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ORIGINAL PAPER

Effect of long-term irrigation with treated wastewater of three soil types on their bulk densities, chemical properties and PAHs content in semi-arid climate

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Abstract This study aims at understanding the effect of soil texture and water quality (treated wastewater and groundwater) on soil physical (bulk density) and chemical (pH, salinity, CEC, total organic carbon and carbonate content) properties and on organic pollutant concentrations (polycyclic aromatic hydrocarbons) in different soil types in semi-arid regions. Results showed that the long-term irrigation with treated wastewater increased the bulk density in lithosoil and saline soil, while it decreased it in the isohumic soil. Moreover, the application of a double volume of treated wastewater enhanced the soil bulk density. However, irrigation with groundwater did not reveal any significant effect on soil bulk density. Also, the long-term impact of groundwater on the physico-chemical properties varies from one soil type to another. Multivariate analysis (principal component analysis) showed that different soil parameters such as soil texture and bulk density were determinant in soil evolution. The treated wastewater is considered as potential source of pollutants, and its long-term application induced high concentration of organic pollutant. Actually, the irrigated soils are heavily contaminated, and the carcinogenic molecule concentrations were about 1.2–7.6 times higher in these perimeters than in control soils.

Keywords Treated wastewater · Soil texture · Bulk density · Total organic carbon · Electric conductivity · Polycyclic aromatic hydrocarbons

Introduction

In arid and semi-arid regions, good water quality resources are becoming an important issue. So, due to freshwater shortage and increasing demand, planning and management of water for either drinking or irrigation are challenging (Şen et al. 2012; Abu-Allaban et al. 2014; Ouelhazi et al. 2014). Therefore, the wastewater reuse has become an important element in water resources planning (Abedi-Koupai and Bakhtiarifar 2003) to offset current scarcity.

Treated wastewater is rich in dissolved organic compounds and nutrients. Therefore, irrigation with treated wastewater (TWW) can have an impact on hydrophysical properties which are affected by interaction between used water and soil compounds (Wang et al. 2003; Coppola et al. 2004). Several authors have studied the effects of effluent used for irrigation on soil physical properties such as hydraulic properties and bulk density (Gharaibeh et al. 2007; Mandal et al. 2008). The percolation of effluent through the soil profile could reduce the pore size distribution. Thus, the water-conducting pores in soils could be blocked due to the relationship between soil structure and porosity (Kutilek et al. 2004; Sacco et al. 2012). Good soil porosity involves a good dynamic of N and C cycle which are positively correlated with root growth and soil enzymatic activity (Juma 1993; Paglia and De Nobili 1993). Thus, the decrease in soil porosity may reduce crop production.

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Treated wastewater (TWW) application can be beneficial by supplying nutrients and organic matter to soil (Horswell et al. 2003; Rattan et al. 2005; Saffari and Saffari 2013) which are favourable for plant growth. But, TWW contains inorganic and organic contaminants (heavy metals, PAHs, etc.), which many of them have an unknown geochemical behaviour (Paglia and De Nobili 1993; Horswell et al. 2003) and can alter soil properties (Magesan et al. 2000; Wang et al. 2003; Coppola et al. 2004; Wallach et al. 2005; Toze 2006; Brindha and Elango 2014).

The impact of the wastewater use on the soil geochemical evolution has been widely investigated (Klay et al. 2010; Khadhar et al. 2012).Variation of salinity, carbon, carbonate percentage, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) contents, etc. are frequently observed in agricultural urban soils.

Many authors reported that different mechanisms such as retention/release of organic and inorganic compounds, and contaminants in these irrigated soils by TWW are directly influenced by the effluent composition and soil properties such as soil texture/porosity, soil pH, soil buffer capacity, cation exchange capacity (Mohammad and Mazahreh 2003) and specific chemical composition (Coppola et al. 2004). Also, local climate plays an important role in soil process (Yang et al. 2014). for example Mediterranean soils under arid and semi-arid conditions (such as Draa Tammar perimeter) are prone to loose organic matter (Anderson 2003). the high temperature (above 40 °C in summer in Draa Tammar) induces a fast organic matter oxidation.

There are three major types of soil in the irrigated perimeter of Draa Tammar, and each soil type has an assigned soil texture. Also, two different water qualities (TWW and GW) are used there. In some areas, a double volume of TWW has been applied. Hence, for the reasons quoted above, the advantage and the disadvantages of long-term irrigation with treated wastewater compared to the soil evolution when groundwater (GW) were used on various soil types should be evaluated.

Since the soil fertility depends greatly on the soil permeability and its organic matter percentage and the soil geochemical evolution depends on TOC, pH, carbonate contents and salinity, the main objectives of this work are the following: (1) to quantify the interactive effects of irrigation of different soil types with different water qualities on hydro-physical properties (bulk density) and (2) to evaluate the impact of these effluents on the chemical characteristics of the soil such as COT, pH, carbonate contents, salinity and organic pollutants in soil (3) to determine the relationship between different physical and chemical soil parameters using a multivariate statistical analysis.

Material and methods

Site description

The irrigated Draa Tammar perimeter is located in the central region of Tunisia (N-W), and 10 km far from Kairouan City and 170 km away from Tunis. It is a semi-arid region where the mean annual rainfall and temperature are 300 mm and 21.6 °C, respectively. The irrigated area covers 225.7 ha, and the soil management has been always the same for the entire perimeter. It has been irrigated since 1989 by TWW with a secondary treatment. In Draa Tammar, perimeter has three soil types which are lithosoil, saline and isohumic soils (Tunis Soil Direction 2009). Irrigated soils with treated wastewater are furrow irrigated and supplied by a flow control valve. As for the irrigated soils by groundwater, spray- irrigation method is used. The demand for irrigation water is greater in summer (16 days per month) than in winter (twice per month); the annual used volumes of treated and groundwater are similar. For the last 10 years, the average annual volume used has been about 2590 $m^3 ha^{-1}$.

Soil

Soil sampling

Depending on the large irrigated area, the apparent heterogeneity of the soil texture, and to allow control of the Tunis Soil Direction classification (Tunis Soil Direction, 2009). 42 profiles (control and irrigated soils) were sampled. For the lithosoil, 2 control soils, 11 irrigated profiles by simple water dose and 3 irrigated profiles by double water doses of TWW were collected. For the saline soil, we sampled two control soils, three irrigated profiles by groundwater (GW) and seven profiles irrigated by treated wastewater (TWW). From the isohumic soil, we sampled five control soils and nine irrigated profiles by TWW. Always, two layers were sampled: the top soil level (0–20 cm) which corresponded to maximum plow depth and 20–40-cm level where the root growth and soil tillage are limited. About 1 kg of soil samples was put in plastic bags and directly lyophilized in the laboratory.

