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

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Abstract. The term non-aqueous phase liquid (NAPL) refers to a group of organic compounds with scarce solubility in water. They are the products of various human activities and may be accidentally introduced into the soil system. Given their toxicity level and high mobility, NAPLs constitute a serious geo-environmental problem. Contaminant distribution in the soil and groundwater entails fundamental information for the remediation of polluted soil sites. The present research explored the possible employment of time domain reflectometry (TDR) to estimate pollutant removal in a silt-loam soil that was primarily contaminated with a corn oil as a light NAPL and then flushed with different washing solutions. Known mixtures of soil and NAPL were prepared in the laboratory to achieve soil specimens with varying pollution levels. The prepared soil samples were repacked into plastic cylinders and then placed in testing cells. Washing solutions were then injected upward into the contaminated sample, and both the quantity of remediated NAPL and the bulk dielectric permittivity of the soil sample were determined. The above data were also used to calibrate and validate a dielectric model (the α mixing model) which permits the volumetric NAPL content (θ_{NAPL}; m³/m³) within the contaminated sample to be determined and quantified during the different decontamination stages. Our results demonstrate that during a decontamination process, the TDR device is NAPL-sensitive: the dielectric permittivity of the medium increases as the NAPL volume decreases. Moreover, decontamination progression can be monitored using a simple (one-parameter) mixing model.

1. Introduction

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

Soil flushing is the technical procedure used for treating polluted soils with water, surfactants and co-solvents (such as methanol, ethanol and propanols). Surfactant-enhanced flushing was developed from the conventional pump-and-treat

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

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

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

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

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

36   and Ayatollahi, 2008).

37   Primary remediation entails the removal of the NAPL free phase by pumping. This extraction mechanism returns

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

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

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

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

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

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

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

45   collection of water samples from aquifers (Mercer and Cohen, 1990). Since the above procedures are costly, different

46   dielectric techniques can be used to detect organic contaminants in soils. The most widely accepted geophysical technique,

47   based on the principle of electromagnetic wave (EMW) propagation, is ground penetrating radar (GPR; Knight, 2001).

48   Redman et al. (1991) described some field experiments in the application of GPR to detect NAPL plumes.

49   Rinaldi and Francisca (2006) used a coaxial impedance dielectric reflectometry (CIDR) technique to measure the complex

50   dielectric permittivity in sands contaminated by a paraffin oil. Their research into the dielectric behavior of NAPL-

51   contaminated soils during a decontamination process mainly focused on the removal efficiency of different washing

52   solutions, and on the spectral response of the contaminated medium during the various tests conducted.

53   TDR is a further geophysical device based on electromagnetic wave (EMW) principles that can also be used for this

54   purpose (Endres and Redman et al., 1993; Redman and De Ryck, 1994; Mohamed and Said, 2005; Moroizumi and Sasaki,

55   2006; Francisca and Montoro, 2012). Few experiments have been conducted coupling the TDR technique and NAPL. In

56   these studies estimation of NAPLs using TDR measurements of dielectric properties relies greatly on various mixing

57   models relating the measured dielectric permittivity to the volume fractions of the pore fluids and various soil phases such

58   as solid, water, air and NAPLs (van Dam et al., 2005).

59   Some interesting results were achieved by Persson and Berndtsson (2002) whilst investigating the influence of different

60   LNAPLs on TDR measurements in a homogeneous silica sand under saturated and unsaturated soil conditions.

61   Measurements of both dielectric permittivity and electrical conductivity allowed a method to be developed (the two-step

62   method) which measured the dielectric properties of the system against the amount of NAPL in soils. Comegna et al.

63   (2016) developed a general TDR-based methodology for evaluating the correlations between the dielectric response and

64   the NAPL content in variable saturated soils with different textures and pedological characteristics.

65   The purpose of this study was as follows: i) to investigate a possible extension of TDR technology to assess the effects

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

67   to predict *"in real time"* the volumetric amounts of NAPL (θ_{NAPL}) within the contaminated soil during the

68   decontamination process.

69   **2. Theoretical concepts of TDR**

70   TDR is a geophysical technique employed to determine the dielectric permittivity of liquids and solids (Ferrè and Topp,

71   2002, described this method in detail). In general, the bulk dielectric permittivity is a complex term (ε_r^*), which may be

72   expressed as follows (Robinson et al., 2003):

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

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

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

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

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

77   minimal (Heimovaara, 1994) and the bulk dielectric permittivity ε_b ($\cong$ the real part of permittivity) of a probe of length

78   L is determined from the propagation velocity $v(=2L/t)$ of an electromagnetic wave along the wave guide across the

79   investigated medium by the following expression:

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

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

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

82   calculated as follows:

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

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

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

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

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

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

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

89   properties of NAPL-polluted soils (Redman et al., 1991; Persson and Berndtsson, 2002; Francisca and Montoro, 2012,

90   Comegna et al., 2013a; Comegna et al., 2016; Comegna et al., 2017).

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

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

93   steady-state remediation process.

94   In the present research, we chose the so-called α model (Birchack et al., 1974; Knight and Endress, 1990; Roth et al.,

95   1990):

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

96   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

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

98   1998; Coppola et al., 2013; Coppola et al., 2015). Under the following hypothesis: i) the soil is homogeneous from a

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

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

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

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

102   where ε_{s-ws} is the soil-washing solution permittivity, and ε_s and ε_{ws} are the permittivities of soil particles and washing

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

104   expressed as follows:

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

105   where ε_{s-NAPL} is the permittivity of the soil-NAPL mixture, and ε_{NAPL} is the oil permittivity.

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

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

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

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

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

109   where θ_f is the volumetric fluid content (m³/m³), sum of the volumetric washing solution content (θ_{ws}) and volumetric

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

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

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

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

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

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

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

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

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

4 Materials and Methods

4.1 Soil and fluid properties

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

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

121   1965) was used to determine soil organic C content. The method developed by Miller and Curtis (2006) was used to

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

123   1988). In textural terms, the soil comprised 15.7% sand, 11.6% clay and 72.4% silt. Soil porosity was 0.57%, organic

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

125   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

126   g/cm^3 (at 25°C). Three different removal solutions were employed for soil cleaning: a) a first solution (referred to below

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

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

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

130   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

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

132    $\varepsilon_{soil+wda\#1}$=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

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

136   a three-rod probe 14.5 cm long with a wire diameter of 0.003 m and a wire spacing of 0.02 m, introduced vertically into

137   the soil samples; iii) a testing cell 0.15 m high and 0.08 m in diameter; iv) a peristaltic pump used for upward movement

138   of the washing solution.

4.2.2 Sample preparation and testing procedures

140   Soil was oven dried at 105°C and passed through a 2-mm sieve. Known amounts of soil and oil were mixed together,

141   shaken and then kept for 24 hours in sealed plastic bags to avoid any evaporation and ensure a uniform distribution of oil

142   within the sample and good oil adsorption by the soil matrix. The samples were then allocated to cylindrical boxes. With

143   a view to achieving different degrees of (initial) soil contamination, volumetric NAPL content (θ_{NAPL}) was varied from

144   0.05 to 0.40 (in steps of 0.05). In all, each washing solution comprised eight oil-contaminated soil samples.

