Soil Contamination by Phthalate Esters in Cultivated and Non-Cultivated Soils in North African Arid Regions: A Tunisian Case Study

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ABSTRACT

Over the last decades, several studies showed that phthalic acid esters (PAEs) were ubiquitous environmental contaminants and became a major threat to human health. This study provided the first case study about the concentration and the potential sources of soil's PAEs, both in Tunisia and North Africa. Soil samples were collected from four cultivated (CS) and two adjacent native soils (NS) at 0-10 cm and 10-30 cm layers in southeastern Tunisia. The PAEs concentrations were analyzed using a gas chromatography-mass spectrometry (GC-MS) system. Results showed that the total concentration of PAEs ranged from 2.40 to 11.05%. Higher values were detected in NS in the 0-10 cm layer contrary to CS which showed higher PAEs concentration in 10-30 cm depth. The di-n-butyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) were the most abundant PAEs. In the 0-10 cm layer, PAEs concentration was highly related to the age of the plastic film in CS. We observed a positive association between PAEs concentration and conductivity (EC) values. The PAEs concentrations were affected by the presence of soil organic matter (SOM) in CS. This decrease of PAEs in CS compared to the NS may be related to the microbial decomposition activity stimulated by the presence of fresh organic residues and fertilizers. These results showed that CS and adjacent NS in the studied regions were contaminated by PAEs which is probably a result of agricultural activities. More investigations on PAEs concentrations in various soil managements are needed to confirm these results.

1. INTRODUCTION

Intensive use of plastic films can induce contamination of microplastics and phthalate esters (PAEs) (Li et al., 2021). Reduction of microplastics contamination is related to the management and mitigation of microplastics pollution (Rahmayanti et al., 2022). However, Phthalic acid esters (PAEs) are extensively used in plastic materials (Zhu et al., 2022), such as, polyvinyl chloride, medical product, cosmetics, clothing, building materials, paints, pesticides, fertilizers, food packaging (Staples et al., 1997; Xu et al., 2008; Wang et al., 2013). As a result of their large scale use, the global PAEs consumption per annum is estimated to 6.0×10^6 tons (Xie et al., 2007). In recent times, there has been an increasing concern over the risk of phthalate exposure leading to adverse effects to human health and the environment (Das et al., 2021).

Several studies have reported health concerns related to endocrine disruptive problems and confirmed that human exposure to PAEs causes particularly cancer and reproductive effects (Hens and Caballos, 2003; Guo and Kannan, 2011). Therefore, they are considered as one of the widespread classes of organic pollutants (Kong et al., 2012) and classified as priority environmental contaminants (USEPA, 2013).

The presence of PAEs is confirmed in various environmental media, such as, air (Wang et al., 2012), water (Xie et al., 2007), sediment, soils (Ma et al., 2013; Kong et al., 2012) and many types of plant species (Fu and Du, 2011). Soils are considered as the main environmental matrices, highly affected by anthropogenic activities, and they act as natural sinks for pollutants, which can lead to the pollution of other spheres of the ecosystems and the human food chain.

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Actually, irrigation methods, the application of pesticides, and the impact of surrounding pollutant sources, waste and diversity of manure may lead to the differences of PAEs concentrations in various types of soils (Kong et al., 2012). Fertilizers contain between 0.01 to 2.8 mg/kg of PAEs as reported by Mo et al. (2008). It can lead to the accumulation of PAEs in the soil (Fu and Du, 2011). Plastic film used in agricultural field is associated to the increase of PAEs contamination (Pedersen et al., 2008). The use modes, and the amount of plastic films, as well as the age of the greenhouse, are the principal sources of PAEs soil contamination. Thus, they are the main factors controlling the PAEs concentration's variation in soil (Guo and Wu, 2011).

Soil contamination by PAEs is controlled by various factors, such as, soil properties and soil uses (Xu et al., 2008; Zeng et al., 2009), as well as the meteorological conditions (Cai et al., 2008; Kong et al., 2012). Zhang et al. (2015) demonstrated that high PAEs concentrations are detected in the summer.

DEHP and DBP are the most identified contaminants in cultivated soils and in multiple environment compartments like surface waters (Kelly et al., 2010). In fact, DEHP and DBP are the dominant components in plastic film (Wang et al., 2013). Moreover, longer/branching alkyl-chain PAEs such as DEHP improve polymer flexibility and they have been extensively used in the polymer industry as plasticizers (Hens and Caballos, 2003). DEHP is a principal component in most widely used-fertilizers (Mo et al., 2008). High concentration of DBP and DEHP in agricultural soils have already been detected in Chinese soils (Ma et al., 2003; Xu et al., 2008).

Our study was carried out in the Gabès Governorate, which is an industrial and commercial town with a population of about 374,300 inhabitants. However, since the foundation of one of the biggest Tunisian industrial complexes in Gabes City (1972), several studies showed that many wastes are produced by the industrial complex and have been directly dumped in the near coastal environment of Gabes region which is considered one of the most polluted areas in the Mediterranean Basin (El Zrelli et al., 2021). In addition, in Gabès region oasis agrosystems and other agricultural soil play a vital role in the life of the local communities. Actually, date palms are one of the most important crops in oasis ecosystems, providing a major source of income for local farmers and for the national economy. Seasonal crops in this region, where soils are poor quality, use fertilizers and greenhouse vegetables are extensively grown. However, in many developing countries, there is a large quantity of agricultural wastes that cause severe pollution problems (El-Hassanin et al., 2020). Hence, degrees of damage on the ecosystem and on human health are detected. We believe that the contamination of atmosphere, groundwater and soils are behind several health damages such as birth defects, negative effects on neurodevelopment and growth in children, cancer, and so on, in the Gabès population. Actually, industrial towns worldwide and particularly in arid regions are subjected to several environmental threats because temperature and wind spread pollutants over large areas. According to Wei et al. (2020) PAEs were detected in all the soil and vegetable samples collected in the economically developed YRD region of China. The main objective of this preliminary study, being the first one in the field in North Africa, is to determine the concentration and the potential sources of soil PAEs under cultivated greenhouse and adjacent non-cultivated native soils. More considerable attention should be given to the PAEs contamination status in soils and potential effects on local resident health (Tao et al., 2020).

