

1 **Dear prof. Vanclooster,**  
2 please find below the replies to the referees, and the marked-up version of our manuscript.  
3 Thank you

4  
5 **Dear Prof. Ferré,**

6  
7 With reference to the paper: **hess 2019-149**, by A. Comegna et al., please find below the replies to  
8 your review. The authors would like to thank prof. Ferré for the invaluable review.

9  
10 In accordance with your comments, we have rearranged the references in order to include some other  
11 relevant manuscripts that were, not intentionally, overlooked. Furthermore in the **Model calibration**  
12 **and validation** section, following your suggestion, we commented on the problem related to the  
13 initial pore-scale distribution of NAPL in the soil sample, which could play a role, with the “*rapid*  
14 *mobility of the fluid*” at the beginning of the removal experiment.

15  
16 **Dear Prof. Persson,**

17 With reference to the paper: **hess 2019-149**, by A. Comegna et al., please find below the replies to  
18 your review.

19 The authors would like to thank Prof. Persson for his useful suggestions which have been **fully**  
20 **accepted**. We explain below how the revised paper was reorganized.

21 **- Major Comments:**

- 22 1. ...**and modeling** was removed from the title. Moreover, in order to eliminate any  
23 misunderstandings about the development of a new dielectric mixing model (we have only  
24 rewritten it for our purposes), we substituted in the text (line 18) the term *develop* with  
25 *calibrate and validate*, and (line 66) the term *build* with *revisit*.
- 26 2. In accordance with your comment we emphasized in the text (**introduction section**: lines 45-  
27 68) the novelty of the present research.
- 28 3. You are right with reference to the possibility of investigating, during remediation, the  
29 dielectric response of an initially four-phase medium (i.e. soil+NAPL+water+air), but (as you  
30 already wrote in your review) the present research is a first attempt to monitor in real time  
31 (with TDR) the dielectric response of the medium during a decontamination process. Thus we  
32 chose a simple initial scenario to avoid possible dielectric “interferences” related with other  
33 phases. This aspect could be explored in further research (a specific sentence regarding this  
34 possibility was introduced in the conclusion). Anyway to carry out our research we followed  
35 the approach of **Francisca and Rinaldi (2006)**, who published a paper entitled: *Removal of*

36 *immiscible contaminants from sandy soils monitored by means of dielectric measurements*  
37 (doi: 10.106/(ASCE)0733-9372(2006)132:8(931)).

- 38 4. I agree with you that the dielectric response of a multiphase medium depends not only on the  
39 NAPL (and eventually water) volumetric content, but is also influenced by their internal  
40 distribution; **In accordance with your comment we sought to emphasize this aspect in the**  
41 **text** (lines 206-209) . Moreover I would like to stress the fact that TDR (as you already know)  
42 cannot allow us to infer how fluid distribution affects dielectric measurement; this aspect  
43 could be a further research topic, which should be developed by coupling TDR with different  
44 geophysical methods, such as the *Gamma Ray Attenuation* technique, that gives more accurate  
45 information on fluid distribution within the contaminated soil sample.

46 - **Technical corrections:**

- 47 1. In accordance with your comment we changed *diverse* to *different* (line 14) and *diverse* to  
48 *varying* (line 15).
- 49 2. In accordance with your comment we substituted in the abstract (and where possible in the  
50 whole manuscript) the terms *hydrocarbon* and *oil* with NAPL.
- 51 3. In accordance with your comment we introduce in the paper the dimensions of the TDR probe  
52 (line 136).
- 53 4. In accordance with your comment we introduced in the text the dimension of the volumetric  
54 NAPL content  $\theta_{\text{NAPL}}$ :  $\text{m}^3/\text{m}^3$  (line 19).
- 55 5. In accordance with your comment we better commented in the paper how was the oil content  
56 determined on the effluent (lines 148-150) and in agreement with the actual description, we  
57 modified figure 1.
- 58 6. In accordance with your comment we better describe how the  $\alpha$  parameters were determined  
59 (lines 187-188). Furthermore, we made some new comments in the paper regarding the  
60 *calibration and validation* data set that we employed for model calibration and validation  
61 (lines 151-152). Finally, we introduce in the text (line 143) the term **initial**, in order to specify  
62 that:  $\theta_{\text{NAPL}}=0.15, 0.20, 0.25, 0.30, 0.35$  and  $0.40$  was the volumetric NAPL content at the  
63 beginning of the different experiments conducted.
- 64 7. With reference to parameter  $\alpha$  in the dielectric mixing model adopted, I would like to  
65 emphasize that  $\alpha$ , in our application is a pure fitting parameter, obtained from the calibration  
66 data set. This means that for a fixed  $\theta_{\text{NAPL}}$  value and washing solution, the dielectric model  
67 was fitted (using a least square algorithm) to the whole set of experimental calibration data  
68 (i.e. the data obtained from the beginning to the end of the remediation test). For this reason  
69  $\alpha$  must be considered constant. This aspect is now commented in the **Model calibration and**  
70 **validation** section (lines 187-188).
- 71 8. In accordance with your comment we introduce a series of 1:1 scatter plots (figure 5a, b, c,  
72 d,e, f).

- 73 9. See comment #6.
- 74 10. In accordance with your comment we elaborated the section **Model calibration and**  
75 **validation**.
- 76 11. No more comments can be made in the manuscript with reference to parameter  $\alpha$  for the  
77 reasons of comment #6.
- 78 12. In accordance with your comment we revisited the conclusions.
- 79 13. In Table 1 the  $\alpha=0.05$  value for  $w_{da\#2}$  and  $\theta_{NAPL}=0.20$  was wrong. Thank you for your  
80 observation. The correct ( $\alpha=0.45$ ) value was inserted.

81

82 **Dear Referee #3,**

83 With reference to the paper: **hess 2019-149**, by A. Comegna et al., please find below the replies to  
84 your review. The authors would like to thank you for your comments on our paper. We would like to  
85 say that part of your observations have been resolved in the revised version of the manuscript, in  
86 accordance with those of the other two referees.

- 87 1. That said, we would like to stress the fact that the purpose of this study was to investigate a  
88 possible extension of TDR technology to assess the effects of NAPL removal in soil organic  
89 mixtures, “*in real time*” during a decontamination process. As is well known, TDR is one of  
90 the most important geophysical methods, with its first applications in Soil Physics in 1980  
91 (see Topp et al., 1980). In recent years several efforts have been made to extend the use of  
92 TDR technology. See for example Kachanoski et al. (1992) who employed TDR for  
93 measuring in the “soil” the presence of a leaching solute. With direct reference to TDR-NAPL  
94 applications, most studies have demonstrated the potential of the TDR technique in estimating  
95 NAPL presence in saturated soils (Redman and DeRyck, 1994; Chenaf and Amara, 2001;  
96 Haridy et al., 2004; Mohamed and Said, 2005; Moroizumi and Sasaki, 2008). Some  
97 experiments have been conducted on unsaturated soils (Persson and Berndtsson, 2002; Rinaldi  
98 and Francisca, 2006; Francisca and Montoro, 2012). In these studies, the estimation of NAPLs  
99 using TDR measurements of dielectric properties has relied greatly on various mixing models  
100 relating the measured dielectric permittivity to the volume fractions of the pore fluids and  
101 various soil phases such as solid, water, air, and NAPLs (van Dam et al., 2005). Finally, I  
102 would like to recall the papers of Comegna et al. (2016) and Comegna et al. (2017) which  
103 tackled the problem of NAPL detection in variously saturated homogeneous and layered  
104 “soils”, respectively.
- 105 2. As already stated in the manuscript, the range of model applicability is:  $0.15 < \theta_{NAPL} < 0.40$ . At  
106  $\theta_{NAPL}=0.05$  and  $0.10$ , TDR is not sensitive to NAPL volumes.

107 3. The present research is a first attempt to monitor via TDR the dielectric response of an NAPL-  
108 contaminated medium during a decontamination process. Thus we chose a simple initial  
109 scenario to avoid possible dielectric “interferences” related to other phases. This aspect could  
110 be explored in further research.

111 Sincerely  
112 The authors

113

114 **A soil non-aqueous phase liquid (NAPL) flushing laboratory experiment based on**  
115 **measuring the dielectric properties of soil-organic mixtures via time domain**  
116 **reflectometry (TDR)**

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123 **Abstract.** The term non-aqueous phase liquid (NAPL) refers to a group of organic compounds with scarce solubility in  
124 water. They are the products of various human activities and may be accidentally introduced into the soil system. Given  
125 their toxicity level and high mobility, NAPLs constitute a serious geo-environmental problem. Contaminant distribution  
126 in the soil and groundwater entails fundamental information for the remediation of polluted soil sites. The present research  
127 explored the possible employment of time domain reflectometry (TDR) to estimate pollutant removal in a silt-loam soil  
128 that was primarily contaminated with a corn oil as a light NAPL and then flushed with different washing solutions. Known  
129 mixtures of soil and NAPL were prepared in the laboratory to achieve soil specimens with varying pollution levels. The  
130 prepared soil samples were repacked into plastic cylinders and then placed in testing cells. Washing solutions were then  
131 injected upward into the contaminated sample, and both the quantity of remediated NAPL and the bulk dielectric  
132 permittivity of the soil sample were determined. The above data was also used to calibrate and validate a dielectric model  
133 (the  $\alpha$  mixing model) which permits the volumetric NAPL content ( $\theta_{NAPL}$ ; m<sup>3</sup>/m<sup>3</sup>) within the contaminated sample to be  
134 determined and quantified during the different decontamination stages. Our results demonstrate that during a  
135 decontamination process, the TDR device is NAPL-sensitive: the dielectric permittivity of the medium rises increases as  
136 the NAPL volume decreases. Moreover, decontamination progression can be monitored using a simple (one-parameter)  
137 mixing model.

138 **1. Introduction**

139 Soil and groundwater contamination with NAPL from point or nonpoint sources is a severe problem  
140 of considerable complexity (Fitts, 2002; Fetter, 1993). The repercussions concern not only the  
141 deterioration of the soil's physical, mechanical and chemical properties, but also account for a  
142 potentially severe hazard to the well-being of humans and other living species (Freeze, 2000).