145   For all experiments, the soil samples were placed in the vessels in various steps at a bulk density of 1.13 g/cm^3. During

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

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

148   supplied at the rate of 90 cm^3/h, corresponding to a Darcian velocity of 1.8 cm/h. After collection of the outflow from the

149   soil columns, the surnatant NAPL was separated from the washing solution and the quantity of NAPL remediated from

150   the soil was determined.

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

152   set, obtained in the same manner as the calibration data set, was used for model validation.

153   **4.3. Numerical indices for model performance evaluation**

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

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

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

156

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

157   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

158   number of observations.

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

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

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

162   **5. Results and Discussion**

163   **5.1 Influence of washing solution on NAPL removal**

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

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

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

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

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

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

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

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

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

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

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

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

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

177   The NAPL volumes removed for different washing solutions and the initial volumetric content of NAPL are compared in

178   Fig. 3. For all the three cleaning solutions adopted, the experiments ultimately demonstrate (for a fixed θ_{NAPL}) the same

179   results in terms of soil decontamination, and they show that NAPL removal increases with increasing θ_{NAPL}. In some cases

180   (i.e. θ_{NAPL}=0.15, 0.20 and 0.30), contaminated samples flushed with the wda#1 solution yield slightly higher removal

181   efficiency values compared to the samples flushed with wd and wda#2. Martel et al. (1998) suggest the need to investigate

182   the best water-surfactant-alcohol combination in order to enhance NAPL solubilization in soil.

183   **5.2 Model calibration and validation**

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

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

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

187   1. The α parameter of the mixing model was determined, for a fixed θ_{NAPL} value and washing solution, by an optimization

188   procedure based on the least squares technique, and was kept constant for each of the remediation tests developed.

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

190   which is commonly employed for estimating the ε_s of soils (Robinson and Friedman, 2003; Kameyama and Miyamoto,

191   2008; Comegna et al., 2013b).

192   For the sake of brevity, a selection of the experimental $\varepsilon_{s\text{-}ws\text{-}NAPL}$-$\theta_{NAPL}$ relationships (validation dataset) is reported in Fig.

193   4a, b, c, d, e and f. The data in Fig. 4 (except for Fig. 4e, f) show that some of the model-simulated values tend to

194   overestimate the measured data. This behavior is mostly restricted to the beginning of the remediation process, when a

195   rapid change in dielectric permittivity may be observed. This behavior was also verified in other tests (not shown here)

196   and may be explained by invoking both NAPL properties such as liquid density, surface tension and viscosity, and soil

197   properties including moisture content, relative permeability and soil porosity (Brost and DeVaull, 2000; Wang et al.,

198   2013).

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

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

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

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

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

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

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

206   few pore volumes. When this fast mobility mechanism is dominant, the predictions of equation 10 fail.

207   Another possible explanation for this discrepancy between the observed and the predicted permittivity values may be

208   linked to the propensity of NAPL-water mixtures to form macroinclusions in the soil (Persson and Berndtsson, 2002),

209   which affected the initial pore-scale distribution of NAPL, and thus the global dielectric response of the medium (Ferré

210   et al, 1996), during the first remediation stages.

211   However, since the phenomenon is mostly limited to the initial part of the washing process, overall model effectiveness

212   is not compromised, as also shown in Table 2, which summarizes the goodness-of-fit statistical indices, and in Fig. 5a, b,

213   c, d, e, f, where the estimated θ_{NAPL} from equation (10) and the known θ_{NAPL} are illustrated in a series of 1:1 scatter plots.

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

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

216   **6. Conclusions**

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

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

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

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

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

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

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

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

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

226   *flow region* may limit its applicability.

227   The approach requires additional experiments and data sets for model calibration and validation in different pedological

228   contexts, mainly to confirm the potential of the methodology developed. Furthermore, an effort should be made,

229   introducing the water phase, *ab initio* in the experimental setup, to simulate a possible natural contamination-

230 decontamination scenario more accurately. Finally, full field-scale tests should also be conducted to evaluate the

231 performance of equation 10 in real field conditions.

232 *Data availability*. The dataset used in this paper is available on request to alessandro.comegna@unibas.it.

233 *Competing interests*: The authors declare that they have no conflict of interest.

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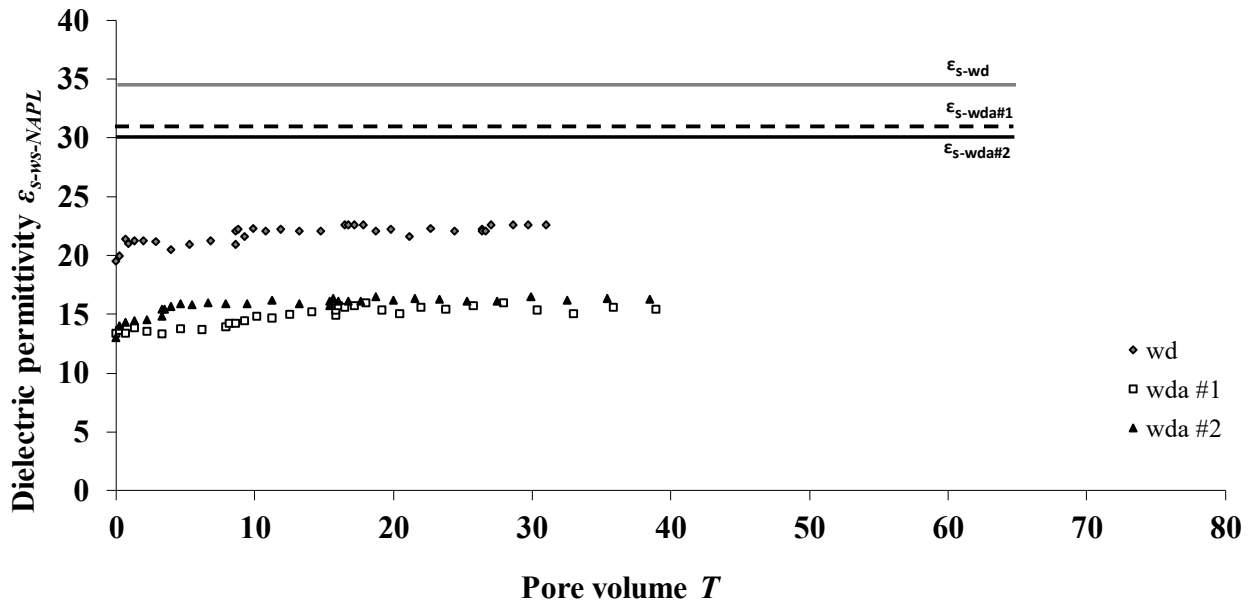
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327