2. METHODOLOGY

2.1 Studied sites and sampling method

All studied sites were located in southeastern arid region of Tunisia, precisely in Gabès governorate (Figure 1). The climate is Mediterranean, dry, hot in summer and mild in winter. The average annual temperatures ranged between 17 and 45°C and irregular precipitation (237 mm/year) is concentrated in the winter. Soils in southren regions of Tunisia are classified as Arenosols or Gypsisols in the WRB classification (Jones et al., 2013; Labiadh et al., 2013). However, in the current study, sampled soils in both sites were classified as Gypsisols. Soil samples were taken from the 0-10 cm and 10-30 cm layers of the profile using pre-cleaned iron soil shovel. In each greenhouse, three profiles were sampled: the first one was about 1m from the door of the greenhouse, the second is at the middle and the third is in the back of the greenhouse. In the laboratory, the three samples from each depth were sieved and mixed to produce composite samples which were reduced and used for analyses. Soil samples were stored in glass bottles and air-dried in a ventilated place at room temperature. Before analysis, samples were sieved through a 2 mm stainless steel sieve to remove plant debris and rock fragments. Six profiles were selected in four vegetable

greenhouse cultivated soils (CS1, CS2, CS3, and CS4) and two adjacent native soils (NS1 and NS2). The ages of the vegetable greenhouses were 8, 10, 15, and 30 years for, respectively, CS1, CS2, CS3, and CS4. In these greenhouses (each one covering 504 m^2, length=56 m, width=9 m) (Figure 2), farmers produce seasonal crops, particularly tomato, pepper, cucumber, melon. The planting date is depending on type of crops.

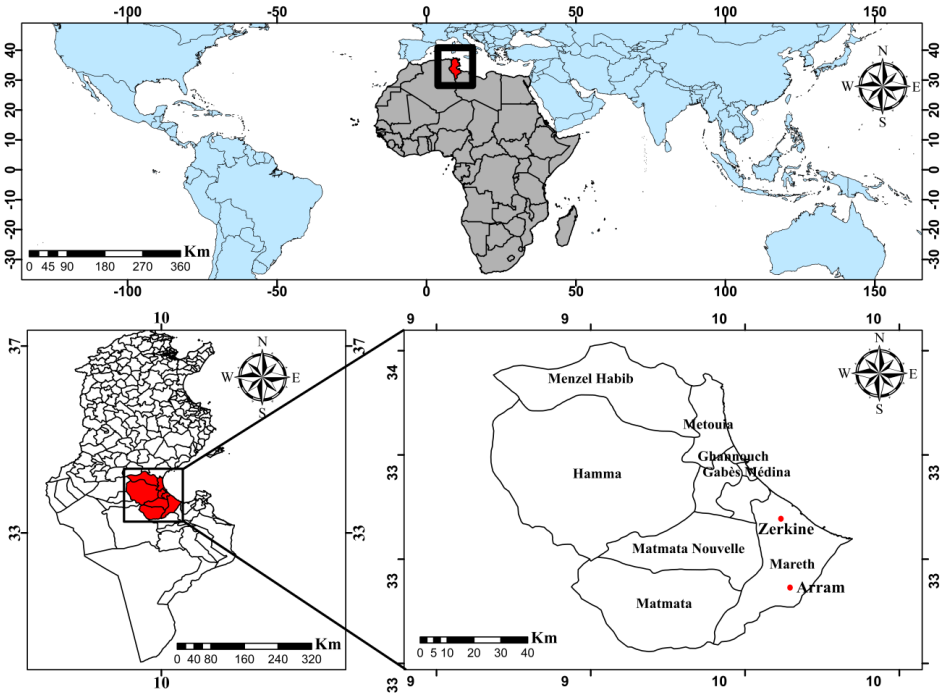

Figure 1. Localization map of the study area in Gabès Governorate

(a)

(b)

Figure 2. The sampling sites of soils (a) Arram (vegetable greenhouse CS1, CS2, and NS1) and (b) Zerkine (vegetable greenhouse CS3, CS4, and NS2)

2.2 Soil analysis

The total soil organic carbon (SOC) was determined by $K_2Cr_2O_7 \cdot H_2SO_4$ oxidation method of Walkey and Black (Nelson and Sommers, 1982) then the soil organic matter (SOM) content was calculated by multiplying SOC content by 1.72 (Dabin, 1967). Soil pH and EC were measured in a 1:5 soil:water suspension. Calcium carbonate ($CaCO_3$) content was estimated by the method of calcimetry (Nelson, 1982). Soil particle size distribution was determined by Robinson's method (Robinson, 1922).

2.3 Organic compounds extraction

Soil organic compounds were obtained by maceration of 50 g of air-dried soil (<2 mm) in 250 mL of methanol (MeOH) for 2 h at room temperature. After filtration, the solvent was evaporated under vacuum at 35°C, using a rotary evaporator (IKA, RV 10 auto V, Germany). The obtained dry concentrated organic residues were placed in hemolysis tubes and stored at -20°C until further analysis (Rahmani et al., 2020).

2.4 Gas chromatography-mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry analysis (a gas chromatography system (7890A) coupled to a mass spectrometry system (5975C, MSD) (Agilent Technologies, USA), was used to identify the volatile compounds from soil organic extracts (Rahmani et al., 2020) (Figure 2).

3. RESULTS AND DISCUSSION

3.1 Soil properties

The cultivated soils and native soils were slightly alkaline because pH values were between 8.12 and 8.90. Specifically, the cultivated soils showed high EC values. However, SOM concentrations were from 0.39 to 1.39% and from 0.55 to 0.87%, respectively, in cultivated soils and in native soils (Table 1). Among soils low concentrations of $CaCO_3$ and gypsum were recorded. The soil textures were loamy sand.

The pH values can be attributed to the high levels of carbonate calcium and gypsum (Corti et al., 2020). Similar pH values are detected by Mlih et al. (2019) and Omar et al. (2020) in the same regions under cultivated and non-cultivated soils. However, higher EC value in CS can be explained particularly by the use of saline water in irrigation (2.5 g/L to 4 g/L) (Omar et al., 2017; Corti et al., 2020). The presence of $CaCO_3$ and gypsum in arid soils of Tunisia was related to the alteration of geological parent materials (Mtimet, 2001). Low SOM concentrations observed in studied regions are similar to the average of SOM contents in soils of arid regions characterized by little accumulation of organic residues and high mineralization rate. SOM concentrations ranged between 0.39 and 1.39%; and between 0.55 and 0.87%, respectively, in CS and NS. Our results are in agreement with those detected by Mlih et al. (2019), Omar et al. (2020), and Znaidi et al. (2020) in soils of arid regions of Tunisia, by Elbasiouny et al. (2017) in reclaimed cultivated soils of the Nile Delta, Egypt and by Shahabinejad et al. (2019) in arid regions of Iran.

