EFFECTS OF OLIVE MILL WASTEWATER APPLICATION ON A MEDITERRANEAN TUNISIAN SOIL UNDER CLIMATIC SEQUENCE SIMULATING SEASONAL CHANGES IN THE COURSE OF ONE YEAR: LYSIMETER EXPERIMENT

by

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Date of the oral examination:

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DECLARATION

I hereby declare that I autonomously conducted the work shown in this Ph.D. thesis entitled "Effects of Olive Mill Wastewater Application on a Mediterranean Tunisian soil under climatic sequence simulating seasonal changes in the course of one year: Lysimeter experiment". All used assistances and involved contributors are clearly declared. This thesis has never been submitted elsewhere for an exam, as a thesis or for evaluation in a similar context; to any department of this university or any scientific institution.

Landau in der Pfalz,

Place, date **signature (Emna Kammoun)**

PARTS OF THE THESIS AND OWN CONTRIBUTIONS

This PhD thesis consists of four chapters, amongst the others, that represent two experiments. The experiments were conducted at the Institute of Environment Sciences, RPTU - Rheinland-Palatine Technical University Kaiserslautern Landau.
My input into the scientific planning of the experiments was guided by the project's objectives and the research outcomes. As a result, research priorities and questions were purposefully adjusted to align with the discoveries made during the project.

The experiments carried out within the framework of the thesis are divided as follows:

Chapter 2 Effects of olive mill wastewater on soil leachate properties under climatic sequence: lysimeter experiment
My own contribution to this experiment includes soil sampling, preliminary field characterization, preliminary experiments, conception of the lysimeter experimental design, water samples analysis, all conducted laboratory measurements and data evaluation.

Chapter 3 Olive mill wastewaters hydrophobic effect on soil vertical degradation - a lysimeter study
All soil analysis in this chapter were carried out at the institute of environmental sciences RPTU - Rheinland-Palatine Technical University Kaiserslautern Landau. Dismantling of soil columns, the additionally conducted soil measurements OCAT, CHNS, SPC, SUVA and detailed data evaluation were done by myself. ^{1}H-NMR relaxometry measurements of soil samples were done with the support of Dr. Christian Buchmann.

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TABLE OF CONTENTS

ABSTRACT

Olive mill wastewater (OMW) is a by-product of olive oil extraction and its disposal on soil has been associated with significant environmental challenges, including toxic effects on soil organisms and quality of groundwater due to its high phenolic content. Recent studies focusing on the dynamics of OMW degradation in soil are handling the environmental conditions as main factors influencing the fate and transport of polyphenols in the soil-water system. The understanding of seasonal-dependent phenol leaching from OMW-treated soil remained elusive, as field studies are hindered by spatial variability and complex environmental dynamics. Therefore, controlled lysimeter experiments were conducted to investigate the leaching and transport mechanisms of OMW-derived phenolic compounds in soil.

This thesis presents the results of an 18-week lysimeter experiment conducted in a laboratory setting, aimed at monitoring and comprehending the distribution and leaching of OMW-derived phenolic compounds in soil after OMW application. The experiment spanned four seasonal simulation phases, including two winter, one spring, and one summer, under semi-arid climate Tunisian conditions. The effects of OMW on soil leachates properties, soil water repellency, and soil water retention capacity were assessed.

The soil leachates exhibited varying degrees of recovery across the different simulation phases. However, persistent salinity in the leachates and high soil water repellency at the top treated OMW-soils were recorded. The findings revealed also that OMW application changed the pore size distribution in treated OMW-soils. Most of the OMW-derived phenols were immobilized in the upper 5 cm of the soil. Notably, soluble phenolic compounds exhibited the formation of coarser pores for the sake of fine pores, suggesting that OMW- organic carbon played a crucial role in controlling the depth-dependent transport mechanisms of OMW within the soil matrix.

In conclusion, this study provides valuable insights into the fate and impact of OMW-derived phenolic compounds in soil. It emphasizes the significance of conducting OMW applications with careful irrigation practices and thorough phenol leaching surveys to minimize the risk of potential groundwater contamination. Additionally, more experiments are warranted to investigate the sorption capacity of the soil during and after OMW application and its influence on the stability of soluble phenolic compounds in soils.

ZUSAMMENFASSUNG

Olivenmühlenabwasser (OMW) ist ein Nebenprodukt der Olivenölgewinnung, dessen Aufbringung auf Böden mit erheblichen Umweltproblemen verbunden ist, einschließlich toxischer Auswirkungen auf Bodenorganismen und Grundwasser aufgrund des hohen Gehalts an phenolischen Verbindungen. Das Verständnis für die saisonabhängige Verlagerung oder Auswaschung von Phenolen aus OMW behandelten Böden ist bisher ungeklärt, da Feldstudien durch räumliche Variabilität und komplexe Umweltdynamik erschwert werden. Daher wurden kontrollierte Lysimeter-Experimente durchgeführt, um die Auswaschung und biologischen Abbaumechanismen von aus OMW stammenden phenolischen Verbindungen im Boden zu untersuchen.

Diese Arbeit präsentiert die Ergebnisse eines 18-wöchigen Lysimeter-Experiments, das unter Laborbedingungen durchgeführt wurde, um die Verteilung und Auswaschung von aus OMW stammenden phenolischen Verbindungen im Boden nach der Anwendung von OMW zu überwachen und zu verstehen. Das Experiment erstreckte sich über vier Phasen saisonaler Simulationen, einschließlich zwei Winter-, einer Frühjahrs- und einer Sommerphase, unter den semi-ariden klimatischen Bedingungen Tunesiens. Dabei wurden die Auswirkungen von OMW auf Bodeneigenschaften, Bodenwasserabweisung und Wasserrückhaltevermögen erfasst und systematisch bewertet. Die Ergebnisse zeigen, dass die Anwendung von OMW sich positiv auf die Bodenfruchtbarkeit auswirkte, aber auch die Bodenbenetzbarkeit erniedrigte und zu einer verstärkten Bindung von Wasser in den behandelten OMW-Böden führte, was zu einer Verstopfung der Bodenporen beitrug. Die meisten der aus OMW stammenden Phenole wurden in den oberen 15 cm des Bodens immobilisiert. Bemerkenswerterweise wiesen lösliche phenolische Verbindungen in gröberen Poren höhere Konzentrationen auf als in feineren Poren, was darauf hindeutet, dass organischer Kohlenstoff aus OMW eine entscheidende Rolle bei der Kontrolle der tiefschichtabhängigen Hydrophobie und Transportmechanismen von OMW innerhalb der Bodenmatrix spielte. Die Studie betont, dass Auswaschung während regnerischer Phasen und Verdunstung sowie kapillarer Aufstieg während trockener Phasen zu wiederholten Zyklen erhöhter Kohlenstoffflüsse in mit OMW behandelten Böden führen können. Darüber hinaus unterstreicht die Forschung die Bedeutung der Berücksichtigung hydraulischer Eigenschaften und saisonaler Variationen bei der Bewertung des Risikos einer mit OMW verbundenen Grundwasserkontamination.

Zusammenfassend liefert die vorliegende Studie wertvolle Erkenntnisse über das Schicksal und die Auswirkungen von aus OMW stammenden phenolischen Verbindungen im Boden. Sie betont die Bedeutung, OMW-Applikationen in der Frühlingszeit durchzuführen, unter sorgfältiger Bewässerung und auf Basis eines versierten Phenol-Monitorings, um das Risiko einer Grundwasserkontamination zu minimieren. Darüber hinaus sind weitere Experimente erforderlich, um die Sorptionskapazität des Bodens während und nach der Anwendung von OMW zu untersuchen und deren Einfluss auf die Stabilität löslicher phenolischer Verbindungen im Boden abschätzen zu können.

1 INTRODUCTION

1.1 OLIVE OIL PRODUCTION

Olive oil is a product with great importance in the Mediterranean diet (Maffia et al., 2020). Each year, about 1.6 million tons of olive oil are extracted in the Mediterranean basin representing more than 96% of the total olive oil extracted worldwide (Souilem et al., 2017). The leading countries in olive oil production are Spain, Italy, Greece and Tunisia (Jeguirim et al., 2020). Tunisia is among the largest olive oil exporters, ranked second after the European Union and fourth after Spain, Italy, and Greece with an annual average export of more than 100,000 tons (Mtimet et al., 2013). The European Community, is by far the most important customer for Tunisian olive oil producers (Bouaziz et al., 2010). The Tunisian market share reached 8.8% on the European market. Most of the exports are carried out in bulk and concern in good part of unrefined oils (B. Karray, 2006). The governorate of Sfax in Tunisia provide 228,000 tons and contains 400 oil mills with a capacity of more than 12,000 tons / d (Mtimet et al., 2013).

The process of olive extraction includes the crushing of olive fruits and obtaining an oleaginous juice and the separation of oil from pomace (Jeguirim et al., 2020). Typically, three kinds of oil extraction techniques are commonly used: The pressure process (olive presses), two-phases separation system and three-phases separation system. A two-phases system is fully applied in Spain while in Italy, Greece and Tunisia still both systems are used, but mainly the three- phases system (Jeguirim et al., 2020). In the three phases system, the extraction of olive oil is achieved through discontinuous (pressing) or continuous (centrifuging) processes in traditional mills or in modern units (Dermeche et al., 2013). Water is used in some of these steps to remove most of the oil from the olive. Once the olive fruit has been crushed, the resulting paste is mixed to increase the percentage of available oil and help small oil droplets to coalesce and agglomerate, thereby facilitating the separation of the oil and water phases (Dermeche et al., 2013).

The discontinuous pressing is the oldest and most widespread method for processing olive fruit to obtain olive oil. The invention of the hydraulic press was a revolution for old mills, and these presses are still used in improved traditional mills (Dermeche et al., 2013). The extraction of olive oil in Sfax is generally carried out using a continuous chain.

It also allows the obtaining of oil yields slightly higher than those obtained by the conventional three-phase decanter and the press system. The quality of olive oil depends harvesting, milling and storage (Jimenez-Lopez et al., 2020). The olive extraction by-products are classified as follows (Figure 1-1): 20% Virgin olive oil, 30% Fresh pomace and 50% olive mill wastewater (OMW) (Alkhalidi et al., 2023).

