MONITORING OF PHENOLS CONCENTRATION IN SOIL OF OLIVE OIL MILL WASTE DISPOSAL SITE

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SUMMARY: Olive oil mills wastes (OOMW), contain several compounds with recognized toxicity towards living organisms. During the milling, almost 3.4 million tons of liquid, OMW are produced annually in Europe, causing enormous environmental problems. The high polyphenols content of olive oil wastewaters makes bacterial degradation more difficult and inhibits vegetation whereas the emulsified fat forms a film on water surfaces. The usual treatment and disposal method in Greece is the evaporation in lagoons/ponds. In practice the evaporation lagoons/ponds are rarely of proper size and construction and wastewaters often overflow affecting the neighboring systems. The base of the lagoons is, in most cases, permeable and thus, the probability for groundwater and deep soil horizons contamination is high. Polyphenols content was found high in the upper soil layers of active and inactive lagoons as well as in areas close to them.

1. INTRODUCTION

In the Mediterranean area, olive oil and table olives production are important agro-alimentary branches in Europe. About 9.7 million tons of olive trees are grown annually from which approximately 1.9 million tons of olive oil is produced in approximately 12,000 olive mills, (FAOSTAT database). In Greece there are about 10^8 olive trees and 2800 olive oil mills while the average oil production in cultivation period of 2006/2007 was about 250.000 tn.

Nowadays there are three systems for olive oil production. Both the traditional and the three phase system produce a liquid residue (olive mill wastewaters, OMW) and a solid residue (pomace). The 3-phase system results in the production of 1.20 I of wastewater per Kg of olives, which means on the average 6 liter of wastewater per liter of olive oil. In the traditional system the wastewater amounts to 0.5 l/Kg of olives, or 2.5 liter of wastewater per liter of olive oil (Vlyssides *et al.*, 1998; Stolting and Bolle, 2000). Thus, during the milling process by the traditional and the 3-phase system, almost 3.4 million tons of liquid, OMW are produced annually in Europe, causing enormous environmental problems due to the very high organic matter content (COD up to 200,000 mg/l and BOD between 10.000 and 150.000 ppm) which excludes state-of-the-art aerobic wastewater treatment (Tunay *et al*., 1998). In addition, the high polyphenols content of olive oil wastewaters makes bacterial degradation more difficult and inhibits vegetation whereas the emulsified fat forms a film on water surfaces, preventing oxygen dissolving and light getting through, and thus hindering aquatic life development. It is estimated that in the milling of 100 Kg of olives, the resulting wastewater is as polluting as a village with a population of 300-500 people.

The most common way of treatment nowadays is just to store the OMW in open basins where they evaporate (leading to noxious odors, with impact on vegetation and landscape and in many cases groundwater contamination due to leakage), or deposit them directly on plantation lands (this can also result in groundwater contamination, and is therefore limited by national legislations, e.g. 8 l/m^2 in Portugal and Italy and 10 l/m^2 in Spain). Lagooning is used widely despite the fact that only reduces the volume of wastes without treating the pollutants and a black foul-smelling sludge, difficult to remove and handle, is produced. Careful design should be considered due to actual risk of leakage of OMW and migration through soil into groundwater (Sayadi et al., 1996; Zaharaki and Komnitsas, 2009).Though other more environment friendly alternatives exist, such as stationary anaerobic degradation, they are not normally affordable for small olive mills due to the high investment cost required (Brunetti *et al*., 2007).

Although the disposal of untreated mills wastes in the environment is not permitted, it is estimated that up to 1.5 million tn of wastes are disposed each year. The usual treatment and disposal method in Greece is the evaporation in ponds after neutralization with lime. There are also many cases of sea, river and underground disposal. In practice the evaporation ponds are rarely of proper size and construction and wastewaters often overflow affecting the neighboring systems (soil, surface and groundwater) but also professional activities of the residents (agriculture, livestock farming). The base of the lagoons is in most cases, permeable and thus, the probability for groundwater and deep soil horizons contamination is high.

