227 subtracted. The yields of each flask were taken into account and the radon activity expressed in  
 228 Bq m<sup>-3</sup> was obtained using previously established calibration. The <sup>222</sup>Rn production (Bq kg<sup>-1</sup>)  
 229 was then calculated (equation 1) taking into account the batch properties (mass of soil, water  
 230 and gas contents):

231

232 Eq. (1) 
$$A = \frac{1}{\left(1 + \frac{\theta_w}{K_H \theta_g} + \frac{K_n \theta_n}{\theta_g}\right)} \frac{m_s}{V_g} E C_{Ra}$$

233 With A the <sup>222</sup>Rn activity (Bq.m<sup>-3</sup>),  $\theta_w$  the water content ( - ),  $K_H$  the gas–water partitioning coefficient  
 234 ( - ),  $\theta_g$  the gas content ( - ),  $K_n$  the NAPL-gas coefficient ( - ),  $\theta_n$  the NAPL content,  $m_s$  the mass of soil  
 235 (kg),  $V_g$  the volume of gas (m<sup>3</sup>), E the <sup>222</sup>Rn emanation coefficient ( - ) and  $C_{Ra}$  the solid <sup>226</sup>Ra content  
 236 (Bq kg<sup>-1</sup>). The NAPL-water partitioning coefficient was also calculated:

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Eq. (2)  $K_{n-w} = K_n \times K_H$

238 In order to test the effect of  $K_{n-w}$  modification on NAPL saturation ( $S_n$ ), the equation  
 239 presented in Hunkeler et al. (1997) was used:

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241 Eq. (3)  $S_n = (Ae^{n_{apl}=0} / Ae^{n_{apl}>0} - 1) / (K_{n-w} - 1)$

242 With  $S_n$  the NAPL saturation ( - ),  $Ae^{n_{apl}=0}$  the  $^{222}\text{Rn}$  activity in the batches without NAPL  
243 ( $\text{Bq}\cdot\text{m}^{-3}$ ),  $Ae^{n_{apl}>0}$  the  $^{222}\text{Rn}$  activity in the batches with NAPL ( $\text{Bq}\cdot\text{m}^{-3}$ ) and  $K_{n-w}$  the NAPL  
244 water partition of  $^{222}\text{Rn}$  ( - ).

## 245 **3. Results**

### 246 **3.1. Porous media and NAPLs densities**

247 The density of the PM is  $2631 \pm 4.2 \text{ kg.m}^{-3}$ . Concerning NAPLs, fresh, UV-degraded and  
248 evaporated diesel fuel densities are about  $813 \pm 3.8$ ,  $812 \pm 3.8$  and  $843 \pm 3.8 \text{ kg m}^{-3}$ ,  
249 respectively, while they are about  $748 \pm 3.8$ ,  $746 \pm 3.8$  and  $796 \pm 3.8 \text{ kg m}^{-3}$  for fresh, UV-  
250 degraded and evaporated gasoline, respectively. Thus, significant density differences can be  
251 observed for NAPL evaporation with an increase of about 4 and 6% for diesel fuel and gasoline,  
252 respectively.

### 253 **3.2. $^{222}\text{Rn}$ production of Porous media**

254 The results concerning the soil  $^{222}\text{Rn}$  production ( $\text{EC}_{\text{Ra}}$ ) in the different batches are presented  
255 in Fig. 1. The results are presented in function of the batches water content ( $\theta_w$ ). For the 20 cm  
256 depth soil,  $\text{EC}_{\text{Ra}}$  increases rapidly from  $1.49 \pm 0.25 \text{ Bq kg}^{-1}$  (dry sample) to  $2.65 \pm 0.25 \text{ Bq kg}^{-1}$   
257 ( $\theta_w 0.02$ ). Then, the  $\text{EC}_{\text{Ra}}$  decreases and remain relatively constant (mean of  $2.49 \pm 0.13 \text{ Bq}$   
258  $\text{kg}^{-1}$ ) for larger water contents ( $\theta_w 0.04 - 0.1$ ). Concerning the 70 cm depth soil, the production  
259 follows the same behavior but presents lower values, with for the dry sample, an  $\text{EC}_{\text{Ra}}$  value of  
260  $0.95 \pm 0.25 \text{ Bq kg}^{-1}$  which increases to  $1.33 \pm 0.32 \text{ Bq kg}^{-1}$  ( $\theta_w 0.1$ ) with a mean of  $1.29 \pm 0.34$   
261  $\text{Bq kg}^{-1}$ . The  $^{222}\text{Rn}$  activities measured in the production batch with a water content of  $\theta_w = 0.02$   
262 are  $2090 \pm 264 \text{ Bq m}^{-3}$  at 20 cm and  $1005 \pm 268 \text{ Bq kg}^{-1}$  at 70 cm. In addition, the  $^{222}\text{Rn}$   
263 production measured in the “check-batches” (7 batches coming from the different sets) are  
264 comprised between 1.3 and  $2.5 \text{ Bq kg}^{-1}$  for the two sets of batches with different soils depth  
265 (Fig. 1). Since the production for the “checked batches” is in the range of the production  
266 batches, for each set of batch, the “checked batch” corresponding production was chosen  
267 instead of the mean production (Fig. 1) due to the  $^{222}\text{Rn}$  production variation.

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### 3.3. NAPL-gas partitioning coefficient ( $K_n$ ) of $^{222}\text{Rn}$ for fresh and altered diesel fuel and gasoline

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#### 3.3.1. Partitioning coefficient ( $K_n$ ) of fresh and altered diesel fuel

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#### 3.3.2. Partitioning coefficient ( $K_n$ ) of fresh and altered gasoline

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The  $^{222}\text{Rn}$  activities in the batches containing fresh diesel fuel at different volumetric contents are presented in Figure 2a. The Supplementary Information (SI) presents the statistical results permitting to conclude to the significant difference between the calculated  $K_{n-w}$ . The  $^{222}\text{Rn}$  activities are presented in function of the batch NAPL contents. The batch without NAPL shows a  $^{222}\text{Rn}$  activity of  $1991 \pm 114 \text{ Bq.m}^{-3}$ , similar to the production experiment ( $2210 \pm 200 \text{ Bq.m}^{-3}$ ). The increase of the NAPL content in the porous media leads to the decrease of the  $^{222}\text{Rn}$  activity reaching a value of  $429 \pm 24 \text{ Bq.m}^{-3}$  for  $\theta_n = 0.2$ . The theoretical Rn activity calculated from Eq.1 with different NAPL contents are also presented in figure 2a (black curve). The best fit with the experimental data is obtained using a  $K_{n-w} = 60.7 \pm 6.1$ .