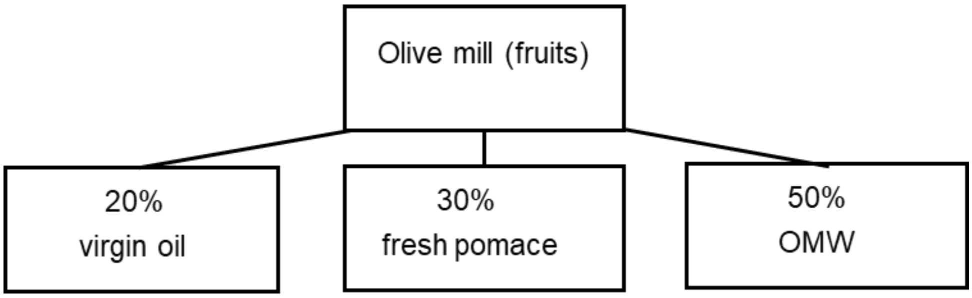

Figure 1-1 Olive processing schemes (Alkhalidi et al., 2023)

1.2 WASTEWATER GENERATION AND CHARACTERISTICS

Although the extraction technology plays an important role in reducing the amount of olive mill wastewater (OMW), the annual production of OMW exceeds 800,000 m³ in Tunisia over the winter season (Mekki et al., 2013).

The composition of OMW is very variable and depends on olive variety, soft tissues of the fruits, and the extraction process (press or centrifuge) (Cabrera et al., 1996). OMW is a turbid liquid with particular smell. Its typical composition by weight is: 83-94% water, 4-16% organic compounds and 0.4-2.5% mineral salts (Davies et al., 2004). Certain common characteristics were defined for OMW: low pH ranges, high biological and chemical oxygen demand, high concentration of oils and greases, high salinity and high load of phenolic compounds (Davies et al., 2004; Kurtz et al., 2015; Tamimi et al., 2016; Peikert et al., 2017).

The presence of high levels of phenolic compounds is the underlying cause of the black coloration in OMW. These compounds also contribute to its well-known toxic properties (R. Karray et al., 2022) and can be divided into those of low-molecular weight such as caffeic acid, tyrosol, p-cumaric acid, ferulic acid, and protocatechuic acid etc.) and of high molecular weight (tannins, anthocianins, etc) (Cbrera et al., 1996).

Phenolic compounds have been enlisted by the United States Environmental Protection Agency (USEPA) and the European Union (EU) as pollutants of priority concern (Anku et al., 2017). Polyphenolic content in OMW ranges from 5 to 25 g l^{-1} (Yangui & Abderrabba, 2018). During the olive extraction, most of the polyphenols get concentrated in the olive mill wastewaters, only 2% remain in the processed olive oil since they are water-soluble substrates of high polarity (Benamar et al., 2020). Much research has been carried out on numerous physicochemical methods for treating OMW, alone or combined, including oxidation, filtration, centrifugation, flocculation, incineration, coagulation, ultrafiltration, reverse osmosis, ozonation, or photolysis (Gomes et al., 2007). Many of these approaches are efficient for pollutant removal—namely monophenolic compounds and high organic charge and consequently quite useful as pre-treatment methods, but they are expensive and do not generate valuable sub-products (de Mattos Gonçalves et al., 2010). Therefore, the most frequently used methods nowadays are the direct discharge of OMW to agricultural soils and evaporation ponds. Actually, the OWM is considered to be 200 times more pollutant than the common urban wastewater (Yao et al., 2018). Furthermore, it was estimated that the load of phenolic compounds in OMW is 1000 times higher than in domestic wastewater (Niaounakis & Halvadakis, 2006). In this way, the pollution derived from OMW represents a social, economic, and environmental problem, which needs to be quickly solved (Rocha et al., 2022).

1.3 OLIVE MILL WASTEWATER DISPOSAL OPTIONS

OMW are characterized by the following chemical properties: a very high content of organic matter (COD between 60 and 185 g l^{-1} ; BOD5 between 14 and 75 g l^{-1}), a low pH, and high polyphenols, potassium and phosphorus contents (Rinaldi et al., 2003). Extremely high organic load and the toxic nature of olive mill wastewaters (OMW) are the main reasons for the prohibition of OMW discharging into municipal sewerage system. Currently, OMW is discharged into a sealed evaporation basin for evaporation, but this generates a lot of sludge and salts (Mekki et al., 2017).

In addition to other OMW treatment technologies that utilize physiochemical, chemical and biological (aerobic or anaerobic) treatment methods (Marques, 2001; Azbar et al., 2004; Kachouri et al., 2005). However, in Mediterranean countries such as in Tunisia, OMW-land disposal has been the most common practice as a low-cost alternative (Magdich et al., 2020).

Because of its geographical position, Tunisia faces two climates, the Mediterranean in the North and the Saharan in the South generating a spatio-temporal variability of water resources in the environment (Mkhinini et al., 2020). This situation makes Tunisia a country with low renewable resources, which is relatively rare and irregular. In addition to water deficiency in this region, the soil has a very low microbial activity and low nutrient availability (Di Bene et al., 2013). Meanwhile, agriculture is typically considered as one of the fields that requires huge amount of water to satisfy irrigation demands (Qadir et al., 2020). In this context, there has been a growing interest in identifying optimal approaches for applying OMW onto agricultural lands, to effectively recycle both the OM and nutrient content within the soil-crop system. OMW is considered a cost-effective and easily accessible alternative to fresh water (Mekki et al., 2013). Agriculturally, OMW can be used as soil biofertilizers (Chaâri et al., 2022). Moreover, positive effects on chemical fertility have been generally reported, but less attention has been paid to the effect on the groundwater quality. Therefore, until now, the application amount of OMW tosoils is limited. In Tunisia, the restriction related to the discharge of raw OMW is defined according to the standard NT.106.002 with an annual spreading of 50 m^3 ha^{-1} a^{-1} (Marks et al.,2020). By these legislations on upper limits for OMW discharge into the soil, countries try to mitigate the expected negative environmental impact on crop and soil. In spite of the restricted OMW disposal on soil, an uncontrolled disposal at even higher quantities than recommended must be assumed (Kavvadias et al., 2014). Although, the direct discharge of OMW into rivers and lakes is strictly forbidden, its illegal direct disposal of OMW into nearby aquatic resources and ecosystems is known to be a common practice (Marks et al., 2020).

1.4 ENVIRONMENTAL IMPACTS OF OLIVE MILL WASTEWATER DISPOSAL

Research during last 30 years ought to investigate extensively the impacts of OMW on the soil physical, chemical and biological properties (Sierra et al., 2001; Barbera et al., 2013; Buchmann et al., 2015; Kurtz et al., 2015; Peikert et al., 2015; Tamimi et al., 2017; Kurtz et al., 2021).
Various research studies have demonstrated the beneficial impact of olive mill wastewater (OMW) on soil fertility and crop growth (Casa et al., 2003; Cereti et al., 2004; Paredes et al., 2005). According to Rinaldi et al., (2003), the application of OMW does not lead to the accumulation of heavy metals in soil. However, recent studies have revealed that the unprocessed application of OMW leads to significant alterations in the composition and function of microbial communities, which ultimately impacts soil fertility (Sierra et al., 2001; Mekki et al., 2007). Moreno et al. (1987) warned against the indiscriminate use of untreated OMW, citing the potential for serious environmental concerns due to its antibacterial properties and phytotoxicity. Levi-Menzi et al. (1992) also highlighted the risk of OMW pollution to

surface and underground waters, given the high COD levels and the presence of phytotoxic and antibacterial polyphenols. Furthermore, the toxicity and ecological hazards associated with OMW can be attributed to the presence of phenolic compounds (Capasso et al., 1992; Aggelis et al., 2003).

In this regard, researchers have also investigated the potential negative impacts of OMW disposal to soil and how it alters soil quality. OMW-OM in soil has been found to have adverse effects such as reducing the saturated hydraulic conductivity and increasing soil water repellency (SWR) due to the accumulation of hydrophobic constituents, such as oil and grease, in the topsoil (Gonzalez et al., 1994; Mahmoud et al., 2010; Steinmetz et al., 2015). The development of soil water repellency in soil can lead to non-equilibrium water flow in soils, as reported by Jarvis et al. (2008). Peikert et al. (2015) concluded that each new and additional application of OMW may intensify the hydrophobic effect on soil. However, the quality of OMW-OM, rather than just its quantity, determines the degree of soil water repellency (Doerr et al., 2000).

All in all, the presence of phenolic substances in OMW has been identified as the main cause of its phytotoxic effects (Dalis et al., 1996; Buchmann et al., 2015). Manifold negative effects of OMW-derived polyphenols on soil physico-chemical properties and soil processes have already been recorded in the course of OMW disposal (Chaari et al., 2015; Kurtz et al., 2015; Tamimi et al., 2016). Further, phytotoxic effects were found when OMW was directly applied on soil as an organic fertiliser, resulting from their partly lipophilic character, which allow them to pass more easily through cell membranes (Buchmann et al., 2015; Enaime et al., 2020).The disposal of OMW on soil alters the soil microbial communities due to the high salinity and abundance of phenolic compounds, leading to inhibition of bacterial growth and an increase in the ratio of fungi to bacteria (Mekki et al., 2006; Barbera et al., 2013; Di Bene et al., 2013; Buchmann et al., 2015; Enaime et al., 2020). However, the adverse effects of OMW disposal on soil are generally observed immediately after discharge and tend to decrease over time.

Studies have found that using controlled doses of 50-100 m^3 ha^{-1} of OMW did not result in any long-term negative effects (Laor et al., 2011; Di Bene et al., 2013). This may be due to the degradation of OMW, its incorporation into soil organic matter (SOM), its adsorption to soil particles, or leaching. It is worth noting that OMW is mainly generated during the winter season and its land disposal mostly takes place during this period. However, the leaching of OMW in winter and its potential impact on groundwater contamination have been studied to a limited extent. The occurrence of phenolic compounds in the aquatic environment is therefore not only objectionable and undesirable but also poses a danger as far as human health and wildlife are concerned (Anku et al., 2017). Tamimi et al. (2016) demonstrated through field experiment that the transport and transformation processes of OMW vary depending on the soil moisture and temperature conditions during and after application. They concluded that throughout allseasons, preferential flow is the primary factor in short-term OMW-soil interaction. However,during the spring and summer months, capillary rise becomes a significant process in subsequent interactions. Azbar et al. (2004) reported potential groundwater contamination dueto OMW leaching during winter. Winter rainfall is known to facilitate the leaching of accumulated salts and phenolic compounds from the soil, which can reach deeper soil layers (up to 1.25m depth) and groundwater (Sierra et al., 2001; Zenjari & Nejmeddine, 2001; Boukhoubza et al., 2008; Tzanakakis et al., 2011; Kapellakis et al., 2015).

