

Effect of irrigation with olive mill wastewater on soil hydraulic and solute transport properties

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Received: 9 October 2012/Revised: 23 January 2013/Accepted: 17 March 2013/Published online: 17 April 2013
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Abstract To evaluate the effect of olive mill wastewater (OMW) application on soil hydraulic and transport properties, two treatment sites, which had been irrigated with OMW for 5 and 15 years, and one control site being irrigated with freshwater were compared. The transport and leaching experiment results showed that a portion of the total soil water was available for transport processes while the remaining of the soil water was considered immobile and not readily accessible for solutes. The separation in water fractions of different mobilities was surprisingly consistent among OMW treatments. The bromide recovery rate decreased with the application of OMW showing that tracer molecules became trapped within immobile water phases. The application of OMW increased significantly the soil water-holding capacity, whereas the soil hydraulic conductivity in the near saturation range decreased significantly with long-term OMW application. The soil irrigated with OMW had significantly higher organic matter content, lower bulk density and relatively higher total porosity, but lower macroporosity than that of control sites. We concluded that the soil was increasingly coated with complex organic molecules originating from OMW, as a result, solute exchange between inter- and intrasoil aggregate water was hindered. Although OMW could cause soil and water pollution, its use in agriculture is promoted because of high nutrients and organic matter contents.

Keywords Breakthrough curves · Hydraulic conductivity · Mobile-immobile soil water · Soil water retention · Soil and water pollution

Introduction

The production of olive oil in the Mediterranean and Middle East countries is regularly increasing. The average annual growth of olive oil production worldwide over the last 15 years is about 5 % (FAOSTAT 2007). However, olive oil producing countries are facing environmental problems because of the lack of practical or reasonable solutions to the disposal of olive mill wastewater (OMW) (Azbar et al. 2004). OMW is the effluent produced during the olive oil extraction process. According to the International Olive Oil Council (IOOC) there are about 789 million olive trees in the world, 95 % of these trees are in the Mediterranean region. Therefore, the disposal and management of OMW from the table olive industry is a serious problem in the Mediterranean region. About 30 million m³ of OMW is generated worldwide (mainly in the Mediterranean region) every year from olive oil production (Niaounakis and Halvadakis 2006). The production of such a high amount of OMW in a short period (3–5 months), its pollution load of high biological oxygen demand (40–80 g l⁻¹), high chemical oxygen demand (50–150 g l⁻¹), and its phytotoxic properties are serious problems for OMW disposal (Rinaldi et al. 2003; Mekki et al. 2006; Mahmoud et al. 2012). As an illustration of the level of the environmental problem of OMW, 10 million m³ year⁻¹ of OMW corresponds to the same load of sewage water generated from about 20 million people (McNamara et al. 2008). Moreover, most olive oil is produced in countries that are scarce in water resources. Thus, the need for efficient treatment and reuse of OMW is critical.

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Discharge of OMW directly to the soil may affect the soil's physical and chemical properties such as porosity and pH (Niaounakis and Halvadakis 2006; Karpouzas et al. 2010) and soil percolation and infiltration capability (Mahmoud et al. 2010). The OMW also contains high level of phytotoxic and microbial inhibitory compounds, such as phenolics and long-chain fatty acids (Mekki et al. 2006; Mechria et al. 2011). The main organic constituents of OMW are sugars and polyphenols. Sugars reported in OMW include fructose, mannose, glucose, saccharose, sucrose and pentose. Phenolic compounds available in olive stones result in concentrations ranging from 0.5 to 25 g l⁻¹ in OMW. The existence of these phenolic compounds also prohibits the use of OMW for irrigation purposes in agricultural production (El Hadrami et al. 2004). The various compositions of OMW and the broad geographical scattering of olive mills cause substantial technical and cost-effective barriers for the treatment of OMW (Marrara et al. 2002).

The need for disposal of OMW on the one hand and water scarcity and low soil fertility in olive producing countries on the other hand has brought about that large amounts of OMW are used for irrigation and fertility purposes in Syria and other Mediterranean countries. Recently, the Italian law has allowed a maximum yearly application of 80 m³ ha⁻¹ of OMW as a reasonable solution to land application of OMW (Giuffrida 2010). In this case, OMW is considered as soil fertilizer, which is not dangerous to crops and can be disposed without causing environmental harm. The nutritional benefits of OMW, as well as its possible herbicidal activity (Ghosheh et al. 1999) and capability of inhibiting soil–plant pathogens (Kotsou et al. 2004) are extra benefits.