The figure 2b shows the  $^{222}\text{Rn}$  activities for the batches containing UV-degraded diesel fuel for different NAPL contents. This set shows, like for the fresh diesel fuel, but more sharply, a decrease of the  $^{222}\text{Rn}$  activity with the increase of the NAPL content ( $356 \pm 63 \text{ Bq.m}^{-3}$ , NAPL  $\theta_n = 0.2$ ). The fitted partitioning coefficient for this altered diesel fuel is  $K_{n-w} = 74.8 \pm 7.5$ . For the evaporated diesel (Fig. 2c), the  $^{222}\text{Rn}$  activity also decreases, but at a lower intensity than the fresh and UV-degraded diesel. Indeed, the batch without diesel fuel shows a  $^{222}\text{Rn}$  activity of  $1413 \pm 215 \text{ Bq.m}^{-3}$  which is lower than for the others because of the type of soil used for this batch, and the most NAPL saturated batch presents a  $^{222}\text{Rn}$  activity of  $547 \pm 28 \text{ Bq.m}^{-3}$  (NAPL  $\theta_n = 0.2$ ). The partitioning coefficient is  $K_{n-w} = 25.1 \pm 2.5$ .

For the fresh gasoline, the porous media without NAPL shows a lower activity than the diesel fuel batch set, with a  $^{222}\text{Rn}$  activity of  $1292 \pm 121 \text{ Bq.m}^{-3}$  (Fig. 3a) which is explained by the type of soil used for this batch. The increase of gasoline content in the batches lead to a decrease of the  $^{222}\text{Rn}$  activity ( $389 \pm 52 \text{ Bq.m}^{-3}$  for  $\theta_n = 0.2$ ). The fitted partitioning coefficient was also calculated and the best fit is obtained

298 for a  $K_{n-w} = 37.4 \pm 5.6$ . The UV-degraded gasoline (Fig. 3b) also shows a decrease of the  $^{222}\text{Rn}$  activities,  
299 but to a lesser extent, reaching  $658 \pm 24 \text{ Bq.m}^{-3}$  ( $\theta_n = 0.2$ ). The partitioning coefficient between NAPL  
300 and water is  $K_{n-w} = 33 \pm 4.9$ . The evaporated gasoline shows a  $^{222}\text{Rn}$  activity of  $1995 \pm 195 \text{ Bq.m}^{-3}$  ( $\theta_n =$   
301  $0$ ) decreasing to  $673 \pm 70 \text{ Bq.m}^{-3}$  ( $\theta_n = 0.2$ ), leading to a  $K_{n-w}$  of  $30.8 \pm 4.6$ . The table 1 summarizes the  
302 different  $K_{n-w}$  found in this study (see SI for statistical results).

303

### 304 **3.4. Molecular investigation of the fresh and degraded NAPLs, identification of by-** 305 **products**

#### 306 **3.4.1 Chemical composition of diesel fuel**

307 The most volatile compounds identified using the HS-GCMS are presented in the figure 4. The  
308 fresh diesel fuel chromatogram (Fig. 4a, Table 2) is principally composed by linear n-alkanes  
309 ranging from n-C5 and n-C15 and by branched n-alkanes. Other compounds such as cyclic  
310 hydrocarbons, alkenes and BTEX are also encountered. The chromatogram corresponding to  
311 the UV treatment (Fig. 4b, Table 2) is rather similar to the fresh diesel without any total loss of  
312 compounds. However, a general decrease of the peaks intensity is observed with a TIC area  
313 representing 73 % of the fresh diesel fuel. The percentage of the different compounds in the  
314 different fractions (<C10 and >C10) confirmed the TIC area decrease, mainly in the <C10  
315 fraction for the UV-degraded diesel fuel. The chromatogram corresponding to the evaporation  
316 treatment is different (Fig. 4c, Table 2). The first 12 minutes of the TIC is characterized by an  
317 absence of peaks, corresponding to the loss of the most volatile compounds (ranging from n-  
318 C5 and n-C8). The area of the evaporated diesel TIC represents 16% of the fresh diesel fuel.  
319 The percentage of the different compounds in the different fractions also shows a decrease in  
320 the evaporated diesel fuel mainly in the <C10 fraction.

321

322 The liquid GC-MS in scan mode permits to identify the different major hydrocarbons of  
323 moderate to low volatility present in the fresh diesel fuel (Fig. 5a, Table 2). The diesel fuel

324 matrix is complex and the separation of the different compounds is limited, reducing the  
325 possible identification of the different compounds. The fresh diesel fuel is principally composed  
326 by n-alkanes such as linear n-alkanes and branched n-alkanes ranging from n-C<sub>8</sub> to n-C<sub>27</sub>. The  
327 diesel fuel is also composed by alkenes, cyclo-alkanes and BTEX. The photodegraded diesel  
328 fuel (Fig. 5b) shows a similar chromatogram pattern with the same by-products and similar  
329 intensity. The percentages of the different families in the different fractions (< C<sub>10</sub>, C<sub>10</sub> – C<sub>15</sub>,  
330 >C<sub>15</sub>) do not show high variations for the fresh and UV-degraded diesel fuel. A slight increase  
331 of the cycloalkanes and methyl alkanes is observed in the >C<sub>15</sub> fraction for the UV-degraded  
332 diesel fuel (Table 2). In contrary, the diesel fuel artificially evaporated (Fig. 5c) under the hood  
333 (30 % in weight) shows variations of the chromatogram compared to fresh and UV-degraded  
334 diesel fuel. The lightest fraction of the diesel fuel (until 17 min) is vaporized resulting in the  
335 absence of peaks. The percentages show high decrease of the different compounds in the  
336 different fractions, mainly in the <C<sub>10</sub> and C<sub>10</sub> – C<sub>15</sub> fractions, containing in particular cyclo-  
337 alkanes.

338

### 339 **3.4.2 Chemical composition of gasoline**

340 The most volatized compounds are presented in the figure 6. The fresh gasoline chromatogram  
341 (Fig. 6a, Table 2) is composed by linear n-alkanes, alkenes (n-C<sub>5</sub> to n-C<sub>8</sub>), branched n-alkanes,  
342 alkenes and cyclic hydrocarbons. In addition, BTEX represents a large fraction of the  
343 chromatogram, eluting between 10 and 20 min. The chromatogram corresponding to the UV  
344 treatment (Fig. 6b, Table 2) is rather similar to the fresh gasoline with similar peaks intensity  
345 in TIC area. The percentage of the different compounds in the different fractions (<C<sub>5</sub> and >C<sub>5</sub>)  
346 also confirms the general observations with the TIC with similar percentages in the different  
347 fractions. The chromatogram corresponding to the evaporation treatment is slightly different  
348 (Fig. 6c, Table 2). Several peaks at the beginning of the chromatogram, corresponding to



349 alkanes and alkenes, disappeared and the area of the evaporated gasoline TIC represents 96%  
350 of the fresh gasoline. The percentage of the different compounds in the different fractions also  
351 shows a decrease in the evaporated gasoline in the <C5 fraction. The >C5 fractions reveals an  
352 increase in the different fractions, resulting from a concentration of the compounds into NAPL  
353 due to evaporation. Indeed, the evaporation results in the removal of the lower boiling  
354 compounds and a relative abundance increase of the higher boiling compounds into NAPL,  
355 leading to higher partial pressure in the gas phase (Raoult law).