Previous studies have not been conclusive on the environmental risk or benefit of OMW disposal in the agricultural system overall. Since, in the field there is a high spatial variability and environmental dynamics in addition to uncontrollable degradation kinetics of OMW constituents. Especially the groundwater system was always questionable in terms of phenols leaching and the extent of contamination depending on the term, the rate and the environmental conditions. So far, little interest has been given to the study OMW phenolic compounds movement on the soil and their consequences on the groundwater. Since a part of phenols are soluble in water, their movement in the soil core should be investigated carefully during the OMW application which was scarcely done in the previous studies. Also, little interest has been given to understand OMW-soil leaching mechanisms causing undesired changes in soil solution quality and whether they are reversible or irreversible during the seasons. This current lack of knowledge results from the restricted adaptability of suitable leaching survey methods to study in-situ water percolation and OMW interaction in soil. Consequently, fundamental relationships between environmental conditions and soil-water interactions are only scarcely known and need to be further investigated under laboratory conditions.

1.5 OBJECTIVE AND STRUCTURE OF THE THESIS

The main objective of this PhD thesis is to understand the effect of OMW, particularly the phenolic fraction on soil leachates quality and soil water interactions in lab scale during and after OMW application to minimize the risk of OMW disposal on groundwater. In order to achieve this objective, it was necessary to develop, optimize and establish suitable testing methods and experimental designs to overcome the limitation of field studies. For this,lysimeter experiment under controlled moisture conditions has been developed in lab over a period of 18 weeks during which soil leachates quality tests were combined with water drop penetration time measurements. OMW has been applied using the same rate performed in Tunisian fields (14 L m^{-2}). The experiment included four simulation phases including all seasons: WS1 (First winter simulation) followed with SPS (Spring simulation), SS (Summer simulation) and finally finished with WS2 (second winter simulation). Temperature andmoisture have been adapted to Tunisian weather conditions. Under these conditions, it was possible to understand 1) how OMW leaching and associated soil-water interactions contributeto soil leachates quality 2) how mutual interactions of OMW constituents, in particular phenoliccompounds and soil particles, affect the water distribution in the porous soil system.

Within the framework of the PhD thesis, different experiments were conducted as subsequently divided into two chapters:

In the first step (Chapter 2) we investigated the potential and limitations of lysimeter setup for the identification of soil leaching quality in function of seasons during and after OMW application.

We hypothesized that OMW-derived, phenolic substances are the main reason for hydrophobic effects on soil due to their long persistence in the top soil and their low (bio-)degradability. Assuming that these phenolic substances have partly hydrophobic character, they ought to increase soil hydrophobicity under specific conditions which were cited above.

The environmental conditions such as temperature and soil moisture during and after the OMW disposal to soil are expected to influence the overall effects in soil leachates quality. Phenolic compounds are assumed to be higher in OMW treated soil leachates due to dilution and leaching of OMW-compounds as a subsequent impact of irrigation during winter simulation.

Under winter conditions, OMW is expected to percolate through the soil matrix, e, g., by a) infiltration: OMW enters the soil matrix through cracks and pores, or b) by dissolution: Some components of OMW dissolve in the soil water, allowing them to move more easily through the soil. So that, the artificial rainfall during the winter simulation is expected to promote leaching of soluble compounds into deeper layers (Tamimi et al., 2017). Through the transport by water flow, OMW is expected to be carried by water moving through the soil matrix.

Lower soluble phenolic compounds are expected to reach soil leachates in spring simulation since the simulation of Tunisian spring conditions is expected to increase and favor soluble phenolic compounds (SPC) biological degradation inside the soil resulting in lower toxicity in the soil leachates and lower repellency effects in the top soil. While under summer conditions SPC brought by OMW are expected to accumulate in the upper soil resulting in a reduction of phenolic content in the leachates. Phenols are assumed to bind by adsorption to soil particles, slowing their movement and most of them should be degraded or immobilized at the top soil horizons (Peikert et al., 2015). Simulating moist conditions in a second winter scenario after hot and dry conditions (summer simulation) is expected to minimize SPC in soil solution in the leachates compared to the first winter simulation.

To validate this hypothesis, the water leached through the polyamide membrane helping to adjust the matric potential under different simulated conditions will be collected from three OMW-treated lysimeters and one control. The leachates will be then quantified and analysed for pH, electrical conductivity (EC), soluble phenolic compounds (SPC), specific ultraviolet absorbance (SUVA) and total organic carbon (TOC) (Figure 1-2).

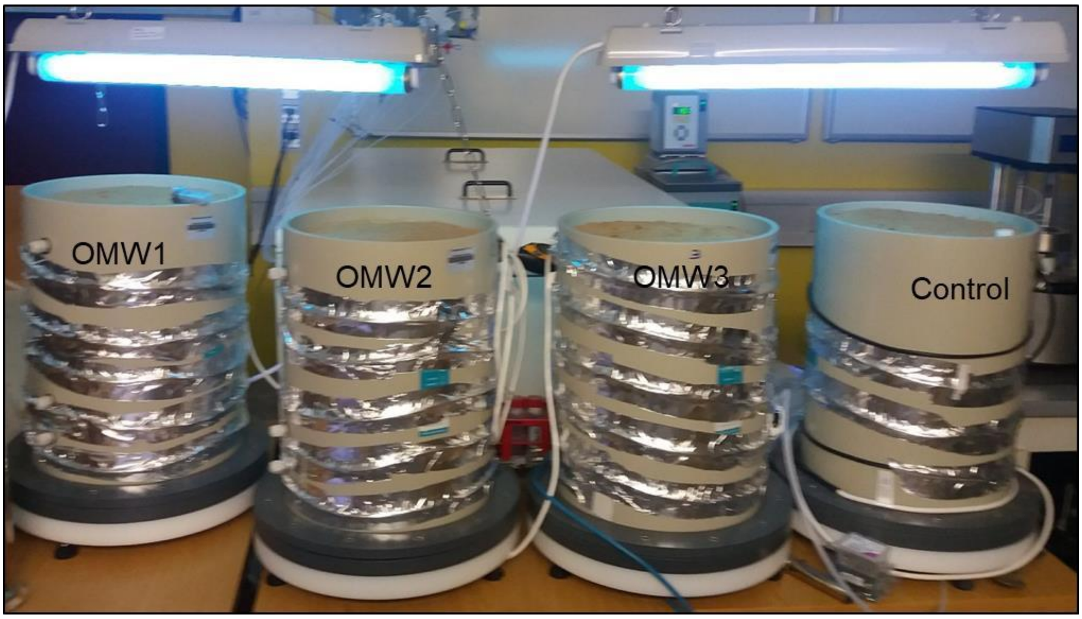

Figure 1-2 Design of laboratory lysimeter experiment for leaching analysis. Three lysimeters for OMW-treatment OMW1, 2 and 3 and one lysimeter control for irrigation with demineralized water only (own figure, Mesocosm laboratory, RPTU - Rheinland-Palatine Technical University Kaiserslautern Landau)

With this, we will obtain time-dependent information about the OMW constituents reaching 40 cm depth. Water balance and OMW constituents' mass balances will be assessed by balancing input and outflow amount and concentration (column outlet). Leachates will be analysed for specific UV absorption (254 nm), electrical conductivity (EC), pH, and soluble phenolic content (SPC). From the time-dependent composition of the leachates, we will conclude on transport times of the OMW constituents, especially the percentage of SPC leaving the top 40 cm of the soil body. Water drop penetration time (WDPT) will be measured daily and this will help to move one step closer to the differentiation of various water populations at the soil surface.

Based on the knowledge gained from the first experiment, we assumed that depth-dependent degradation of phenolic compounds in general should come along with a reduction of soil water repellency (SWR) since most of the hydrophobic components are expected to be immobilized in the upper layer (Chapter 3).

It has already been shown that both single and repeated OMW applications increased dissolved organic carbon content (Piotrowska et al., 2006; Brunetti et al., 2007; Di Bene et al., 2013; Kurtz et al., 2015) characterized by a higher ratio of aliphatic: aromatic compounds than in untreated control soils (Peikert et al., 2015). This hydrophobizing effect on soil may further increase and remain with each additional application of OMW (Peikert et al., 2015). Since SWR is a surface phenomenon that strongly depends on the surface areas coated and governed by the strength of mineral-organic interactions, a better understanding of the mechanisms that define the fate of OMW-OM in soil is needed to reduce these and other potential negative effects.

To test the second hypothesis, the incubated lysimeters were dismantled and the respective soil was collected slicewise (Chapter 3): soil crust, 0-1cm, 1-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-25 cm, 25-30 cm, 30-35 cm and 35-40 cm. After homogenization, each sample was analyzed for pH, TOC, SPC, and wettability (optical contact angle). With this, we obtained retention profiles for the different OMW constituents in the soil core after the sequence of the different simulated seasons. From a conducted total mass balance, we concluded on the transport pathways.

The analysis of phenols allowed for distinguishing i) the readily available soluble phenols in leachates that could reach deeper soil layers and ii) those physically immobilized at the top layers.

By combining the time-dependent leachate information in the first part of this work (chapter 2) with the information gained from depth-dependent soil analysis in the second part (chapter 3), it was possible to calculate the mass balance and estimate leaching of OMW constituents.

By bringing these together with soil wettability and porosity investigation results (OCAT and ^{1}H-NMR), it was further possible to deduce the fate of OMW hydrophobic compounds on the water path flows in the soil.