Physical soil properties: granulometric analysis and bulk density

Granulometric analysis has been achieved according to the Anderson pipettes-method (Afnor 1999). Selected soils had different textures which were determined according to the U.S.D.A. textural classification (U. S. D. A. 1954).

Several studies presented numerous methods to quantify the soil bulk density (Rossi et al. 2006; Timm et al. 2005). One of the conventional and standard methods that are commonly used by many researchers is the volumetric ring method (Grossman and Reinsch 2002). Different volumetric rings were used and results indicated that the standard deviation of soil bulk density values from rectangular box were higher than those from volumetric cylinder (Lestariningsih and Hairiah 2013). Therefore, in Draa Tammar soil profiles, core samplers (5-cm diameter, 5-cm height) were used to remove undisturbed soil samples in three triplicates at 5-cm depth increments.

A total of 24 soil profiles were dug in control and irrigated soils in order to collect undisturbed soil samples at different depths (from 0 to 40 cm): three soil profiles in each control soil type (total 9), six profiles in both lithosoil and saline soils, and three profiles in isohumic soil.

In laboratory, these samples were placed in an oven at 105 °C for 24 h and then weighted. The bulk density was obtained by dividing the oven dry mass of the sample by the sample volume (Blake and Hartge 1986).

Chemical and mineralogical soil analysis

Soil pH was measured at the soil/distilled water ration of 1:2.5. The samples were stirred every 5 min until the saturation period was reached (0.5 h). Soil pH was then determined with pH-meter LPH 230 T-type. The electric conductivity (EC) was measured in extracts of soil [1:5, soil/water ratio] with a conduct meter model ORION 150. Total organic carbon (TOC) was analysed by ANNE method according to AFNOR X 31–109. Cation exchange capacity was determined by copper ethylenediamine complex (Bergaya and Vayer 1997). Total carbonate was determined using Bernard calcimeter (AFNOR, 1999). Mineralogical identification was done by X-ray diffraction (XRD) Philips Model.

PAHs soil analysis

Fifteen grams of soil was mixed with 2 g of anhydrous sodium sulphate. Organic fraction of the mixtures was extracted by Soxhlet method in a pre-washed (dichloromethane) cellulose thimble for 16 h with 150 ml dichloromethane/hexane (1:1, *v*/*v*). The extracts were concentrated to 1 ml using rotary evaporation, and PAHs clean-up was done on activate silica gel and alumina gel columns, which were conditioned with 20 ml of hexane and 2 ml of dichloromethane, in order to remove the aliphatic hydrocarbon fraction (eluted with 30 ml of *n*-hexane) from aromatic hydrocarbons fraction (eluted with 80 ml of *n*-hexane/dichloromethane 3:2 mixture). This last fraction was concentrated and analysed by HPLC Shimadzu-type.

The recovery efficiency was checked by analysing soil samples spiked with known amount of PAHs. Standard recoveries ranged from 71 to 85 % for the reported PAHs in soil samples. Procedural blanks were performed periodically to prevent contamination. The relative standard deviation for triplicate analyses ranged from ±7 to ±15 %.

Irrigation water

During a year, we collected 21 TWW samples and 3 wells were sampled for groundwater (GW). Both TWW and GW samples were collected in polyethylene bottles after measuring the pH and the electric conductivity (EC), in situ. The major elements (Na, K, Mg and Ca) in water samples were determined with Atomic Absorption Spectrophotometry (AAS), PerkinElmer type HGA900. Total suspended solids (SS) were determined by 0.45-μm membrane filtration; chemical oxygen demand (COD) by oxidation with potassium dichromate, DBO_5 using a DBO meter with an OxiTop system, and nutrient salts (Rodier et al. 1996) were analysed.

Statistical analysis

Experimental results were statistically subjected to variance analysis. It was performed for each parameter of soil using STATISTICA software version 6. A principal component analysis was conducted in order to determine the relationship between the different soil types and their physical and chemical soil parameters, and also to evaluate the impact of irrigation with TWW on the evolution of the soils.

Results and discussion

Treated wastewater (TWW) and groundwater (GW) characteristics

The main characteristics of different types of irrigation water are shown in Table 1. TWW was slightly alkaline (average pH was 7.9). The SAR (8.24) level, biochemical oxygen demand (BOD_5), and chemical oxygen demand (COD) concentrations were above the limit allowed by Tunisian Norm NT 106.03.

Based on SAR of TWW, EC (>2 mS cm^{-1}) and FAO guidelines (FAO 1998). this water category was considered moderate to severe and exceeded the water quality reused in agriculture. Moreover, the combination of the electrical conductivity and the SAR of TWW according to the diagram of classification of Riverside showed that the TWW of Kairouan had a low alkalising power and high salinity risk.

The BOD_5/COD mean ratio showed that this water contained more or less readily biodegradable compounds (Table 1). Treated wastewater of Kairouan plant had a poor quality compared to other plants (Khadhar 2011).

Groundwater had a slightly acidic pH and moderate salinity (EC) which was lower than of those treated wastewater. But, TWW was richer in nutrients than the groundwater.

Table 1 Mean physical-chemical concentrations of different parameters of treated wastewater and groundwater

	TWW	GW	Standards[a]
pH	7.9	6.7	6.5–8.5
EC, mS cm^{-1}	3.99	3.20	7
COD, mg L^{-1}	160	nd	90
BOD_5, mg L^{-1}	45	nd	30
SS, mg L^{-1}	38	nd	30
TP, mg L^{-1}	3.61	0.48	0.05
TN, mg L^{-1}	158.18	nd	–
NO_2^-, mg L^{-1}	0.54	nd	0.5
NO_3^-, mg L^{-1}	3.86	0.31	50
NH_4^+, mg L^{-1}	36.25	0	1
Ca^{2+}, mg L^{-1}	174.5	66.8	500
Mg^{2+}, mg L^{-1}	116.85	231.5	200
Na^+, mg L^{-1}	105.61	30.25	500
K^+	61	6.7	50
SAR	8.75	2.47	–
Cl^{-1}, mg L^{-1}	818.58	31.51	600
HCO_3^-, mg L^{-1}	1703.67	985	–
SO_4^{2-}, mg L^{-1}	722	420	600

EC electric conductivity, *TDS* total dissolved solids, *SS* suspended matter, *COD* chemical oxygen demand, *BOD* biochemical oxygen demand, *Pt* total phosphorous, *Nt* total nitrogen, *SAR* sodium absorption ratio, *nd* not detected

[a] Tunisian standards for wastewater reuse in irrigation (NT106.03)

Physical soil properties: granulometry and bulk density

Granulometric analyses of Draa Tammar soil are shown in Table 2. The plotting of these results on the soil texture triangle of the U.S.D.A. (1954) showed three different textures (Table 2):

- For the lithosoil, a clay texture which was mainly a clay-silt texture and the dominant fractions were clay (from 32.54 to 39.23 %) and silt (from 51.55 to 62.82 %).
- For the saline soil, a silt-clay texture which was and the abundant fraction was silt. Its percentages ranged from 52.87 to 62.83 %.
- For the isohumic soil, a sandy-clay-silt texture with a dominant sand (from 59.9 to 63.64 %).