143 Soil flushing is the technical procedure used for treating polluted soils with water, surfactants and co-  
144 solvents (such as methanol, ethanol and propanols). Surfactant-enhanced flushing was developed  
145 from the conventional pump-and-treat method. The success of this approach is related to the capacity  
146 of such chemical compounds to greatly enhance the aqueous solubility of oils (Pennell et al., 1994;  
147 Parnian and Ayatollahi, 2008).

148 There is high interfacial tension between NAPL and water molecules that makes water a non-efficient  
149 cleaning material in removing NAPL from the soil. Instead, surfactants and co-solvent agents can  
150 promote the enhanced removal of NAPL from the subsurface through mobilization and solubilization  
151 (Martel et al., 1998; Rinaldi and Francisca, 2006; Parnian and Ayatollahi, 2008).

152 Primary remediation refers to the removal of the NAPL free phase by pumping. This extraction  
153 mechanism returns appreciable effects if there is a region of high NAPL saturation. After primary  
154 pumping, a considerable portion of NAPL remains constrained within the soil as capillary forces  
155 overcome viscous and buoyancy forces. This discontinuous NAPL phase is referred to as trapped  
156 residual NAPL (or NAPL residual saturation), and its remediation is referred to as secondary  
157 remediation (Parnian and Ayatollahi, 2008). Residual NAPL is a long-term source of soil and  
158 groundwater pollution (Mercer and Cohen, 1990; Troung Hong and Bettahar, 2000).

159 To develop powerful decontamination procedures, the characterization of polluted soils is required.  
160 Practices usually employed to characterize polluted soil sites are coring, soil sampling and the  
161 installation of monitoring wells for the collection of water samples from aquifers (Mercer and Cohen,  
162 1990). Since the aforementioned procedures are costly, different dielectric techniques can be used to  
163 detect organic contaminants in soils. The most accepted geophysical technique, based on the principle  
164 of electromagnetic wave (EMW) propagation, is the ground penetrating radar (GPR; Knight, 2001).  
165 Redman et al. (1991), described some field experiments in the application of GPR to detect NAPL  
166 plumes.

167 Rinaldi and Francisca (2006) used a coaxial impedance dielectric reflectometry (CIDR) technique to  
168 measure the complex dielectric permittivity in sands contaminated by a paraffin oil. Their research

169 mainly focused on the dielectric behavior of NAPL-contaminated soils during a decontamination  
170 process, however their research mainly focused on the different washing solution removal efficiency,  
171 and on the spectral response of the contaminated medium during the different tests conducted.

172 TDR is a further available geophysical device based on electromagnetic wave (EMW) principles that  
173 can also be used for this purpose (Endres and Redman et al., 1993; Redman and De Ryck,  
174 1994; Mohamed and Said, 2005; Moroizumi and Sasaki, 2006; Francisca and Montoro, 2012).

175 Few experiments have been conducted coupling TDR technique and NAPL. In these studies  
176 estimation of NAPLs using TDR measurements of dielectric properties relies greatly on various  
177 mixing models relating the measured dielectric permittivity to the volume fractions of the pore fluids  
178 and various soil phases such as solid, water, air and NAPLs (van Dam et al., 2005).

179 Some interesting results have been achieved by Persson and Berndtsson (2002) whilst investigating  
180 the influence of different LNAPLs on TDR measurements in a homogeneous silica sand under  
181 saturated and unsaturated soil conditions. Measurements of both dielectric permittivity and electrical  
182 conductivity allowed a method to be developed (two-step method) which measured the dielectric  
183 properties of the system against the amount of NAPL in soils.

184 Comegna et al., (2016) developed a general TDR-based methodology for evaluating the correlations  
185 between the dielectric response and the NAPL content in variable saturated soils with different  
186 textures and pedological characteristics.

187 The purpose of this study was to the following: i) investigate a possible extension of TDR technology  
188 to assess the effects of NAPL removal in soils, and ii) **rewrite**, on the basis of the acquired data and  
189 the experimental results, a dielectric model to predict "**in real time**" the volumetric amounts of NAPL  
190 ( $\theta_{NAPL}$ ) within the contaminated soil during the decontamination process.

## 191 **2. Theoretical concepts of TDR**

192 TDR is a geophysical technique employed to determine the dielectric permittivity of liquids and solids  
193 (Ferrè and Topp, 2002, described this method in detail). In general, the bulk dielectric permittivity is  
194 a complex term ( $\epsilon_r^*$ ), which may be expressed as follows (Robinson et al., 2003):

$$\varepsilon_r^* = \varepsilon'_r - J \left[ \varepsilon''_r + \frac{\sigma}{\omega \varepsilon_0} \right] \quad (1)$$

195 where  $\varepsilon'_r$  is the real part of dielectric permittivity, which gives the energy stored in the dielectrics at  
 196 a certain frequency and temperature, and  $\varepsilon''_r$  is the imaginary part due to relaxations. The zero  
 197 frequency conductivity  $\sigma$ , the angle frequency  $\omega$ , the imaginary number  $J = \sqrt{-1}$  and the  
 198 permittivity  $\varepsilon_0$  in free space contribute to define  $\varepsilon_r^*$ .

199 When the frequency of a TDR cable tester ranges between 200 MHz to 1.5 GHz, dielectric losses can  
 200 be considered minimal (Heimovaara, 1994) and the bulk dielectric permittivity  $\varepsilon_b$  ( $\cong$  the real part of  
 201 permittivity) of a probe of length  $L$  is determined from the propagation velocity  $v (= 2L/t)$  of an  
 202 electromagnetic wave along the wave guide across the investigated medium by the following  
 203 expression:

$$\varepsilon_b = \left( \frac{c}{v} \right)^2 \quad (2)$$

204 where  $c$  ( $= 3 \times 10^8 \text{ m s}^{-1}$ ) is the velocity of an electromagnetic wave in vacuum (Topp et al., 1980) and  
 205  $t$  is travel time, i.e. the time required by the generated signal to go back and forth through the TDR  
 206 probe of length  $L$  (m). This can be calculated as the following:

$$t = \frac{2L}{c} \sqrt{\varepsilon_b} \quad (3)$$

207 The direct dependence of the signal's travel time  $t$  upon soil dielectric permittivity is expressed by  
 208 equation 3.

### 209 **3. Estimating volumetric NAPL content during a decontamination process in soils**

210 Dielectric mixing models, in their classical application, have been proposed to estimate the bulk  
 211 dielectric permittivity of a multi-phase medium, that is, a combination of three or four dielectric  
 212 phases, and to couple the dielectric permittivity of the medium to the dielectric permittivity of each  
 213 single phase (Hilhorst, 1998). Recently, after analyzing the effects of organic contaminants on soil  
 214 dielectric properties, the above models were further developed to estimate the dielectric properties of



215 NAPL-polluted soils (Redman et al. 1991; Persson and Berndtsson, 2002; Francisca and Montoro,  
216 2012, Comegna et al., 2013a; Comegna et al., 2016; Comegna et al., 2017).

217 Based on such models, in the present study, we analyze the possibility of predicting the correlations  
218 between the volumetric contents of NAPL ( $\theta_{NAPL}$ ) and the dielectric response ( $\epsilon_b$ ) of contaminated  
219 soil during the progression of a steady-state remediation process.

220 In the present research, we chose the so-called  $\alpha$  model (Birchack et al., 1974; Knight and Endress,  
221 1990; Roth et al., 1990):

$$\epsilon_b = \left[ \sum_{i=1}^n V_i \epsilon_i^\alpha \right]^{1/\alpha} \quad (4)$$

222 where  $V_i$  is the volume and  $\epsilon_i$  is the permittivity of each component of the complex medium; the  
223 exponent  $\alpha$  is a fitting parameter ( $\alpha$  varies between -1 and 1), which may be related to the internal  
224 structure of the investigated medium (Hilhorst, 1998; Coppola et al., 2013; Coppola et al., 2015).

225 Under the following hypothesis: i) the soil is homogeneous from a textural point of view, and ii) the  
226 soil porosity ( $\phi$ ) is constant, equation 4 was reformulated for our purposes.

227 For mixtures of soil ( $s$ ) saturated with a certain amount of washing solution ( $ws$ ), in rearranging the  
228 model formulation of Rinaldi and Francisca (2006), the  $\alpha$  model yields the following:

$$\epsilon_{s-ws}^\alpha = \left[ (1-\phi)\epsilon_s^\alpha + \phi\epsilon_{ws}^\alpha \right] \quad (5)$$

229 where  $\epsilon_{s-ws}$  is the soil-washing solution permittivity, and  $\epsilon_s$  and  $\epsilon_{ws}$  are the permittivities of soil  
230 particles and washing solutions, respectively. By the same token, for soil organic ( $s-NAPL$ )  
231 compounds at saturation, the  $\alpha$  model can be expressed as the following:

$$\epsilon_{s-NAPL}^\alpha = \left[ (1-\phi)\epsilon_s^\alpha + \phi\epsilon_{NAPL}^\alpha \right] \quad (6)$$

232 where  $\epsilon_{s-NAPL}$  is the permittivity of the soil-NAPL mixture, and  $\epsilon_{NAPL}$  is the oil permittivity.

233 A medium consisting of soil particles, washing solution and NAPL ( $s-ws-NAPL$ ) can be viewed as a  
234 mix of soil-washing solution (equation 5) and soil-NAPL (equation 6):

$$\epsilon_{s-ws-NAPL}^\alpha = \left[ \beta\epsilon_{s-NAPL}^\alpha + (1-\beta)\epsilon_{s-ws}^\alpha \right] \quad (7)$$

235 where  $\beta$  is the relative volume of NAPL contained in the whole fluid phase:

$$\beta = \frac{\theta_{NAPL}}{(\theta_{ws} + \theta_{NAPL})} = \frac{\theta_{NAPL}}{\theta_f} \quad (8)$$

236 where  $\theta_f$  is the volumetric fluid content ( $\text{m}^3/\text{m}^3$ ), sum of the volumetric washing solution content ( $\theta_{ws}$   
237 ) and volumetric NAPL content ( $\theta_{NAPL}$ );  $\beta$  varies between 0 (i.e. a soil-washing solution mixture) and  
238 1 (i.e. a soil-NAPL mixture).