328   **Figures**
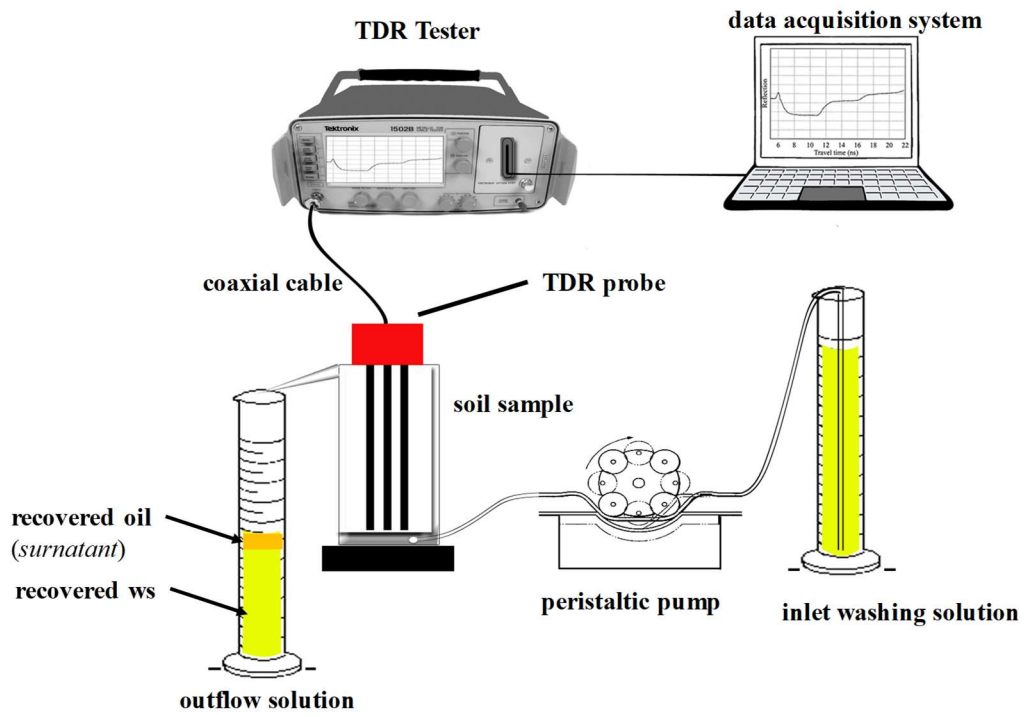
329

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

331

a) $\theta_{NAPL}=0.15$

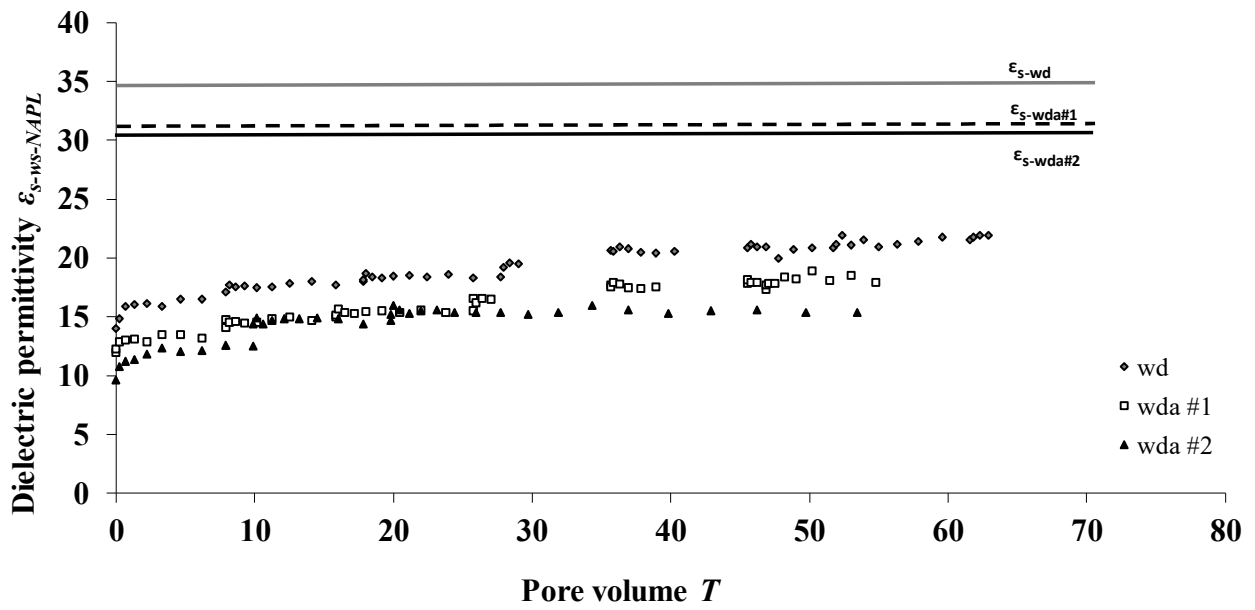b) $\theta_{NAPL}=0.20$

332
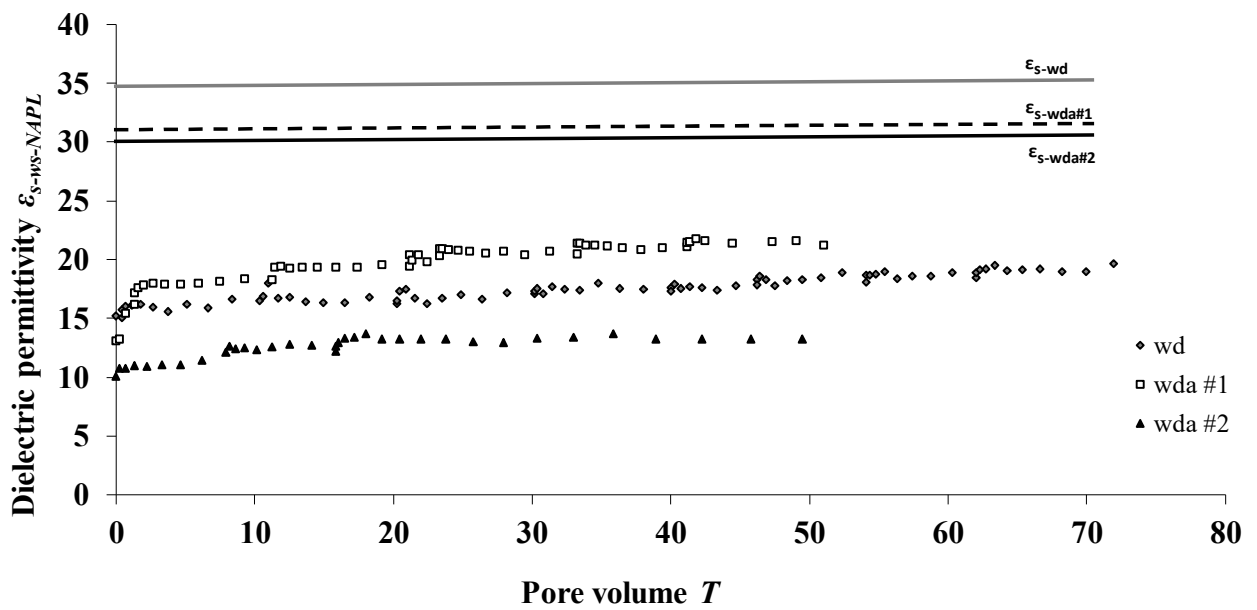