356 The fresh gasoline (Fig. 7a, table 2) is characterized by low molecular-mass hydrocarbons  
357 mainly eluting before 10 min. Monoaromatic compounds are predominant in the sample.  
358 Alkanes (n-C<sub>8</sub> to n-C<sub>16</sub>), alkenes, cycloalkanes and isoalkanes complete the composition. The  
359 UV-degraded gasoline (Fig. 7b, Table 2) chromatogram pattern is similar to the fresh  
360 chromatogram pattern with the predominance of low molecular-mass hydrocarbons at similar  
361 intensity. In contrast to the evaporated diesel fuel (Fig. 7c), the evaporated gasoline does not  
362 clearly show difference with the fresh gasoline. The percentage of the different compounds in  
363 the <C10 and >C10 fractions for the fresh, UV-degraded and evaporated gasoline does not show  
364 clear and logical variations (Table 2).

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## 370 **4. Discussion**

### 371 **4.1. Radon production in the porous media**

372 Radon production can evolve in two different ways depending on soil moisture. Low soil  
373 moisture contents can lead to an increase of soil emanation (Nazaroff, 1992; Hosoda et al.,  
374 2007) in comparison with dry soil. Actually, for dry soil, a significant fraction of  $^{222}\text{Rn}$  that  
375 escape from a grain due to recoil enters in another grain and thus does not stay in porosity,  
376 inducing low  $\text{EC}_{\text{Ra}}$  as can be seen for the first batch without water (Fig. 1). When a small amount  
377 of water is added, a higher fraction of  $^{222}\text{Rn}$  is trapped in the porosity, leading to an increase of  
378  $\text{EC}_{\text{Ra}}$ . This behavior is also observed in this study with the increase of  $\text{EC}_{\text{Ra}}$  for the batches with  
379 small content of water ( $\theta_w$  0.01 – 0.02) (Fig. 1). However, higher soil moisture reduces gas  
380 mobility.

381 Different factors influence the  $^{222}\text{Rn}$  emanation from soils (*ie.* temperature, soil physical and  
382 chemical properties). When the temperatures are lower, the number of radon atoms adsorbed to  
383 particles increases, leading to a decrease of the  $^{222}\text{Rn}$  activity (Baskaran, 2016). The different  
384 set of batches were carried out at different time and the room temperature changed slightly  
385 (from 25 °C to 15 °C). This temperature change could explain the variation of  $^{222}\text{Rn}$  activity.  
386 Another explanation can come from the soil material used in this study. The soil was sampled  
387 from a pond area, close to the laboratory. A large amount of soil was necessary for the different  
388 set of batches and a hole of approximately 1.5 m deep was dug. The composition of the soil  
389 was not the same from the surface and the bottom with more fine particles encountered deeper.  
390 This soil composition variation could explain the  $^{222}\text{Rn}$  activity variation between the batch  
391 sets. Thu et al., (2020) investigated the  $^{222}\text{Rn}$  emanation and diffusion from soil in function of  
392 different soil compositions. They noted a dependence of the radon emanation on iron content  
393 and pH.

### 394 **4.2. Molecular composition**

395 Diesel fuel is a complex mixture of different hydrocarbons. The major compounds encountered  
396 are straight n-alkanes, isoprenoids (branched n-alkanes), cyclo-alkanes and aromatics  
397 (Christensen et al., 1987). A typical fresh diesel fuel chromatogram is characterized by a  
398 dominance of n-alkanes peaks, appearing in a regular pattern and covering all the chromatogram  
399 (Christensen et al., 1993). Gasoline fuel is obtained from the distillation and cracking of crude  
400 oil (El Naggat et al., 2017). Cracking produces, from long chain alkanes, smaller alkenes at  
401 high temperature. Typical gasoline fuel is composed by over 200 petroleum-derived chemicals  
402 (El Naggat et al., 2017) with a dominance of aromatic compounds and branched alkanes over  
403 n-alkanes.

404 The fresh commercial diesel fuel and gasoline used in this study, characterized with MS in scan  
405 mode using GC-MS reveals similar patterns than the ones observed in literature. On the  
406 contrary, the artificial degradations carried out in this study permit to reveal different behaviors.  
407 The different chromatographic techniques employed in this study do not permit to observe any  
408 difference concerning the UV-light degradation with the fresh material except a diminution of  
409 the area of the total chromatogram for the UV-degradation compared to the fresh diesel fuel  
410 with the HS-GCMS analyses. Garrett et al., (1998) also performed artificial weathering of  
411 Alaskan crude oil, by its exposure to UV-light, and observed no effect of the illumination on  
412 the total ion chromatograms as well. However, the use of thin layer chromatography showed  
413 variations with the conversion of the aromatics hydrocarbons to resins or polar compounds.  
414 Douglas et al., (2002) also investigated the effect of UV light on oil molecular composition  
415 using Single Ion Monitoring (SIM) mode. They showed that large polycyclic aromatic  
416 hydrocarbons are more affected by photooxidation as well as the more alkylated compounds.  
417 Further investigation of the degraded products, focusing on certain molecules could help to  
418 distinguish some variations between fresh and UV-degraded chromatograms patterns.

419 The artificial evaporation effect on the molecular composition is quite different from the  
420 artificial photooxidation. In this study, the artificial diesel fuel evaporation under the hood  
421 removes the compounds presenting a chromatographic retention time below 12 min, as  
422 observed in liquid and head-space chromatographs (Fig 4c and 5c). Villa et al., (2010) studied  
423 the effects of the evaporation on the molecular composition of diesel fuel. They showed a loss  
424 of hydrocarbons with chain lengths less than 14 carbons in addition to other unsaturated and  
425 cyclic hydrocarbons. Prince et al., (2003) also showed the release of the lightest compounds  
426 (C4 – C18) in result to the evaporative process. As a general feature, the evaporative process  
427 will start with the removal of all components with short retention times including n-alkanes and  
428 isoprenoids. Sometimes, the process can lead to the evaporation of components with higher  
429 retention times. However, the ratio between the n-alkanes and isoprenoids will not change  
430 (Wang et al., 1990). In the present study, the gasoline chromatograms do not show any variation  
431 of the composition or peak intensity between fresh and evaporated material except a removal  
432 of the first peaks (first two minutes, Fig. 7c) and a relative increase of the high boiling  
433 compounds in the HS-GCMS. Turner et al., (2012) also studied the effects of weathering  
434 (evaporation) on the molecular composition of gasoline using liquid GCMS. They reported no  
435 special variation of the chromatogram pattern between a 0% weathered sample and 50%  
436 weathered sample. This could explain the absence of variation in this study with gasoline  
437 subject to 50% evaporation in weight.