Soils in arid and semiarid regions have a very low microbial activity, low levels of microbial biomass, low nutrient availability and low organic matter content (OM) (Yaakoubi et al. 2010). As OMW is rich in OM, it represents an important source of nutrients for plants (Rinaldi et al. 2003). Inclusion of OMW into soil can encourage microbiological activity. Microbial activity and soil fertility are strongly correlated because of their role in mineralization of the OM elements (Saadi et al. 2007; Mechri et al. 2008). Yaakoubi et al. (2010) found that OMW is known to increase soil OM and the concentration of essential inorganic elements for plant growth. Piotrowska et al. (2006) and Cabrera et al. (1996) showed a temporary decrease in soil pH and increased salinity following agronomic application of OMW. Tardioli et al. (1997) mention that the addition of fresh OMW to soil increases the number of soil microorganisms, and induces a change in the microbial community. The addition of OM causes an increase in the number of bacteria, which form the first colonizers of the added OM (Stenström et al. 2001).

However, OMW application changes the biological, chemical and physical properties of soil (Jarboui et al. 2008; Saadi et al. 2007). Irrigation with wastewater has also been shown to decrease the saturated hydraulic conductivity and to enhance the soil's water repellency because of grease and oil accumulation in the topsoil (Gharaibeh et al. 2007; Travis et al. 2008). Soil water repellency could lead to non-equilibrium water flow and solute transport in soils (Jarvis et al. 2008). Negative effects of OMW on soil properties have also been recorded, including the immobilization of available N (Mechria et al. 2011) and either decreases or increases of available elements and salts (López et al. 1996). In many studies, various effects of wastes applied to soil were recorded, but mainly occurred shortly after amendment (Albich et al. 2000; Martens et al. 1992). Additionally, not enough information is available to allow the safe agricultural use of OMW (Azbar et al. 2004). The results sometimes differed and were impractical in that they did not provide realistic conclusions. Moreover, very few studies, to our knowledge, investigated the impact of OMW on the transport and hydraulic properties of the soil. Most of these studies were performed, at laboratory and small scales, to assess the impact of the direct application of OMW on the fertility of bare soils (Cabrera et al. 1996) and on the chemical properties and plant performance (Mekki et al. 2006). So far, little interest has been given to the impact of OMW land application on selected soil hydraulic properties and on the soil flow and transport properties. The main objectives of this study were to investigate the effects of OMW application on selected soil hydraulic properties (soil moisture retention and unsaturated hydraulic conductivity) and on the flow and transport behavior of soil being irrigated with OMW for 5 and 15 years at field sites located in southwestern part of Syria, 15 km to the east of the city of Daraa for 2 years from 2007 to 2009.

Materials and methods

Field experiment site

This study was conducted at a field site located in southwestern Syria, 15 km to the east of the city of Daraa, at an altitude of 435 m above sea level. Three nearby farms were selected with different irrigation practices: farm 1 was irrigated with freshwater and farms 2 and 3 were frequently irrigated with untreated OMW for 5 and 15 years, respectively. The freshwater-irrigated farm and the farms irrigated with OMW for 5 and 15 years are noted as T0, T5, and T15, respectively. The olive orchards at all sites were irrigated by drip irrigation during the growth period. However, during the olive mill operation (from early October to late

December), farms T5 and T15 were irrigated with OMW by furrow irrigation. The annual OMW contaminant in the irrigated lands mostly depends on the annual OMW production. Farms were plowed once in spring and early summer and one to three times in late summer and autumn according to the local agricultural management practices. The soils are Cambisols (FAO classification), characterized by high calcium carbonate content and moderately alkaline pH (Table 1). The OMW characteristics depend on the olive variety and ripeness, as well as on the oil extraction method. Some physical and chemical properties of the OMW at the experimental site are shown in Table 2.