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c) $\theta_{NAPL}=0.25$
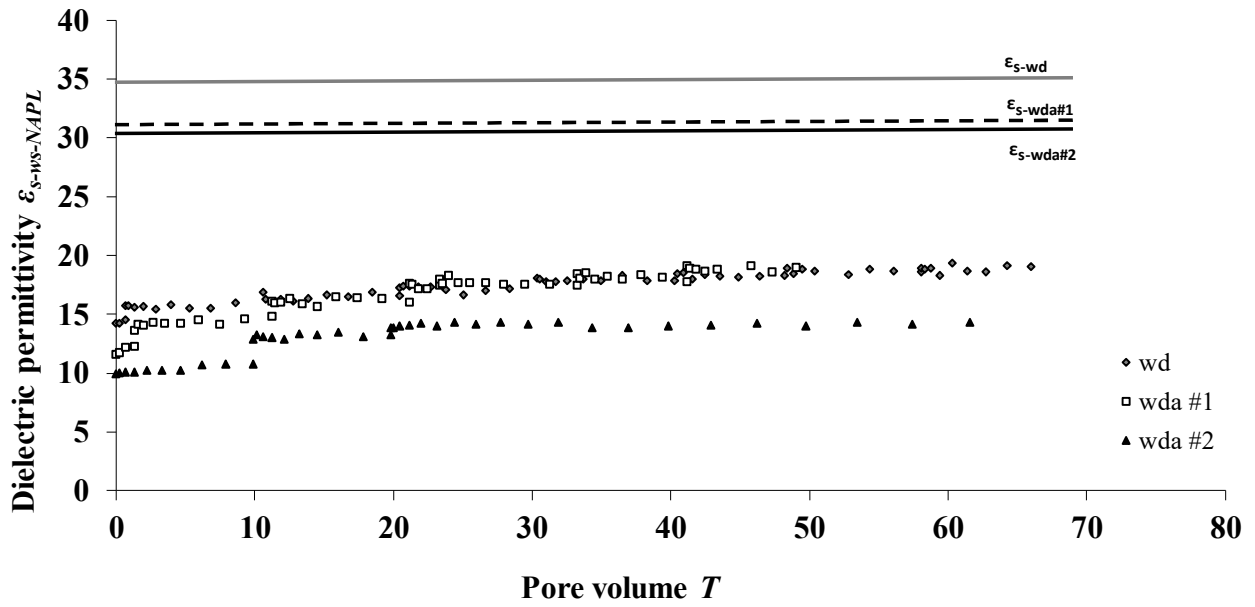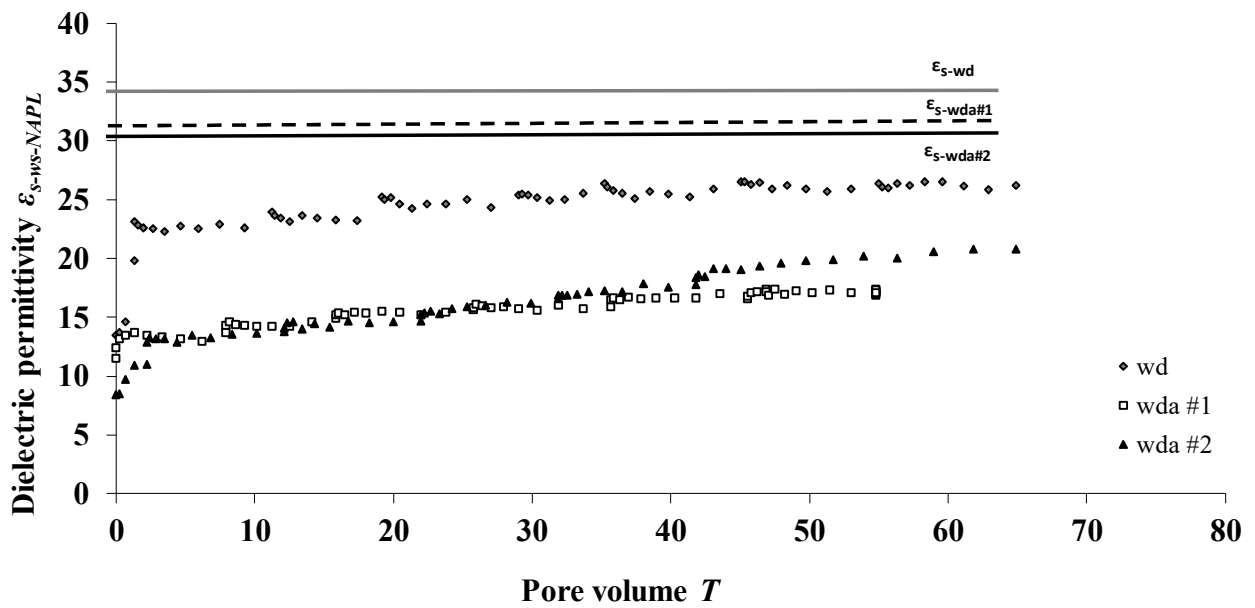

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d) $\theta_{NAPL}=0.30$
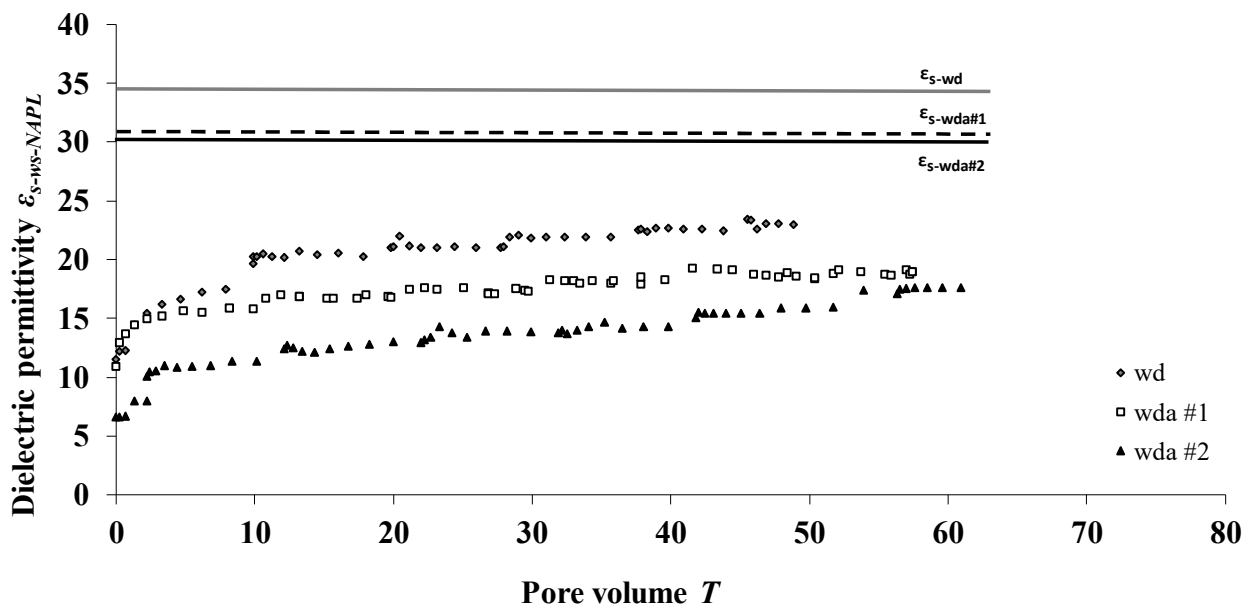
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336

