Disposal of olive oil mill wastes in evaporation ponds: Effects on soil properties

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ABSTRACT

The most common practice followed in the Med countries for the management of olive oil mill wastes (OMW) involves disposal in evaporation ponds or direct disposal on soil. So far there is lack of reliable information regarding the long-term effects of OMW application on soils. This study assesses the effects of OMW disposal in evaporation ponds on underlying soil properties in the wider disposal site as well as the impacts of untreated OMW application on agricultural soils. In case of active disposal sites, the carbonate content in most soils was decreased, whereas soil EC, as well as Cl^-, SO_4^{2-}, PO_4^{3-}, NH_4^+ and particularly K^+ concentrations were substantially increased. Soil pH was only marginally affected. Phenol, total N, available P and PO_4^{3-} concentrations were considerably higher in the upper soil layers in areas adjacent to the ponds. Available B as well as DTPA extractable Cu, Mn, Zn and Fe increased substantially. Most surface soil parameters exhibited increased values at the inactive site 6 years after mill closure and cease of OMW disposal activities but differences were diminished in deeper layers. It is therefore concluded that long-term uncontrolled disposal of raw OMW on soils may affect soil properties and subsequently enhance the risk for groundwater contamination.

1. Introduction

The annual olive oil mill wastewater (OMW) generation in the Mediterranean olive oil producing countries varies between 7×10^6 and 30×10^6 m^3. OMW is an aqueous, dark, foul-smelling and turbid liquid that is characterized by relatively acidic pH (4.5–5.5), high electrical conductivity (3.5–12.5 dS/m), high organic content (40–165 g/L) and increased COD/BOD ratio (2.05–2.35). OMW is easily fermentable and exhibits different characteristics depending on the variety and ripeness of olives, climate, soil type as well as the extraction method used [1–3].

Traditional methods used for treatment of OMW in the Med region include: (a) disposal in shallow evaporation ponds (b) disposal on soil (c) incineration and (d) utilization for the production of fermentation products, fat and oils preservatives (i.e. phenolic compounds), etc. [4]. In Greece there are about 14×10^7 olive trees and 2800 olive oil mills, while the average olive oil production for the cultivation period of 2007–2008 reached 419,000 tons (Greek Ministry of Rural Development and Food). The volumes of OMW produced are extremely big and each mill produces daily 15–20 tons. The volume of OMW generated per ton of olive oil varies between 3.25 m^3 for the traditional (pressure type) and 5 m^3

for modern (centrifuge type) mill respectively. Although direct disposal of untreated OMW in environmental receptors is not allowed in Greece it is estimated that almost 1.5 million tones of OMW are disposed of every year in aquatic streams [5]. The usual treatment and disposal practice followed in Greece involves neutralization with lime and disposal in evaporation ponds/lagoons. There are cases where OMW are disposed of in sea, river or underground. The construction of evaporation ponds/lagoons rarely meets engineering criteria for stability and safe accommodation of liquid wastes, therefore OMW often overflow and affect neighboring systems (agricultural soils, surface- and groundwater). The base of the ponds is in most cases permeable and thus the probability for groundwater and deep soil contamination is considered high [6].

Several studies related with direct application of OMW, either as a fresh liquid or sludge, to soil as fertilizer have been carried out during the last 20 years [7]. The results indicate that acceptable application rates of OMW on soils enhance herbicidal activity [2] and have beneficial effects for both crops [8–10] and hosting soils [11,12]. Controlled land application results in increase of soil organic matter and nutrient availability and thus, improves soil fertility and productivity by controlling the nutritional and biological equilibrium in the soil–plant interface [13–17]. However, negative effects may appear when some factors, such as soil properties and type, moisture content, water table and crop type are either underestimated or not considered at all. It is also known that OMW contain oil compounds that may result in increased soil hydrophobicity and decrease water retention and infiltration rate

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[18]. The use of OMW in agriculture may also affect acidity, salinity, N immobilization, microbial response, leaching of nutrients and concentration of lipids, organic acids and phenolics [9,19–22]. These latter compounds with bactericide and phytotoxic properties may cause alterations in N cycle, changes in soil microbial activity as well as contamination of surface- and groundwater [23–25,21].

Despite the number of research studies focused on the appropriate use of OMW in agriculture, there are only few studies available that try to assess the effect of long-term OMW disposal in evaporation ponds on soil physical and chemical properties as well as on the fate of nutrients, organic matter and toxic substances. Such studies are considered important since they provide valuable information pertinent to the response of soil to the receiving organic load and elucidate the mechanisms of dispersal and transfer of OMW constituents. This information may be used to define effective OMW management strategies as well as to select and apply appropriate remediation schemes in case of soil contamination. The present study, carried out in the framework of the LIFE+ project, entitled "PROSODOL: Strategies to improve and protect soil quality from the disposal of olive oil mill wastes in the Mediterranean region" aims to assess (a) the impact of active and inactive OMW evaporation ponds on underlying soil properties in the wider disposal areas and (b) the effects of direct application of untreated OMW on soils.

2. Materials and methods

2.1. Study area and soil sampling

The area under study belongs to the municipality of Nikiforos Fokas, prefecture of Rethymnon, Crete, Greece; North latitude is $35°$ $17'$ while the East longitude is $24°$ $21'$. The region has subtropical/Mediterranean climate and is characterized by mild winters and dry-hot summers [26]. The annual temperature varies between $7.9 °C$ in February (mean minimum temperature) and $28.4 °C$ in July (mean maximum temperature). Average precipitation is 692 mm; most of it falls between October and April while no precipitation is seen during summer.

Limestones cover almost 40% of the total area ($8300 km^2$) of the island of Crete; dolomites, marbles and alluvial deposits are also seen. Soils in the area under study are clayey or silty clayey, slightly to moderately alkaline and rich in carbonates (Table 1).

Four sites representing different disposal cases were studied. All evaporation ponds were constructed by using native soil and simple engineering, while no impermeable membranes or other protective media were used. The ponds located in active sites ACTS-1, ACTS-2 and ACTDS-3 sites are in operation for more than 10 years while the forth one, located in the site INACTS-4, has been used for the disposal of OMW for 20 years but for the last 6 years is inactive. ACTS-1 is a typical disposal site located in a field with almost 10% slope; pond dimensions are 50 m × 10 m × 10 m. ACTS-2 represents a different case; the pond (21 m × 8 m × 1.70 m) was constructed by using native soil material excavated from the top of an adjacent hill. ACTDS-3 is a large field (1 ha) with almost 5% slope and contains two evaporation ponds with dimensions 32 m × 4.20 m × 1.70 m and of 30 m × 44 m × 1.75 m, respectively. Direct disposal of OMW on soil takes place at ACTDS-3 every 2–3 days between May and September each year. The dimensions of the inactive pond at INACTS-4 site are 24 m × 17 m × 1.75 m.

