https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences
Discussions

Time domain reflectometry (TDR) for dielectric characterization of olive mill wastewater (OMW) contaminated soils

Alessandro Comegna[a*], Antonio Coppola[a], Giovanna Dragonetti[b]

[a]School of Agricultural Forestry Food and Environmental Sciences (SAFE), University of Basilicata, Potenza, Italy.
[b]Mediterranean Agronomic Institute, Land and Water Division, IAMB, Bari, 70010, Italy.

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

Abstract

Olive mill wastewater (OMW) is a compound originating from oil mills during oil extraction processes. In the Mediterranean area, more than 30 million m^3 of OMW are produced each year, which represents 95-97% of world production. Such volumes of untreated OMW are usually directly disposed of into drainage systems, water bodies (such as streams, lagoons and ponds), or else are sprinkled on soils, causing potentially severe environmental problems to soils and groundwater. There is thus a serious waste management problem related to the olive oil industry, such practices no longer being acceptable. In the case of on-land OMW disposal, characterization and identification of this contaminant in soils is a fundamental task especially with a view to maintaining the integrity and quality of agroecosystems. In recent years, soils have been extensively studied to detect contaminants by using various geophysical methods. Among such techniques, time domain reflectometry (TDR) has shown, in different contexts, evident sensitivity and resolution capability for characterizing contaminated soil sites. In order to further exploit the potential of the TDR technique, in the present study we conducted a series of laboratory-controlled tests to explore how OMW influences the dielectric response of contaminated soils. The research led to the development of an empirical dielectric model to estimate the presence of OMW in variably saturated-contaminated soils with different textures and pedological features.

1. Introduction

The olive oil industry is one of the chief agricultural sectors in the Mediterranean basin. Every year about 2 million tons of olive oil are produced (Piotrowska et al., 2011), and this production is regularly increasing (Caputo et al., 2013; Sahraoui et al., 2015).

The extraction process of olive oil generates olive mill wastewater (OMW) which is a mixture of vegetation water initially present in the drupes and the water used during the different stages of oil extraction (Colarieti et al., 2006; Sahraoui et al., 2015). The volumes of OMW produced depend on the extraction method (i.e. traditional pressing, or two-phase/three-phase centrifugation systems) and may vary between 40 and 100 liters per 100 kg of processed olives (Kavvadias et al., 2014).

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences
Open Access
Discussions

OMW is a waste product with a high pollution load. It is generally characterized by a low pH, high salinity and organic content, high chemical and biological oxygen demand, a high concentration of suspended solids, and abundant presence of mineral elements especially nitrogen, phosphorus, potassium, calcium and magnesium (Mekki et al., 2006). Furthermore, considerable concentrations of phenolic compounds may be detectable in this wastewater, such concentrations usually varying between 1.0 and 10 g/l (Capasso et al., 1992; Piotrowska et al., 2011).

Due to its complex composition, OMW cannot be directly added to domestic wastewater treatment plants (Caputo et al., 2013), and there is a lack of practical and sustainable alternative solutions to OMW disposal. This aspect represents a potential environmental problem for olive oil-producing countries (Kavvadias et al., 2014). One solution adopted for OMW discharge which has been legally regulated in several countries (e.g. Italy under *Legislative Decree 152/2006*) is its use for soil fertilization. However, the benefits conferred by this practice are questionable due to its proven toxic effect on the soil biota (Isidori et al., 2005). Furthermore, long-term OMW application may cause severe alteration of soil chemical and physical properties.

For all the above reasons, the problem of evaluating the spatial and temporal distribution of OMW in situ represents a research topic of great interest. It can now be dealt with, for example, by using non-invasive geophysical methods (Huisman et al., 2003; Robinson et al., 2003).

Starting from the findings of Comegna et al. (2016), in this study we show the suitability of the TDR technique in determining the presence of OMW in a contaminated medium. Indeed, we observed that OMW affected the dielectric behavior of the contaminated soil. A direct dependence of the bulk electrical conductivity (EC_b) on OMW concentration was experimentally documented. This dependence was investigated in depth and exploited to develop, calibrate and validate a dielectric logarithmic model, which provides, under different levels of soil contamination, the possibility of quantifying the presence of OMW.

2. Dielectric permittivity and electrical conductivity determination using TDR

TDR allows concomitant determination of soil bulk dielectric permittivity (ε_b) and soil bulk electrical conductivity (EC_b) on the same observation volume (Dalton et al., 1984). The ε_b determined by TDR requires measurement of the propagation velocity and attenuation of an applied electromagnetic wave along a transmission line in the soil (Topp et al., 1980). At TDR frequencies between 200 MHz to 1.5 GHz, the dielectric losses can be assumed to be negligible, and ε_b along a wave-guide line of length L is a function of the propagation velocity v (=$2L/t$) according to:

$$\varepsilon_b = \left(\frac{c}{v}\right)^2 = \left(\frac{ct}{2L}\right)^2 \tag{1}$$

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences
Discussions

where c (=3 × 10^8m s^{-1}) is the velocity of an electromagnetic wave in vacuum, and t is the travel time, that is the time that the TDR signal requires to travel to and from the wave-guide.

Attenuation of the TDR signal can also be used as a measure of EC_b. According to the *thin section approach*, originally proposed by Giese and Tiemann (1975), EC_b can be calculated as follows:

$$EC_b = \frac{\varepsilon_0 c}{L}\frac{Z_0}{Z_c}\left(\frac{2V_0}{V_f} - 1\right) \tag{2}$$

where ε_0 is the dielectric permittivity of free space, Z_0 is the characteristic probe impedance, Z_c is the TDR cable tester output impedance, V_0 is the incident pulse voltage, and V_f is the return pulse voltage at relatively long distances along the waveform (Or et al., 2004).