Due to the serious environmental problems caused by the uncontrolled disposal of these wastes, European Commission co-funded in the framework of LIFE+ funding scheme a four-year project entitled "*Strategies to improve and protect soil quality from the disposal of olive oil mills' wastes in the Mediterranean region*". One of the main project's objective is to record and evaluate the effect of the disposal of olive oil mills' wastes on soil quality. First results of PROSODOL project in relation to soil polyphenols content at wastes disposal areas are presented in this study.

2 MATERIALS AND METHODS

2.1 Implementation area

The project area is located in the municipality of Nikiforos Fokas, prefecture of Rethymnon, Crete. The municipality has a total area of 95 km^2 and a population of approximately 6600. Geological formations of the area under study are mainly identified as limestones, dolomites and marbles. Soils are slightly alkaline to alkaline (pH between 7,3 and 8,0), rich in carbonates (40%-60%) and clay or silty clay in texture.

2.2 Soil sampling

Soil samples were collected from four disposal areas : three active and one inactive for more than 6 years. All of them contain lagoons which were built by excavating the superfacial materials of soil, and by heaping excavating materials around the lagoon to form low retaining walls. Protective impermeable membranes or other protective media were not used. The disposed wastes derived from three-phase mills with continuous centrifuge extraction systems.

Four ponds located in NF-1, NF-2 and NF-4 sites (two ponds in the disposal field) respectively are active for 10 years while the forth one (NF-6 site) which has been used as disposal area for 20 years is inactive for the last 6 years. Although the owners of NF-1 and NF-2 do not dispose wastes directly on land, the owner of NF-4 uses a pump to directly dispose unprocessed wastes on soil. In the direct OMW disposal locations surface soil has a dark color. The pump station and the waste pipe are located near the one of the two ponds which is emptied periodically (almost every 2-3 days). This uncontrolled land disposal occurred every year between May and September and wastes covered a large part of the field. Soil sampling took place one month after completion of wastes disposal, between 6^{th} and 9^{th} May, 2009. Soil samples were collected from the pond walls and at selected down slope distances, up to 105 m; in depth, samples were collected at 25 cm intervals up to 175 cm. Control samples collected from uphill points located far away from the disposal sites.

2.3 Total phenols measurement

Thirty ml of methanol /water (80:20) were added to 10 g of soil and mixed with ultra turrax T 25 at 15000 g for 1 min and then centrifuged at 5000 x g for 10 min. The extraction was repeated two times. The combined methanolic extracts were concentrated in vacuum rotary evaporator at <35 °C. Finally, the sample was dissolved in 5 ml gradient grade methanol and was analyzed colorimetrically.

The concentration of total phenols in the methanolic extract was determined colorimetrically using the Folin-Ciocalteau reagent. The absorbance was measured at 725 nm (in the range 0.01-1.00 mg ml^{-1}) against a blank, using a UV-VIS spectrophotometer (GBS model 916). Results were expressed in mg kg^{-1} of gallic acid (Gutiérrez *et al.*, 1977; Box, 1983).

3 RESULTS AND DISCUSSION

3.1 Sampling area NF1.

The concentrations of phenolic compounds in control soils of all disposal areas varied from 16.5 to 22.6 mg kg^{-1}; these values are considered in our study as guideline values for soils unaffected by OMW (Kavvadias et al., 2010).Figure 1 sketch the sampling area NF1 as well as the concentration of polyphenols in soil. The concentration of phenols was found very high (134.8 mg kg^{-1}) only for the surface pond soil and significantly increased for one sampling point away from the lagoon (69,33 mg kg^{-1}). In this case, the limited polyphenols dispersion is due to the fact that wastes do not disposed on soil but in the evaporation pond