e) $\theta_{NAPL}=0.35$
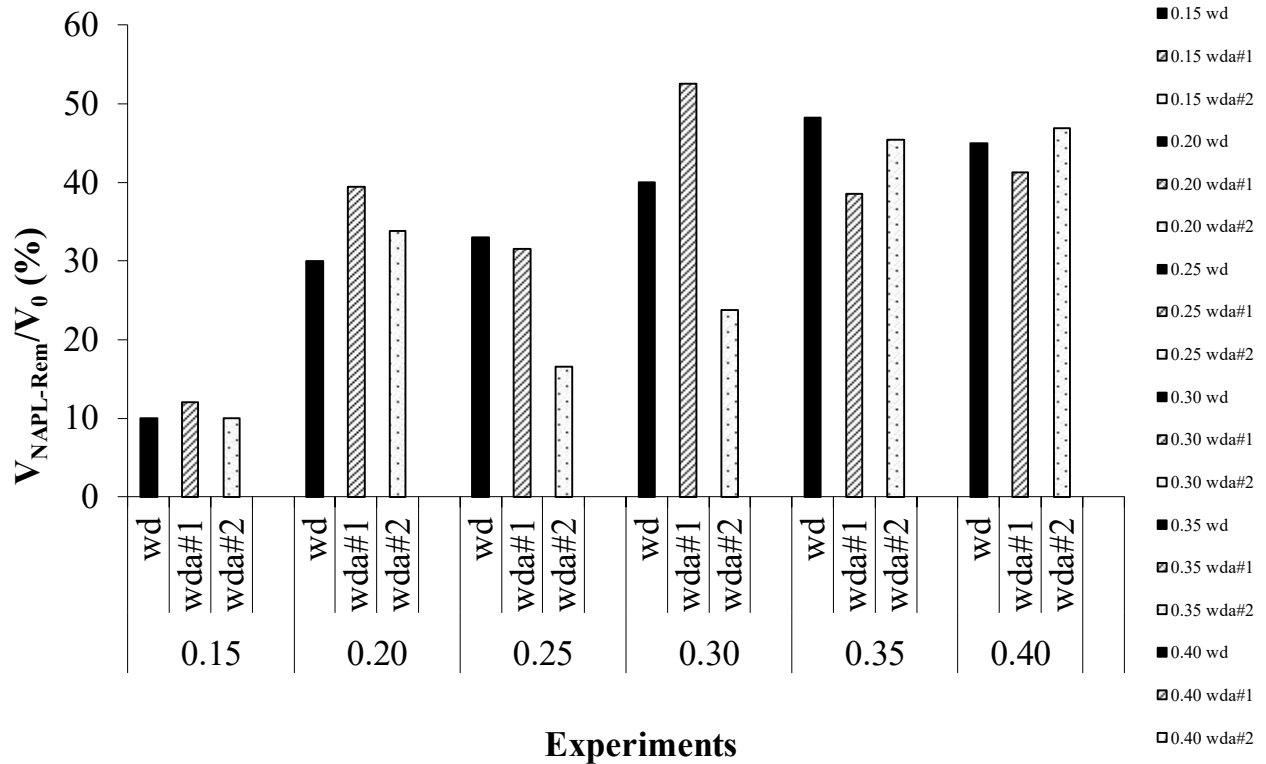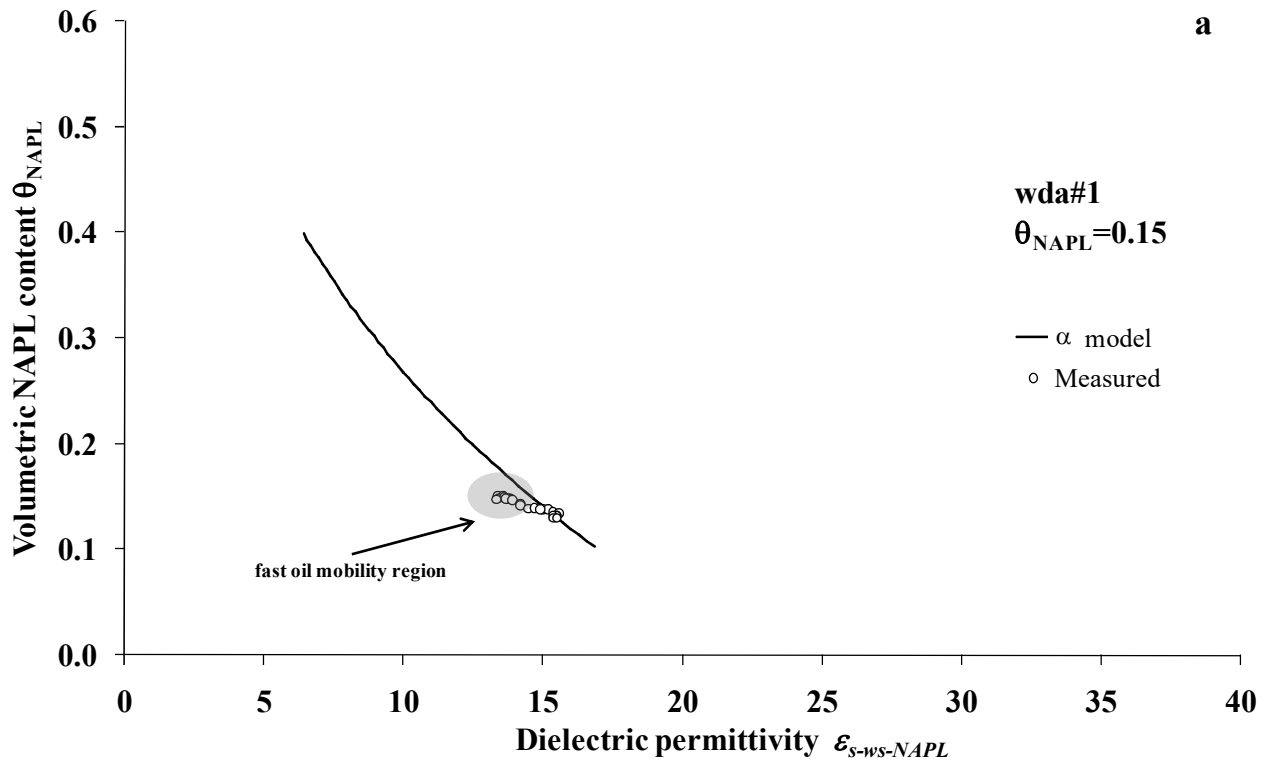