3. Volumetric OMW content determination in soils

Detection of contaminants in multiphase soil systems by means of geophysical methods is problematic even if the pollutant is homogeneously distributed within the soil matrix (Redman and De Ryck, 1994; Persson and Berndtsson, 2002; Haridy et al., 2004; Moroizumi and Sasaki, 2006; Francisca and Montoro, 2012, amongst others). The TDR technique has the potential to reveal the presence of a contaminant in soils (see Comegna et al., 2013a; Comegna et al., 2016, Comegna et al., 2017; Comegna et al., 2019). However, as the TDR waveform only returns *"aggregate"* information that depends on all the distinct phases involved (Comegna et al., 2016), the challenge is to find a way to extrapolate the dielectric weight of the pollutant from the whole dielectric response (Comegna et al., 2013b).

In the present research, we followed the same methodological approach as that of Comegna et al. (2016), which was developed to detect and quantify the presence of organic contaminants such as non-aqueous phase liquids (NAPLs) in variable saturated soils. We observed that the presence of an NAPL in the soil affected the dielectric response of the medium in terms of bulk dielectric permittivity (ε_b decreases as the amount of NAPL increases). Analysis of dielectric NAPL behavior allowed us to establish a univocal relationship between the amount of NAPL in the contaminated soil (θ_{NAPL}), the bulk dielectric permittivity of the multiphase medium (ε_b), and the final value of the reflection coefficient (ρ_f) which, as known, can only be determined at long TDR-travel times (Or et al. 2004). Starting from these findings, we concentrated our efforts on OMWs, which are fluids with dielectric characteristics quite unlike those of NAPLs.

In the case of OMWs, we observed that their presence in soils scarcely alters the global dielectric response of the medium in terms of permittivity, which for increasing amounts of OMW, varies randomly (see section 5.1 below). By contrast, at higher propagation times (i.e. those useful for TDR-EC_b calculation), a functional relationship between θ_{OMW} and EC_b can be hypothesized. Such considerations allowed us to develop a logarithmic relationship between EC_b, calculated in the contaminated medium, and the so-called relative volume of OMW in water (β):

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

$$\beta = a\,ln(EC_b) + b \qquad (3)$$

where *a* and *b* are coefficients which have to be experimentally determined, and the relative volume of OMW in water, β, is defined as (Rinaldi and Francisca, 2006):

$$\beta = \frac{\theta_{OMW}}{(\theta_w + \theta_{OMW})} = \frac{\theta_{OMW}}{\theta_f} \qquad (4)$$

where θ_f and θ_w are respectively the volumetric content of the whole fluid phase and the volumetric water content. Values of β vary in the range between 0 for a soil-water mixture and 1 for a soil-OMW mixture.

Substituting equation 4 into equation 3, θ_{OMW} can be calculated as:

$$\theta_{OMW} = \theta_f[a\,ln(EC_b) + b] \qquad (5)$$

We observed that, for a selected soil, coefficients *a* and *b* depend on θ_f values (see section 5.3 below), in the sense that for each θ_f a pair of *a* and *b* parameters can be estimated. Further data examination coupled with statistical analysis based on an ANCOVA test, conducted at a significance level of α=0.05 (for more details see Comegna et al., 2016), allowed us to assume the coefficient *a* of equation 5 to be constant ($a = a_c = cost$, thus independent of θ_f), whereas the term *b* can be related to θ_f via a second-order polynomial equation:

$$b = b_1\theta_f^2 + b_2\theta_f + b_3 \qquad (6)$$

where b_1, b_2 and b_3 are fitting parameters of the equation.

As a result, θ_{OMW}can be finally written as follows:

$$\theta_{OMW} = \theta_f\left[a_c + ln(EC_b) + \left(b_1\theta_f^2 + b_2\theta_f + b_3\right)\right] \qquad (7)$$

Using Equation 7 θ_{OMW} may be estimated once the bulk electrical conductivity (EC_b) and the volumetric fluid content (θ_f) of the contaminated medium are determined.

4. Materials and methods

4.1 Soil and OMW properties

The soils selected to conduct the present research were a loam *Eutric Cambisol* (IUSS Working Group WRB, 2006) and a silt-loam *Anthrosol* (IUSS Working Group WRB, 2006, both of which are found in southern Italy. Table 1 reports the main physical and chemical properties of the two soils, while Table 2 shows a characterisation of the OMW employed in the laboratory experiments.

Total polyphenol content was obtained using the Folin-Ciocalteu colorimetric method (APHA, 1995). Absorbance was measured at 760 nm with a SpectroVis Plus (Vernier Software & Technology) UV-visible spectrophotometer. Total nitrogen (TN), total organic content (TOC) and chemical oxygen demand (COD) were determined by using the IRSA-

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

CNR 4060 method (IRSA-CNR, 2003), the IRSA-CNR 5040 method (IRSA-CNR, 2003) and the IRSA-CNR 5130 method (IRSA-CNR, 2003), respectively.

4.2. Experimental equipment

The experimental apparatus consists of a TDR unit (Tektronix 1502C cable tester) and a three-wire TDR probe (with wave guides 14.5 cm long) connected via an RG58 coaxial cable to the tester. The TDR signals once acquired were post-processed for ε_b and EC_b calculation with a homemade Matlab code. The laboratory system used during the experiments is illustrated in Figure 1.