Finally, chapter 4 includes the main conclusions and synthesis of the current thesis with an answer deduces OMW-soil leaching and interactions mechanism during and after the sequence of different climatic conditions. Also, this last part includes recommendations for the best conditions of OMW disposal to soil and leaching survey schedule during every application in order to reduce the toxic effects of phenolic derived from OMW in soil and groundwater system. Further, open questions and further research needs are presented in the outlook.

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2 EFFECTS OF OLIVE MILL WASTEWATER ON SOIL LEACHATES PROPERTIES UNDER CLIMATIC SEQUENCE: LYSIMETER EXPERIMENT

2.1 ABSTRACT

Olive mill wastewater (OMW) disposal on soil causes serious problems due to its phenols-related toxic effects to soil and water system. Seasonal-dependent phenol leaching remains unclear since it cannot be controlled in field studies due to the high spatial variability and environmental dynamics. Thus, further research is needed to distinguish leaching and biodegradation mechanisms under controlled conditions. Lysimeter experiments allow to study the fate of chemicals such as phenols in soil system as well as transformation and leaching dynamics as function of time and space. The objective of this study was to monitor and understand the distribution and leaching of OMW-derived phenolic compounds in soil after OMW application. In this study, an 18 weeks lysimeter experiment was carried out in laboratory and the leaching of OMW-derived components was investigated as function of time. The degree and persistence of soil acidification, accumulation of soluble phenolic compounds in leachates and soil water drop penetration time were assessed for various simulated seasons. In contrast to the untreated soil, the OMW-treated soils, revealed both higher soil water repellency and soluble phenolic compounds in leachates. Leaching of OMW components through the soil varied in dependence on moisture dynamics and water redistribution and was higher under winter conditions. Under spring conditions, a partial recovery in soil leachates quality was recorded and SPC concentration in leachates was significantly lower than the OMW input level. However, a continued increase in salinity in soil leachates was recorded along with high water repellency at the soil surface which persisted until the second winter simulation. All in all, OMW application in winter should be avoided and better carried out in spring season, including a careful irrigation and leaching survey.

2.2 INTRODUCTION

The increasing worldwide demand for olive oil results in a strong growth of operating mills and, therewith, milling wastes and olive mill wastewater (OMW) (Bellumori et al., 2018).

Nowadays, OMW is most frequently applied to agricultural soils as organic fertilizer since it provides positive characteristics such as high content in water, organic matter (OM), nitrogen, phosphorous, potassium and magnesium (Magdich et al., 2012; Chaari et al., 2014; Chatzistathis & Koutsos, 2017; Tamimi et al., 2017).

Several studies have already demonstrated that OMW increase soil organic matter (SOM) (Ayoub et al., 2014; Peri & Proietti, 2014). However, OMW-derived OM is very rich in polyphenols. It was estimated that the load of phenolic compounds in OMW is 1000 times higher than in domestic wastewater (Niaounakis & Halvadakis, 2006). OMW-related phenolic compounds could contaminate the environment because they can be toxic to plants and microorganisms, as well, they could accumulate in soil or leach to the groundwater (Buchmann et al., 2015; Kurtz et al., 2015; Mekki et al., 2006).

By applying OMW in agricultural fields, phenols ought to increase soil water repellency and increase soil water retention capacity. In fact, polymerization reactions of phenolic compounds into larger molecules induced abiotic acidification and repellency effects (Buchmann et al., 2015; Kurtz et al., 2015; Peikert et al., 2015; Steinmetz et al., 2015; Tamimi et al., 2016). This increase in soil water repellency is influenced by variations of environmental conditions such as temperature, moisture content, organic carbon content and pH (Täumer et al., 2005; Diehl & Schaumann, 2007; Lebron et al., 2012). Therefore, it is highly relevant to understand the fate of OMW-derived phenolic compounds in soil and to find the optimum conditions of OMW disposal to reduce their negative impact on the environment.

Many field studies showed contradictory results for the persistence of phenolic compounds in soil (Piotrowska et al., 2006). Several works showed that the repellency effect induced by phenolic compounds partly disappeared after OMW application depending on the seasonal variations. A rapid decrease in phenolic compounds to almost 50 % of their initial concentration was recorded within the first 2 - 3 weeks following OMW application to soil (Sierra et al., 2001; Saadi et al., 2007; Tsiknia et al., 2014). In the same context, Buchmann et al., (2015) reported that during rainy season two days after OMW application 40 % for total phenolic compounds decreased. Also, Tamimi et al., (2016) reported that during the first rain season the repellency effects clearly disappeared and soluble phenolic compounds significantly decreased in soil which indicate that hydrolysis reactions mobilized the condensed and polymerized compounds and consequently enabled their leaching. Other studies showed the persistence of soluble phenolic compounds even after rainy season, which indicated their immobilization in the top layers (Steinmetz et al., 2015). However, several studies showed that negative effects of OMW in soil are lower during spring season than during winter season.

Diamantis et al., (2013) reported that moderate conditions of moisture and temperature during the spring season resulted in lower toxicity and repellency effects in soil. Nevertheless, under hot and dry conditions e.g., during summer season, condensation reactions of amphiphilic from the residual oil induced repellency in soil. Similarly, Tamimi et al., 2016 showed also that sunlight or drought during spring and summer induce polymerization processes and cause OMW-derived soluble organic constituents to raise to the soil surface by capillary action, accumulate and remain there upon drying (Steinmetz et al., 2015). Therefore, a better understanding of the mechanisms that govern the fate of OMW-OM in soil is needed to reduce these and other potential negative effects.

The aim of the present work was to study the accumulated effect of OMW application under different climatic conditions to investigate the relationship between the degree of OMW-OM degradation or accumulation and the changes in soil leachates quality. In this, context, the trend of OMW-OM in leachates can be used to describe the degradation of organic substances from OMW. Additionally, the knowledge of time-dependent phenolic fraction availability in soil leachates would be useful to estimate effects of OMW on groundwater contamination and might give reasonable solutions regarding the appropriate application of OMW to soil.

Field studies were conducted to assess the direct effect of OMW application on groundwater contamination (Zenjari & Nejmeddine, 2001; Boukhoubza et al., 2008; Kapellakis et al., 2015). Most empirical studies dealing with field management effects on runoff water quality rely on edge-of-field monitoring, which is generally unreplicated and prone to high variances (Duncan, 2016). However, studies concerning the evolution of OMW phenolic compounds on the soil leachates and their consequences on the groundwater are rare. Therefore, monitoring leaching processes of OMW-derived substances during and after OMW disposal is highly relevant to estimate the risk of groundwater contamination (Tamimi et al., 2016). To our best knowledge, lab experiments investigating phenols leaching as a function of seasonal conditions have not yet been investigated. Lysimeters are one of the most promising tools due to reduced sample preparation time and a fully automated extraction process. The advantages of lysimeter experiments are their function as proxies to field scale studies that include improved control over the operation, monitoring and sample collection that would be impractical on site (Gilbert et al., 2014).

Lysimeter have already been used to evaluate the leaching potential of OMW and the subsequent groundwater (Caputo et al., 2013), to investigate the impact of OMW land spreading on both soil properties and mature olive plant performance (Chartzoulakis et al., 2010), to determine the flux density of the water through potassium bromide applied as a nonreactive tracer in the soil column experiments (Mohawesh et al., 2014), but they have not been yet applied to assess the dynamic of phenolic compounds in deeper soil layers under controlled environmental compartments.

This study explored the response of the soil system to OMW application by monitoring the time-dependent leachates quality during and after OMW application in laboratory scale using lysimeters (total of 18 weeks). The experiment includes four simulation phases including all seasons: WS1 (First winter simulation) followed with SPS (Spring simulation). Then SS (Summer simulation) and finished with WS2 (second winter simulation). Due to the any irrigation and therefore an overall low soil water content, no leachate was collected during the extreme summer simulation period.

Therefore, in this study, we focused on the soil surface water drop penetration time (WDPT) and the time-dependent variations of soluble phenolic compounds (SPC), pH, electrical conductivity (EC), water drop penetration time (WDPT) and the quality of dissolved organic carbon (DOC) by specific ultraviolet absorbance ($SUVA_{254}$) balance in 40 cm soil depth. In the current work, we addressed four main research questions: (i) How does OMW spreading change the organic matter content and composition of the soil leachates? (ii) What are the underlying mechanisms of OMW-OM immobilization? and (iii) How do soil characteristics influence the leaching of OMW-derived organic substances such as phenolic compounds?

To answer these questions, we hypothesized that If OMW-derived, phenolic substances are the main reason for hydrophobic effects on soil, the soluble phenolic compounds in OMW treated soil leachates and its extracts should be related with changes in the WDPT during all simulated seasons. Under winter conditions, OMW is expected to percolate through the soil matrix. The artificial rainfall is expected to promote leaching of soluble compounds into deeper layers. A part of phenolic substances is expected to be collected in the leachates and a part is expected be degraded or immobilized at the top soil horizons. Under spring conditions, moderate conditions of moisture and temperature are expected to allow for considerable biological degradation, and result in lower toxicity and repellency effects in soil. Moist conditions during a second winter simulation after hot and dry conditions under summer simulation are expected to minimize OMW overall negative effects in soil consequently, to reduce the phenolic content in the leachates compared to the first winter simulation.

To test these hypothesis, OMW was applied to the soil incubated in lysimeters by mimicking typical seasonal conditions in Tunisian. Leachates were analysed for pH, EC, total organic carbon (TOC), the dissolved organic carbon (DOC) by specific UV absorption (254 nm), as well as soluble phenolic content (SPC). The experiment provided time-dependent information on the quantities of OMW constituents leaving the soil at 40 cm depth.