The XRD diffractograms indicated that the dominant minerals were carbonate and phyllosilicate (41 and 32 %, respectively) in lithosoil. Whereas in saline and isohumic soils, the dominant minerals were carbonate and quartz (70.1 and 18 %, respectively), and Quartz and carbonate (56.2 and 26.8 %), respectively. These results were in agreement with soil texture. Also, XRD patterns of the clay analysis indicated that kaolinite was the only clay present in the isohumic soil. While in lithosoil and the saline soil, the clay fraction consisted of a mixture of 1:1 (kaolinite) and 2:1 clay minerals (illite). The lithosoil is composed by 28.16 % of kaolinite and 3.84 % of illite. As for the saline soil, the kaolinite and illite percentages were 19.18 and 3.65 %, respectively. The XRD diffractograms, also, showed the presence of fluorapatite which had more intense peak in irrigated soils.

The analysis of field samples collected from the different profiles showed that the standard deviations of mean bulk density (BD) values are always below 10 %. Thus, it indicates that the used method was globally valid for this study. BD values ranged from 1.21 to 1.65 g cm^{-3}, from 1.19 to 1.50 g cm^{-3} and from 1.19 to 1.35 g cm^{-3} in lithosoil, saline and isohumic soils, respectively (Fig. 1).

The average bulk density (BD) values of lithosoil, saline and isohumic control soils were 1.3675, 1.3650 and 1.2775 g cm^{-3}, respectively (Fig. 1). These control soils had similar soil porosity in top soil layer, which was probably due to the presence of vegetation roots. Lithosoil was the least permeable especially in 30- and 40-cm levels. Besides, this soil type had the highest clay content (from 32.54 to 39.53 %) and the lowest sand (5.26–9.22 %) percentages. The isohumic soil was more permeable than the two other soil types (Fig. 1) due essentially to its high sand fraction (from 59.9 to

Table 2 Mean granulometric variation (in %) of the three soil types of Draa Tammar perimeter with depth in centimetre

	Lithosoil					Saline soil						Isohumic soil			
	CU		$I_{W1}U$		$I_{W2}U$	CS		I_GS		I_WS		CI		I_WI	
Depth (cm)	0–20	20–40	0–20	20–40	0–20	0–20	20–40	0–20	20–40	0–20	20–40	0–20	20–40	0–20	20–40
Clay	32.54	38.47	38.07	39.23	39.53	23.58	22.86	26.32	21	20.66	22.67	29.16	30.34	29.28	27.8
Silt	62.82	54.88	54.69	51.55	51.95	60.82	58.38	52.87	60.6	62.62	62.83	8.11	7.88	11.225	11.68
Sand	5.26	6.65	7.24	9.22	8.52	15.6	18.76	20.83	19.4	16.72	14.5	63.64	59.9	60.53	60.44

CU control lithosoil, *$I_{W1}U$* lithosoisoil irrigated with one dose of treated waste water (TWW), *$I_{W2}U$* lithosoil soil irrigated with double dose of TWW, *CS* control saline soil, *I_GS* saline soil irrigated with groundwater, *I_WS* isohumic soil irrigated with one dose of TWW, *CI* control isohumic soil, *I_WI* isohumic soil irrigated with one dose of TWW

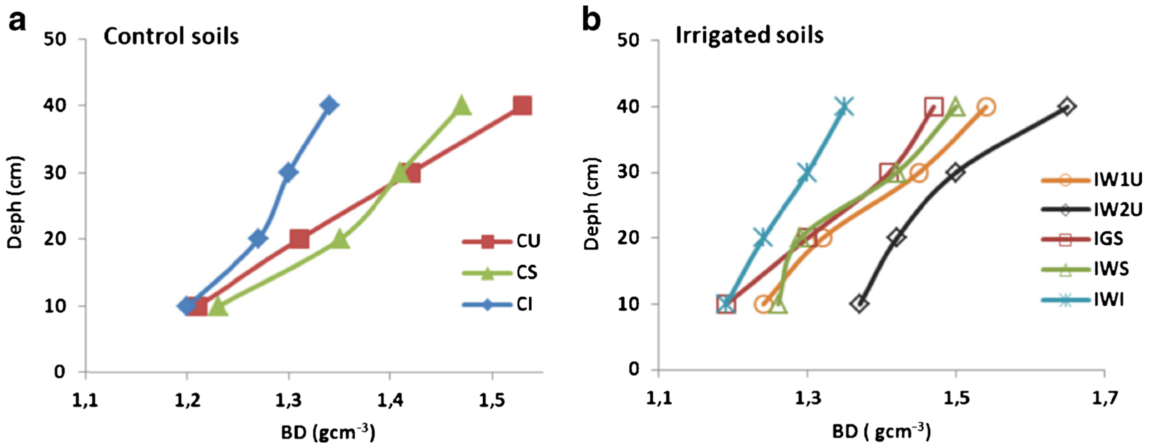

Fig. 1 Bulk density variations of the three soil types with depth: **a** control soils, and **b** irrigated soils with treated wastewater and groundwater

63.64 %). The average BD values were 1.4362, 1.3675 and 1.3650 g cm^{-3} in wastewater irrigated lithosoil, saline and isohumic soils, respectively. Irrigation with TWW decreased the soil porosity in lithosoil and saline soil especially in the upper level (0–10 cm) and only in 30–40-cm level in the isohumic soil (Fig. 1).

In the lithosoil, irrigated soil with double dose of TWW ($\mathrm{I_{W2}U}$) has lower porosity than the soil receiving a single dose ($\mathrm{I_{W1}U}$) (Fig. 1). The porosity was especially lower in 20- and 30-cm levels.

In the saline soil, water quality was an important parameter that influenced the soil porosity evolution. Indeed, the irrigation with groundwater, generally, increased the soil porosity (Fig. 1), contrary to irrigation with treated wastewater which decreased the soil porosity especially in 10-, 30- and 40-cm levels.

The irrigation of isohumic soil by treated wastewater improved soil porosity (Fig. 1) especially in upper layers (10 and 20 cm) where the average clay content was low (Table 2, Fig. 1).