4.3. Laboratory experiments

The laboratory experiments were carried out on repacked soil samples. Simultaneous measurements of ε_b and EC_b have been made on soil samples that were adequately prepared as a mix of known amounts of soil and volumetric water (θ_w) and OMW (θ_{OMW}) content, following the scheme of table 3. Soil samples were oven dried at 105°C and sieved at 2 mm. The different combinations of soil, water and OMW were mixed and then kept for 24 hours in plastic bags to ensure that OMW and water were uniformly distributed within the soil. Since the TDR signal (hence the dielectric response of a medium) is influenced by soil porosity ϕ (see, for example, Jung et al., 2013), soil samples were cautiously placed in plastic cylindrical containers (15 cm high and 9.5 cm in diameter) until the bulk densities of 1.27 g cm^{-3} (*Eutric Cambisol*) and 1.13 g cm^{-3} (*Anthrosol*) were reached. Finally, a TDR probe was inserted vertically into the samples. The same procedure was replicated on a second set of samples for model validation. The laboratory tests were conducted at a constant temperature of 25°C.

4.4. Model performance evaluation

Three statistical indices were selected and calculated for evaluating model performance (equation 7): i) mean absolute percentage error (*MAE*), ii) model efficiency (*EF*), and iii) maximum absolute percentage error (*ME*), determined according to the following relations (Legates and McCabe Jr, 1999; Goovaerts et al., 2005):

$$MAE(\%) = \frac{\sum_{i=1}^{N} |E_i - O_i|}{N} \cdot 100 \quad (8)$$

$$EF = 1 - \frac{\sum_{i=1}^{N} (E_i - O_i)^2}{\sum_{i=1}^{N} \left(O_i - \overline{O}\right)^2} \quad (9)$$

$$ME(\%) = MAX|E_i - O_i| \cdot 100 \quad (10)$$

where E_i is the prediction (model-simulated data) and O_i is the true value (observed data), $\overline{O}$ is the mean of the observed data, and N is the number of observations.

Hydrology and Earth System Sciences
Discussions

5. Results and discussion

5.1 Dielectric characterization of OMW-contaminated soil

Figures 2a and b show respectively the experimental ε_b vs θ_f and EC_b vs θ_f relationships, obtained for selected β values. As can be observed in Figure 2a, in the observed θ_f domain (i.e. $0.05\leq \theta_f \leq 0.40$), the measured dielectric permittivity of OMW-contaminated soil samples increases overall as the volumetric fluid content increases. At the same time, for fixed θ_f values, it may be noted that the calculated ε_b values more or less overlap. This means that differences in β (i.e. differences in soil contamination levels) do not affect the dielectric response of the contaminated medium in terms of permittivity. In other words, ε_b is not OMW-sensitive. By contrast, on observing the graphs in figures 2b, especially in the θ_f range 0.20-0.40, a clear correlation appears between EC_b and θ_f and, for a fixed θ_f, between EC_b and β. Indeed, EC_b values increase with θ_f and with β.

5.2 Model calibration and validation

In order to confirm the approach adopted, as described in section 3 above, figures 3a and b show the experimental (colored dots) and inferred (continuous line) β vs $\ln(EC_b)$ relationships for different values of the volumetric fluid content (θ_f). On such data, an ANCOVA analysis performed at a significance level of 0.05 confirmed a parallelism among the β-$\ln(EC_b)$ regression lines. As a consequence, a common slope a_c can be assumed for each of the tested soils. Furthermore, as demonstrated by figures 4a and b, the intercepts b of the different β-$\ln(EC_b)$ relationships can be suitably inferred from a second order polynomial equation (R^2 is 1.0 for the *Eutric Cambisol* and 0.99 for the *Anthrosol*). Coefficients a_c, b_1, b_2 and b_3 resulting from model calibration are shown in table 4.

As mentioned above, model reliability was evaluated by applying the model with the calibrated coefficients to an independent validation dataset. Figure 5 compares the computed (equation 7) and the measured volumetric OMW content. The corresponding statistical indices are reported in table 5. Overall, both figure 5 and table 5 confirm the satisfactory agreement of the model predictions with the experimental data: model efficiency is very close to 1 for both soils; maximum absolute percentage error and mean absolute error are, respectively, 8.8% and 3.4% for the *Eutric Cambisol* and 6.5% and 2.8% for the *Anthrosol*.

Considering the complexity of the modeled process, these results are appreciable and validate the scientific consistency of the approach and its general applicability to determining volumetric OMW content in a contaminated medium by means of TDR.

6. Conclusions

In the present study, we conducted a series of laboratory experiments on soil samples subjected to variable degrees of OMW contamination. Measurements of soil bulk dielectric permittivity (ε_b) and soil bulk electrical conductivity (EC_b)

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

were simultaneously taken, via TDR, within each investigated sample. The experimental framework was set up in order to accomplish, as far as possible, a full factorial plan of electromagnetic characterization of the OMW-contaminated soil samples in the 0.05≤ θ_f ≤0.40 domain. It was shown that the presence of olive mill wastewater in the soil had a low or null effect on ε_b. However, an interesting correlation between θ_{OMW} and EC_b was found. On the basis of the results attained, a dielectric model (equation 7) which allows the volumetric OMW content to be quantified was developed and appropriately validated. The research in question can be considered an enhancement in monitoring soil affected by OMW contamination using the time domain reflectometry technique.

In order to expand the available data set, further experiments should be conducted, for example in other pedological contexts. Full field-scale tests should also be carried out to evaluate the performance of the proposed model in real field conditions.

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

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

References

APHA (American Public Health Association).: Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995. Washington, D.C.

Capasso, R., Cristinzio, G., Evidente, A., and Scognamiglio, F.: Isolation, spectroscopy and selective phytotoxic effects of polyphenols from vegetable waste waters. Phytochemistry, 31, 4125-4128, 1992.

Caputo, M. C., De Girolamo, A. M., and Volpe, A.: Soil amendment with olive mill wastes: Impact on groundwater. J. Environ Manage., 131, 216-221, 2013.