2.3 MATERIALS AND METHODS

2.3.1 FIELD SITES AND OLIVE MILL WASTEWATER

The soil used in this incubation study was sampled from a field located in the Mediterranean country of Sfax/Tunisia (North Africa, Lambert coordinates X = 38G 70 ’50’’and 38G 73’ 80’’ Y = 8G 97 ’60’ ’and 9G 05’ 90’’ Z = 130). The sampling area was characterized by extensive arboriculture based on olive trees. The climatological data used were those of the Sfax weather station. The sampling area was characterized by insufficient and irregular rainfall, the influence of the sea on temperature and humidity in summer. The average annual rainfall is in the order of 213 mm (National Institute of Metrology, INM, Sfax). Temperatures are generally moderate with mild winters and short and long hot summers. The average of the maxima is 35.1 °C in August and that of the minima is 6.2 °C in January. The average annual temperature is 18.7 °C with August as the hottest (average of 26.5 °C) and January as the coldest month (average of 11.3 °C), respectively. During the sampling period, no pesticides or fertilizers were applied. In a preliminary field characterization, the soil was tested with hydrogen peroxide for pesticide tracers and HCl for carbonate detection. Additionally, bulk density was measured. For the incubation experiment, soil material was sampled from 3 depths (0-10 cm, 10-20 cm, 20-40 cm), dried, homogenized, sieved to 2 mm and stored in textile boxes prior to the experiment.
Additionally, OMW from a three-phase system from olive mill from Sfax was conditioned in plastic bottles for shipping. OMW was stored in freezer until used. Three soil profiles were sampled and prepared for the lysimeter experiments: Profile n°1 and n°2: 0-10 cm and 10-20 cm: very little stony surface, light brown color, fresh, sandy loam texture, very crumbly, hairy root, effervescence at HCl, particulate structure, shell debris. Profile n°3 20-40 cm: Pale brown horizon, fresh inconsistent, diffuse gypsum, calcareous pseudo mycelium, fine porous blocky structure, effervescence with HCl for carbonates detection, sandy loam.

2.3.2 LYSIMETER EXPERIMENT SET UP AND MONITORING OF SEASONAL REGIMES

The lysimeter study was conducted at the mesocosm laboratory of RPTU - Rheinland-Palatine Technical University Kaiserslautern Landau using Tunesian soil and OMW (see section 2.3.1). Four lysimeters (ecoTech-bonn, Germany) were filled layerwise with the soil as described by Lewis & Sjöstrom, (2010). Each lysimeter (30 cm diameter and 40 cm depth) was filled layer-wise with 2 mm air-dried soil (previous section 2.3.1) with a final bulk density of 1.4 g cm^{-3} (Figure 2-1).

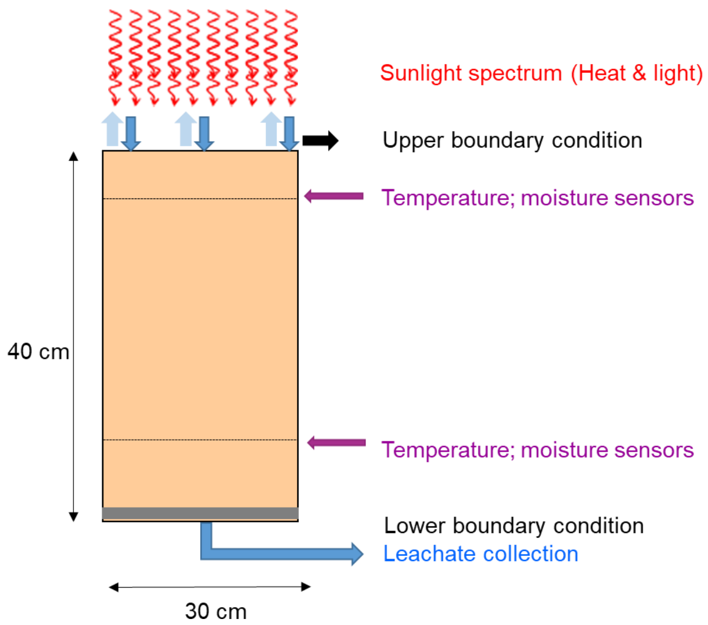

Figure 2-1 Design of laboratory lysimeters for leaching analysis. Upper boundary condition is given by inflow as function of time; Lower boundary condition is given by matric potential anticipated in 40 cm soil depth (own figure)

Moisture conditions of each lysimeter was pre-equilibrated until reaching the Tunisian winter conditions (15%, water volume). Afterwards, three lysimeters were irrigated with OMW, one Lysimeter was set as control (irrigated with Milli-Q water).

The amount of applied OMW was 1.1 L (equivalent to 50 m^3 ha^{-1} at the field scale) and therefore based on the recommendation of the Ministry of Environmental Protection in Tunisia for one single application on soil (14 L m^{-2}). OMW was applied manually using water gardening cans to avoid soil disturbance and to allow equal distribution. Throughout the whole incubation time of 18 weeks, three leachates sampling campaigns took place (Figure 2-2) with 15 samplings for the first winter simulation (WS1), 9 samplings for spring simulation (SPS) and 6 samplings for the second winter simulation (WS2).

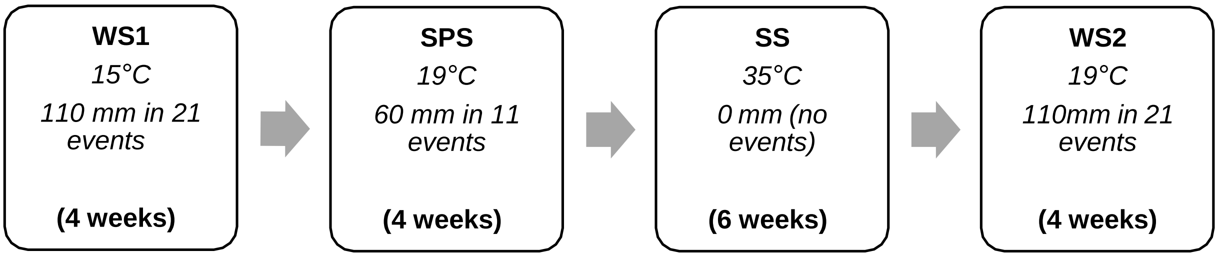

Figure 2-2 Successive seasonal simulation after OMW application. In total 18 weeks for the simulation of one scenario. WS1: 1st winter simulation, SPS: spring simulation, SS: summer simulation, WS2: 2nd winter simulation.

Temperature was adjusted following the respective Tunisian seasonal conditions in the field (15 °C, 21 °C and 35 °C for winter, spring and summer, respectively). One movable sprinkler head allowing uniform distribution of the irrigation and rain water was used for simulation of season-specific rainfall typical for Sfax (upper boundary condition: for winter: 110 mm in 21 events; spring: 60 mm in 11 events and extreme summer: no rainfall). source during the summerperiod mimicking the sunlight spectrum (intensity :100.000 lux for 12 h per day), simulating strong extreme summer conditions and allow potential sunlight-induced reactions, the columnswere irradiated by a light daylight and allowing influence of light and excess heat on the very top soil layer. Due to the low soil water content, no leachate was collected during the extreme summer simulation period.

The lysimeters were equipped with a polyamide membrane at the bottom to adjust matric potential using a dosing pump (ecoTech-bonn, Germany). The lower boundary condition was set to -83 hPa for the first and second winter simulation (WS1 and WS2) and -600 hPa for summer (SS) and spring simulation (SPS). In addition, two moisture and temperature sensors (Hydra probes, ecoTech-bonn, Germany) at 10 cm and 30 cm soil depth were inserted in each column to monitor the development of depth-dependent soil moisture and temperature via data logger (envilog-GP5W-Shell, ecoTech-bonn, Germany).

We monitored the spatio-temporal changes in soil water drop penetration time (WDPT) and the time-dependent leachates quality in terms of pH, electrical conductivity (EC), specific ultraviolet absorbance ($SUVA_{254}$) as proxy for soluble organic compound quality and the amount of soluble phenolic compounds (SPC).

2.3.3 DETERMINATION OF BASIC SOIL AND LEACHATES PHYSICO-CHEMICAL PROPERTIES

OMW was diluted 1:1000 and filtered (Whatmann, 0.45 μm) prior to the analyzes. Aqueous extracts of the soil samples were prepared by shaking soil-water mixtures (1:5 w/v) for 24 h and centrifugation at 3720 g for 15 min using laboratotry centriguge (UNIVERSAL 320, Hettich, Germany). Soil extracts were filtered through a 0.45 μm filter (Whatmann) prior to measurements. Soil dry density was measured according to DIN ISO 11272 (2001), gravimetric water content (WC) was determined on a dry mass basis (38 h oven-drying at 105 °C). pH and electrical conductivity (EC) were determined according to DIN ISO 11265 (1997) and DIN ISO 38404–5 (2009), respectively. Total cation concentrations (K^+, Na^+, Mg^{2+}, Ca^{2+}) were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 720, Germany) in microwave-assisted reverse aqua regia (HCL+ 3HNO3) extraction at a pH < 2. Chloride concentration was determined using an ion chromatograph (881 Compact IC pro, Metrohm, Switzerland). Organic carbon (OC) was determined by the difference of total carbon (TC) and total inorganic carbon (TIC) concentrations obtained by Multi N/C Analyser 2100/2100S (Analytik Jena, Germany). Elemental analysis (carbon, hydrogen and nitrogen, DIN ISO 10694 :1996-08, Vario micro cube, Elementar Analysensysteme GmbH, Germany). Freeze-dried OMW were used to determine soluble cations, an OMW solution ratio of 1:10 was used. Cations and anions were determined using ion chromatography (881 Compact IC pro, Metrohm, Herisau, Switzerland). Soluble phenolic compounds (SPC) were determined by Folin-Ciocalteu (FC) method according to Box, 1983: 300 μl of the concentrated OMW extract were added to 1.5 ml of 1:10 dH_2O-diluted Folin-Ciocalteu reagent. After 4 min, 1200 μl of saturated sodium carbonate solution (200 g l^{-1}) were added. Absorbance was measured after 1 h at 760 nm against a matrix blank using a Specord 50 UV/VIS spectrometer (Analytik Jena, Jena, Germany). To evaluate the photosensitivity of the FC reagent towards phenolics, calibration curve with gallic acid was prepared. Gallic acid (0 – 500 mg l^{-1}) was used as standard calibration curve for the total phenolic content calculations. Results are presented in mg Gallic acid units (GAU) per gram dry soil. $SUVA_{254}$ were also investigated using Specord 50 UV/VIS spectralphotometer (Analytik Jena, Germany) to assess the degree of OMW-OM decomposition or accumulation in soil, and therefore, the persisting effects of OMW disposal to soil (Tamimi et al., 2016). Under laboratory conditions, $SUVA_{254}$ is sufficiently sensitive to detect changes in the concentration of dissolved organic carbon (DOC) in OMW-treated soil. The measured absorbance was normalized to the concentration of dissolved organic C giving the specific UV absorption ($SUVA_{254}$), which serves as an indicator of the aromatic character of the organic matter. The percentage of retained compounds by the soil column as well as leached amount of TOC, SPC and $SUVA_{254}$ as a result of OMW application was calculated according to (Aharonov-Nadborny et al., 2017) (equation 1).

$$\%\text{Soil retained compounds} = \frac{\mathbf{Cin-Cout}}{\mathbf{Cin}} * \mathbf{100} \quad (1)$$

with C_{in} as the concentration of a given component in the OMW solution added to each soil, and C_{out} as the concentration of a given component leached directly after OMW application. Positive results mean that the amount retained in the soil column was higher than the amount leached through the soil.

