Assessing impact of Olive Mill Waste disposal on soil at nine randomly selected disposal areas in Crete, Greece.

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Abstract In European Mediterranean countries the disposal of Olive Mill Wastes (OMW) is a major environmental problem. Following an extent study on the risks for soil quality caused by the disposal of OMW, in the framework of the LIFE PROSODOL project, eight soils indicators appropriate for defining soil degradation risk at OMW disposal areas were defined, namely pH, organic matter, electrical conductivity, total nitrogen, polyphenols, exchangeable potassium, available phosphorus and iron. In order to confirm the indicators and also other results as regards impact on soil quality outside the main pilot area of PROSODOL project in Rethymnon, Crete, nine OMW disposal areas were randomly selected and studied. It was confirmed that soils that accept OMW have high electrical conductivity; increased amount of organic matter and nitrogen; high concentrations of exchangeable K and Mg as well as of available P, B, Fe and Cu. Available Mn and Zn were also high, however Zn was above threshold only in two cases while Mn in three. Finally it was also confirmed that soils with high $CaCO_3$ content, maintain their pH values and neutralize OMW acidity.

Keywords: Olive mill waste-OMW, soil, indicators.

1. Introduction

As soil formation is an extremely slow process, soil can be considered as a non-renewable resource. European Union acknowledges that soil is subject to a series of degradation processes or threats. In the European Soil Thematic Strategy soil degradation is recognized as a serious problem in Europae. Especially for the Mediterranean countries, in which huge amounts of agricultural wastes are produced and disposed annually, the potential risk for soil degradation and desertification should be always considered by carrying out risk assessment studies for all practices to be implemented and under the specific environmental conditions. Specifically, in European Mediterranean countries the disposal of OMW is considered as a major environmental problem since the three main olive oil productive countries worldwide are Spain, Italy and Greece. To assess the risk for soils that receive the disposal of OMW, a monitoring system - based on land characteristics - was designed and implemented in Crete, South Greece, in 2010-2011, which included periodical soil samplings and analysis of 23 soil parameters from five OMW disposal areas located in the prefecture of Rethymnon; in total more than 16,200 analyses were performed. The statistical processing and the evaluation of the results revealed that eight soil parameters were mostly affected by the disposal of OMW on soils, namely pH, organic matter, electrical conductivity (EC), total N, polyphenols, exchangeable K, available P and available Fe (Doula *et al*., 2013). Soil pH is a parameter that can be affected mainly in soils poor in $CaCO_3$. In order to evaluate and validate these results, nine randomly selected disposal areas located at the wider area of the main pilot area were selected and monitored once, during 2011 by colecting soil samples from inside the disposal ponds. Control samples were collected, as well.

2. Materials and methods

2.1. Areas under study

Nine OMW disposal areas were selected in Crete (red marks in Map 1, Table 1) and soil samples were collected once (June 2011). The management practice for all areas was the same, which concerned the disposal in evaporation ponds. For almost all the cases the ponds were deep (up to 1.5-2 m), poorly constructed by simple soil excavation (Photo 1) and without using any protective media to prevent leaching to aquifers through soil soil (e.g. geotextiles). Samples were collected from inside the disposal ponds. Control samples from the wider area were collected, as well.

2.2. Soil analysis

Soil analysis was carried out using conventional and ISO methodologies (Page *et al*., 1982; Doula *et al*., 2013, Kavvadias *et al*., 2010). Specifically, particle size distribution was carried out using the Bouyoukos method; pH and EC were measured in the paste extract; organic matter was determined by dichromate oxidation; carbonates by using Bernard calcimeter; total N by the Kjeldahl method; available phosphorus using $NaHCO_3$ extraction; exchangeable K, Ca and Mg using $BaCl_2$ extraction, while available Mn, Fe, Cu and Zn using DTPA extraction. Soil B was extracted by boiling water using the azomethine-H method. Methanol extractable phenol compounds were quantified by means of the Folin–Ciocalteu colorimetric method (Box, 1983). K, Ca, Mg, Cu, Mn, Fe, Zn were measured in a Varian SPECTRAA 220 Atomic Absorption. Na was measured with the use of a Korning Spectrometer while P was measured in a HITACHI U3010 Spectrophotometer.