#### 438 **4.3. Determination of $^{222}\text{Rn}$ partitioning coefficients of fresh and aged NAPLs**

439 Very little data is available concerning the radon partitioning coefficient for NAPL mixtures.  
440 Hunkeler et al. (1997) measured the  $^{222}\text{Rn}$  partitioning coefficient for an unspecified diesel fuel  
441 and Schubert et al. (2007a) determined  $^{222}\text{Rn}$  partitioning coefficient for three synthetic NAPL  
442 mixtures representing gasoline, and diesel fuel (Table 3). To our knowledge, no data is currently  
443 available concerning the partitioning coefficient of complex degraded NAPLs.

444 On the other side, pure NAPLs such as Benzene and Toluene radon partitioning coefficient can  
445 be encountered in the literature (Clever, 1979; Abraham et al., 1994; Schubert et al., 2007a, b).  
446 The table 3 gathers several coefficient partitions of pure NAPLs of interest from the literature.  
447 The next paragraph is dedicated to the comparison of the different complex NAPLs mixtures  
448 and pure NAPLs.

449 First of all, the results show that, in spite of a wide range covered by the radon partitioning  
450 coefficients  $K_{n-w}$  (26 – 75), the different commercial NAPLs investigated have a strong affinity  
451 with radon. The fresh diesel fuel shows higher partitioning coefficient than fresh gasoline. For  
452 both fresh NAPL used in this study, the partitioning coefficient  $K_{n-w}$  are similar to those  
453 presented in Schubert et al. (2007b) ( $60.7 \pm 6.1$  vs  $60 \pm 1.3$  and  $37.4 \pm 5.6$  vs  $38.9 \pm 0.9$ , for  
454 diesel fuel and gasoline, respectively), despite the fact that this study used commercial mixture  
455 while Schubert et al. (2007b) used simplified synthetic mixtures. Indeed, the gasoline used in  
456 Schubert et al., (2007b) study was a laboratory made mixture composed by 50 % of iso-octane,  
457 40 % of BTEX and 10 % alkene while the commercial gasoline used in this study is composed  
458 by multiple compounds and especially a large proportion of BTEX. Coefficient partition of  
459 several BTEX has been determined in the literature indicating intermediate  $K_{n-w}$  values  
460 (between 44.7 and 51.3, table 3). This could explain the lower  $K_{n-w}$  encountered for gasoline.  
461 The diesel fuel used in Schubert et al., (2007b) was composed at 60% by hexadecane and 15%  
462 cyclohexane while the one used in this study is mainly composed by different alkanes from C8  
463 to C27. One explanation for this  $K_{n-w}$  similarity is that the compounds used by Schubert et al.,  
464 (2007b) may drive the partitioning coefficient behavior. The main result brought by this study  
465 is the variation of the partitioning coefficient (compared to fresh NAPLs) when the diesel fuel  
466 is degraded. On the other hand, the gasoline did not show any significant variations related to  
467 degradation, probably due to the too slight degradation (see part 4.2). The evaporation of 50%  
468 in weight of the gasoline was extremely rapid. However, the chromatogram pattern does not

469 show large differences for the evaporation treatment. This could be due to the evaporation of  
470 an extremely volatile compound. The evaporation leads to a reduction of the diesel fuel affinity  
471 for  $^{222}\text{Rn}$ , whereas the UV-degradation engenders higher affinity of diesel fuel for  $^{222}\text{Rn}$ . This  
472 feature demonstrates that for diesel, the degradation processes will change the affinity of  
473 NAPLs toward  $^{222}\text{Rn}$  compared to fresh products. The partitioning coefficients gathered in the  
474 literature (Table 3) may explain the variations of  $K_{n-w}$ . When a diesel fuel is artificially  
475 evaporated, the results show a removal of the lightest fraction which is composed by short  
476 alkanes chains and cycloalkanes. The  $K_{n-w}$  of hexane and cyclohexanes are 58.1 and 63.3,  
477 respectively. When those molecules are removed by evaporation, a modification of the  $K_{n-w}$  is  
478 then expected, as measured in this study. In addition, the hexadecane  $K_{n-w}$  has also been  
479 reported with a value of 33.3 (Abraham et al., 1994).

480 As Schubert et al., (2007a) stated, the use of Radon method is not applicable without  
481 restrictions. Indeed, as found in this study, the partitioning coefficient evolves in relation with  
482 the NAPL alteration. This change in the partitioning coefficient will lead to incorrect  
483 interpretation of the Radon Deficit Factor. A simple calculation of the NAPL saturation (eq. 3)  
484 permits to estimate the NAPL saturation changes in relation with the  $K_{n-w}$ . The use of a fresh  
485 diesel fuel  $K_{n-w}$  (60) instead of a  $K_{n-w}$  of evaporated diesel fuel (26) in an area where diesel fuel  
486 has been exposed to air will lead to an overestimation of approximately 50% of the NAPL  
487 saturation. In the same way, if a  $K_{n-w}$  of a fresh diesel fuel is used instead of fresh gasoline, the  
488 overestimation of the NAPL saturation would be about 30%. However, semi-quantitative  
489 measurements are still operable since  $^{222}\text{Rn}$  shows a strong affinity to NAPLs either fresh or  
490 degraded.