2.3.4 WATER DROP PENETRATION TIME

Soil water repellency (SWR) was determined in the course of the incubation via water drop penetration time (WDPT). For this, 20 water drops of each 100 µl were placed directly but randomly distributed on the top soil in each lysimeter. The time for complete penetration was determined. The soil was considered water repellent when the WDPT exceeded 5 seconds (Bisdom et al., 1993). Pore-size distribution (PSD) of the sampled soil before incubation was measured with proton nuclear magnetic resonance relaxometry (^{1}H-NMR relaxometry) using a Bruker Minispec MQ (Bruker, Karlsruhe, Germany) at a magnetic field strength of 0.176 T (proton Larmor frequency of 7.5 MHz). A Carr– Purcell–Meiboom–Gill (CPMG) pulse sequence was used to obtain the transverse relaxation time T_2 and the corresponding relaxation rates of the water protons in the samples (Meiboom & Gill, 1958; Jaeger et al., 2009). The derived relaxation time distribution was transferred into a soil pore-size distribution (PSD) (Meyer et al., 2018). The respective PSD was further converted into a water retention curve (matric potential as a function of volumetric water content) using Young-LaPlace equation (Hartge & Horn, 2014).

2.3.5 STATISTICAL ANALYSIS

Results were statistically analyzed with R statistics using person´s product-moment correlation to assess the relationships between different water parameters. Tukey's multiple comparison test at $p < 0.05$ to find significant differences between treated soil leachates and untreated soil leachates. ANOVA was used to compare means across different groups. Specifically, we conducted a one-way ANOVA to assess the effect of the factor “Season” on different leachates parameters for OMW1, OMW2, and OMW3.

2.4 RESULTS

2.4.1 PHYSICO-CHEMICAL PROPERTIES OF SOIL AND OMW

Prior to OMW application, OMW-treated and control soil did not significantly differ in temperature, WC, pH, EC and SPC. Thus, observed differences after application to be presented in the following sections should be attributed to the effect of OMW. The physicochemical characteristics of the investigated crude OMW and soil are summarized in Table 2-1.

Table 2-1 Selected physico-chemical proprieties of the investigated soil and olive mill wastewater (OMW)

Parameter	**Soil**	**OMW**
pH	8.8 ± 0.1	5.35 ± 0.1
EC (µS cm^{-1})	64.95 ± 0.1	530 ± 0.1
Water content oven dried (%)	0.8 ± 0.1	91.68 ± 0.1
Total Carbon (mg l^{-1})	8.7 ± 0.1	376.7 ± 0.1
Organic carbon (mg l^{-1})	4.4 ± 0.1	298.6 ± 0.1
Total nitrogen (mg l^{-1})	0.17 ± 0.1	8.6 ± 0.1
SUVA254 nm (L mg C^{-1} m^{-1})	0.37 ± 0.1	2.8 ± 0.1
Phenols (g l^{-1})	0.036 ± 0.1	6.47 ± 0.1
Na (g l^{-1})	0.001 ± 0.3	1.4 ± 0.4
K (g l^{-1})	0.02 ± 0.5	10.3 ± 0.3
Ca (mg l^{-1})	18.36 ± 0.5	749 ± 0.2
Fe (mg l^{-1})	0.74 ± 0.9	27 ± 0.5
Mg (mg l^{-1})	1.73 ± 0.4	397 ± 0.4
Sand (%)	80 ± 0.1	-
Silt (%)	12 ± 0.1	-
Clay (%)	8 ± 0.1	-

The OMW applied was acidic with high content of organic carbon, phenols, potassium and ion load. The soil used in this study was a sandy loam with 80% sand, 12% silt, 8% clay. It had a bulk density of 1.4 g cm^{-3} and a pH of 8.8.

PSD of the soil and the gradient of the hydraulic potential for the three sampled layers 0-10 cm, 10-20 cm and 20-40 showed that the soil had an overall high porosity with about 80% coarse pores and a water holding capacity of about 25% of its dry mass (Figure 2-3).

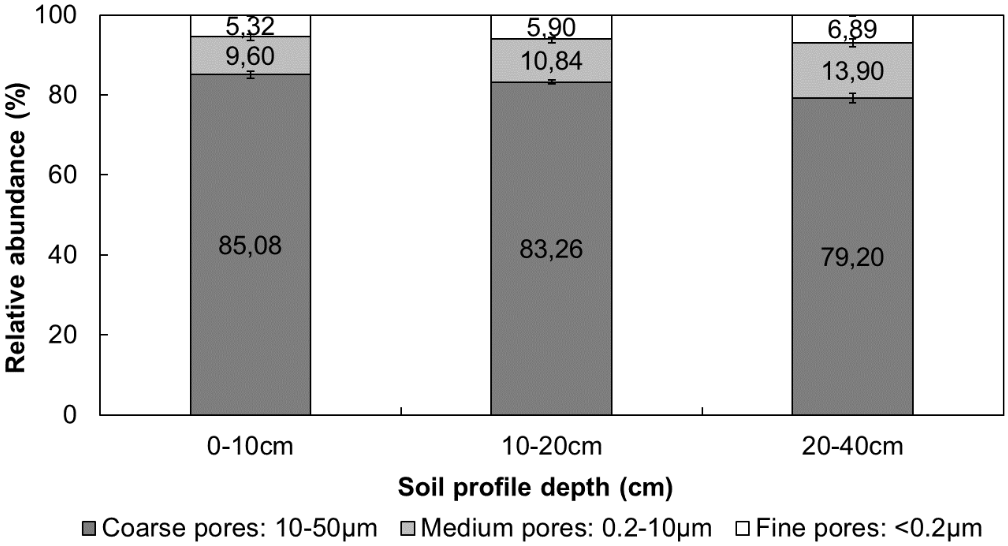

Figure 2-3 Pore size distribution (PSD) of three soil profiles sampled from the field experiment 0-10cm, 10-20cm and 20-40cm based on the pore diameter 10µm-50µm, 0.2µm-10µm and <0.2µm for the coarse pore, medium pore and fine pore respectively

2.4.2 WATER CONTENT DEVELOPMENT

One important aspect which is subject to significant seasonal variations was the distribution of water and its transport within the soil profile inside each lysimeter (Figure 2-4). The total amount of water applied to each lysimeter throughout the 18 weeks of incubation was equal to 16.1 L, (15 L irrigation water and 1.1 L OMW for treated or demineralized water for control lysimeter). Water irrigation two days after OMW application caused the first release of leachate, clearly identifiable in the highest peaks of volume (upper left side). OMW application increased the water content (WC) in the treated soils (OMW1, OMW2 and OMW3) comparing to the control soil. Generally, WC increased during the first winter simulation (WS1) then slightly decreased during spring simulation (SPS) and significantly decreased during summer simulation. WC increased again during the second winter simulation (WS2).

During the first winter simulation (WS1) and the spring simulation (SPS), OMW2 and control had similar development of water content in both depths. OMW3 and OMW1 had higher WC´s in the upper layer but lower WC in the lower layers than OMW2 and control.

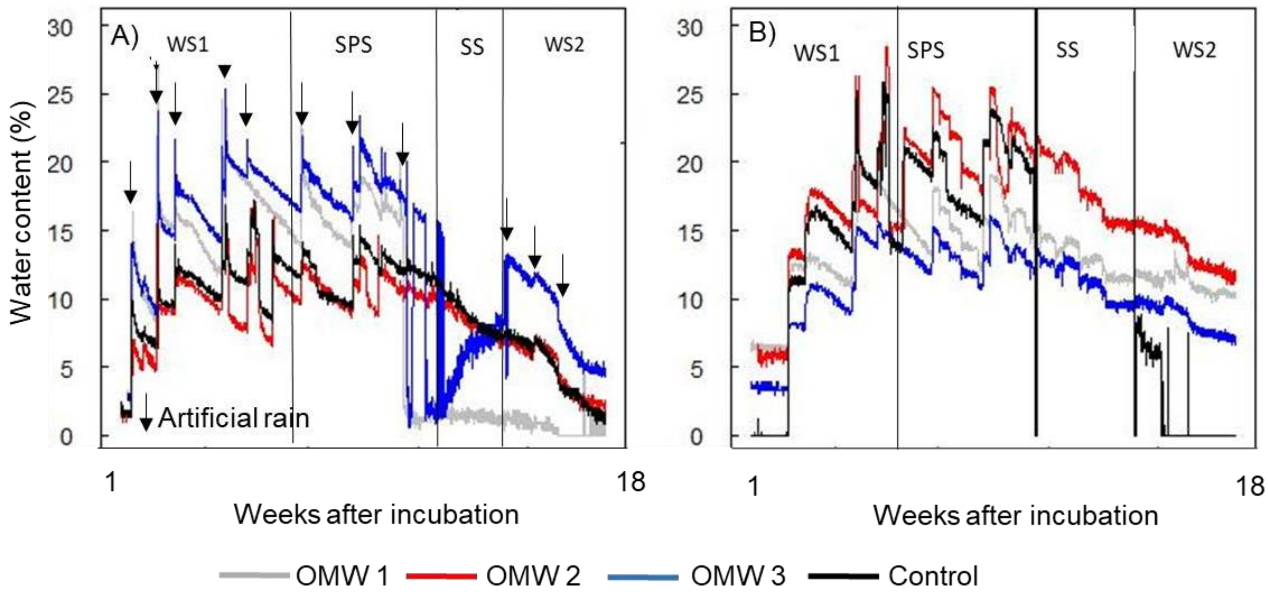

Figure 2-4 Soil water content evolution A) at 10cm and B) at 30cm during different seasonal simulations (four phases are recognized: WS1 (first winter simulation: week1-week4), SPS (spring simulation: week4-week8), SS (summer simulation: week8-week14) and WS2 (second winter simulation: week14-week18).

