

**Dear Referee #2,**

With reference to the paper: **hess 2020-69**, by A. Comegna et al., please find below the replies to your review. The authors would like to thank the anonymous Referee for his useful suggestions which have been **fully accepted**. We explain below how the revised paper was reorganized.

### **Question 1**

#### *General premises*

Solute monitoring in the soil can be achieved through the analysis of the variation of a certain physico-chemical property that is able to characterize the solute concentration. Methods commonly used to characterize contaminated sites involve soil drilling, sampling, and the installation of monitoring wells for the collection of soil and water samples (Mercer and Cohen, 1990). Given the cost of these technologies, other noninvasive techniques that belong to geophysical methods have been sought to characterize contaminated sites extensively.

Olive mill wastewater (OMW), like other contaminants (such as for e.g. hydrocarbons), is a very complex mixture made of different elements (Mahmoud et al., 2010; Piotrowska et al., 2011; Caputo et al., 2013, Mohawesh et al., 2014; Sahraoui et al., 2015; among others). Because of this composite nature, OMW detection can be a very difficult task.

OMWs are known to be wastewaters rich in salts (especially potassium, calcium and magnesium). For this reason one may imagine to relate the concentration of a selected salt to the whole OMW amount in the soil. This approach is to be considered impractical for at least two reasons: i) soils may in turn contain a background concentration of the candidate salt. As a consequence, this background concentration must be determined in order to avoid mis-estimating the OMW final concentration, ii) the OMW composition changes in accordance with the quality of the olives, the type of maceration and the type of solvents used for cleaning the machines. Thus, again exactly as for the soil, chemical analysis of the wastewater should be carried out, from time to time, to establish the initial salt concentration.

In order to overcome these difficulties, in this study we developed a general methodology, based on a dielectric approach for evaluating OMW presence in a contaminated soil. The methodology does not need, a priori, for the soil and OMW chemical composition to be known.

That said, since OMWs are characterized by very high values of electrical conductivity ( $EC_{sol}$ ), we selected, on the basis of several laboratory tests, electrical conductivity as a candidate dielectric parameter for our approach, being furthermore easy to detect via the time domain reflectometry (TDR) technique.

We explain in the following how the experimentation was fully implemented. A series of preliminary experiments (**data not shown in the paper**) were conducted in order to characterize the OMW dielectric response. Laboratory tests, in which simultaneous measurements were made of dielectric permittivity  $\epsilon_{sol}$  and electrical conductivity  $EC_{sol}$ , were carried out on solutions that were suitably prepared as a mix of known amounts of OMW and water. Measurements were carried out via the TDR technique; electrical conductivity was also measured using a Cyberscan conductivity meter (model 500). Data are shown in **table 1** as a function of the relative volume of OMW in water  $\beta$ :

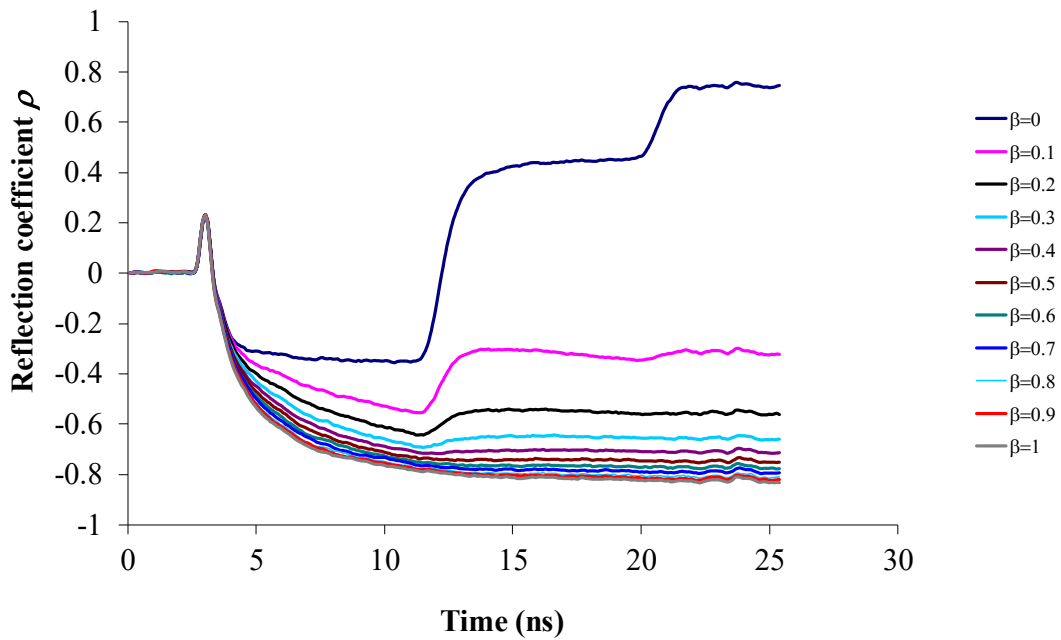
$$\beta = \frac{\theta_{OMW}}{(\theta_w + \theta_{OMW})} = \frac{\theta_{OMW}}{\theta_f}$$