f) $\theta_{NAPL}=0.40$

Figure 2. Selection of experimental relationships between the measured dielectric permittivity ($\varepsilon_{s\text{-}ws\text{-}NAPL}$) 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).
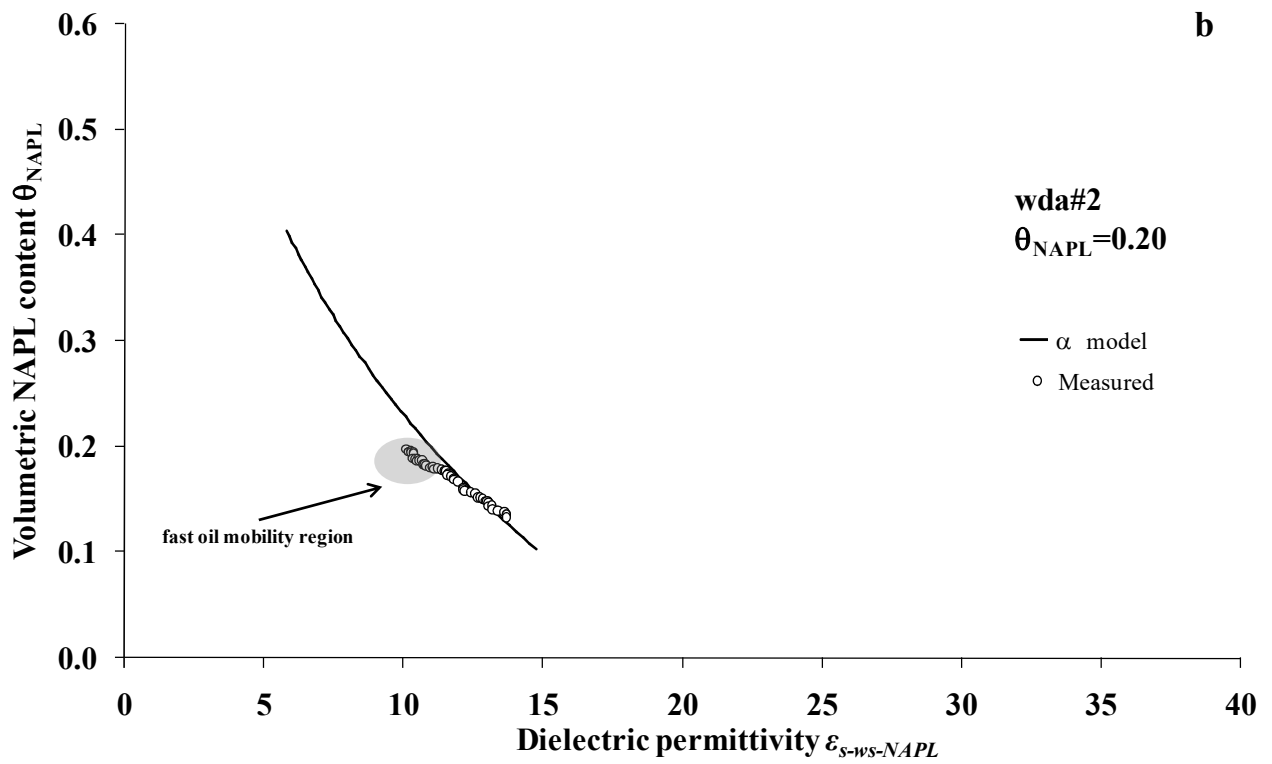
The chart legend (right side) reads:

- 0.15 wd
- 0.15 wda#1
- 0.15 wda#2
- 0.20 wd
- 0.20 wda#1
- 0.20 wda#2
- 0.25 wd
- 0.25 wda#1
- 0.25 wda#2
- 0.30 wd
- 0.30 wda#1
- 0.30 wda#2
- 0.35 wd
- 0.35 wda#1
- 0.35 wda#2
- 0.40 wd
- 0.40 wda#1
- 0.40 wda#2

Y-axis: $V_{NAPL\text{-}Rem}/V_0$ (%)

X-axis: Experiments (0.15, 0.20, 0.25, 0.30, 0.35, 0.40 with wd, wda#1, wda#2)