During summer simulation (SS), WC information was incomplete due to the high simulated temperature and dryness which impede the detection of very low WC through the water probes. In the second winter simulation (WS2), WC increased in the upper layer and decreased in the deeper layer in all treated soils. At the end of the experiment differences disappeared only partly at the upper soil. The WC in OMW3 was significantly higher than OMW1 and OMW2 which recorded WC comparable to the control.

2.4.3 pH AND EC

The changes in pH and electrical conductivity (EC) of soil leachates after OMW application in the first winter simulation (WS1), spring simulation (SPS), summer simulation (SS) and second winter simulation (WS2) were depicted in Figure 2-5.

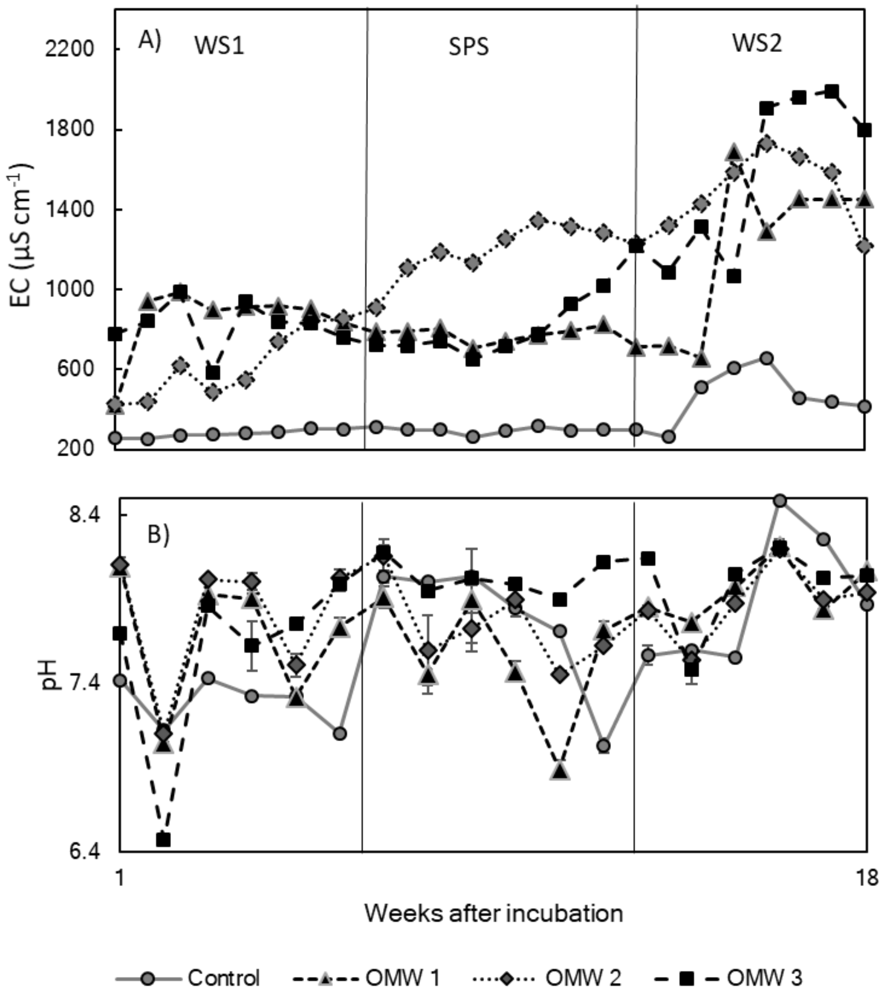

Figure 2-5 A) Electrical conductivity (EC) and B) pH treated soil leachates incubated in lysimeter 1, 2 and 3 respectively OMW1, OMW2 and OMW3. Non treated soil leachate (irrigated only with water) incubated in lysimeter 4 (control). The incubation time=18 weeks, WS1: first winter simulation from week 1 to week 4, SPS: spring simulation from week 4 to week 8, SS: summer simulation from week 8 to week 14 (no leachates), WS2: second winter simulation from week 14 to week 18.

Generally, OMW application increased EC and reduced pH in all soil leachates with respect to the untreated control soil. OMW significantly affected the initial soil pH. The pH of the leachate was always between 6.8 ± 0.01and 8.2 ± 0.01 for OMW1, between 7.1 ± 0.01 and 8.2 ± 0.01 for OMW2 and between 6.4 ± 0.01 and 8.2 ± 0.01 for OMW3.

In the first winter simulation (WS1) from the first until the second week, pH seems to be lower in the leachates of OMW3 than OMW1 and OMW2. OMW1 and OMW2 had similar development. In the second week, pH significantly increased in all treatments comparing with the control. Up to the third week, pH was lower in OMW1 than in OMW2 than in OMW3. Between the second and the fourth week, pH was always lower in the control than in the treated

soils. At the end of WS1, pH was significantly higher in OMW-treated soils than in the control. OMW2 and OMW3 had similar pH development which was slightly higher than OMW1.
In the spring simulation (SPS) higher salinization effects than in WS1 were detected with values of 1432 ± 0.01 µS $cm^{-1}$for OMW2 and 1314 ± 0.01 µS cm^{-1} for OMW3 and 823 ± 0.01 µS $cm^{-1}$for OMW1. The differences between treated and untreated soil were significant (p <0.05).
In the second winter simulation (WS2), the most significant higher salinization effects (p <0.01) were observed, 2000 ± 0.01 µS cm^{-1} for OMW3, 1730 ± 0.01 µS cm^{-1} for OMW2, 1690 ± 0.01 µS $cm^{-1}$for OMW1.

2.4.4 TRENDS OF SOLUBLE OMW-OM CONCENTRATIONS

The variation in soluble OMW-OM in soil leachates after OMW application in the first winter simulation (WS1), the spring simulation (SPS), summer simulation (SS) and in the second winter simulation (WS2) was depicted in figure 2-6. Leaching as profiles showed that OMW increased of total organic carbon (TOC), OM quality expressed by $SUVA_{254}$ and soluble phenolic compounds (SPC) in the soil leachates.
Generally, results showed that the difference in TOC in the leachates between the simulated seasons was not significant WS1-SPS (p=0.06), WS2-SPS (p=0.08) and WS2-WS1 (p=0.95). OMW application affected the quality of soluble organic compounds expressed as $SUVA_{254}$ and favoured higher aromacity in the OMW-treated soils than in the control (Figure 2-6).
Soluble phenolic compounds (SPC) in the leachates were measured as an index of leachates contamination (Sanchez-Hernandez et al., 2020). The effect of OMW is better highlighted in Figure 2-6 showing the average concentration of SPC collected throughout the entire incubation time.

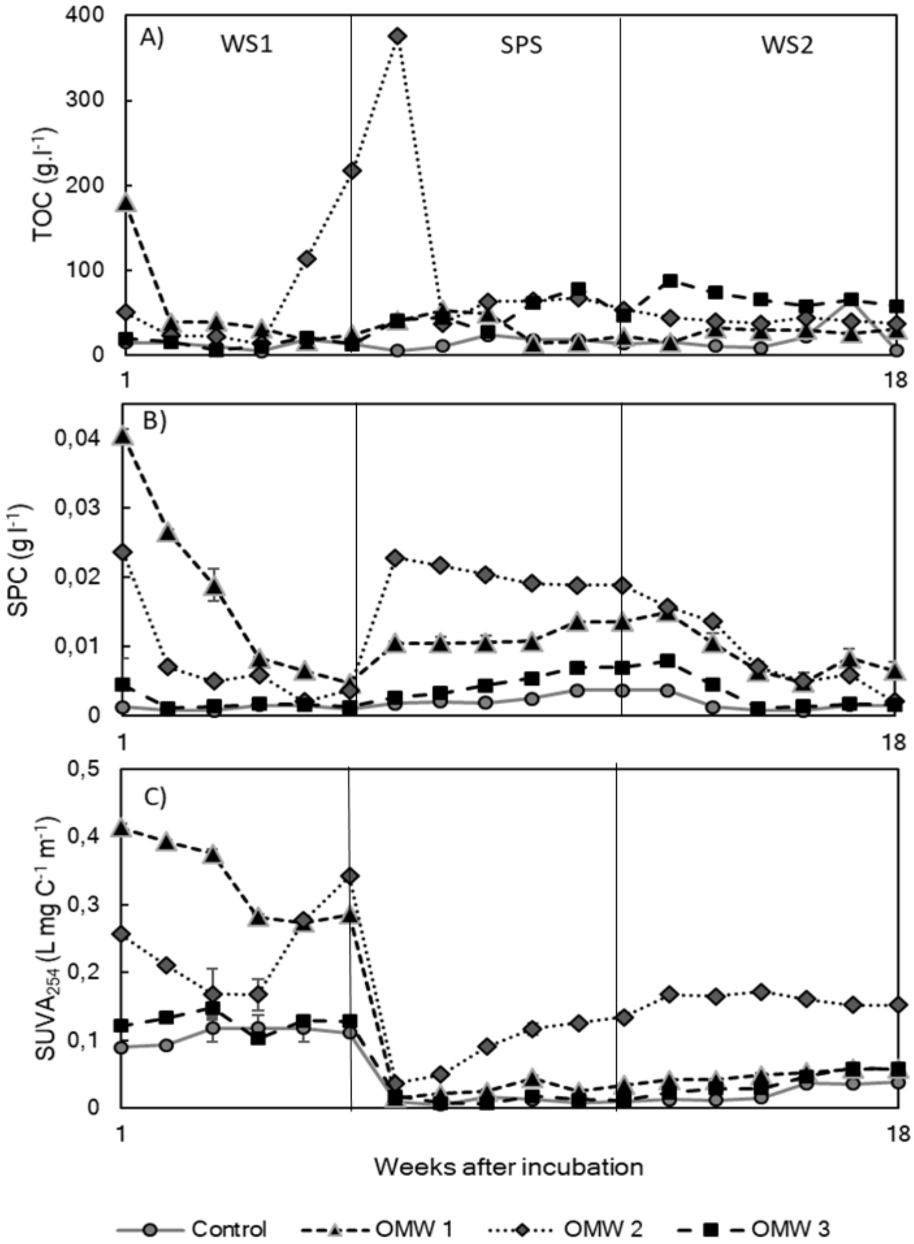

Figure 2-6 A) Total organic carbon (TOC), B) Soluble phenolic compounds (SPC) and C) Specific Ultraviolet absorbance (SUVA $_{254nm}$) olive mill wastewaters (OMW) treated soil leachates incubated in lysimeter 1, 2 and 3 respectively OMW1, OMW2 and OMW3. WS1: winter simulation 1 from week 1 to week 4, SPS: spring simulation from week 4 to week 8, SS: summer simulation from week 8 to week 14 (no leachates), WS2: second winter simulation from week 14 to week 18.