Colarieti, M. L., Toscano, G., and Greco, G.: Toxicity attenuation of olive mill wastewater in soil slurries. Environ. Chem. Lett. 4, 115-118, 2006.

Comegna, A., Coppola, A., Dragonetti, G., and Sommella, A.: Dielectric response of a variable saturated soil contaminated by Non-Aqueous Phase Liquids (NAPLs). Procedia Environmental Sciences, 19, 701-710, 2013a.

Comegna, A., Coppola, A., Dragonetti, G., Severino, G., and Sommella A.: Basile A. Dielectric properties of a tilled sandy volcanic-vesuvian soil with moderate andic features. Soil Till. Res., 133, 93-100, 2013b.

Comegna, A., Coppola, A., Dragonetti, G., and Sommella, A.: Estimating non-aqueous phase liquid (NAPL) content in variable saturated soils using time domain reflectometry (TDR). Vadose zone J., 15, doi:10.2136/vzj2015.11.0145, 2016.

Comegna, A., Coppola, A., Dragonetti, G., Severino, G., and Sommella, A.: Interpreting TDR Signal Propagation through Soils with Distinct Layers of Nonaqueous-Phase Liquid and Water Content. Vadose Zone J. 16(13). doi:10.2136/vzj2017.07.0141.

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Comegna, A., Coppola, A., Dragonetti, G., and Sommella, A.: 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). Hydrol. Earth Syst. Sci., 23, 3593–3602, https://doi.org/10.5194/hess-23-3593-2019, 2019.

Dalton, F. N., Herkelrath, W. N, Rawlins, D. S., and Rhoades, J. D.: Time-domain reflectometry: Simultaneous measurements of soil water content and electrical conductivity with a single probe. Science, 224, 989-990, 1984.

Francisca, M., and Montoro, M. A.: Measuring the dielectric properties of soil-organic mixtures using coaxial impedance dielectric reflectometry, J. Appl. Geophys., 80, 101–109, 2012.

Giese, K., and Tiemann, R.: Determination of the complex permittivity from thin-sample time domain reflectometry: Improved analysis of the step response waveform. Adv. Mol. Relaxation Processes, 7, 45-49, 1974.

Goovaerts, P., AvRuskin, G., Meliker, J., Slotnick, M., Jacquez, G., and Nriagu, J.: Geostatistical modeling of the spatial variability of arsenic in groundwater of southeast Michigan. Water Resour. Res., 41, W07013, doi:10.1029/2004WR003705, 2005.

Haridy, S. A., Persson, M., and Berndtsson, R.: Estimation of LNAPL saturation in fine sand using time-domain reflectometry. Hydrological Sciences, 49, 987-1000, 2004.

Huisman, J. A., Hubbard, S.S., Redman, J.D., and Annan, A.P.: Measuring soil water content with ground penetrating radar: A review. Vadose Zone J., 2, 476-491, 2003.

IUSS Working Group WRB.: World reference base for soil resources 2006: A framework for international classification, correlation and communication. 2nd ed. World Soil Resour. Rep. 103, FAO, 2006, Rome.

Kavvadias, V., Doula, M., and Theocharopoulosm S.: Long-Term Effects on Soil of the Disposal of Olive Mill Waste Waters (OMW). Environmental Forensic, 15, 37-51, 2014.

Jung, S., Drnevich V. P., and Abou Najm, M. R.: New methodology for density and water content by time domain reflectometry. J. Geotech. Geoenviron. Eng., 139, 659–670. doi:10.1061/(ASCE)GT.1943-5606.0000783, 2013.

IRSA-CNR.: Metodi analitici per le acque. Volume Primo, 2003, pp 781-789.

Isidori, M., Lavorgna, M., Nardelli, A., and Parrella, A.: Model study on the effect of 15 phenolic olive mill wastewater constituents on seed germination and vibro fischeri metabolism. J. Agric. Food Chem., 53, 8414-8417, 2005.

Legates, D. R., and McCabe Jr, G. J.: Evaluating the use of "goodness-of-fit" measures in hydrologic and hydroclimatic model validation. Water Resour. Res., 35, 233-241, 1999.

Mekki, A., Dhouib, A., and Sayadi, S.: Changes in microbial and soil properties following amendment with treated and untreated olive mill wastewater. Microbiol. Res., 161, 93-101. 2006.

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Moroizumi, T., and Sasaki, Y.: Estimating the nonaqueous-phase liquid content in saturated sandy soil using amplitude domain reflectometry. Soil Sci. Soc. Am. J., 72, 1520-1526, 2006.

Or, D., Jones, S. B., VanShaar, J. R., Humphries, S., and Koberstein, L.: Win TDR Soil Analysis Software User Guide. 2004, Utah State University.

Piotrowska, A., Rao, M. A, Scotti, R., and Gianfreda, L.: Changes in soil chemical and biochemical properties following amendment with crude and dephenolized olive mill waste water (OMW). Geoderma, 161, 8-17, 2011.

Persson, M., and Berndtsson, R.: Measuring nonaqueous phase liquid saturation in soil using time domain reflectometry, Water Resour. Res, 38, doi: 10.1029/2001WR000523, 2002.

Redman, J. D., and De Ryck, S. M.: Monitoring non-aqueous phase liquids in the subsurface with multilevel time domain reflectometry probes. Proc Symp. on Time Domain Reflectometry in Environmental, Infrastructure, and Mining Applications, Evanston, IL. Spec. Publ. SP19-94. U.S. Bur. of Mines, Washington, DC, 1994.

Rinaldi, V. A., and Francisca, F. M.: Removal of Immiscible Contaminants from Sandy Soils monitored by Means of Dielectric Measurements. J. Environ. Eng., 132, 931-939, 2006.

Robinson, D. A., Jones, S. B., Wraith, J. M., and Or, D.: A review of advances in dielectric and electric conductivity measurements using time domain reflectometry. Vadose Zone J., 2, 444-475, 2003.

