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ORIGINAL ARTICLE

Assesing the effect of an olive mill wastewater evaporation pond in Sousse, Tunisia

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Abstract Olive oil is a typical and valuable agro-industrial product in Mediterranean countries. In Tunisia, olive mill wastewaters (OMW) reach an amount of about 1,000,000 t year^{-1} and constitute a serious organic pollution risk because of the high chemical oxygen demand values and the presence of phytotoxic and antibacterial polyphenols. OMW have been generally stored in pond sites to be eliminated by natural evaporation or valorised by spreading on cultivated soils or by composting. Many researches on the interactions of OMW with soils at laboratory scale (columns) have been reported, but less attention have been paid to the effect of OMW on soils at field scale. The aim of this work is to investigate an area used for >15 years as an uncontrolled OMW pond site. The transformations of soil properties and groundwater occurring during OMW storage were characterised by the pH, phenolic contents, electrical conductivity (EC), moisture content and organic contents. The soil samples were taken from two borings and compared to those of a control one located near the pond site. Groundwater samples were taken on the accessible and nearest water wells to the evaporation ponds. The permeable silty and sandy layers in the site support the infiltration of OMW near the evaporation ponds. This infiltration has reached a depth of 6 m at a distance of almost 50 m laterally. The results show that the OMW infiltration in the subsoil has affected the pH, EC, organic content, phenolic compounds and the moisture.

Keywords Olive mill wastewater · Evaporation pond · Contamination · Soil · Groundwater

Introduction

Olive oil is a typical and valuable agro-industrial product in the Mediterranean region. Tunisia is one of the most important producers of olive oil. In fact, the average Tunisian production is about 22 × 10^4 tons of olive oil per year representing >8% of the worldwide production. The extraction of olive oil which is carried out in small seasonally operating units, generates two by-products, namely solid residues, constituted by olive husk, and liquid residues: the olive mill wastewater (OMW).

The quantities and qualities of these by-products vary according to the technology used in olive processing. The batch-pressure system, also known as the traditional system, produces from 400 to 500 l of OMW per ton of olives (Bonari and Ceccarini 1990). In the continuous process with three-phase decanter system, the amount of OMW ranges between 500 and 1,400 l t^{-1} (Sierra et al. 2001) whereas, in the continuous process with two-phase decanter system, the liquid residue remains mixed with the solid residues.

The purpose of this work is to characterize the Kalâa Kebira (Sousse, Tunisia) OMW evaporation pond, to analyze its environmental impact particularly and to evaluate the evolution and propagation of phenolic compounds on underlying soil and groundwater. This has been achieved by using chemical analysis on soil and groundwater samples taken around the OMW pond site.

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Table 1 Overall composition of OMW (adapted from S'habou et al. 2005; Martin et al. 1991)

Parameters	Range
pH	4.5–5.2
Electrical conductivity (mS cm^{-1})	8–16
COD (g l^{-1})	45–130
BOD (g l^{-1})	35–100
Suspended solids (g l^{-1})	1–9
Total solids (g l^{-1})	60–120
Mineral solids (g l^{-1})	5–15
Volatile solids (g l^{-1})	55–105
Sugar (g l^{-1})	10–80
Pectins, mucilage and tannins (g l^{-1})	3.7–15
Polyalcohols (g l^{-1})	1.1–15
Polyphenols (g l^{-1})	5–24
Fats (g l^{-1})	0.5–10
Organic acids (g l^{-1})	5–10
Amino acids (g l^{-1})	2.8–20
PO_4^{2-} (g l^{-1})	0.8
Cl^- (g l^{-1})	0.27
SO_4^{2-} (g l^{-1})	0.01
Na^+ (g l^{-1})	5.37
K^+ (g l^{-1})	15.29
Ca^{++} (g l^{-1})	1.17
Mg^{++} (g l^{-1})	0.41
Mn^{++} (g l^{-1})	0.01

OMW characteristics and management attempts

The OMW comes from the vegetable water of the fruit and the water used in the different steps of oil production and contains olive pulp, mucilage, pectin, oil, etc., suspended in a relatively stable emulsion (Paredes et al. 1999) and constitutes a dark, full smelling and turbid liquid. Its characteristics are strongly influenced by the oil extraction method, the variety of olive fruit and ripeness, climate and soil condition.

The overall composition and constituents of OMW is summarized in Table 1.

The pH of OMW is low around 5, its electrical conductivity (EC) is relatively high (compared to wastewaters which do not exceed 7 mS cm^{-1}), and it has high free polyphenol content (Martinez et al. 1986).