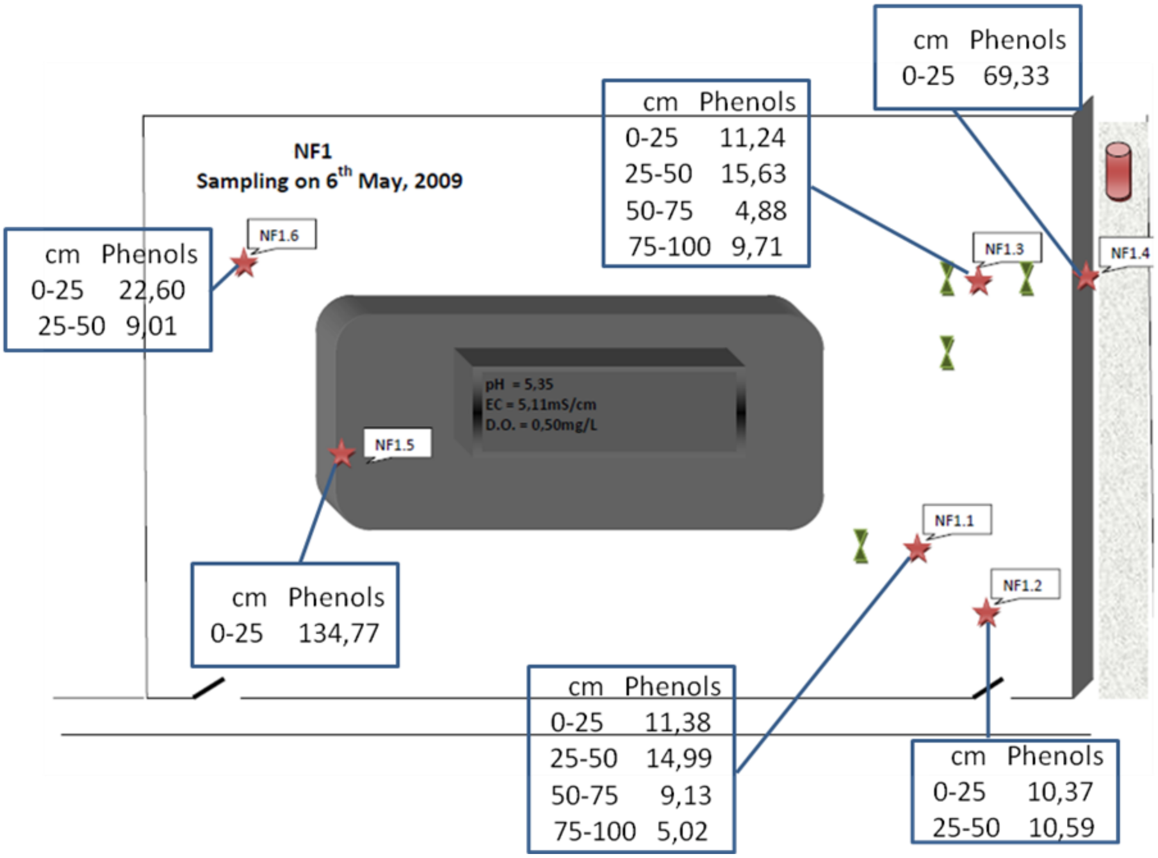

Figure 1. Sampling area NF1 and polyphenols concentration (mg kg^{-1}soil gallic acid)

3.2 Sampling area NF2.

Figure 2 sketch the sampling area NF2 as well as the concentration of polyphenols in soil. As for the case of NF-1 disposal area, very high polyphenols concentration (311 mg kg^{-1}) was measured for the surface pond soil.