344

Figure 3. Volume of NAPL recovered ($V_{NAPL\text{-}Rem}$) with respect to the initial volume of NAPL present in the soil sample (V_0) of 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).
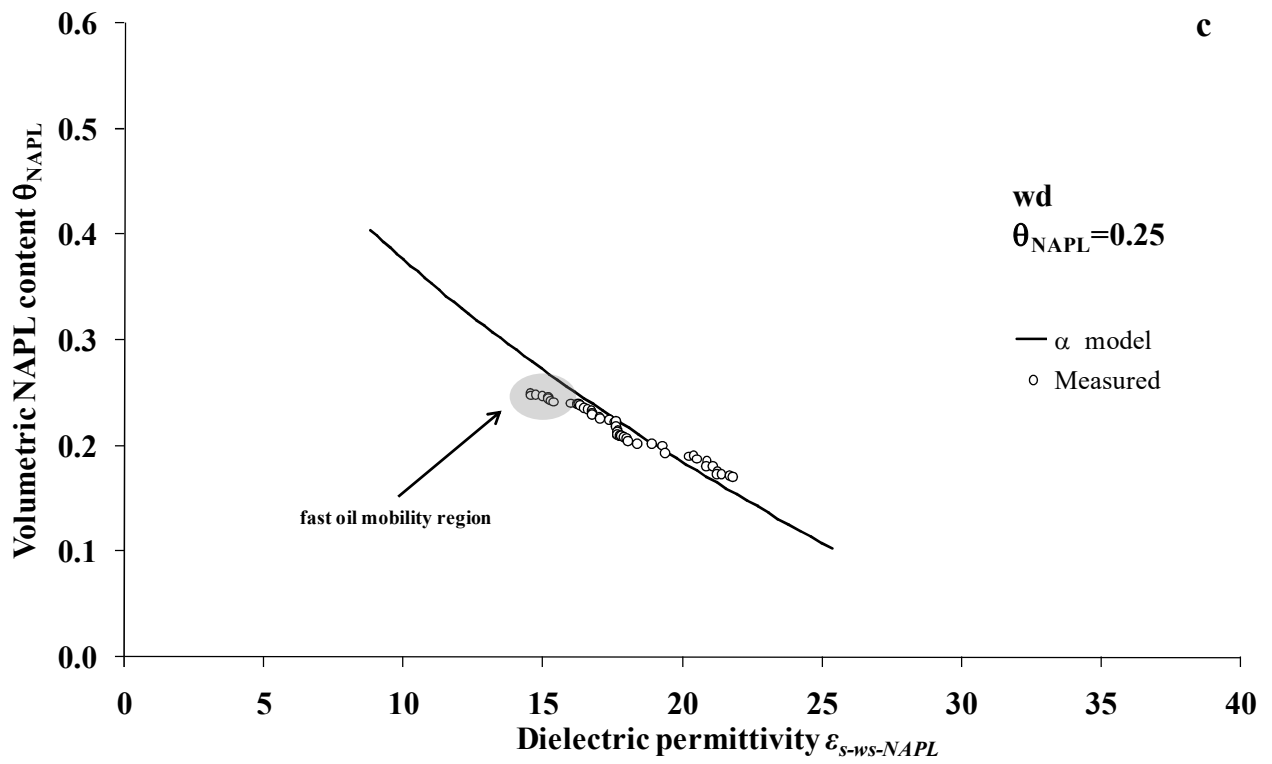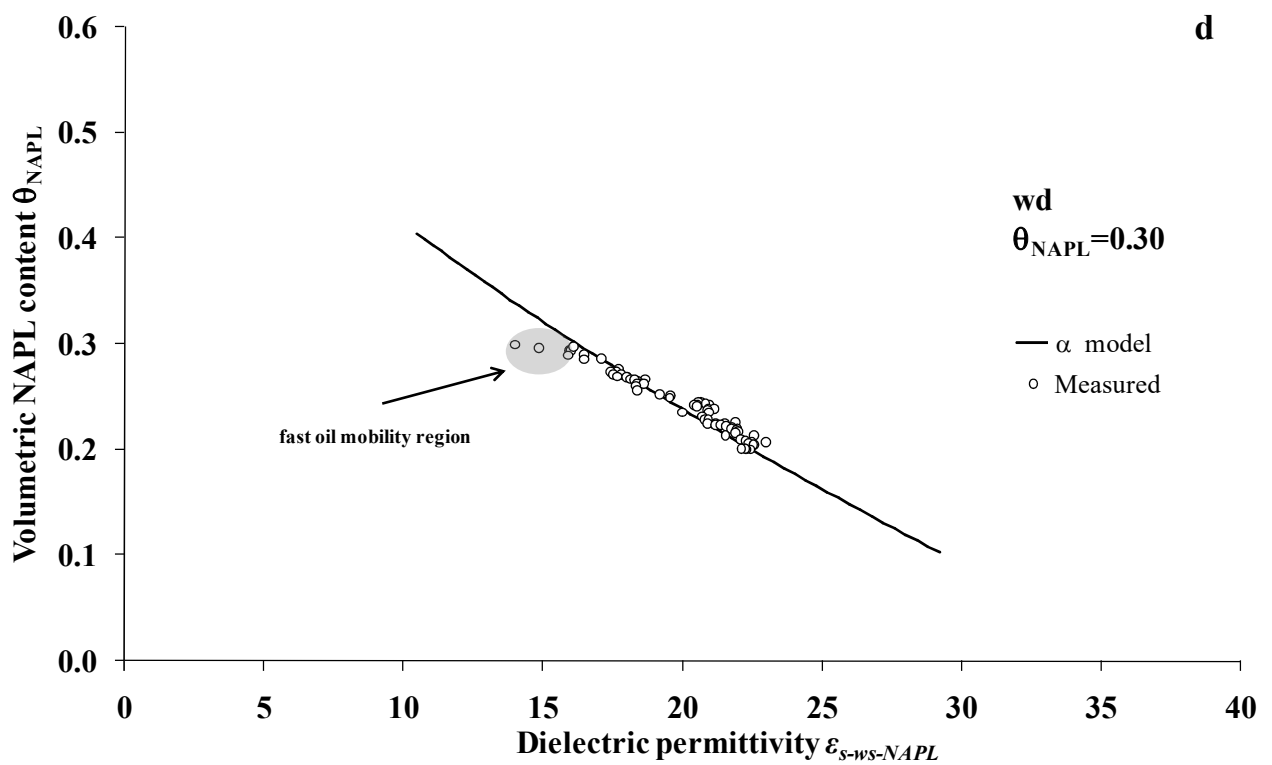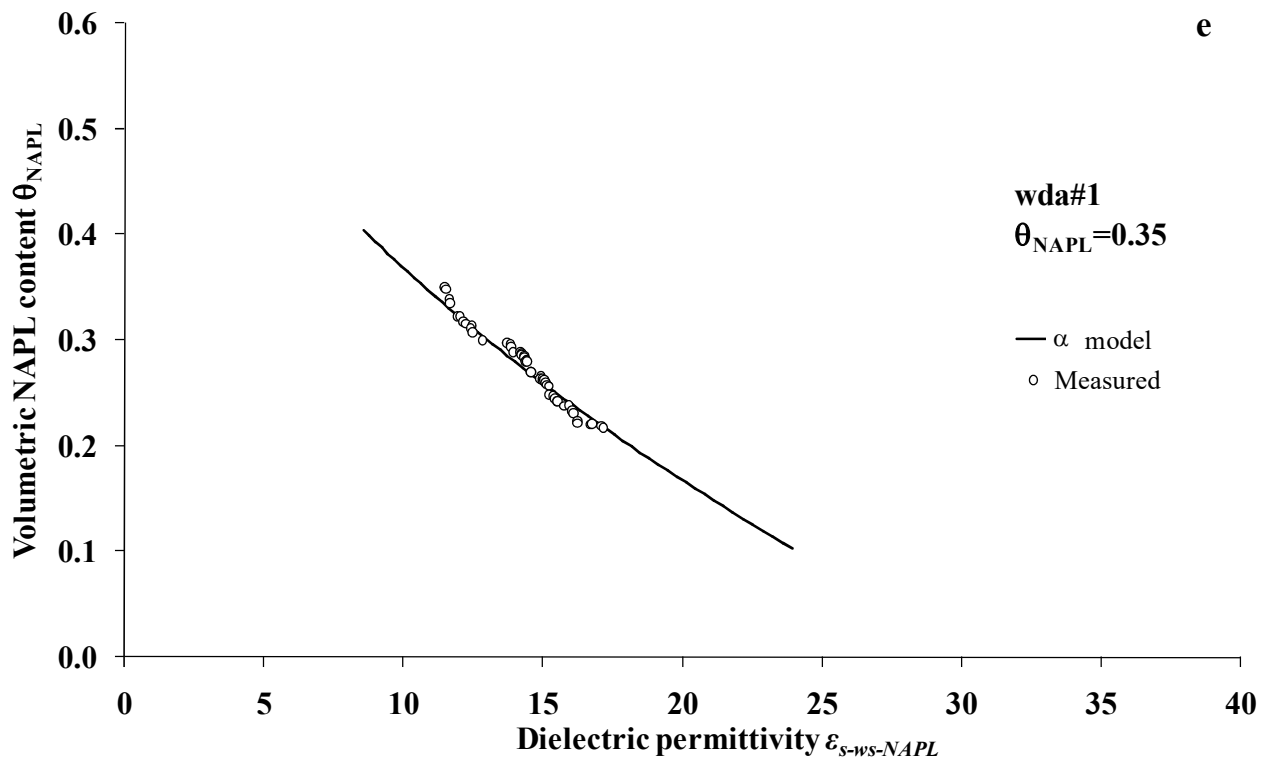
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346

