1 **A soil non-aqueous phase liquid (NAPL) flushing laboratory**

2 **experiment based on time domain reflectometry (TDR) and**

3 **modeling**

4 Alessandro Comegna[a*], Antonio Coppola[a], Giovanna Dragonetti[b], Angelo Sommella[c]

5 [a]School of Agricultural Forestry Food and Environmental Sciences (SAFE), University of Basilicata, Potenza, Italy.
6 [b]Mediterranean Agronomic Institute, Land and Water Division, IAMB, Bari, 70010, Italy.
7 [c]Department of Agriculture, University of Naples "Federico II", Italy.

8 *Correspondence*: Alessandro Comegna (alessandro.comegna@unibas.it)

9 **Abstract.** The term non-aqueous phase liquid (NAPL) refers to a group of organic compounds with scarce solubility in

10 water. They are the products of various human activities and may be accidentally introduced into the soil system. Given

11 their toxicity level and high mobility, NAPLs constitute a serious geo-environmental problem. Contaminant distribution

12 in the soil and groundwater entails fundamental information for the remediation of polluted soil sites. The present research

13 explored the possible employment of time domain reflectometry (TDR) to estimate pollutant removal in a silt-loam soil

14 that was primarily contaminated with a light hydrocarbon and then flushed with diverse washing solutions. Known

15 mixtures of soil and NAPL were prepared in the laboratory to achieve soil specimens with diverse pollution levels. The

16 prepared soil samples were repacked into plastic cylinders and then placed in testing cells. Washing solutions were then

17 injected upward into the contaminated sample, and both the quantity of remediated oil and the bulk dielectric permittivity

18 of the soil sample were determined. The above data was also used to develop a dielectric model (the α mixing model)

19 which permits the volumetric NAPL content (θ_{NAPL}) within the contaminated sample to be determined and quantified

20 during the different decontamination stages. Our results demonstrate that during a decontamination process, the TDR

21 device is NAPL-sensitive: the dielectric permittivity of the medium increases as the NAPL volume decreases. Moreover,

22 decontamination progression can be monitored using a simple (one-parameter) mixing model.

23 **1. Introduction**

24 Soil and groundwater contamination with NAPL from point or nonpoint sources is a severe problem of considerable

25 complexity (Fitts, 2002; Fetter, 1993). The repercussions concern not only the deterioration of the soil's physical,

26 mechanical and chemical properties, but also account for a potentially severe hazard to the well-being of humans and

27 other living species (Freeze, 2000).

28 Soil flushing is the technical procedure used for treating polluted soils with water, surfactants and co-solvents (such as

29 methanol, ethanol and propanols). Surfactant-enhanced flushing was developed from the conventional pump-and-treat

30   method. The success of this approach is related to the capacity of such chemical compounds to greatly enhance the

31   aqueous solubility of oils (Pennell et al., 1994; Parnian and Ayatollahi, 2008).

32   There is high interfacial tension between NAPL and water molecules that makes water a non-efficient cleaning material

33   in removing NAPL from the soil. Instead, surfactants and co-solvent agents can promote the enhanced removal of NAPL

34   from the subsurface through mobilization and solubilization (Martel et al., 1998; Rinaldi and Francisca, 2006; Parnian

35   and Ayatollahi, 2008).

36   Primary remediation refers to the removal of the NAPL free phase by pumping. This extraction mechanism returns

37   appreciable effects if there is a region of high NAPL saturation. After primary pumping, a considerable portion of NAPL

38   remains constrained within the soil as capillary forces overcome viscous and buoyancy forces. This discontinuous NAPL

39   phase is referred to as trapped residual NAPL (or NAPL residual saturation), and its remediation is referred to as secondary

40   remediation (Parnian and Ayatollahi, 2008). Residual NAPL is a long-term source of soil and groundwater pollution

41   (Mercer and Cohen, 1990; Troung Hong and Bettahar, 2000).

42   To develop powerful decontamination procedures, the characterization of polluted soils is required. Practices usually

43   employed to characterize polluted soil sites are coring, soil sampling and the installation of monitoring wells for the

44   collection of water samples from aquifers (Mercer and Cohen, 1990). Since the aforementioned procedures are costly, the

45   time domain reflectometry (TDR) technique is suggested as a valid technical alternative since it exhibits adequate

46   sensitivity for the characterization of NAPL saturation (Persson and Berndtsson, 2002; Mohamed and Said, 2005;

47   Moroizumi and Sasaki, 2006; Francisca and Montoro, 2012; Comegna et al., 2013a; Comegna et al., 2016).

48   The purpose of this study was to the following: i) investigate a possible extension of TDR technology to assess the effects

49   of NAPL removal in soils, and ii) build, on the basis of the acquired data and the experimental results, a dielectric model

50   to predict the volumetric amounts of NAPL (θ_{NAPL}) within the contaminated soil during the decontamination process.

51   **2. Theoretical concepts of TDR**

52   TDR is a geophysical technique employed to determine the dielectric permittivity of liquids and solids. In general, the

53   bulk dielectric permittivity is a complex term (ε_r^*), which may be expressed as follows (Robinson et al., 2003):

$$\varepsilon_r^* = \varepsilon'_r - j\left[\varepsilon''_r + \frac{\sigma}{\omega\varepsilon_0}\right] \tag{1}$$

54   where ε'_r is the real part of dielectric permittivity, which gives the energy stored in the dielectrics at a certain frequency

55   and temperature, and ε''_r is the imaginary part due to relaxations. The zero frequency conductivity σ, the angle

56   frequency ω, the imaginary number $j = \sqrt{-1}$ and the permittivity ε_0 in free space contribute to define ε_r^*.

57 When the frequency of a TDR cable tester ranges between 200 MHz to 1.5 GHz, dielectric losses can be considered

58 minimal and the bulk dielectric permittivity ε_b ($\cong$ the real part of permittivity) of a probe of length L is determined from

59 the propagation velocity $v (= 2L/t)$ of an electromagnetic wave along the wave guide across the investigated medium by

60 the following expression:

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

61 where c ($= 3 \times 10^8$ m s^{-1}) is the velocity of an electromagnetic wave in vacuum (Topp et al., 1980) and t is travel time, i.e.

