SOIL QUALITY MONITORING IN OLIVE OIL MILL WASTE DISPOSAL SITES

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SUMMARY: The uncontrolled disposal of olive oil mill wastes in not properly designed evaporation ponds or directly on soil can cause severe damages to soil properties, affect its quality and subsequently deteriorate the quality of surface- and groundwater in neighboring areas. The aim of this work was to monitor the effects of wastes disposal on soil properties and to develop a soil information and monitoring system for olive oil mills wastes disposal sites with the use of GIS and parameters-indicators for soil quality. Five olive oil mills sites were selected in a pilot municipality in Rethymnon, Crete, South Greece, three of them are active for more than 10 years and two are inactive for the last 6 years. Periodical soil sampling campaigns reveal significant changes in soil properties. The sampling regions have been connected to map layers and an accompanying database of the measured parameters. On-the-fly diagrams that show the temporal fluctuations of the chemical parameters were formed and updated continuously following the corresponding analysis phase. At the same time, surfaces of the most critical parameter-indicators are formed based on kriging interpolation to define their spatial distribution in the wider waste disposal areas. The particular maps are superimposed on other available map layers (e.g. land use, vegetation, geology, erosion, a.o.) contributing to the study of the correlation and effects of the specific pollution parameters to the rest of the environmental attributes of the area.

1. INTRODUCTION

The large quantities of Olive Mill Wastes (OMW) generated in the area under study located in the municipality of Nikiforos Fokas, prefecture of Rethymnon, Crete, are disposed of in unprotected evaporation lagoons or directly on soil causing thus deterioration of the quality of soils as well as ground- and surface water. 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.

The fate of contaminants (e.g. polyphenols) present in OMW disposed of in lagoons is defined by a number of physical, geochemical and biological processes which may attenuate, concentrate, immobilize, liberate, degrade or otherwise transform them. Therefore the precise calculation of risk depends on the concentration of each contaminant, the route of exposure and the properties of soils which define the type of physical/chemical interactions (Zaharaki and Komnitsas, 2009). Moreover, when OMW is properly mixed and incorporated at acceptable loading rates herbicidal activity is enhanced (Kotsou et al. 2004), soil organic matter and nutrient availability for plant growth is increased and thus, soil fertility status and productivity are improved (Mechri et al. 2008). On the other hand, the use of wastes for agricultural purposes may cause acidity, salinity, N immobilization, microbial response, excessive leaching of nutrients, as well as lipids, organic acids and phenolic compounds accumulation (Brunetti et al. 2007).

Despite the large number of research works which were focused on the appropriate use of OMW on the agricultural sector, there are only few studies dealing with the effect of long term disposal of OMW in evaporation ponds on soil properties relative to climatic conditions and time. In the framework of LIFE+ funding scheme a four year project entitled "PROSODOL: *Strategies to improve and protect soil quality from the disposal of olive oil mills' wastes in the Mediterranean region*" is carried out since January 2009. In this study we present some characteristics of OMW and water samples and initially assess the impact of active and inactive olive mill waste evaporation ponds on underlying soil properties as well as the effects of untreated OMW application on soils. We also present the characteristics of OMW and water samples and the WEB portal (www.prosodol.gr) that gathers information from all project participants, organizes measurements and data in databases and information libraries and allows access to external user groups.

2 MATERIALS AND METHODS

2.1 Study area

Municipality of Nikiforos Fokas belongs to the Subtropical or Mediterranean climate with soft winters and dry-hot summers. Limestones, dolomites, marbles and alluvial deposits are mainly identified. Soils in the area under study are rich in carbonates, slightly to moderate alkaline and have clayey or silty clayey texture.

