Journal of Environmental Management 351 (2024) 119861

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

The impact of olive mill wastewater on soil properties, nutrient and heavy metal availability – A study case from Syrian vertisols

Jehan Khalil[a], Abd Al Karim Jaafar[a,**], Hassan Habib[a], Sirine Bouguerra[b,c], Verónica Nogueira[c,d], Andrés Rodríguez-Seijo[e,f,*]

[a] Department of Soil Science, Faculty of Agricultural, Damascus University, Damascus, Syrian Arab Republic
[b] GreenUPorto, Sustainable Agrifood Production Research Center & Inov4Agro | Rua da Agrária 747, 4485-64, Vairão, Portugal
[c] Department of Biology, Faculty of Sciences, University of Porto, Rua do Campo Alegre S/N. 4169-007 Porto, Portugal
[d] CIIMAR - Interdisciplinary Centre of Marine and Environmental Research (CIIMAR), University of Porto, Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4450-208, Matosinhos, Portugal
[e] Department of Plant Biology and Soil Science, Área de Edafoloxía e Química Agrícola, Facultade de Ciencias, Universidade de Vigo, 32004, Ourense, Spain
[f] Agroecology and Food Institute (IAA), University of Vigo – Campus Auga, 32004, Ourense, Spain

ARTICLE INFO

Handling editor: Lixiao Zhang

Keywords:
Abiotic stress
Arid environment
Circular economy
Irrigation
Nutrient deficiency
Soil fertility

ABSTRACT

Olive oil mill wastewater (OMW) is an environmental concern in olive oil producers' regions due to its use in agricultural soils as an organic amendment. However, OMW can also be used as organic fertilizer due to their high organic matter and nutrient levels, but its use, when it occurs without environmental management, can cause serious environmental implications for soils and waters. This work evaluated the impact of different OMW levels on a set of physicochemical parameters from an agricultural vertisol where wheat grew (*Triticum aestivum* L var. Douma 1). A set of physicochemical parameters were conducted before adding different levels of OMW (0, 5, 10 and 15 L m^{-2}) at two soil depths (0–30 and 30–60 cm) and for the two growing seasons to determine: i) the effect of OMW treatments on the studied physicochemical soil properties (bulk density, soil porosity, soil pH, electrical conductivity and organic matter), ii) available primary (N, P, K) and secondary macronutrients (Ca, Mg and Na), ii) micronutrients (Cu Fe, Mn and Zn), and iv) available heavy metals (Cd and Pb). The results indicated that soil physicochemical parameters were slightly improved, mainly due to improvement in organic matter, macro- and micronutrients, usually proportionally to the olive mill wastewater dose. Cadmium and Pb were within the permissible limits. The increased OMW had different behaviour on the soil nutritional balances of different elements, leading to nutrient imbalances, although in some cases, they were improved. However, the plant growth was not affected, and it was improved under 10 L m^{-2} and 15 L m^{-2} doses. The results offer valuable data about the use of OMW as organic fertilizer for crops and their potential impact on soil properties.

1. Introduction

The olive crop in Syria is considered one of the essential strategic crops, as Syria today occupies third place in production in the Arab world after Tunisia and Morocco (D'Auria et al., 2020). In some regions, especially in the Mediterranean regions, with severe water and organic matter (OM) deficiencies, the waste resulting from the pressing of olive fruits, as its liquid waste (Olive Mill Wastewater, OMW), is disposed of directly without any treatment to the agricultural soils. This is a simple and inexpensive disposal method that can also be reused as organic amendments due to the high percentage of OM contents, essential mineral elements necessary for plants (N, P, K) and a reasonable quantity of necessary and essential microelements (e.g., Cu, Mn, Zn) (Barbera et al., 2013). However, this direct disposal can lead to soil and water pollution and deterioration of its physical, chemical, and biological properties due to their high salinity (especially due to high available K

---

* Corresponding author. Department of Plant Biology and Soil Science, Área de Edafoloxía e Química Agrícola, Facultade de Ciencias, Universidade de Vigo, 32004, Ourense, Spain.

** Corresponding author.

E-mail addresses: jehan5.khalil@damascusuniversity.edu.sy (J. Khalil), abdalkarim.jaafar@damascusuniversity.edu.sy (A.A.K. Jaafar), hassan3.habib@damascusuniversity.edu.sy (H. Habib), sirine.bouguerra@fc.up.pt (S. Bouguerra), veronica.nogueira@fc.up.pt (V. Nogueira), andresrodriguezseijo@uvigo.gal (A. Rodríguez-Seijo).

https://doi.org/10.1016/j.jenvman.2023.119861
Received 5 August 2023; Received in revised form 7 December 2023; Accepted 12 December 2023
Available online 23 December 2023

contents) and a high percentage of solid and organic pollutants, such as phenolic substances (Justino et al., 2011; Mekki et al., 2013; Aly et al., 2014; Kavvadias et al., 2015).

When these OMW are directly added to the soil, in terms of the impact on soil properties, different studies (e.g., Al-Budi, 2011; Mohawesh et al., 2014; Haifa et al., 2016) showed that the soil treated with OMW increased its ability to retain water; since bulk density was reduced, the soil porosity increased, and stable aggregates are formed (Chatzistathis and Koutsos, 2017). Besides, adding peat water to the soil at rates up to 60 m^3 ha^{-1} can increase the soil OM and N contents (Mohawesh et al., 2019). Cegarra et al. (1996), Magdich et al. (2013) or Chatzistathis and Koutsos (2017) also indicated an increase in available macronutrients (i.e., P and K), micronutrients, and soil salinity, while soil pH can decrease due to strong to slight acid conditions of OMW (pH between 3 and 5.9). However, adding OMW could increase the soil bioavailability of non-essential elements such as Cd or Pb, and their potential uptake by plants (Arienzo and Capasso, 2000; Justino et al., 2011), as reported for wheat-inhibited germination (Sassi et al., 2006) or by Danellakis et al. (2011) for OMW elutriates and their impact on mussels. Heavy metal contamination can take place during the handling and processing of olive fruits with variable contents according to the olive oil extraction processes (traditional, semi-modern and continuous) (Sassi et al., 2006; Zbakh and Abbassi, 2012), although metal accumulation in soils treated with OMW seems reduced under permissible levels (Feria, 2000; Rinaldi et al., 2003; Moraetis et al., 2011).

Besides, the impact of OMW has been reported to have adverse effects on plant growth, such as a delay in germination and plant growth due to high contents of phenolic compounds or heavy metals, especially under non-diluted solutions (i.e., Sassi et al., 2006; Justino et al., 2011). A previous work (Khalil et al., 2021) showed that the application of OMW at 0, 5, 10 and 15 L m^2 (eq. 0, 50, 100 and 150 m^3 ha^{-1}) can improve wheat growth and increase the number of bacterial and fungi cells by increasing OMW concentrations. In this sense, Dakhli et al. (2021) recently demonstrated that the rate of 15 m^3 ha^{-1} applied in sandy soil results in a great improvement of the faba bean (*Vicia faba* L.) growth and, the soil fertility without compromising soil pH, phosphorous content, and salinity, for three consecutive years. This question was also previously observed by Magdich et al. (2013), who noticed a negative effect on soil salinity when using 200 m^3 ha $year^{-1}$ of OMW (no significative effects below this application rate). In general, potential beneficial effects (i.e., increased OM or macronutrients in soils) are highly dependent on OMW concentration and frequency of application.

In this sense, this work aims to know the impact of different levels of OMW on vertisols, which constitute a good percentage of the area of Syria, and the use of these soils mainly in rainfed crops. To achieve this, the changes resulting from the addition of different doses of OMW in some physicochemical properties of Vertisols, including the bioavailability of macro- (N, P, K, Ca, Mg and Na), micro-nutrients (Cu Fe, Mn and Zn) and heavy metals (Cd and Pb), were determined.

2. Material and methods

2.1. Olive mill wastewater characterization

The OMW was collected from a local centrifugation-based system press in Isim village in Qatana city (southern Syria; 25 km from Damascus). The collected OMW samples were placed in 20-L plastic containers and stored at 4 °C to avoid chemical and biological transformations during the study. Once at the laboratory, the OMW was analyzed before they were added to the soil. The pH and EC were analyzed by direct measurement (Conyers and Davey, 1988; Jones, 2001), while ash contents were through incineration of samples at 550 °C. Regarding the macronutrients, total Nitrogen was analyzed with concentrated sulfuric acid and then using the Kjeldahl distillation (Bremner, 1996); the P was analyzed using ammonium molybdate solution and estimating the absorbance at a wavelength of 470 nm using a spectrophotometer, while the total K was analyzed through flame photometer (Jackson, 1958). Besides, the available heavy metals and micronutrient contents (Cd, Cu, Fe, Mn, Pb and Zn) were analyzed by Atomic Absorption Spectrometer (AAS) (Varian SpectrAA-880/GTA100 Atomic Absorption Spectrometer) (Jones, 2001).

The phenolic substances were extracted with a solution of ethyl acetate (1:2, v/v, OMW/ethyl acetate), and phenolic contents were determined using Folin−Ciocalteu reagent, while the determination of absorbance was carried out by spectrophotometer at a wavelength of 760 nm (Lee et al., 2003; Abu-Lafi et al., 2017). Regarding the oil content, the oil was extracted from the OMW using a Gerber tube with a capacity of 11 ml by adding 9 ml of OMW and 1 ml of amyl alcohol and then completing the volume using concentrated sulfuric acid until reaching the black colour. Then, the tube was placed in the centrifuge at a speed of 500 rpm, and the oil percentage was read from the numbers listed from bottom to top. This method is based on a modification from the Gerber method for milk and the Gerber-Van Gulik method (ISO, 1975), as indicated by (El-Chami et al., 2023; Mohana et al., 2023). Finally, the biological oxygen demand (BOD) and the chemical oxygen demand (COD) were measured using a closed system for oxidation so that it provides greater contact with the oxidant following the methodology indicated by Muthuvel and Udayasoorian (1999).

2.2. Soil characterization

The study was conducted on Vertisol samples taken from the Al-Thala village in the Al-Suwayda governorate from a 0–30 and 30–60 cm depth. Vertisol constitutes about 9% of Syria's area. Cracked clay soils can be present in most of the moisture systems of the soil, and what distinguishes it in Syria is its presence in rain-fed areas. Usually, these soils are calcareous with a high percentage of smectite clay minerals that are flexible during hydration, which makes them prone to cracking when dry. Besides, Ca^{2+} and Mg^{2+} mainly dominate the total exchange complex, have low OM and N contents, and usually have deficiencies by N and P (Virmani et al., 1982; Hailu et al., 2015; Khalil et al., 2021).