Generally, more dilute wastewaters are produced with the continuous process, but the polluting organic load expressed in weight of processed olives, is practically independent of the processing method and ranges between 45 and 55 kg biological oxygen demand (BOD) per ton of olive (Hamdi et al. 1991).

Different minerals were identified and it has been found that potassium (K^+), sodium (Na^+) calcium (Ca^{2+}) and phosphorous (PO_4^{2-}) are the most present minerals in OMW and showing concentrations of about 15.3, 5.4, 1.2 and 0.8 g l^{-1}, respectively (Salvemini 1985).

Pollution by olive wastewater is becoming a crucial problem particularly in the four main olive oil producer countries: Italy, Spain, Greece and Tunisia (Hamdi and Ellouz 1992). In fact, >30 × 10^6 m^3 of OMW are produced per year which is generated during a few months of the year (November to February).

To overcome the pollution problems related to this effluent, many valorization alternatives are tested by researchers (Roig et al. 2006). OMW is often used as soil fertilizer and amendment, and thus its effects on nutrient evolution, seed germination, crop production and agronomic soil properties and soil organic matter have been reported in several studies (Mekki et al. 2007; Komilis et al. 2005; Ehaliotis et al. 1999; Perez and Gallardo-Lara 1989; López et al. 1996). The effect of The OMW as soil amendment on soil porosity and on leaching of the herbicides resulted in an increase of the organic carbon content of the soil and a reduction in soil porosity by decreasing the volume of large size pore and increasing the smallest pores (Cox et al. 1997).

Actually, valorization studies are focused on the degradation of phenolic compounds which seem responsible of the dark color. The enzymatic degradation was developed by many authors (Kissi et al. 2001; Perez et al. 1987; Robles et al. 2000). The process of combining the clayey soils and the hydrogen peroxide is capable to remove black-brownish color of OMW with elimination of the polyphenols (Oukili et al. 2001).

Some experimental studies (Mellouli et al. 1998) have shown that OMW is characterized by their adhesive and stabilizing behavior for non-agricultural purposes such as the beneficial effect on soil aggregation, soil structure stability and hydrodynamic properties of sandy soils, by reducing the evaporation losses.

Different elimination methods were developed based on physical, chemical and biological treatments (Fiestas Ros De Ursinos and Borja-Padilla 1992, 1996; Ramos-Cormrnzana et al. 1996). Many researches have shown the effect of ultra-son treatment in biogas production (Chui et al. 1997; Forester et al. 2000).

All studies and experiments carried out to treat and valorize this effluent have not reached the industrial or in situ scale for economic reasons. Besides, OMW cannot be used in all soil types and only limited amounts are consumed compared to quantities generated annually.

The storage of OMW in evaporation ponds is the most economic and frequently used method nowadays, but the high level of chemical oxygen demand (COD) values (up to 130 g l^{-1}) and the presence of phytotoxic and antibacterial phenols present a serious pollution risk for superficial and underground waters (Arambarri and Cabrera 1986;

Sierra et al. 2001) in addition to the release of polluting gases namely phenols and sulfur dioxide (Gianfranco et al. 2003).

In Tunisia passive evaporation (natural) in wild sites or in poor-engineered sites is the only used technique to manage the huge amounts of OMW, so far. However this technique needs a long time for evaporation and large space is required, besides the environmental annoyances and the residues left after achieving evaporation.

The kalâa Kebira OMW pond site

The studied site is located in Kalâa Kebira at Sousse city, East of Tunisia at an altitude of 70 m and 1.5 km far from the M'derej wadi (Fig. 1). It covers a total area of about 2 ha including the evaporation ponds built directly on the site without an impervious layer. It is divided into two small basins Br and Bf used for receiving the OMW and eventually for suspended solids elimination via filtration, respectively; and two evaporation ponds, B1 and B2 with an area of 8,000 and 7,000 m^2, respectively (Fig. 2).

The evaporation basins were built by excavating the soil and heaping it around to form retaining walls. The mean depth of these evaporation ponds is 11 m, with a storage capacity of almost 160,000 m^3 of OMW. During the olive oil campaign, the site receives OMW generated from the traditional and three-phase extraction systems with rates of 140 and 650 m^3 day^{-1}, respectively.