62 the time required by the generated signal to go back and forth through the TDR probe of length L (m). This can be

63 calculated as the following:

$$t = \frac{2L}{c}\sqrt{\varepsilon_b} \tag{3}$$

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

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

66 Dielectric mixing models, in their classical application, have been proposed to estimate the bulk dielectric permittivity of

67 a multi-phase medium, that is, a combination of three or four dielectric phases, and to couple the dielectric permittivity

68 of the medium to the dielectric permittivity of each single phase (Hilhorst, 1998). Recently, after analyzing the effects of

69 organic contaminants on soil dielectric properties, the above models were further developed to estimate the dielectric

70 properties of NAPL-polluted soils (Persson and Berndtsson, 2002; Francisca and Montoro, 2012, Comegna et al., 2013a;

71 Comegna et al., 2016; Comegna et al., 2017).

72 Based on such models, in the present study, we analyze the possibility of predicting the correlations between the

73 volumetric contents of NAPL (θ_{NAPL}) and the dielectric response (ε_b) of contaminated soil during the progression of a

74 steady-state remediation process.

75 In the present research, we chose the so-called α model (Birchack et al., 1974; Roth et al., 1990):

$$\varepsilon_b = \left[\sum_{i=1}^{n} V_i \varepsilon_i^{\alpha}\right]^{1/\alpha} \tag{4}$$

76 where V_i is the volume and ε_i is the permittivity of each component of the complex medium; the exponent α is a fitting

77 parameter (α varies between -1 and 1), which may be related to the internal structure of the investigated medium (Hilhorst,

78 1998; Coppola et al., 2013; Coppola et al., 2015). Under the following hypothesis: i) the soil is homogeneous from a

79 textural point of view, and ii) the soil porosity (ϕ) is constant, equation 4 was reformulated for our purposes.

80 For mixtures of soil (*s*) saturated with a certain amount of washing solution (*ws*), in rearranging the model formulation of

81 Rinaldi and Francisca (2006), the α model yields the following:

$$\varepsilon_{s-ws}^{\alpha} = \left[(1-\phi)\varepsilon_s^{\alpha} + \phi\varepsilon_{ws}^{\alpha} \right] \tag{5}$$

82 where $\varepsilon_{s\text{-}ws}$ is the soil-washing solution permittivity, and ε_s and ε_{ws} are the permittivities of soil particles and washing

83 solutions, respectively. By the same token, for soil organic (*s-NAPL*) compounds at saturation, the α model can be

84 expressed as the following:

$$\varepsilon_{s-NAPL}^{\alpha} = \left[(1-\phi)\varepsilon_s^{\alpha} + \phi\varepsilon_{NAPL}^{\alpha} \right] \tag{6}$$

85 where $\varepsilon_{s\text{-}NAPL}$ is the permittivity of the soil-NAPL mixture, and ε_{NAPL} is the oil permittivity.

86 A medium consisting of soil particles, washing solution and NAPL (*s-ws-NAPL*) can be viewed as a mix of soil-washing

87 solution (equation 5) and soil-NAPL (equation 6):

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

88 where β is the relative volume of NAPL contained in the whole fluid phase:

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

89 where θ_f is the volumetric fluid content (cm^3/cm^3), sum of the volumetric washing solution content (θ_{ws}) and volumetric

90 NAPL content (θ_{NAPL}); β varies between 0 (i.e. a soil-washing solution mixture) and 1 (i.e. a soil-NAPL mixture).

91 To estimate θ_{NAPL}, equation 7 is first reformulated in terms of β:

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

92 Substituting equation 8 into equation 9, and considering that for a saturated medium, the volumetric fluid content is equal

93 to soil porosity (i.e. $\theta_f = \phi$), θ_{NAPL} can be calculated as the following:

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

94 Equation 10 correlates the dependence of volumetric NAPL content with soil porosity; θ_{NAPL} can be estimated (within the

95 contaminated soil) during the progression of a remediation process once the dielectric permittivity of the soil-

96 contaminated mixture ($\varepsilon_{s-ws-NAPL}$) is known.

97 **4 Materials and Methods**

98 **4.1 Soil and fluid properties**

99   A silt-loam Anthrosol (IUSS Working Group WRB, 2006) from the region of Puglia (Italy) was used for this study. The

100   soil texture was measured by means of the hydrometer method (Day, 1965), while the Walkley–Black procedure (Allison,

101   1965) was used to determine soil organic C content. The method developed by Miller and Curtis (2007) was used to

102   measure soil electrical conductivity (EC_w), while soil pH was determined on the basis of a 1:1 soil/water ratio (Eckert,

103   1988). In textural terms, the soil comprised 15.7% sand, 11.6% clay and 72.4% silt. Soil porosity was 0.57%, organic

104   content 1.84%, EC_w 0.17 dS/m and soil pH 8.40.

105   The NAPL employed for the laboratory tests was corn oil (ε_{NAPL}=3.2; EC_{NAPL}=0.055 dS/m at 25°C) with a density of 0.905

106   g/cm³ (at 25°C). Three different removal solutions were employed for soil cleaning: a) a first solution (referred to below

107   as wd) composed of 99% distilled water and 1% commercial detergent (ε_d=9.22, at 25°C), b) a second solution (wda#1)

108   composed of 90% distilled water, 1% commercial detergent and 9% methanol as co-solvent ($\varepsilon_{alcohol}$=26.13, at 25°C) and

109   c) a third solution (wda#2) composed of distilled water (85%) with commercial detergent (1%) and methanol (14%). The

110   dielectric permittivity of the washing solutions, measured at 25°C, was ε_{wd}=75.04, $\varepsilon_{wda\#1}$=68.98 and $\varepsilon_{wda\#2}$=65.92, whereas

111   the dielectric permittivity of the tested soil saturated with each of the three cleaning solutions was $\varepsilon_{soil+wd}$=34.59,

112   $\varepsilon_{soil+wda\#1}$=31.04 and $\varepsilon_{soil+wda\#2}$=30.10.