491 In this study, the different pure compounds forming the diesel fuel and gasoline present a  $K_{n-w}$   
492 ranging from 33 to 63 (fresh compounds). The fresh diesel fuel detains a  $K_{n-w}$  of 60.7 and the  
493 gasoline a  $K_{n-w}$  of 37. This could suggest that the  $K_{n-w}$  for this kind of NAPLs mixtures should

494 reasonably ranging between 30 and 60. Despite the remaining uncertainty in the  $K_n$  of one  
495 degraded NAPL, the presented results allowed to specify the full range of  $R_n$  for field NAPL.  
496

## 497 **5. Conclusion**

498 This study investigates the variations of the partitioning coefficient ( $K_{n-w}$ ) of different fresh  
499 commercial NAPL mixtures (diesel fuel and gasoline) and commercial NAPL mixtures  
500 degradations (evaporation and photooxidation). The results show different partitioning  
501 coefficients of the fresh diesel fuel and gasoline which are similar with previous  $K_{n-w}$  reported  
502 in the literature. The NAPL artificial degradations carried out in this study engender variations  
503 of the  $K_{n-w}$ . The evaporated diesel fuel shows lower  $K_{n-w}$  than the fresh diesel fuel whereas the  
504 UV-degraded diesel fuel shows higher  $K_{n-w}$  than fresh diesel fuel. For the gasoline, the  
505 variations of the  $K_{n-w}$  in relation with the degradation processes are more tenuous. The  
506 molecular characterization of the diesel fuel, using GCMS in scan mode, do not permit to  
507 differentiate fresh and UV-degraded products (except the diminution of the intensity concerning  
508 the HS approach). The evaporated diesel fuel chromatogram is different with the absence of  
509 peaks at the beginning of the chromatogram (first 17 min). The gasoline molecular composition  
510 is not variable between the different treatments using the GCMS method in scan mode, except  
511 a removal of the first peaks (first 2 min) in the HS approach. As previously reported in the  
512 literature, the  $^{222}\text{Rn}$  is a good proxy parameter for soil NAPL delineation. In the calculation and  
513 modelling, the partitioning coefficient is of pivotal importance. This study emphasis the  
514 importance of the study of the  $K_{n-w}$  variability as it can lead to an false estimation of NAPL  
515 saturation. Therefore, it is extremely important to explore the effects of different parameters  
516 that could modify the  $K_{n-w}$ . This study reveals that NAPL degradation modify the partitioning  
517 coefficient in relation with the molecular composition. Future researches are thus needed to  
518 decipher the relationship between NAPL molecular composition and  $^{222}\text{Rn}$  partitioning  
519 coefficient  $K_{n-w}$  in order to:

- 520 – better understand the evaporation intensity effects on the diesel fuel and gasoline  $K_{n-w}$
- 521 – Investigate the microbial degradation effects on the  $K_{n-w}$



522 – Investigate the effects of different degradation processes on the same NAPL mixture  
523 (evaporation coupled to photooxidation, evaporation coupled to microbial degradation).

## 524 **Conflict of Interest**

525 The authors declare that the research was conducted in the absence of any commercial or  
526 financial relationships that could be construed as a potential conflict of interest.

527

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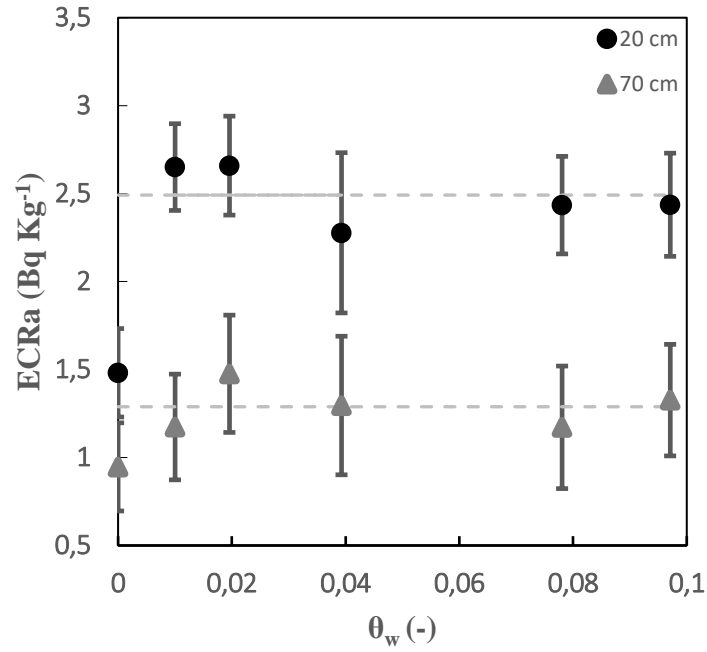
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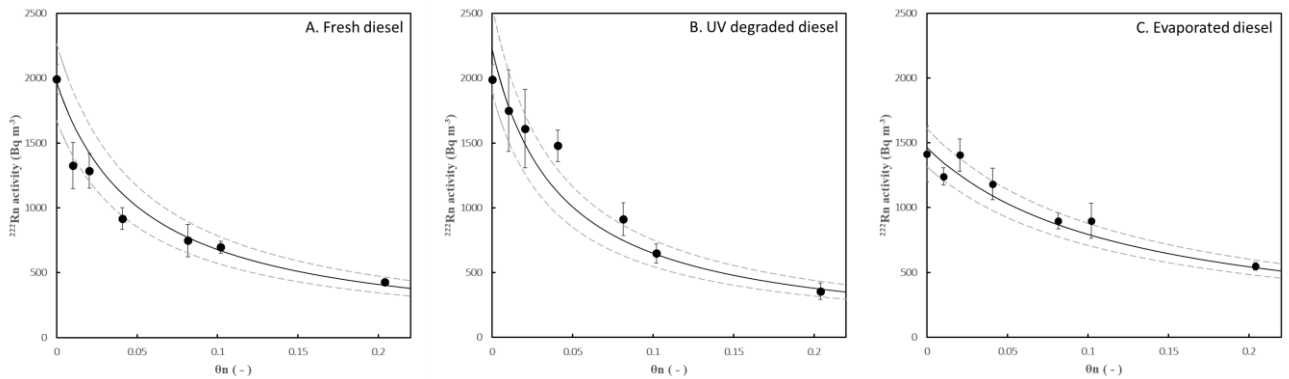
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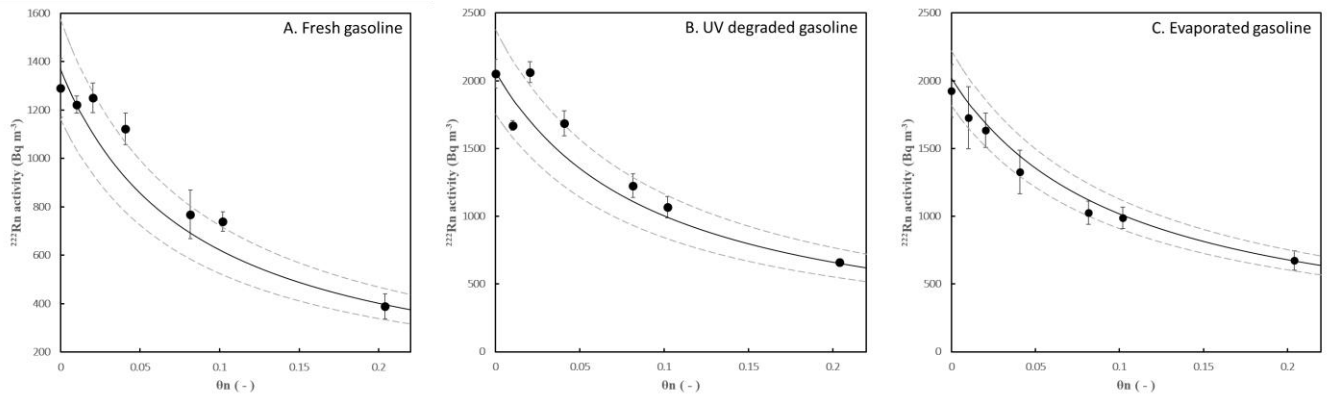
757 Fig. 1.  $^{222}\text{Rn}$  production ( $EC_{Ra}$ ) for the soil used in this study in relation with the water content ( $\theta_w$ ). Grey dashed  
 758 line corresponding to  $EC_{Ra}$  mean (dry sample not included).  
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761 Fig. 2 Experimental (black dots) and theoretical (black curve)  $^{222}\text{Rn}$  activity ( $\text{Bq}\cdot\text{m}^{-3}$ ) for (a) Fresh diesel fuel,  
 762 (b) UV-degraded diesel fuel and, (c) evaporated diesel fuel as a function of the NAPL content ( $\theta_n$ ). Dotted lines  
 763 represent errors of 15% in the gas-diesel partitioning-coefficient.  
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767 *Fig. 3 Experimental (black dots) and theoretical (black curve)  $^{222}\text{Rn}$  activity ( $\text{Bq m}^{-3}$ ) for (a) Fresh gasoline, (b)*  
 768 *UV-degraded gasoline, (c) evaporated gasoline and, (d) on site NAPL as a function of the NAPL content ( $\theta_n$ ).*  
 769 *Dotted lines represent errors of 15% in the gas-gasoline partitioning-coefficient.*