Sahraoui, H., Kanzari, S., Hachicha, M., and Mellouli, H. J.: Olive Mill Wastewater Spreading Effects On Hydraulic Soil Properties. The experiment, 30, 2002-2011, 2015.

Topp, G. C., Davis, J. L., and Annan, A. P.: Electromagnetic determination of soil water content: Measurement in coaxial transmission lines, Water Resour. Res., 16, 574-582, 1980.

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences
Discussions

Tables

Table 1. Main physico-chemical properties of the two soils investigated.

Soil	Depth (cm)	Soil Texture and Classification (USDA)				Porosity (%)	*C* (%)	EC_w (dSm^{-1})	*pH*
		Sand (%)	Clay (%)	Silt (%)					
E. Cambisol	0-20	41.4	16.4	42.2	Loam	0.52	0.30	0.13	8.40
Anthrosol	0-20	15.7	11.6	72.7	Silt Loam	0.57	1.84	0.17	8.37

Table 2. Main physico-chemical properties of the OMW used in the experimentation.

Parameter	**Value**
pH	3.85
Electrical conductivity at 20°C (dS/m)	10.20
Dissolved oxygen: *DO* (mg/l)	0.23
Total organic carbon: TOC (mg/l)	6016
Total N (mg/l)	650
Chemical oxygen demand: COD (mg/l)	65000
Total polyphenols (mg/l)	1718

Table 3. Combinations of moisture volume (V_w) and OMW volume (V_{OMW}) for β and θ_f values.

θ_f	Volume of fluids (cm^3)	Relative volume of OMW in water: β					θ_f	Volume of fluids (cm^3)	Relative volume of OMW in water: β				
		1	0.75	0.50	0.25	0.10			1	0.75	0.50	0.25	0.10
0.05	V_w	0	13	27	40	48	0.25	V_w	0	66	133	199	239
	V_{OMW}	53	40	27	13	5		V_{OMW}	266	199	133	66	27
0.10	V_w	0	27	53	80	96	0.30	V_w	0	80	159	239	287
	V_{OMW}	106	80	53	27	11		V_{OMW}	319	239	159	80	32
0.15	V_w	0	40	80	120	144	0.35	V_w	0	93	186	279	335
	V_{OMW}	159	120	80	40	16		V_{OMW}	372	279	186	93	37
0.20	V_w	0	53	106	159	191	0.40	V_w	0	106	213	319	383
	V_{OMW}	213	159	106	53	21		V_{OMW}	425	319	213	106	43

Table 4. Estimated a_c, b_1, b_2 and b_3 coefficients of β vs ln(EC_b) relationships at different θ_f values.

Soil	a_c	b_1	b_2	b_3
Eutric Cambisol	1.185	-16.103	-1.367	2.989
Anthrosol	1.569	-22.646	4.7463	1.927

Table 5. Range of model applicability and: i) mean absolute error (*MAE*), ii) maximum absolute percentage error (*ME*), iii) model efficiency (*EF*), referring to measured and predicted (equation 7) volumetric OMW content (θ_{OMW}).

Soil	***Range of model applicability***	***MAE* (%)**	***ME* (%)**	***EF***
Eutric Cambisol	$0.20 \leq \theta_f \leq 0.40$	3.4	8.80	0.95
Anthrosol	$0.20 \leq \theta_f \leq 0.40$	2.8	6.53	0.96