Once in the laboratory and before the pot experiment, the soil was air-dried, homogenized, and sieved using a 2 mm diameter sieve, and different physicochemical properties were analyzed. The particle-size distribution was analyzed using the hydrometer method with the addition of a soil dispersant (sodium hexametaphosphate) (Gupta, 2000), while the bulk and particle densities were analyzed using the cylinder and the pycnometer method, respectively (ASTM, 1958). The soil pH_{H2o} and electrical conductivity (EC) were analyzed through a soil suspension in water (1:2.5 and 1:5 soil/water extract, respectively) (Conyers and Davey, 1988; ISO, 1994). Soil organic matter (OM) content was determined by oxidation method with potassium dichromate (Walkley and Black, 1934). Regarding the macronutrients, the total Kjeldahl-N (organic plus ammonium-N) was analyzed by Kjeldahl digestion with sulfuric acid and distillation with boric acid (Bremner, 1996). The available soil available P was extracted by the Olsen method ($NaHCO_3$ 0.5 M, pH 8,5; 1:20 soil:extractant ratio) (Olsen and Sommers, 1982), while the available K was analyzed using a solution of ammonium acetate (1 M), with an extraction ratio of (1:10 soil:extractant ratio) (Jackson, 1958). Finally, the bioavailable contents of Cd and Pb were extracted by DTPA and their measurement by AAS (Jones, 2001).

2.3. Pot experiments: impact of OMW on soil properties

The experiment was conducted during two consecutive agricultural seasons where a hard wheat variety such as Douma 1 was used as crop culture to assess the impact of OMW. The first planting was carried out from December 2019 to June 2020 when it was harvested, while the second planting was carried out in December 2020, and the harvest was conducted in June 2021. The weather from the study zone has a semi-arid, cool climate with warm to hot and dry summers and moderately rainy winters (Kattan and Nasser, 2023). The first season was characterized by more rainfall and less average temperature than the second season. The soil, from the topsoil (0–30 cm depth) and subsoil (30–60 cm), were then distributed in plastic pots with a diameter of 18 cm (7 L), where 4 kg of soil dry weight was placed in each pot. Each layer was placed separately in a pot. Peat water was added to these pots at four different treatments: control soil with no OMW addition (0 L m^{-2}), 5 (eq. 120 cm^3 pot^{-1}), 10 (eq. 240 cm^3 pot^{-1}) and 15 L m^{-2} (eq. 360 cm^3 pot^{-1}). At the end of each season, soil from each depth was analyzed to see the extent of the effect. This addition of OMW was made only one time, about two months before planting wheat for a previous assay (Khalil et al., 2021), according to the recommendations of Garcia-Ortiz et al. (1999), who mentioned that a period should be left between adding OMW and planting wheat seeds, estimated at 45 days, and the OMW was mixed well with the soil in pots and watered until 80% of their field water capacity. Ten wheat grains were planted in each pot. During the experimental period (around six months), all the pots were spiked with distilled water to encourage the biological activity contributing to the dissolution of phenolic compounds and mitigate their negative impact. The experiment was designed according to a completely randomized design. Data for wheat growth was studied before, and their results can be found at Khalil et al. (2021).

2.4. *Statistical analysis*

Results from all parameters were expressed as the mean ± standard deviation (SD). All analyses were carried out in triplicate. After verifying the homogeneity of the variances (Levene's test), a bi-factorial analysis of variance (two-way ANOVA) was performed, defining as fixed factors the season, depth, and treatment and assuming a significance value of 0.05. In cases of significant differences for any of the factors, a one-way ANOVA was performed to test for significant differences between treated soils; when the interaction between factors was significant, the one-way ANOVA was performed with correction for the simple main effects. A Spearman's correlation analysis was carried out between OMW dose, season, and physicochemical properties for each soil depth (Supplementary material, Tables S1 and S2). All statistical procedures were performed in Prism 8 (GraphPad Software Inc, USA) and IBM SPSS Statistics v23 (IBM®, USA).

3. Results and discussion

3.1. *Physicochemical characterization of the OMW and soil samples previous OMW amendment*

The physicochemical characterization of the olive mill wastewater (OMW) and soil samples before the OMW amendment are shown in Tables 1 and 2. The OMW showed the typical values reported by other authors for untreated OMW (Sierra et al., 2001; Justino et al., 2011; Dermeche et al., 2013; El-Abbassi et al., 2013; Pierantozzi et al., 2013; Solomakou and Goula, 2021; Domingues et al., 2022), with acid pH values and moderate to high EC levels, that reflects a high content of salts in these effluents as shown by Ca^{2+} and K^{+} values (Table 1). Although macro- and micronutrients seem within the indicated by typical values, they were high when compared with recommended levels by international guidelines for safety release to water bodies (EU, 2016). Cadmium and Pb were over the permissible levels for drinking water (EPA US, 2009; Mahmoud et al., 2021) and higher than reported by other authors for OMW (Rajib et al., 2016; Tajini et al., 2019). In this sense, the pollution load indicated by COD, BOD or total phenols are moderate to high, which reflects their high polluting ability to waters and soils due to the predominance of potentially toxic substances and, therefore, with potential toxicity impacts for aquatic and terrestrial biota (Justino et al., 2011; Benamar et al., 2020). In this sense, the studied OMW had a BOD/COD >0.33, which indicates that effluent could be readily biodegradable (Rajib et al., 2016).

Table 1
Physicochemical characterization of olive mill wastewater.

	Units	Collected OMW	Typical OMW values[a]	Environmental Guidelines[b]
$pH_{H2o\ (1:2.5)}$		4.63 ± 0.08	2.2–5.9	6.5–7
Electrical conductivity	dS m^{-1}	8.82 ± 0.07	5.5–10	–
Ash content	%	0.80 ± 0.02	1	–
Water content	%	92.40 ± 0.25	83–94	–
Organic matter	g l^{-1}	68.00 ± 2.00	57.2–62.1	–
Nitrogen content	mg L^{-1}	812.63 ± 5.25	500–15000	5–25
Phosphorous content	mg L^{-1}	284.36 ± 3.24	300–1100	0.5–3
Ca	mg L^{-1}	154.65 ± 3.26	120–750	–
Mg	mg L^{-1}	78.41 ± 2.00	100–400	–
Na	mg L^{-1}	54.6 ± 0.69	40–900	–
K	mg L^{-1}	2231 ± 26.57	2700–7200	–
Fe	mg L^{-1}	18.3 ± 1.93	–	–
Cu	mg L^{-1}	2.92 ± 0.69	0.0021 (%)	0.005–1.3
Mn	mg L^{-1}	3.46 ± 0.50	0.0015	–
Zn	mg L^{-1}	2.83 ± 0.06	0.0057	0.002–0.3
Cd	mg L^{-1}	0.12 ± 0.01	–	0.005
Pb	mg L^{-1}	0.56 ± 0.05	–	0.015
Total phenol	g L^{-1}	8.12 ± 0.63	0.01–15	1–3
Oil	g L^{-1}	3.16 ± 0.29		–
COD	g L^{-1}	142.26 ± 3.59	3.5–132	0.03–0.1
BOD	g L^{-1}	58.37 ± 2.83	32–320	≤20
BOD/COD		0.41 ± 0.06	0.2–0.88	

Average values (n = 3) ± standard deviation.

[a] Sierra et al., (2001); Davies et al., (2004); Justino et al., 2011; Dermeche et al., (2013); Benamar et al., (2020); Solomakou and Goula (2021).

[b] EPA US, 2009; EU 2016.

Regarding the studied soil for the pot experiment, it has typical values from a vertisoil, which are characterized by neutral to alkaline pH_{H2o} due to high carbonate content and very high clay content. Besides, it also has very low OM, macro- and micronutrients contents (Table 2), a typical issue at vertisols where N, P or K can be limiting nutrients for plants due to their low bioavailability (Virmani et al., 1982; Mamo et al., 2002; Hailu et al., 2015). These neutral to slightly alkaline values, carbonate contents and high clay contents are reflected in the available heavy metal contents, which are low, although according to soil micronutrients for arid soils (FAO, 2007), Fe and Zn can be easily bioavailable.

3.2. *Effect of added OMW rates on soil properties*

The effect of added OMW rates on soil physical and chemical properties can be observed in Fig. 1. The results of the statistical analysis of the bulk density values in both seasons indicated a decrease in the bulk density value in all studied treatments compared to the control treatment.

Although a significant correlation was found between added OWM and bulk density for 0–30 ($r = -0.77$, $p < 0.01$, Table S1) and 30–60 cm ($r = -0.81$, $p < 0.01$, Table S2), significative differences were only found with 15 L m^{-2} treatment. No significative differences between seasons were found ($p > 0.05$) (Fig. 1a). The soil porosity increased as the OMW dose (Fig. 1b) for 0–30 ($r = 0.54$, $p < 0.01$, Table S1) and

Table 2
Physicochemical characterization of soil samples before OMW amendment.

Parameter	Units	0–30 cm depth	30–60 cm depth
Bulk density	g cm^{-3}	1.13 ± 0.02	1.18 ± 0.03
Total porosity	%	55.85 ± 1.03	53.90 ± 2.44
Sand	%	19.72 ± 1.01	17.36 ± 0.98
Silt	%	22.34 ± 1.31	21.35 ± 1.08
Clay	%	57.94 ± 0.98	61.29 ± 1.35
Soil texture	USDA classification	Clay	Clay
pH	anumerical	7.58 ± 0.23	7.67 ± 0.12
Electrical conductivity$_{(1:5)}$	dS m^{-1}	0.12 ± 0.01	0.15 ± 0.02
Soil Organic matter	%	0.97 ± 0.04	0.63 ± 0.04
$CaCO_3$	%	9.80 ± 0.89	11.20 ± 1.12
Nitrogen content	%	0.04 ± 0.00	0.04 ± 0.00
Available Phosphorous	mg kg^{-1}	1.82 ± 0.06	1.23 ± 0.15
Available K	mg kg^{-1}	370.5 ± 46.8	304.20 ± 31.2
Ca^{2+}	cmol$_{(+)}$ kg^{-1}	30.46 ± 2.55	32.86 ± 0.29
Mg^{2+}	cmol$_{(+)}$ kg^{-1}	9.83 ± 0.50	11.23 ± 0.41
Na^{+}	cmol$_{(+)}$ kg^{-1}	0.75 ± 0.01	0.93 ± 0.03
Cation exchange capacity	cmol$_{(+)}$ kg^{-1}	44.30 ± 1.09	46.23 ± 2.95
Fe	mg kg^{-1}	8.23 ± 0.29	7.31 ± 0.17
Cu	mg kg^{-1}	1.83 ± 0.17	1.67 ± 0.017
Mn	mg kg^{-1}	3.19 ± 0.08	1.64 ± 0.06
Zn	mg kg^{-1}	6.23 ± 0.21	4.15 ± 0.66
Cd	mg kg^{-1}	0.12 ± 0.00	0.08 ± 0.01
Pb	mg kg^{-1}	0.162 ± 0.00	0.134 ± 0.00

Average values (n = 3) ± standard deviation.

30–60 cm (r = 0.79, $p < 0.01$, Table S2), although no significant differences were found between treatments within and comparing between seasons ($p > 0.05$) (Fig. 1b).