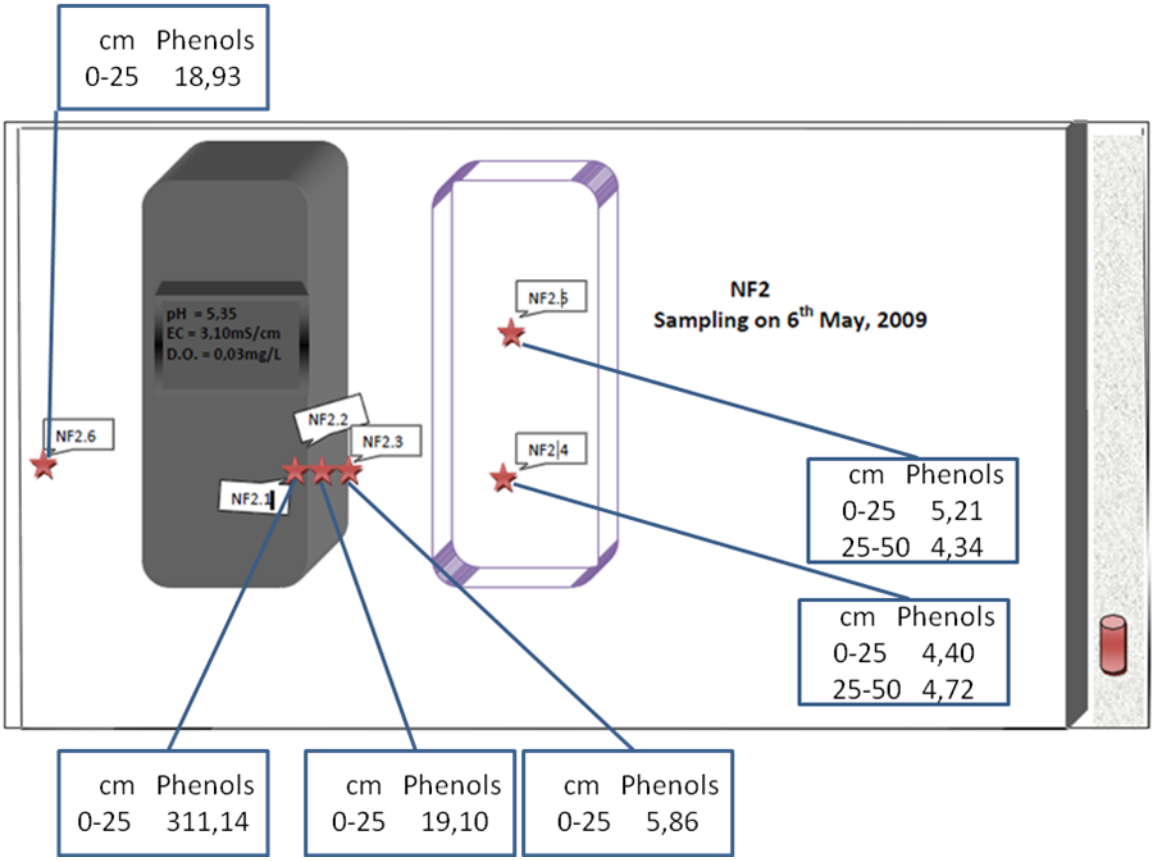

Figure 2. Sampling area NF2 and polyphenols concentration (mg kg^{-1} soil gallic acid)

3.3 Sampling area NF4.

Figure 3 sketch the sampling area NF4 as well as the concentration of polyphenols in soil. Very high polyphenols concentration was measured for surface pond soil (450 mg kg^{-1}), while the concentration of polyphenols remains high up to 100cm depth. Surface wastes disposal affects mainly NF4.7; NF4-8 points because the pump emptied lagoon D2 close to them; as well as areas from a neighboring field (NF 5.1in Figure 4). The soil disposal results in the presence of high polyphenol concentrations for NF4.7 (80 mg kg^{-1}) and NF4.8 (67.60 mg kg^{-1}) points as well as for NF5.1 (147.33 mg kg^{-1}) which is almost 105m away from the pumb.