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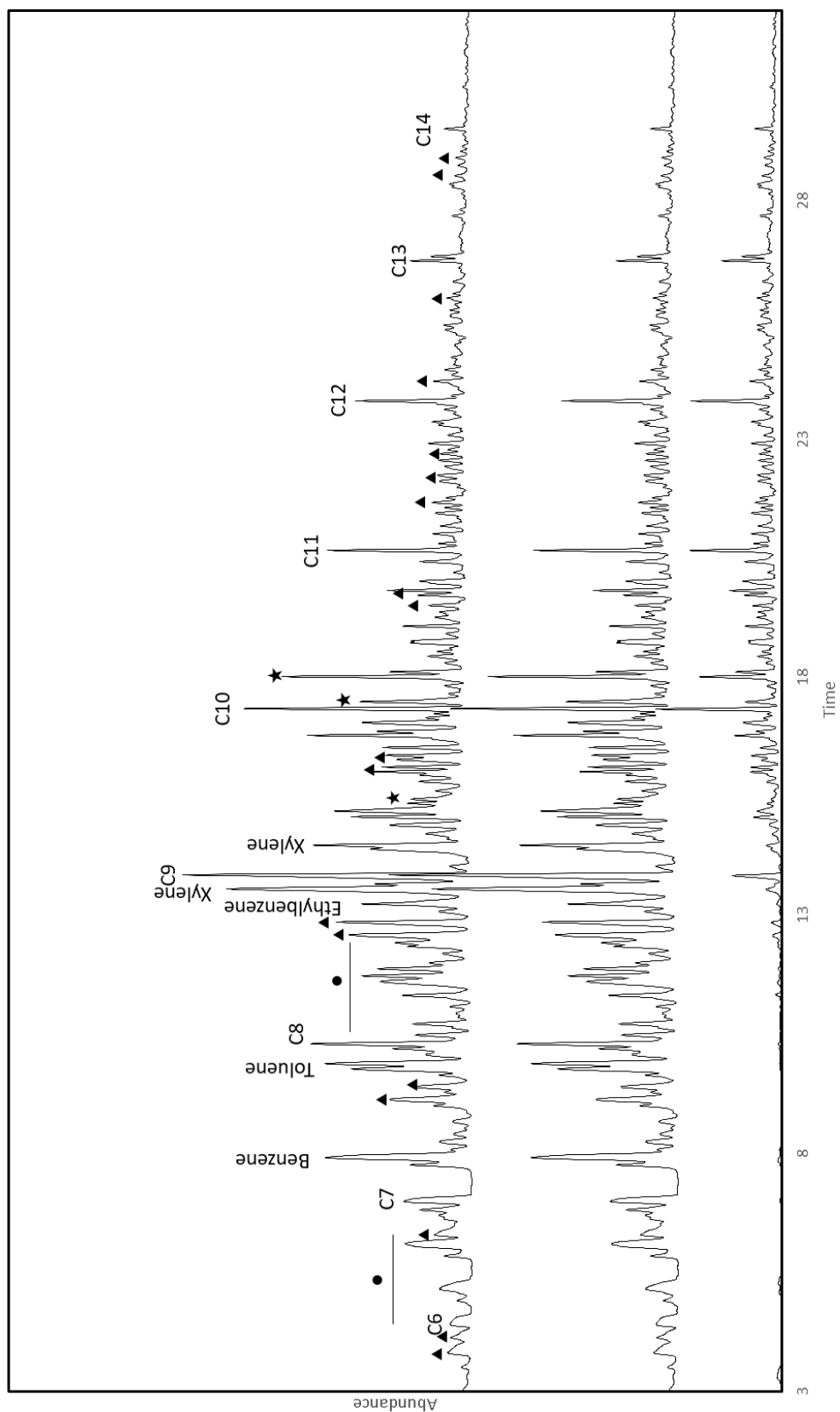
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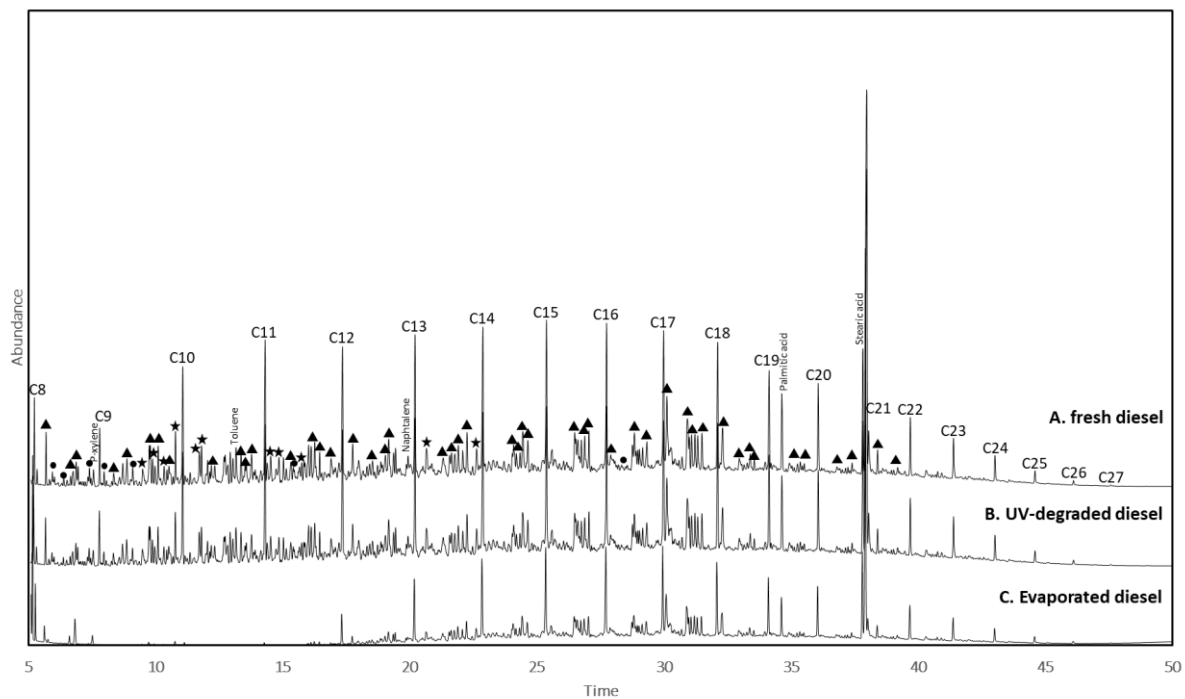
780 Fig. 4 Head-Space GC-MS in scan mode chromatograms of the (a) fresh diesel, (b) UV-degraded diesel and, (c)  
 781 evaporated diesel. The C<sub>5</sub> to C<sub>15</sub> correspond to the linear n-alkanes, triangle refers to ramified alkanes, circles  
 782 refer to cycloalkanes, stars correspond to BTEX.