A similar pattern has been found for EC, in which values have been increased proportionally to the OMW dose (r = 0.77 and 0.69, $p < 0.01$, for 0–30 (Table S1) and 30–60 (Table S2). However, it was not statistically different between seasons or treatments ($p > 0.05$) (Fig. 1d). A reduction in soil pH to the OMW dose was also observed. However, no correlations were observed between pH and doses for both depths (Tables S1 and S2), as well no significant differences were observed between treatments ($p > 0.05$). But a significant difference between seasons was found only for 15 L m^{-2} (p = 0.0203) (Fig. 1c).

In general, soil pH can be acidified after OMW application, although this reduction can be recovered after soil cultivation (Barbera et al. 2013; Zahra El Hassani et al. 2023). Besides, our soils have a chalky nature that can neutralize the OMW acidity due to the carbonate's contents (Table 2), which makes the OMW effect on pH insignificant, as reported by Aguilar (2009), Vella et al. (2016) or Pierantozzi et al. (2013) for similar soils to ours. Although EC was increased, this was not statistically significant similar to those indicated by Vella et al. (2016), and the potential increment could be related to solid parts of the olive (Pierantozzi et al. 2013) or due to the olive-mill extraction method (Barbera et al. 2013). Besides, although some authors (Mahmoud et al. 2010; Barbera et al. 2013) indicated that OMW application could improve the physical properties of soils, such as the bulk density and porosity, the increment was not statistically significant since improvements in these parameters are usually dependent on the environmental conditions of moisture and temperature for soil biological activity (Barbera et al. 2013).

Organic matter contents in soil were significantly increased under all treatments, especially under 10 and 15 L m^{-2} doses ($p < 0.05$) (Fig. 1e). Significant differences were also observed between seasons ($p < 0.05$) (Fig. 1e), although OM contents were reduced over time. Organic matter increments were significantly correlated with dose application (r = 0.89 and 0.82 $p < 0.01$), for 0–30 and 30–60 cm, respectively (Tables S1 and S2), while a significative correlation between OM and season was only observed for 0–30 cm (r = -0.47 $p < 0.05$, Table S1). The OMW has a high content of different forms of organic matter and nutrients. In general, the results agree with the reported literature with a significative increase by OM under increased doses since OMW is highly loaded with different forms of OM (Barbera et al. 2013; Mohawesh et al. 2019; Zahra El Hassani et al. 2023). Regarding the reduction in OM values compared to the previous season and between depths, it was also observed by different authors (Zema et al., 2019; Mohawesh et al. 2019; Zahra El Hassani et al. 2023) since although OMW has high OM contents, OM can be unstable. Further studies should analyze labile organic carbon (LC), particulate organic carbon (POC) or mineral mineral-associated carbon (MAOC) to understand the behaviour of soil Carbon under OMW application (Massaccesi et al. 2018).

3.3. *Effect of added OMW rates on soil macronutrients: nitrogen, phosphorous and potassium*

Significant differences were observed for all treatments and between seasons for N and P contents, especially for 10 and 15 L m^{-2} treatments (Fig. 2a–c). In our case, N, P and K increased significantly and proportionally to the OMW dose applied, the same pattern indicated for Argentinian soils by Pierantozzi et al. (2013). Significant correlations were found between N, P and K regarding the OMW dose and for both depths (Tables S1 and S2). The OMW has a high content of different forms of organic matter and nutrients. Consequently, OMW can significantly increase the soil organic matter (Fig. 1e), macro and micronutrients (Barbera et al., 2013; Pierantozzi et al., 2013; Mohawesh et al., 2019; Zahra El Hassani et al., 2023).

As observed by OM, N and P tended to decrease with time. In the case of N, this situation was observed at 0–30 cm depth, while P was reduced at 30–60 cm (Fig. 2a and b, respectively). A similar tendency was also observed for potassium (Fig. 2c), with a significant correlation between K levels and season for 0–30 cm (r = −0.68, p < 0.01) and 30–60 cm (r = −0.41 $p < 0.05$). However no significant differences were found ($p > 0.05$). Zahra El Hassani et al. (2023) reported that N tends to accumulate at deeper soil layers, while P can be stored in upper and deeper layers, and this situation seems to be verified according to our results. Besides, the potential reduction of macronutrients over time was also observed by Zema et al. (2019) or Pierantozzi et al. (2013), although Zema et al. (2019) also indicated that no clear tendency regarding the time after OMW application (from no effects to reduction).

In any case, the OMW application could be a sustainable alternative to chemical fertilizers and, in some cases, especially indicated to arid areas due to the ability of P to help water stress tolerance (López-Piñeiro et al., 2011; Zahra El Hassani et al., 2023), although OMW pretreatment could be required to reduce phenolic substances or heavy metals. Besides, nitrites and nitrates analysis (not measured in this study) should be carried out to avoid potential issues of leaching into water bodies.

3.4. *Effect of added OMW rates on exchangeable cations and cation exchange capacity*

The exchangeable cations values are incrementally proportional to the OMW dose, although with different patterns (Fig. 3a–d).

An increment proportionally to OMW dose was observed for exchangeable Ca^{2+} and Mg^{2+} (Fig. 3a and b), although no significative differences were observed between treatments for Ca^{2+} and significant differences were only observed for Mg^{2+} at the second season and 30–60 cm depth. No significant differences were found between treatments for exchangeable Na^{+} (Fig. 3c), but their content was significantly increased over time, as shown for the growing seasons. Finally, significant differences were found between all treatments and depths for CEC (Fig. 3d) for the first season ($p < 0.05$), while for the second season, although an increment was observed, it was not significant ($p > 0.05$). Significant correlations between Mg^{2+} and CEC were found with OMW added dose for 0–30 (r = 0.79 and 0.77, $p < 0.01$, respectively Table S1) and 30–60 cm (r = 0.83 and 0.84, $p < 0.01$, respectively, Table S2).

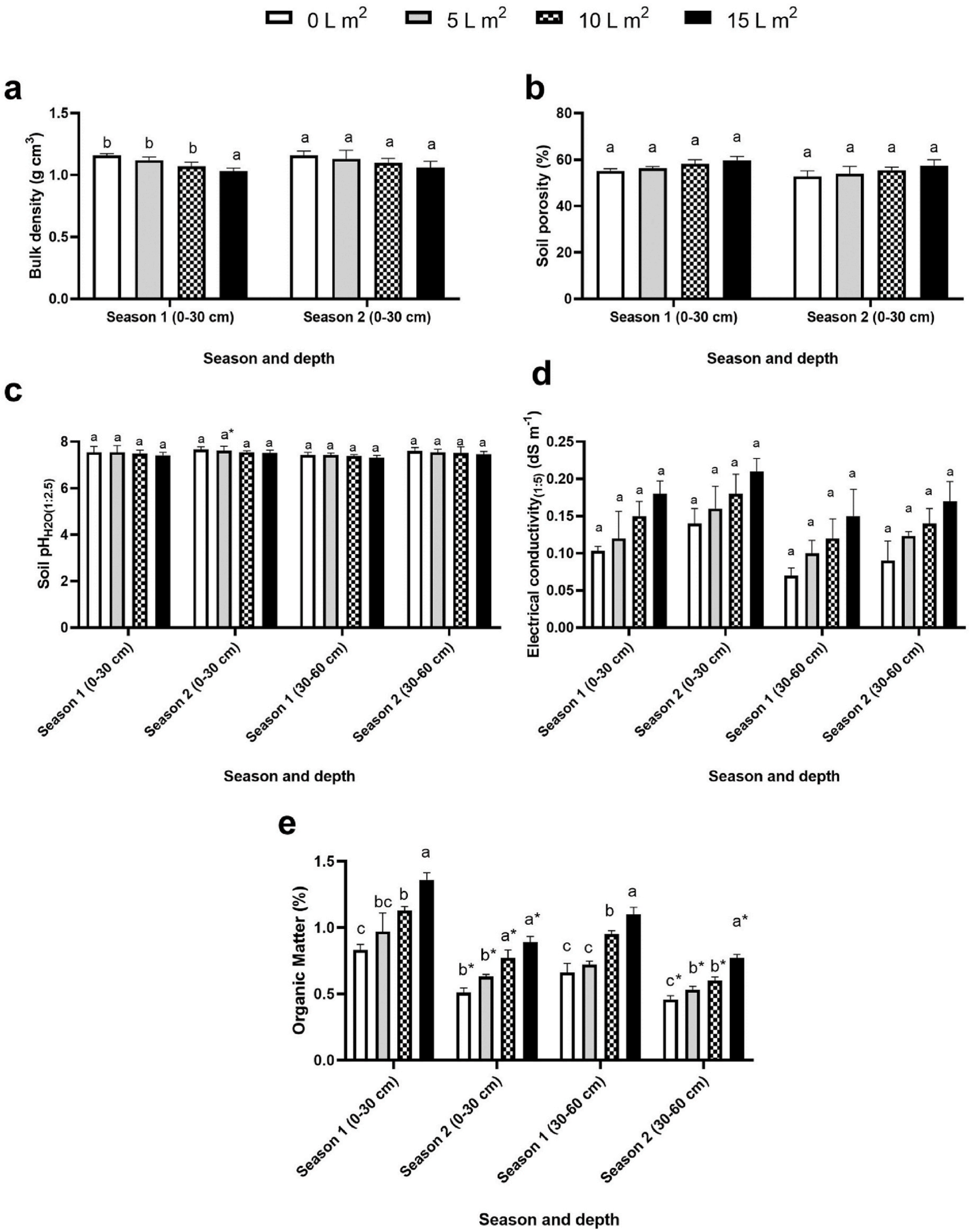

Fig. 1. Bulk density (a), soil porosity (b), soil pH$_{H2O\ (1:2.5)}$ (c), electrical conductivity$_{(1:5)}$ (d) and organic matter (e) after OMW treatments and between seasons. Data are shown as means ± standard deviation of three replicates. Bars marked by different letters indicate significant differences for each season and depth ($p < 0.05$). Bars marked with * indicate significant differences between depths for the same season ($p < 0.05$).

These results agree with several other studies since OMW spread can increase the CEC values, especially on the layer 0–30 cm (Barbera et al., 2013; Rusan and Malkawi et al., 2016; Chaâri et al., 2022; Zahra El Hassani et al., 2023). Zahra El Hassani et al. (2023) reported that a successive spreading of OMW to soils can modify the soil's cation exchange capacity by increasing the exchangeable Na^+, as observed for our soils, being these results similar to those reported by Chaari et al. (2015; 2016). Repetitive OMW could favour soil salinization problems due to the increase of Ca^{2+} and Na^+(Fig. 3a and c), although soil EC values were appropriated (<0.25 dS m^{-1}). This question should be assessed to avoid further soil salinization issues (Chaari et al., 2015; Chatzistathis and Koutsos, 2017). Besides, El Zahra El Hassani et al. (2023) also reported a potential reduction of Ca^{2+} and Mg^{2+}, but in our case, this situation was not observed.