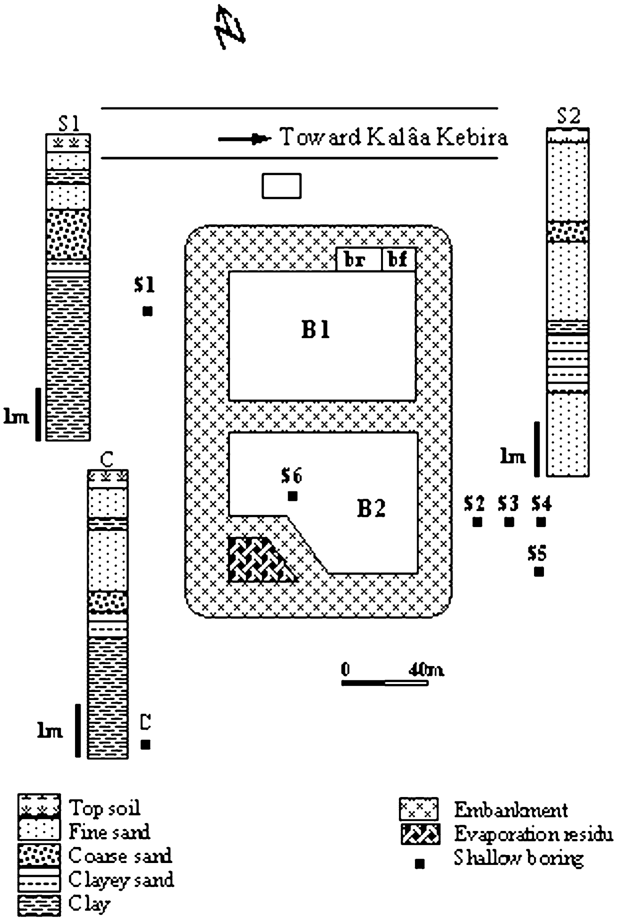

Fig. 2 Detailed Site map with investigation borings

Geological and hydrogeological framework

The Sousse region is formed by weak elevated hills separated by shallow depressions with lakes and sebkha. This region is located in an arid zone. In fact, the mean annual temperature recorded during 30 years was 19°C and the mean annual precipitation was 336 mm $year^{-1}$. The evaporation was weak in January (86 mm) and reached 147 mm on July. If we consider that OMW losses in such conditions are similar to water losses, the OMW evaporation rate in the site will be around 1,019 mm $year^{-1}$. The air humidity was 71% and the wind speed was around 22 m s^{-1} with slightly higher values in winter (25 m s^{-1}). Thus, these meteorological conditions favored elimination of OMW by natural evaporation.

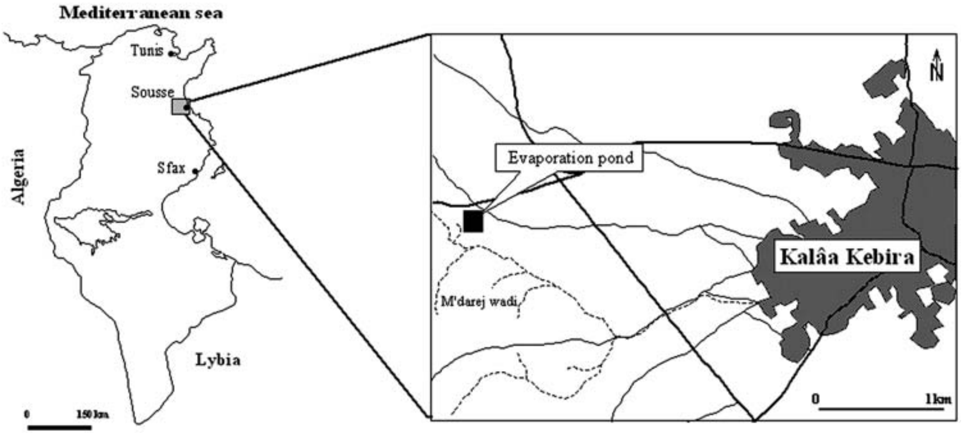

Fig. 1 Location map of the study area

The geologic outcrops are of Mio-Pliocene and old and recent Quaternary ages. The Mio-Pliocene layers are formed by sand, sandstone and salty clayey sand material. The old Quaternary outcrops are constituted by red clays and the recent quaternary ones are formed by alluvial deposits and sand dunes.

The aquifer in the study area has an extension of 217 km^2 and it is located in the Plio-Quaternary clayey sand deposits. The groundwater level depth ranges between 10 and 40 m. The unsaturated levels in the site were around 25 m. The groundwater salinity varied from 2 g l^{-1} to almost 10 g l^{-1} and was around 2 g l^{-1} in the site vicinity. The main groundwater uses are for human consumption and agricultural irrigation.