Table 1. Main characteristics of the vegetable greenhouse cultivated soils (CS1, CS2, CS3, and CS4) and adjacent native soils (NS1 and NS2).

		pH	EC (mS/cm)	Clay (%)	Silt (%)	Sand (%)	SOM (%)	$CaCO_3$ (%)	Gypsum (%)
CS1	0-10 cm	8.19±0.03	2.67±0.02	5.6	7.8	83.9	1.37±0.03	10.09±1.36	1.10±0.28
	10-30 cm	8.20±0.04	2.62±0.08	4.2	18	77.1	0.49±0.02	6.25±1.10	1.10±0.56
CS2	0-10 cm	8.17±0.12	6.89±0.61	6.7	7.2	83.5	0.39±0.05	6.25±1.30	8.70±0.74
	10-30 cm	8.18±0.08	6.23±0.45	8.1	7.7	83.9	0.96±0.06	5.28±1.30	12.25±0.42
CS3	0-10 cm	8.12±0.05	5.27±0.09	13.3	6.5	78.1	1.39±0.04	7.70±0.90	1.25±0.09
	10-30 cm	8.14±0.04	5.90±0.05	12.9	4.8	79.5	1.04±0.03	7.20±1.87	1.77±0.10
CS4	0-10 cm	8.39±0.04	9.40±1.10	14.2	3.3	80.9	0.73±0.03	8.18±1.91	2.06±0.12
	10-30 cm	8.28±0.03	12.20±1.80	12.5	4.5	81.6	0.84±0.03	7.24±2.44	0.44±0.01
NS1	0-10 cm	8.12±0.09	2.92±0.02	6.6	8.8	82.9	0.55±0.01	3.63±1.51	0.44±0.05
	10-30 cm	8.13±0.06	1.65±0.03	6.2	16.7	77.3	0.67±0.02	10.90±2.86	0.22±0.02
NS2	0-10 cm	8.19±0.02	1.48±0.01	14.9	5.3	78.9	0.87±0.01	8.20±2.55	0.29±0.02
	10-30 cm	8.38±0.02	2.36±0.02	13.5	5.1	81.5	0.60±0.03	8.60±3.22	0.44±0.02

C: cultivated; N: Native; EC: electrical conductivity; SOM: soil organic matter

3.2 PAEs soil concentrations and sources

Four types of PAEs are detected in studied soils DBP, DEHP, Dimethyl phthalate (DMP), and Dipentyl phthalate (DPP), which indicated that studied soils, as expected, were polluted by PAEs (Table 2). The total PAEs concentrations (∑PAEs) are ranging from 2.40 to11.05%. Across depth, PAEs concentration in CS was between 2.40 and 8.33% and in NS between 5.01 and 11.05%. Several previous studies have reported that soils of various agrosystems and uncultivated surrounding soil are contaminated by PAEs (Zhang et al., 2015). However, in our study as unexpected in NS the ∑PAEs was more than two or three times higher compared to CS. For example the ∑PAEs in NS2 in 0-10 cm was equal to 10.05% but in CS1 and CS2 we recorded, respectively, 2.4 and 3.97%. This finding is in agreement with those by Zhang et al. (2014) which found that total PAEs and individual concentrations of phthalate contaminants were all relatively low in the areas that used plastic films compared with other samples. They considered this fact is due to the greatest usage amount of plastic

products in people's daily lives and other factors like diffusion of PAEs in the atmosphere. In our study, probably, these differences can be the result of the impact of factors controlling PAEs accumulation in soil, such as, distance from a pollution source, soil type and properties, land use, rainfall and temperature, which can make transverse, vertical and seasonal changes (He et al., 2015). Xu et al. (2008) thought that precipitation, atmospheric deposition, drainage, or seepage could cause PAEs contaminations in cultivated and uncultivated soils. Moreover, building materials and domestic garbage at surroundings can cause native PAEs soil contamination. Actually, high concentrations of PAEs in urban soils were observed for roadside sites (Kong et al., 2012). Moreover, the less PAEs in cultivated soils in the present study is probably because sampling in the present study was performed in summer when fewer agricultural activities were involved, leading to less PAEs input. In addition, in CS, we hypothesize that the presence of organic matter (Gao et al., 2021), water and fertilizers increase microbial activity in CS which in turn increases organic matter and PAEs mineralization (Boll et al., 2020; Das et al., 2021; Wang et al., 2020). Microbial degradation could efficiently reduce the residue of organic pollutants in soil and crop plants (Liu et al., 2022; Wang et al., 2020). This is perhaps why in CS the PAES concentration is low than in NS.

Table 2. The concentrations (%) of different PAEs detected in the vegetable greenhouse cultivated soils (CS1, CS2, CS3, and CS4) and adjacent native soils (NS1 and NS2)

Soil	CS1		CS2		CS3		CS4		NS1		NS2	
	8years		10years		15years		30 years					
	0-10 cm	10-30 cm	0-10 cm	10-30 cm	0-10 cm	10-30 cm	0-10 cm	10-30 cm	0-10 cm	10-30 cm	0-10 cm	10-30 cm
DEHP (%)	2.40	6.00	3.97	4.99	4.30	5.39	5.34	6.38	7.12	3.30	6.74	5.30
DBP (%)	ND	1.74	ND	0.78	0.97	1.26	0.00	1.95	1.05	1.33	3.40	3.00
DPP (%)	ND	0.41	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DMP (%)	ND	ND	ND	ND	ND	ND	0.59	ND	ND	0.38	0.91	0.00
Total (%)	2.40	8.15	3.97	5.77	5.27	6.65	5.93	8.33	8.17	5.01	11.05	8.30

C: cultivated; N: native; DEHP: di-(2-ethylhexyl) phthalate; DBP: di-n-butyl phthalate; DPP: dipentyl phthalate; DMP: dimethyl phthalate; ND: not detected