Laboratory measurements

Soil sampling

The soil samples were collected from December 2007 until January 2008. Six undisturbed soil columns (14.4 cm in diameter and 20 cm long) were collected for leaching experiments in two replicates at water content relatively lower than field capacity. Before soil sampling, the soil surface layer was cleaned and the soil columns taken from a depth of 5 to 25 cm. The soil columns were stored at 4 °C until transport and leaching experiments were conducted. After the experiments were performed completely, eight undisturbed soil samples were collected at two depths of 0–10 and 10–20 cm (four soil samples of size 7.2 cm in diameter and 6.15 cm long, and four soil samples of size 5.0 cm in diameter and 5.1 cm long) for soil hydraulic properties and bulk density measurements, respectively. Disturbed soil samples also were collected from the soil

Table 1 Chemical and physical characteristics of soil properties of control (T0), 5 (T5) and 15 (T15) years of OMW application

Treatments	T0	T5	T15
ρ_b (g cm ⁻³)	1.33 ^a	1.16 ^b	1.11 ^b
CO ₃ (%)	15.40 ^a	16.35 ^a	18.54 ^b
C _{org} (%)	0.64 ^a	4.65 ^b	7.68 ^c
N (%)	0.093 ^a	0.29 ^b	0.60 ^c
C/N	6.87 ^a	15.85 ^b	12.77 ^b
Humus (%)	2.63 ^a	6.82 ^b	11.12 ^c
pH	7.93 ^a	7.73 ^a	7.81 ^a
Clay (%)	24.20	21.90	18.60
Silt (%)	74.50	76.50	78.80
Sand (%)	1.30	1.70	2.60
Total porosity (%)	50 ^a	56 ^a	58 ^b
Drainable porosity (%)	7.40 ^a	6.47 ^a	4.18 ^b

ρ_b soil bulk density (g cm⁻³), C_{org} organic carbon (%), N nitrogen content (%), C/N carbon-to-nitrogen ratio

Superscripts indicate significant differences ($P < 0.05$) between treatments

Table 2 Chemical characteristics of olive mill wastewater and fresh water used for irrigation

Parameters	Olive mill wastewater	Fresh water
pH	5.07	7.60
Electric conductivity (dS m ⁻¹)	9.75	1.01
Dry matter (g l ⁻¹)	33.25	
Organic matter (g l ⁻¹)	30.57	
Mineral matter (g l ⁻¹)	2.69	
Specific weight (g cm ⁻³)	1.03	
Cl (mg l ⁻¹)	763.8	82.0
Br (mg l ⁻¹)	18.42	Non detectable
NO ₃ (mg l ⁻¹)	1.19	1.11
PO ₄ (mg l ⁻¹)	426.12	0.08
SO ₄ (mg l ⁻¹)	174.48	54.90
Na (mg l ⁻¹)	128.8	50.70
K (mg l ⁻¹)	1,050.9	6.75
Ca (mg l ⁻¹)	137.5	51.80
Mg (mg l ⁻¹)	168.3	28.30

columns from the same depths. The disturbed soil samples were analyzed for each soil column (four soil samples per treatment). The soil bulk density (ρ_b) was measured by the core method (Blake and Hartge 1986). Total carbon and nitrogen were determined with the Elementar Vario EL analyzer (Elementar Analysensysteme GmbH, Hanau, Germany), while carbonate content was determined separately with Scheibler equipment. The macroporosity was assumed to be equal to the drainable porosity (Φ_d). The drainable porosity was calculated as $\Phi_d = \theta_s - \theta_{fc}$, where θ_s (cm³ cm⁻³) is volumetric water content at saturation and θ_{fc} (cm³ cm⁻³) is volumetric content at field capacity.

Transport and leaching experiment

Transport and leaching experiments were conducted in all columns under unsaturated steady-state flow conditions, using laboratory equipment described by Rambow and Lennartz (1993) (Fig. 1). The apparatus can be used under many upper and lower conditions to study the leaching behavior of chemical transport in undisturbed soil columns (Fig. 2). Four columns were simultaneously mounted on the experimental setup; a pressure of -20 hPa was maintained throughout the experiment at the lower end of the soil columns. After 2 days of steady-state equilibration, 20 ml of bromide (700 mg L⁻¹ of Br) in the form of potassium bromide (KBr) was applied pulse-wise with a surface density of 0.088 mg cm⁻² as a nonreactive tracer in the column experiments. Following pulse application of bromide at the soil surface of the columns, effluent volumes were measured at regular intervals to determine the flux density of water. The column leachate was collected at 2, 3 and 24 h intervals