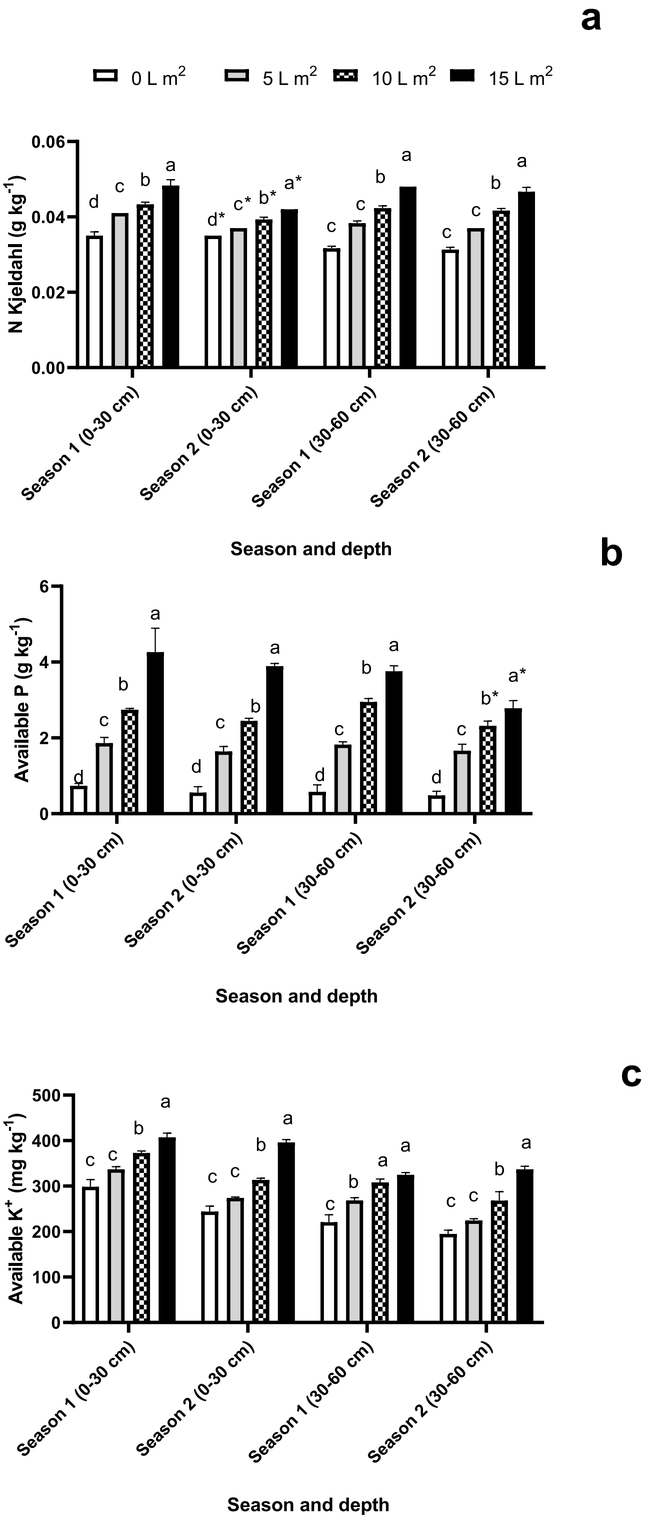

Fig. 2. Nitrogen (a), available phosphorous (b) and potassium (c) contents after OMW treatments and between seasons. Data are shown as means ± standard deviation of three replicates. Bars marked by different letters indicate significant differences for each season and depth ($p < 0.05$). Bars marked with * indicate significant differences between depths for the same season ($p < 0.05$).

3.5. Effects of added OMW on the available soil micronutrients: Cu, Fe, Mn and Zn

Olive mill wastewater application has been indicated as a low-cost source of soil macro-, micronutrients and water for plants (Chatzistathis and Koutsos, 2017). However, their continuous application can favour the release and metal accumulation in soils and, therefore, a potential environmental risk due to high accumulation or due to potential imbalances with other nutrient elements. Different authors (Lindsay and Norvell, 1978; Agrawal, 1992; Voss, 1998; Chung and Lee, 2008; Kabata-Pendias, 2010) suggested that critical levels for wheat growth of the available micronutrients should be ranged from 0.4 to 0.78 mg kg^{-1} for Cu, 2.5–5 mg kg^{-1} for Fe, 1–5 mg kg^{-1} for Mn and 0.6–0.8 mg kg^{-1} for Zn. When comparing the obtained values with these critical levels, the bioavailable levels of Cu, Fe, and Zn are in excess, while Mn seems to be within the optimum levels for wheat growth. In any case, Cu and Zn levels were lower than the maximum limits for crop toxicity of 17–25 and 15–20 mg kg^{-1}, respectively (Fan et al., 2012; Vázquez-Blanco et al., 2023).

A significant correlation has been found between Cu and OM contents for 0–30 cm (r = 0.45, $p < 0.05$, Table S1), while Cu was significantly correlated with seasons for both depths (r = −0.67 and 0.58 for 0–30 and 30–60 cm, respectively, Table S1 and Table S2). However, significant differences between treatments or seasons were not detected for Cu (Fig. 4a). No increase in the available Cu content at both depths can be explained because Cu is one of the essential micronutrients that can be uptaken by wheat, as reflected by changes between seasons since their deficiency is reflected by chlorosis, deformed leaves, and small grain. Besides, Cu is considered one of the most closely related minor elements to organic matter, as it is strongly associated with organic matter through oxygen functional groups such as carboxyl and phenolic or alcoholic hydroxyls, forming stable complexes, especially the complexes that form between Cu and organic acids with high molecular weights (humic acids). In this sense, a significant correlation has been found between Cu and OM contents for 0–30 cm (r = 0.45, $p < 0.05$, Table S1).

As these complexes become insoluble, and the presence of calcium carbonate in the soil reduces the availability of Cu, these carbonates interact with Cu, forming the insoluble alkaline Cu carbonate [$CaCO_3.Cu(OH)_2$], which reduces who facilitated this element, which is agreed with (Cegarra et al., 1996; Badran, 2011).

Besides, it was observed a slight increment of Fe, Mn and Zn (Fig. 4b, c and 4d) when compared with previous values before addition for both depths (Table 2), an increment that seems proportionally with OMW dose, were also the treatments were significantly high to the control treatment in both seasons and depths (Fig. 4b–d). In this sense, significant correlations between Fe, Mn and Zn were found with OM and dose application for both depths (Table S1 and Table S2), while Mn contents were significantly correlated with time (r = −0.78 and −0.71 for 0–30 and 30–60 cm, respectively, Tables S1 and S2). These results are similar to those reported by Aharonov-Nadborny et al. (2018), since OMW application can increase the Fe and Mn bioavailability.

3.6. Effects of added OMW on the available heavy metals: Cd and Pb

As previously mentioned, OMW is an agro-alimentary by-product characterized by high acidity and salt contents and can contain different levels of heavy metals (Zahra El Hassani et al., 2023). Although heavy metals are usually in reduced amounts, the repetitive application can favour their accumulation in the release and metal accumulation in soils (Zahra El Hassani et al., 2023). As indicated by different authors (de la Fuente et al., 2011; Kalyvas et al., 2020; Zahra El Hassani et al., 2023), the application of fresh OMW can reinforce the solubility of heavy metals in soils and the amount of heavy metals in soils can be increased proportionally with the OMW doses and soil pH. In our case, we have an acid OMW (Table 1), which can favour the solubility of several heavy metals (Bejarano and Madrid, 1996), but our soil samples are calcareous, which will reduce the metal availability, as reported by de la Fuente et al. (2011) for calcareous soils in Spain.

Cadmium and Pb are two heavy metals without biological function

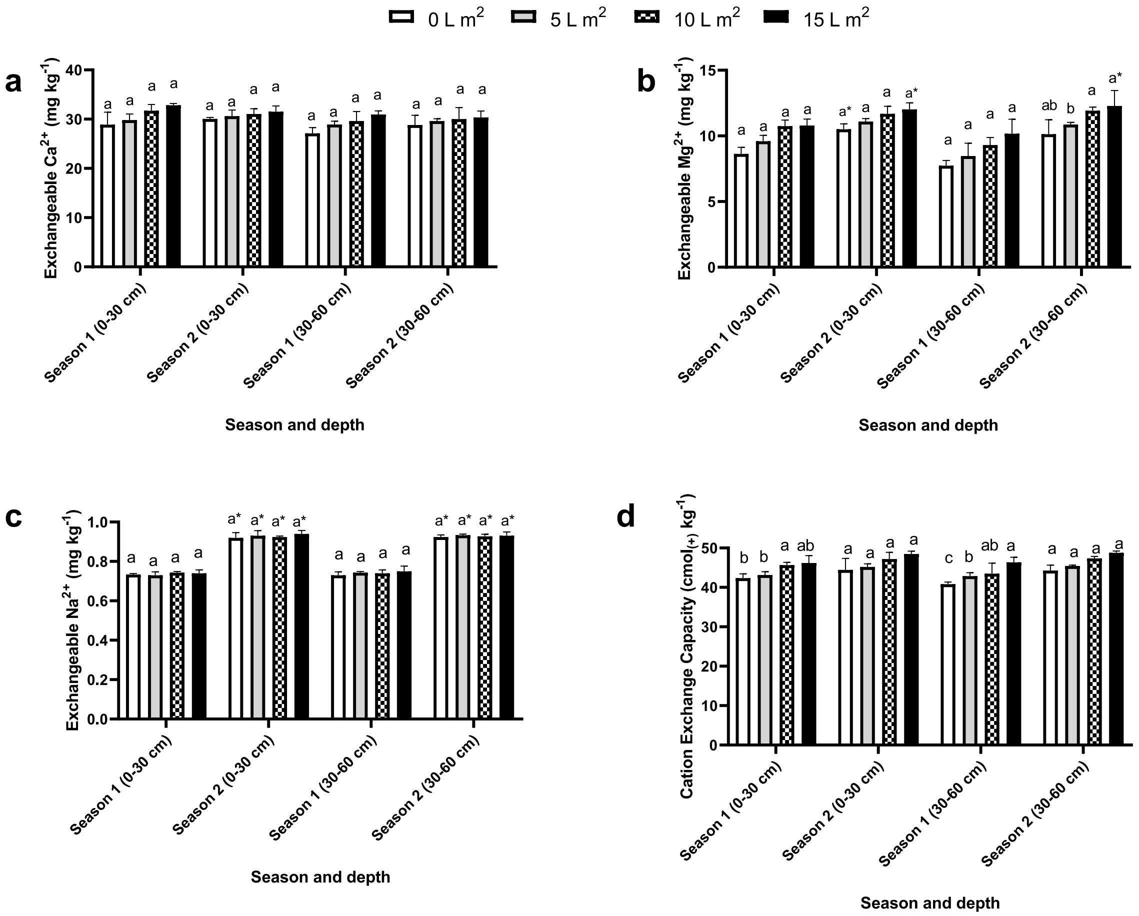

Fig. 3. Exchangeable Ca^{2+} (a), Mg^{2+} (b), Na^{+} (c) and cation exchange capacity (d) after OMW treatments and between seasons. Data are shown as means ± standard deviation of three replicates. Bars marked by different letters indicate significant differences for each season and depth ($p < 0.05$). Bars marked with * indicate significant differences between depths for the same season ($p < 0.05$).