Bulk density always increases with depth. Generally, application of TWW increased the soil bulk density in all soil types. Also, granulometric variations have a great impact on soil porosity. Indeed, we found that bulk density was well correlated with soil texture, and especially the fine fractions (clay+silt) rates and the soil permeability.

In lithosoil, saline and isohumic soils, the quality of water used for irrigation did alter the physical properties of the soil.

Table 3 Mean values of physical-chemical parameters of the three soil types of Draa Tammar perimeter

		Depth (cm)	Number of samples	pH	TOC (%)	EC (mS cm^{-1})	$CaCO_3$ (%)	CEC $cmol^{+}$ kg^{-1}
Lithosoil soil	CU	0–20	2	7.81	0.54	0.62	34.21	37.66
		20–40	2	7.71	0.71	0.72	37.23	36
	$\mathrm{I_{W1}U}$	0–20	11	8.02	0.69	1.05	28.67	39.72
		20–40	11	8.01	0.53	1.09	29.46	38.45
	$\mathrm{I_{W2}U}$	0–20	3	7.52	0.94	0.83	37.64	33.23
Saline soil	CS	0–20	2	8.1	0.69	5.93	33.28	32.47
		20–40	2	8.4	0.53	6.93	44.66	29.53
	$\mathrm{I_GS}$	0–20	3	7.94	0.66	1.49	33.9	22.87
		20–40	3	7.7	0.64	5.72	35.05	19.98
	$\mathrm{I_WS}$	0–20	7	8.15	0.75	3.26	35.62	32.76
		20–40	7	8.06	0.74	2.31	32.44	27.25
Isohumic soil	CI	0–20	5	8.05	1.22	0.1	50.63	10.41
		20–40	5	7.95	1.46	0.08	51.46	10.08
	$\mathrm{I_WI}$	0–20	9	7.95	1.03	0.16	51.68	8.37
		20–40	9	7.6	1.11	0.15	51.01	7.1

For other abbreviations, see Table 2

pH potential hydrogen, *TOC* total organic carbon, *EC* electric conductivity, *$CaCO_3$* carbonates

When the initial soil porosity was low, the suspended solids and the dissolved compounds of treated wastewater decreased the soil porosity. Whereas when the TWW was used in a permeable soil (isohumic soil), it improved the soil permeability by water drainage. This leaching caused an increase of the macro- and meso-porosity but also reduced the micro-porosity (Sacco et al. 2012; Hu et al. 2009).

Chemical soil properties: CEC, salinity (electric conductivity), TOC, pH and carbonates

In Draa Tammar irrigated perimeter, two types of clays minerals 1:1 (kaolinite) and 2:1 clay (illite) were detected. As shown in Table 3, CEC values were similar in lithosoil and saline soil, despite the differences in their clay percentages. These results could be explained by the higher amount of illite in saline soil (16 % of the clay fraction) than in lithosoil (12 % of the clay fraction). Although CEC depends greatly on soil organic matter which has a higher cation exchange capacity than clays, its low content in soil limited its contribution to soil exchange capacity. The isohumic soil had the lowest CEC values that ranged from 7.1 to 10.41 $\text{cmol}^+ \text{kg}^{-1}$. These lower values of CEC might be attributed to the clay type (kaolinite) and also to the high content of sand (>60 %).

The average salinity of the TWW (3.99 mS cm^{-1}) was higher than that of the lithosoil and isohumic controls soils. Unlike the saline soil, the EC of the control profile was higher (6.3 mS cm^{-1}) than salinity of irrigation water (TWW and GW (3.20 mS cm^{-1})) (Table 1). Long-term irrigation with TWW increased the soil salinities both in lithosoil and isohumic soils. The average EC values variations were about + 0.05 mS cm^{-1} in isohumic soil and +0.30 mS cm^{-1} in lithosoil soil which was less permeable. This increase in soil salinity was observed by many researchers such as Klay et al. (2010) and Garcia and Hermandez (1996). it was, probably, due to high EC of TWW (higher than of control soils salinities). Despite the high salinity of the irrigation water, isohumic soil which was well drained and had the lowest mean bulk density (1.2775 g cm^{-3}), the soil salinity increase was very low (+ 0.05 mS cm^{-1}) compared to other soil types. However, the low permeability of the lithosoil which its mean bulk density was 1.3675 g cm^{-3} led to more salt retention. In addition to the saline irrigation water (TWW), the increase of EC might be also due to 2:1 clay minerals (illite) and humic substances which have a much higher ability to retain positively charged ions and in return can enhance soil EC in the lithosoil.

In saline soil, EC values decreased both in soils irrigated with TWW and groundwater. So, when the soil salinity level was greater than irrigation water salinities (TWW and GW), application of TWW seemed to be beneficial since the mean bulk density was relatively good (1.3650 g cm^{-3}). Although the high CEC, water movement controlled salt movement and distribution (Nakayama and Bucks 1986) in the saline soil.

Also, based on the good relationship between bulk densities, control soil salinities, water irrigation salinities and soil permeability, we suggested that salts were leached to lower horizons (Stewart et al. 1990).

The average percentage of total organic carbon (Table 3) in isohumic soil which was irrigated by TWW (1.07 %) was lower than in control soil (1.34 %). The mean TOC in wastewater-irrigated lithosoil (0.61 %) and saline soils (0.75 %) was higher than in control soils (0.54 and 0.69, respectively). But, in soil irrigated by groundwater, the TOC percentage was stable (0.66 %). We, also, noticed that in 20–40-cm level, we had some fluctuations which probably depended on the soil's permeability and drainage conditions.

The TWW brought organic compounds, and their amounts depended on water quantities. Indeed, the increase of water quantities used (from single to double dose) was associated to an increase of COT percentage (from 0.69 to 0.94 %). Organic carbon supplied in soil by TWW was observed elsewhere (Polglase et al. 1995; Gloaguen et al. 2007; Gharbi Tarchouna et al. 2010). Part of this organic carbon might accumulate in the surface soil, whereas others will progress toward the bottom of soil levels based on the soil bulk density of each layer, soil texture and soil drainage. These variations of TOC in soils irrigated by effluents might be explained by the "priming effect" according to Jueschke et al. (2008) through which TWW brought nutrient that enhanced the microbial activity like in the isohumic soil. Also, the kinetic rate of organic compounds biodegradation depends directly on soil type and its permeability. So, when the soil permeability was good, the oxygen which is a key component in biodegradation process penetrated and trigged this mechanism. Its celerity was proportional to organic and biological compound quantities. Hence, the increase of organic compounds promoted the biodegradation, and the TOC increased. The biodegradability ratio DCO/DBO_5 of the effluents of Kairouan plant is greater than three ($\text{DCO/DBO}_5>3$). Thus, these effluents are more or less readily biodegradable (Hill and Spiegel 1980). Therefore, the repeated addition of organic matter brought by TWW, and its accumulation masked the priming effect in the lithosoil and saline soil.