Materials and methods

Seven borings, with 1.5–7 m depth, were executed in the site (Fig. 2). The different material profiles were used to determine the site lithology and to examine the contamination degree in the area. Material sampling were conducted in all the borings, but only three representative borings, the deepest ones, have been characterized in this study; namely S1 and S2 situated near the basins B1 and B2, respectively and C located at 100 m far from the disposal area serving as a control material.

Two samples of the stored OMW, E1 and E2 were sampled from the surface and at the bottom of the basin B1, respectively.

In December 2005, representative groundwater samples were obtained from the 15 accessible and nearest pumping water wells to the evaporation ponds. Most of the selected wells are used for irrigation and their groundwater levels ranged from 20 to 36 m. Samples were collected in glass flask and stored in a dark refrigerator at 4°C prior to analysis.

Laboratory analyses were carried out on samples of groundwater, stored OMW and soil samples taken from borings.

The groundwater and OMW samples were tested for EC, and pH by direct measurement in the liquid samples. The dosage of Mg^{++} and Na^{+} consists on acidic decomposition at a temperature of 120°C with nitric and perchloric acids. Mg^{++} was determined according to the atomic absorption spectrophotometry method with a polarized Zeeman Z6100 spectrophotometer. Na^{+} was analyzed using a Jenmay PFP.7 flame photometer.

Chemical oxygen demand was determined by oxidation through boiling (148°C) with excess of potassium dichromate in acid medium and BOD was estimated with respiratory apparatus.

Phenolic compounds were extracted with ethyl acetate by mixing the OMW samples with the organic solvent (1:1 v/v) during 8–10 min. Concentrations in the extracts were measured by means of the Folin–Ciocalteau Colorimetric method, using 4-methl-cathecol as standard.

Total nitrogen (TKN), N$_{\text{org.}}$, NH$_4{}^{+}$ were determined by Kjeldahl method. The total solids were determined after drying the sample 24 h at 105°C. The ash content was determined after calcination of the dry sludge at 550°C for 2 h. The difference between total solids and ash content is defined as volatile solids (VS).

For soil samples, the analyses were conducted on air dried and 2 mm sieved fraction. Total organic content was estimated by 2 h calcination at 550°C. EC and pH were determined in a 1/2.5 (w/v) water soluble extract of the soil sample. Phenolic compounds were extracted with ethyl acetate, a 1/4 (w/v) soil/solvent extract was shaken for 48 h in a mechanical shaker, then filtrated and concentrated in a rotary evaporator at 40°C. Concentrations in the extracts were quantified by means of the Folin–Ciocalteau colorimetric method, using 4-methl-cathecol as standard.

The relative analytical uncertainties for the previous parameters were within 0.1 for the pH and the EC, 3% for Polyphenols, 4% for organic contents and 2% for moisture content.

The soil identification parameters consisted of sieve analysis using dry sieving technique, permeability test and liquid and plastic limits for clayey sample.

Results and discussion

OMW in the storage basins

The analysis results of the sampled OMW, E1 and E2 taken from the storage basin B1 are shown in Table 2 including pH, EC, COD, BOD, TS, TKN, N$_{\text{org.}}$, NH$_4{}^{+}$, polyphenols, oils and soluble Na^{+}, Mg^{++} and NO$_3{}^{-}$.

All analysis results of sampled OMW were compared with those of raw OMW mentioned in Table 1.

pH

The OMW taken in the storage pond (E1 and E2) showed that the pH was slightly higher than the raw OMW, but still acid.

Electrical conductivity

The EC values of the stored OMW were around 16 mS cm^{-1}. This parameter shows the high mineral contents. As it can be seen in Table 2, on the surface and even at the bottom of the basin B1, the Na^{+} and Mg^{++} concentrations were 1.2 and 0.4 g l^{-1}, respectively.

Table 2 Analysis results and characteristics of OMW samples from storage basin

Parameters	Sample E1	Sample E2
pH	5.3	5.4
EC (mS cm$^{1-1}$)	15	16
COD (g l^{-1})	405	547
BOD (g l^{-1})	1.34	1.79
Total solids (g l^{-1})	237	236
Volatile solids (g l^{-1})	25.40	34.20
Oils (g l^{-1})	14.47	6.85
Polyphenols (g l^{-1})	6.37	61.17
TKN (g l^{-1})	2.45	1.83
NH_4^+ (g l^{-1})	0.46	0.51
$N_{org.}$ (g l^{-1})	1.99	1.32
NO_3^- (g l^{-1})	0.38	0.13
NO_2^- (g l^{-1})	0.07	0.21
Na^+ (g l^{-1})	1.15	1.22
Mg^{++} (g l^{-1})	0.34	0.37

Polyphenols

Polyphenols concentrations varied during the OMW storage from 6 to 61 g l^{-1} on the surface and at the bottom pond, respectively. These values indicated that the long storage period in the pond (>15 years) has enhanced the accumulation of these toxic compounds at the bottom whereas on the surface, OMW underwent natural biodegradation during its storage in the evaporation pond (Martin et al. 1991).