where  $\theta_f$ ,  $\theta_{OMW}$  and  $\theta_w$  are respectively the volumetric content of the whole fluid phase, the volumetric OMW content and the volumetric water content.

**Table 1.**

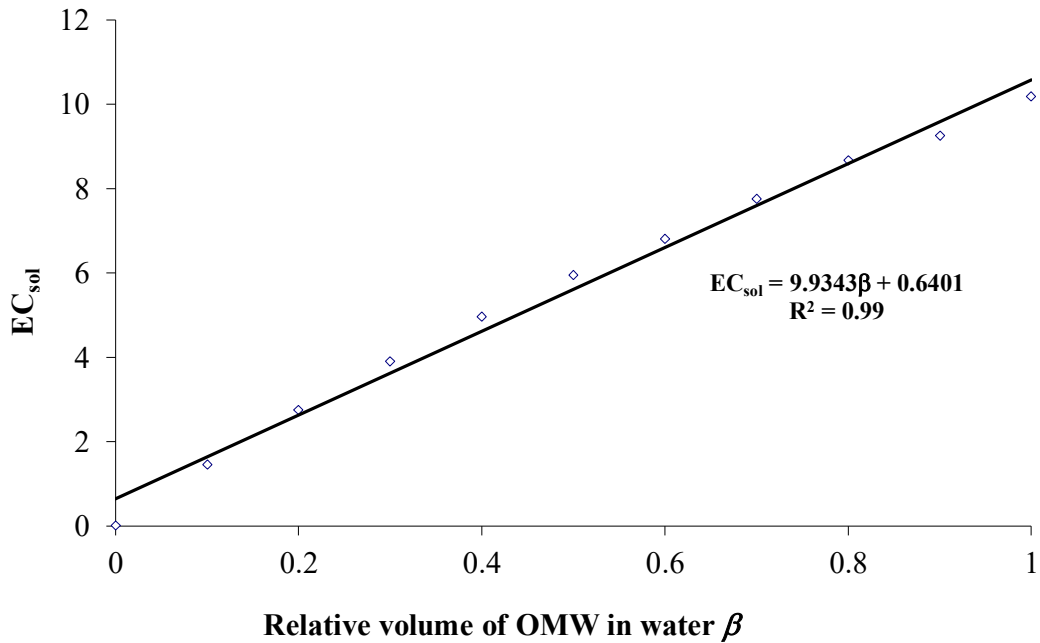
| $\beta$             | $\epsilon_{sol}$ | $EC_{sol}$ (TDR)<br>(dS/m) | $EC_{sol}$ (Cyberscan)<br>(dS/m) |
|---------------------|------------------|----------------------------|----------------------------------|
| 0 (distilled water) | 78.89            | 0.013                      | 0.012                            |
| 0.10                | 77.86            | 1.45                       | 1.52                             |
| 0.20                | 75.77            | 2.76                       | 2.79                             |
| 0.30                | 73.46            | 3.90                       | 3.86                             |
| 0.40                | n.a.             | 4.97                       | 4.99                             |
| 0.50                | n.a.             | 5.95                       | 6.02                             |
| 0.60                | n.a.             | 6.81                       | 6.78                             |
| 0.70                | n.a.             | 7.75                       | 7.70                             |
| 0.80                | n.a.             | 8.66                       | 8.61                             |
| 0.90                | n.a.             | 9.25                       | 9.20                             |
| 1.0 (OMW)           | n.a.             | 10.20                      | 10.18                            |

As deducible from **table 1**, it can be seen that the permittivity changes slightly with  $\beta$ , and that for  $\beta > 0.30$ ,  $\epsilon_{sol}$  cannot be estimated because the reflection point completely disappears (**figure 1**).



**Figure 1.** Reflection coefficient versus time, for different  $\beta$  values.

On the contrary,  $EC_{sol}$  changes significantly, with a linear dependence, in the  $0 < \beta < 1$  domain (**figure 2**).