4.2 Measurement of dielectric permittivity of soil-NAPL contaminated samples during soil remediation

4.2.1 Experimental setup

As illustrated in Figure 1, the experimental layout consisted of the following: i) a Techtronix (model 1502C) cable tester;

ii) a three-wire TDR probe 14.5 cm long, introduced vertically into the soil samples; iii) a testing cell 15 cm high and 8

cm in diameter; iv) a peristaltic pump used for upward movement of the washing solution.

4.2.2 Sample preparation and testing procedures

After oven-drying at 105°C and sieving at 2 mm, the soil was mixed with oil in known quantities and then placed for 24

hours in plastic bags to prevent evaporation and ensure a complete distribution of oil in the soil. The samples were then

allocated to cylindrical boxes. With a view to achieve different degrees of soil contamination, volumetric NAPL content

(θ_{NAPL}) was varied from 0.05 to 0.40 (in steps of 0.05). In all, each washing solution comprised eight oil-contaminated

soil samples.

For all experiments, the soil samples were placed in the vessels in various steps at a bulk density of 1.13 g/cm³. During

TDR measurements, the soil samples were conserved at a temperature of 25°C by using a thermostat box. Remediation

was performed using an upward flux of diverse pore volumes T of three washing solutions (wd, wda#1 and wda#2)

supplied at the rate of 90 cm³/h, corresponding to a Darcian velocity of 1.8 cm/h. After collection of the outflow from the

128   soil columns, the oil was separated from the washing solution and the quantity of oil remediated from the soil was

129   determined.

130   The obtained data series were employed to calibrate the proposed dielectric model of equation 10.

131   **4.3. Numerical indices for model performance evaluation**

132   The goodness of equation 10 was evaluated using two different criteria: i) the mean bias error (*MBE*), and ii) the model

133   efficiency (*EF*), computed according to the following relations (Legates and McCabe Jr, 1999):

$$MBE = \frac{\sum\limits_{i=1}^{N}\left(E_i - O_i\right)}{N} \tag{11}$$

134

$$EF = 1 - \frac{\sum\limits_{i=1}^{N}\left(E_i - O_i\right)^2}{\sum\limits_{i=1}^{N}\left(O_i - \overline{O}\right)^2} \tag{12}$$

135   where E_i and O_i are respectively the expected and the observed value, $\overline{O}$ is the mean of the observed data, and N is the

136   number of observations.

137   *MBE* measures the differences between model-simulated data and measured values (positive *MBE* values are used to

138   indicate average overprediction, while negative values indicate underprediction). The model's ability to forecast θ_{NAPL} is

139   described by parameter *EF*, according to which *EF*=1 indicates perfect accord between predicted and measured data.

140   **5. Results and Discussion**

141   **5.1 Influence of NAPL removal on bulk dielectric permittivity**

142   Figures 2a, b, c, d, e and f, with reference to the most representative experimental results, reveal the influence of pore

143   volumes T on evaluated bulk dielectric permittivity ($\varepsilon_{s-ws-NAPL}$) for the soil specimens initially polluted with oil. As the

144   washing solution started to remove oil, the dielectric permittivity rose due to the larger dielectric permittivity of the

145   flushing mixture. As the remediation solution continued to move upward, the rising rate of the dielectric permittivity

146   decreased and asymptotically approached a constant value. This steady value was smaller than that observed when the

147   soil specimens were completely saturated by only the flushing solution (i.e. wd, wda#1 or wda#2), which in our tests

148   corresponds to the condition of a completely decontaminated soil. This difference in values is undoubtedly due to oil

149   confined in soil pores (i.e. NAPL residual saturation). For the same reason, residual saturation may explain why

150   insignificant oil remediation was observed for θ_{NAPL} values less than 0.15. This aspect may be explained by the fact that

151   for low volumetric NAPL contents, the non-wetting fluid (oil) is disconnectedly distributed (i.e. immobile) in the soil

152   samples, which means that θ_{NAPL} is close to the limiting *residual value*, and thus NAPL loses its ability to move in the

153   soil in response to a hydraulic gradient [i.e. capillary retention forces are greater than gravitational forces, which tend to

154   immobilize the NAPL (Brost and DeVaull, 2000)].

155   Figure 3 showed, for different washing solutions, the percentages of NAPL volumes recovered ($V_{NAPL-Rem}$) with respect

156   to the initial volume of NAPL present in the soil sample (V_0). For all the three cleaning solutions adopted, the experiments

157   ultimately demonstrate (for a fixed θ_{NAPL}) the same results in terms of soil decontamination, and they show that NAPL

158   removal increases with increasing θ_{NAPL}. In some cases (i.e. θ_{NAPL}=0.15, 0.20 and 0.30), contaminated samples flushed

159   with the wda#1 solution yield slightly higher removal efficiency values compared to the samples flushed with wd and

160   wda#2. Martel et al. (1998) suggest the need to investigate the best water-surfactant-alcohol combination in order to

161   enhance NAPL solubilization in soil.

162   **5.2 Model calibration and validation**

163   For the model (equation 10) calibration methodology, with reference to the three washing solutions (wd, wda#1 and

164   wda#2), we analyze the effect of the measured dielectric permittivity on volumetric NAPL content (θ_{NAPL}) in order to

165   estimate the α parameter of the model. The complete data set of estimated α parameters is reported in Table 1.

166   A permittivity value of 3.70 was adopted for the solid phase. This value was determined using the *"immersion method"*

167   which is commonly employed for estimating the ε_s of soils (Robinson et al., 2003; Kameyama and Miyamoto, 2008;

168   Comegna et al., 2013a; Coppola et al., 2013).

169   For the sake of brevity, a selection of the experimental $\varepsilon_{s-ws-NAPL}$-θ_{NAPL} relationships (validation dataset) is reported in

170   figures 4a, b, c, d, e and f. The data in figures 4 (except for figures 4e, f) show that some of the model-simulated values

171   tend to overestimate the measured data. This behavior is mostly restricted to the beginning of the remediation process,

172   when a rapid change in dielectric permittivity may be observed. This behavior was also verified in other tests (not shown

173   here) and may be explained by invoking both NAPL properties such as liquid density, surface tension and viscosity, and

174   soil properties including moisture content, relative permeability, soil heterogeneity and porosity (Brost and DeVaull,

175   2000; Wang et al., 2013).