OMW are produced from three-phase mills using the continuous centrifuge extraction process and have the following characteristics: pH 4.9–5.4, EC 7.6–8.1 dS m^{-1}, total organic carbon 34–37 g L^{-1}, BOD 35–42 g L^{-1}, COD 55–74 g L^{-1}, total Kjeldahl N 750–790 mg L^{-1}, NH$_4^+$ 121–164 mg L^{-1}, total phenols 8500–9200 mg L^{-1}, Mg 152–160 mg L^{-1}, P 430–480 mg L^{-1}, K 4200–4700 mg L^{-1}, Ca 430–500 mg L^{-1}, Na 106–118 mg L^{-1},

Table 1
Selected surface soil properties at studied sites.

Soil properties	Sites			
	ACTS-1	ACTS-2	ACTDS-3	INACTS-4
Clay (%)	36	38	42	58
Silt (%)	30	22	30	23
Sand (%)	34	40	28	19
SP (%)	68	58	68	56
pH	7.8	7.9	7.7	7.3
EC$_{25}$ (dS m^{-1})	0.64	0.44	0.61	0.49
CaCO$_3$ (%)	41.2	40.7	35.7	5
Organic matter (%)	4.24	4.7	4.34	2.7
Phenols (mg kg^{-1})	23	18.9	16	19
Kjeldahl N (mg g^{-1})	3.3	3.9	3.1	3.3
C/N	7.4	4.6	8.1	4.7
NH$_4^+$ (mg kg^{-1})	25	35	70	45
NO$_3^-$ (mg kg^{-1})	25	20	7	20
Available P (mg kg^{-1})	41	14	10	1.50
PO$_4^{3-}$ (mg kg^{-1})	10	7	9	30
Exc. K (cmol kg^{-1})	1.1	0.8	0.95	0.5
exc. Mg (cmol kg^{-1})	1.1	2.1	2.0	3.2
Exc. Na (cmol kg^{-1})	0.14	0.12	0.15	0.17
Cl$^-$ (mg kg^{-1})	45	25	75	60
SO$_4^{2-}$ (mg kg^{-1})	85	220	440	630
Cu-DTPA (mg kg^{-1})	3.5	3.2	1.4	2.8
Mn-DTPA (mg kg^{-1})	23	19	12	8
Fe-DTPA (mg kg^{-1})	40	20	13	6
Zn-DTPA (mg kg^{-1})	1.7	1.10	0.72	0.7
Available B (mg kg^{-1})	1.2	1.0	2.1	0.4

S 180–210 mg L^{-1}, Cl 89–118 mg L^{-1}, Al 12.3–12.8 mg L^{-1}, B 5.1–5.4 mg L^{-1}, Cu 8.6–10 mg L^{-1}, Fe 21–26 mg L^{-1}, Zn 10–11 mg L^{-1} and Mn 7–9 mg L^{-1}. The concentration of Pb, Cr, Pb and other heavy metals is in general lower than 0.5 mg L^{-1}.

Soil sampling took place almost 1 month after the end of the olive harvesting season, between 6th and 9th of May, 2009.

Surface soil samples were collected from the pond walls and selected downslope distances, up to 105 m (ACTS-1 and ACTS-2 sites); in depth samples were collected at 25 cm intervals up to 175 cm (ACTDS-3 and INACTS-4 sites). Control samples were collected from uphill points located far away from the disposal sites, where soil contamination is practically nonexistent.

2.2. Analytical methods

2.2.1. Waste analysis

The main chemical parameters of OMW, namely pH, EC, TOC, BOD, COD, total Kjeldahl N, NH$_4$, NO$_3$, Mg, PO$_4$, K, Ca, Na, SO$_4$, Cl, Al, B, Cu, Fe, Zn, Mn, Pb, Cr, Ni, and Pb were determined in duplicates using established methodologies [27]. The total phenol content was determined using the Folin–Ciocalteu method [28].

2.2.2. Soil analysis

Soil analysis was carried out using standard methodologies [29]. Particle size distribution was carried out using the Bouyoukos method [30]; pH and electrical conductivity were measured in the paste extract using pH/EC meter equipped with glass electrode; organic matter was determined by dichromate oxidation; carbonates by using Bernard calcimeter; total N by the Kjeldahl method; available phosphorous using sodium hydrogen carbonate extraction; exchangeable K, Ca and Mg using BaCl$_2$ extraction, while available Mn, Fe, Cu and Zn using DTPA extraction. Determination of NH$_4^+$, NO$_3^-$, Cl$^-$, PO$_4^{3-}$, and SO$_4^{2-}$ was performed in 1:10 water extracts using 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 [28].

Table 2
ACTS-1 site: soil properties for control, pond and downslope samples collected from various depths and distances.

	Soil depth cm	Control soil	Pond soil	Distance from pond			
				2 m	4 m	10 m	12 m
pH	0–25	7.8	7.3	7.8	7.9	7.8	8
	26–50	7.9		7.8	7.8	7.9	
	51–75			7.8		7.8	
	76–100			7.9		7.9	
CaCO$_3$ (%)	0–25	41.2	4.2	17.6	7.1	9.7	7.6
	26–50	50.4		16.0	4.2	10.1	
	51–75			9.7	3.4	8.8	
	76–100			3.4		26.3	
EC$_{25}$ (dS m^{-1})	0–25	0.64	3.59	0.99	0.65	0.29	0.53
	26–50	0.49		0.88	0.88	0.48	
	51–75			0.8		0.4	
	76–100			0.8		0.48	
K$^+$ (cmol kg^{-1})	0–25	1.11	15	4.42	1.80	1.71	0.92
	26–50	0.41		4.34	1.22	0.65	
	51–75			5.81	0.87	0.55	
	76–100			3.90		0.47	
Mg^{2+} (cmol kg^{-1})	0–25	1.12	2.51	1.20	1.86	1.84	1.68
	26–50	0.74		1.01	1.36	1.42	
	51–75			1.42	1.06	1.35	
	76–100			1.07		1.10	
Cl$^-$ (mg kg^{-1})	0–25	45	290	45	15	70	70
	26–50	15		45	50	30	
	51–75			160	35	10	
	76–100			160		20	
SO$_4^{2-}$ (mg kg^{-1})	0–25	85	1650	175	20	80	400
	26–50	15		170	140	90	
	51–75			1300	315	12	
	76–100			1700		110	
Organic matter (%)	0–25	4.24	23.35	4.41	3.28	3.65	3.34
	26–50	1.14		4.26	2.31	2.28	
	51–75			3.92	1.49	2.13	
	76–100			2.13		2.13	
Total phenolic compounds (mg kg^{-1})	0–25	22.6	134.8	11.4	10.4	11.2	69.3
	26–50	9.0		15.0	10.6	15.6	
	51–75			9.1	0.5	4.9	
	76–100			5.0		9.7	
Kjeldahl N (mg g^{-1})	0–25	3.3	4.2	3.7	2,1	2.6	1.7
	26–50	1.2		4.9	1.5	1.7	
	51–75			2.8	1.1	1.9	
	76–100			1.7		1.5	
NH$_4^+$ (mg kg^{-1})	0–25	25	170	30	20	25	30
	26–50	10		20	20	10	
	51–75			25	7	10	
	76–100			10		10	
P (mg kg^{-1})	0–25	41	283	189	6.2	18	14
	26–50	4.7		99	10	3.5	
	51–75			77	3.1	2.5	
	76–100			48		1.7	
PO$_4^{3-}$ (mg kg^{-1})	0–25	10	205	35	8	15	8
	26–50	7		25	30	23	
	51–75			15	9	8	
	76–100			10		11	

3. Results and discussion

3.1. Soil acidity

Soil pH indicates that disposal of OMW does not considerably affect soil acidity (Tables 2 and 3; Fig. 1(a and b)). The only exception was seen in surface samples collected from pond walls where pH was, as expected, lower (pH = 4.93–5.15) due to the acidity induced by the disposal of raw OMW. It is concluded therefore that most of the acidity present in OMW is neutralized by the carbonate content of the soil and that surface application of OMW does not markedly

affect soil pH in the long term [31]. Similar pH values are mentioned in other studies dealing with OMW disposal on calcareous, carbonate and clayey soils [32–36]. According to Levi-Minzi et al. [37] OMW application has a temporary acidifying effect just after application and after approximately fifteen days soil original acidity is restored.