Total solids and volatile solids

With regards to both samples, E1 and E2, the concentration of total solids was around 237 g l^{-1}. VS concentrations (organic content) decreased from 34.2 g l^{-1} at the bottom to 25.4 g l^{-1} on the pond surface. These values demonstrated, once again, the decomposition of certain organic compounds present in the OMW on the pond surface.

Oils

As shown in Table 2, the stored OMW contains a high concentration of oils which reached 14.5 g l^{-1} on the pond surface whereas it was around 7 g l^{-1} at the bottom. These oils inhibit the evaporation and the biological activity.

COD and BOD

With regard to COD, the values of stored OMW were higher than those of the raw OMW, especially at the bottom which had probably an accumulation of organic matter. Concerning BOD values, considerable decreases were observed in the stored OMW (1.79 g l^{-1}) compared to the raw one (35–100 g l^{-1}). These values confirm the decomposition and eventually, the biodegradation of OMW during its storage.

Nitrate

High nitrate concentrations probably derived from organic matter mineralization and transformation are present on the surface storage basin (0.38 g l^{-1}). At the bottom the concentration decreased and reached 0.13 g l^{-1}. This might be due to the high reducing properties of OMW and also to the activity of heterotrophic denitrifier favored by anaerobic conditions.

The great variation found in the characteristics of the two OMW samples indicates a stratification of the OMW during its storage with accumulation of organic matter, particularly phenolic compounds, at the pond bottom, and loss of these substances on the pond surface where the organic matter degrades aerobically (and even anaerobically at deeper levels).

The stored OMW which had a high pollutant load was a potential source for soil and groundwater contamination.

Site lithology

The borings realized in the site contributed a fine description of the different subsoil profiles (Fig. 2). In the S1 boring, situated at a distance of about 40 m to the basin B1, a 1.2-m thickness superficial level, essentially formed by yellow fine sand with thin clay intercalations was encountered. Then, the profile shows a 1-m coarse sand layer followed by a sand level with clay concretions. At 2.8 m depth, a layer of >3 m thickness which is formed by consistent clay with few OMW accumulations was found. In fact, the soil moisture increased with depth, with a dark waste coating on the clay level at a depth of 3.5 m.

The profile of the boring S2, which is about 30 m far from the basin B2, consists of a first 3.5 m thick level of yellow fine sand. The second layer is composed by a thin consistent clay level (20 cm) which overcomes a thick sand layer (1.2 m) with clayey concretions. At depth of 5.5 m, a yellow sand level was also present.

Thus, the lithological succession in the southern part of the site is dominated by sandy and silty clayey levels with a layer of fine yellow sand at depth of >5 m.

In the northern part near the old basin B1, we notice the predominance of >3 m thick clayey levels impregnated with OMW accumulations.

The lithological study of the pond site contributed to the identification of four material types: yellow sand (M1), coarse sand (M2), sand with clay concretions (M3) and clay (M4).

The permeability of sandy samples M1, M2 and M3 was 1.85×10^{-5}, 3.18×10^{-5} and 1.8×10^{-5} m s^{-1} respectively. They could be classified to fine sand (M3) and medium sand (M2 and M1) according to the sieve analysis.

Regarding the liquid and plastic limits, the clayey material (M4) is considered as a high plastic clay with a plasticity index of 50%. The permeability test carried out in laboratory on intact clay sample, shows a permeability of about 10^{-10} m s^{-1}.

Despite the presence of thick clay level, the evaporation ponds of the Sousse region could be considered as permeable allowing infiltration of OMW.

Analytical results of subsoil profiles

The representative subsoil samples issued from borings S1 and S2 were analyzed in the laboratory and then compared to the control one. The analytical results referred to air-dried soil are shown in Figs. 3 and 4.

S1 boring

The moisture content of the pond soil profile showed relatively high values ranging from 3.2 to 21.3%, whereas for the control soil they were <2%. The organic matter content was low in superficial level, and increased in deeper levels reaching a rate of 5% at 3.5 m depth. The rates recorded in the control soil did not exceed 1%. A similar behavior is noticed for the concentrations of phenolic substances. In fact, in the control soil, they were <1 ppm, and reached greater concentrations (70 ppm) in contaminated clay at 3.5 m depth.