Map 1. The nine studied OMW disposal areas in Crete (red marks). The blue marks are the ponds of the main pilot area of PROSODOL project.

Photo 1. A simply constructed OMW evaportation pond in Crete, Greece.

Table 1. Coordinates of the nine OMW disposal areas.

Disposal Area	Latitude	Longitude
Episkopi village, Rethymno	35°19′34.68′′N	24°20′21.47′′E
Sellia village, Rethymno	35°12′08.21′′N	24°22′39.64′′E
Akoumia village, Rethymno	35°10′8.72′′N	24°34′48.99′′E
Agouseliana village, Rethymno	35°14′7.72′′N	24°26′36.62′′E
Koxare village, Rethymno	35°13′39.28′′N	24°28′20.95′′E
Asomatos village, Rethymno	35°11′26.00.′′N	24°26′23.39′′E
Spili village, Rethymno	35°12′22.02′′N	24°32′6.98′′E
Adele village, Rethymno	35°21′57.17′′N	24°33′39.70′′E
Achlada village, Heraklio	35°23′38.65′′N	24°59′49.07′′E

3. Results and discussion

Figure 1 presents the pH values and the $CaCO_3$ content of the pond and the control soil samples collected from the nine disposal areas. As it can be seen and also proved for the samples from the pilot area, soils with high content in $CaCO_3$ (i.e. Episkopi, Adele and Asomatos) maintain their pH values and neutralize the OMW acidity (pH_{OMW}=4.5 approximately). On the contrary, most of the soils with low $CaCO_3$ content seem to be unable to neutralize the acidity of OMW and incurred a decrease in pH values mainly for the two upper soil layers (i.e. 0-25cm and 25-50cm). It seems that a reduction in $CaCO_3$ could occur due to wastes disposal in soil rich in $CaCO_3$ (Episkopi, Adele).

The EC of all pond soils were significantly higher than the EC of the respective control soils, not only for the upper soil layers, but also for the deeper ones (Fig. 2). However, in contrast with the pond soils of the main pilot area, 95% of EC data had lower values than the threshold value for salinity i.e. 4mS/cm (Doula, *et al*., 2013; Kavvadias t al., 2010). In two of the disposal areas (i.e. Adele and Agouseliana) EC was very high. In general, there is a trend of EC increasing with the increase in soil clay content, however, this is not valid for all of the monitored areas. It should, however, be highlighted that the selected areas had not been monitored in the past and no further information, such as years of disposal, pretreatment of wastes, etc., were available. As regards organic matter (OM), high concentrations were measured up to 1m depth in many areas (data not shown). For top soils (0-25cm), OM content was higher than 2% while there were cases of very high OM concentrations (>8%). As confirmed also in the case of the main pilot area of the project, high values of OM could be found up to 1m depth, indicating significant build up of organic carbon (Kavvadias *et al*., 2010). In general, OM and total nitrogen were well correlated; the total nitrogen content of the upper soil layer was very high for almost all the cases studied, while high values were also measured up to 1m depth (data not shown). High levels of OM and residual N were found in the control soils of some areas (e.g. Sellia) and may attributed to sheep grazing effects, since the area of central Crete is well known for its livestock farming. Kavvadias *et al*.

(2010) concluded that the positive effect of OMW application on the total organic nitrogen content is due to the provision of a high carbon source and immobilization of inorganic nitrogen by microorganisms.