347

fast oil mobility region

wda#1
$\theta_{NAPL}=0.15$

— α model
○ Measured

348

fast oil mobility region

wda#2
$\theta_{NAPL}=0.20$

— α model
○ Measured

349
350

c

wd
$\theta_{NAPL}=0.25$

— α model
○ Measured

fast oil mobility region

Volumetric NAPL content θ_{NAPL}

Dielectric permittivity $\varepsilon_{s\text{-}ws\text{-}NAPL}$

351

d

wd
$\theta_{NAPL}=0.30$

— α model
○ Measured

fast oil mobility region

Volumetric NAPL content θ_{NAPL}

Dielectric permittivity $\varepsilon_{s\text{-}ws\text{-}NAPL}$

352

e

wda#1
$\theta_{NAPL}=0.35$

— α model
○ Measured
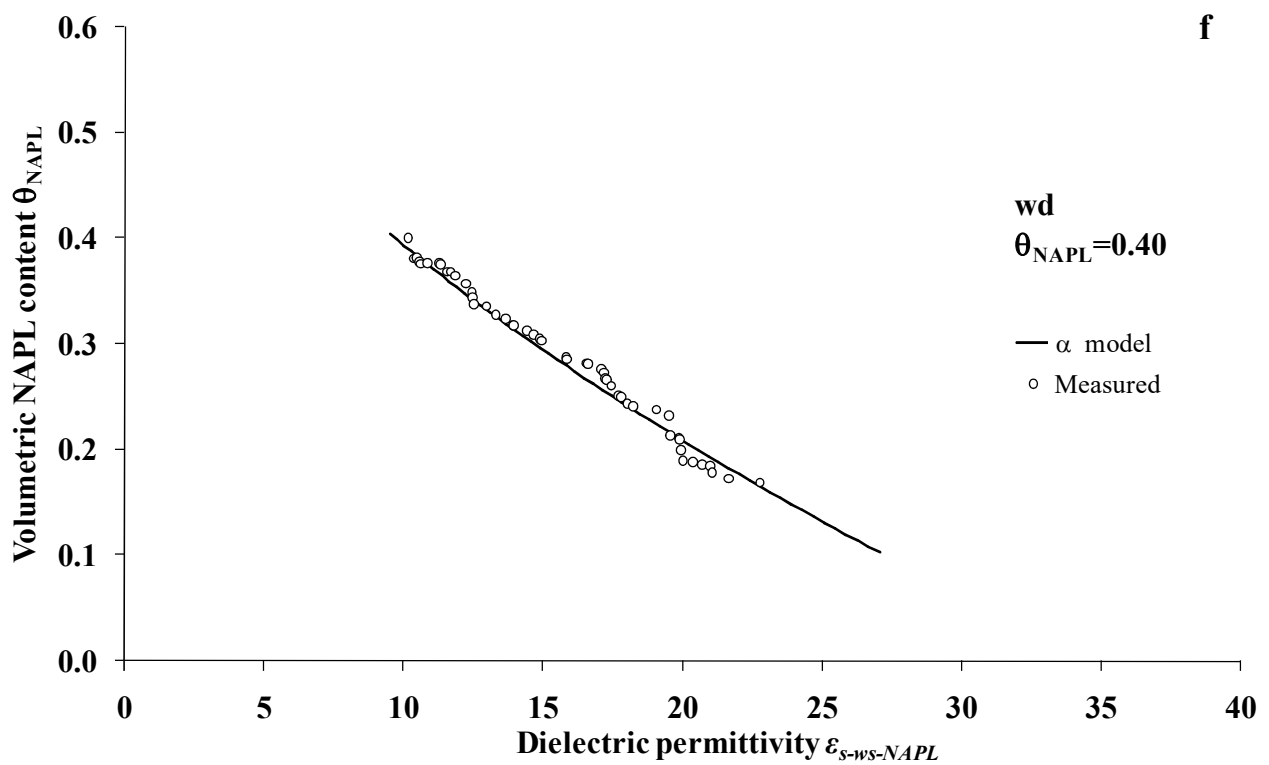
353

f

wd
$\theta_{NAPL}=0.40$

— α model
○ Measured

354
355 **Figure 4 a, b, c, d, e, f. Selection of observed (symbols) and modeled (dashed lines) volumetric NAPL content (θ_{NAPL}) versus**

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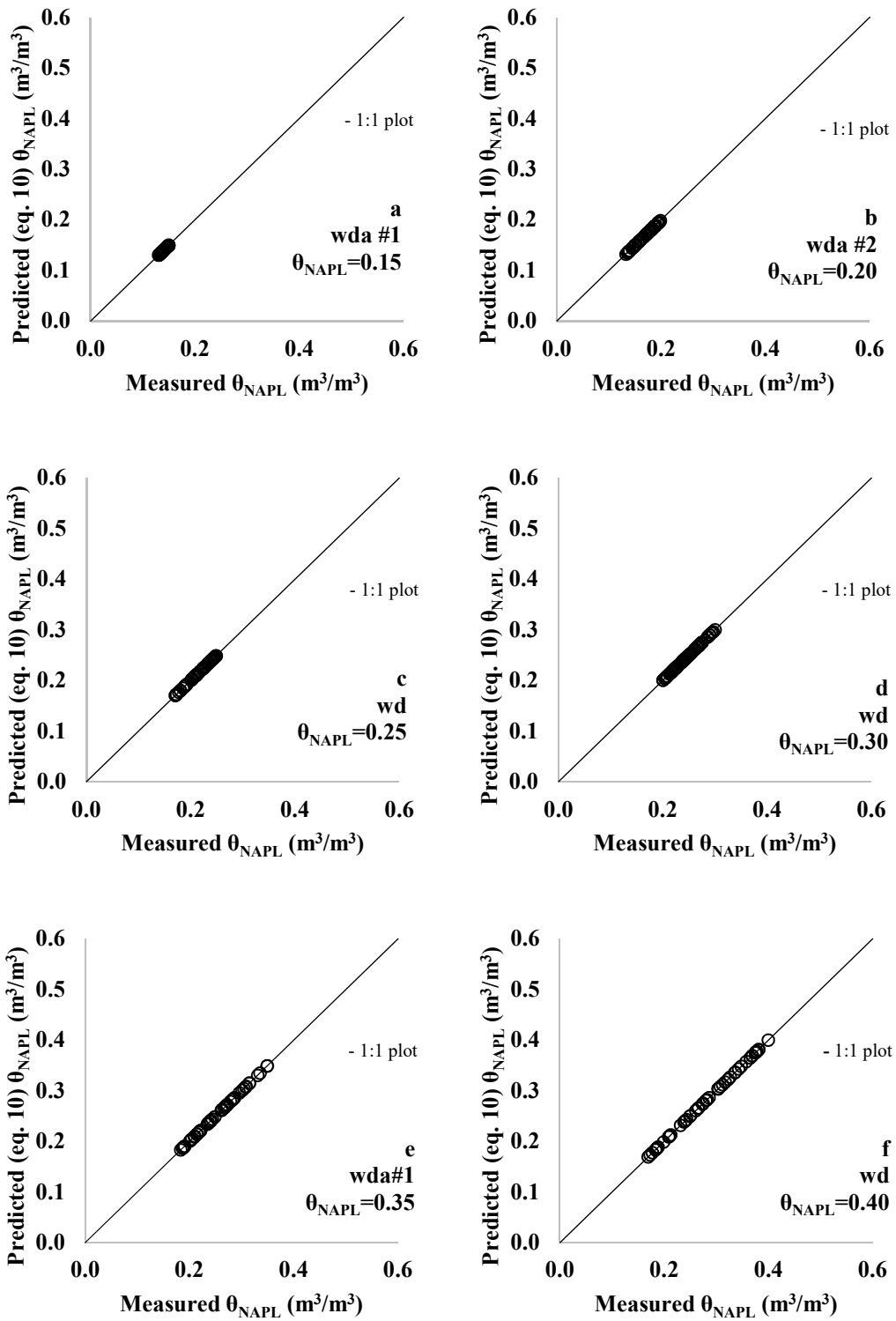
357 **remediation tests.**

358

Figure 5 a, b, c, d, e, f. Measured (equation 10) vs. known volumetric NAPL content (θ_{NAPL}) of contaminated soils, with reference to the different remediation tests in figure 4.

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	0.25	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 (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.