(Sadiku and Rodríguez-Seijo, 2022), and their critical levels are better when lower. In our case, the found levels were very low and within the permissible levels. According to Kabata-Pendias (2010), permissible levels for Pb and Cd are <0.5 and 0.2 mg kg^{-1}, respectively, while phytotoxic effects are over 100 and 3 mg kg^{-1}, respectively. Both heavy metals were within the permissible levels. Only Cd could represent a potential risk due to soil pH and, therefore, their increased bioavailability, but both Cd and Pb were reduced between seasons ($p < 0.05$, Fig. 5a and b).

3.7. Impact of OMW on soil nutritional status and plant development

Different authors have reviewed the impact of OMW application on soil chemical parameters and nutrient contents (e.g., Sierra et al., 2007; Barbera et al., 2013; Chaâri et al., 2022). However, the impact on nutrient imbalances has been less studied. In this sense, different soil nutrient ratios have been determined according to the reported literature for wheat-grown and their values were compared through different soil profiles and seasons after OMW application (Table 3).

The soil C:N ratio was improved under OMW application, although this ratio was slightly reduced over time (Table 3). In general, the values for 0–30 cm were within the optimum values (10–20) for the soil microbial activity stimulation of the release of soil nutrients to crops, while the subsoil (30–60 cm) was slightly reduced due to an excess of N (Luo et al., 2016; Liu et al., 2023). Barbera et al. (2013) explained that the low N content of the OMW can increase the C:N ratio in soils where they are applied, as observed in our soils for 0–30 cm. This low N concentration means that there is no imbalance with K, as observed by the N:K ratio, which value below <2.1 is optimum for plant growth (Olde Venterink et al., 2003).

Vertisoils are deficient in soil nutrients, such as P and Zn. This situation is reflected in soil nutrient ratios. First, $N:P_{available}$ ratios were improved under all treatments and depths, although insufficient to avoid imbalances since the applied OMW is moderately rich in N but with a P deficiency in comparison with typical OMW values (Table 1). A similar question was also observed for $P_{available}:Zn_{available}$ (Ayamba et al., 2023), $P_{available}:Fe_{available}$ (Slunjski et al., 2012), $P_{available}:Mn_{available}$ (Slunjski et al., 2012) with a significant deficiency by P (Table 3). Regarding other soil ratios, the $Fe_{available}:Zn_{available}$ ratio suggests inhibition of Fe uptake (Zare et al., 2009), although improved with increased concentration with better ratios obtained under 10 L m^2. Similar issues were also observed for $K_{exchangeable}:Mg_{exchangeable}$ and $K_{exchangeable}:Na_{exchangeable}$, which represents a potential K deficiency (Table 3). No issues were observed for $Na_{exchangeable}:Mg_{exchangeable}$, $Na_{exchangeable}:Ca_{exchangeable}$, since their ratios were <1. This low ratio suggests no phytotoxicity due to excess Na^{+} or Ca^{2+}, a relatively common issue in vertisols where both cations dominate the exchange complex and can generate nutritional imbalances (Pierre et al., 2019; Kasno et al., 2021). This question is reflected in soil ratios with $Ca_{exchangeable}:Mg_{exchangeable}$ and $Ca_{exchangeable}:K_{exchangeable}$. First, the $Ca_{exchangeable}:Mg_{exchangeable}$ ratios were within the optimum values for plant growth (1.5–4.5) (Osemwota et al., 2007; Loke et al., 2014; Ayamba et al., 2023), but $Ca_{exchangeable}:K_{exchangeable}$ were

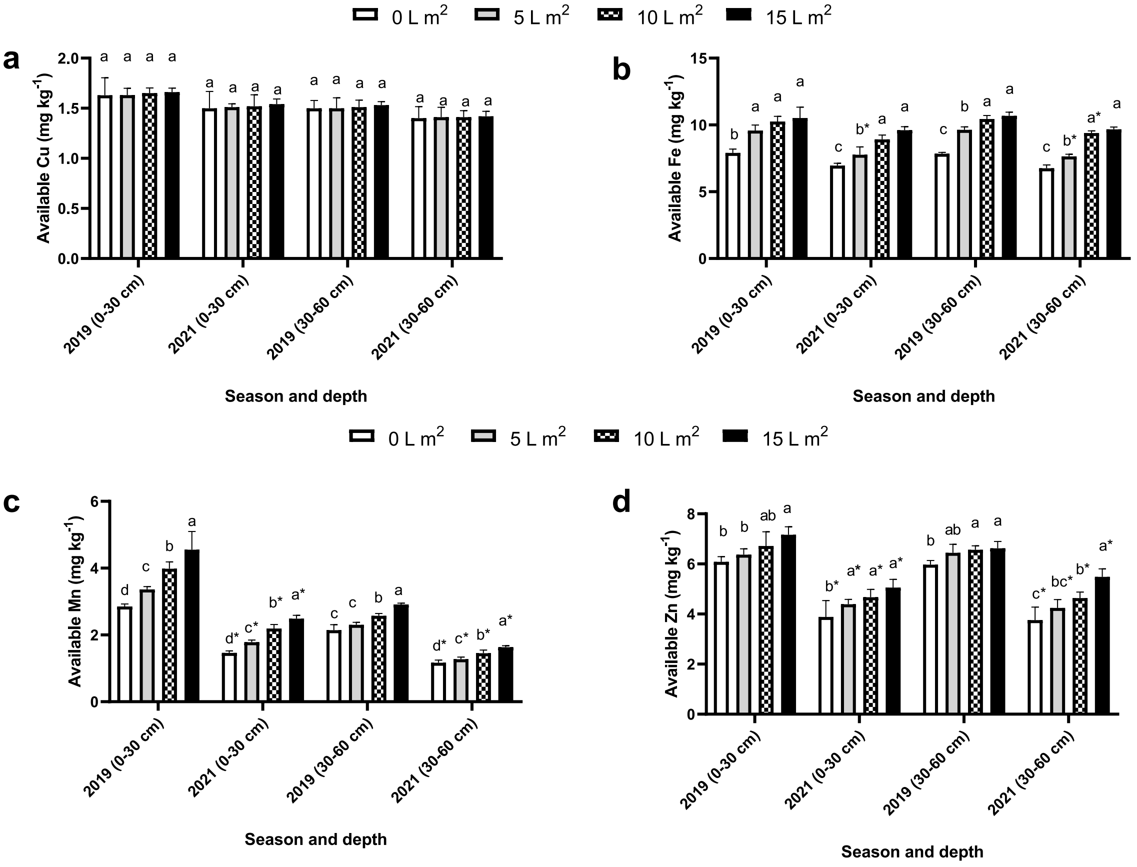

Fig. 4. Available contents of Cu (a), Fe (b), Mn (c) and Zn (d) after OMW treatments and between seasons. Data are shown as means ± standard deviation of three replicates. Bars marked by different letters indicate significant differences for each season and depth ($p < 0.05$). Bars marked with * indicate significant differences between depths for the same season ($p < 0.05$).

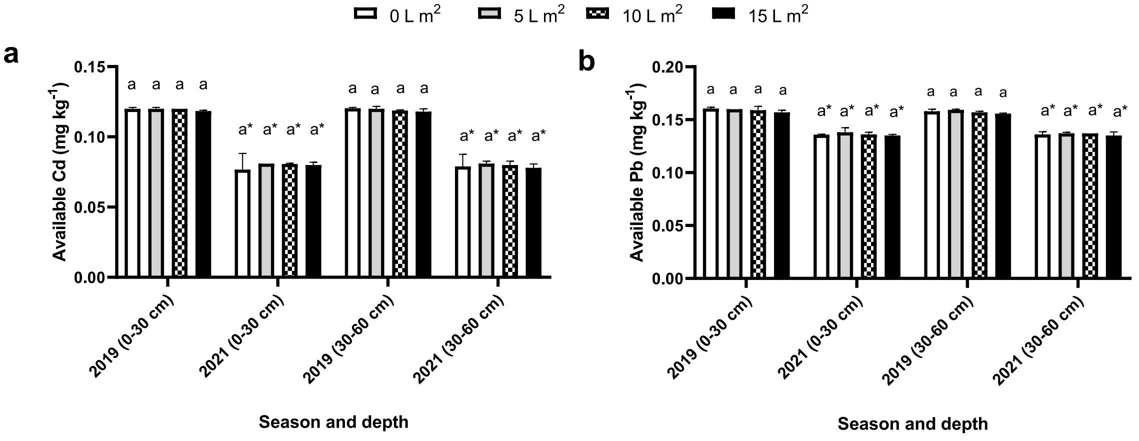

Fig. 5. Available contents of Cd (a) and Pb (b) after OMW treatments and between seasons. Data are shown as means ± standard deviation of three replicates. Bars marked by different letters indicate significant differences for each season and depth ($p < 0.05$). Bars marked with * indicate significant differences between depths for the same season ($p < 0.05$).

very high, although improved with increased OMW dose (Table 3).

Despite these imbalances due to the P and K deficiencies, the plant growth was improved, as indicated in a previous study where the impact of OMW was assessed for wheat production and soil microbiological activities (Khalil et al., 2021). This previous study achieved the best wheat yield under 10 L m^2, followed by 15, 5 and 0 L m^2, with increments proportional to the OMW dose applied to be these results similar to those indicated by other researchers (Piotrowska et al., 2006; Al-Ibrahim et al., 2008; Mekki et al., 2013). The OMW can be enriched with OM, which, when decomposed, gives nutrients in addition to

Table 3

Nutrient rations in soils treated with different olive-mill wastewater doses (average values, n = 3).