2.2 The WEB portal – Soil quality monitoring

Most of the sampling points are imported into ArcGIS according to their coordinates which are given in the Greek grid reference system GGRS/EGSA'87. Apart from the sampling areas, three more thematic group layers were integrated to the GIS: modern characteristics, land use elements and geomorphologic features. A total of 13 GIS services have been published and are shown as layers on top of the Google map. To insure compatibility all GIS services had to be published using WGS 1984 web Mercator projection. The maps were synthesized in two different GIS projects through the use of cashing and Google Maps API. Customization of each project was carried out for the labelling of the different layers as a function of the scale, the transparency degree of each layer, the hierarchical sequence of layers and the symbolism and colors that were used for the better visualization of the data.

Modern characteristics included first level local administration units (OTA), villages and the road network comprising main roads and dust roads. All the above were digitized from topographic maps of 1:50,000 scale produced by the Hellenic Military Geographical Service. Land use elements comprised of layers holding information in respect to the NATURA 2000 ecological network of protected areas, CORINE land cover as well as artificial vegetation, erosion, land region, soil depth, forestry capability codes and land use codes digitized from maps produced by the Greek Ministry of

Agriculture. Geomorphologic features consisted of the Digital Elevation Model (DEM) and the Hillshade Model, created by processing SPOT stereoscopic images, as well as rivers and mountains digitized from topographic maps. In addition to the group layers, individual layers were also included to the GIS interface. Geological formations and faults were digitized from geological maps of 1:50.000 scale produced by the Institute of Geology and Mineral Exploration and thematic layers concerning hydrolithology and springs, were vectorized by hydrological maps of 1:100.000 scale. Although not all of the above layers have been published in the WEB_GIS application of the project, they will contribute to the further analysis of the risk assessment in the wider OMW disposal sites in the region of Nikiforos Fokas.

2.3 OMW and water sampling

After five sampling campaigns, over a period of more than one year, OMW samples were collected from four lagoons in the three active disposal areas. Water samples were also collected from wells, springs, water supply pipes and streams located in the vicinity of the disposal areas within a maximum distance of 10 km. An indicative characterization of OMW and water samples, as well as drinking water standards is seen in Table 1.

2.4 Soil sampling

Five sites representing different disposal cases were included in the study. Evaporation ponds in each site were constructed by excavating the superficial soil and using this to form pond walls. No protective impermeable membranes or other protective media were used. Three ponds located in ACTS-1, ACTS-2 and ACTDS-3 sites respectively are active for at least 10 years while the forth (INACTS-4 site) and fifth one (INACTS-4 site) are inactive for the last 6 years. In addition, the owner of ACTDS-3 uses a pump to directly dispose unprocessed wastes on soil. The pond is emptied periodically (almost every 2-3 days) between May and September and OMW are released and cover a large part of the field. Soil sampling took place every two months starting in May, 2009. Soil samples were collected from the ponds and the down slope side at a distance of 105 m to a maximum depth of 175 cm at 25 cm depth intervals. Control samples collected from the upper slope side of the ponds. In this study changes in selected soil properties during the initial sampling campaign (May, July and September 2009) from the direct disposal site ACTDS-3 and the inactive site INACTS-4 are presented (Table 2).

2.5 Analytical methods

2.5.1 Waste and water analysis

The principal chemical properties of OMW and water samples pH, EC, salinity, LDO, COD, TS, TDS, NH_4^+, NO_3^-, Hardness$_{tot}$, SO_4^{2-} , PO_4^{3-}, Cl^-, K, Mn, Fe, Cu, Zn, were determined in duplicates according to standard procedures (Clesceri et al. 1998). The total phenol content was determined by the Folin- Ciocalteau method (Box, 1983).

2.5.2 Soil analysis

Laboratory determinations were performed according to the methods usually used for soil characterization (Page et al. 1982). Particle size distribution was carried using the Bouyoukos method; pH and electrical conductivity were measured in paste extract using a glass electrode pH/EC meter; organic matter was determined by dichromate oxidation; carbonates by using Bernard calcimeter; total N by the Kjeldahl method; available phosphorous with sodium hydrogen carbonate extraction; exchangeable K, Ca and Mg by $BaCl_2$ extraction, available Mn, Fe, Cu and Zn with DTPA extraction. The determination of NH_4^+, NO_3^-, Cl^-, PO_4^{3-}, and SO_4^{2-} were performed in 1:10 water extract with the use of a Dionex-100 Ionic Chromatography. Soil B was extracted with boiling water using the azomethine-H method. Methanol extractable phenol compounds were quantified by means of the Folin–Ciocalteu colorimetric method (Box, 1983).