In lithosoil, the mean soil pH increased by 0.22 units when a single volume of TWW was applied ($\text{I}_{\text{W1}}\text{U}$). This increase in pH was associated with an increase in soil cation exchange capacity, whereas the soil pH decreased by 0.29 U when the soil received a double volume of TWW ($\text{I}_{\text{W2}}\text{U}$) (Table 3) and a decrease in CEC was observed. In the lithosoil, cation exchange capacities were well correlated with pH (R^2=0.97). Irrigation with treated wastewater increased the CEC by the additional input of exchangeable cations, mostly sodium, which induced an increase in soil pH (Gelsomino et al. 2006).

In saline soil, the soil pH variations depended on the quality of irrigation water. A slight variation of soil pH has been observed since the application of TWW (from 8.2 to 8.1).

However, irrigation by groundwater decreased the mean soil pH by 0.42 U (Table 3). In saline soil, the decrease in soil pH was consistent with the slightly acidic pH values of the groundwater (Table 1). The drop of pH occurred as a result of displacing cations or leaching of basic cations, while the stability of pH in the topsoil under TWW irrigation is explained by the buffering capacity of both TWW and saline soil.

In isohumic soil, the pH decreased only in 20–40-cm level by 0.5 U (Table 3). Typically, humic substances contribute to a high CEC and thus to a high buffering capacity of the soil. But, due to the low percentage of carbon and the low CEC values of the isohumic soil, the humic substances contribution were not enough to impact the pH under irrigation. Thus, the low buffering capacity of the soil and the CEC decrease led to a decrease in the soil pH.

In summary, the soil pH decline was detected in many irrigated soil by TWW. It was considered as the result of important loss of nutrients (Kiziloglu et al. 2007). The pH decrease was also observed in many same contexts (e.g. Sing et al. 2012). The pH increase could be due to the irrigation water pH. Due to soil buffering, the soil pH evolution might have occurred in different steps: soil pH decreased initially; this decline was the result of organic matter decomposition through the high microbial biomass in the soil irrigated by TWW (Adrover et al. 2012). Then, organic matter mineralization produced carbon dioxide (CO_2), negative charges and basic cations (Mohammad and Athamneh 2004; Mkhabela and Warman 2005). Exchangeable cations which were adsorbed by soil contributed to soil pH increase (Jardao et al. 2006; Gelsomino et al. 2006). This proposed process was always closely related to soil porosity which was variable in our studied perimeter. When the mean BD was low such as in isohumic soil, the pH level evolution was directly related to ambient conditions and movement of irrigation water and soil compounds (Nakayama and Bucks 1986).

The percentage of $CaCO_3$ varied from 29.46 to 54.23 % (Table 3). Irrigation of lithosoil by only one dose of TWW decreased the carbonate rate by 6.65 % and increased the pH soil, whereas the increase of used water volume increased the carbonate rate and hence increased the soil pH. In saline soil, TWW decreased the carbonate rate (4.95 %), and consecutively, a decrease in soil pH was observed. In isohumic soil, a small increase of carbonate percentage (0.20 %) was detected which was reflected by a decrease in soil pH level (0.2). Irrigation with groundwater decreased the carbonate percentage (4.50 %) and also the soil pH (0.43). According to the soil pH values which were always below 8.5 and due to the high carbonate contents, any soil sodification could be suspected (Fernangez-Galvez et al. 2012). The carbonate rate variation was observed elsewhere (Mahmoud et al. 2010, 2012; Sierra et al. 2001).

The supply and decomposition of organic matter increased the number of negative charges in acid, organic-poor soils. This latter adsorbed soil protons and caused an increase of the soil pH and in return increased the soil CEC. Consequently, the liberated H^+ contributed to carbonate decomposition and thus to a decrease in soil $CaCO_3$ (Table 3).

In addition, TWW was very rich in HCO_3^- and Ca^{2+} (Table 1). Hence, the application of a double volume of TWW brought excessive amounts of Ca^{2+} and HCO_3^- which resulted in precipitation of calcium carbonate ($CaCO_3$ increased in soil). This reaction released CO_2 that contributed to more acidification of soil solution and to CEC decrease.

The good permeability of the isohumic soil (the lowest bulk density) involved a relatively high evaporation of the soil solution. So, calcium and bicarbonate were retained although the low CEC of this soil subsequently led to $CaCO_3$ formation. Also, particularly, the humic substances could retain H^+ cations which might explain the CEC decrease and in return the pH decrease.

Groundwater had a slight acidic pH which involved a pH drop of the soil due to leaching of the basic cations (CEC decrease). In return, the decrease in pH and with the produced CO_2 by the soil fauna and roots activity could dissolve calcium carbonate and thus contribute to its decrease.

PAHs content, distribution and carcinogenic potential

Dissolved organic matter (DOM) of TWW is a complex mixture of compounds poly-dispersed. Part of it is derived from humics and contributes to soil fertility, while the other part can be considered as anthropic contaminants such as polycyclic aromatic hydrocarbons (PAHs). These organic contaminants have dangerous health impacts. Investigating the concentrations of these carcinogenic and mutagenic organic pollutants and their geochemical behaviour in long-term irrigated soil by TWW was very crucial.

Although several hundred PAHs exist, most studies focus on a limited number of them, namely the 16 PAHs listed by the US Environmental Protection Agency (USEPA) and the European Community as pollutants (Samanta et al. 2002; Puglisi et al. 2007). Only 14 PAHs were detected in soil samples from the perimeter of Draa Tammar.

Draa Tammar irrigated perimeter with TWW showed elevated concentrations of PAHs (Table 4). The average concentration of total PAHs of dry material (TPAHs) was 2252.18 $\mu g\ kg^{-1}$ for all soils together (Fig. 2); it ranged from 204.16 $\mu g\ kg^{-1}$ (in 20–40-cm level of control isohumic soil) to 8845.41 $\mu g\ kg^{-1}$ (in 20–40 cm level of irrigated by TWW lithosoil). On the whole, the highest TPAH quantities were always in 0–20-cm layer soil (3426.66 $\mu g\ kg^{-1}$), and the lowest concentrations were in 20–40-cm layer (791.18 $\mu g\ kg^{-1}$, 20–40 cm). Studied samples showed, also, a relatively large proportion of B[ghi] (Table 4). This compound was, usually, associated with motor vehicle exhaust (Grimmer 1983; Khalili et al. 1995; Harrison et al. 1996). In Draa tammar, these high

Table 4 Concentration in micrograms per kilogram variation of the 14 analysed PAHs in different soil types with depth