176   Mercer and Cohen (1990) referred to the existence, in NAPL-contaminated soils, of a *"double fluid domain,"* defined as

177   the composition of the following: i) mobile pools, which are NAPL-connected phases that move in the soil and ii)

178   immobile residuals (i.e. low permeability regions), which depend on small disconnected blobs or ganglia within the

179   contaminated soil (see also section 5.1 above). As long as the flushing continues, mobile pools are reduced and the oil

180   tends increasingly to be trapped in the immobile areas. This means that, during soil cleaning, the capacity of non-wetting

181   fluids to respond to gravitational forces gradually diminishes (Luckner et al., 1989). From a dielectric point of view, this

182   mechanism may appear as a rapid dielectric permittivity increase (identified in figures 4 as *fast oil mobility region*) within

183 a few pore volumes. When this fast mobility mechanism is dominant, the predictions of equation 10 fail. However, since

184 the phenomenon is mostly limited to the initial part of the washing process, overall model effectiveness is not

185 compromised, as also shown in Table 2, which summarizes the goodness-of-fit statistical indices.

186 Overall, both graphical and quantitative evaluations in terms of *MBE* and *EF* reveal the suitability of the dielectric model

187 adopted to estimate the volumetric NAPL content in the θ_{NAPL} range 0.15-0.40.

188 **6. Conclusions**

189 This paper presented an extensive dataset of remediation experiments that were conducted at a laboratory scale using corn

190 oil as a soil contaminant, and three different solutions for soil cleaning. The results of these tests were employed to

191 investigate the potential of the TDR technique in monitoring the development of a steady-state decontamination process.

192 Dielectric data analysis showed that, during soil flushing, dielectric permittivity behavior is highly dependent on the initial

193 volumetric content and intrinsic permittivity of the specific NAPL: *removal of NAPL produces an increase in bulk*

194 *dielectric permittivity*, due to the low value of oil permittivity. The experiments conducted also allowed us to calibrate

195 and validate a dielectric mixing model (equation 10). The model outcomes are encouraging; the calculated statistical

196 indices confirmed a high accuracy in NAPL predictions of the α-model at different stages during soil cleaning, with the

197 only exception of the very initial cleaning stage (confined to the low values of *T*) where the eventual presence of a *fast*

198 *flow region* may limit its applicability.

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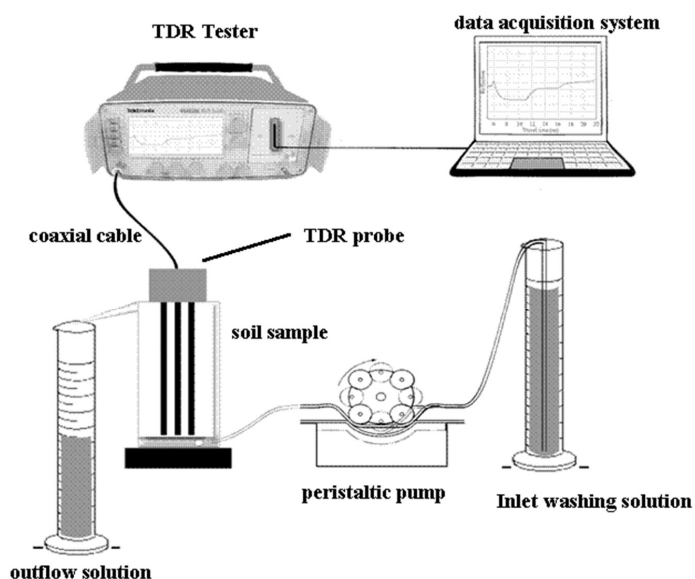
271