Among different sampled soils four types of phthalates were detected DBP, DEHP, DPP, and DMP which showed different concentrations. The DPP is closely present in CS1 in Arram region. However, the DMP was detected in NS and cultivated soil CS4. The DEHP and DBP are the most abundant PAEs in NS and CS but varied widely between sites and across soil depth. This result is in agreement with those found by Ma et al. (2020). The DEHP and DBP are the principal components of wide ranges of industrial products. For example, according to Mo et al. (2008) and Kong et al. (2012), the concentrations of DBP and DEHP were influenced by fertilizers and plastic films, as well as differences in the use of irrigation mode. An increase in the annual average temperature causes the reduction in bond strength of the plasticizer and Polyvinyl chloride (PVC) chain thus leading to increased discharge of PAEs into the surrounding soil (Chen et al., 2011). DEHP is not easily biodegradable; therefore, it easily accumulates in the soil at high levels (Cartwright et al., 2000). An increase in the annual average temperature causes the reduction in bond strength of the plasticizer and PVC chain thus leading to increased discharge of PAEs particularly into the surrounding soil (Chen et al., 2011). That is probably why sampled soils showed relatively high accumulation of DEHP and DBP.

3.3. The DEHP and DBP concentrations and repartition across depth

Among sites, the DEHP concentration ranged between 2.40 and 7.12% and 3.30 and 6.38% in 0-10 cm and 10-30 cm depth, respectively. Native soils showed the highest contamination by DEHP which was located at surface layer (0-10 cm) (Figure 3(a)). In 0-10 cm the largest proportion of DEHP in cultivated soil (5.34%) was detected in CS4 which showed also the greatest DEHP percentage (6.38%) in 10-30 cm depth. Soil cultivation increases deep layer contamination by PAEs. For example, in CS1 the DEHP concentration in 10-30 cm depth was more than two times higher than in 0-10 cm depth. Conversely, in NS the surface layer 0-10 cm concentrated more DEHP than the 10-30 cm layer depth. Contrarily to

DEHP, the presence of DBP is recorded in only four samples at 0-10 cm depth and five samples in 10-30 cm (Figure 3(b)). The maximum of DBP concentration was detected in NS2 with 3.40 and 3.00%, respectively, in 0-10 cm depth and 10-30 cm depth. However, in the cultivated sites, the DBP concentration did not exceed 2%. Our results are in agreement with those found by Chai et al. (2014) who indicated that the maximum of PAEs concentration was detected in 10-20 cm layer in soils of vegetable greenhouses. Also, sampled soils from different regions of China, showed that the DEHP and DBP are concentrated in 0-20 or 0-30 cm layer, but DEHP was the dominant congener at 20 cm to 40 cm depth (Chai et al., 2014; Zhang et al., 2015).

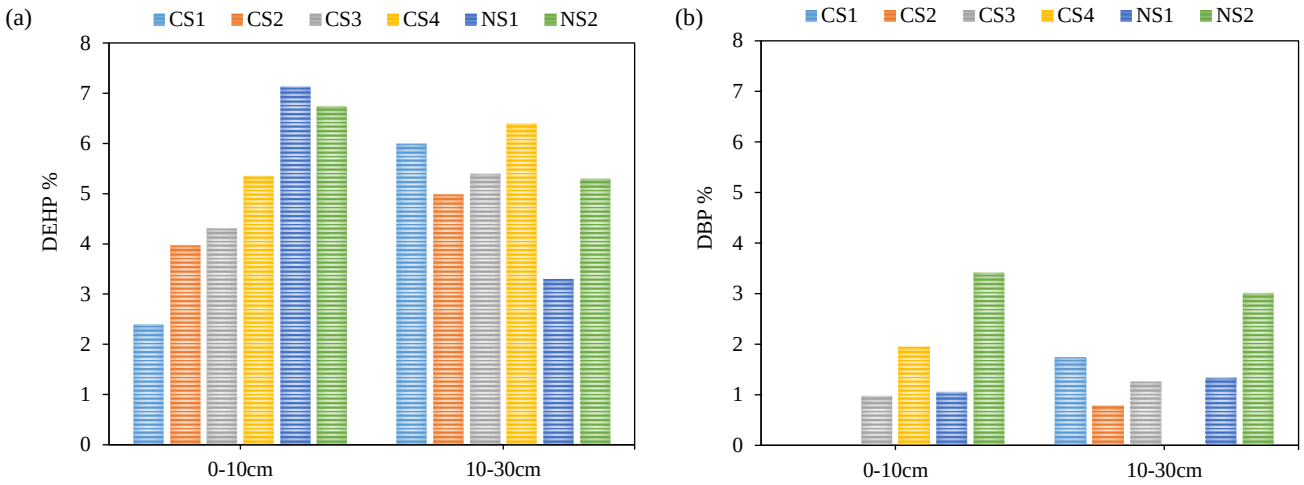

Figure 3. The (a) DEHP and (b) DBP concentrations of different sampled soil

Actually, the consumption of plastic films would lead to the continuous input of the PAEs into the soil, which leads to an increase in the concentration of DBP and DEHP in the soil (Tao et al., 2020). DEHP and DBP are the dominant components in plastic films (Wang et al., 2013, Tao et al., 2020). The amount of DEHP added in flexible PVC products could reach up to 40% (Chao and Cheng, 2007). DEHP is a principal component in most widely used-fertilizers (Mo et al., 2008), and it is typically used in plastic products in high volume compared to DBP (Zeng et al., 2009; Chai et al., 2014). In recent studies (Tao et al., 2020; Wei et al., 2020; Zhou et al., 2021) in Chinese soils the DBP and DEHP were the dominant pollutants among large numbers of PAEs.

Our results were in agreement with the finding of the Chinese study which concluded that cultivation is a principal source of soil's contamination by DBP and DEHP. However, in the current study we found that less DBP and DEHP concentrations were recorded in cultivated soils which are in disagreement with the previously mentioned study in China. For example the DBP and DEHP levels for cultivated fields were about 3.5 fold higher than those for non-cultivated fields in Chinese soils (Xu et al., 2008). We can suggest that differences between soil properties in arid Tunisia and in China make the studied CS show low concentrations of PAEs compared to surrounding soils. The higher accumulation in surface layer was the result of the rapprochement to the source of contamination. Actually, in 0-10 cm depth we remark a strong relationship between DEHP and DBP percentages (Figure 4). This supports our suggestion that these two compounds have the same source.