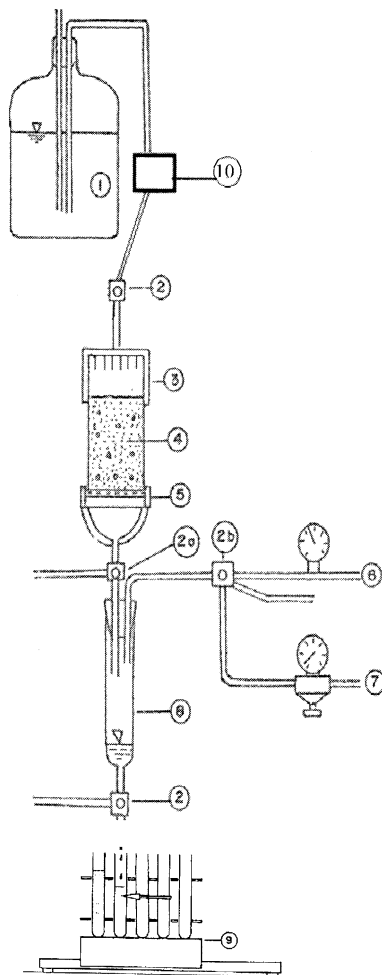


Fig. 1 Schematic diagram of the experimental set-up. 1 Mariotte bottle, 2 magnetic valve (2a and 2b), 3 sprinkler, 4 soil column, 5 porous plate and nylon membrane, 6 suction supply, 7 pressure supply, 8 vacuum lock, 9 fraction sampler, 10 impulse pump

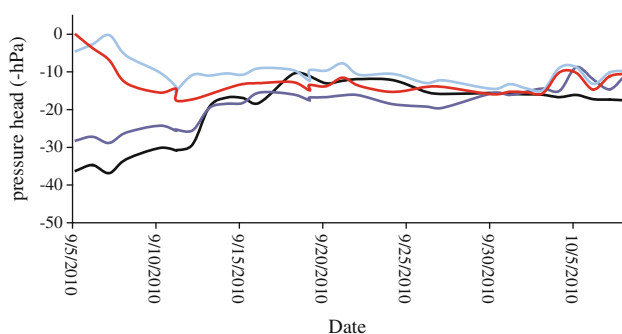


Fig. 2 Observed tensiometers suction during the test of T15 treatments

for T0, T5 and T15, respectively. The total duration was 12, 18 and 94 days for T0, T5 and T15, respectively, which corresponded to approximately two pore volumes. After termination of the experiment, irrigation was stopped for 1 day. Soil samples were taken for hydraulic conductivity,

soil water retention curve (WRC), water content and soil bulk density measurements. All leachate samples were stored at 4 °C until analyzed.

Determination of WRC and unsaturated hydraulic conductivity

The WRC was determined at eight different matric suctions (ψ). The undisturbed saturated samples were drained at 0, -30, -50, -100, -200, -300 and -600 hPa on ceramic plates. When the samples attained equilibrium with the applied vacuum, the soil sample weights were taken. Finally, the samples were dried in an oven at 105 °C for 24 h to determine the water content at each applied pressure (Hartge and Horn 1989). Bulk density, ρ_b , was calculated with the core method for each soil sample to calculate volumetric water content (θ) (Hartge and Horn 1989). WRCs were integrated between top and bottom boundaries for comparison of WRCs among treatments. The van Genuchten's model was selected (Van Genuchten's 1980). The van Genuchten's model is:

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{[1 + (\alpha_v \psi)^n]^m} \quad (1)$$

where ψ is the matric suction (hPa); θ is the volumetric water content ($\text{cm}^3 \text{cm}^{-3}$); θ_s is the saturated water content ($\text{cm}^3 \text{cm}^{-3}$); θ_r is the residual water content ($\text{cm}^3 \text{cm}^{-3}$); α_v is a parameter, the inverse of which, $1/\alpha_v$, is an indication of the suction at the air-entry point (hPa^{-1}); and n and m are the dimensionless parameters related to the homogeneity of the pore size distribution. The experimental data for soil water retention were best fitted to van Genuchten's model with optimization software RETC (US Salinity Laboratory, USDA, ARS) (Marquardt 1963). θ_r was considered equal to soil water content at the permanent wilting point ($\theta_{-15,000 \text{ hPa}}$) (Mohawesh et al. 2005).