272 **Figures**

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

a) $\theta_{NAPL}=0.15$

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b) θ$_{NAPL}$=0.20

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c) θ$_{NAPL}$=0.25

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d) θ$_{NAPL}$=0.30

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e) θ$_{NAPL}$=0.35

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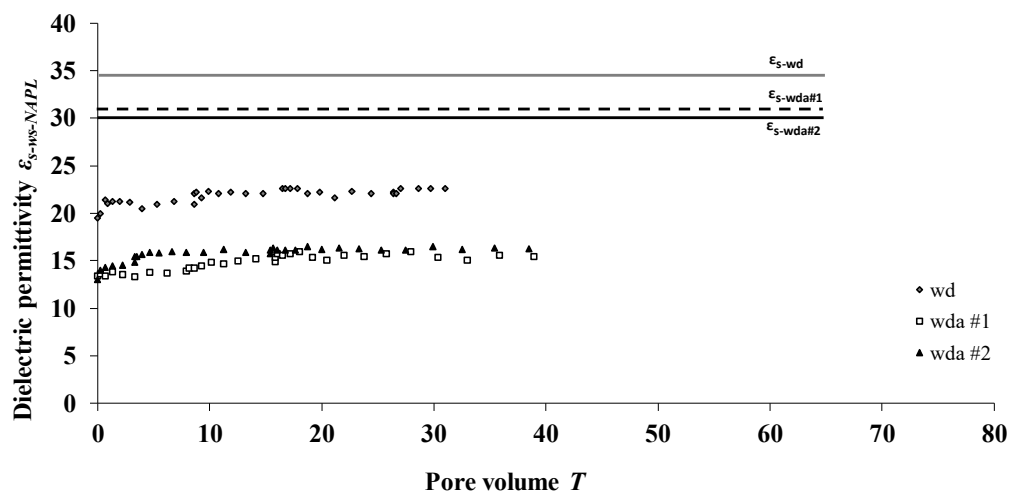
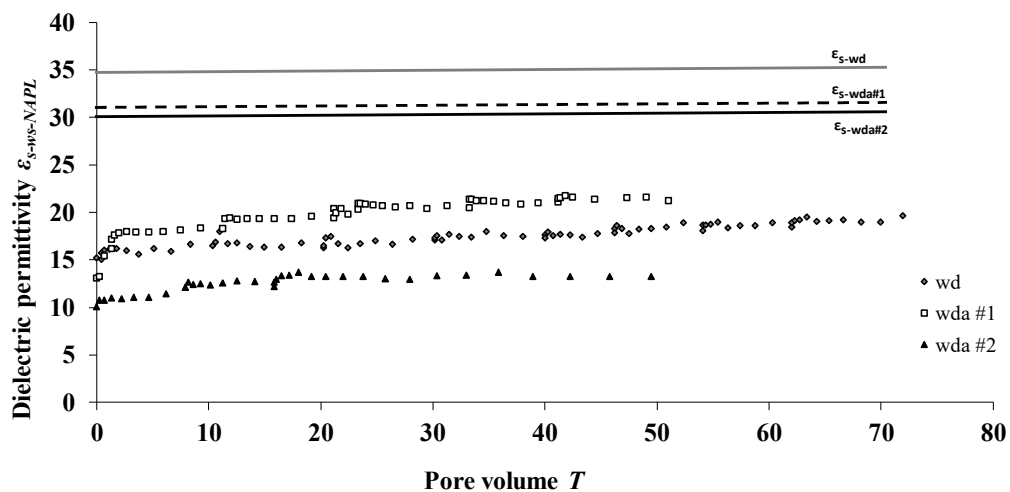
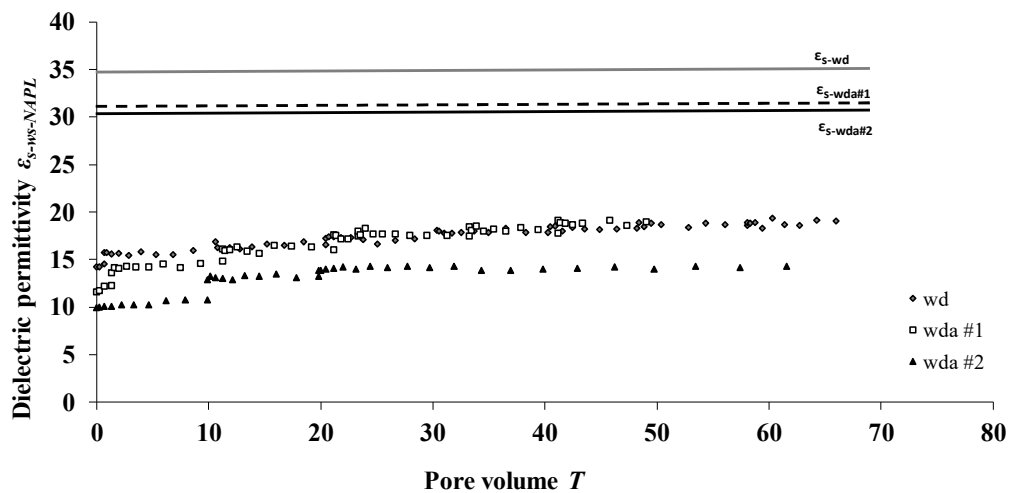
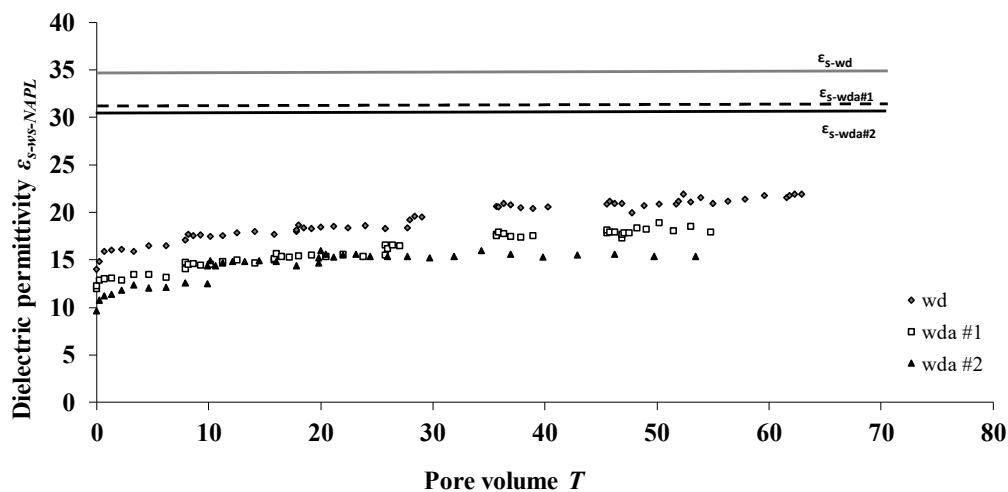
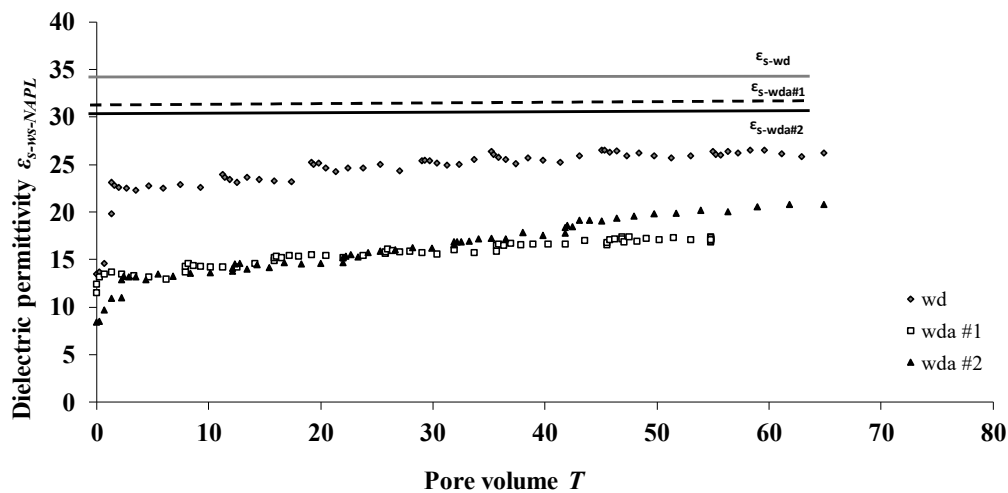
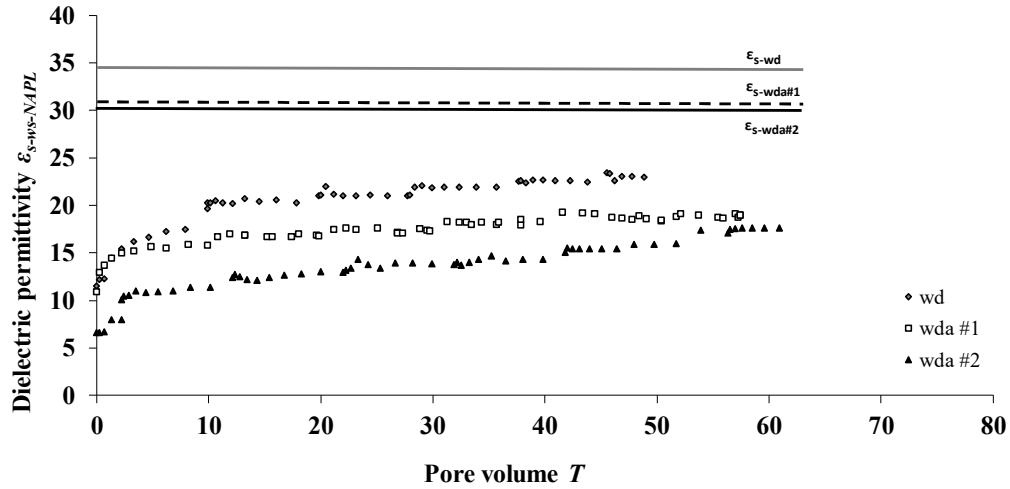