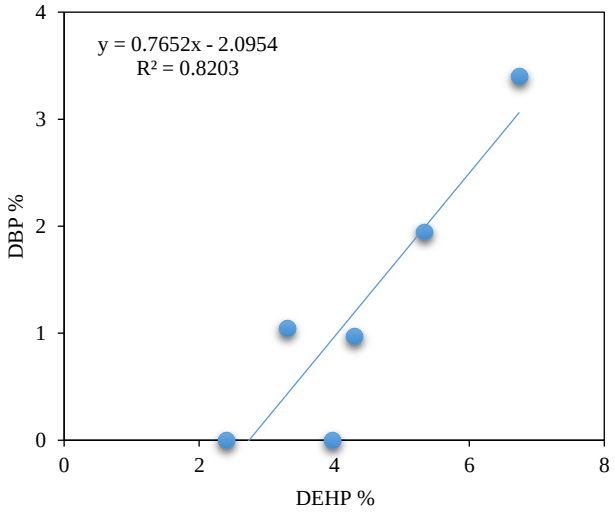

Figure 4. Relationship between the DEHP and the DBP percentages in different vegetable greenhouse cultivated soils

3.4. Effect of plastic film use period on PAEs concentration

As shown in Figure 5, the PAEs concentration appears to be related to the period of plastic film use. Interestingly, in 0-10 cm layer, the PAEs concentration increases with the age of the used plastic film. Similarly, Fu and Du (2011), remarked that the variation of PAEs concentration in soil could be related to the age of plastic greenhouse or the amounts of remaining plastic film residues. Due to the use of a large amount of agricultural film, greenhouse vegetable soil has become a key area of PAE pollution, and it has also become a pollution source of PAEs (Zhou et al., 2021).

According to Wang et al. (2013), the time over which the soil is exposed to the plastic film and the use mode can influence PAEs concentration. Larger value of PAEs concentrations in soils at 0-10 cm and 10-20 cm appeared in the region with a long history of vegetable production and particularly for extensive greenhouse cultivation (Chai et al., 2014). In their previous study, Wang et al. (2013) found that Chinese soil exhibited elevated levels of PAEs caused by large amounts of plastic film and compost fertilizers, which had been used for several years. In addition, they demonstrated that in soil covered with new plastic film the PAEs concentration is high. High PAEs levels have been previously reported in soils with residual plastic film (Kong et al., 2012). In addition, it was noticed that the PAEs soil concentration is significantly correlated to the period of plastic film coverage because the PAEs compounds in plastic films are released to the soils with the passage of time (Hens and Caballos, 2003). Soils using plastic mulch for long or using black plastic mulch were found to have a relatively higher PAEs content. The application of large amounts of plastic film over long periods of time can raise PAEs concentrations and environmental risk in soils (Wang et al., 2013). Guo and Wu (2011) and Chai et al. (2014) demonstrated that DBP and DEHP contents in soils were high with long periods of plastic film utilization or the use of greenhouse vegetable cultivation over years. Recently, Wang et al. (2022) confirmed that the duration of plastic film used and air temperature affect phthalate soil-air migration. In our study this positive relationship between soil PAEs concentrations and the period of use of plastic film strongly supports the hypothesis that plastic films are the main source of the contamination by PAEs.

However, PAEs concentration in 10-30 cm showed no link with the age of plastic film use. In the deeper layer from 10-30 cm depth the concentration of PAEs was not correlated to the period of plastic film use and fertilizers addition. The current results were in agreement with those found by Chai et al. (2014) which record a low correlation between PAEs and the age of vegetable greenhouses in deeper soil layer. This may be due to the soil properties, soil land use or the soil leaching by water, which caused the migration of PAEs through the soil (Chai et al., 2014). Soil leaching of studied soils is considered high because of their coarse texture (developed porosity).

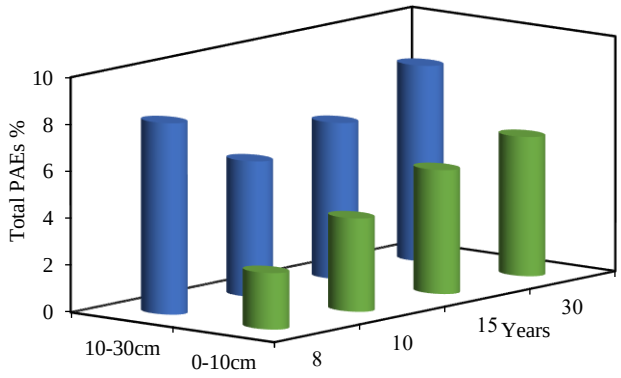

Figure 5. Effect of period of plastic film use of vegetable greenhouse on total PAEs concentrations across soil depth in cultivated soils.

3.5. Relation between soil properties and PAEs concentration

Globally, the soil properties and the soil use types affect largely the concentration, mobility and the decomposition rate of pollutants. According to Zeng et al. (2009), the soil's PAEs concentration levels and variation were, also, affected by many factors, such as, land use and soil properties.

As shown in Figures 6 and 7 we can draw positive correlations between PAES concentrations and particular soil properties in the current study. Indeed, Figure 6(a) shows positive relationship (R^2=0.16) between PAEs concentrations and EC (soil salinity) in CS. Similarly positive association (R^2=0.28) was observed between DEHP percentages and EC values (Figure 6(b)). However, we recorded negative correlation between the amount of SOC in CS and the PAEs and DEHP percentages in soil (Figure 7 and Figure 7(b)). Similar positive correlations with similar R-squared are recorded by Li et al. (2016), particularly between SOM and PAEs in contrast with our study. It means that these soil properties affect directly or indirectly the concentration of PAEs of soil in studied region. Though, these weak associations between soil

properties and PAEs in this work make it hard to draw any conclusive statements on the observed values. We can make hypothesis about the origins of this correlation. Generally, soil salinity, in arid regions, is related to the soil irrigation by saline water and the use of PVC irrigation system increases the soil's PAEs concentration by dissolved plastic compounds in the water. In addition, several studies indicated the presence of PAEs in water used for irrigation in polluted regions (Zeng et al., 2009; Wang et al., 2012). Hence we can consider that irrigation increases simultaneously EC and PAEs concentration in soil which can explain the association between them. Similarly, the negative association between SOC and PAEs or DEHP concentrations is in contrast with both results found by Zhang et al. (2015) and Li et al. (2022) which recorded high significant positive correlation between PAEs and organic matter. We can suggest that the difference in results can be related to other soil properties such as soil microbiology or CEC, the type of fertilizers and the type of agro-systems. This makes it crucial to start further studies to give more accurate data about factors controlling PAEs concentration, origins and dynamic in soil of Tunisia and MENA regions.