		Depth (cm)	Naph	Ace	Fl	Phen	Anthr	Fluo	Pyr	Chry	B[b]Fl	B[k]Fl	B[*a*]P	DB[ah]A	IP	B(ghi]P	∑14 PAHs
Lithosoil soil	CU	0–20	28.46	52.07	57.53	7.50	2.77	33.24	89.91	25.72	27.39	61.58	86.02	29.66	1.99	13.29	517.20
		20–40	12.76	45.66	67.98	5.67	16.56	51.78	76.76	4.78	7.96	10.34	5.67	1.87	1.23	2.67	311.70
	$I_{W1}U$	0–20	42.87	2415.35	20.19	69.07	383.72	278.98	227.97	20.67	242.87	921.34	254.63	3513.83	31.24	431.68	8854.41
		20–40	nd	305.46	13.69	2.51	32.23	130.86	141.31	131.55	136.23	61.03	6.88	76.75	23.48	163.81	1225.85
	$I_{W2}U$	0–20	51.50	884.29	71.97	24.29	31.98	226.46	189.27	23.61	35.99	106.48	56.51	488.07	15.73	386.91	2593.10
Saline soil	CS	0–20	27.56	35.74	36.34	4.35	3.69	44.92	82.92	17.98	18.17	54.89	38.18	27.11	nd	147.32	539.24
		20–40	17.69	26.04	7.64	3.03	18.59	35.79	62.16	9.92	16.10	7.10	1.80	3.21	nd	118.80	327.90
	I_GS	0–20	nd	37.92	19.11	19.67	33.76	69.31	88.25	52.64	17.34	38.27	5.26	16.44	nd	107.34	505.36
		20–40	nd	47.82	41.61	8.60	31.98	74.43	52.60	4.70	8.36	51.27	17.82	20.71	nd	13.94	373.88
	I_WS	0–20	30.87	3065.65	18.09	67.87	323.98	208.98	187.97	21.67	102.87	845.98	209.98	3124.67	23.98	404.08	8636.64
		20–40	27.95	1027.83	42.75	23.37	36.31	264.16	209.36	6.95	250.55	77.25	10.39	206.04	6.43	207.32	2396.73
Isohumic soil	CI	0–20	25.34	34.56	5.76	11.39	6.98	27.76	56.76	56.98	27.68	51.34	19.45	40.76	14.12	123.45	502.37
		20–40	11.87	21.202	3.97	6.082	13.22	21.998	30.22	4.784	15.062	15.412	20.22	7.815	9.604	22.68	204.16
	I_WI	0–20	59.66	1908.86	37.81	37.68	163.37	208.98	198.94	23.69	240.13	453.78	148.00	1562.33	12.98	208.68	5264.96
		20–40	45.35	686.74	55.36	14.52	26.43	157.97	143.06	5.86	129.25	43.79	8.03	103.95	3.83	104.99	1529.22

For others abbreviations: see Table 2

Naph naphtalene, *Ace* acenaphtene, *F* fluorene, *Anth* anthracene, *Phen* phenanthrene, *Flua* fluoranthene, *Pyr* pyrene, *Chr* chrysene, *B[a]P* benzo(a)pyrene, *B[b]Fl* benzo(b)fluoranthene, *DB[ah]Anth* dibenzo(ah)anthracene, *B[k]Fl* benzo(k)fluoranthene, *B[ghi]P* benzo(ghi)perylene, *IP* indeno(1.2.3-cd)pyrene

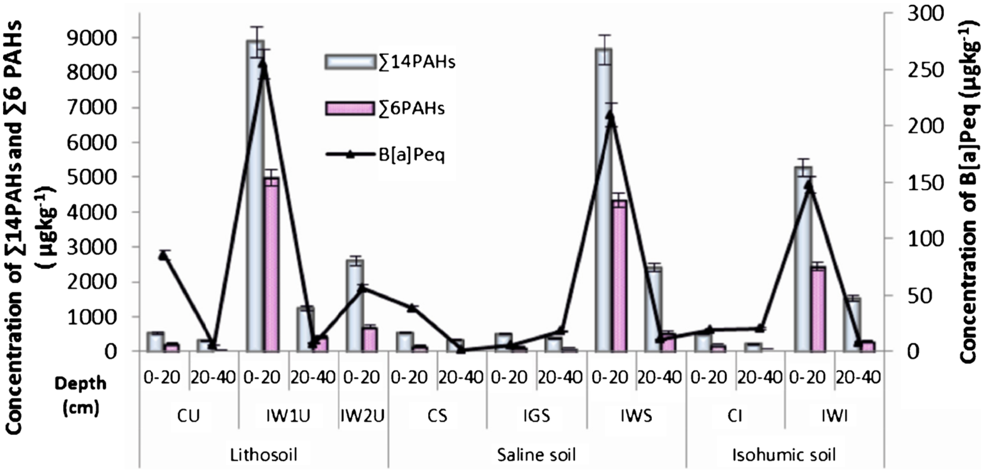

Fig. 2 Repartition of total ∑14 PAHs, ∑6 PAHs probable, or possible human carcinogens by IARC (1987) on primary *Y*-axis and total B[a]Peq concentrations on the secondary *Y*-axis in Draa Tammar perimeter

concentrations were probably due to the use of labour tractors and also to the domestic heating.

TPAH concentrations were strongly related to the soil type and irrigation history (irrigated or not, irrigation water quality). The lithosoil irrigated by TWW had the highest total PAHs concentrations, followed by saline soil (Table 4, Fig. 2), then isohumic soil

Based on soil BD, the soil porosity order was isohumic soil > saline soil > lithosoil. Isohumic soil has an important sand fraction and high permeability. Thus, an important oxygen quantity could infiltrate at least to the first 20 cm of soil where the highest TPAH quantities were found. Consequently, the high microbial biomass of TWW would enhance the kinetic rate of the aerobic biodegradation of TPAHs and decreased their concentrations in the soil. Also, isohumic soil was well drained. Hence, the TPAH molecules could be leached to deeper levels. The highest TPAH amounts were found in the top soil layer and the pollutants level despite the variability of BD in the three soil types. PAHs tend to sorb strongly to soil organic matter and diffuse into micropores and hence become less or non-bioavailable. Therefore, we suggest that the TPAH retention was mainly by chemisorptions of these molecules onto clay fraction and soil organic matter, which reduce their bioavailability and led to their accumulation in the top soil. In isohumic soil, the important water movement (leaching) may cause the redistribution of these pollutants (Maxin and Kogel-Knabner 1995; Pierzynski et al. 2000).