The soil hydraulic conductivity (K) was determined for undisturbed soil samples (250 cm^3 , 7.2 cm in diameter and 6.15 cm long) in four replicates; two tensiometers were installed at depths of 1.5 and 4.5 cm from the surface. The samples were saturated with water from the bottom. After saturation, water was again released by free drainage. The samples were then sealed at the bottom with the surface remaining open to evaporation. Tensiometer readings (ψ) and sample mass (m) were measured at regular time intervals. The hydraulic gradient ($\Delta h/\Delta x$) was calculated on the basis of the tension values. The flux (q) was derived from the soil water volume difference ΔV (1 cm^3 of water = 1 g) per surface area (A) and time unit (Δt). The experimental data of soil hydraulic conductivity were fitted to Mualem's model (Mualem 1976) (Eq. 3) by using RETC optimization software:

$$K(\theta) = K_s \Theta^l [1 - (1 - \Theta^{1/m})^m]^2 \quad (2)$$

where K_s is the saturated hydraulic conductivity (cm day^{-1}), l is a fitting parameter (dimensionless), Θ is the dimensionless water content ($\Theta = (\theta - \theta_r)/(\theta_s - \theta_r)$), and n and m ($m = 1 - 1/n$) are dimensionless parameters. For the optimization of soil hydraulic conductivity parameters, logarithmic values of $K(\theta)$ were used to account for its log-normal distribution (Mohawesh et al. 2005).

Analytical procedure

Leachate samples were analyzed for bromide with an ion chromatography system consisting of a Metrohm pump (model 709) and a Metrohm conductivity detector (model 732) with a temperate measuring cell. A Metrohm ion separation column (Super-Sep; 10,054.6 mm i.d.) served for the stationary phase. The flow rate of the mobile phase [2.5 mM phthalic acid buffered at pH 4.2 with tris (hydroxymethyl)-aminomethane] was adjusted at 1.5 ml min^{-1} .

Breakthrough curve and data treatment

The analytical solution of equilibrium and non-equilibrium for the prescribed boundary condition was used to estimate the transport parameters of Br. The conventional equilibrium model for one-dimensional solute can be written as follows (Van Genuchten and Alves 1982):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D(x, t) \frac{\partial C}{\partial x} - u(x, t) C \right) \quad (3)$$

where C is the solute concentration at position x along the longitudinal direction at time t (M L^{-3}), D is the solute dispersion coefficient ($\text{L}^2 \text{T}^{-1}$), and u is the medium's flow velocity (L T^{-1}), t is the time (T), x is the distance (L).

The non-equilibrium model assumes the liquid phase to be partitioned into a mobile and an immobile region, with water flow limited to the mobile region. The model can be given in dimensionless form as follows (van Genuchten and Wierenga 1976):

$$\begin{aligned} \beta R \frac{\partial C_m}{\partial T} + (1 - \beta) R \frac{\partial C_{im}}{\partial T} &= \frac{1}{P_m} \frac{\partial^2 C_m}{\partial X^2} - \frac{\partial C_m}{\partial X} \\ (1 - \beta) R \frac{\partial C_{im}}{\partial T} &= \omega(C - C_{im}) \end{aligned}$$

where

$$\begin{aligned} P_m &= v_m L / D_m \\ \beta &= (\theta_m + \rho_b f k_d) / (\theta + \rho_b k_d) \\ \omega &= \alpha L / q \end{aligned} \quad (4)$$

where subscripts m and im refer to the mobile and immobile regions, respectively; f is the fraction of adsorption sites in the mobile region (dimensionless); v_m is the mean pore velocity of the mobile region ($=q/\theta_m$); $\omega = \alpha L/q$, α is the first-order mass transfer coefficient

between mobile and immobile regions (T^{-1}); D_m (cm^2/day) is the dispersion coefficient of the mobile region; k_d is the linear adsorption coefficient (L m^{-3}); P is the column Péclet number ($=vL/D$), ρ_b is the soil bulk density (M L^{-3}), L is the column length (L); θ_m and θ_{im} are the volumetric water contents of the mobile and immobile regions ($\theta = \theta_m + \theta_{im}$), respectively; and C_m and C_{im} are the solute concentrations in mobile water and immobile water, respectively. Assuming equal R for the two regions and the fraction f equal to θ_m/θ (Wierenga and van Genuchten 1989), β and $1 - \beta$ represent the relative fractions of mobile and immobile water, respectively.