3.2. Carbonates

The carbonate content of the upper soil layers in pond walls and surface disposal points (at 75 m, 90 m and 105 m distance from

Table 3
ACTS-2 site: soil properties for control, pond and downslope samples collected from various depths and distances.

Soil properties	Soil depth (cm)	Control soil	Pond soil	Distance from pond			
				2 m	4 m	10 m	14 m
pH	0–25	7.9	6.9	7.8	7.8	7.9	7.9
	26–50					7.8	7.9
CaCO$_3$ (%)	0–25	40.7	4.2	46.2	21	2.1	5.9
	26–50					1.3	3.4
EC$_{25}$ (dS m^{-1})	0–25	0.44	2.72	0.71	0.34	0.23	0.33
	26–50					0.25	0.37
K$^+$ (cmol kg^{-1})	0–25	0.8	15.9	0.74	0.64	0.52	0.43
	26–50					0.54	0.47
Mg^{2+} (cmol kg^{-1})	0–25	2.1	3.7	1.4	2.9	2.3	2.4
	26–50					2.6	1.9
Cl$^-$ (mg kg^{-1})	0–25	25	330	12	40	19.6	12.8
	26–50					10.1	9.0
SO$_4^{2-}$ (mg kg^{-1})	0–25	220	1500	85	280	110	155
	26–50					30	50
Organic matter (%)	0–25	4.72	36.1	1.63	2.05	0.32	0.61
	26–50					0.42	0.54
Total phenolic compounds (mg kg^{-1})	0–25	18.9	311.1	19.1	5.9	4.4	5.2
	26–50					4.7	4.3
Kjeldahl N (mg g^{-1})	0–25	3.9	4.3	1.4	1.8	0.9	0.6
	26–50					0.6	3.1
NH$_4^+$ (mg kg^{-1})	0–25	35	185	25	30	8	7
	26–50					6	8
P (mg kg^{-1})	0–25	14	296	1.7	0.8	1.4	1.3
	26–50					0.9	1.2
PO$_4^{3-}$ (mg kg^{-1})	0–25	7	365	5	7	9	6
	26–50					6	7

the pond) in active sites ACTDS-3 (Fig. 1c), ACTS-1 and ACTS-2 (Tables 2 and 3) was considerably lower than the control. The only exception was one sampling point at ACTS-2 site just 2 m away from the pond wall; this is probably due to the higher elevation of this point (+2 m) which prohibits reaction of OMW with soil carbonates; since at this site no OMW surface disposal takes place, the movement of OMW constituents takes only place with gravity affecting thus only subsurface soil horizons. Carbonates buffer OMW acidity by generating soluble calcium bicarbonate that moves to lower horizons and precipitates again as calcium carbonate [14]. This process is clearly evident in pond soils at ACTDS-3 site and in most other surface sampling points. On the other hand, samples collected from the pond located at the inactive site exhibited higher carbonate content compared to control (Fig. 1d); this is probably due to liming of OMW prior to disposal. Soil samples collected from a depth higher than 125 cm showed increased carbonate content compared to control probably due to their higher clay content (57–70% and 58–61% respectively).

3.3. Electrical conductivity

Electrical conductivity of pond soils in active disposal sites (Tables 2 and 3 and Fig. 2a) as well as in most other sampling points where direct application of OMW took place (ACTDS-3) was higher than the control (0.44–0.61 mS/cm), but still below the EC threshold value for salinity (4 mS/cm). EC values in pond soils at ACTDS-3 site increased in general with depth, indicating thus infiltration of OMW from surface to deeper soil horizons. In general, the EC increase seems to be irreversible especially in the upper soil layers when excessive OMW rates are applied [23,16,34]. This was not seen at the inactive disposal area (Fig. 2b), however EC values in pond soil 6 years after mill closure remained slightly higher (0.43–0.87 mS/cm) than the control (0.23–0.49 mS/cm); this is due to precipitation which induces transfer of ions to deeper soil horizons [21]. Differences in EC values were more evident in higher depths (125–170 cm) where the OMW flux is restrained due to the presence of compact sedimentary rocks [37].

3.4. Concentration of K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, and SO$_4^{2-}$

Increase in soil EC is mainly due to ionic species, namely potassium, chloride, sulfate, ammonium and nitrates, present either in OMW or generated through waste mineralization and transformation [38]. This is confirmed in the present study by the significant positive correlations between EC and concentrations of K$^+$, Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$ and NH$_4^+$ at ACTS-1 and ACTS-2 sites on the one hand and Cl$^-$ and PO$_4^{3-}$ at ACTDS-3 site on the other hand (Table 4). Therefore the increase in soil salinity can be a major concern if long-term application of OMW takes place on soils at high rates.

The exchangeable K content in pond soils was very high (Tables 2 and 3), whereas, potassium reached high levels even at deeper soil layers at ACTDS-3 (Fig. 2c). The K content (Table 2 and Fig. 2c) decreased with distance from the pond and with soil depth at ACTS-1 and ACTDS-3 sites. An exception was seen, mainly at upper soil layers, in areas directly receiving OMW. This may cause adverse effects on soil physical properties, enhance potassium mobility and subsequently the risk for groundwater contamination. Arienzoa et al. [22] underlined that increased exchangeable levels of K affect negatively soil hydraulic conductivity and infiltration rates. Potassium surplus does not seem to be an issue of concern at ACTS-2 site (Table 3) as a result of pond construction characteristics. Nevertheless, the K content is in most soil samples extremely high and incidents of phytotoxicity and inhibition of seed germination may be anticipated.

Table 4
Correlation coefficients between electrical conductivity (EC) and exchangeable K$^+$, water soluble Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$, and NH$_4^+$ in the studied sites.