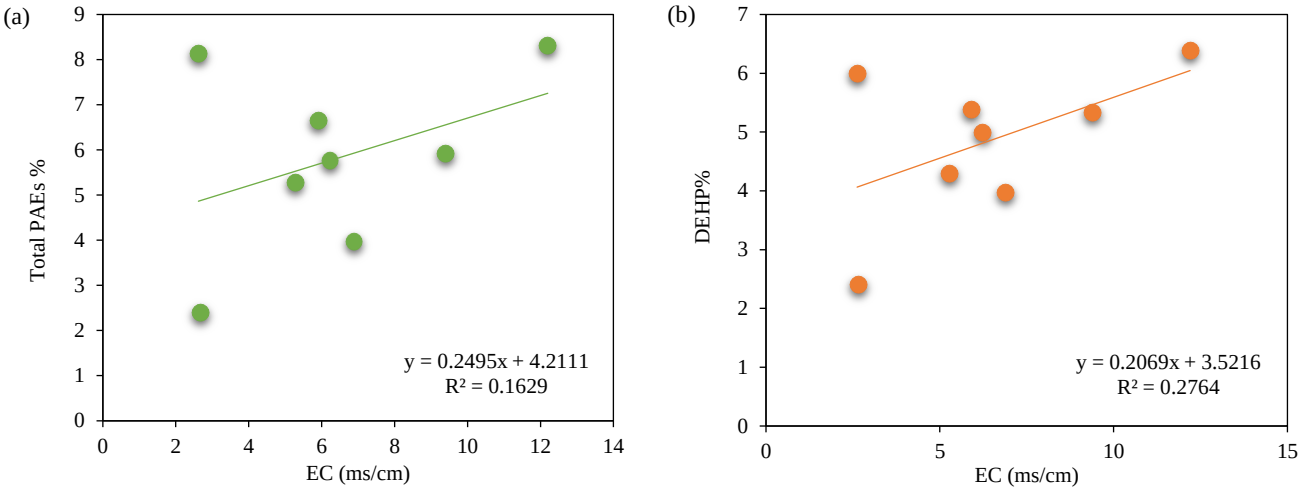

Figure 6. Relationships between soil's electrical conductivity EC (a) Total PAEs concentrations and (b) the DEHP concentrations in vegetable greenhouse cultivated soils

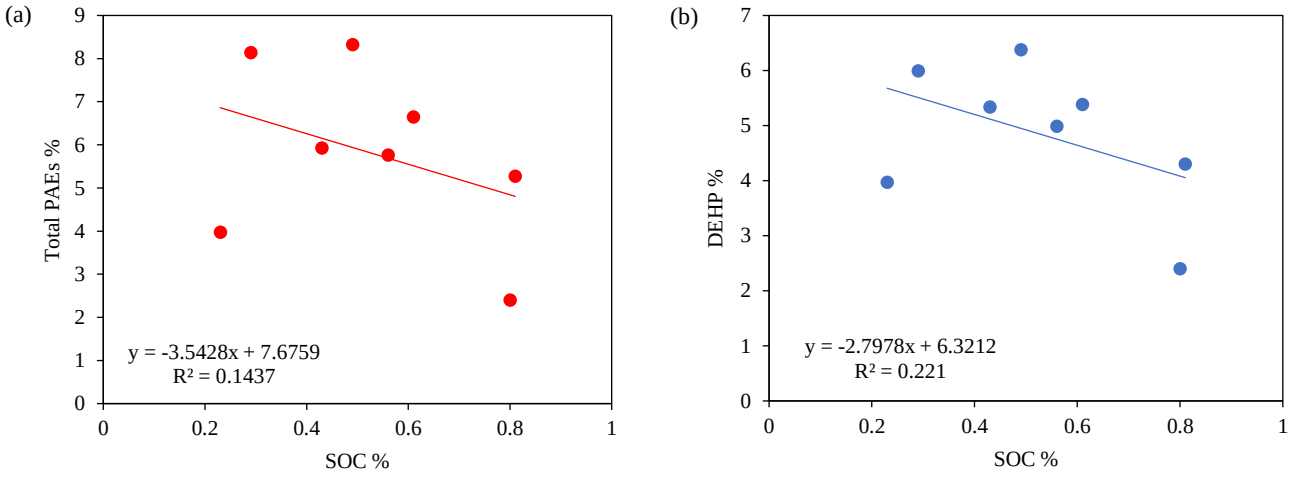

Figure 7. Relationships between SOC and (a) total PAEs concentrations and (b) the DEHP concentrations in vegetable greenhouse cultivated soils

4. CONCLUSION

The current preliminary study has provided baseline information about the concentration and distribution of phthalate acid esters (PAEs) in the soils of arid regions of Tunisia. Only four types of PAEs were detected with different concentrations. Cultivated soils under greenhouses showed low PAE concentrations than in adjacent native soils. The main PAEs detected were DBP and DEHP. Soil PAEs, DBP and DEHP concentrations seem to be related to the age

of greenhouses, the EC and to the SOC content. This primary data confirmed that PAEs are emerging organic contaminants in agricultural soils of Tunisia. Data on PAEs in various types of soils in different regions and in various types of irrigation water are needed for future research on human exposure to these emerging toxic contaminants. Effective measures should be taken to control the migration of PAEs from soil to plants. The soil pollution by PAEs and human health threats should receive more attention in developed country in MENA regions.

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REFERENCES

Boll M, Geiger R, Junghare M, Schink B. Microbial degradation of phthalates: Biochemistry and environmental implications. Environmental Microbiology Reports 2020;12(1):3-15.

Cai QY, Mo CH, Wu QT, Katsoyiannis A, Zeng QY. The status of soil contamination bysemivolatile organic chemicals (SVOCs) in China: A review. Science of the Total Environment 2008; 389(2-3):209-24.