f) θ_{NAPL}=0.40

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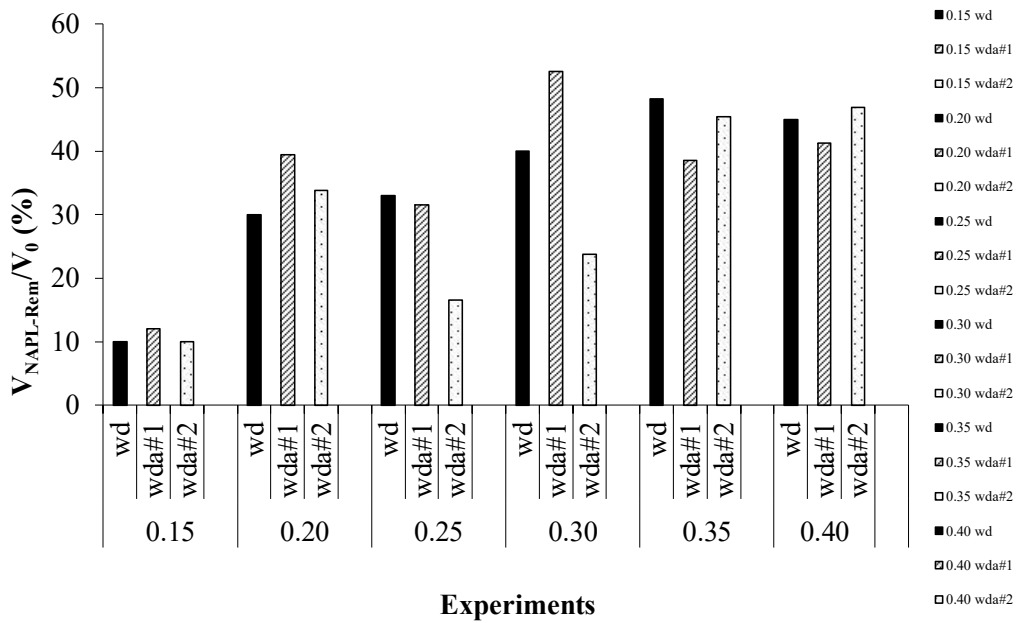
283 **Figure 2. Selection of experimental relationships between the measured dielectric permittivity ($\varepsilon_{s\text{-}ws\text{-}NAPL}$) and number of pore**

284 **volumes T under the effect of different washing solutions: i) water-detergent (wd) and ii) water-detergent-alcohol (wda#1 and**

285 **wda#2).**

286

287 **Figure 3. Volume of NAPL recovered ($V_{NAPL-Rem}$) with respect to the initial volume of NAPL present in the soil sample (V_0) of**

288 **different washing solutions (wd, wda#1 and wda#2) for different experiments (θ_{NAPL}=0.15, 0.20, 0.25, 0.30, 0.35, 0.40).**