3. RESULTS AND DISCUSSION

3.1 Characterization of OMW and water samples

Table 1: Characterization of diluted OMW and water samples

Parameter	OMW samples	Water samples	Drinking water standars
pH	5-6	7-8	*6.5-8.5 (FPTC, 2008)*
Electrical conductivity, μS/cm	350-5000	400-870	*~2500 (98/83/EC)*
Liquid dissolved oxygen (LDO), mg/L	0-3.8	5-10	*No health-based guideline value (WHO, 2008)*
Total solids (TS), g/L	~10	–	*≤0.5 (FPTC, 2008)*
Mineral solids, g/L	~0.5	–	-
Total dissolved solids (TDS), g/L	~9.5	–	*<0.5 (FPTC, 2008)*
Salinity, g/L	0.2-3.2	–	-
COD, g/L	5-15	0	*<255 mg/L (WHO, 2008)*
Phenol, mg/L	20-100	0-5	*<0.5 μg/L (98/83/EC)*
Tannic acid, mg/L	160-560	0-0.6	*No health-based guideline value (FPS, 1999)*
Hardness$_{tot}$, mg/L $CaCO_3$	320-2400	145-420	*No health-based guideline value (WHO suggests safe levels around 100-200 mg/L)*
NO_3, mg/L	300-1000	0-13	*<45 (FPS, 1999; FPTC, 2008)*
SO_4, mg/L	250-1400	5-60	*≤500 (FPS, 1999; FPTC, 2008; WHO, 2008)*
PO_4, mg/L	25-270	0-1.3	*No health-based guideline value (WHO suggests a maximum safe level of 5 mg/L)*
Cl, mg/L	120-360	5-30	*<250 (98/83/EC; FPS, 1999)*
NH_3-N, mg/L	50-200	0	*<3 (WHO, 2008)*
K, mg/L	75-1400	0.2-10	*<12 (98/83/EC)*
Mn, mg/L	10-90	0-1	*<0.05 (98/83/EC; FPS, 1999; FPTC, 2008)*
Fe, mg/L	0.1-1	<0.1	*<0.2 (98/83/EC)*
Cu, mg/L	0.1-9	<0.1	*<2 (98/83/EC)*
Zn, mg/L	0.8-1.7	0	*≤5 (FPTC, 2008)*

Results show (Table 1) that OMW samples are characterized by relatively low pH and LDO values (between 5-6 and up to 3.8 mg/L, respectively). Total and mineral solids are ~10 and ~0.5 g/L respectively, while the concentration of total dissolved solids is around 9.5 g/L. COD values are quite high ranging between 5-15 g/L. Concentration of other significant parameters such as NO_3, SO_4, Cl, K, Mn and Cu are higher than drinking water standards. Water samples are in general characterized by neutral pH (7-8), electrical conductivity ranging from 400 to 870 μS/cm and LDO between 5 and 10 mg/L. Water samples collected in the near vicinity of the lagoons (within a maximum distance of 1 km) show a high phenol concentration (up to 5 mg/L). The concentration of NO_3, SO_4, PO_4, Cl, K, Mn, Zn and Cu is lower than drinking water standards.

3.2 Effect of OMW on soil properties

Table 2: Mean values of soil properties in control, pond and down slope at various distances in ACTDS-3 and INACTS-4 site (soil data were averaged across samplings and soil layers).