Cartwright CD, Thompson IP, Burns RG. Degradation and impact of phthalate plasticizers on soil microbial communities. Environmental Toxicology and Chemistry 2000;19(5):1253-61.

Chai C, Cheng H, Ge W, Ma D, Shi Y. Phthalic acid esters in soils from vegetable greenhouses in Shandong Peninsula, East China. PloS One 2014;9:Article No. 95701.

Chao WL, Cheng CY. Effect of introduced phthalate-degrading bacteria on the diversity of indigenous bacterial communities during di-(2-ethylhexyl) phthalate (DEHP) degradation in a soil microcosm. Chemosphere 2007;67:482-8.

Chen YS, Luo YM, Zhang HB, Song J. Preliminary study on PAEs pollution of greenhouse soils. Acta Pedologica Sinica 2011; 48:516-23.

Corti G, Cocco S, Hannachi N, Cardelli V, Weindorf DC, Marcellini M, et al. Assessing geomorphological and pedological processes in the genesis of pre-desert soils from southern Tunisia. Catena 2020;187:Article No. 104290.

Dabin B. Application de dosage automatique à l'analyse des sols, 3éme partie. Cahier ORSTOM, Série Pédologie 1967;7:257-63. (in French).

Das MT, Kumar SS, Ghosh P, Shah G, Malyan SK, Bajar S, et al. Remediation strategies for mitigation of phthalate pollution: Challenges and future perspectives. Journal of Hazardous Materials 2021;409:Article No. 124496.

Elbasiouny H, Bowaly A, Gad A, Abu-Alkheir A, Elbehiry F. Restoration and sequestration of carbon and nitrogen in the degraded northern coastal area in Nile Delta, Egypt for climate change mitigation. Journal of Coastal Conservation 2017;21: 105-14.

El- Hassanin AS, Samak MR, Radwan SR, El- Chaghaby GA. Preparation and characterization of biochar from rice straw and its application in soil remediation. Environment and Natural Resources Journal 2020;18(3):283-9.

El Zrelli R, Baliteau JY, Yacoubi L, Castet S, Grégoire M, Fabre S, et al. Rare earth elements characterization associated to the phosphate fertilizer plants of Gabes (Tunisia, Central Mediterranean Sea): Geochemical properties and behavior, related economic losses, and potential hazards, Science of the Total Environment 2021;791:Article No. 148268.

Fu XW, Du QZ. Uptake of di-(2-ethylhexyl) phthalate of vegetables from plastic film greenhouses. Journal of Agricultural and Food Chemistry 2011;59:11585-8.

Gao M, Chang X, Xu Y, Guo Z, Song Z. Effects of Fe-Mn impregnated biochar on enzymatic activity and bacterial community in phthalate-polluted brown soil planted with wheat. Environmental Pollution 2021;284:Article No. 117179.

Guo Y, Kannan K. Comparative assessment of human exposure to phthalate ethers from house dust in China and the United States. Environmental Science and Technology 2011;45:3788-94.

Guo DM, Wu Y. Determination of phthalic acid esters of soil in south of Xinjiang cotton fields. Arid Environmental Monitoring 2011;25:76-9.

He L, Gielen G, Bolan N, Zhang X, Qin H, Huang H, et al. Contamination and remediation of phthalic acid esters in agricultural soils in China: A review. Agronomy for Sustainable Development 2015;35:519-34.

Hens AG, Caballos MPA. Social and economic interest in the control of phthalic acid esters. Trends in Analytical Chemistry 2003;22:847-57.

Jones A, Breuning-Madsen H, Brossard M, Dampha A, Deckers J, Dewitte O, et al. Soil Atlas of Africa: An Introduction to the First Ever Soil Atlas of Africa. Luxembourg: European Commission: Publications Office of the European Union; 2013.

Kelly MA, Reid AM, Quinn-Hosey KM, Fogarty AM, Roche JJ, Brougham CA. Investigation of the estrogenic risk to feral male brown trout (*Salmotrutta*) in the Shannon International River Basin District of Ireland. Ecotoxicology and Environmental Safety 2010;73:1658-65.

Kong S, Ji Y, Liu L, Chen L, Zhao X, Wang J, et al. Diversities of phthalate esters in suburban agricultural soils and wasteland soil appeared with urbanization in China. Environmental Pollution 2012;170:161-8.

Labiadh M, Bergametti G, Kardous M, Perrier S, Grand N, Attoui B, et al. Soil erosion by wind over tilled surfaces in South Tunisia. Geoderma 2013;202-203:8-17.

Li K, Ma D, Wu J, Chai C, Shi Y. Distribution of phthalate esters in agricultural soil with plastic film mulching in Shandong Peninsula, East China. Chemospher 2016;164:314-21.

Li Q, Zeng A, Jiang X, Gu X. Are microplastics correlated to phthalates in facility agriculture soil? Journal of Hazardous Materials 2021;412:Article No. 125164.

Li X, Li N, Wang C, Wang A, Kong W, Song P, et al. Occurrence of phthalate acid esters (PAEs) in protected agriculture soils and implications for human health exposure. Research Square 2022:preprint;1-11.

Liu LH, Yuan T, Zhang JY, Tang GX, Huixiong Lü, Zhao HM, et al. Diversity of endophytic bacteria in wild rice (*Oryza meridionalis*) and potential for promoting plant growth and degrading phthalates. Science of the Total Environment 2022;806(1):Article No. 150310.

Ma LL, Chu SG, Xu XB. Phthalate residues in greenhouse soil from Beijing suburbs, People' s Republic of China. Bulletin of Environmental Contamination and Toxicology 2003;71:394-9.

Ma TT, Christie P, Luo YM. Phthalate esters contamination in soil and plants on agricultural land near an electronic waste recycling site. Environmental Geochemistry and Health 2013;35:465-76.

Ma T, Zhou W, Chen L, Li Y, Luo Y, Wu P. Phthalate esters contamination in vegetable-soil system of facility greenhouses in Jingmen, Central China and the assessment of health risk. Environmental Geochemistry and Health 2020;36:505-15.

Mlih R, Gocke MI, Bol R, Berns AE, Fuhrmann I, Brahim N. Soil organic matter composition in coastal and continental date palm systems-insights from Tunisian oases. Pedosphere 2019;29:444-56.