The transport parameters of both equilibrium and non-equilibrium breakthrough curves (BTCs) were estimated with the curve fitting program CXTFIT (Parker and van Genuchten 1984). Br concentrations were expressed in dimensionless form, $C(T)/C_0$, with $T = vt/L$.

Statistical analysis

Statistical assessments of differences at $P = 0.05$ between mean values were performed using the software package SPSS 17.

Results and discussion

Effect of OMW application on soil physical and chemical properties

Soil analyses showed unexpected results that soil organic carbon and humus content increased significantly from 0.64 and 2.63 % for T0 to 4.65 and 6.82 % for T5 and 7.68 and 11.12 % for T15, respectively (Table 1). The total nitrogen of soil also increased significantly by OMW application from 0.093 % for T0 to 0.29 and 0.60 % for T5 and T15, respectively (Table 1). Bulk density, ρ_b , decreased significantly with the application of OMW, a trend that was expected because of the increasing content of organic matter in the soil (Table 1). The soil texture was silt loam, and the soil color was 7.5 YR 4/3. Chemical characteristics of OMW were determined using a repeated-measures analysis (Table 2).

Impact of OMW on bromide transport and BTC

The bromide behaviors are characterized by the occurrence of peak BTCs at less than 0.7 pore volumes, indicating the presence of immobile water in all treatments (Fig. 3). The maximum concentration peak of the BTCs appeared slightly earlier in the soils irrigated with OMW than in the soil irrigated with freshwater (Table 3). This behavior could be related to the presence of dissolved organic matter which initially facilitates the leaching of the tracer by

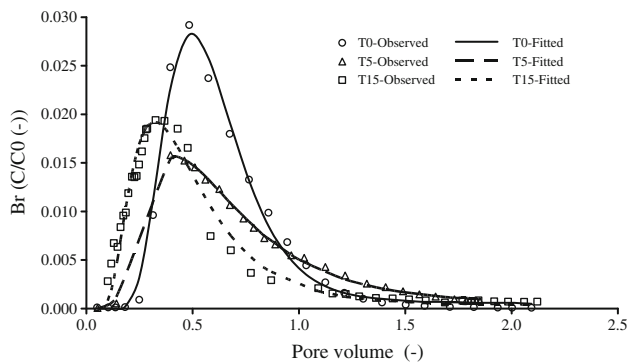


Fig. 3 Observed and fitted breakthrough curves of T0, T5 and T15 treatments

Table 3 Fitted transport parameters of breakthrough curves of T0, T5 and T15 treatments

Treatment	T0	T5	T15
Pulse duration (<i>T</i>) (day)	12	18	94
Pore velocity (<i>v</i>) (cm day ⁻¹)	4.01	1.78	0.47
Dispersion coefficient (<i>D</i>) (cm ² day ⁻¹)	4.861	5.896	1.951
Dispersivity (<i>λ</i>) (cm)	1.215	3.4279	4.151
Relative fractions of mobile water (<i>β</i>)	0.6065	0.6148	0.6023
First-order mass transfer coefficient (<i>ω</i>)	0.1779	0.1711	0.1783
Peak concentration (<i>C/C₀</i>)	0.028	0.016	0.019
Pore volume at peak (-)	0.5	0.4	0.3
Mass transfer coefficient (<i>α</i>) (day ⁻¹)	0.01779	0.004114	0.000157
Soil bulk density (<i>ρ_b</i>) (g cm ⁻³)	1.33	1.16	1.11
Coefficient of determination (<i>R</i> ²)	0.98	0.99	0.94

enhancing the water solubility through an organic matter tracer association, giving rise to an earlier breakthrough (Santos-Buelga et al. 1992). However, the Br BTC in T0 has a higher concentration peak ($C/C_0 = 0.028$) compared with the BTCs of T5 ($C/C_0 = 0.016$) and T15 ($C/C_0 = 0.018$) treatments, indicating an overall effect of reduction in the total amounts leached from soil that was irrigated with OMW (Table 3). The total Br recovery decreased from 98 % in T0 to 88 and 78 % in T5 and T15 soils, respectively.