239 To estimate  $\theta_{NAPL}$ , equation 7 is first reformulated in terms of  $\beta$ :

$$\beta = \frac{\varepsilon_{s-ws}^\alpha - \varepsilon_{s-ws-NAPL}^\alpha}{\varepsilon_{s-ws}^\alpha - \varepsilon_{s-NAPL}^\alpha} = \frac{(1-\phi)\varepsilon_s^\alpha + \phi\varepsilon_{ws}^\alpha - \varepsilon_{s-ws-NAPL}^\alpha}{((1-\phi)\varepsilon_s^\alpha + \phi\varepsilon_{ws}^\alpha) - ((1-\phi)\varepsilon_s^\alpha + \phi\varepsilon_{NAPL}^\alpha)} \quad (9)$$

240 Substituting equation 8 into equation 9, and considering that for a saturated medium, the volumetric  
241 fluid content is equal to soil porosity (i.e.  $\theta_f = \phi$ ),  $\theta_{NAPL}$  can be calculated as the following:

$$\theta_{NAPL} = \frac{(1-\phi)\varepsilon_s^\alpha + \phi\varepsilon_{ws}^\alpha - \varepsilon_{s-ws-NAPL}^\alpha}{\varepsilon_{ws}^\alpha - \varepsilon_{NAPL}^\alpha} \quad (10)$$

242 Equation 10 correlates the dependence of volumetric NAPL content with soil porosity;  $\theta_{NAPL}$  can be  
243 estimated (within the contaminated soil) during the progression of a remediation process once the  
244 dielectric permittivity of the soil-contaminated mixture ( $\varepsilon_{s-ws-NAPL}$ ) is known.

## 245 4 Materials and Methods

### 246 4.1 Soil and fluid properties

247 A silt-loam Anthrosol (IUSS Working Group WRB, 2006) from the region of Puglia (Italy) was used  
248 for this study. The soil texture was measured by means of the hydrometer method (Day, 1965), while  
249 the Walkley–Black procedure (Allison, 1965) was used to determine soil organic C content. The  
250 method developed by Miller and Curtis (2007) was used to measure soil electrical conductivity ( $EC_w$ ),  
251 while soil  $pH$  was determined on the basis of a 1:1 soil/water ratio (Eckert, 1988). In textural terms,  
252 the soil comprised 15.7% sand, 11.6% clay and 72.4% silt. Soil porosity was 0.57%, organic content  
253 1.84%,  $EC_w$  0.17 dS/m and soil  $pH$  8.40.

254 The NAPL employed for the laboratory tests was corn oil ( $\varepsilon_{NAPL}=3.2$ ;  $EC_{NAPL}=0.055$  dS/m at 25°C)  
255 with a density of 0.905 g/cm<sup>3</sup> (at 25°C). Three different removal solutions were employed for soil

256 cleaning: a) a first solution (referred to below as wd) composed of 99% distilled water and 1%  
257 commercial detergent ( $\epsilon_d=9.22$ , at 25°C), b) a second solution (wda#1) composed of 90% distilled  
258 water, 1% commercial detergent and 9% methanol as co-solvent ( $\epsilon_{alcohol}=26.13$ , at 25°C) and c) a  
259 third solution (wda#2) composed of distilled water (85%) with commercial detergent (1%) and  
260 methanol (14%). The dielectric permittivity of the washing solutions, measured at 25°C, was  
261  $\epsilon_{wd}=75.04$ ,  $\epsilon_{wda\#1}=68.98$  and  $\epsilon_{wda\#2}=65.92$ , whereas the dielectric permittivity of the tested soil  
262 saturated with each of the three cleaning solutions was  $\epsilon_{soil+wd}=34.59$ ,  $\epsilon_{soil+wda\#1}=31.04$  and  
263  $\epsilon_{soil+wda\#2}=30.10$ .

## 264 **4.2 Measurement of dielectric permittivity of soil-NAPL contaminated samples during soil** 265 **remediation**

### 266 **4.2.1 Experimental setup**

267 As illustrated in Figure 1, the experimental layout consisted of the following: i) a Techtronix (model  
268 1502C) cable tester; ii) a three-rod probe 14.5 cm in length with a wire diameter of 0.003 m and a  
269 wire spacing of 0.02 m, introduced vertically into the soil samples; iii) a testing cell 15 cm high and  
270 8 cm in diameter; iv) a peristaltic pump used for upward movement of the washing solution.

### 271 **4.2.2 Sample preparation and testing procedures**

272 Soil was oven dried at 105°C and passed through a 2-mm sieve. Known amounts of soil and oil were  
273 mixed together, shaken and then kept for 24 hours in sealed plastic bags to avoid any evaporation and  
274 to ensure a uniform distribution of oil within the sample and good oil adsorption by the soil matrix.

275 The samples were then allocated to cylindrical boxes. With a view to achieve different degrees of  
276 (initial) soil contamination, volumetric NAPL content ( $\theta_{NAPL}$ ) was varied from 0.05 to 0.40 (in steps  
277 of 0.05). In all, each washing solution comprised eight oil-contaminated soil samples.

278 For all experiments, the soil samples were placed in the vessels in various steps at a bulk density of  
279 1.13 g/cm<sup>3</sup>. During TDR measurements, the soil samples were conserved at a temperature of 25°C  
280 by using a thermostat box. Remediation was performed using an upward flux of diverse pore volumes  
281  $T$  of three washing solutions (wd, wda#1 and wda#2) supplied at the rate of 90 cm<sup>3</sup>/h, corresponding

282 to a Darcian velocity of 1.8 cm/h. After collection of the outflow from the soil columns, the surnatant  
283 NAPL was separated from the washing solution and the quantity of NAPL remediated from the soil  
284 was determined.

285 The obtained data series were employed to calibrate the proposed dielectric model of equation 10. An  
286 independent data set, obtained in the same manner of the calibration data set was used for model  
287 validation.

### 288 4.3. Numerical indices for model performance evaluation

289 The goodness of equation 10 was evaluated using two different criteria: i) the mean bias error (*MBE*),  
290 and ii) the model efficiency (*EF*), computed according to the following relations (Legates and  
291 McCabe Jr, 1999):

$$292 \quad MBE = \frac{\sum_{i=1}^N (E_i - O_i)}{N} \quad (11)$$

$$EF = 1 - \frac{\sum_{i=1}^N (E_i - O_i)^2}{\sum_{i=1}^N (O_i - \bar{O})^2} \quad (12)$$

293 where  $E_i$  and  $O_i$  are respectively the expected and the observed value,  $\bar{O}$  is the mean of the observed  
294 data, and  $N$  is the number of observations.

295 *MBE* measures the differences between model-simulated data and measured values (positive *MBE*  
296 values are used to indicate average overprediction, while negative values indicate underprediction).

297 The model's ability to forecast  $\theta_{NAPL}$  is described by parameter *EF*, according to which *EF*=1  
298 indicates perfect accord between predicted and measured data.

## 299 5. Results and Discussion

### 300 5.1 Influence of washing solution on NAPL removal

301 Figures 2a, b, c, d, e and f, with reference to the most representative experimental results, reveal the  
302 influence of pore volumes  $T$  on evaluated bulk dielectric permittivity ( $\epsilon_{s-ws-NAPL}$ ) for the soil specimens  
303 initially polluted with oil. As the washing solution started to remove oil, the dielectric permittivity  
304 rose due to the larger dielectric permittivity of the flushing mixture. As the remediation solution

305 continued to move upward, the rising rate of the dielectric permittivity decreased and asymptotically  
306 approached a constant value. This steady value was smaller than that observed when the soil  
307 specimens were completely saturated by only the flushing solution (i.e. wd, wda#1 or wda#2), which  
308 in our tests corresponds to the condition of a completely decontaminated soil. This difference in  
309 values is undoubtedly due to oil confined in soil pores (i.e. NAPL residual saturation). For the same  
310 reason, residual saturation may explain why insignificant oil remediation was observed for  $\theta_{NAPL}$   
311 values less than 0.15. This aspect may be explained by the fact that for low volumetric NAPL  
312 contents, the non-wetting fluid (oil) is disconnectedly distributed (i.e. immobile) in the soil samples,  
313 which means that  $\theta_{NAPL}$  is close to the limiting *residual value*, and thus NAPL loses its ability to move  
314 in the soil in response to a hydraulic gradient [i.e. capillary retention forces are greater than  
315 gravitational forces, which tend to immobilize the NAPL (Brost and DeVaul, 2000)].

316 The NAPL volumes removed for different washing solutions and the initial volumetric content of  
317 NAPL are compared in Figure 3. For all the three cleaning solutions adopted, the experiments  
318 ultimately demonstrate (for a fixed  $\theta_{NAPL}$ ) the same results in terms of soil decontamination, and they  
319 show that NAPL removal increases with increasing  $\theta_{NAPL}$ . In some cases (i.e.  $\theta_{NAPL}=0.15, 0.20$  and  
320  $0.30$ ), contaminated samples flushed with the wda#1 solution yield slightly higher removal efficiency  
321 values compared to the samples flushed with wd and wda#2. Martel et al. (1998) suggest the need to  
322 investigate the best water-surfactant-alcohol combination in order to enhance NAPL solubilization in  
323 soil.

## 324 **5.2 Model calibration and validation**

325 For the model (equation 10) calibration methodology, with reference to the three washing solutions  
326 (wd, wda#1 and wda#2), we analyze the effect of the measured dielectric permittivity on volumetric  
327 NAPL content ( $\theta_{NAPL}$ ) in order to estimate the  $\alpha$  parameter of the model. The complete calibration  
328 data set of estimated  $\alpha$  parameters is reported in Table 1. The  $\alpha$  parameter of the mixing model was  
329 determined, for a fixed  $\theta_{NAPL}$  value and washing solution, by an optimization procedure based on the  
330 least square technique, and was kept constant for each of the developed remediation test.

331 A permittivity value of 3.70 was adopted for the solid phase. This value was determined using the  
332 “immersion method” which is commonly employed for estimating the  $\epsilon_s$  of soils (Robinson et al.,  
333 2003; Kameyama and Miyamoto, 2008).

334 For the sake of brevity, a selection of the experimental  $\epsilon_{s-ws-NAPL}-\theta_{NAPL}$  relationships (validation  
335 dataset) is reported in figures 4a, b, c, d, e and f. The data in figures 4 (except for figures 4e, f) show  
336 that some of the model-simulated values tend to overestimate the measured data. This behavior is  
337 mostly restricted to the beginning of the remediation process, when a rapid change in dielectric  
338 permittivity may be observed. This behavior was also verified in other tests (not shown here) and  
339 may be explained by invoking both NAPL properties such as liquid density, surface tension and  
340 viscosity, and soil properties including moisture content, relative permeability and soil porosity (Brost  
341 and DeVaul, 2000; Wang et al., 2013).