This illustrates the high mobility rates of OMW phenolic compounds even in fine textured soils. The concentrations of phenolic substances in sandy levels were lower, which confirms the inert behavior of OMW phenolic compounds in contact with permeable soils.

With regard to the EC, the values for pond soils were higher than those for the control one, especially in the clayey deeper levels probably due to adsorption and ion exchange. The highest values were around 2.2 and 0.3 mS cm^{-1}, respectively.

The pH values in pond soil levels were around 7 whereas those recorded in control soils reached 8.3. The decrease of pH with depth, especially in clayey soil indicates that these soils have been neutralized by acidic OMW during its infiltration.

S2 boring

The moisture content was increasing progressively to reach 11% at a depth of 4 m and then it decreased to 1.7% at 6 m depth.

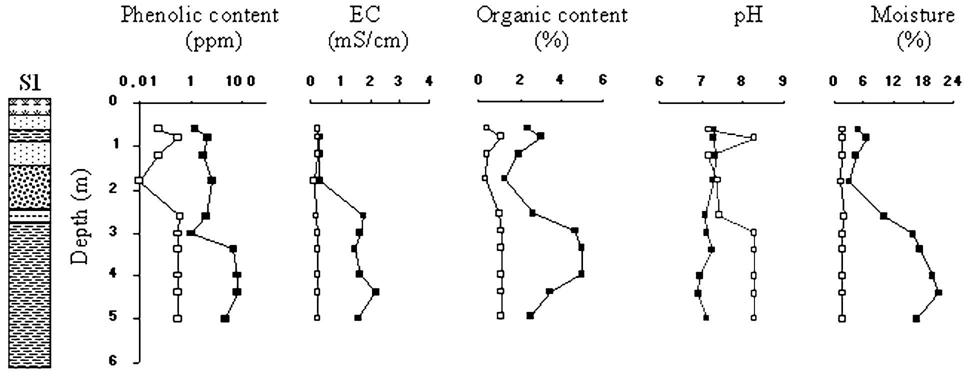

Fig. 3 Variation of different parameters versus depth in S1 boring (*dark symbol*) and control boring (*white symbol*)

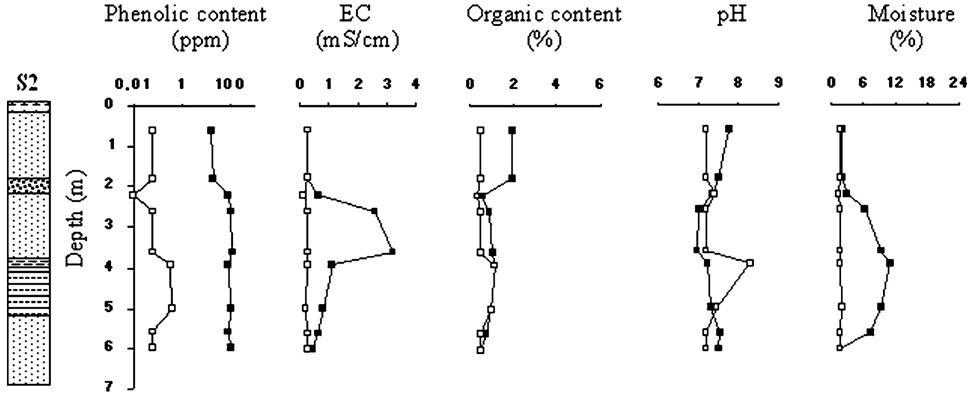

Fig. 4 Variation of different parameters versus depth in S2 boring (*dark symbol*) and control boring (*white symbol*)

Table 3 pH, electrical conductivity (EC) and polyphenol concentration in groundwater

Sample reference	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
pH	7.5	8	8.2	8	8.6	7.5	8.8	7.9	7.6	7.4	8	8.2	8.1	7.8	7.7
EC (mS cm^{-1})	1.9	1.6	1.5	1.7	0.9	2.2	2.5	2.3	3.4	5.8	2.5	2	1.9	1.9	2.2
Polyohenol (ppm)	198	10	41	35	16	145	36	81	113	232	114	103	92	193	222

For the pond soil, phenolic substances reached greater concentrations compared to control soil even at 6 m depth, with 115 and 16 ppm, respectively. A similar behavior was recorded for organic matter with a weak increase in the pond soils (2%) compared to the control soil (1%).