The actual water movement through the soil columns was considerably slower in the case of T5 and T15 treatments due to the significant changes that occurred in pore size distribution (lower macropore and higher micropore content). The combined effect of the suspended and soluble organic matter and salts in OMW caused these changes in pore size distribution (Table 2). The different pore size distributions were also found with OMW amendments because of the high OM and salt content of these liquid

wastes (López et al. 1996), which cement and aggregate the soil particles together, blocking large-sized pores (Mahmoud et al. 2010).

The slow exchange of Br by diffusion between the mobile and immobile phase that developed in the small pore sizes increases the resident time of Br in soil columns and even the physical sorption by pore entrapment. The assumption of limited mass transfer between the mobile and immobile phase is supported by the fitted mass transfer coefficient values ($\alpha = w\theta v/L$), which decreased with OMW application. α values were decreased from 0.01779 in T0 to 0.00414 and 0.000157 day⁻¹ in T5 and T15, respectively. The dispersivity ($\lambda = D/v$) increased in soil irrigated with OMW; λ values were 1.215, 3.4279 and 4.151 cm for T0, T5 and T15 treatments, respectively (Table 3). The application of water may cause clay dispersion, as a result, its movement and lodgement into conducting pores might cause a reduction in the measured hydraulic parameters. However, as the water was used in the whole experiments, its effect was relatively the same among the whole experiments. Thus, it does not affect the comparison between the treatments. Although ρ_b was significantly decreased with OMW for irrigation, a significant

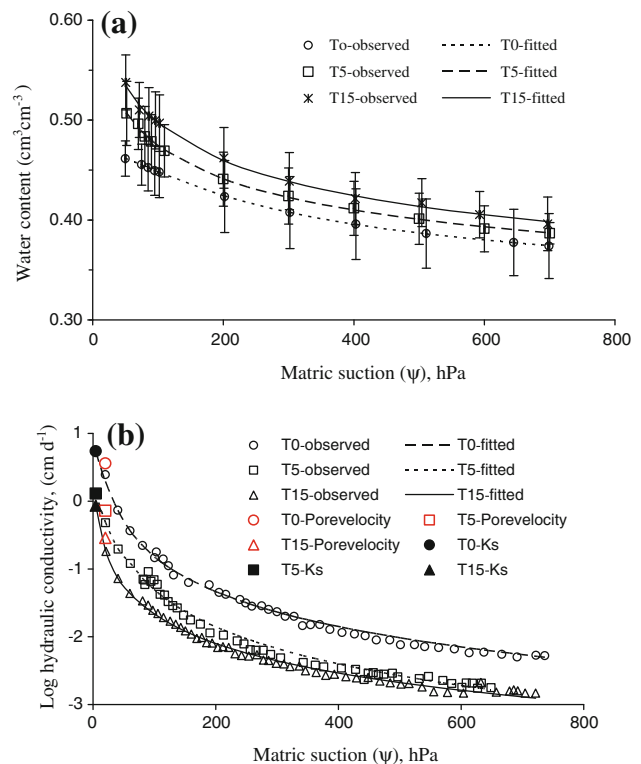


Fig. 4 Effect of OMW on soil water retention curves (a) and soil hydraulic conductivity (b) for T0, T5 and T15 treatments. Large symbols represent pore velocity for each treatment from transport and leaching experiments. Dark symbols represent saturated hydraulic conductivity measured for undisturbed soil samples from the soil columns

Table 4 The fitted van Genuchten's model parameters of soil water retention and soil hydraulic conductivity for T0, T5 and T15 treatments