Soil properties	ACTIVE SITE ACTDS-3										INACTIVE SITE INACTS-4	
	Control soil	Pond soil	Distance from pond								Control soil	Pond soil
			1m	3m	4m	25m	50m	75m	90m	105m		
pH	7.7	7.7	7.9	7.8	7.7	7.8	7.6	7.8	7.6	7.7	7.5	7.6
$CaCO_3$ (%)	52	59	61	53	26	46	22	5	25	27	2	8
EC_{25} (dS m^{-1})	0.7	2.8	1.7	1.3	0.9	2.0	3.2	2.6	1.8	0.8	0.4	0.7
K^+ (cmol kg^{-1})	0.5	7.4	3.2	3.2	0.8	7.9	9.3	13.7	7.9	3.8	2.6	2.6
Mg^{2+} (cmol kg^{-1})	2.1	2.9	3.2	3.5	4.0	2.6	5.7	4.7	2.7	2.7	0.5	3.3
Cl^- (mg kg^{-1})	45	114	113	95	44	112	160	415	115	32	22	22
SO_4^{2-} (mg kg^{-1})	98	74	90	107	44	155	297	393	465	158	154	154
Organic matter (%)	3.4	5.7	1.6	3.5	4.9	3.6	5.0	4.2	5.5	4.8	2.3	2.4
Total phenols (mg kg^{-1})	19	54	13	12	14	33	38	20	53	38	20	38
Kjeldahl N (mg g^{-1})	1.7	2.2	0.8	1.9	3.5	2.7	5.3	3.6	3.6	2.9	2.1	1.5
NH_4^+ (mg kg^{-1})	70	40	15	30	50	2	12	32	57	43	18	16
P (mg kg^{-1})	8	180	15	44	4	60	116	151	195	6	2	45
PO_4^{3-} (mg kg^{-1})	7	74	18	13	113	12	60	73	45	7	12	11
B (mg kg^{-1})	0.5	1.2	0.6	0.5	0.5	0.9	0.9	0.9	2.0	0.6	1.2	0.8
Cu (mg kg^{-1})	1.9	7.2	3.7	3.3	2.6	4.4	5.8	5.5	4.8	2.7	4.4	5.9
Mn (mg kg^{-1})	7.3	6.9	5.8	11.9	14.9	18.7	36.7	25.0	13.6	10.7	10.7	12.1
Fe (mg kg^{-1})	21	148	59	76	17	105	163	148	203	30	9	37
Zn (mg kg^{-1})	0.3	4.1	0.5	0.6	0.7	1.4	3.4	1.7	1.7	0.8	1.0	1.3

3.2.1 Soil acidity and carbonate content

Regarding pH levels (Table 1) and compared to the control, no marked differences were recorded, with the exception of the first 25 cm of soil in evaporation pond where pH in the first two samplings (May and July) was lower (pH=6.6-7.3) due to the acidity of OMW (pH=4.93-5.15). Therefore, surface application does not markedly change soil pH. In the case of carbonates and in comparison to control (47-49 % $CaCO_3$), the carbonate content of the upper soil layer in pond in surface disposal points was considerably lower in all soil samplings. Carbonates, present in soil, buffer the wastes acidity by generating soluble calcium bicarbonate, which infiltrates to the lower horizons and precipitates again as calcium carbonate (Sierra et al., 2001; Mechri, 2007).

3.2.2 Electrical conductivity

In comparison to control soil (EC: 0.60-0.91 mS/cm), electrical conductivity of pond soil and in most sampling points where direct application of OMW took place was substantially enhanced, however for most sampling points EC levels were still below the threshold EC value for salinity (4 mS/cm). Electrical conductivity in soil pond increased with soil depth at the first two samplings suggesting thus infiltration of OMW from the surface to the deeper soil layers whereas at the 3rd sampling EC was decreased with soil depth probably due to xerothermic conditions prevailing in this sampling period.