Table 5 Maliszewska-Kordybach (1996) Classification of soil contamination class by 16 PAHs

Class of soil contamination	∑16 PAH (µg kg^{-1} dry weight)
Not contaminated	<200
Weakly contaminated	500–600
Contaminated	600–1000
Heavily contaminated	>1000

Compared to other agriculture lands, Draa Tammar perimeter did not have the highest level of PAHs, for example, in Tianjin (China) agricultural soil irrigated with TWW, the mean TPAHs amounts ranged from 3000 to 5000 µg kg^{-1} (Chen et al. 2003). In Tunisia, these TPAH concentrations were clearly higher than those of Zaouit Sousse irrigated perimeter (Tunisia) which ranged from 46.23 to 129.51 µg kg^{-1} (Khadhar et al. 2012) despite that the irrigation period by TWW was the same. These differences were, probably, due to two parameters, (a) the water quality of the TWW of Zaouit Sousse which was widely better (e.g., the dissolved organic matter in TWW Kairouan plant were much higher) and (b) the soil of Zaouit Sousse had better permeability and leaching.

According to Maliszewska-Kordybach (1996) classification (Table 5), control soils and soil irrigated by groundwater (GW) can range between non-contaminated to weakly contaminated soils. According to Skrbic et al. (2005). they proposed that regions and countries with 300–400 µg kg^{-1} dry weight are considered as not polluted soils. Therefore, control and irrigated soils by groundwater (GW) were not polluted. But, the irrigated soils with TWW were, always, considered heavily contaminated (Maliszewska-Kordybach 1996).

The rings number is one parameter which permits knowing the degradation degree of different PAHs. Thus, the lighter PAHs are easily degraded or exported (Wilcke et al. 1996). The PAHs could be divided into three groups according to the ring numbers, i.e. two to three rings, four rings and five to six rings (Fig. 3).

In saline and isohumic control soils, we had relatively homogeneous distribution of the three ring number groups of PAHs (Fig. 3), and the five- to six-ring group was predominant, in both layers. For the lithosoil, the dominant rings were five to six rings in top soil layer and two to three rings in the second soil layer (20–40 cm).

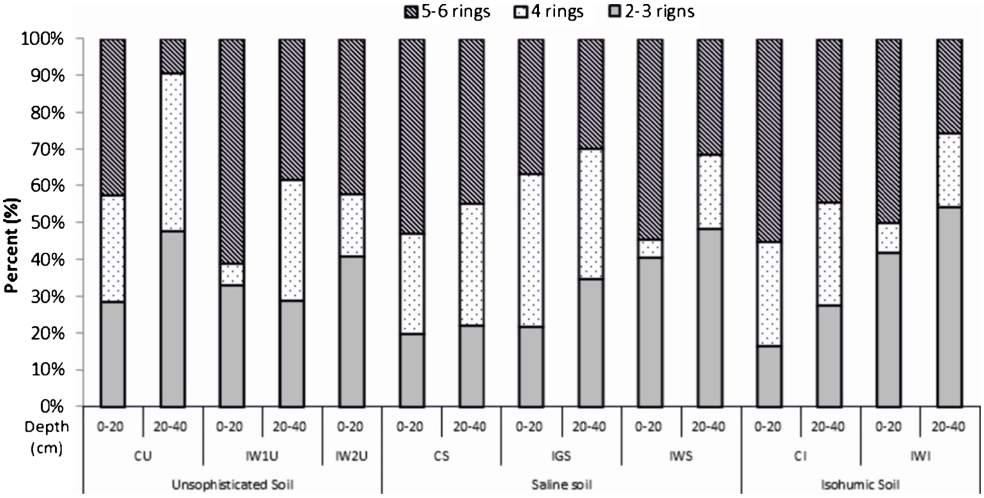

Fig. 3 Percentage distributions of two- to six-ring PAHs in all control and irrigated soils with treated wastewater and groundwater

The irrigated soil with groundwater showed a predominance of four-ring group (170 μg kg^{-1}) in both layers. Irrigated soil by TWW had the same predominance of the five- to six-ring group in the first layer (0–20 cm) and two- to three-ring group for the second layer (20–40 cm). Except the lithosoil which maintained the same predominance in both layers. On the whole, the highest molecular weights were predominant in soil. Also, distribution varied according to depth. Generally, in control and groundwater irrigated soils, we have homogeneous distribution of the three ring number groups of PAHs. But, in soils irrigated with TWW, five- to six-ring numbers were dominant in top soil layer, and two- to three-ring numbers were dominant in 20–40-cm soil level (Fig. 3). So, it likely that the first mechanism proposed above for TPAHs retention was the more probable. The infiltrated oxygen and microbiological biomass controlled the organic biodegradation of light rings number. Consequently, the PAHs with high rings numbers became dominant. But, in deeper soil level where the BD was higher, the aeration was not enough, and the light rings number was persistent. In soil, PAH might undergo chemical oxidation, photolysis, and volatilization and microbial degradation. Hence, biodegradation of PAHs in soil is usually very slow (Wilson and Jones 1993) because of their extremely low bioavailability which is limited by a poor mass transfer due to strong or irreversible sorption (Bosma et al. 1997). Also, PAH molecules tend to strongly bind with the clay minerals and organic matter present in soils because these contaminants have a low aqueous solubility. Therefore, since in isohumic, lithosoil and saline soils, the ring number distribution was not different, the chemisorptions mechanism had played, in part, an important role in PAHs retention.

IARC (1987) listed seven PAHs which were B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A and IP as into probable (2A) or possible (2B) human carcinogens. In Draa Tammar perimeter, only six PAHs on seven were detected which were Chry, B[b]F, B[k]F, B[a]P, DB[ah]A and IP. The PAH_{carc} percentage ranged between 17 and 31 % in control soils and between 32 and 40 % in irrigated soils (Fig. 2).

Toxic equivalency factors (TEFs) were used to quantify the carcinogenicity of other PAHs relative to B[a]P and to estimate benzo[a]pyrene-equivalent concentration (B[a]P)eq (Nadal et al. 2004; Rey-Salgueiro et al. 2008). According to the USEPA, calculated TEFs for B[a]A, B[a]P, B[b]F, B[k]F, IP, DB[ah]A and Chry were 0.1, 1, 0.1, 0.01, 0.1, 1 and 0.001, respectively (Qiao et al. 2006). The total benzo[a]pyrene-equivalent concentration (B[a]P)eq was calculated as follows:

$$\text{Total B[a]Peq} = \sum \text{i Ci} \times \text{TEFi} \,;\ \text{Ci}$$

$$: \text{concentration of individual PAH},\ \text{TEFi}$$

$$: \text{toxic equivalency factor.}$$

The B[a]Peq average total concentration was 59.25± 80.88 μg kg^{-1}. The measured values varied from 1.8 μg kg^{-1} (control saline soil, at 20–40 cm) to 254.63 μg kg^{-1} (irrigated by TWW lithosoil, at 0–20 cm). Generally, the highest total B[a]P concentration was in top soil layer irrigated with TWW (Fig. 2); it was 1.2–7.6 times higher than those of control soils. We noted, also, that the top layer of lithosoil ($I_{W1}U$) retained the highest carcinogenic potential (4894.58 μg kg^{-1}).