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences
Discussions

Figures

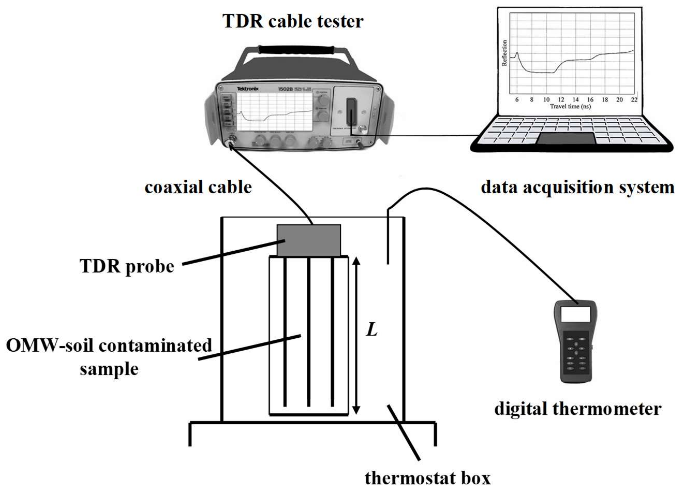
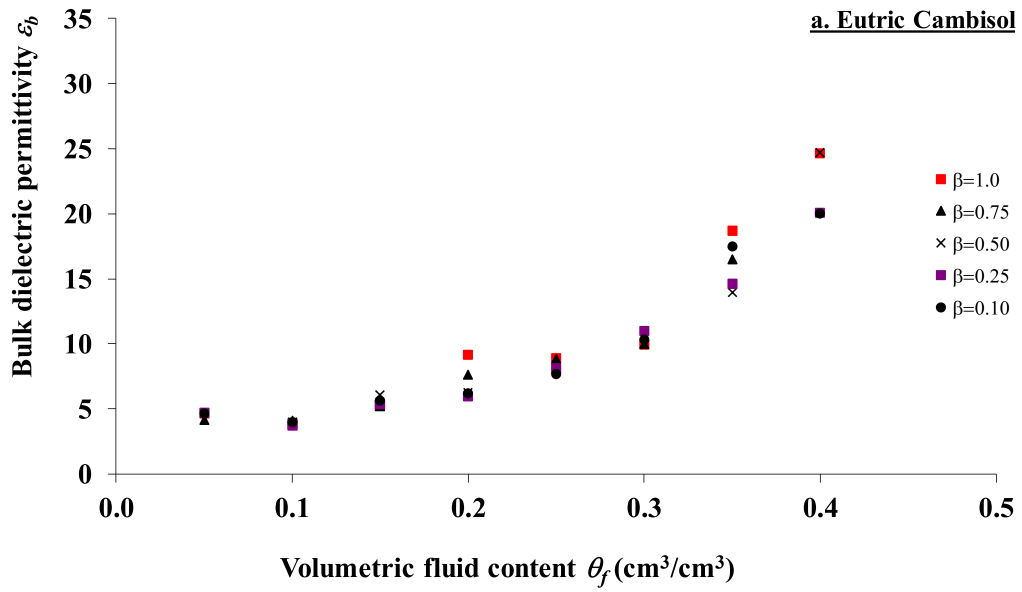
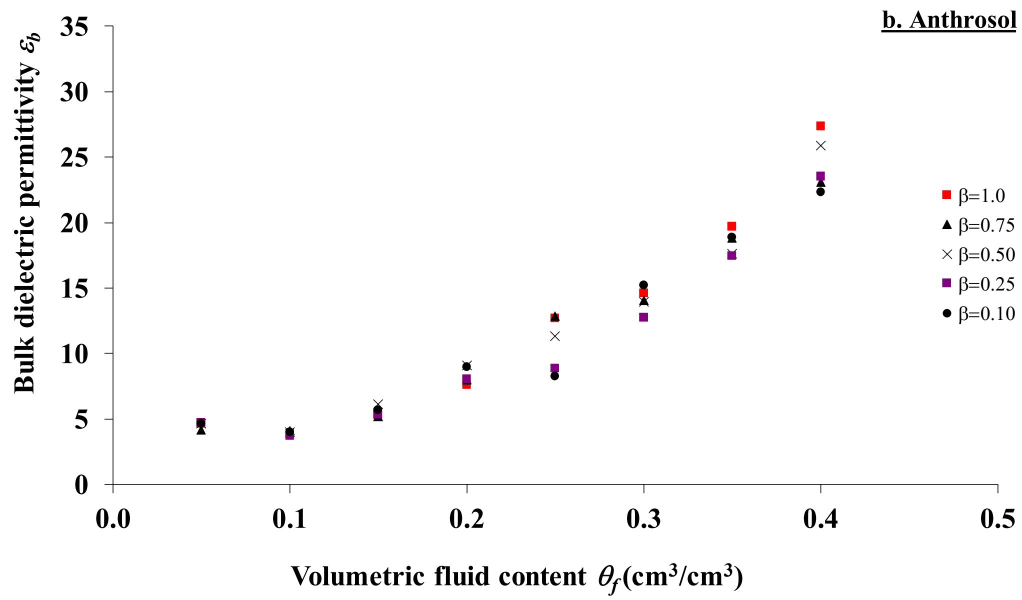


Figure 1. Experimental setup used in laboratory experiments (from Comegna et al., 2016).