3.2.3 Concentration of K^+, Mg^{2+}, Cl^-, and SO_4^{2-}

The exchangeable K content in pond soil, reached high levels even at deeper soil layers (8-11 cmol kg^{-1}). Moreover many of the soil locations receiving OMW exhibited higher K content (up to 17 cmol kg^{-1}) than pond soil mainly at the upper soil layers. This may have deleterious effects on soil physical properties with potential effects on enhancement of potassium mobility and groundwater contamination (Arienzoa et al. 2009). Regarding the inactive disposal site and in comparison to control, high levels of exchangeable K were found in the upper soil layers (0-25 and 25-50 cm) of pond soils, being 13 to 18 times higher (8.80 and 5.5 cmol kg^{-1} respectively).

Pond surface soil was rich in exchangeable Mg (2.8 cmol kg^{-1}) and direct soil application favours Mg availability (3.3-7.3 cmol kg^{-1}) as compared to control values (2.1-3.8 cmol kg^{-1}). This may potentially endanger soil quality. Previous studies reported that, in general, application of OMW on soil increases available Mg (Walker and Bernal, 2008). Considerably higher levels of SO_4^{2-} and Cl^- were recorded for most sampling points at ACTDS-3 site compared to control in the upper soil horizons (up to 50 cm) whereas differences were diminished in deeper layers.

3.2.4 Organic matter and total nitrogen

The content of organic matter was very high in the top soil layer of pond (42 %) but it was sharply reduced with increasing depth and time of sampling. Moreover, there was a small increase in the content of organic matter in the top soil in places where direct disposal of OMW occurs in comparison to control. According to Yasemin and Killi (2008), the significant enhancement in the organic carbon content recorded after 1-2 months of increased application of OMW is a short term effect. As with organic matter in soil, the content of N does not seem to be affected by N surplus in top soil of pond (4.2-6.8 mg g^{-1}) and it is gradually decreased with soil depth except for the upper layer (0-25 cm) of the surface disposal points which are rich in total nitrogen (>0.3 %).

3.2.5 Available P

Pond soil was very rich in available P and water soluble phosphates compared to control. Surface disposal of OMW increased the concentration of extractable P in top soil up to 30 times. The overloading of soils with phosphate ions could result in P leaching, increasing the risk for surface water contamination. The environmental concern of allowing P to accumulate to very high levels in soil is the long period required to reduce P to levels normally recommended for agronomic production. This is why at the inactive site surface P concentration was still very high compared to control.

3.2.6 Total phenols

The concentrations of phenolic compounds in control soils varied from 16.5 to 26.6 mg kg^{-1} and these values are considered, in our study, as background values for soils unaffected by OMW (Sierra et al. 2001). In the first sampling (May) phenol content was very high in the top soil in pond and in sampling points where direct disposal of OMW takes place and remains higher than the control up to 100 cm depth. However differences between control soil and soil treated with OMW were diminished in the following samplings suggesting a short term effect of high total phenol content in the studied soils treated with raw OMW.

Although the inactive pond has been abandoned for more than six years, the concentration of phenols in surface soil layers (62-77 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 application.

3.2.7 Micronutrients

In pond soils the levels of available B and metals, Cu and Fe and Zn (0.8-4.3 mg kg^{-1}, 8.5-9.9 mg kg^{-1}, 101-183 mg kg^{-1}), were markedly higher than the control soil (0.2-0.4 mg kg^{-1}, 1.8-2.5 mg kg^{-1}, 8.2-18 mg kg^{-1}). Marked differences were also recorded between the control and soil received OMW in respect to extractable Cu, Fe, Mn, and Zn fractions. Moreover the six year period after abandonment of disposal ponds was not adequate to reduce Cu and Fe concentrations in pond surface soil layers (6.6-10.3 mg $kg^{-1}$and 66-117 mg kg^{-1} respectively) to normal values.

3.3 Monitoring of soil quality

On-the-fly diagrams showing the temporal fluctuations of the chemical parameters were formed and updated continuously following the corresponding analysis phase. The results of the chemical analyses of the samples were entered in databases that make specific discrimination for the location and depth of the samples and the period of the sample collection. At the same time, surfaces of the most critical parameter-indicators were formed based on IDW interpolation to define their spatial distribution in the wider waste disposal areas (Figure 1). The particular maps are superimposed on the rest of the cartographic layers contributing to the study of the correlation and effects of the specific pollution parameters to the rest of the environmental attributes of the area. Such an integrated methodology may help scientists and local authorities to evaluate potential risks and also monitor and control degraded areas and consequently to take all the required measures for their protection and sustainable management.