342 Mercer and Cohen (1990) referred to the existence, in NAPL-contaminated soils, of a “double fluid  
343 domain,” defined as the composition of the following: i) mobile pools, which are NAPL-connected  
344 phases that move in the soil and ii) immobile residuals (i.e. low permeability regions), which depend  
345 on small disconnected blobs or ganglia within the contaminated soil (see also section 5.1 above). As  
346 long as the flushing continues, mobile pools are reduced and the oil tends increasingly to be trapped  
347 in the immobile areas. This means that, during soil cleaning, the capacity of non-wetting fluids to  
348 respond to gravitational forces gradually diminishes (Luckner et al., 1989). From a dielectric point of  
349 view, this mechanism may appear as a rapid dielectric permittivity increase (identified in figures 4 as  
350 *fast oil mobility region*) within a few pore volumes. When this fast mobility mechanism is dominant,  
351 the predictions of equation 10 fail.

352 Another possible explanation, of this disagreement between the observed and the predicted  
353 permittivity values, may be associated with the propensity of NAPL-water mixtures to form  
354 macroinclusions in the soil (Persson and Berndtsson, 2002), that affected the initial pore-scale  
355 distribution of NAPL, and thus the global dielectric response of the medium (Ferré et al, 1996), during  
356 the first remediation stages.

357 However, since the phenomenon is mostly limited to the initial part of the washing process, overall  
358 model effectiveness is not compromised, as also shown in Table 2, which summarizes the goodness-  
359 of-fit statistical indices, and figures 5a, b, c, d, e, f, were the estimated  $\theta_{NAPL}$  from equation (10) and  
360 the known  $\theta_{NAPL}$  are illustrated in a series of 1:1 scatter plots.

361 Overall, both graphical and quantitative evaluations in terms of MBE and EF reveal the suitability of  
362 the dielectric model adopted to estimate the volumetric NAPL content in the  $\theta_{NAPL}$  range 0.15–0.40.

## 363 6. Conclusions

364 This paper presented an extensive dataset of remediation experiments that were conducted at a  
365 laboratory scale using corn oil as a soil contaminant, and three different solutions for soil cleaning.  
366 The results of these tests were employed to investigate the potential of the TDR technique in  
367 monitoring the development of a steady-state decontamination process.

368 Dielectric data analysis showed that, during soil flushing, dielectric permittivity behavior is highly  
369 dependent on the initial volumetric content and intrinsic permittivity of the specific NAPL: *removal*  
370 *of NAPL produces an increase in bulk dielectric permittivity*, due to the low value of oil permittivity.

371 The experiments conducted also allowed us to calibrate and validate a dielectric mixing model  
372 (equation 10). The model outcomes are encouraging; the calculated statistical indices confirmed a  
373 high accuracy in NAPL predictions of the  $\alpha$ -model at different stages during soil cleaning, with the  
374 only exception of the very initial cleaning stage (confined to the low values of  $T$ ) where the eventual  
375 presence of a *fast flow region* may limit its applicability.

376 The approach requires additional experiments and data sets for model calibration and validation in  
377 different pedological contexts, mainly to confirm the potential of the methodology developed.

378 Furthermore an effort should be done, introducing the water phase, “*ab initio*”, in the experimental  
379 setup, in order to simulate more accurately a possible natural contamination-decontamination  
380 scenario. Finally full field-scale tests should also be conducted to evaluate the performance of  
381 equation 10 in real field conditions.

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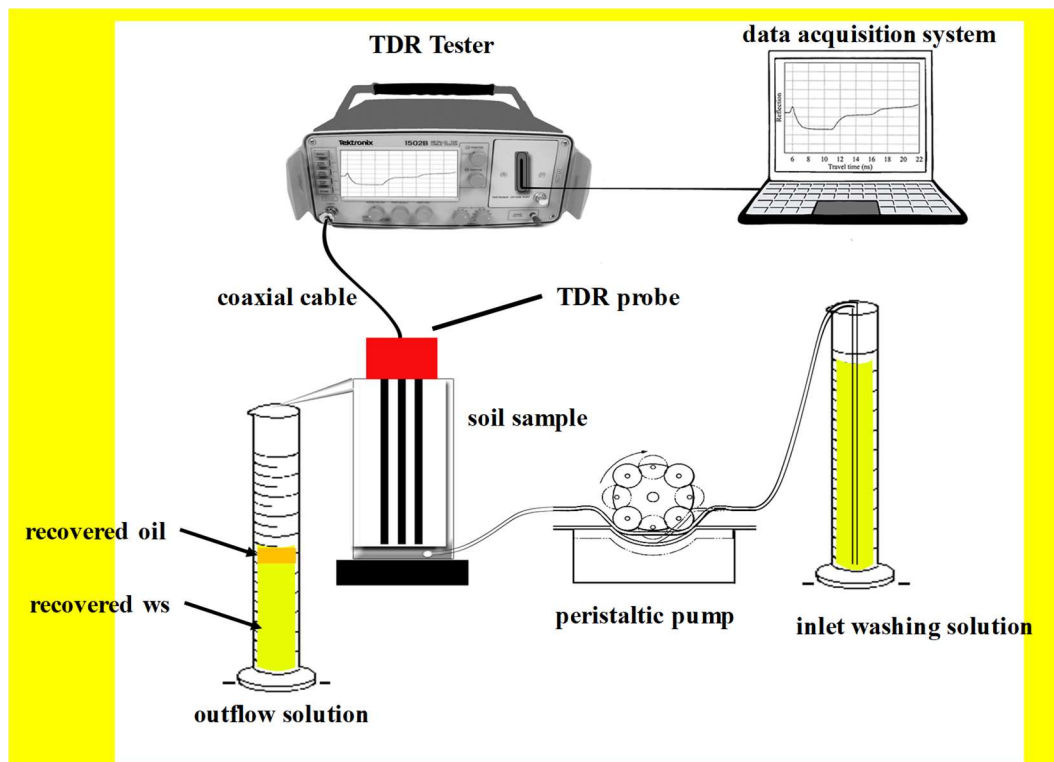
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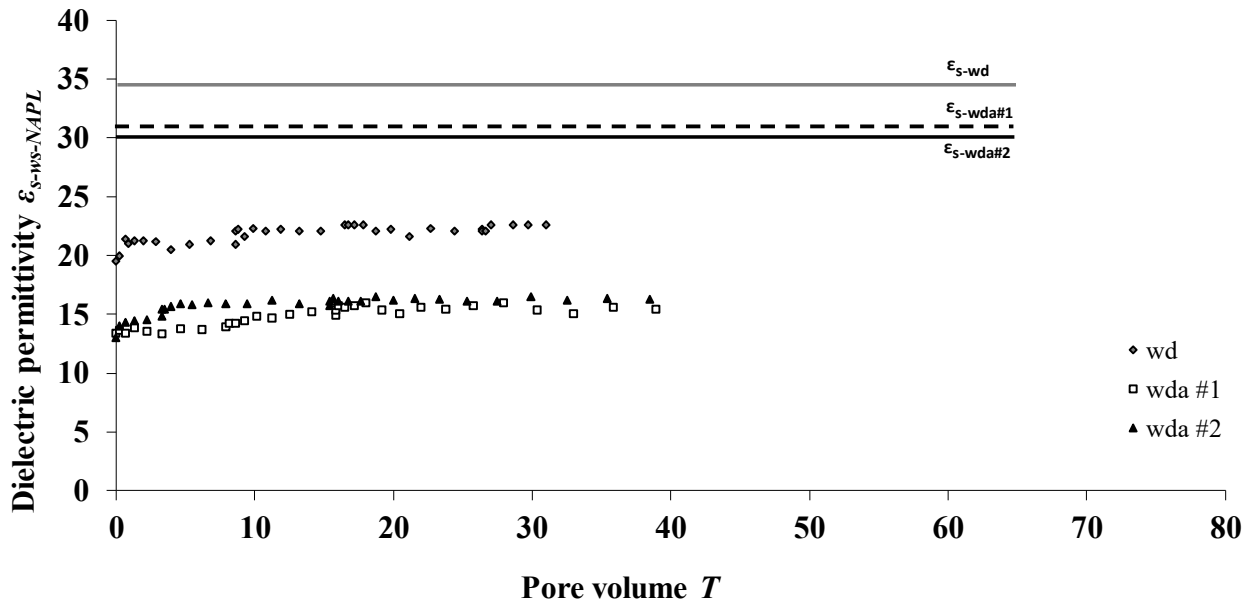


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489 **Figure 1. Experimental setup used in the NAPL removal experiments (from Comegna et al.,**  
490 **2013b).**

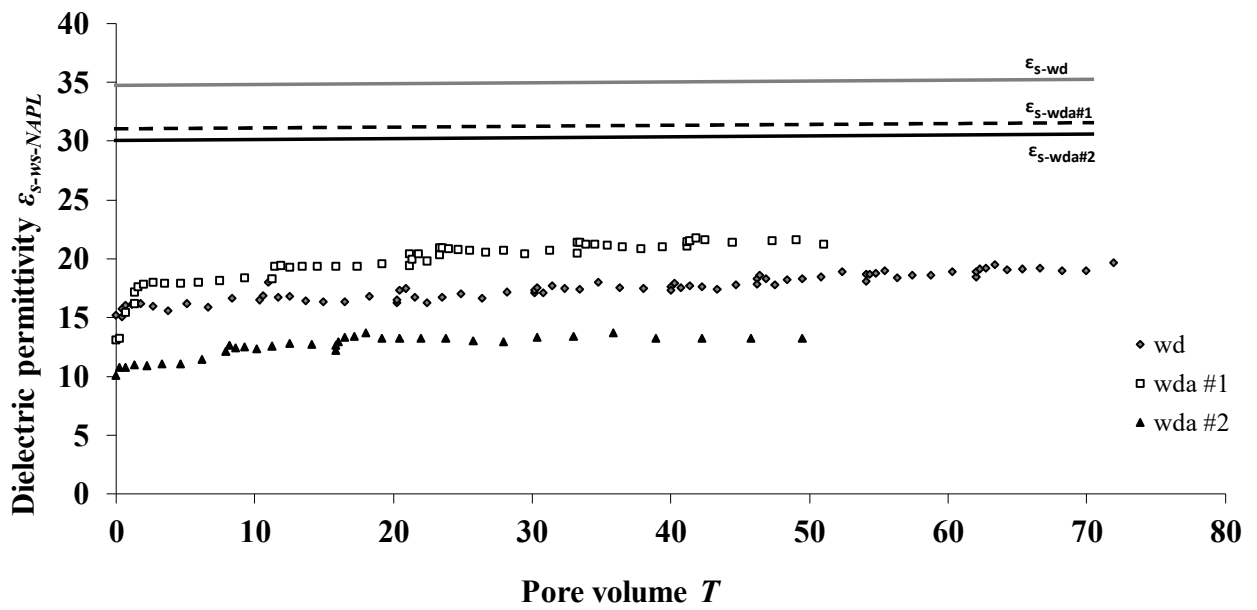
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a)  $\theta_{NAPL}=0.15$