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences
Discussions





https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences Discussions

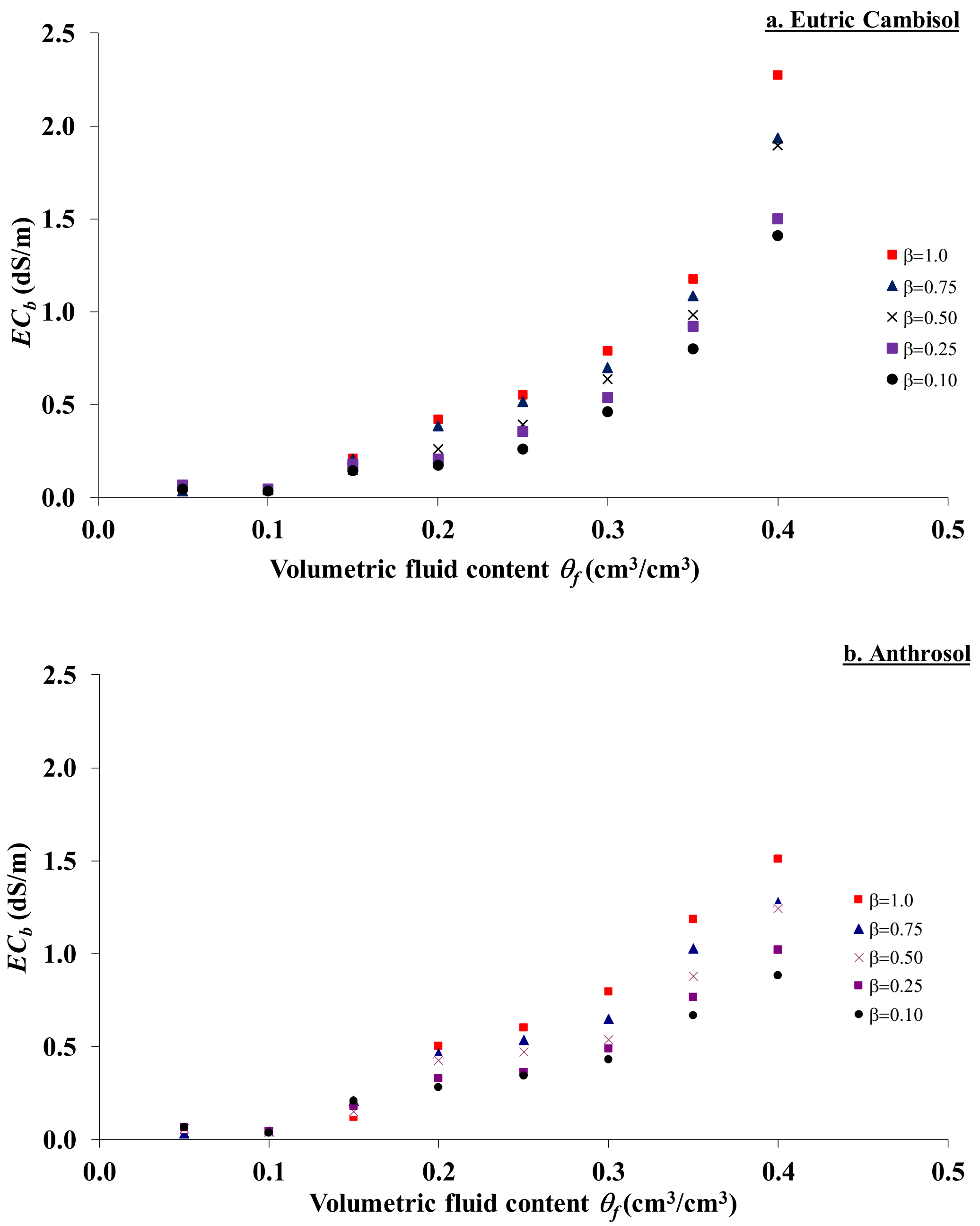


Figure 2. Effect of volumetric fluid content (θ_f) on: a) bulk dielectric permittivity (ε_b), and b) bulk electrical conductivity (EC_b), of soil-water-OMW-air mixtures, for different β values.

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences Discussions
Open Access

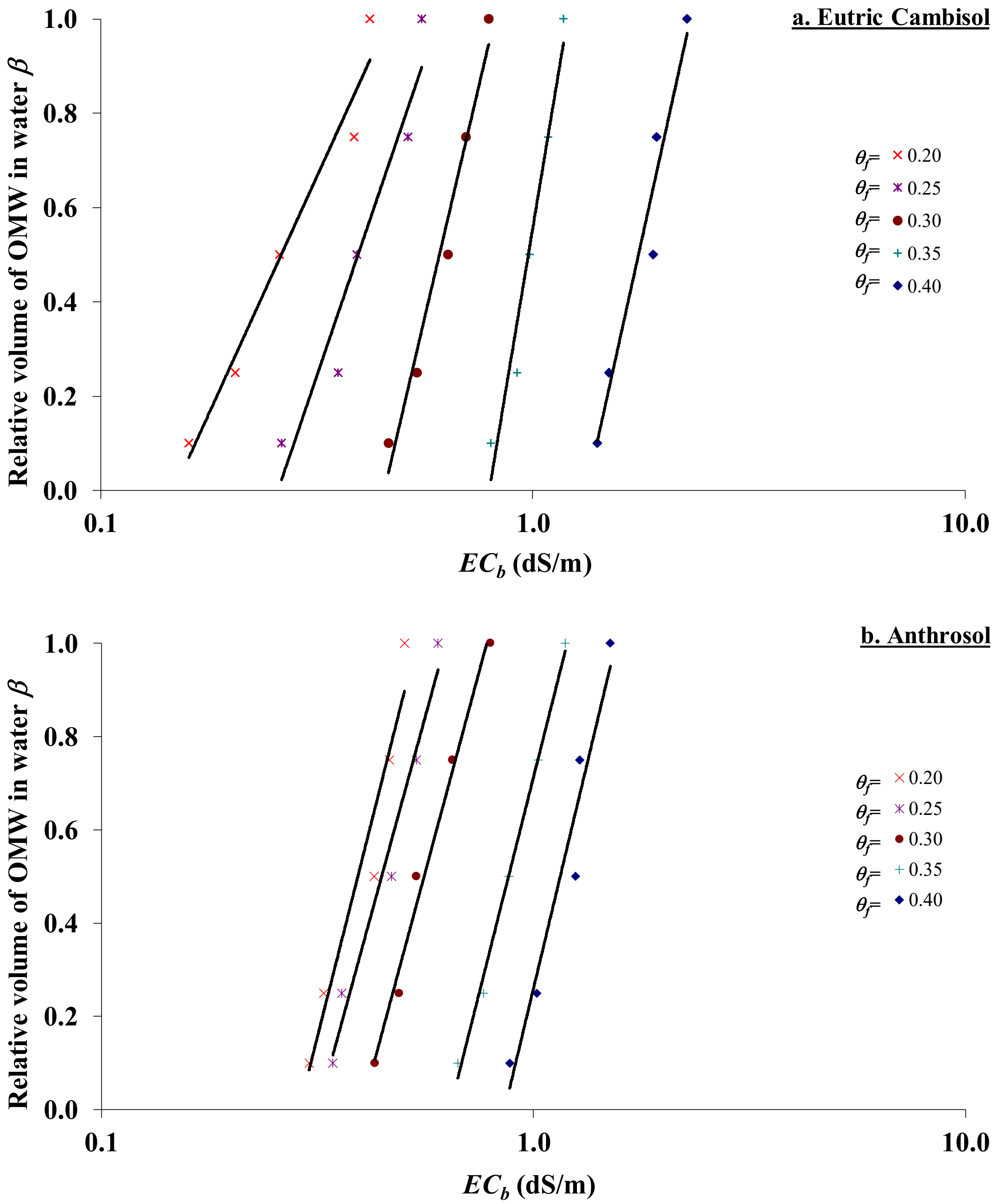


Figure 3 Experimental relationship between bulk electrical conductivity EC_b and the relative volume of OMW in water, for constant θ_f values: a) *Eutric Cambisol* and b) *Anthrosol*.