Statistical results

Four principal components (PCs) were extracted from the PCA analysis and only eigenvalues >1 were retained. The PCA analysis of the different results obtained from the studied site (Fig. 4) showed that 83.14 % of the variances were explained by the first three factorial axes. The PCA analysis had showed, too, that three groups were distinguished: The first group involved isohumic soils (control and irrigated); the second consisted of the control and irrigated (GW and TWW) saline soils; and the third group was represented by control and irrigated lithosoil.

The first factor which implied 46.08 % of the total variance was heavily weighted by silt fraction (0.97), $CaCO_3$ (−0.90), TOC (−0.92) and sand fraction (−0.94). The second factor with 13.25 % of total variance was predominated by the pH (0.72), EC (0.69) and clay fraction (−0.89). Thus, the first and second factor represented the chemical and textural parameters. The third factor corresponded to 15.19 % of the total variance. The principal components were PAHs (0.89) and BD (−0.63). This last factor illustrated the physical parameter and organic pollutants; the PAHs and BD variances confirmed that the organic pollutant mobility was controlled by other factors as seen above the aerobic biodegradation and chemisorption.

Thus, the isohumic soil was mainly distinguished by the higher TOC, $CaCO_3$ and sand fraction values (Fig. 4). The control and irrigated soils with TWW depend essentially on textural and chemical parameters. Also, this classification showed that organic pollutants (PAHs) behaviour in soil depended on both textural (clay and silt fractions) and physical parameters (BD), and not only on the organic matter of TWW irrigation water. Moreover, PCA analysis, also, showed that Bulk density was, for the three textural soils, an important parameter which influences chemical soil evolution (Fig. 4).

We noted that when the depth parameter was, directly, considered, the total variances were not associated to the same factor. The absolute variance values were lower or equal, except for PAHs which increased from 0.69 to 0.89. But, in fact, the depth was indirectly implied by BD parameter which was closely correlated with depth.

Summary and conclusion

Draa Tammar irrigated perimeter (Central Tunisia) has three soil types and different textural characteristics. Therefore, it presented an opportunity to investigate TWW impact over time on soil evolution in semi-arid climate.

Results showed that application of TWW decreased the soil permeability when the soil has high bulk density in lithosoil and saline soil. However, it improved the soil permeability when the soil had relatively low bulk density (isohumic soil). When the leaching potential of the soil is reduced thanks to 2:1 clay minerals (Illite) and soil texture, a decrease in $CaCO_3$ percentage was associated to pH, EC and CEC increase. Also, the continuous input of HCO_3^- contributed to the precipitation of $CaCO_3$ and thus a decrease in soil pH and CEC. Irrigation with groundwater which has a slight acidic pH involved a decrease in soil pH and CEC, and consequently led to the decrease of carbonates.

Irrigation with treated wastewater for over 20 years was not recommended as it ends up with high level of organic contaminants in soils. These irrigated soils by treated wastewater are classified as heavily contaminated, while control and irrigated with groundwater soils are considered as none to weakly contaminated.

The overall results showed that the soil texture and mineralogy, water quality and volume, soil fauna and roots

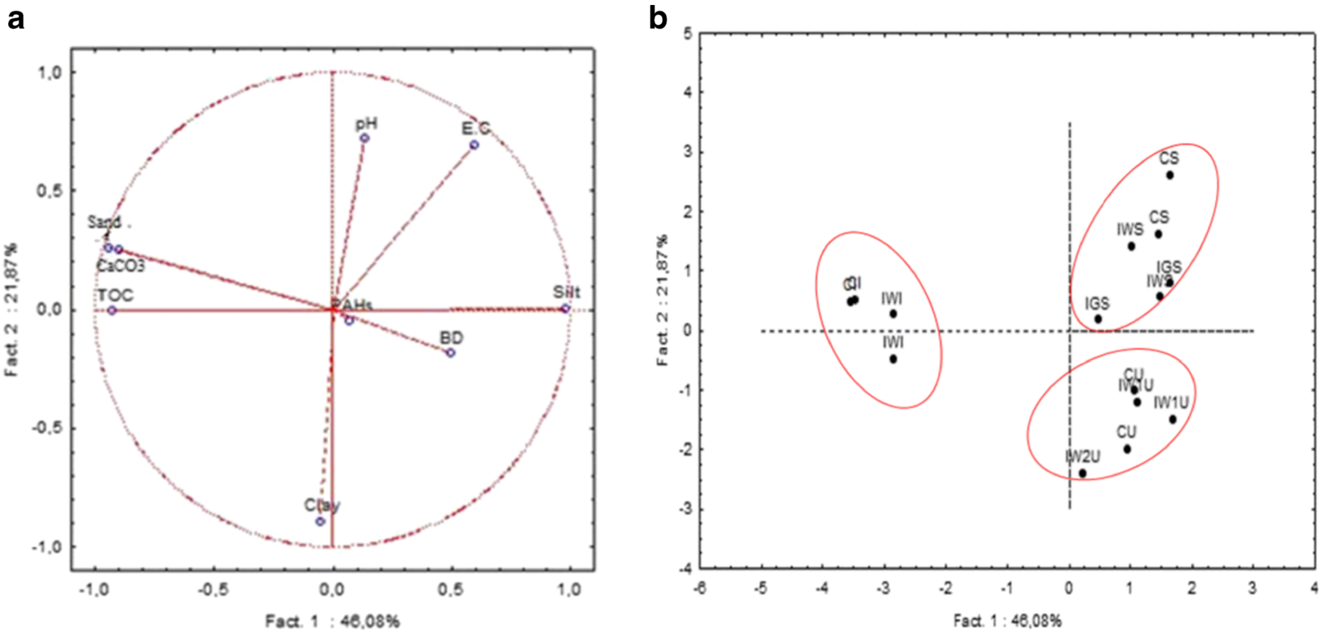

Fig. 4 Scatter plot of PCA analysis: **a** variables and **b** observations

respiration are key parameters which controlled the soil pH, CEC, salinity, carbonate evolution and PAH retention.

Also, PCA analysis confirmed that the impact of long time irrigation with treated wastewater on soil evolution is mainly dependent of the initial chemical and physical parameters of the soil and that the soil contamination with PAHs is principally related to soil texture and bulk density.

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