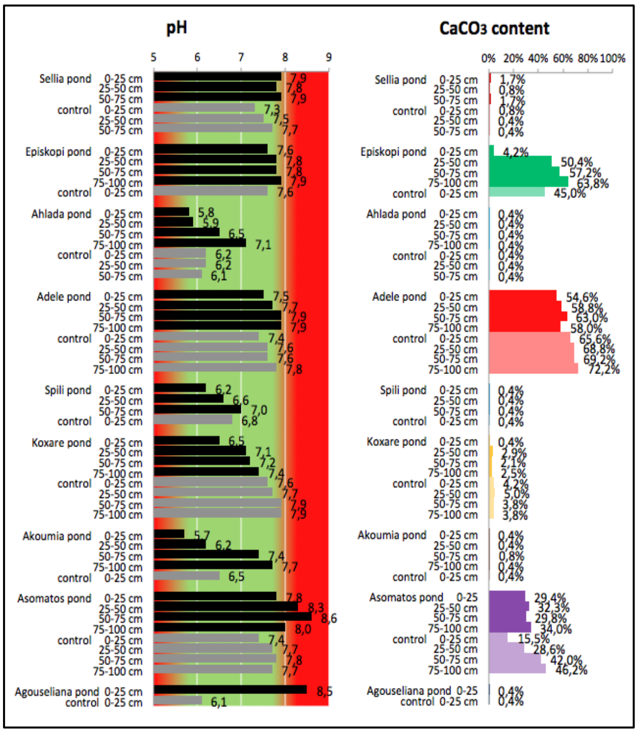

Figure 1. pH values and $CaCO_3$ content of soil samples collected from the nine disposal area in Crete.

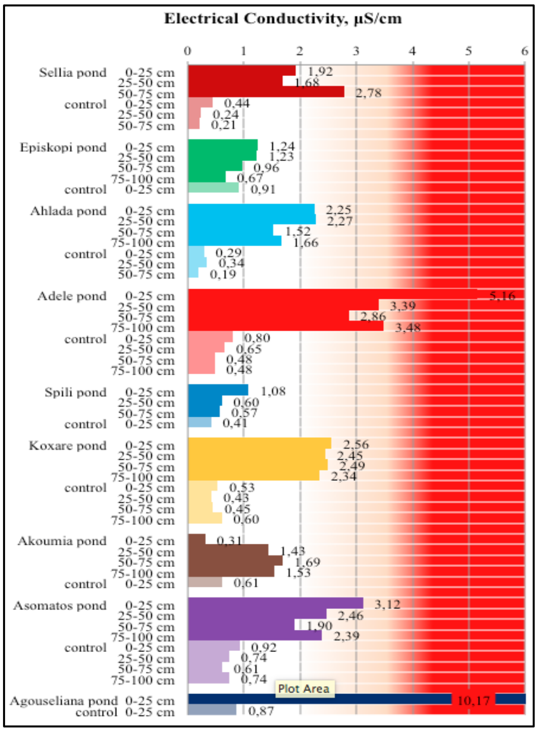

Figure 2. Electrical conductivity of soil samples collected from the nine disposal area in Crete.

As shown in Fig. 3, available P ranged in low levels (0.4-13 mg/kg) for control soils while high values were measured in pond soils, ranging from 2.4 to 297 mg/kg located across soil profile.

Generally, the assessment of polyphenols concentration in soils is considered difficult and with high degree of uncertainty due to the lack of generally accepted thresholds (Kavvadias *et al.*, 2010). Thus, local and site specific threshold are often established, as in the case of the study of Sierra *et al.* (2001), who decided to consider as guideline values the concentrations of phenolic substances in the control soils of their study, which were between 14 and 25 mg/kg. In the present study, a high percentage of the control samples (45 %) had polyphenol values between 41 and 108 mg/kg while in most of the areas, pond soils had higher polyphenols concentrations than the control samples. However, although the measured concentrations in the ponds of the nine disposal areas were high (up to 185 mg/kg), did not reach the levels recorded in pond soils of the main pilot area, for which, the 46%, of total polyphenols data in pond soils varied from > 40 mg/kg up to the very high value of 638 mg/kg. This can be attributed to the fact that OMW survey took place once in June 2011, a few months later from OMW disposal after olives milling and thus organic load has been subjected to decomposition processes. On the contrary, for he main pilot area of the project, pond soils were collected and analyzed for polyphenols bimonthly for one and a half years.