**Figure 2.** Electrical conductivity ( $EC_{sol}$ ) versus  $\beta$  values.

Starting from the above experimental evidence we further investigated in depth the OMW behavior in contaminated soil samples. From an experimental point of view, with reference to two distinct soils, 160 measurements, for a full factorial analysis, were carried out for model calibration and validation. Several statistical indices ( $MAE$ ,  $EF$ ,  $ME$ ) were calculated, and finally a statistical ANCOVA test was performed at a significance level of 0.05 so as to consolidate from a statistical point of view the proposed methodology.

Specific comments

**1a and 1c)** In accordance with the Referee’s comments contained in question #1, it should be emphasized that the soils selected belong to two typical pedological units of southern Italy which account for approximately 90% of the Italian olive plantations and the highest concentration of the olive oil industry in Italy. In these districts, despite European and Italian laws, there is the controversial propensity to spread olive mill wastewater (OMW) on soils, causing critical environmental problems. Under these considerations, in addition to what has already been stated in the general premise, one may assume that, in such field conditions, the main source of high electrical conductivity values is exclusively due to OMW.

**1b) Line 105:** polyphenols are known to be constituents of OMW. Their concentration can be relevant, and may cause, of course, several problems to soil biota. In the present paper, in order to characterize, from a physico-chemical point of view, the OMW used in the experimentation, we reported in table 2 (of the paper) the concentration of “Total polyphenols”: “*Total polyphenol content, in OMW, was obtained using the Folin-Ciocalteu colorimetric method*”.

**Question 2**

The soil extract method for salinity measurements, as proposed by US Salinity Laboratory Staff (1953) is laborious and destructive.

New devices have been developed such as TDR (Topp et al., 1980), which exploit the variation in the dielectric behavior that a medium exhibits in the presence of an electromagnetic field. This behavior is described by the

dielectric permittivity which is in general a complex function. The TDR technique is widely employed in Soil Physics to predict the volumetric water content ( $\theta$ ) of a soil through the dielectric permittivity ( $\epsilon_b$ ). TDR also allows us to estimate the soil bulk electrical conductivity ( $EC_b$ ) of the multiphase medium.

The electrical conductivity of the bulk soil  $EC_b$  is of course strongly related to the electrical conductivity of the soil solution ( $EC_w$ ) by means of empirical or theoretical correlations. Such correlations have been extensively investigated, notably by Rhoades et al. (1976), Rhoades et al. (1989), and Hilhorst (2000).

Hilhorst (2000) presented a linear model relating  $\epsilon_b$  and  $EC_b$  in the form  $\epsilon_b = AEC_b + B$ , where  $A = \epsilon_w/EC_w \cong 80/EC_w$ , and  $B=K_0$  is the intercept of the line  $\epsilon_b = f(EC_b)$ .

Hilhorst concluded that his model could be validated for water contents up to saturation and for  $EC_w$  values up to 0.3 S/m. He found that  $K_0$  depends on soil type and varies between 1.9 and 7.6. He recommended the value of 4.1 as generic offset.

Many researchers (Hamed et al., 2003; Regalado et al., 2007; Persson 2002, among others) applied the deterministic model of Hilhorst to their experiments to convert  $EC_b$  to  $EC_w$  but did not use the same  $K_0$  offset value to achieve their study objectives. Nevertheless,  $K_0=4.1$  was proposed as a representative value for all soil types. The Hilhorst's model must be applied for cases where  $\theta > 0.1$  since the conceptual model does not include the contribution due to ions moving through the lattice of ionic crystals in dry or almost dry soils. This same reason renders the above model inappropriate for the cases where bound water might be present, as may happen, for instance, in clays.

Hilhorst's model appears to be a rather simplistic special case of the model reported by Rhoades et al. (1976), and Rhoades et al. (1989), in the sense that it does not take into account that  $\epsilon_b$  might be affected by the surface conductance of the soil matrix.

The other most practical model of Rhoades et al. (1989) is based on the dual pathway parallel conductance (DPPC) approach and is applicable in open fields. The DPPC model demonstrated that  $EC_b$  can be reduced to a nonlinear function of five soil properties: i) salinity as measured by the electrical conductivity of the saturated extracts ( $EC_e$ ), ii) the saturation percentage ( $SP$ ), iii) the volumetric soil water content ( $\theta$ ), iv) the soil bulk density ( $\rho_b$ ), and v) the soil temperature ( $t$ ). These parameters must be kept in mind when interpreting  $EC_b$  data.

We conclude that the DPPC model is not easy to parametrize, and together with the Hilhorst model is subject to many limitations.

**We would like to say that referee's observations have been resolved in the revised version of the manuscript (abstract, section 3, and conclusions).**

Sincerely

The authors