Site		K$^+$	Cl$^-$	SO$_4^{2-}$	PO$_4^{3-}$	NH$_4^+$
ACTS-1	EC	0.94**	0.89**	0.63*	0.56*	0.97**
ACTS-2	EC	0.99**	0.98**	0.97**	0.98**	0.98**
ACTDS-3	EC	0.36	0.59*	−0.04	0.59*	−0.21
INACTS-4	EC	0.66*	0.60*	0.58*	0.42	0.49

* Significant at the 0.05 level.
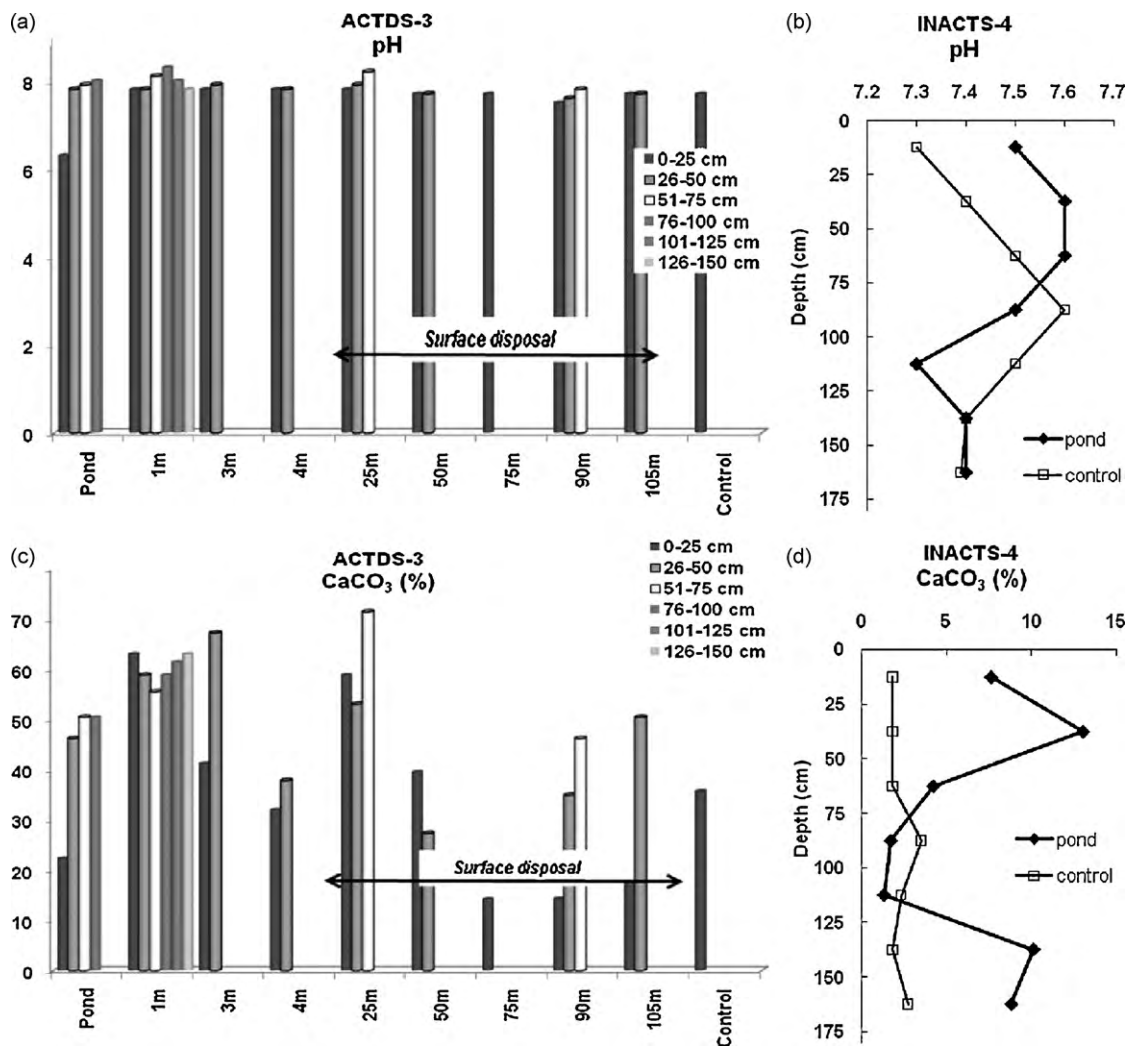** Significant at the 0.01 level.

Fig. 1. ACTDS-3 and INACTS-4 sites: evolution of soil pH and content of carbonates (%) vs. depth.

Regarding the inactive disposal site (Fig. 2d), high levels of exchangeable K were determined in pond soils compared to control (8.80 and 5.5 cmol kg^{-1}, respectively), especially in the upper soil layers (0–25 and 25–50 cm); no considerable differences were noticed in deeper layers. Increased plant available nutrient contents, due to organic fertilization, were also observed in soils by Cabrera et al. [39], who investigated the residual effects of different applications of sludge compost produced by OMW.

Lopez-Pineiro et al. [40] noted that the high content of soluble organic carbon present in OMW facilitates transport and accelerates ion exchange through soil, while the contact of OMW with clayey soils promotes dissolution of carbonates and increases permeability [41]. Potassium present in soil solutions is vulnerable to loss through leaching, particularly in soils with limited potassium fixing capacity (i.e. have low content of hydrous micas and illite clays) as well as in soils where large quantities of K$^+$ are introduced (e.g. disposal of wastes rich in K, fertilizers). Hence, during long-term application of OMW, replacement of soil Ca by K and Na could result in increase of osmotic pressure, degradation of soil structure and formation of saline soils [42,38].

Pond surface soils were rich in exchangeable Mg (2.5–3.7 cmol kg^{-1}) (Tables 2 and 3; Fig. 2e and f). Direct soil application favours Mg availability (3.3–4.6 cmol kg^{-1}) in comparison to control (3.7 cmol kg^{-1}) (Fig. 2e) and may also potentially endanger soil quality. Previous studies mention that application of

OMW on soils increases available Mg [43] and to a lesser degree Ca [21].

Concentrations of Cl$^-$ were also high in pond soils and decreased in general with distance from the pond (Tables 2 and 3; Fig. 2g and h). Direct disposal of OMW resulted also in higher Cl$^-$ content (ACTDS-3 site), which decreased with distance and reached the levels of control after 90 m (Fig. 2g). K and Cl$^-$ levels were also considerably higher, compared to control, in the upper soil horizons (up to a depth of 75 cm) at the inactive site, whereas almost identical Cl$^-$ concentrations were determined in deeper pond soil samples (Fig. 2h).

Relatively higher levels of SO$_4^{2-}$, compared to control, were also recorded in most sampling points at ACTS-1 and in surface points at ACTDS-3 site but not at ACTS-2. Six years after mill closure the pond surface soil layer (0–25 cm) at INACTS-4 site was very rich in SO$_4^{2-}$ compared to control (1100 and 630 mg kg^{-1}, respectively), however differences were diminished in deeper layers (Fig. 2j).