The very high exchangeable K content of the pond soils (Fig.4), especially for the upper soil layer, confirms the observations of the main pilot area of the project, i.e. the 89% of K data in pond soils had values from >2cmol(+)/kg up to 26cmol(+)/kg, which were found throughout the soil profile. Potassium in the control soils of the nine disposal areas of this study ranged below the threshold value of 2cmol(+)/kg; from 0.1 to 1.7cmol(+)/kg. On the contrary, accumulation of K was high in pond soils and more than 80% of K data had values > 2 cmol(+)/kg up to 12 cmol(+)/kg, which were found in all soil layers. The potential for accumulation of K in soils from OMW disposal is high and can adversely alter soil properties. Moreover, since excessive concentrations of the element were also found in deeper soil layers, the uncontrolled disposal of OMW in evaporation ponds may cause significant amounts of K to leach through the soil in ground waters. Same as K, available B was significant higher in pond soils compared to control ones (Fig. 5). Both exchangeable K and available B may cause significant phytotoxicity problems and substantial soil degradation.

In general, for all soils monitored, exchangeable Mg content was measured higher than the control samples (data not shown). Approximately, 25% of Mg data in pond soils ranged from 2.3 to 11mg/kg, located across soil profile. Regarding exchangeable Ca, it was observed that soils with high $CaCO_3$ content (Episkopi, Adele and Asomatos-Fig. 1) underwent a significant reduction in exchangeable Ca content (data not shown) because of the OMW acidity, which caused dissolution of $CaCO_3$. In soils with low $CaCO_3$, no significant differences were found between pond and control samples.

Very high concentration of available Fe and Cu were measured in soil samples collected from inside the disposal ponds (Fig. 6), confirming the threat for serious soil degradation. In the case of Fe, measured values were above threshold for toxicity, i.e. 100mg/kg (Kavvadias *et al*., 2010).

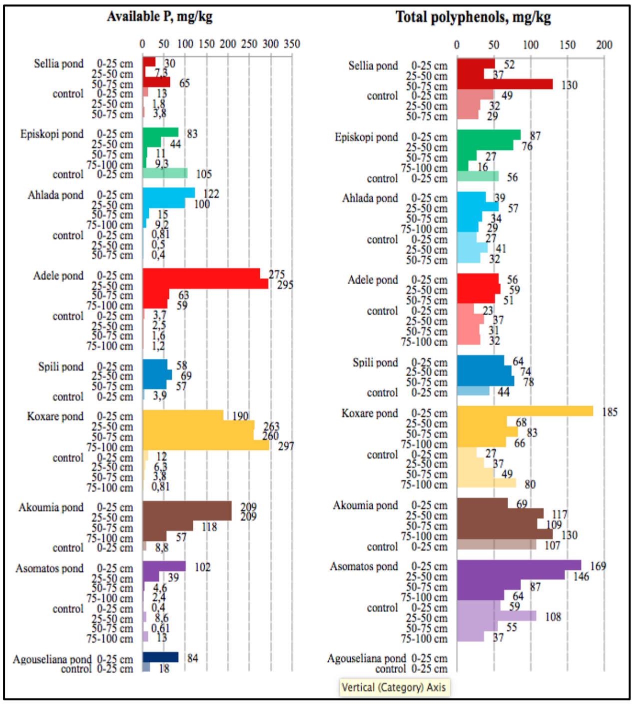

Figure 3. Available P and total polyphenols content of soil samples collected from the nine disposal area in Crete.