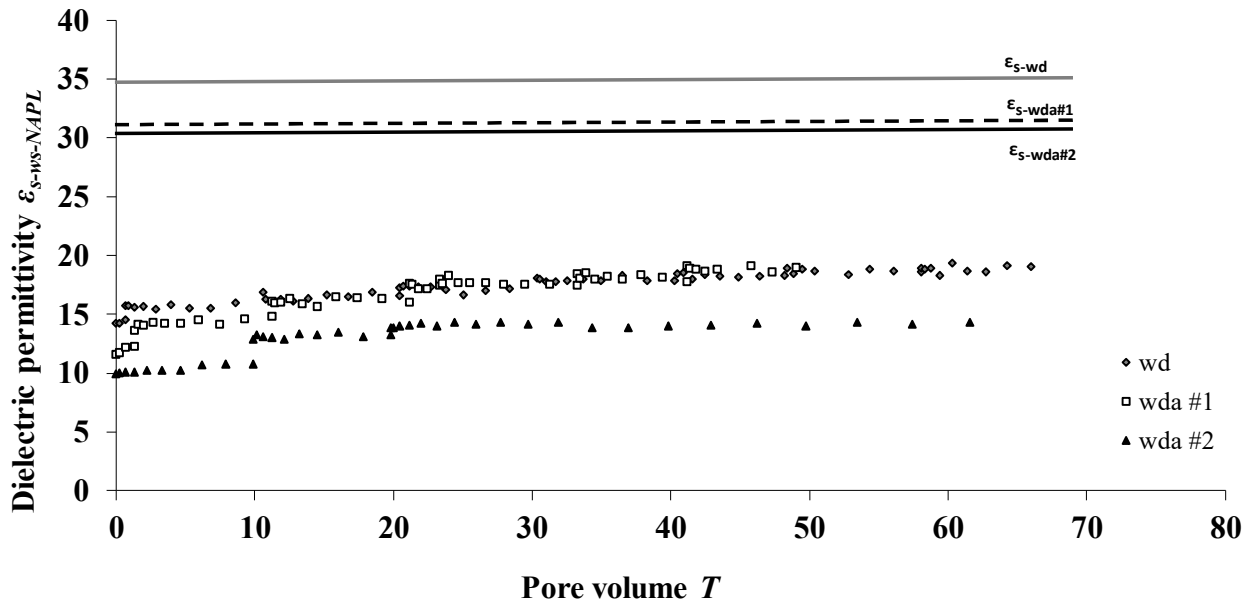
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b)  $\theta_{NAPL}=0.20$



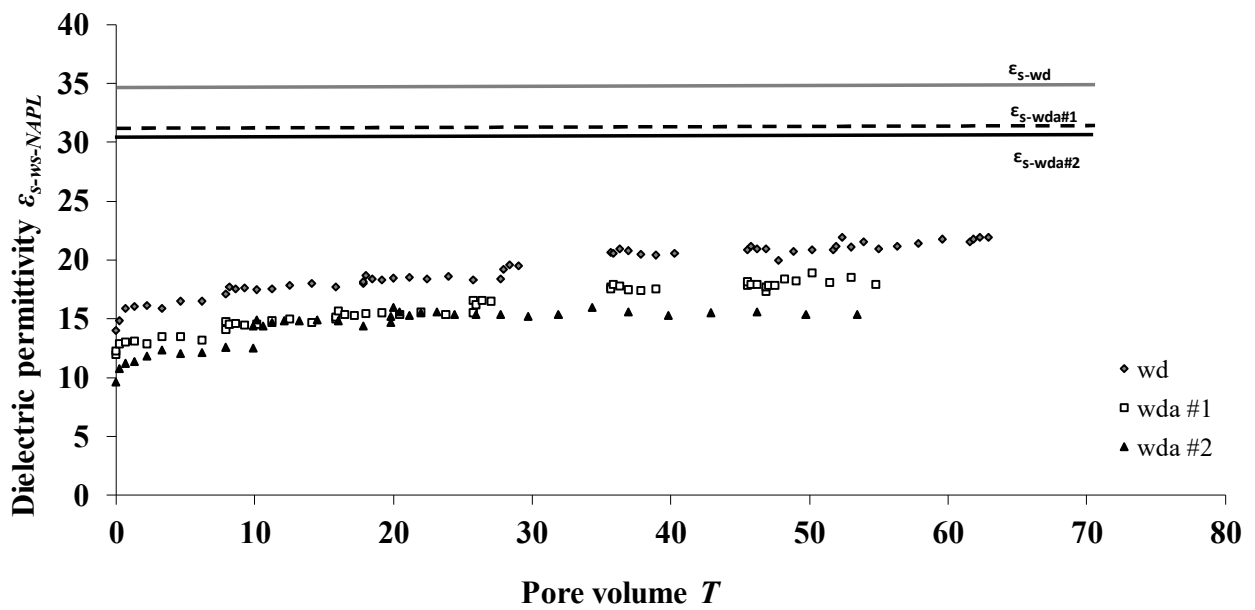
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c)  $\theta_{NAPL}=0.25$



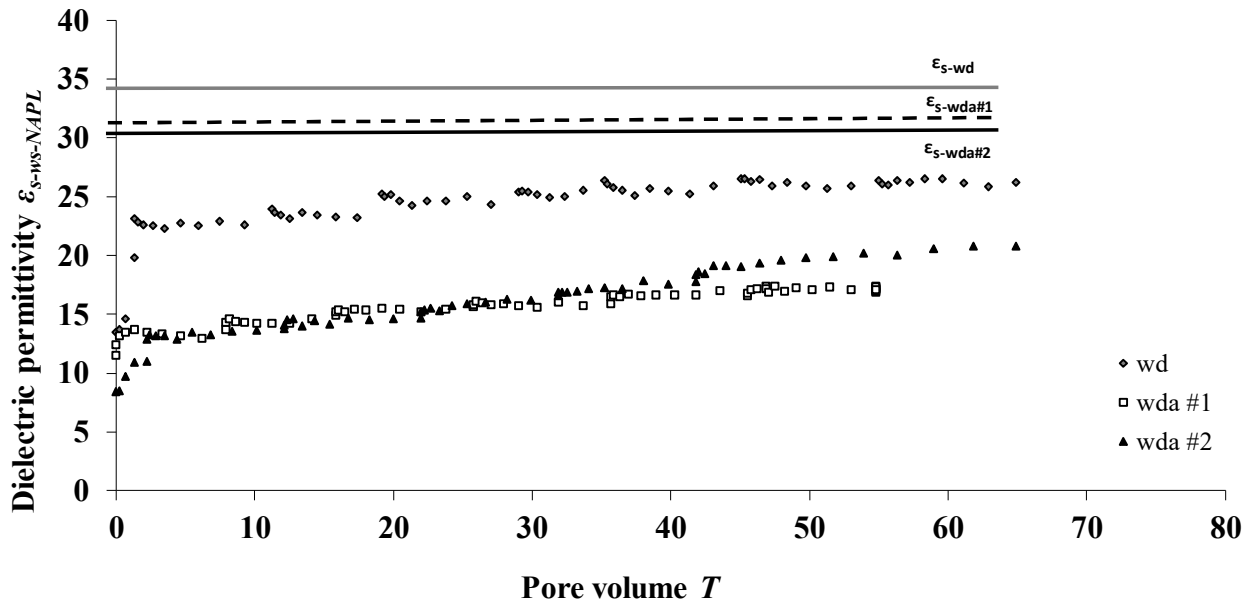
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d)  $\theta_{NAPL}=0.30$



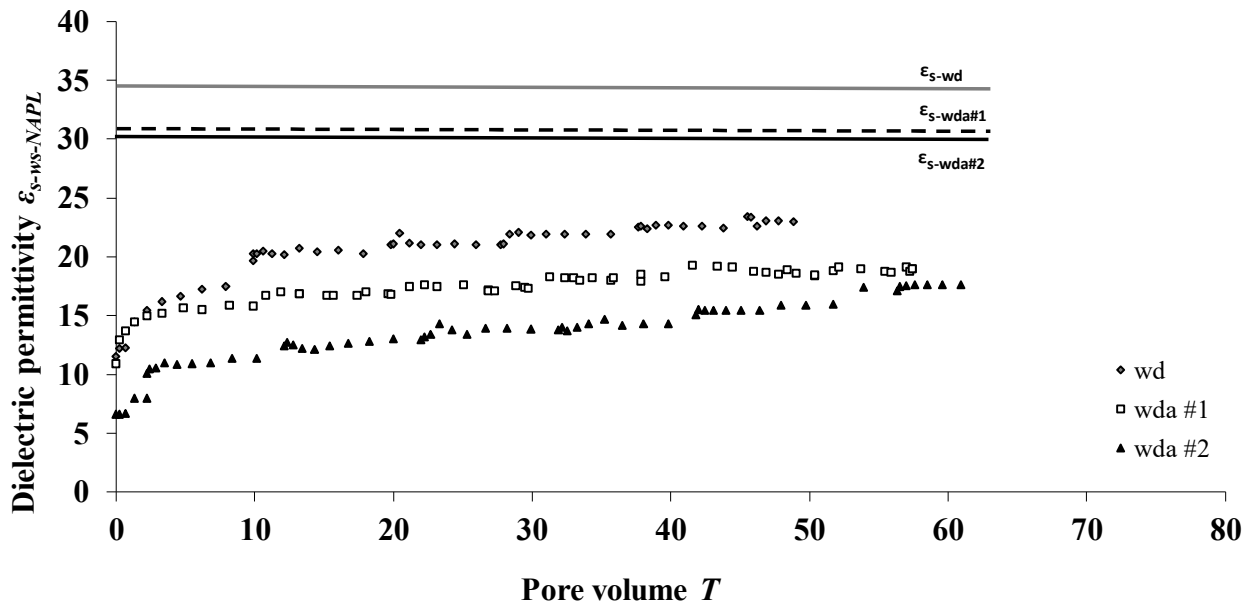
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e)  $\theta_{NAPL}=0.35$