3.5. Organic matter

The content of organic matter at the active ponds was very high in upper soil layers (0–25 cm) but decreased sharply with depth (Tables 2 and 3; Fig. 3a). Moreover, a small increase in the content of organic matter, compared to control, was seen in the topsoil in areas where direct application of OMW takes place. It
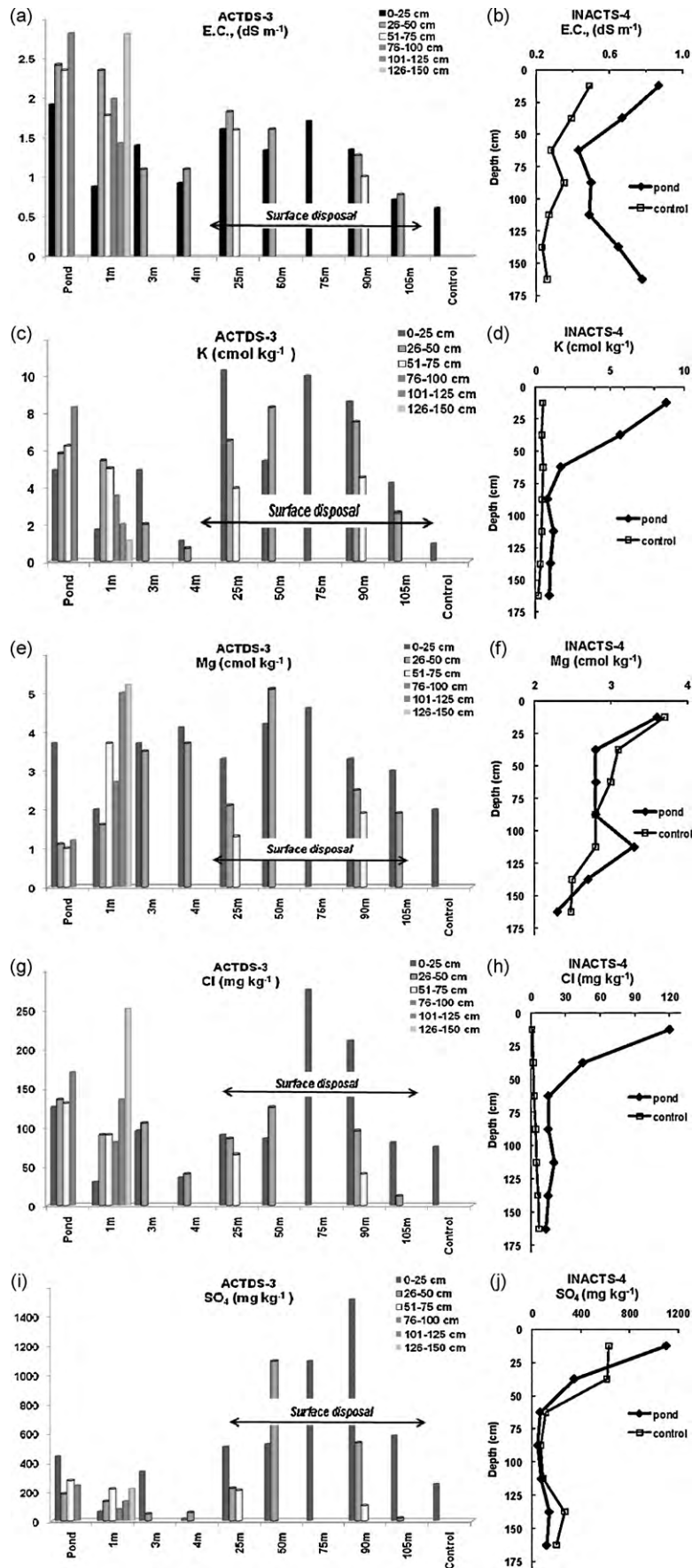
Fig. 2. ACTDS-3 and INACTS-4 sites: evolution of soil EC (dS m^{-1}) and concentration of available K (cmol kg^{-1}), available Mg (cmol kg^{-1}), water soluble Cl (mg kg^{-1}) and SO$_4$ (mg kg^{-1}) vs. depth.
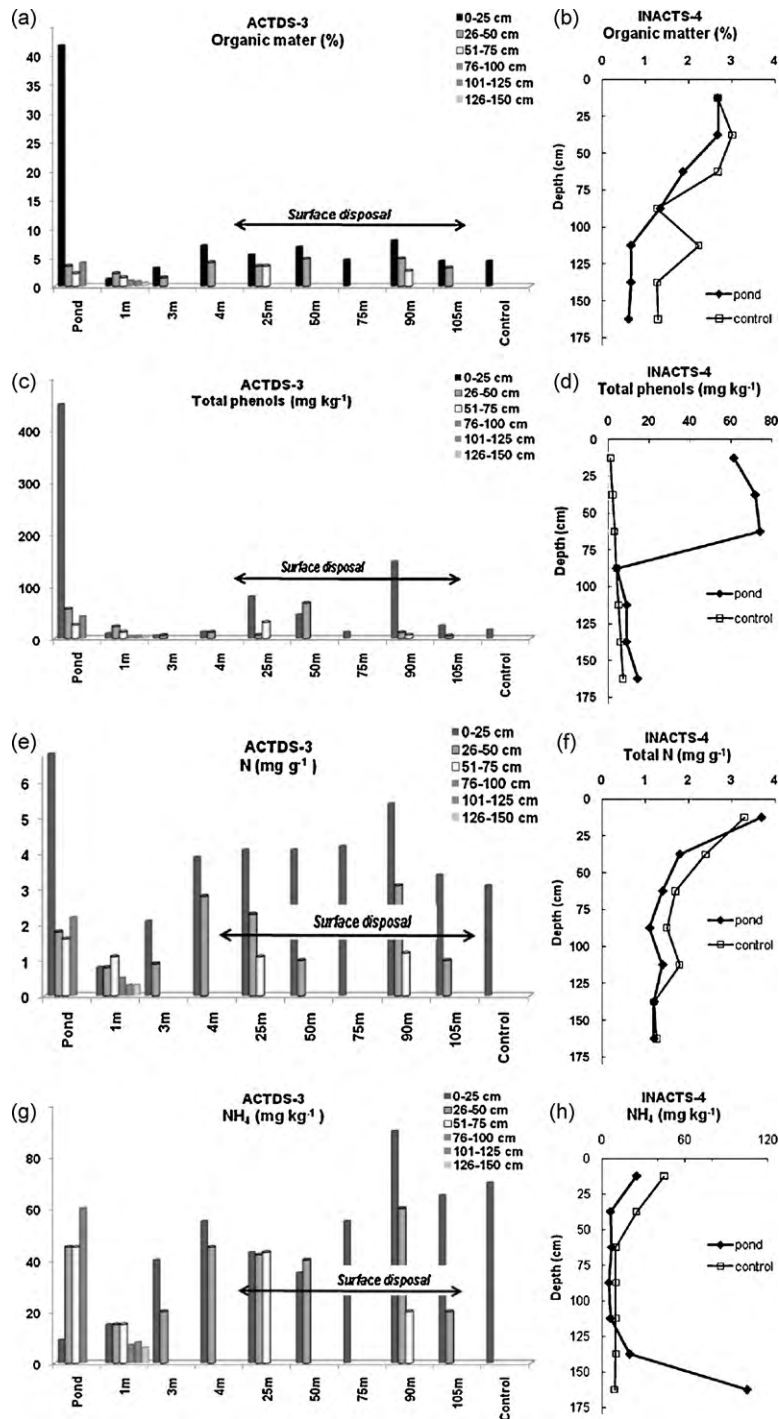
Fig. 3. ACTDS-3 and INACTS-4 sites: evolution of soil organic matter (%), and concentration of total phenols (%), total N (mg kg^{-1}) and NH$_4$ (mg kg^{-1}) vs. depth.

is anticipated though that this property will not increase noticeably with depth and distance from the pond, since the movement of large organic molecules through soil layers is difficult. The low response of organic matter accumulation on soil treated with OMW was also reflected in the C/N ratios; control samples exhibited slightly lower values (4.6–8.1) than those obtained from active disposal sites with or no direct application of OMW (5.2–12.9) (data not shown). According to Yasemin and Killi [44], the significant increase in the content of organic carbon recorded after 1–2 months of increased olive solid waste application is a short-term effect. However, it should be pointed out that application of insufficiently stable organic matter may cause various negative effects on soil

properties such as increase in mineralization rate of native soil organic C, generation of anaerobic conditions and release of phytotoxic substances that may adversely affect plant growth [45,46].