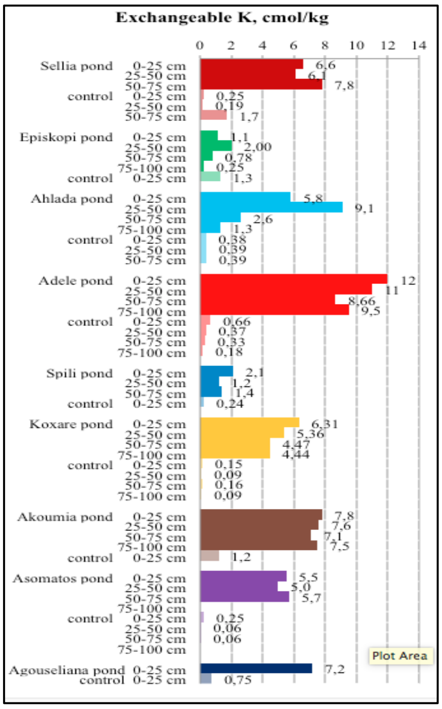

Figure 4. Exchangeable K of soil samples collected from the nine disposal area in Crete.

Most of Fe data for control soils had values lower than threshold levels (50mg/kg) while excess accumulation of available Fe was measured in pond soils. 90% of Fe data had values ranging from 80 to 550mg/kg measured throughout the soil profile. Cu in control soils ranged from 0.3 to 4.7mg/kg (Fig. 6). High accumulation of available Cu, was recorded in pond soils, where values ranged from 3 to 15mg/kg across soil profile, slightly lower than the limit of toxicity (>15-16mg/kg) (Kavvadias *et al.*, 2010). Fe is, without doubt, a threat for soil health, however, if no measures are not to be taken, then Cu will be a similar threat, as well.

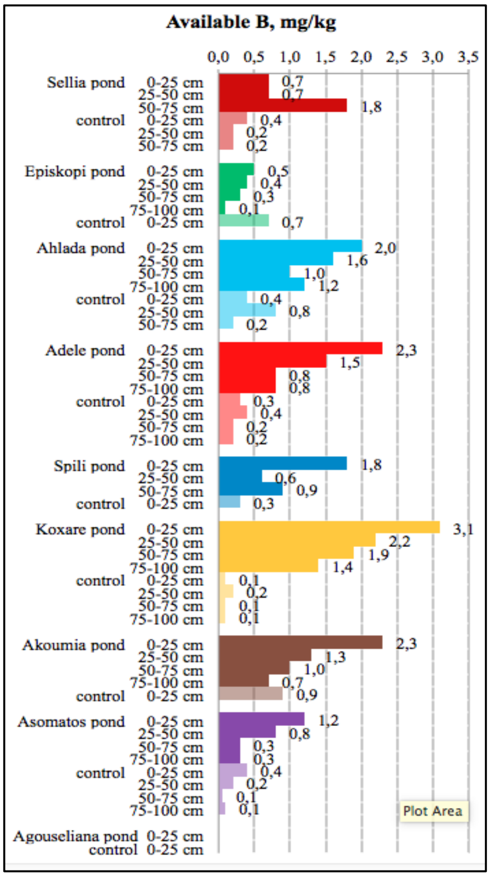

Figure 5. Available B of soil samples collected from the nine disposal area in Crete.

For Mn (Fig.7), it was detected that there were cases (also in the main pilot area of the project) for which increased concentrations were measured. The increase was slight or substantial. In pond soils Mn generally had higher values (8-148mg/kg) compared to control soils; approximately 45 % of Mn data were above the threshold value of 45 mg/kg (Kavvadias *et al.*, 2010), being measured across soil profile. However, there were also cases for which the high natural Mn content was decreased after OMW disposal, mainly due to waste's acidity, which caused the dissolution of naturally occurring metals (e.g. Spili, Akoumia, Asomatos, Agouseliana). On the contrary, available Zn (Fig. 7) was significantly higher in pond soils than in control soils. This trend was also detected for soils collected from the main pilot area of the project.