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences Discussions

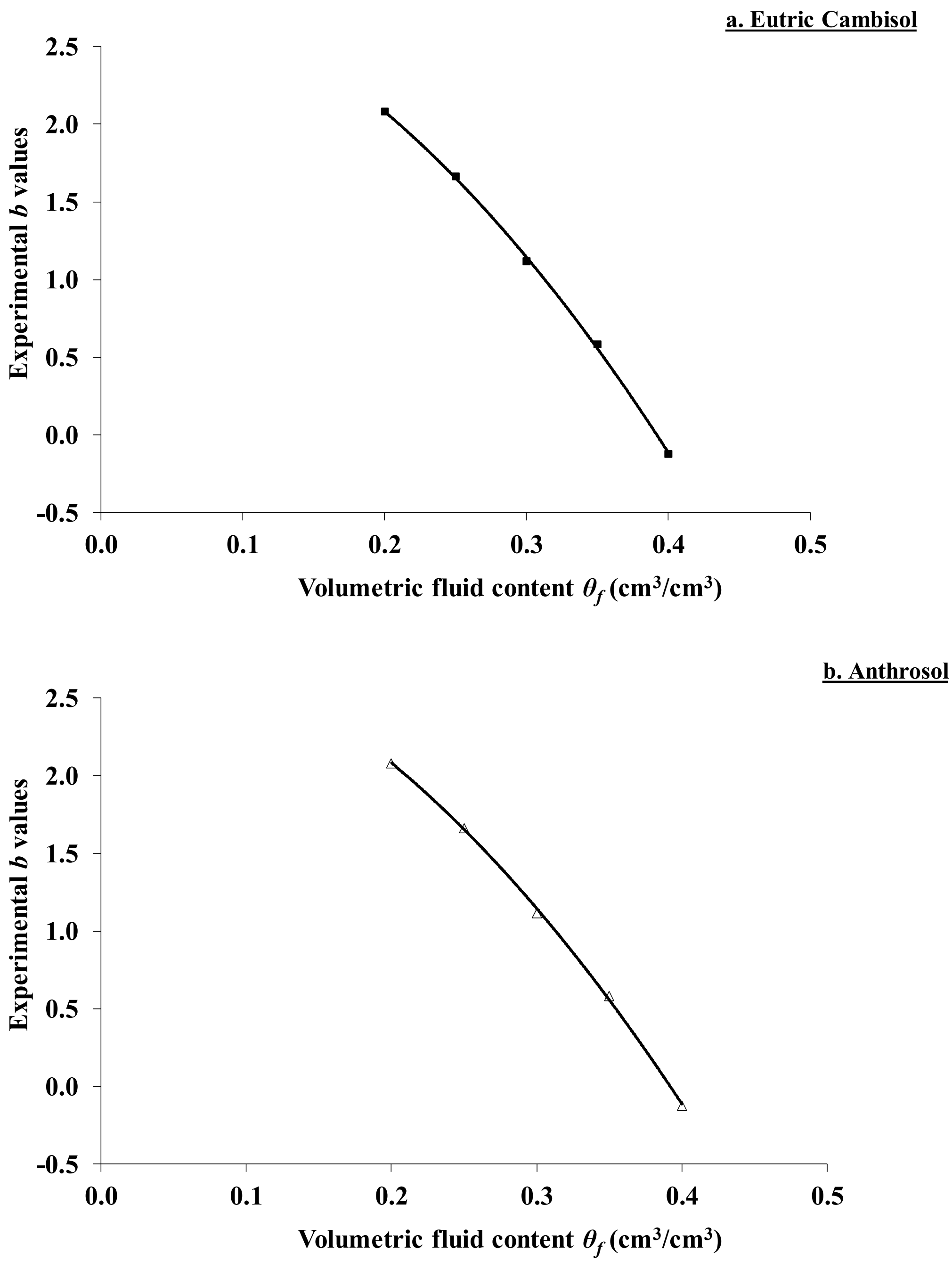


Figure 4. Experimental b values of the β-ln(EC_b) relationships versus volumetric fluid content (θ_f): a) *Eutric Cambisol* and b) *Anthrosol*.

https://doi.org/10.5194/hess-2020-69
Preprint. Discussion started: 24 February 2020

Hydrology and Earth System Sciences
Discussions

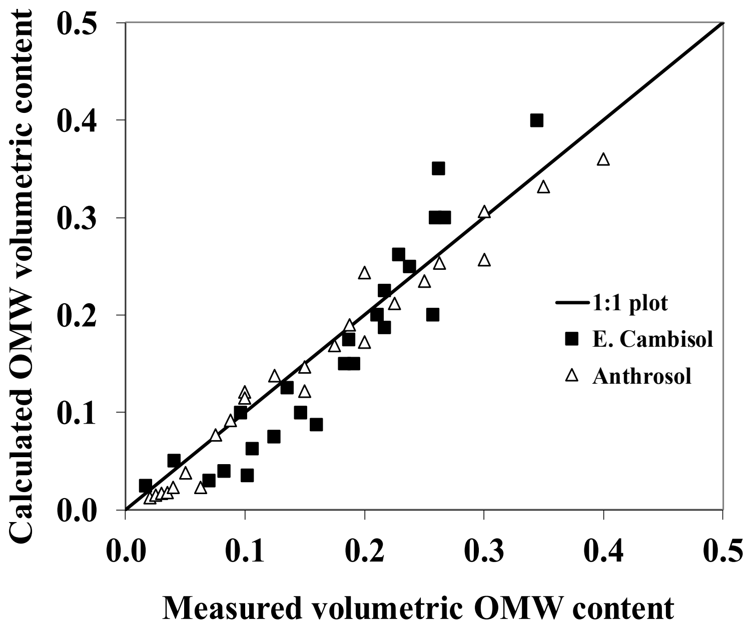


Figure 5. Calculated (equation 7) versus measured volumetric OMW content (θ_{OMW}) for the two contaminated soils.