Season	Depth (cm)	OMW dose (L m^2)	C:N*	N: K_{AV}	N:P_{av}	P_{av}: Zn_{av}	P_{av}: Fe_{av}	P_{av}: Mn_{av}	Ca_{ex}: Mg_{ex}	K_{ex}:Mg_{ex}	K_{ex}: Na_{ex}	Fe_{av}: Mn_{av}	Fe_{av}: Zn_{av}	Na_{ex}: Mg_{ex}	Na_{ex}: Ca_{ex}	Ca_{ex}: K_{ex}
2019–2020	0–30	0	13.77	1.18	475.13	0.12	0.09	0.26	3.34	0.09	1.04	2.78	1.30	0.09	0.03	37.73
		5	13.72	1.22	221.41	0.29	0.19	0.55	3.11	0.09	1.18	2.85	1.50	0.08	0.02	34.52
		10	15.13	1.16	158.16	0.41	0.27	0.69	2.95	0.09	1.29	2.58	1.53	0.07	0.02	33.21
		15	16.33	1.19	115.41	0.59	0.41	0.95	3.04	0.10	1.41	2.32	1.47	0.07	0.02	31.44
	30–60	0	8.45	1.44	655.49	0.14	0.08	0.38	2.86	0.06	0.68	4.77	1.83	0.09	0.03	48.18
		5	9.88	1.35	226.59	0.37	0.21	0.92	2.76	0.06	0.76	4.37	1.77	0.08	0.03	43.59
		10	11.35	1.25	160.61	0.53	0.27	1.12	2.66	0.07	0.87	4.08	1.91	0.08	0.03	38.63
		15	12.29	1.06	107.99	0.77	0.41	1.56	2.63	0.08	1.08	3.86	1.90	0.08	0.03	31.03
2020–2021	0–30	0	12.10	1.44	579.78	0.10	0.07	0.27	3.51	0.07	0.78	3.68	1.31	0.09	0.03	47.97
		5	10.89	1.43	210.84	0.28	0.19	0.79	3.45	0.08	0.93	4.19	1.50	0.09	0.03	42.04
		10	13.02	1.37	143.60	0.45	0.28	1.15	3.19	0.09	1.07	4.06	1.59	0.08	0.03	37.51
		15	13.29	1.48	127.78	0.57	0.35	1.29	3.06	0.08	1.11	3.67	1.61	0.07	0.02	37.15
	30–60	0	8.51	1.61	673.51	0.13	0.07	0.41	2.87	0.05	0.54	5.79	1.82	0.09	0.03	57.70
		5	8.31	1.65	224.41	0.39	0.22	1.31	2.73	0.05	0.62	6.03	1.81	0.09	0.03	51.46
		10	8.36	1.56	179.98	0.50	0.25	1.61	2.52	0.06	0.74	6.50	2.03	0.08	0.03	43.64
		15	9.58	1.39	168.68	0.51	0.29	1.71	2.48	0.07	0.93	5.94	1.77	0.08	0.03	35.13
	Deficiency		<8		12		<15	<20	<1.5	<0.25		<1.5	<2			
	Optimum value		10–20	<2.1	15	10	15–30	25–40	1.5–4.5	0.25–0.5	3–4.1	1.5–2.5	2–3			13
	Deficiency		>25		16		>30	>40	>7-8	>0.7–1		>2.5	>4	>1	>1	

The deficiencies and optimum values were calculated according to those reported by different authors for C_{org}:N (Luo et al., 2016; Liu et al., 2023), N:$K_{available}$ (Olde Venterink et al., 2003), N:$P_{available}$ (Luo et al., 2016; Zhang et al., 2019), $P_{available}$:$Zn_{available}$ (Ayamba et al., 2023), $P_{available}$:$Fe_{available}$ and $P_{available}$:$Mn_{available}$ (Slunjski et al., 2012), $Ca_{exchangeable}$:$Mg_{exchangeable}$ (Osemwota et al., 2007; Loke et al., 2014; Ayamba et al., 2023), $K_{available}$:$Mg_{exchangeable}$ (Loke et al., 2014; Laekemariam et al., 2018; Vázquez-Blanco et al., 2023), $K_{available}$:$Na_{exchangeable}$ (Ali et al., 2013), $Fe_{available}$:$Mn_{available}$ (Hodges, 2010; Ayamba et al., 2023), $Fe_{available}$:$Zn_{available}$ (Zare et al., 2009), $Na_{exchangeable}$:$Mg_{exchangeable}$ and $Na_{exchangeable}$:$Ca_{exchangeable}$ (Prasad and Power, 1997) and $Ca_{exchangeable}$:$K_{available}$ (Bear et al., 1945).

*Organic carbon for C:N ratio was calcuated using the van Bemmelen Conversion factor. For K ratios, available K was used for N:K ratio, while K content was converted to $cmol_{(+)}kg^{-1}$ for exchangeable cations ratios.

organic acids, especially humic acid, which plays an important role in increasing seed germination by stimulating enzymatic activity inside the seeds. It provides a quick energy source for the embryo to move inside the seed from the non-autotrophic stage to the self-feeding stage (Mekki et al., 2013).

4. Conclusions and recommendations

The addition of OMW with its three doses led to an improvement in the physical properties of the studied soil, as observed for organic matter, the cation exchange capacity and macronutrients, especially under 10 and 15 L m^2. Also, the addition of the OMW with its three treatments did not cause any significant increase in Cd and Pb levels. In contrast, their addition improved the studied soil content of micronutrients, especially Fe, Mn and Zn, under all studied treatments compared to the no-addition dose in both seasons and depths. The increased OMW doses improved some nutrient balances, although insufficient to improve the optimum soil nutrient balances. In general, P deficiencies were observed.

The 10 L m^2 dose offered more balanced results with an adequate improvement of soil properties. However, more assays are needed to assess the potential toxicity to soil organisms or the impact on other understudied soil properties, such as LC, POC, MOC, nitrates, nitrates or other heavy metals such as Ni. In any case, this research provides results for using olive mill wastewater in an eco-friendly way under arid conditions and, therefore, as an adequate alternative to chemical fertilizers.

Ethical approval, consent to participate or for publication

Not applicable.

Funding

This research received no external funding.

CRediT authorship contribution statement

Jehan Khalil: Conceptualization, Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Abd Al Karim Jaafar:** Conceptualization, Data curation, Formal analysis, Investigation, Supervision, Writing - original draft, Writing - review & editing. **Hassan Habib:** Conceptualization, Investigation, Supervision, Writing - original draft, Writing - review & editing. **Sirine Bouguerra:** Writing - original draft, Writing - review & editing. **Verónica Nogueira:** Writing - original draft, Writing - review & editing. **Andrés Rodríguez-Seijo:** Data curation, Supervision, Visualization, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All generated data are published in this version.

Acknowledgements

This research was also supported by the Foundation of Science and Technology through the Strategic Funding UIDB/05748/2020 & UIDP/05748/2020 (GreenUPorto), and UIDB/04423/2020, UIDP/04423/2020 & LA/P/0101/2020 (CIIMAR). V.N. thanks FCT for funding through program DL 57/2016 –Norma transitória. S.B. thanks the NORTE 2020 Program funded by FEDER through the project S4Hort Soil & Food (REF: Norte-01-0145-FEDER-000074) for the financial support of her investigation contract. A.R.S. wants to acknowledge MCIN/AEI/UVigo for their JdCi contract under the “Actuación financiada por IJC 2020-044197-I, funded by MCIN/AEI/10.13039/501100011033 and the European Union NextGenerationEU/PRTR". Funding for open access charge: Universidade de Vigo/CISUG.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.119861.

References

Abu-Lafi, S., Al-Natsheh, M.S., Yaghmoor, R., Al-Rimawi, F., 2017. Enrichment of phenolic compounds from olive mill wastewater and in vitro evaluation of their antimicrobial activities. Evidence-based Complementary and Alternative Medicine. eCAM, 3706915. https://doi.org/10.1155/2017/3706915.

Agrawal, H.P., 1992. Assessing the micronutrient requirement of winter wheat. Commun. Soil Sci. Plant Anal. 23 (17–20), 2555–2568. https://doi.org/10.1080/00103629209368756.

Aguilar, M.J., 2009. Olive oil mill wastewater for soil nitrogen and carbon conservation. J. Environ. Manag. 90 (8), 2845–2848. https://doi.org/10.1016/j.jenvman.2009.02.015.

Aharonov-Nadborny, R., Tsechansky, L., Raviv, M., Graber, E.R., 2018. Mechanisms governing the leaching of soil metals as a result of disposal of olive mill wastewater on agricultural soils. Sci. Total Environ. 630, 1115–1123. https://doi.org/10.1016/j.scitotenv.2018.02.270.

Al-Budi, M., 2011. Studying the cumulative effect of adding olive mill wastewater on soil nematode communities, growth and productivity in protected cultivation of tomato plants. Agricultural Scientific Research Center in Lattakia. PhD thesis.

Al-Ibrahim, A., Al-Nawab, H., Ghadry, M., 2008. The Effect of Using Olive Pressing Water in Agricultural Lands Planted with Wheat on Soil Properties and Production. Agricultural Research Center, Idlib.

Ali, L., Ashraf, M., Maqbool, M., Ahmad, R., Aziz, A., 2013. Optimization of soil K: Na ratio for cotton (*Gossypium hirsutum* L.) nutrition under field conditions. Pakistan J. Bot. 45 (1), 127–134.

Aly, A.A., Hasan, Y.N., Al-Farraj, A.S., 2014. Olive mill wastewater treatment using a simple zeolite-based low-cost method. J. Environ. Manag. 145, 341–348. https://doi.org/10.1016/j.jenvman.2014.07.012.

Arienzo, M., Capasso, R., 2000. Analysis of metal cations and inorganic anions in olive oil mill waste waters by atomic absorption spectroscopy and ion chromatography. Detection of metals bound mainly to the organic polymeric fraction. J. Agric. Food Chem. 48 (4), 1405–1410. https://doi.org/10.1021/jf990588x.

ASTM, 1958. Procedures for Testing Soils. American Society for Testing and Materials, Philadelphia.

Ayamba, B.E., Abaidoo, R.C., Opoku, A., Ewusi-Mensah, N., 2023. Mechanisms for nutrient interactions from organic amendments and mineral fertilizer inputs under cropping systems: a review. PeerJ 11, e15135. https://doi.org/10.7717/peerj.15135.

Badran, A., 2011. The effect of adding different levels of olive pressing water on some fertility and productivity properties of citrus cultivated soil. PhD Thesis. Faculty of Agriculture, Tishreen University.

Barbera, A.C., Maucieri, C., Cavallaro, V., Ioppolo, A., Spagna, G., 2013. Effects of spreading olive mill wastewater on soil properties and crops, a review. Agric. Water Manag. 119, 43–53. https://doi.org/10.1016/j.agwat.2012.12.009.

Bear, F.E., Prince, A.L., Malcolm, J.L., 1945. Potassium needs of New Jersey soils. Bull. 721. New Jersey Agric. Exp. Stn., New Brunswick.

Bejarano, M., Madrid, L., 1996. Solubilization of heavy metals from a river sediment by an olive oil mill effluent at different pH values. Environ. Technol. 17 (4), 427–432. https://doi.org/10.1080/09593331708616403.

Benamar, A., Mahjoubi, F.Z., Barka, N., Kzaiber, F., Boutoial, K., Ali, G.A.M., Oussama, A., 2020. Olive mill wastewater treatment using infiltration percolation in column followed by aerobic biological treatment. SN Appl. Sci. 2, 655. https://doi.org/10.1007/s42452-020-2481-1.

Bremner, J.M., 1996. Nitrogen—total. In: Sparks, D.L. (Ed.), Methods of Soils Analysis: Chemical Methods. American Society of Agronomy, Soil Science Society of America, Madison, WI, pp. 1085–1211.