The content of organic matter in pond soils at the inactive disposal site (INACTS-4) did not differ appreciably compared to control, up to depth of 125 cm (Fig. 3B). Similar results were also seen in other studies involving much shorter application periods (120 days) [21]; this can be attributed to organic matter mineralization which, according to Paredes et al. [47] is a key parameter for the decrease in the content of organic carbon in calcareous soils amended with organic OMW compost. However, pond soils in deeper layers exhibited slightly lower organic matter content

compared to control; this results in different C/N ratios (6.0–7.2 and 2.7–3.2 in control and pond soil respectively) and indicates that mineralization rates are relatively higher for organic carbon than organic N [48].

3.6. Total phenols

The concentrations of phenolic compounds in control soils varied from 16.5 to 22.6 mg kg^{-1} (Tables 2 and 3; Fig. 3c and d); these values are considered in the present study as background values for soils unaffected by OMW disposal [14]. Phenol content was very high in the upper soil layer (0–25 cm) in the ponds as well as in topsoil at ACTDS-3 site, where direct disposal of OMW takes place, and remains higher compared to control up to a depth of 100 cm. Sierra et al. [21] mentioned that phenols are detected in concentrations of approximately 200 mg kg^{-1} even at depths of 125 cm. This value indicates mobility of phenolic compounds even in fine textured soils and enhances the risk for groundwater contamination. The concentration of phenols decreased substantially with distance from the ponds. It is therefore seen that direct disposal of OMW increases phenol concentration in upper soil layers to values above threshold levels while deeper layers, rich in clay content (34–48%), are not seriously affected due to sorption of phenols by clays. Caravaca et al. [49] outlined that soils rich in clay minerals and thus characterized by high specific surface area, adsorb humic substances and thus application of OMW enhances the stability of soil aggregates [50]. Zenjari and Nejmeddine [42] reported that clayey soils have very strong adsorption capacity and may remove over 99% of nutrients and phenols after the first application of OMW; this capacity is though substantially reduced after the second application increasing thus the phenol concentration in leachates and thus the risk for groundwater contamination. Phenols concentration in the inactive pond (INACTS-4) remained up to a depth of 75 cm (61.5–71.4 mg kg^{-1}); then decreased rapidly until 100 cm and remained stable and similar to the control up to a depth of 170 cm (Fig. 3d). Thus, even though the pond has been abandoned for more than six years, the concentration of phenols in surface soils is higher than the control; this is in agreement with Feria [51], who reported that residual levels of polyphenols may be significant even 6 years after OMW application. Mekki et al. [38] also determined, one year after irrigation with untreated OMW, high content of phenolic monomers in soils at 1.2 m depth. It has been shown that the presence of clay minerals in soils affect markedly transformations of organic material and increase the concentration of some slowly decomposed polyphenols that persist for a long period [52,20,53].

Moreover, the absence of vegetation on the surface and the walls of the inactive pond can be considered as a sign of phytotoxicity for seed germination and plant growth [46,54–56] not only due to the presence of polyphenols but also of other organic and inorganic constituents which may remain phytotoxic even after complete removal/degradation of polyphenols [57].

3.7. Total organic and inorganic N

The mean organic N content in surface pond soils at ACTS-1, ACTS-2 and ACTDS-3 sites (4.2, 4.3, and 6.8 mg g^{-1}) was relatively higher than the values recorded in the respective control sites (3.3, 3.9 and 3.1 mg g^{-1}) (Tables 2 and 3; Fig. 3e). As with organic matter content, the content of N in the areas under study does not seem to be affected by N surplus in ponds and it is gradually decreased with depth except for the upper layers at ACTDS-3 site, which are rich in total nitrogen (>0.3%). Ammonium concentration in pond surface soils at ACTS-1 and ACTS-2 sites (170 and 185 mg kg^{-1} respectively) was markedly higher compared to other sampling points (Tables 2 and 3); this was not the case though at ACTDS-3 site (Fig. 3g) where NH$_4$ concentration was lower compared to control (70 mg kg^{-1}).

Considering the high C/N ratio of the OMW, varying between 43 and 49, it seems that one of the reasons for the lower NH$_4^+$ content in sites receiving waste is the bacterially induced immobilization of inorganic N. Sorensen and Amato [58] also reported that most of ammonium-N present in soils, after application of pig slurry, was due to immobilization phenomena during microbial decomposition of waste organic matter. By considering the high total
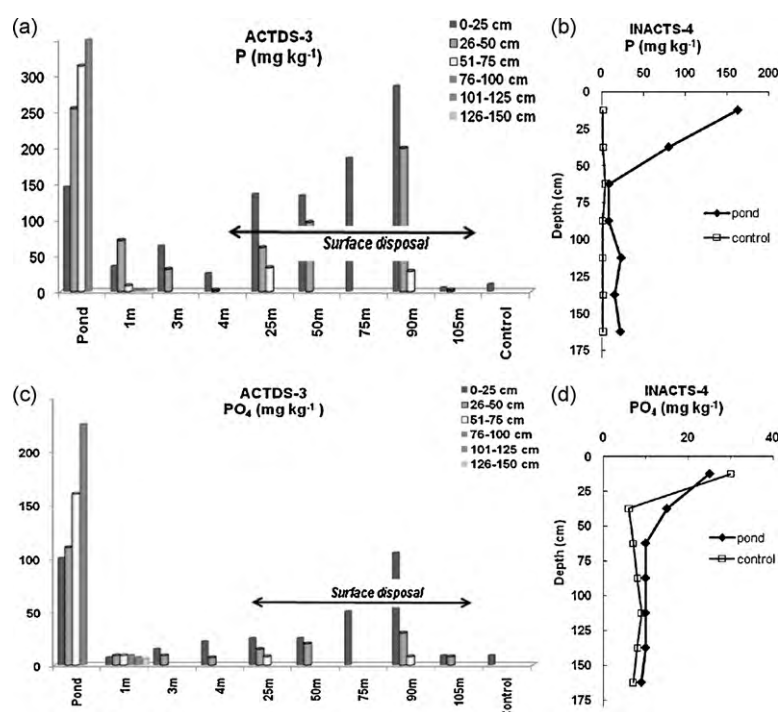