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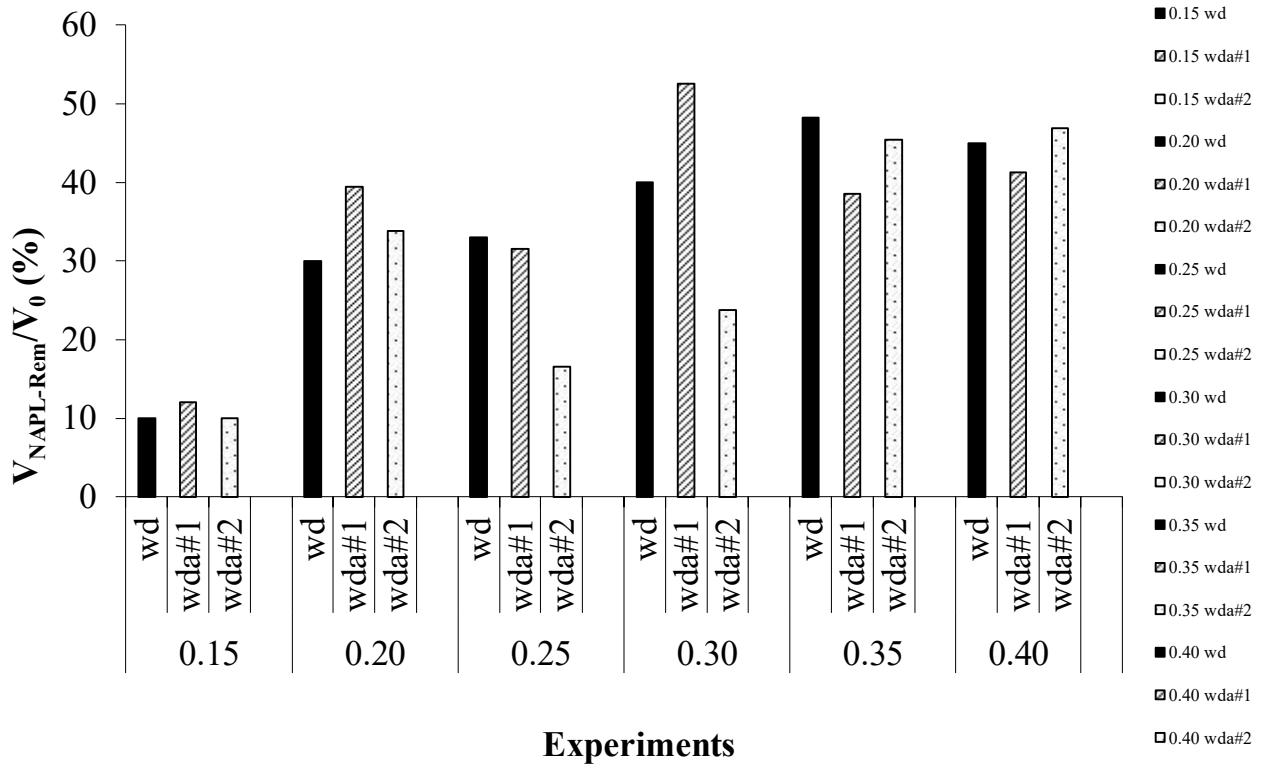
f)  $\theta_{NAPL}=0.40$



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**Figure 2. Selection of experimental relationships between the measured dielectric permittivity ( $\epsilon_{S-WS-NAPL}$ ) and number of pore volumes  $T$  under the effect of different washing solutions: i) water-detergent (wd) and ii) water-detergent-alcohol (wda#1 and wda#2).**

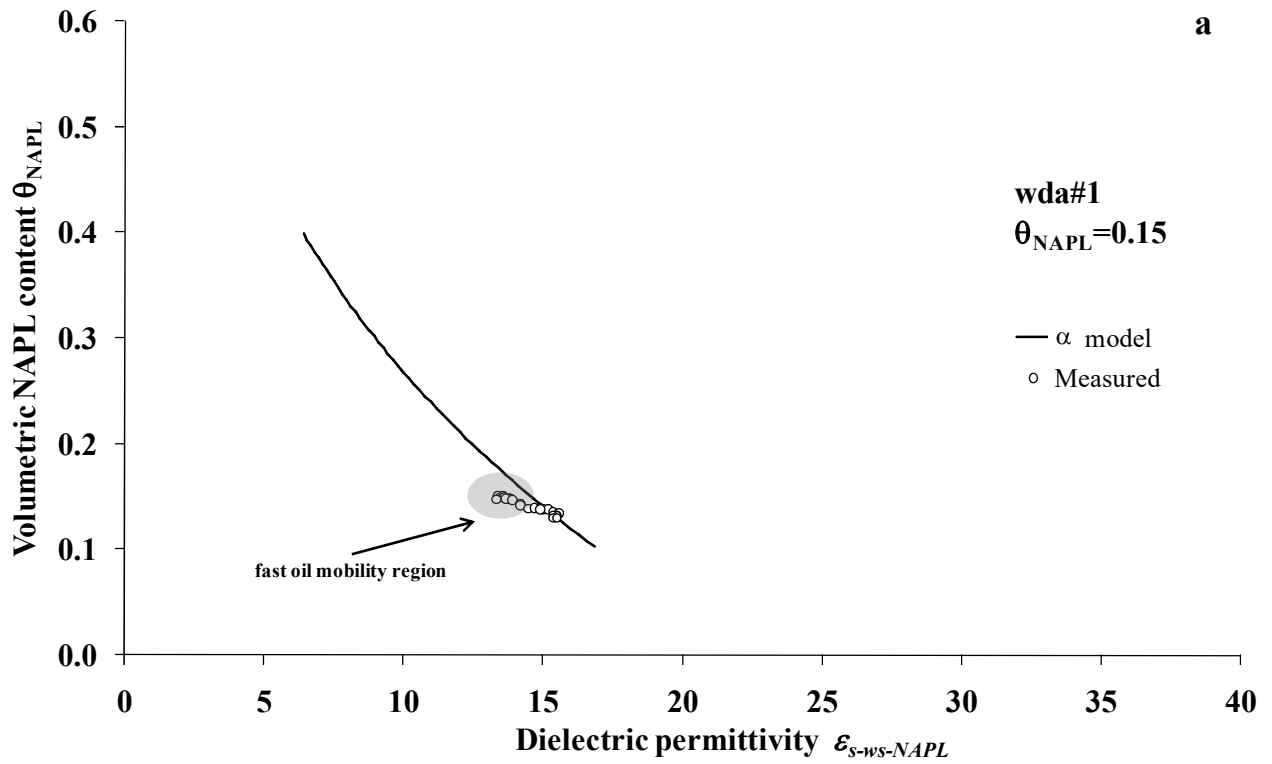




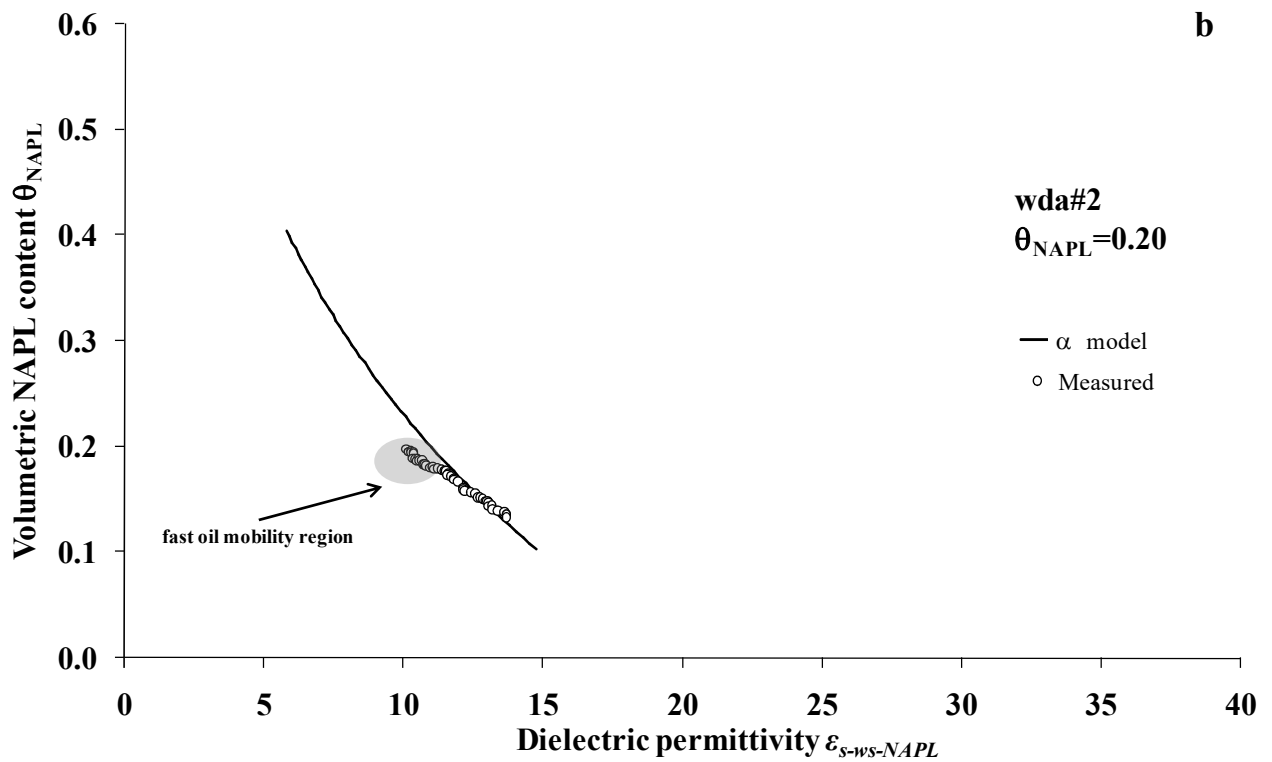
504

505 **Figure 3. Volume of NAPL recovered ( $V_{NAPL-Rem}$ ) with respect to the initial volume of NAPL**  
 506 **present in the soil sample ( $V_0$ ) of different washing solutions (wd, wda#1 and wda#2) for**  
 507 **different experiments ( $\theta_{NAPL}=0.15, 0.20, 0.25, 0.30, 0.35, 0.40$ ).**