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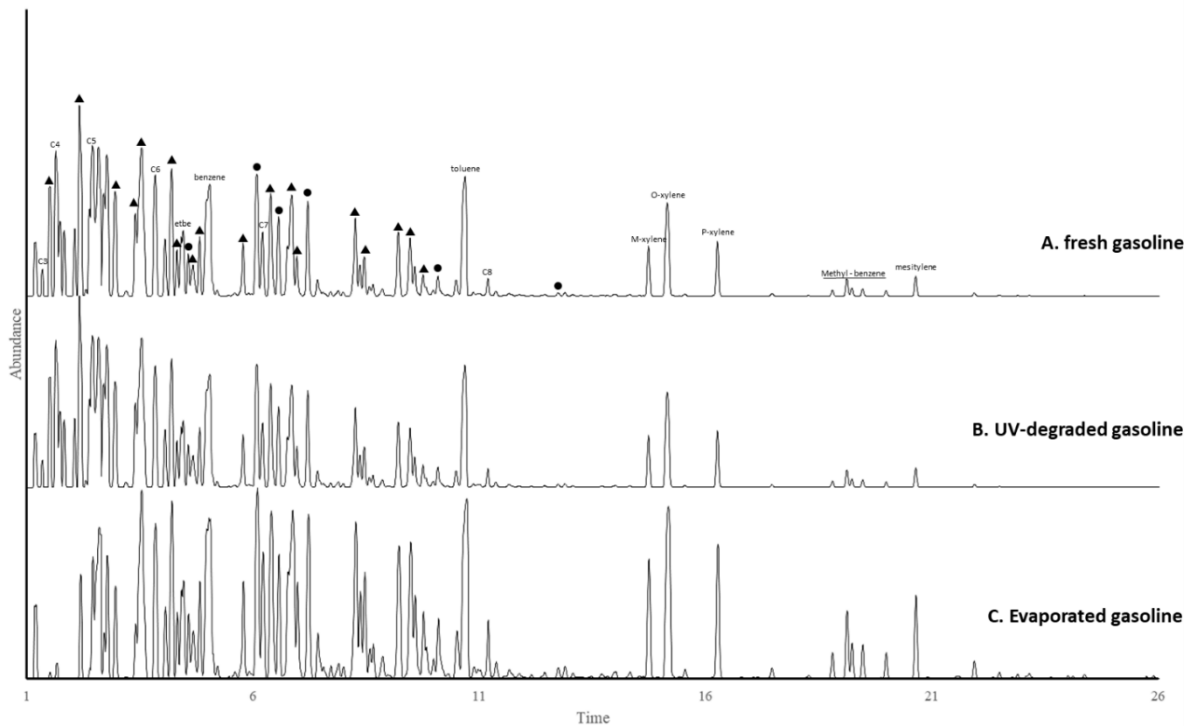
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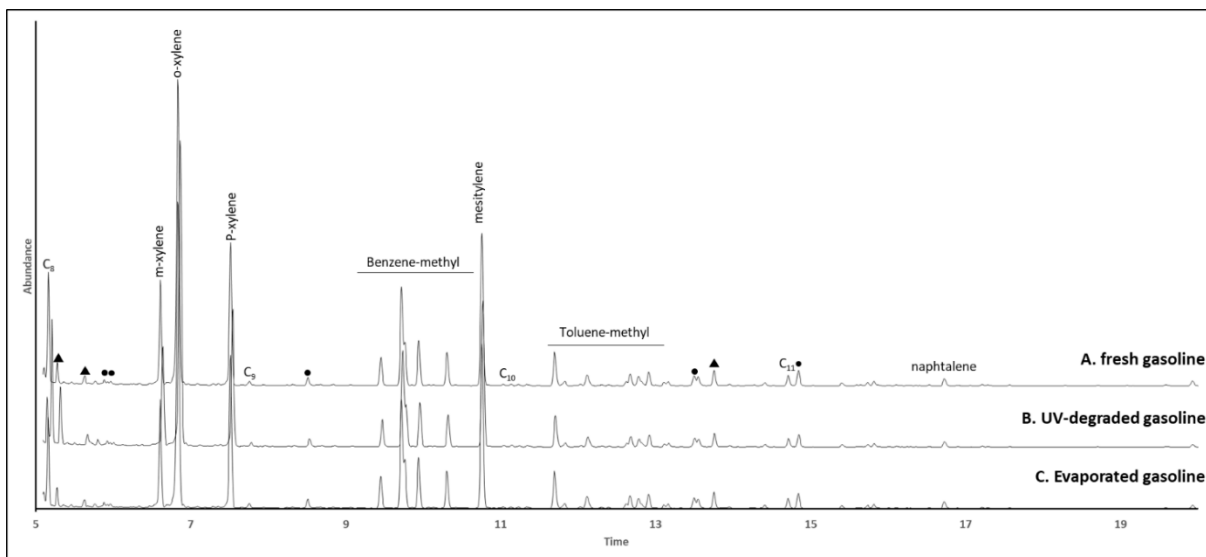
787 *Fig. 5 Liquid GC-MS in scan mode chromatograms of the (a) fresh diesel, (b) UV-degraded diesel and, (c)*  
788 *evaporated diesel. The C<sub>8</sub> to C<sub>27</sub> corresponds to the linear n-alkanes, triangle refers to ramified alkanes, circle*  
789 *refers to cycloalkanes, stars correspond to BTEX.*  
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792 *Fig. 6 Head-Space GC-MS in scan mode chromatograms of the (a) fresh gasoline, (b) UV-degraded gasoline*  
 793 *and, (c) evaporated gasoline. The C<sub>4</sub> to C<sub>8</sub> correspond to the linear n-alkanes, triangle refers to ramified*  
 794 *alkanes, circle refers to cycloalkanes.*