Fig. 4. ACTDS-3 and INACTS-4 sites: evolution of soil available P (mg kg^{-1}) and water soluble PO$_4$ concentration (mg kg^{-1}) vs. depth.
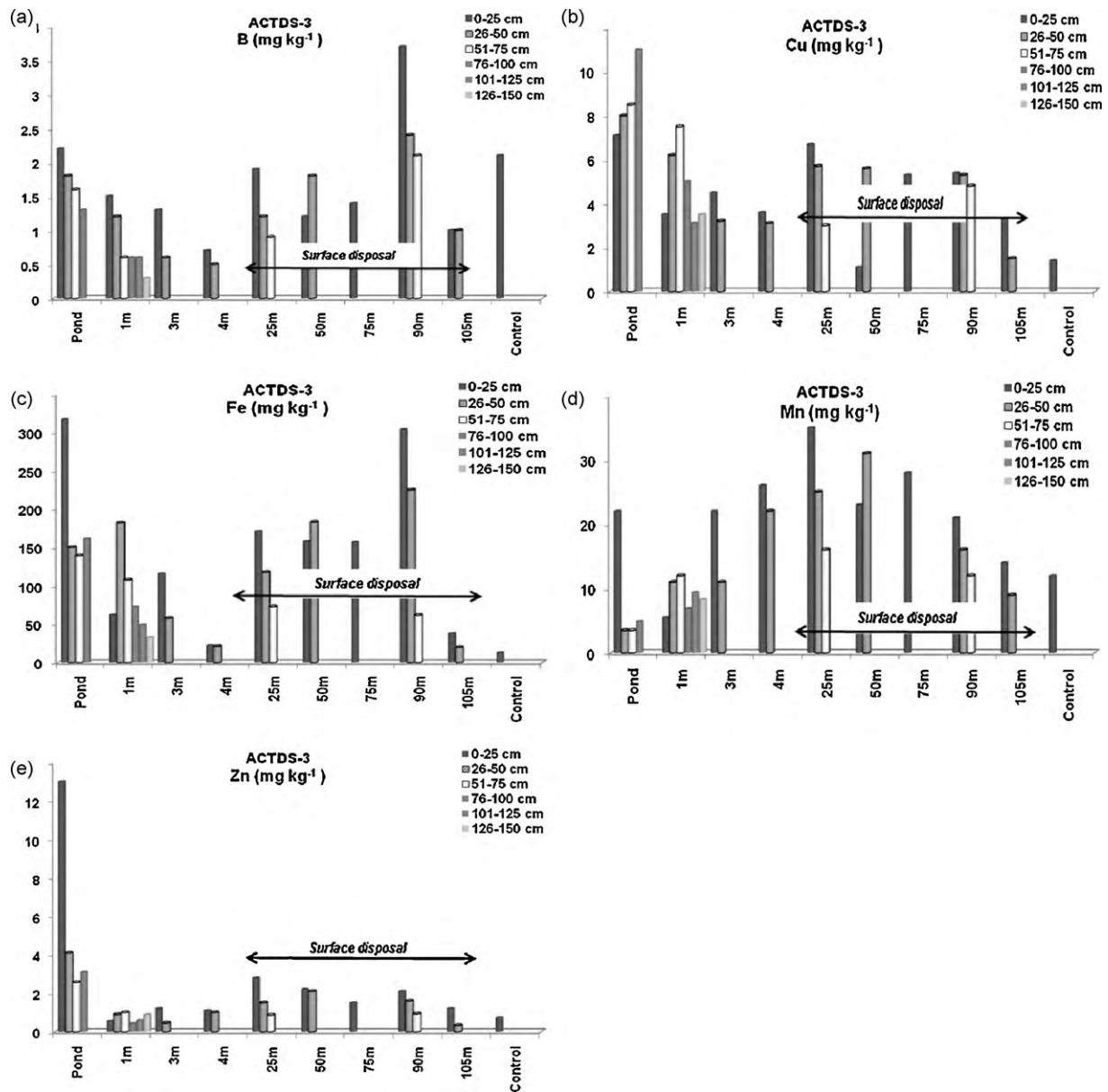
Fig. 5. ACTS-3: evolution of soil available micronutrients B, Cu, Mn, Fe and Zn ($mg\,kg^{-1}$) vs. depth.

carbon (2.65–4.58%) and the low NH_4^+ content (35–55 mg kg^{-1}) in comparison with control (2.49% and 70 mg kg^{-1}, respectively), it is concluded that the positive effect of OMW application on the total organic nitrogen content is due to the provision of a high C source and immobilization of inorganic nitrogen by microorganisms [44]. Aguilar [59] reported that application of OMW on soils enhances immobilization of inorganic or mineralized N; when OMW is mixed with a solid inorganic nitrogenous fertilizer a slow-release fertilizer suitable for different types of soils is produced. Moreover, ammonium fixation by clay minerals retards mineralization of organic N present in OMW.

The above interactions may be the cause for the contradictory NO_3^- concentration determined in soils of the active sites (data not shown). Moreover, nitrate values were low probably due to the activity of heterotrophic denitrifiers [14] and, as has been shown in a series of incubation experiments, application of wastes to calcareous soils decreases NO_3^- production [60,35,61].

The content of N in pond soils at the inactive disposal site (Fig. 3f) decreases with time and is restored due to mineralization of organic

nitrogen provided by the olive mill waste [21]. Moreover, no considerable differences in NH_4^+ content between pond and control soils are seen (Fig. 3h), except for the increased NH_4^+ levels determined in pond soils at 150–175 cm depth. Regarding NO_3^-, slightly higher concentrations were measured in the upper soil layers of the control compared to pond soil (data not shown).