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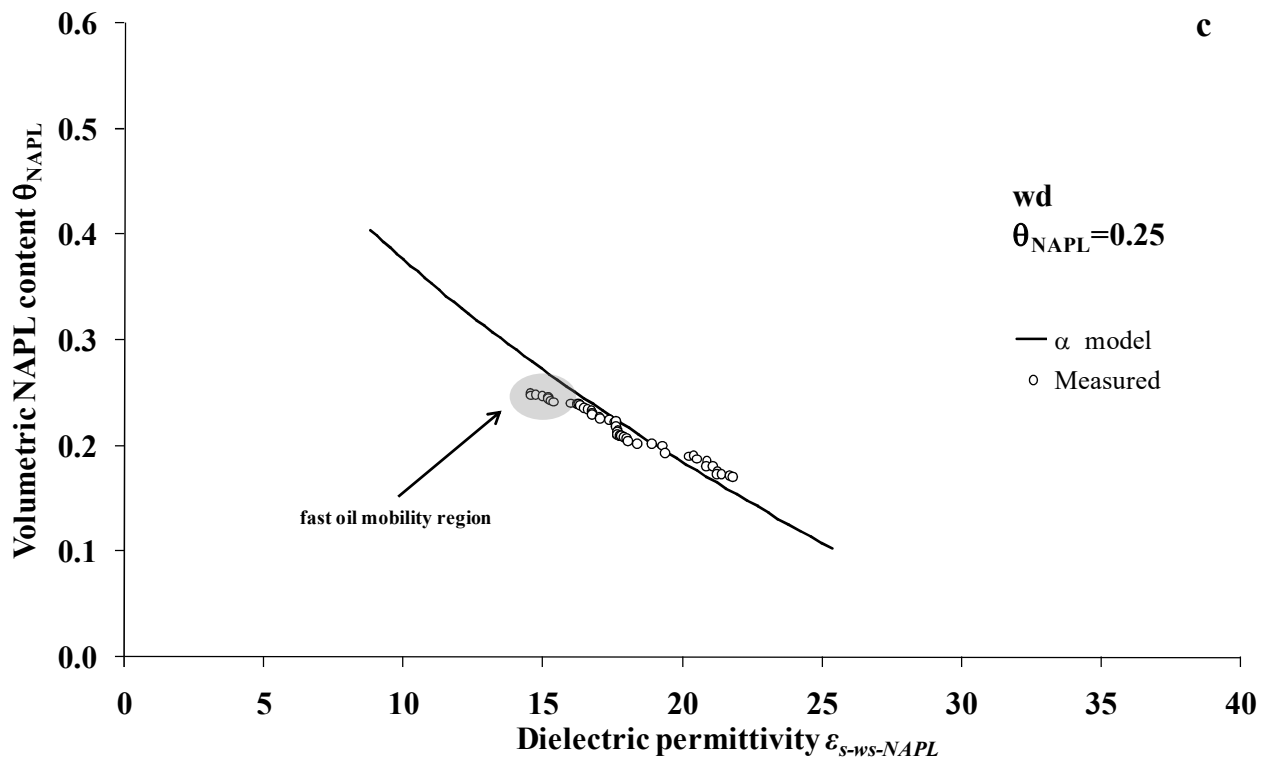


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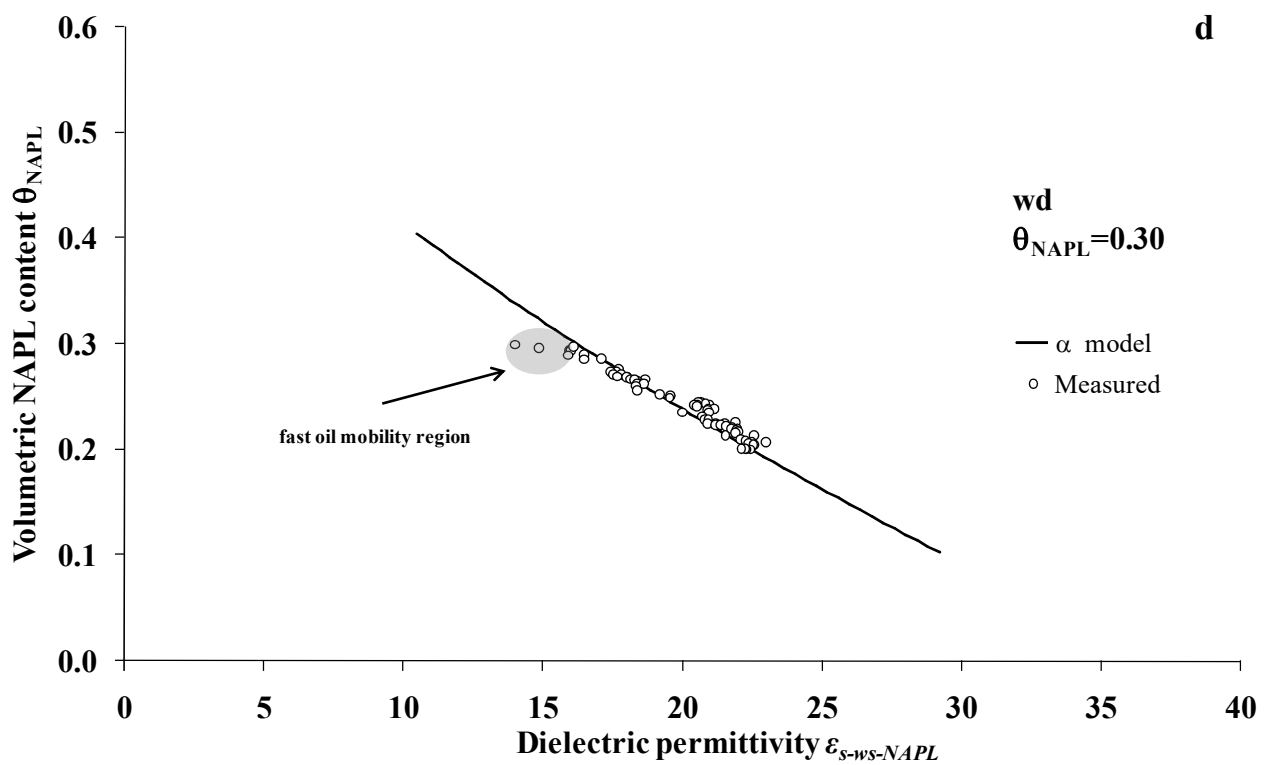