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797 *Fig. 7 Liquid GC-MS in scan mode chromatograms of the (a) fresh gasoline, (b) UV-degraded gasoline and, (c)*  
 798 *evaporated gasoline. The C<sub>4</sub> to C<sub>10</sub> correspond to the linear n-alkanes, triangle refers to ramified alkanes, circle*  
 799 *refers to cycloalkanes.*

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	Diesel fuel	Gasoline
Fresh	60.7 ± 6.1	37.4 ± 5.6
UV-degraded	74.8 ± 7.5	33 ± 4.9
Evaporated	25.1 ± 2.5	30.8 ± 4.6

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Table 1. NAPL-water partitioning coefficient for the fresh and altered diesel fuel and gasoline.

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		Fresh D	UV D	Evaporated D	Fresh G	UV G	Evaporated G	
Liquid GCMS	< n-C10	4.38	4.38	0.61	6.38	2.29	7.05	
	cyclo < n-C10	1.27	1.27	0.00	0.79	0.29	1.14	
	BTEX < n-C10	4.55	4.64	0.30	73.45	68.34	95.30	
	methyl < n-C10	3.39	3.50	0.00	0.88	0.72	1.24	
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	n-C10-C15	14.76	15.01	1.61	0.40	0.07	0.10	
	cyclo n-C10-C15	0.40	0.43	0.00	0.00	0.00	0.00	
	BTEX n-C10-C15	6.90	6.89	0.21	16.61	12.66	16.85	
	methyl n-C10-C15	14.53	14.33	1.12	1.50	0.67	1.02	
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	>C15	15.11	16.09	2.46				
	cyclo > n-C15	0.27	0.50	0.07				
	BTEX > n-C15	0.00	0.00	0.00				
	metheyl > n-C15	15.02	16.78	2.49				
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HS GCMS	< n-C10	20.92	12.95	1.82	13.30	13.51	2.12	
	cyclo < n-C10	26.20	17.79	0.79	7.69	7.77	1.52	
	BTEX < n-C10	17.11	13.86	1.72	0.00	0.00	0.00	
	methyl < n-C10	18.35	13.14	1.37	0.00	0.00	0.00	
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	> n-C10	3.88	3.65	2.76	20.42	20.62	17.32	
	cyclo > n-C10	2.51	1.98	1.47	29.36	29.53	38.35	
	BTEX > n-C10	7.07	6.38	3.49	7.12	7.60	11.67	
methyl > n-C10	3.80	3.36	2.50	13.78	13.99	23.54		

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Table 2. Proportion (%) of the different families (linear alkanes, ramified alkanes, monoaromatics, cycloalkanes) in the different chromatograms.

Compound	$K_{\text{NAPL-water}}$ measured	Temperature of experiment (°C)
n-hexane	58.1*	23°C
n-hexadecane	33.1"	
cyclohexane	63.3*	23°C
benzene	44.9*	23°C
toluene	51.3*	23°C
o-xylene	44.7*	23°C
Ethanol	27.9°	23°C
Diesel	60°	23°C
Diesel	40'	12°C
Gasoline	38.9°	23°C

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819 *Table 3. Coefficient partitions of several pure NAPLs from the literature (\* Schubert et al. (2007b); °Schubert*  
820 *et al. (2007a); "Abraham et al. (1994); ' Hunkeler et al. (1997)).*

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841 Effect of NAPL mixture and alteration on <sup>222</sup>Rn partitioning  
842 coefficients: implications for NAPL subsurface contamination  
843 quantification

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### Supplementary information

855 This supplementary material presents the statistical results permitting to indicate that the Kn-w  
856 calculated from the equation 1 in the paper are significantly different. To test the significant  
857 differences between the groups, ANCOVA was used. For the ANCOVA, NAPL content ( $\theta$ )  
858 was treated as fixed factors and the activity as the covariates. Statistical tests were performed  
859 using the software Xcel Stat (version 2021.1) with the significant level set at 0.05. All the  
860 variables were normalized by 1/A transformation prior to analysis.

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863 Step 1: linear approximation of the equation :  $A = \frac{1}{\left(1 + \frac{\theta_w}{K_H \theta_g} + \frac{K_n \theta_n}{\theta_g}\right)} \frac{m_s}{V_g} EC_{Ra}$

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865 The linear approximation is:  $\frac{1}{A} = \frac{(1 + \theta_w / K_H \theta_g) V_g}{(m_s EC_{Ra})} + \frac{K_n V_g}{m_s \theta_g EC_{Ra}} * \theta_n$

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Table 1. statistical results for NAPLs and 1/A activities (R squared = 0.997, Ajusted R squared = 0.993)

Source	DF	Sum of squares	Mean squares	F	sig
Model	3	0.031	0.010	288.819	<b>0.000</b>
Error	3	0.000	0.000		
Corrected					
Total	6	0.031			

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We found a significant linear regression between the NAPL content and the fresh diesel ( $F = 3.72$ ;  $p < 0.05$ ). However, the NAPL did not show significant linear regression between UV degraded diesel fuel and evaporated diesel fuel ( $F = 2.45$   $p > 0.05$ ;  $F = -0.20$   $p > 0.05$ ). We can state that the different 1/A of the diesel are significantly different.

Table 2. statistical results for NAPLs and 1/A activities (R squared = 0.997, Ajusted R squared = 0.994)

Source	DF	Sum of squares	Mean squares	F	Pr > F
Model	3	0.031	0.010	327.309	<b>0.000</b>
Error	3	0.000	0.000		
Corrected					
Total	6	0.031			

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We found a significant linear regression between the NAPL content and the evaporated gasoline ( $F = 4.96$ ;  $p < 0.05$ ). However, the NAPL did not show significant linear regression between UV degraded gasoline and fresh gasoline ( $F = 0.49$   $p > 0.05$ ;  $F = 0.55$   $p > 0.05$ ). We can state that the different 1/A of the diesel are significantly different.