Mo CH, Cai QY, Li YH, Zeng QY. Occurrence of priority organic pollutants in the fertilizers, China. Journal of Hazardous Materials 2008;152:1208-13.

Mtimet A. Soils in Tunisia. In: Zdruli P, Steduto P, Lacirigola C, Montanarella L, editors. Soil Resources of Southern and Eastern Mediterranean Countries, Options Méditerranéennes: Serie B. Etudes et Recherche; 2001. p. 243-62. (in French).

Nelson R. Carbonate and gypsum. In: Page AL, editor. Methods of Soil Analysis. 2nd ed. Madison, USA: American Society of Agronomy and Soil Science Society of America; 1982. p. 181-97.

Nelson DW, Sommers LE. Total carbon, organic carbon, and organic matter In: Page AL, editors. Methods of Soil Analysis. 2nd ed. Madison, USA: American Society of Agronomy and Soil Science Society of America; 1982. p. 539-77.

Omar Z, Bouajila A, Brahim N, Grira M. Soil property and soil organic pools and stocks of soil under oases in arid regions of Tunisia. Environmental Earth Science Journal 2017;76: Article No. 415.

Omar Z, Bouajila A, Bouajila J, Rahmani R, Besser H, Hamed Y. Spectroscopic and chromatographic investigation of soil organic matter composition for different agrosystems from arid saline soils from Southeastern Tunisia. Arabian Journal of Geosciences 2020;13:Article No. 524.

Pedersen GA, Jensen LK, Fankhauser A, Biedermann S, Petersen JH, Fabech B. Migration of epoxidized soybean oil (ESBO) and phthalates from twist closures into food and enforcement of the overall migration limit. Food Additives and Contaminants 2008;25:503-12.

Rahmani R, Bouajila J, Jouaidi M, Debouba M. African mustard (*Brassica tournefortii*) as source of nutrients and nutraceuticals properties. Journal of Food Science 2020;85:1856-71.

Rahmayanti R, Adji BK, Nugroho AP. Microplastic pollution in the inlet and outlet networks of Rawa Jombor Reservoir: Accumulation in aquatic fauna, interactions with heavy metals, and health risk assessment. Environment and Natural Resources Journal 2022;20(2):192-208.

Robinson GW. A new method for mechanical analysis of soil and other dispersion. Journal of Agricultural and Food Chemistry 1922;212:306-21.

Shahabinejad N, Mahmoodabadi M, Jalalian A, Chavoshi E. In situ field measurement of wind erosion and threshold velocity in relation to soil properties in arid and semiarid environments. Environmental Earth Sciences. 2019;78:Article No. 501.

Staples CA, Peterson DR, Urbanerton TF, Adams WJ. The environmental fate of phthalate esters: a literature review. Chemosphere 1997;35:667-749.

Tao H, Wang Y, Liang H, Zhang X, Liu X, Li J. Pollution characteristics of phthalate acid esters in agricultural soil of Yinchuan, northwest China, and health risk assessment. Environmental Geochemistry and Health 2020;42:4313-26.

United States Environmental Protection Agency (USEPA). Electronic Code of Federal Regulations (e-CFR), Part 423-Steam electric power generating point source category: Appendix A to part 423-126, Priority pollutants [Internet]. 2013 [cited 2021 Jun]. Available from: https://www.law.cornell.edu/cfr/text/40/appendix-A_to_part_423.

Wang J, Luo YM, Teng Y, Ma WT, Christie P, Li ZG. Soil contamination by phthalate esters in Chinese intensive vegetable production systems with different modes of use of plastic film. Environnemntal Pollution 2013;180:265-73.

Wang Q, Wu X, Jiang L, Fang C, Wang H, Chen L. Effective degradation of di-nbutyl phthalate by reusable, magnetic Fe_3O_4 nanoparticle- immobilized *Pseudomonas* sp. W1 and its application in simulation. Chemosphere 2020;250: Article No. 126339.

Wang W, Zhang Y, Wang S, Fan CQ, Xu H. Distributions of phthalic esters carried by total suspended particulates in Nanjing, China. Environmental Monitoring and Assessment 2012;184:6789-98.

Wang X, Zhang Y, Huang B, Chen Z, Zhong M, Lu Q, et al. Phthalate pollution and migration in soil-air-vegetable systems in typical plastic agricultural greenhouses in northwestern China. Science of the Total Environment 2022;809: Article No. 151101.

Wei L, Li Z, Sun J, Zhu L. Pollution characteristics and health risk assessment of phthalate esters in agricultural soil and vegetables in the Yangtze River Delta of China. Science of the Total Environment 2020;726:Article No. 137978.

Xie Z, Ebinghaus R, Temme C, Lohmann R, Caba A, Ruck W. Occurrence and air-sea exchange of phthalates in the Arctic. Environmental Science and Technology 2007;41:4555-60.

Xu G, Li FS, Wang QH. Occurrence and degradation characteristics of dibutylphthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in typical agricultural soils of China. Science of the Total Environment 2008;393:333-40.

Zeng F, Cui KY, Xie ZY, Wu LN, Luo DL, Chen LX, et al. Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. Journal of Hazardous Materials 2009; 164:1171-8.

Zhang Z, He G, Peng X, Lu L. Distribution and sources of phthalate esters in the topsoils of Beijing, China. Environmental Geochemistry and Health 2014;36:505-15.

Zhang Y, Wang P, Wang L, Sun G, Zhao J, Zhang H, et al. The influence of facility agriculture production on phthalate esters distribution in black soils of northeast China. Science of the Total Environment 2015;506-507:118-25.

Zhou B, Zhao L, Sun Y, Li X, Weng L, Li Y. Contamination and human health risks of phthalate esters in vegetable and crop soils from the Huang-Huai-Hai region of China. Science of the Total Environment 2021;778:Article No. 146281,

Zhu Z, Rao R, Zhao Z, Chen J, Jiang W, Bi F, et al. Research progress on removal of phthalates pollutants from environment. Journal of Molecular Liquids 2022;355:Article No. 118930.

Znaidi A, Brahim N, Ibrahim H, Bol R, Chaouachi M. Comparison of organic carbon stock of Regosols under two different climates and land use in Tunisia. Arabian Journal of Geosciences 2020;13:Article No. 1011.