3.8. Available P

Active pond soils were very rich in available P and water soluble phosphates compared to control (Tables 2 and 3; Fig. 4a and c); these concentrations in ACTDS-3 site increased with depth enhancing thus the risk for groundwater contamination (Fig. 4a and c). This could be due to P infiltration and accumulation in deeper soil horizons, exhibiting high free carbonate content, in the form of sparingly soluble Ca–P compounds [62]. On the other hand, direct application of OMW to soil (ACTDS-3) revealed an opposite trend and increased the concentration of Olsen extractable P up to 28 times compared to control. Soil water soluble PO_4^{3-} exhibited sim-
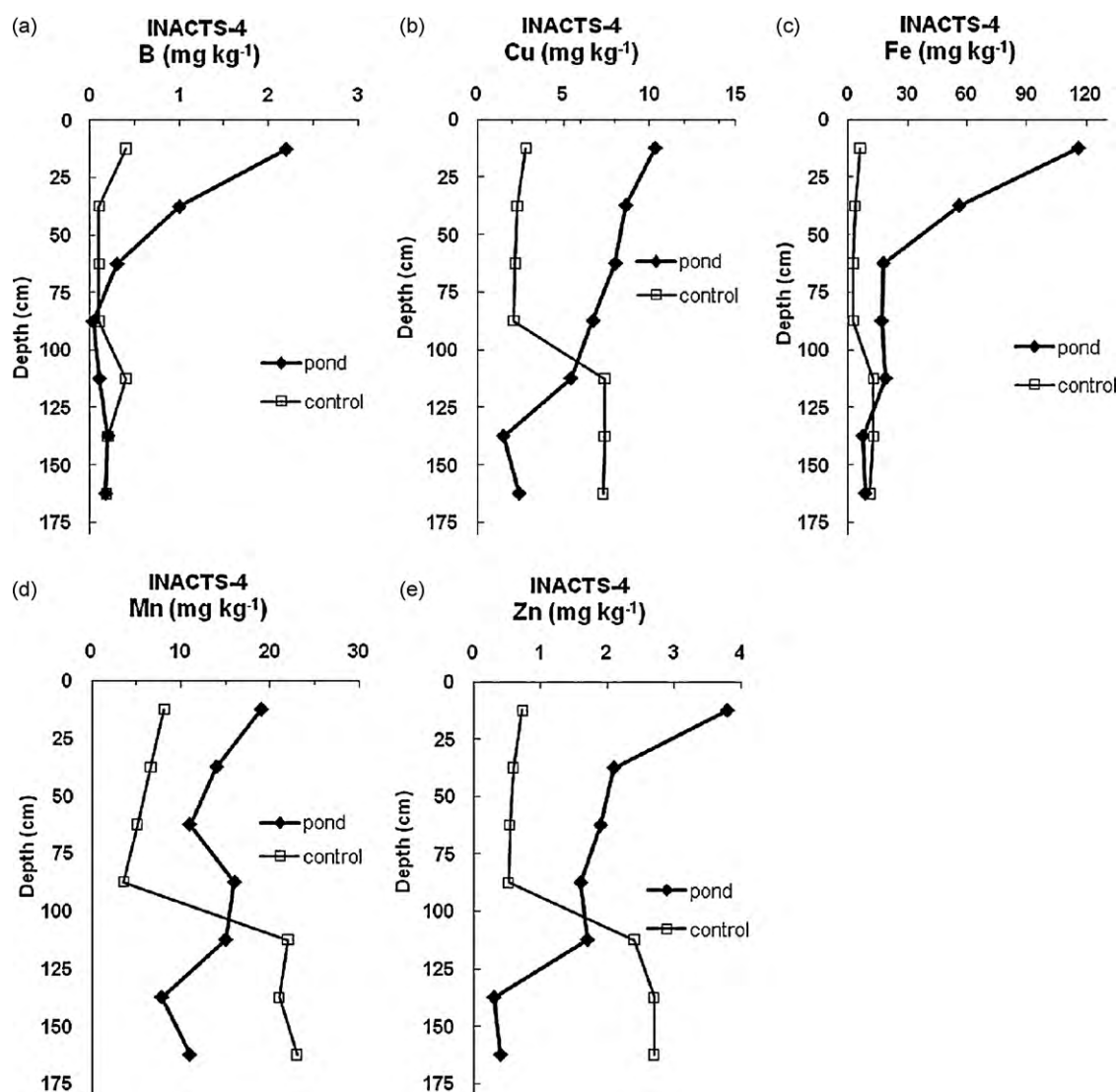
Fig. 6. INACTS-4: residual effect of OMW disposal on available micronutrients B, Cu, Mn, Fe and Zn (mg kg^{-1}).

ilar patterns with distance from the pond, between 25 and 90 m. Overloading of soils with phosphate ions could result in P leaching, increasing thus the concentration of dissolved P in surface runoff, and thus the risk for surface water contamination [63]. At locations where no direct application of OMW on soils took place (ACTS-1 and ACTS-2 sites), the concentration of available P decreased with distance probably due to its immediate precipitation in ponds.

The environmental concern of P accumulation in soil is the long period required to reduce P to levels normally allowed for agronomic production. High levels of P can be reduced only after 15–20 years of continuous crop harvesting, provided that no additional P from any source is added during this period [64,65]. This is why surface P concentration at INACTS-4 site was 50–100 times higher, at 25–50 and 0–25 cm depth, respectively, compared to control (Fig. 4b). Similar levels of extractable P were determined in deeper soil layers. Fig. 4d shows that the levels of soluble PO_4^{3-} were similar in pond and control soil and were sharply decreased up to 75 cm depth.

3.9. Micronutrients

In pond soils (data are shown only for ACTDS-3 and INACTS-4 sites) the levels of available B and heavy metals, Cu and Fe in

particular, were markedly higher compared to control and sampling points in areas where no direct OMW application takes place (Figs. 5 and 6). Distinct differences are seen for extractable Cu, Fe and Mn between control and soil received OMW (ACTDS-3 site) (Fig. 5b–d). At all sites, significant positive correlations were observed between total phenolic content and available Fe and Zn; correlation coefficients vary between 0.71** and 0.99* (Table 5) indicating that the presence of phenols in OMW enhances metal availability in soils. Increased concentrations of Zn and Fe after OMW application were also reported by Aqeel et al. [66]; these values are due to enhanced soil microbial activity producing natural chelates that increase micronutrient availability [67]. According

Table 5
Correlation coefficients between phenolic content and DTPA extractable Cu, Mn, Fe and Zn in the studied sites.

Site		DTPA-Cu	DTPA-Mn	DTPA-Fe	DTPA-Zn
ACTS-1	Phenols	0.16	0.12	0.71**	0.87**
ACTS-2	Phenols	0.97**	0.98**	0.99**	0.99**
ACTDS-3	Phenols	0.29	0.21	0.69**	0.96**
INACTS-4	Phenols	0.54	0.19	0.58*	0.56*

* Significant at the 0.05 level.
** Significant at the 0.01 level.

to Piotrowska et al. [68], the increase of extractable Fe and Mn can be attributed to the fact that these metals catalyze the oxidative transformation of phenols present in soil. Fe and Mn oxides contribute to this process [69]; manganese is reduced to extractable forms of Mn^{2+} while Fe(III) is reduced to Fe(II) and then is oxidized again by the reaction products (i.e. quinones) and reports to soil solution as Fe^{3+} [70]. Fig. 6 reveals that 6 years after cease of OMW disposal in ponds is not an adequate period to reduce the concentration of micronutrients in surface soils to normal levels. Gondar and Bernal [71] reported that application of OMW increases the long-term capacity of soils to retain Cu since the humified fractions (fulvic and humic-like) of the waste exhibit high persistence in soils and high affinity for copper.

4. Conclusion

Disposal of untreated OMW in permeable evaporation ponds has significant impacts on the chemical properties of underlying soil. In particular, soil samples are characterized by increased EC, low carbonates, increased organic load, high content of total nitrogen and NH_4^+, available P, water soluble Cl^-, PO_4^{3-} and SO_4^{2-}, exchangeable K and DTPA extractable metals.

Disposal of acidic OMW on calcareous soils enables neutralization of the waste pH but soil pH is only temporarily affected. Clay substratum is able to retain most of the organic load and nutrients, the concentration of which decreases with distance from the ponds. Residual levels of total phenols, P, K, SO_4^{2-}, Cl^-, B, Cu, Mn, Fe and Zn in surface soils are still present even 6 years after the mill closure; this may cause contamination of surface- and groundwater.

Additional studies are required to assess the long-term effect of uncontrolled OMW disposal in evaporation ponds and agricultural land and assess the risk for soil and water contamination. Particular interest should be also paid to the fate of recalcitrant heavy metals present in soils.

Acknowledgments

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