Treatment	θ_s (cm ³ cm ⁻³)	θ_r (cm ³ cm ⁻³)	α_v (hPa ⁻¹)	n	m	l	Ks (cm day ⁻¹)	R^2 (K)	R^2 (pF)
T0	0.472 ^a	0.303 ^a	0.067 ^a	1.536 ^a	0.350	-2.484 ^a	5.472 ^a	0.97	0.99
T5	0.592 ^b	0.318 ^a	0.0512 ^b	1.193 ^b	0.162	-3.033 ^b	1.296 ^b	0.96	0.99
T15	0.623 ^b	0.318 ^a	0.0455 ^b	1.202 ^b	0.168	-3.880 ^b	0.864 ^c	0.99	0.99

reduction in large pores (macropores) and an increase in finer pores (meso- and micropores) were observed (Table 1). The change in pore size distribution and lower bulk density in T5 and T15 enhances bromide diffusion as a result of significant higher soil water-holding capacity and more organic matter. While the chemical composition of OMW might cause soil and water pollution, its use in agriculture is promoted because of the high content of plant nutrients and OM (Lozano-García et al. 2011). In semi arid and arid regions, OMW can be applied to soil to improve its physical, chemical and biological properties (Mekki et al. 2006; Mechri et al. 2008).

WRC and unsaturated hydraulic conductivity

The OMW significantly increased the water retention capacity of the soils in all treatments (Fig. 4a). This effect can be seen from the shape of the WRC, primarily in the low-suction range. The high organic matter content in OMW significantly improved the soil water-holding capacity, despite significantly reducing the large macropore percentage. On the other hand, the volume of intermediate-sized pores is significantly greater in OMW treatments (Table 1). Table 4 shows the van Genuchten's model parameters for T0, T5 and T15 treatments. The significant reduction of large soil pores was found with OMW amendment because of the higher organic matter and salt content of these liquid wastes, which blocked large-sized pores (Mahmoud et al. 2010). It is also apparent that fluctuation in soil water retention capacity among different treatments resulted from the aggregation effects of OMW application on pore size rather than from other factors; hence, this fluctuation is mainly affected by soil structure (Gharaibeh et al. 2007).

The experimental data of soil hydraulic conductivity were fitted to Mualem's model (Eq. 3) with RETC optimization software (Table 4). The hydraulic conductivity significantly decreased with the application of OMW at applied matric suctions (Fig. 4b). It is reasonable to assume that the application of OMW plays an important role in pore size, shape and orientation and, as a result, these are the principal factors influencing hydraulic conductivity. The soil irrigated with OMW had a significantly higher organic matter content, a lower bulk density (1.33, 1.16 and 1.11 g cm⁻³ for T0, T5 and T15, respectively) and relatively significant higher total porosity (50, 56 and 58 % for T0, T5 and T15, respectively), but a significantly lower

macroporosity than that of control sites (7.40, 6.47 and 4.18 % for T0, T5 and T15, respectively). The significant decrease in macroporosity with OMW application can be explained by the higher air-entry point of the soil retention curve and lower soil hydraulic conductivity (Mahmoud et al. 2010; Vogeler 2008; Gharaibeh et al. 2007).

Conclusion

This study investigated the effects of OMW application on selected soil hydraulic properties of soil that had been irrigated with OMW. Bromide behavior was characterized by the occurrence of peak BTCs at less than 0.5 pore volumes, indicating the presence of immobile water in all treatments. Initial breakthrough in T5 and T15 occurred earlier than it did for T0 treatment. The slow exchange of bromide by diffusion between the mobile and immobile phase was supported by the fitted mass transfer coefficients. The soil water retention capacity was significantly higher in T15 and T5 treatments compared with that for T0. The high organic matter content in OMW improved the soil water-holding capacity despite reducing significantly the large pore (macropore) percentage. The hydraulic conductivity decreased significantly with the application of OMW at the applied suction head. We concluded that the soil aggregates were increasingly coated with complex organic molecules originating from OMW, as a result, solute exchange between inter- and intrasoil aggregate water was hindered. Although OMW application affected relative total porosity, the pore space available, for nutrient exchange processes, for instance, was less. Even though OMW could cause soil and water pollution, its use in agriculture is promoted because of the high content of plant nutrients, such as N, P, and K and OM. In arid and semi arid regions, OMW can be applied to soil to improve its physical, chemical and biological properties.

Acknowledgments This study was kindly supported by a Deutsche Forschungsgemeinschaft (DFG) grant and the sponsor of the Institute of Land Use, Rostock University.

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