Thus, the increase of the clay fraction in soil contributed to the retention of organic matter with consequent increase in phenolic substance concentrations.

The samples taken in the superficial levels showed neutral pH values in the pond soil and control soil (7.45 and 7.2, respectively). In deeper levels, the pH in pond soil decreased particularly in the clay horizon in which the values reached 7.2, whereas in the control soil it was alkaline in the range of 8.3. This confirms the neutralizing effect of acid OMW in contact with the clayey levels.

With regard to EC, the values for pond soil were higher than those for control soil, especially at depth levels between 3 and 4 m.

In spite of the fact that the soil stratum presents low hydraulic conductivity, which restrained OMW propagation, many researches pointed out the morphological and textural changes due to acidic attack (Hamdi et al. 2005). In deed, the contact of OMW with clayey levels promotes to the formation of discrete aggregates (D'Acqui et al. 2002), and leads to the dissolution of carbonates present in the medium, yielding an increase in porosity, and thus in the permeability (Brown 1994).

On the other hand, the clay minerals affected markedly the organic material transformations. The net effect is a relative increase in some polyphenol substances which are slow to decompose and persist even after a long period (D'Acqui et al. 2002; Mekki et al. 2007).

These findings show the negative effect of OMW on soil, mainly on clay level, yielding the propagation of polyphenols, especially the monomers, by infiltrating rain water to deeper levels, and thus a considerable risk of groundwater contamination (Mekki et al. 2007).

Groundwater analysis

The analysis of pH, EC and polyphenols of groundwater samples are reported in Table 3.

The concentrations of polyphenols varied from 10 to 232 ppm where the highest values were observed at the wells with neutral pH (samples n°1, 10, 14 and 15).

These results indicate the OMW infiltration in deeper levels and consequently the contamination of groundwater by organic compounds.

Conclusion

This paper shows the evaluation of the pollution impact of an OMW disposal site in Tunisia using field sampling and laboratory analysis of soil and groundwater. The results of this study indicate that the uncontrolled and massive disposal of OMW contributes to its infiltration near the evaporation ponds, particularly in the permeable sandy layers of high hydraulic conductivity. This infiltration has reached a depth of 6 m at a distance of almost 50 m laterally. The acidity of OMW allows the neutralization of soil alkaline clay. An enrichment of organic matter was detected, as well as an increase in EC and phenolic compounds concentration. The contamination with phenolic substances has reached the groundwater. In fact, as long as the OMW remains on the evaporation pond, phenolic substances can be released and leached down to deeper horizons and laterally far from the site through the permeable subsoil levels.

In order to limit the environmental impact of the OMW evaporation pond and contaminants release below and around the site, it is recommended to implement a confining layer in the bottom of earth storage and evaporation basins combined to a perimeter slurry trench.

References

Arambarri P, Cabrera F (1986) Vegetation waters as spreading agents of water contamination by heavy metals. In: International symposium on olive by-products valorisation, FAO, UNDP, Sevilla, Spain, 1986, pp 145–146

Bonari E, Ceccarini L (1990) Sugli effetti dello spargimento delle acque di vegetazione sul terreno agrario: risultati di una ricerca sperimentale. Genio Rurale 5:60–67

Brown K (1994) Fluids in deforming sediments, in the geological deformation of sediments. In: Maltman A (ed) Chapman & Hall, London, pp 239–244

Chui YC, Chang CN, Lin JG, Huang SJ (1997) Alkaline and ultrasonic pre-treatment of sludge before anaerobic digestion. Water Sci Technol 36:155–162

Cox L, Celis R, Hermosin MC, Becker A, Cornejo J (1997) Porosity and herbicide leaching in soils amended with olive mill waste water. Agric Ecosyst Environ 65:151–161

D'Acqui LP, Sparvoli E, Agnelli A, Santi CA (2002) Olive oil mills waste waters and clay minerals interactions: organics transformation and clay particles aggregation. In: Transaction of the 17th World Congress Soil Science, International Soil Society, Bangkok, Thailand, 14–21 August 2002, Symposium no. 47-1578, pp 1–7

Ehaliotis C, Papadopoulou K, Kotsou M, Mari I, Balis C (1999) Adaptation and population dynamics of *Azotobacter vinelandii* during aerobic biological treatment of olive-mill wastewater. FEMS Microbiol Ecol 30:301–311

Fiestas Ros De Ursinos JA, Borja-Padilla R (1992) Use and treatment of olive mill wastewater: current situation and prospects in Spain. Grasas Aceites 43:101–106