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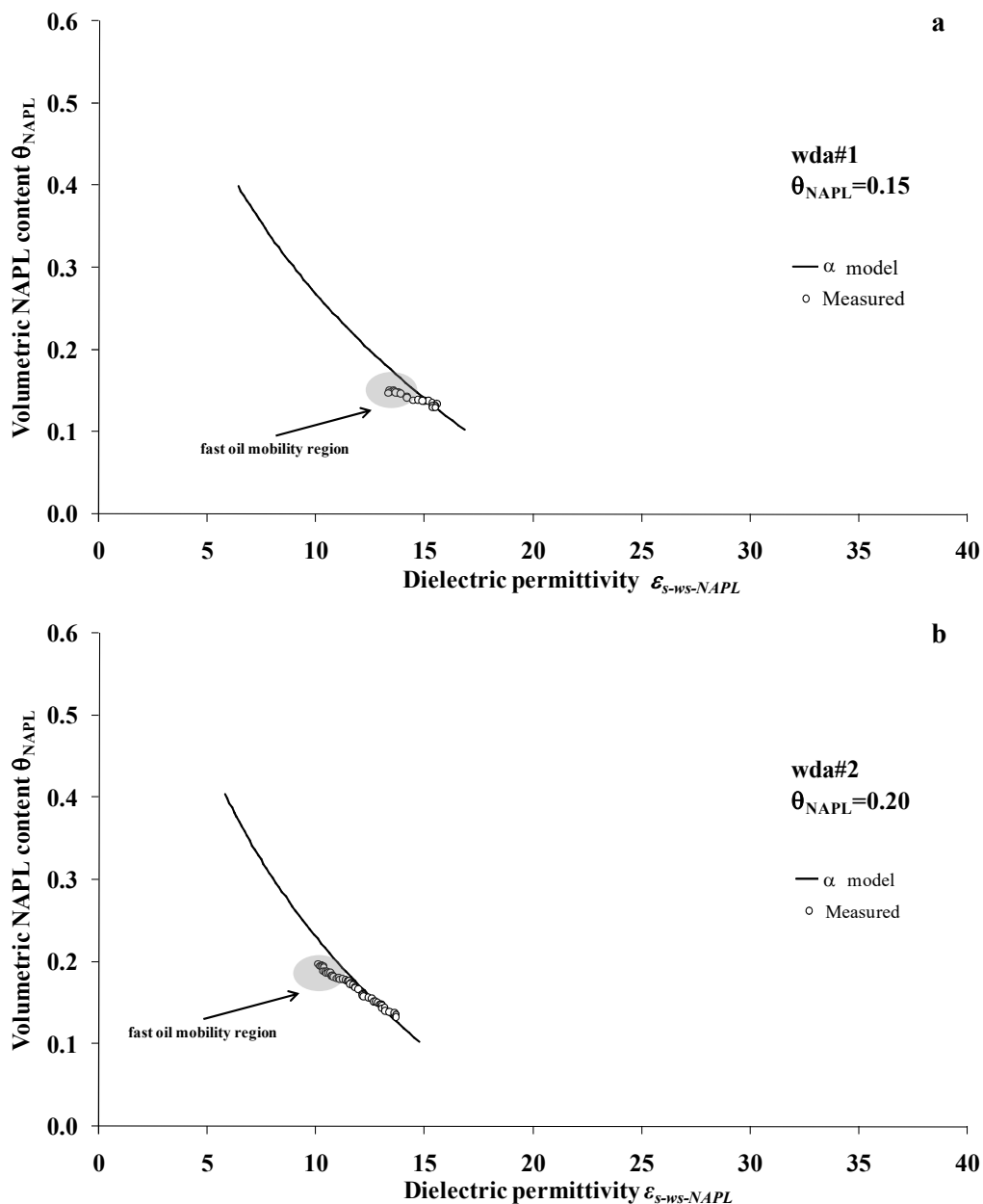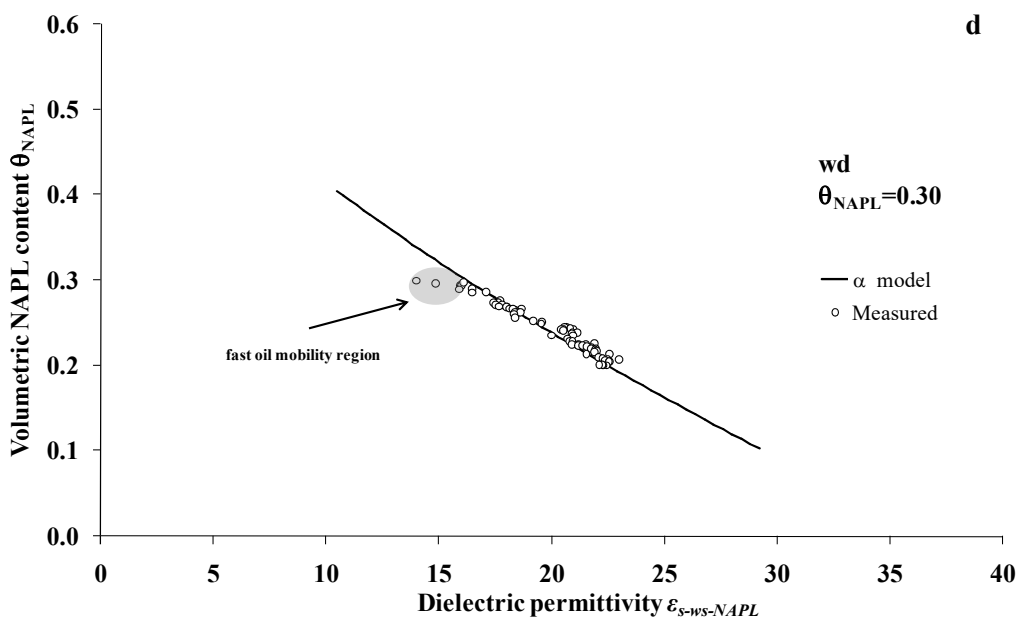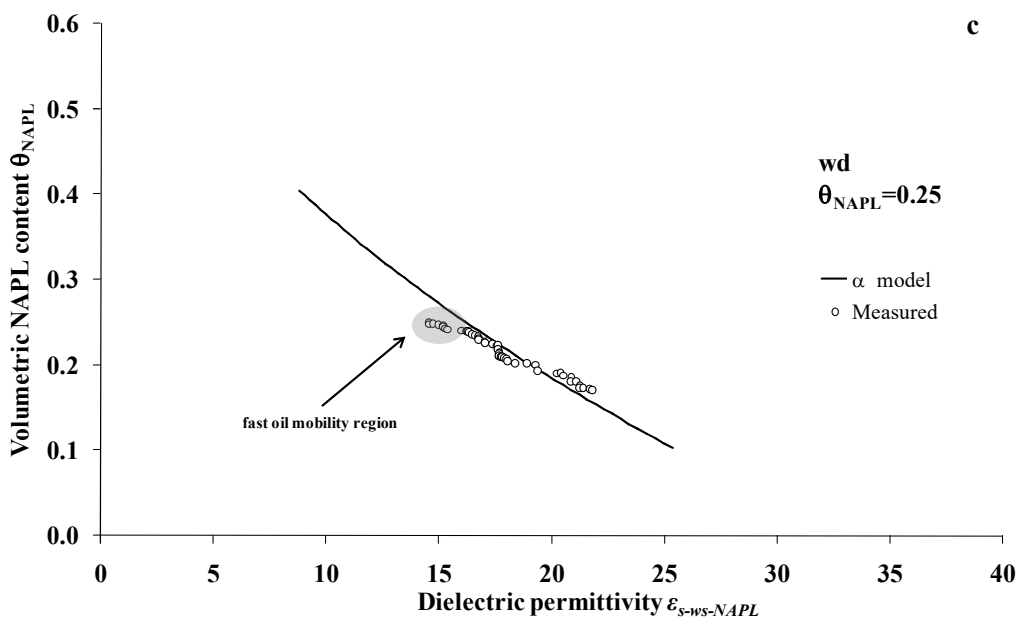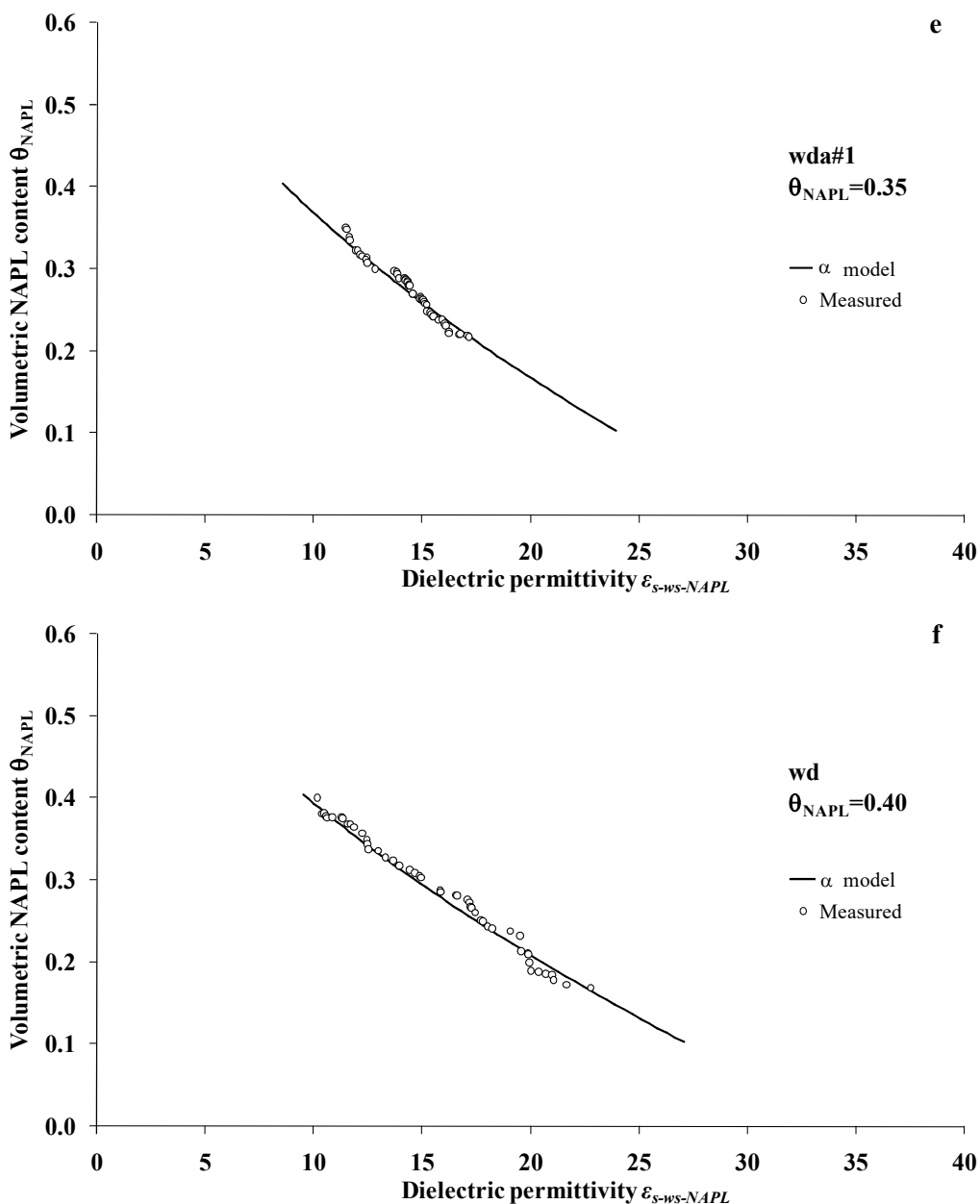
295
296 **Figure 4 a, b, c, d, e, f. Selection of observed (symbols) and modeled (dashed lines) volumetric NAPL content (θ_{NAPL}) versus**

297 **dielectric permittivity ($\varepsilon_{s\text{-}ws\text{-}NAPL}$), with reference to the three washing solutions (wd, wda#1 and wda#2) used during the**

298 **remediation tests.**

299

Tables

Table 1. Estimated α parameter of equation 10 for all three washing solutions (wd, wda#1 and wda#2) and volumetric NAPL content (θ_{NAPL}) tested.

parameter	washing solution	θ_{NAPL}					
		0.15	**0.20**	**0.25**	**0.30**	**0.35**	**0.40**
α	wd	0.45	0.30	0.49	0.65	0.67	0.55
	wda#1	0.15	0.45	0.45	0.42	0.50	0.55
	wda#2	0.20	0.05	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 (θ_{NAPL}).

Washing solution	θ_{NAPL}=0.15		θ_{NAPL}=0.20		θ_{NAPL}=0.25	
	EF	**MBE**	**EF**	**MBE**	**EF**	**MBE**
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	0001
Washing solution	θ_{NAPL}=0.30		θ_{NAPL}=0.35		θ_{NAPL}=0.40	
	EF	**MBE**	**EF**	**MBE**	**EF**	**MBE**
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≤ θ_{NAPL}≤0.40.