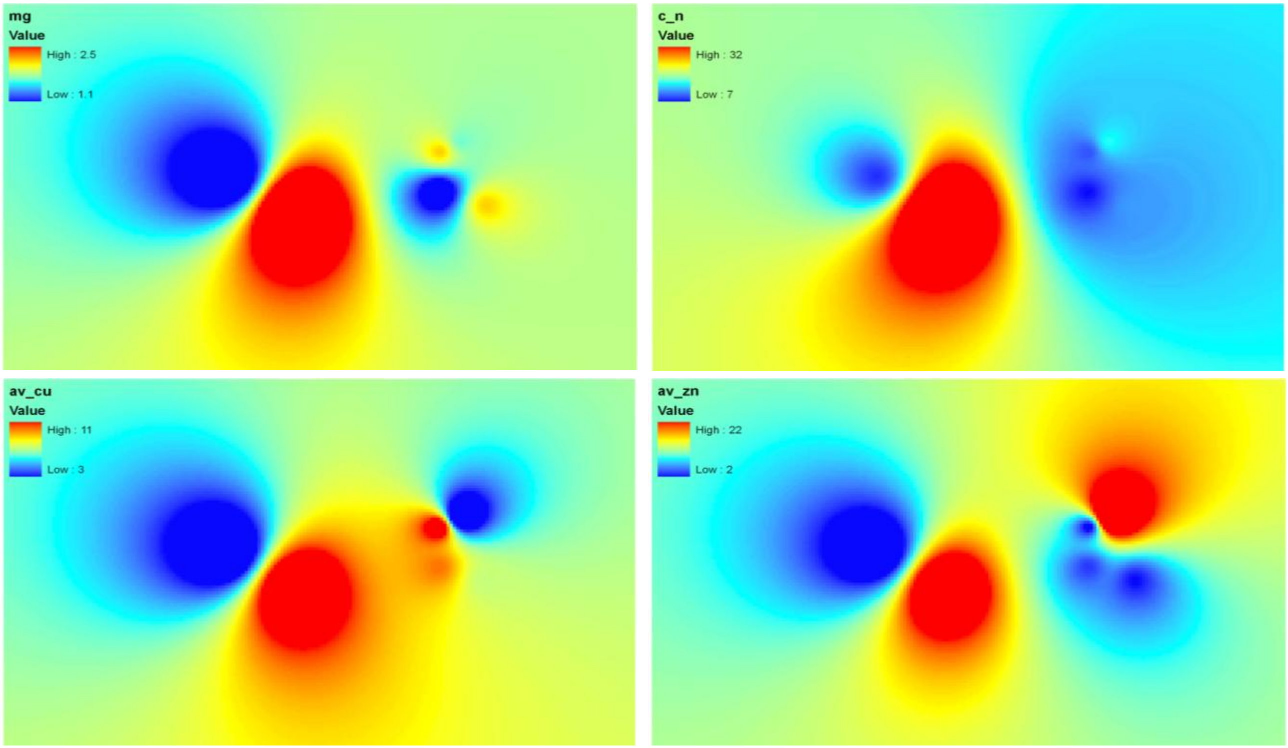

Figure 1. Interpolation surfaces indicating the distribution of chemical parameters in the vicinity of the disposal areas using the inverse distance weighted (IDW) technique.

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4. CONCLUSIONS

The long term uncontrolled disposal of raw OMW on soil causes degradation of its quality as well as contamination of surface- and groundwater. The study of the fate of major organic and inorganic contaminants in underlying soil as well as in water systems in combination with WEB_GIS applications will contribute to the assessment of the risk due to OMW disposal in the region of Nikiforos Fokas.

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