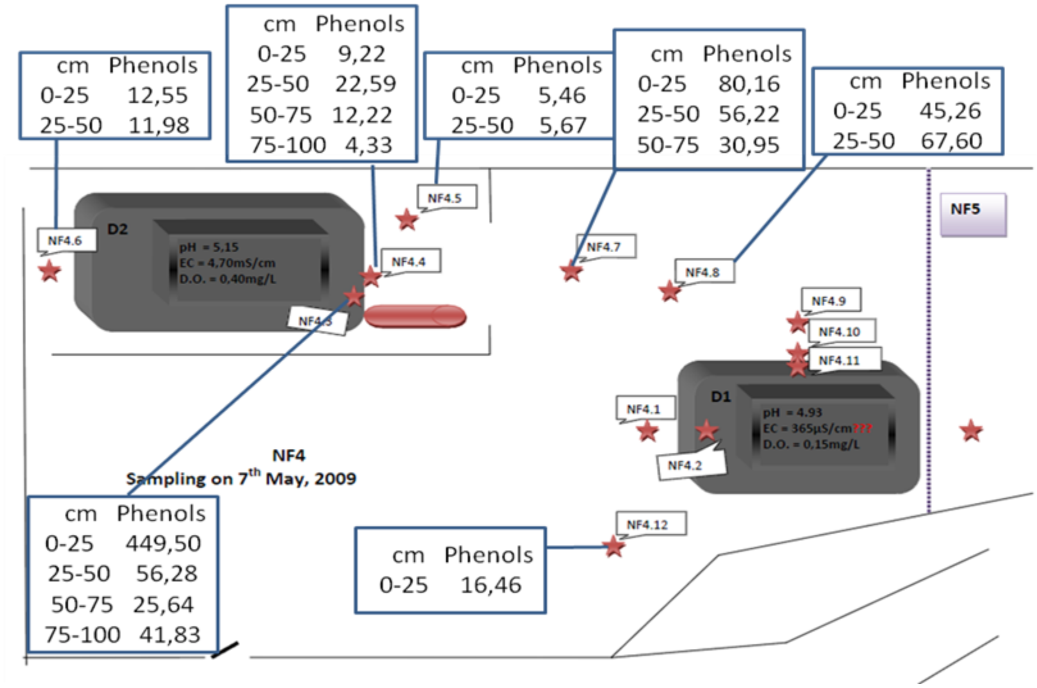

Figure 3. Sampling area NF4 and polyphenols concentration (mg kg^{-1} soil gallic acid)

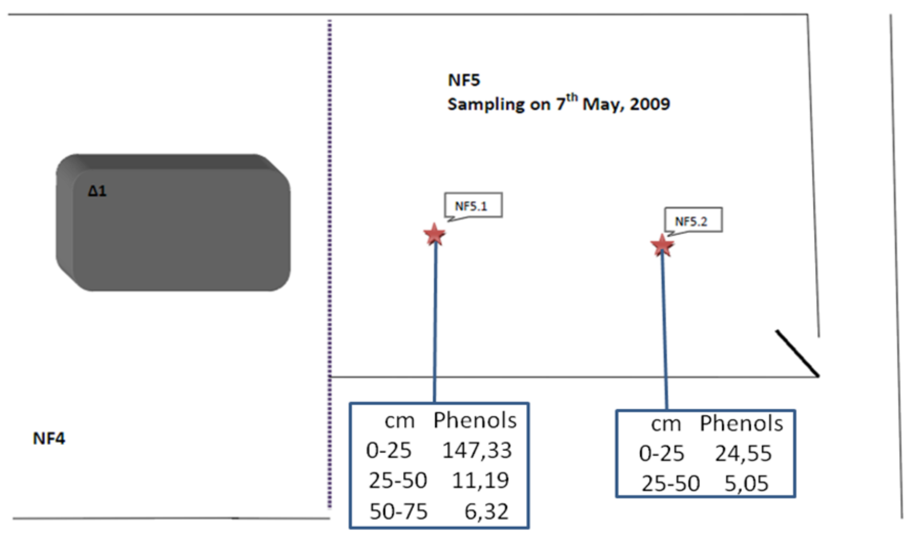

Figure 4. Sampling area NF5 and polyphenols concentration (mg kg^{-1} soil gallic acid)