4. Conclusions

The study focused on soil properties affected by the disposal of OMW. Nine randomly selected OMW disposal areas in Crete, Greece were monitored once and the results were compared with the results obtained during a previous systematic study of five OMW disposal areas in Crete, during which, five OMW disposal areas were monitored for one and a half years. In general, the conclusions of the present study are in accordance with the results obtained by the systematic one. Soils with high content in $CaCO_3$ maintained their pH values and neutralized the OMW acidity. On the contrary, most of the soils with low $CaCO_3$ content seemed to be unable to neutralize the acidity of OMW and incurred pH decrease.Electrical conductivity of all pond soils at the random areas were higher than the EC of the respective control soils, not only for the upper soil layers, but also for the deeper layers. High concentrations of organic matter and nitrogen found in soils up to 1m depth confirm a significant build up of organic matter and nitrogen. Regarding available P, high concentrations were measured in pond soils located across soil profile, same as in the main pilot area. Regarding the majority of the areas, pond soils had higher polyphenols concentrations than the control samples. Exchangeable K, exchangeable Mg and available B content of the pond soils were significantly higher compared to control soils. For exchangeable Ca, it was observed that soils with high $CaCO_3$ content underwent a reduction in exchangeable Ca because of the OMW acidity, which caused dissolution of $CaCO_3$. For soils with low $CaCO_3$, no significant differences were found between pond and control samples.

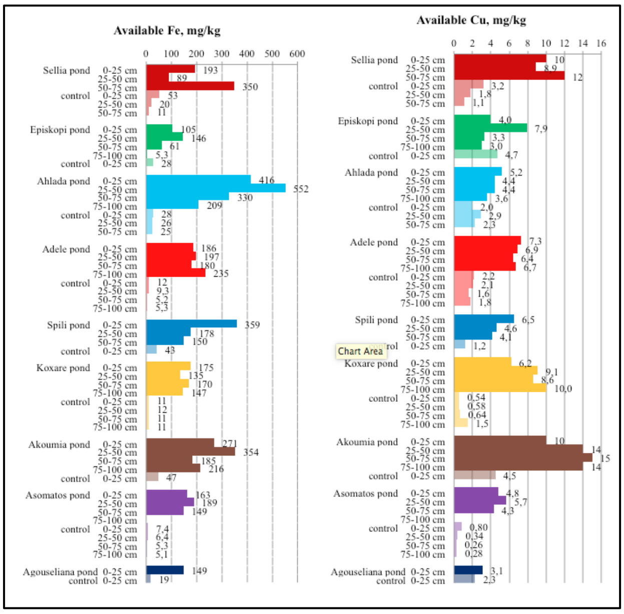

Figure 7. Available Fe and Cu (DTPA extractable) of soil samples collected from the nine disposal area in Crete.

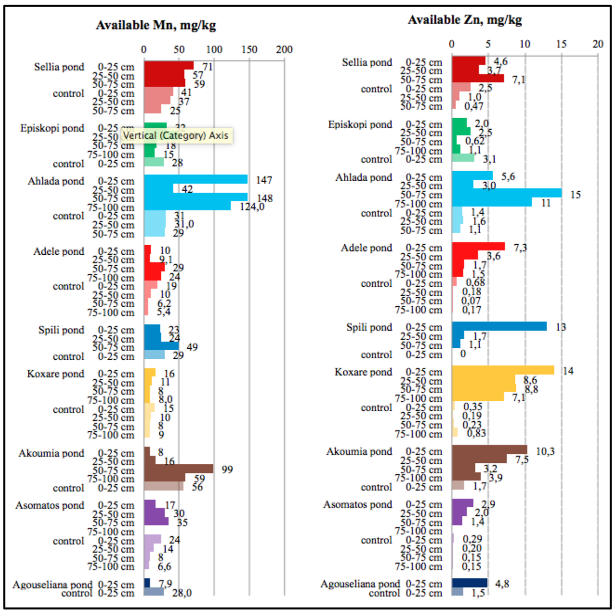

Figure 8. Available Mn and Zn (DTPA extractable) of soil samples collected from the nine disposal area in Crete.

In the line of the conclusion regarding the high concentrations of available Fe and Cu in the main pilot area, it was found that these metals had also high concentrations at the randomly selected disposal areas. Available Mn and Zn had high values in pond soils; this trend was also detected in soils collected from the main pilot area of the project, however Zn was above threshold only in two cases while Mn in three.

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