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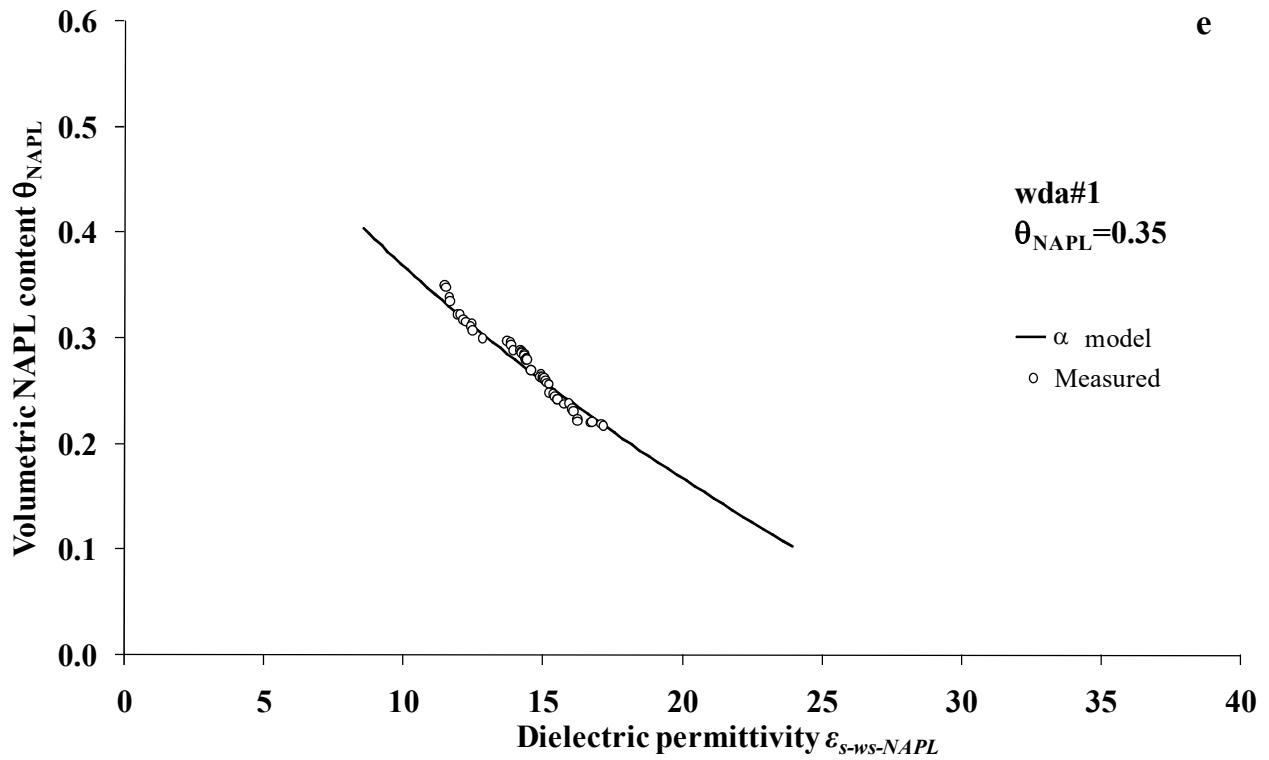
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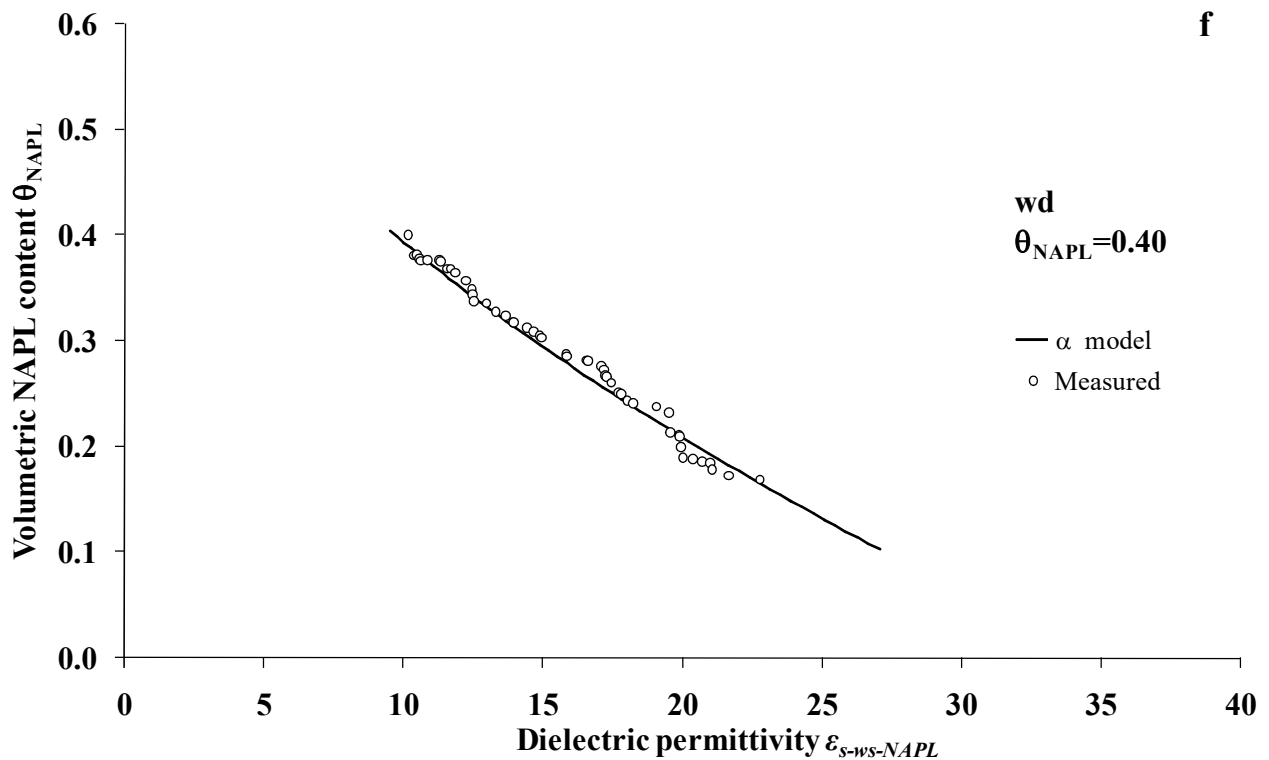
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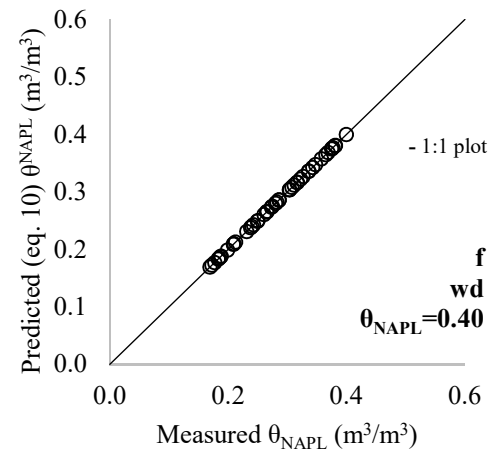
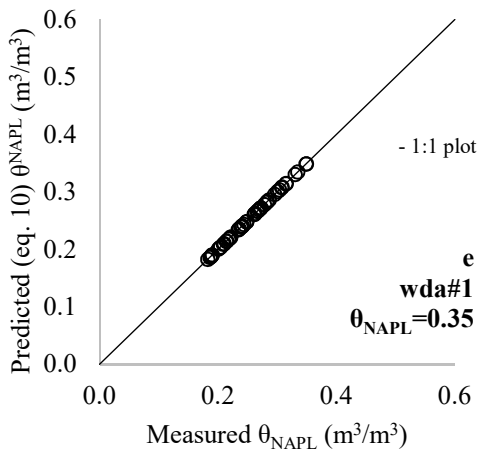
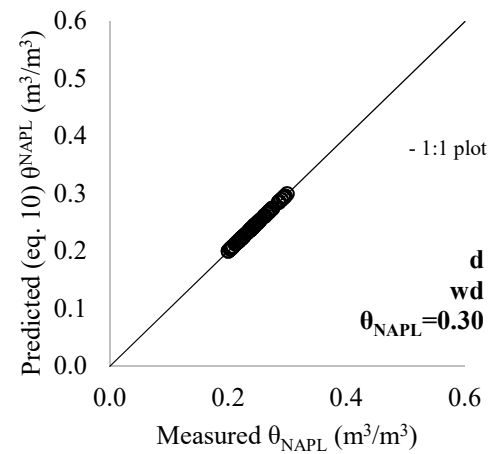
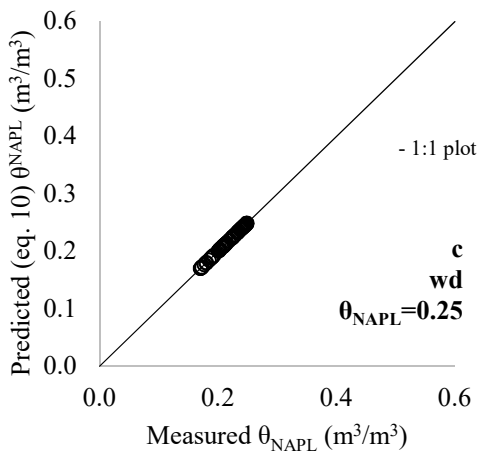
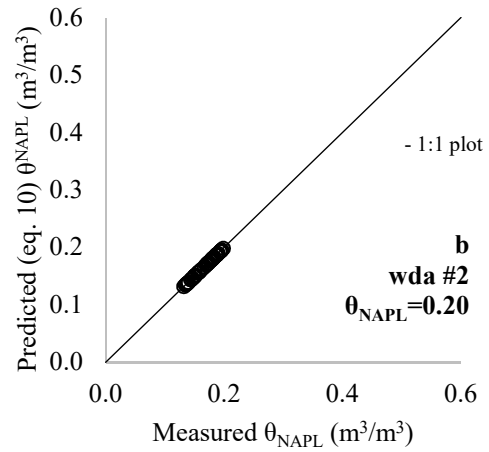
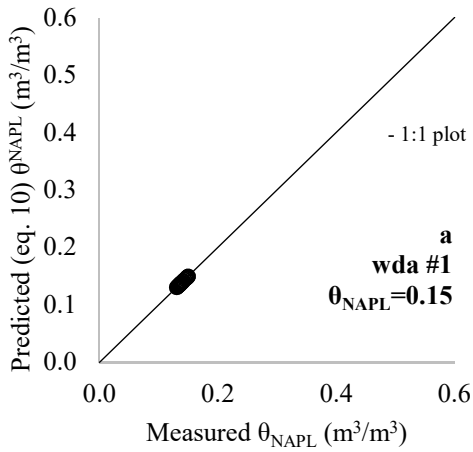
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516 **Figure 4 a, b, c, d, e, f. Selection of observed (symbols) and modeled (dashed lines) volumetric**

517 **NAPL content ( $\theta_{NAPL}$ ) versus dielectric permittivity ( $\epsilon_{s-ws-NAPL}$ ), with reference to the three**

518 **washing solutions (wd, wda#1 and wda#2) used during the remediation tests.**

519



**Figure 5 a, b, c, d, e, f. Measured (equation 10) vs. known volumetric NAPL content ( $\theta_{\text{NAPL}}$ ) of contaminated soils, with reference to the different remediation tests of figures 4.**

## Tables

**Table 1.** Estimated  $\alpha$  parameter of equation 10 for all three washing solutions (wd, wda#1 and wda#2) and volumetric NAPL content ( $\theta_{NAPL}$ ) tested.

parameter	washing solution	$\theta_{NAPL}$					
		<b>0.15</b>	<b>0.20</b>	<b>0.25</b>	<b>0.30</b>	<b>0.35</b>	<b>0.40</b>
$\alpha$	wd	0.45	0.30	0.49	0.65	0.67	0.55
	wda#1	0.25	0.45	0.45	0.42	0.50	0.55
	wda#2	0.20	0.45	0.30	0.45	0.55	0.52

**Table 2.** Model efficiency ( $EF$ ) and mean bias error ( $MBE$ ) statistical indices, referring to measured and predicted (equation 10) volumetric NAPL content ( $\theta_{NAPL}$ ).

Washing solution	$\theta_{NAPL}=0.15$		$\theta_{NAPL}=0.20$		$\theta_{NAPL}=0.25$	
	<b>EF</b>	<b>MBE</b>	<b>EF</b>	<b>MBE</b>	<b>EF</b>	<b>MBE</b>
wd	0.98	1.548	0.93	-0.422	0.96	0.570
wda#1	0.86	0.405	0.99	0.516	0.97	-0.048
wda#2	0.84	0.148	0.94	0.420	0.66	0.001
Washing solution	$\theta_{NAPL}=0.30$		$\theta_{NAPL}=0.35$		$\theta_{NAPL}=0.40$	
	<b>EF</b>	<b>MBE</b>	<b>EF</b>	<b>MBE</b>	<b>EF</b>	<b>MBE</b>
wd	0.98	-0.023	0.99	-0.153	0.99	-0.179
wda#1	0.95	-0.074	0.99	-0.066	0.99	0.303
wda#2	0.91	0.014	0.97	0.326	0.99	0.019

\*Range of model applicability:  $0.15 \leq \theta_{NAPL} \leq 0.40$ .