3.4 Sampling area NF6.

Figure 5 sketches the sampling area NF6 (inactive for more than 6 years)and the concentration of polyphenols in soil. The concentration of phenols in surface soil layers (62 mg kg^{-1}) was higher than the values measured in the control site. This is in agreement with Feria (2000), who reported that the residual levels of polyphenols can remain significant even 6 years after OMW spreading. It has been shown that clay minerals present in soils affect markedly the organic material transformations and cause an increase in the concentration of some slowly decomposed polyphenol substances which persist even after a long period

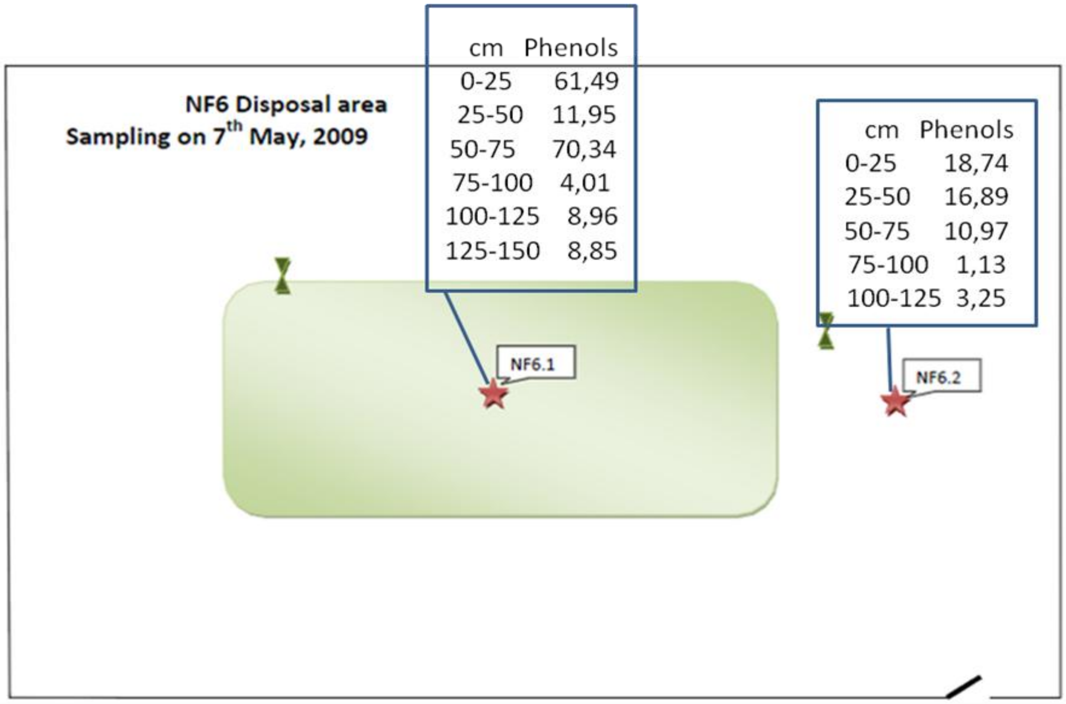

Figure 5. Sampling area NF6 and polyphenols concentration (mg kg^{-1} soil gallic acid)

4. CONCLUSION

The usual treatment and disposal method of OMW in Greece is the evaporation in ponds after neutralization with lime. In the upper soil layers in the evaporation ponds, the polyphenols concentration was measured particularly high, both in active and inactive disposal areas. The distance from the ponds had no substantial effect on soil phenolic load. On the other hand, direct disposal increased phenolic concentration in upper soil layers to values above threshold levels; By measuring polyphenols content in soils from an inactive disposal area, it was found that their concentration remained high even after 6 years from the last wastes application.

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