Cegarra, J., Paredes, C., Roig, A., Bernal, M.P., Garcia, D., 1996. Use of olive mill wastewater compost for crop production. Int. Biodeterior. Biodegrad. 38 (3–4), 193–302. https://doi.org/10.1016/S0964-8305(96)00051-0.

Chaari, L., Elloumi, N., Mseddi, S., Gargouri, K., Rouina, B.B., Mechichi, T., Kallel, M., 2015. Changes in soil macronutrients after a long-term application of olive mill wastewater. J. Agric. Food Chem. 4, 1–13. https://doi.org/10.4236/jacen.2015.41001.

Chaâri, L., Alsaiari, N.S., Amari, A., Ben Rebah, F., Kallel, M., Mechichi, T., 2022. Soil responses to high olive mill wastewater spreading. Agronomy 12, 972. https://doi.org/10.3390/agronomy12040972.

Chatzistathis, T., Koutsos, T.M., 2017. Olive mill wastewater as a source of organic matter, water and nutrients for restoration of degraded soils and for crops managed with sustainable systems. Agric. Water Manag. 190, 55–64. https://doi.org/10.1016/j.agwat.2017.05.008.

Chung, J., Lee, Y., 2008. Comparison of soil nutrient status in conventional and organic apple farm. Korean J. Soil Sci. Fert. 41 (1), 26–33. https://koreascience.kr/article/JAKO200828066505008.page.

Conyers, M.K., Davey, B.G., 1988. Observations on some routine methods for soil pH determination. Soil Sci. 145, 29–36.

Dakhli, R., Gosh, A., Wali, A., Manna Chandra, M., Khatteli, H., 2021. Agricultural valorization of olive mill wastewater in arid regions of Tunisia: short-term impact on soil biochemical properties and faba bean growth. Pol. J. Environ. Stud. 30 (2), 1117–1128. https://doi.org/10.15244/pjoes/123903.

Danellakis, D., Ntaikou, I., Kornaros, M., Dailianis, S., 2011. Olive oil mill wastewater toxicity in the marine environment: alterations of stress indices in tissues of mussel Mytilus galloprovincialis. Aquat. Toxicol. (N. Y.) 101, 358–366. https://doi.org/10.1016/j.aquatox.2010.11.015.

Davies, L.C., Vilhena, A., Novais, J., Martins-Dias, S., 2004. Olive mill wastewater characteristics: modelling and statistical analysis. Grasas Aceites 55, 233–241.

de la Fuente, C., Clemente, R., Martínez-Alcalá, I., Tortosa, G., Bernal, M.P., 2011. Impact of fresh and composted solid olive husk and their water-soluble fractions on soil heavy metal fractionation; microbial biomass and plant uptake. J. Hazard Mater. 186 (2–3), 1283–1289. https://doi.org/10.1016/j.jhazmat.2010.12.004.

Dermeche, S., Nadour, M., Larroche, C., Moulti-Mati, F., Michaud, P., 2013. Olive mill wastes: biochemical characterizations and valorization strategies. Process Biochem. 48 (10), 1532–1552. https://doi.org/10.1016/j.procbio.2013.07.010.

Domingues, A., da Costa, J.P., Rocha-Santos, T.A.P., Gonçalves, F.J.M., Pereira, R., Pereira, J.L., 2022. Biosorption potential of the shell of Corbicula fluminea towards olive oil mill waste. Int. J. Environ. Sci. Technol. 19, 5689–5696. https://doi.org/10.1007/s13762-021-03404-0.

D'Auria, A., Marano-Marcolini, C., Čehić, A., Tregua, M., 2020. Oleotourism: a comparison of three mediterranean countries. Sustainability 12, 8995. https://doi.org/10.3390/su12218995.

El Chami, A., Conte, P., Hassoun, G., Piga, A., 2023. Effect of region of cultivation, tree age, and harvest time on the quality of Lebanese virgin olive oil. Ital. J. Food Sci. 35 (1), 57–71. https://doi.org/10.15586/ijfs.v35i1.2286.

El-Abbassi, A., Hafidi, A., Khayet, M., García-Payo, M.C., 2013. Integrated direct contact membrane distillation for olive mill wastewater treatment. Desalination 323, 31–38. https://doi.org/10.1016/j.desal.2012.06.014.

EPA US, 2009. National primary drinking water guidelines. Epa 1, 7, 816-F-09-004. 2009.

EU, 2016. Commission Implementing Decision (EU) 2016/902 of 30 May 2016 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for common waste water and waste gas treatment/management systems in the chemical sector (notified under document C(2016) 3127) (Text with EEA relevance). Off. J. Eur. Union L152/23. http://data.europa.eu/eli/dec_impl/2016/902/oj.

Fan, J., Ding, W., Chen, Z., Ziadi, N., 2012. Thirty-year amendment of horse manure and chemical fertilizer on the availability of micronutrients at the aggregate scale in black soil. Environ. Sci. Pollut. Res. 19, 2745–2754. https://doi.org/10.1007/s11356-012-0774-7, 2012.

FAO, 2007. Methods of Analysis for Soils of Arid and Semi-arid Regions. Food and Agriculture Organization, Rome, Italy.

Feria, A.L., 2000. The generated situation by the OMW in Andalusia. Actas/Proceedings-Workshop Improlive-2000-Anexo A 1, 55–63, 7.

Garcia-Ortiz, A., Beltrán, G., Uceda, M., Hermoso, M., González, P.M., Ordóñez, R., Giráldez, J.V., 1999. Vegetation water (alpechin) application effects on soils and plants. Acta Hortic. 474, 749–752. https://doi.org/10.17660/ActaHortic.1999.474.156.

Gupta, P.K., 2000. Soil, Plant, Water and Fertilizer Analysis. Agrobios (India), Jodhpur, New Delhi, India, p. 438.

Haifa, S., Ahmed, E., Al-Budi, M., Qashou, B., 2016. The effect of adding olive mill wastewater on some soil properties, its content of some microelements, and the quality of tomato plants grown in a plastic house. Al-Baath University Journal. 38 (46), 127–153.

Hailu, H., Mamo, T., Keskinen, R., Karltun, E., Gebrekidan, H., Bekele, T., 2015. Soil fertility status and wheat nutrient content in Vertisol cropping systems of central highlands of Ethiopia. Agric. Food Secur. 4, 19. https://doi.org/10.1186/s40066-015-0038-0.

Hodges, S.C., 2010. S Soil Fertility Basics: NC Certified Crop Advisor Training. North Carolina State University Soil Science Extension. http://www.soil.ncsu.edu/programs/nmp/Nutrient%20Management%20for%20CCA.pdf, 06.08.2023.

ISO, 1975. Cheese. Determination of Fat Content. International Organization for Standardization, Geneva, Switzerland. Van Gulik Method. ISO Standard 3433.

ISO, 1994. ISO 11265:1994 Soil Quality. Determination of the Specific Electrical Conductivity. International Organization for Standardization, Geneva, Switzerland.

Jackson, M.L., 1958. Soil Chemical Analysis. Prentice- Hall, Inc., Englewood Cliffs, New Jersey.

Jones Jr., J.B., 2001. Laboratory Guide for Conducting Soils Tests and Plant Analysis. CRC Press, Boca Raton Florida, USA.

Justino, C.I.L., Pereira, R., Freitas, A.C., Rocha-Santos, T.A.P., Panteleitchouk, T.S.L., Duarte, A.C., 2011. Olive oil mill wastewaters before and after treatment: a critical review from the ecotoxicological point of view. Ecotoxicology 21, 615–629. https://doi.org/10.1007/s10646-011-0806-y.

Kabata-Pendias, A., 2010. Trace Elements in Soils and Plants. CRC Press, p. 548. https://doi.org/10.1201/b10158.

Kalyvas, G., Gasparatos, D., Liza, C.A., Massas, I., 2020. Single and combined effect of chelating, reductive agents, and agro-industrial by-product treatments on As, Pb, and Zn mobility in a mine-affected soil over time. Environ. Sci. Pollut. Res. 27, 5536–5546. https://doi.org/10.1007/s11356-019-07230-3.

Kasno, A., Setyorini, D., Widowati, L.R., 2021. Cations ratio and its relationship with other soil nutrients of Java intensified lowland rice. IOP Conf. Ser. Earth Environ. Sci. 648, 012015 https://doi.org/10.1088/1755-1315/648/1/012015.

Kattan, Z., Nasser, S., 2023. Temporal variability of precipitation isotopes in Damascus, Syria — implications for regional climate change. Asian J. Atmos. Environ 17, 5. https://doi.org/10.1007/s44273-023-00004-x.

Kavvadias, V., Doula, M., Papadopoulou, M., Theocharopoulos, S., 2015. Long-term application of olive-mill wastewater affects soil chemical and microbial properties. Soil Res. 53, 461–473. https://doi.org/10.1071/SR13325.

Khalil, J., Habib, H., Alabboud, M., Mohammed, S., 2021. Olive mill wastewater effects on durum wheat crop attributes and soil microbial activities: a pilot study in Syria. Energy Ecol. Environ. 6, 469–477. https://doi.org/10.1007/s40974-021-00209-2.

Laekemariam, F., Kibret, K., Shiferaw, H., 2018. Potassium (K)-to-magnesium (Mg) ratio, its spatial variability and implications to potential Mg-induced K deficiency in Nitisols of Southern Ethiopia. Agric. Food Secur. 7, 13. https://doi.org/10.1186/s40066-018-0165-5.

Lee, K.W., Kim, Y.J., Lee, H.J., Lee, C.Y., 2003. Cocoa has more phenolic phytochemicals and a higher antioxidant capacity than teas and red wine. J. Agric. Food Chem. 51 (25), 7292–7295.

Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42, 421–428. https://doi.org/10.2136/sssaj1978.03615995004200030009x, 1978.

Liu, J., Qiu, T., Peñuelas, J., Sardans, J., Tan, W., Wei, X., Cui, Y., Cui, Q., Wu, C., Liu, L., Zhou, B., He, H., Fang, L., 2023. Crop residue return sustains global soil ecological stoichiometry balance. Glob. Chang. Biol. 29, 2203–2226. https://doi.org/10.1111/gcb.16584.

Loke, P.F., Kotzé, E., Du Preez, C.C., 2014. Long-Term effects of wheat production management practices on exchangeable base cations and cation exchange capacity of a plinthosol in semi-arid South Africa. Commun. Soil Sci. Plant Anal. 45 (8), 1083–1105. https://doi.org/10.1080/00103624.2013.867060.

López-Piñeiro, A., Albarrán, Á., Cabrera, D., Peña, D., Nunes, J.R., 2011. De-oiled two-phase olive mill waste application impact on phosphorus sorption and fractionation in a mediterranean soil under olive production. Soil Sci. 176, 22–32.

Luo, X., Mazer, S.J., Guo, H., Zhang, N., Weiner, J., Hu, S., 2016. Nitrogen:phosphorous supply ratio and allometry in five alpine plant species. Ecol. Evol. 6 (24), 8881–8892. https://doi.org/10.1002/ece3.2587.