Fiestas Ros De Ursinos JA, Borja-Padilla R (1996) Biomethanization. Int Biodeterior Biodegradation 38:145–153

Forester CF, Chacin E, Fernandez N (2000) The use of ultrasound to enhance the thermophilic digestion of waste activated sludge. Environ Technol 21:357–362

Gianfranco R, Michele R, Introna M (2003) Volatilisation of substances after spreading olive oil wastewater on the soil in a Mediterranean environment. Agric Ecosyst Environ 96:49–58

Hamdi M, Ellouz R (1992) Use of *Aspergillus niger* to improve filtration of olive mill wastewaters. J Chem Technol Biotechnol 53:195–200

Hamdi M, Khadir A, Garcia JL (1991) The use of *Aspergillus niger* for the bioconversion of olive mill wastewaters. Appl Microbiol Biotechnol 34:828–831

Hamdi N, Della M, Srasra E (2005) Experimental study of the permeability of clays from the potential sites for acid effluent storage. Desalination 185:523–534

Kissi M, Mountadar M, Assobhei O, Gargiulo E, Palmieri G, Giardina P, Sannia G (2001) Roles of two white-rot basidiomycete fungi in decolourisation and detoxification of olive mill waste water. Appl Microbiol Biotechnol 57:221–226

Komilis DP, Aratzas E, Halvadakis CP (2005) The effect of olive mill wastewater on seed germination after various pretreatment techniques. J Environ Manage 74:339–348

López R, Martinez Bordiu A, Dupuy De Lome E, Cabrera F, Sánchez MC (1996) Soil properties after application of olive oil mill wastewater. Fresenius Environ Bull 5:49–54

Martin A, Borja R, Garcia I, Fiesta JA (1991) Kinetics of methane production from olive mill wastewater. Process Biochem 26:101–107

Martinez J, Perez J, Moreno E, Ramos-Cormenzana A (1986) Incidencia del efecto antimicrobiano del alpechin en su posible aprovechamiento. Grasas Aceites 37:215–223

Mekki A, Dhouib A, Sayadi S (2007) Polyphenols dynamics and phytotoxicity in a soil amended by olive mill wastewaters. J Environ Manage 84:134–140

Mellouli HJ, Hartmann R, Gabriels D, Cornelis WM (1998) The use of olive mill effluents ("margines") as soil conditioner mulch to reduce evaporation losses. Soil Till Res 49:85–91

Oukili O, Chaouch M, Rafiq M, Hadji M, Hamdi M, Benlemlih M (2001) Bleaching of olive mill wastewater by clay in the presence of hydrogen peroxide. Ann Chim Sci Mat 26:45–53

Paredes C, Cegarra J, Roig A, Sánchez-Monedero MA, Bernal MP (1999) Characterization of olive mill wastewater (alpechin) and its sludge for agricultural purposes. Bioresour Technol 67:111–115

Perez JD, Gallardo-Lara F (1989) Sulphur transformation affected by the application of wastewater from olive processing on soil. Commun Soil Sci Plant Anal 20:75–84

Perez JD, Hernandez MT, Ramos-Cormrenzana A, Martinez J (1987) Caracterizacon de fenoles del pigmento del alpechin y transformacion por *Phanerochaete chrysosporiwn*. Grasas Aceites 38:367–371

Ramos-Cormrnzana A, Juarez-Jimenez A, Garcia-Pareja MP (1996) Antimicrobial activity of olive mi1l waste-waters (alpechin) and biotransformed olive oil mi1l wastewater. Int Biodeterior Biodegradation 38:283–290

Robles A, Lucas R, De Cienfuegos AG, Ga1vez A (2000) Phenoloxidase (laccase) activity in strains of the hyphomycete *Chalara paradoxa* isolated from olive mi1l wastewater disposal ponds. Enzyme Microb Technol 26:484–490

Roig A, Cayuela ML, Sanchez-Monedero MA (2006) An overview on olive mill wastes and their valorization methods. Waste Manage 26:960–969

Salvemini F (1985) Composizione chimica e valutazione biologica di un mangime ottenuto essicando tercamente le acque di vegetazione delle olive. Riv Ital Sostanze Grasse 112:559–564

S'habou R, Zairi M, Ben Dhia H (2005) Characterisation and environmental impacts of olive oil wastewater disposal. Environ Technol 26:35–45

Sierra J, Marti E, Montserrat G, Cruanas R, Garau MA (2001) Characterisation and evolution of a soil affected by olive oil mill wastewater disposal. Sci Total Environ 279:207–214