Magdich, S., Ben Ahmed, C., Jarboui, R., Ben Rouina, B., Boukhris, M., Ammar, E., 2013. Dose and frequency dependent effects of olive mill wastewater treatment on the chemical and microbial properties of soil. Chemosphere 93 (9), 1896–1903. https://doi.org/10.1016/j.chemosphere.2013.06.066.

Mahmoud, M., Janssen, M., Haboub, N., Nassour, A., Lennartz, B., 2010. The impact of olive mill wastewater application on flow and transport properties in soils. Soil and Till. Res. 107, 36–41.

Mahmoud, E.N., Fayed, F.Y., Ibrahim, K.M., Jaafreh, S., 2021. Removal of cadmium, copper, and lead from water using bio-sorbent from treated olive mill solid residue. Environ. Health Insights 15, 1–10. https://doi.org/10.1177/11786302211053176.

Mamo, T., Richter, C., Heiligtag, B., 2002. Phosphorus availability studies on ten Ethiopian Vertisols. J. Agric. Rural Dev. Tropics Subtropics 103, 177–183. https://www.jarts.info/index.php/jarts/article/view/12.

Massaccesi, L., Feudis, M.D., Agnelli, A., Nasini, L., Regni, L., D'Ascoli, R., Castaldi, S., Proietti, P., Agnelli, A., 2018. Organic carbon pools and storage in the soil of olive groves of different age. Eur. J. Soil Sci. 69 (5), 843–855. https://doi.org/10.1111/ejss.12677.

Mekki, A., Dhouib, A., Sayadi, S., 2013. Review: effects of olive mill wastewater application on soil properties and plants growth. Int. J. Recycl. Org. Waste Agric. 2, 15. https://doi.org/10.1186/2251-7715-2-15.

Mohana, A.A., Roddick, F., Maniam, S., Gao, L., Pramanik, B.K., 2023. Component analysis of fat, oil and grease in wastewater: challenges and opportunities. Anal. Methods 15, 5112–5128. https://doi.org/10.1039/D3AY01222K.

Mohawesh, O., Mahmoud, M., Janssen, M., Lennartz, B., 2014. Effect of irrigation with olive mill wastewater on soil hydraulic and solute transport properties. Int. J. Environ. Sci. Technol. 11 (4), 927–934. https://doi.org/10.1007/s13762-013-0285-1.

Mohawesh, O., Al-Hamaiedeh, H., Albalasmeh, A., Qaraleh, S., Haddadin, M., 2019. Effect of olive mill wastewater (OMW) application on soil properties and wheat growth performance under rain-fed conditions. Water Air Soil Pollut. 230, 160. https://doi.org/10.1007/s11270-019-4208-8.

Moraetis, D., Stamati, F.E., Nikolaidis, N.P., Kalogerakis, N., 2011. Olive mill wastewater irrigation of maize: impacts on soil and groundwater. Agric. Water Manag. 98 (7), 1125–1132. https://doi.org/10.1016/j.agwat.2011.02.006.

Muthuvel, P., Udayasoorian, C., 1999. Soil, Plant, Water and Agrochemical Analysis. Tamil Nadu Agricultural University, Coimbatore, India, p. 315.

Olde Venterink, H., Wassen, M.J., Verkroost, A., Ruiter, P.C., 2003. Species richness–productivity patterns differ between n-, p-, and k-limited wetlands. Ecology 84, 2191–2199. https://doi.org/10.1890/01-0639.

Olsen, S.R., Sommers, L.E., 1982. Phosphorus. In: Page, A.L., Miller, R.H., Keeney, R.S. (Eds.), Method of Soil Analysis: Part 2. Chemical and Microbiological Properties. Agronomy Monographs No. 9, second ed. American Society of Agronomy and Soil Science Society of America, Madison, pp. 403–430.

Osemwota, I.O., Omueti, J.A., Ogboghodo, A.I., 2007. Effect of calcium/magnesium ratio in soil on magnesium availability, yield, and yield components of maize. Commun. Soil Sci. Plant Anal. 38, 2849–2860. https://doi.org/10.1080/00103620701663081.

Pierantozzi, P., Torres, M., Verdenelli, R., Basanta, M., Maestri, D.M., Meriles, J.M., 2013. Short-term impact of olive mill wastewater (OMWW) applications on the physico-chemical and microbiological soil properties of an olive grove in Argentina. J. Environ. Sci. Health B. 48 (5), 393–401. https://doi.org/10.1080/03601234.2013.742398.

Pierre, T.J., Primus, A.T., Simon, B.D., Philémon, Z.Z., Hamadjida, G., Monique, A.A., Pierre, N.J., Lucien, B.D., 2019. Characteristics, classification and genesis of vertisols under seasonally contrasted climate in the Lake Chad Basin, Central Africa. J. Afr. Earth Sci. 150, 176–193. https://doi.org/10.1016/j.jafrearsci.2018.11.003.

Piotrowska, A., Iamarino, G., Rao, M.A., Gianfreda, L., 2006. Short-term effects of olive mill waste water (OMW) on chemical and biochemical properties of a semiarid Mediterranean soil. Soil Biol. Biochem. 38 (3) https://doi.org/10.1016/j.soilbio.2005.06.012, 600-.016.

Prasad, R., Power, J.F., 1997. Soil Fertility Management for Sustainable Agriculture. CRC Press.

Rajib, B., Elmidaoui, A., Chaouch, A., larif, M., 2016. Physicochemical characterization of olive oil mill wastewaters samples collected from four different oil mills located in the Meknès-Tafilalt region of Morocco. Moroc. J. Chem. 4 (3), 775–784. https://doi.org/10.48317/IMIST.PRSM/morjchem-v4i3.5365.

Rinaldi, M., Rana, G., Introna, M., 2003. Olive-mill wastewater spreading in southern Italy: effects on a durum wheat crop. Field Crops Res. 84 (3), 319–623. https://doi.org/10.1016/S0378-4290(03)00097-2.

Rusan, M.J.M., Malkawi, H.I., 2016. Dilution of olive mill wastewater (OMW) eliminates its phytotoxicity and enhances plant growth and soil fertility. Desalin. Water Treat. 57 (57), 27945–27953. https://doi.org/10.1080/19443994.2016.1186397.

Sadiku, O.O., Rodríguez-Seijo, A., 2022. Metabolic and genetic derangement: a review of mechanisms involved in arsenic and lead toxicity and genotoxicity. Arh. Hig. Rad. Toksikol. 73 (4), 244–255. https://doi.org/10.2478/aiht-2022-73-3669.

Sassi, A., Boularbah, A., Jaouad, A., Walker, G., Boussaid, A., 2006. A comparison of Olive oil Mill Wastewaters (OMW) from three different processes in Morocco. Process Biochem. 41, 74–78. https://doi.org/10.1016/j.procbio.2005.03.074.

Sierra, J., Martí, E., Montserrat, G., Cruañas, R., Garau, M.A., 2001. Characterisation and evolution of a soil affected by olive oil mill wastewater disposal. Sci. Total Environ. 279 (1–3), 207–214. https://doi.org/10.1016/s0048-9697(01)00783-5.

Sierra, J., Martí, E., Garau, M.A., Cruañas, R., 2007. Effects of the agronomic use of olive oil mill wastewater: field experiment. Sci. Total Environ. 378 (1–2), 90–94. https://doi.org/10.1016/j.scitotenv.2007.01.009.

Slunjski, S., Coga, L., Herak Ćustić, M., Petek, M., Spoljar, A., 2012. Phosphorus, manganese and iron ratios in grapevine (*Vitis Vinifera* L.) Leaves on acid and calcareous soils. Acta Hortic. 938, 299–306. https://doi.org/10.17660/ActaHortic.2012.938.39.

Solomakou, N., Goula, A.M., 2021. Treatment of olive mill wastewater by adsorption of phenolic compounds. Rev. Environ. Sci. Biotechnol. 20, 839–863. https://doi.org/10.1007/s11157-021-09585-x.

Tajini, F., Ouerghi, A., Hosni, K., 2019. Effect of irrigation with olive-mill waste-water on physiological and biochemical parameters as well as heavy-metal accumulation in common bean (*Phaseolus vulgaris* L.). J. New Sci. Agric. Biotech. 66 (6), 4193–4203.

Vázquez-Blanco, R., González-Feijoo, R., Campillo-Cora, C., Fernández-Calviño, D., Arenas-Lago, D., 2023. Risk assessment and limiting soil factors for vine production—Cu and Zn contents in vineyard soils in galicia (rías baixas D.O.). Agronomy 13 (2), 309. https://doi.org/10.3390/agronomy13020309.

Vella, F.M., Galli, E., Calandrelli, R., Cautela, D., Laratta, B., 2016. Effect of olive mill wastewater spreading on soil properties. Bull. Environ. Contam. Toxicol. 97, 138–144. https://doi.org/10.1007/s00128-016-1830-7, 2016.

Virmani, S.M., Sahrawa, K.L., Burford, J.R., 1982. Physical and chemical properties of vertisols and their management. In: 12 Th International Congress of Soil Science. New. Delhi, India. https://doi.org/10.13140/2.1.2604.1284, 8-16 February 1982.

Voss, R., 1998. Micronutrients. Department of Agronomy, Iowa State University, Ames, IA, USA. https://www.agronext.iastate.edu/soilfertility/info/Micronutrients_VossArticle.pdf, 30.07.2023.

Walkley, A., Black, C.A., 1934. An examination of degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37, 29–83.

Zahra El Hassani, F., El Karkouri, A., Errachidi, F., Merzouki, M., Benlemlih, M., 2023. The impact of Olive Mill Wastewater spreading on soil and plant in arid and semi-arid areas. Environ. Nanotechnol. Monit. Manag. 20, 100798 https://doi.org/10.1016/j.enmm.2023.100798.

Zare, M., Khoshgoftarmanesh, A.H., Norouzi, M., Schulin, R., 2009. Critical soil zinc deficiency concentration and tissue iron: zinc ratio as a diagnostic tool for prediction of zinc deficiency in corn. J. Plant Nutr. 32 (12), 1983–1993.

Zbakh, H., Abbassi, A.E., 2012. Potential use of olive mill wastewater in the preparation of functional beverages: a review. J. Funct.Foods 4, 53–65. https://doi.org/10.1016/j.jff.2012.01.002.

Zema, D.A., Esteban Lucas-Borja, M., Andiloro, S., Tamburino, V., Zimbone, S.M., 2019. Short-term effects of olive mill wastewater application on the hydrological and physico-chemical properties of a loamy soil. Agric. Water Manage. 221, 312–321. https://doi.org/10.1016/j.agwat.2019.04.011.

Zhang, Y., Li, C., Wang, M., 2019. Linkages of C: N: P stoichiometry between soil and leaf and their response to climatic factors along altitudinal gradients. J. Soils Sediments 19, 1820–1829. https://doi.org/10.1007/s11368-018-2173-2.