2.4.4.1 TOTAL ORGANIC CARBON

In the first winter simulation (WS1), total organic carbon (TOC) was higher in leachates of OMW1 and OMW2 than in control. OMW3 and control had similar development of TOC. As an initial effect (two days after OMW application) a peak of TOC concentration was detected for OMW1 (200 ± 0.5 mg l^{-1}) and OMW2 (50 ± 0.5 mg l^{-1}) suggesting that winter conditions significantly increased soil organic matter content determined as a loss of TOC. In contrast to OMW3, the differences between OMW1, OMW2 and the control were significant ($p<0.05$). A sudden decrease of TOC in OMW1 during the second week was recorded. Near to the beginning of the spring simulation (SPS), a high increase of TOC concentration was detected in OMW2. This effect was especially evident, as the outcoming TOC was significantly higher than the control with an amount of 376 ± 0.5 mg l^{-1} and eight time higher than OMW1 and OMW3. This result may be explained by considering, the high OMW2 water content at 30 cm depth (approx. 30%). For OMW1 the TOC, was lower than during WS1 with a maximum of 70 ± 0.5 mg l^{-1}. However, it was slightly higher for OMW3 50 ± 0.5 mg l^{-1}.

During summer simulation (SS), TOC information was incomplete due to the absence of leaching for OMW1, OMW2 and OMW3 as well as for the control. In the second winter simulation (WS2) despite simulating a comparable rainfall amount to WS1, a slightly decreasing trend was detected for TOC concentration, that reached the lowest values. TOC of OMW1 and control developed similarly. OMW3 had higher TOC 80 ± 0.5 mg l^{-1} than OMW2, which reached the lowest values of 50 ± 0.5 mg l^{-1}. In the end of the second winter simulation (WS2), TOC became similar between control and treatment.

2.4.4.2 DISSOLVED ORGANIC CARBON

During the first winter simulation (WS1), specific ultraviolet absorbance ($SUVA_{254)}$ significantly ($p < 0.05$) increased for OMW1 (0.4 L mg C^{-1} m^{-1}) and OMW2 (0.2 L mg C^{-1} m^{-1}) compared to the control (0.07 L mg C^{-1} m^{-1}). For OMW3, no significant differences were observed. These effects decreased during the spring simulation (SPS) for OMW1 and OMW3 (0.05 L mg C^{-1} m^{-1}) as well as OMW2 (0.15 L mg C^{-1} m^{-1}). During the second winter simulation (WS2), $SUVA_{254}$ slightly increased for OMW2 but disappeared for OMW1 and OMW3 (not significant to the control ($p>0.05$)).

2.4.4.3 SOLUBLE PHENOLIC COMPOUNDS

In the first winter simulation (WS1), soluble phenolic compounds (SPC) seems to be higher in the leachates of treated soils than in control. However, the differences were significant only for OMW1 which recorded the highest SPC concentration 0.04 g l^{-1} ±0.01 (p > 0.05). For OMW2 and OMW3 lower SPC values were detected (0.025 g l^{-1} ±0.01 and 0.005 g l^{-1} ±0.01, respectively). In the spring simulation (SPS), SPC decreased in OMW1 and increased in OMW2. OMW3 and control had similar development. In the end of the second winter simulation (WS2), SPC became similar between control and treatment. All in all, the out-coming SPC concentrations were of the same order of magnitude for all treated soils and were always lower than the incoming concentration of OMW 6.47g l^{-1} ± 0.1.

2.4.5 TOPSOIL WATER REPELLENCY

The results of the water drop penetration time (WDPT) for the three soils receiving an OMW application rate of 50 m^3 OMW ha^{-1} y^{-1} and the control during the different simulated seasons are given in figure 2-7. Olive mill wastewater (OMW) significantly increased water drop penetration time (WDPT) for the topsoil. Differences between control and treated soils were significant (p<0.05) during all simulation phases.

Directly after OMW application under winter conditions (WS1), severe water repellency developed at the topsoil which was only partly reduced during the spring simulation (SPS) and persisted during summer simulation (SS) and the following second winter simulation (WS2) with a total of 70% of all spots of WDPT<60 s. Among the scenarios within OMW treated soils, the differences between the first winter simulation (WS1), the spring simulation (SPS), the summer simulation (SS) and the second winter simulation (WS2) were significant (p<0.05) for the topsoil of the OMW treated lysimeters.

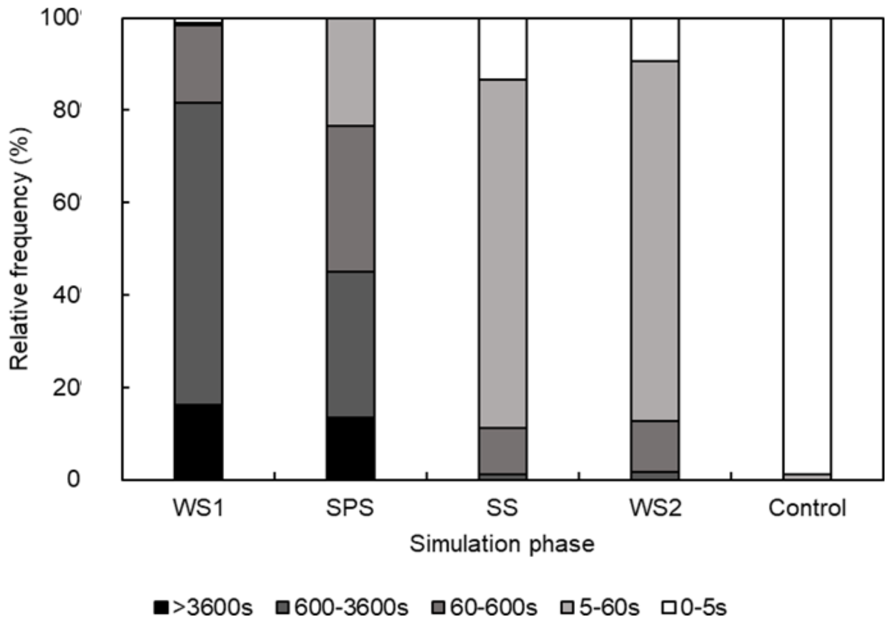

Figure 2-7 Relative frequencies of soil water drop penetration times (WDPT) according to Bisdom et al. (1993), three replicates irrigated with olive mill wastewater (OMW) and one control irrigated with MQ water, WS1: winter simulation 1, SPS: spring simulation, SS: summer simulation.WS2: winter simulation 2)

The repellency classes showed the strongest hydrophobic effects during the first winter simulation (WS1) with more than 80% of the spots showing a WDPT > 600 s. According to Bisdom et al., 1993, these spots were severely water repellent (> 600 s), single spots even showed WDPT above 3600 s.

2.5 DISCUSSION

The results of the current study demonstrate that OMW application significantly affected soil leachates quality as function of the different simulated seasons. Several soil leachate parameters changed due to the olive mill wastewater (OMW) application. These include increases in the soil salinity, the soil acidity, soluble phenolic compound (SPC), soil organic carbon (TOC), and dissolved organic carbon (DOC) concentrations as well as an increase in repellency. All these observations are in agreement with other studies (Di Bene et al., 2013; Mekki et al., 2013; Kurtz et al., 2015; Peikert et al., 2015; Steinmetz et al., 2015).

Generally, OMW-effects on soil increased in the first winter simulation (WS1) then decreased in the spring simulation (SPS) and slightly increased again during the second winter simulation (WS2). However, it was validated that these effects were compensated differently in each soil and during each simulated season and were dependent on the water transport which was different between the control and OMW-treated soils.

During the first winter simulation (WS1), EC increased significantly in all treated leachates since artificial rain helped leach the OMW-salts in soil (Boukhoubza et al., 2008; Tzanakakis et al., 2011; Kapellakis et al., 2015). Water content (WC) and electrical conductivity (EC) correlated significantly (*p*<0.01). This suggest that OMW salts transport was related to the water content development in the soil matrix. OMW3 had higher WC than OMW1 and OMW2.As a result, OMW salts transport was faster in OMW3 than OMW1 than OMW2. This indicates that slow mineralization effect helped OMW-salts to accumulate faster down in OMW3 than in OMW1 and OMW2 before draining or being sucked out in the leachates. In all treatments, the EC of the effluent was higher than the influent one and this can be explained by OMW-OM mineralization and evaporation of a certain volume of water in each lysimeter (Mekki et al., 2015).

It was validated that during the first winter simulation (WS1), OMW-OM transport was faster in OMW1 than in OMW2. However, OMW-OM in OMW3 and control had similar development. This could explain the lower pH in OMW1 than in OMW2 than in OMW3. Indicating that the transport of the OMW-OM through the soil matrix induced the acidity detected in the leachates. The acidity detected in the leachates can be attributed to the transport of OMW-OM through the soil matrix. This phenomenon occurs due to several interconnected processes. First, as OMW-OM percolates through the soil, it can release organic acids and other acidic compounds into the surrounding environment (Keren et al., 2015). These compounds may originate from the decomposition of organic matter present in the OMW or from chemical reactions within the soil matrix itself. Second, OMW-OM can alter the pH of the soil as it moves through it, creating conditions conducive to increased acidity in the leachates. Additionally, OMW-OM may interact with mineral components of the soil, leading to the release of ions that can contribute to acidity (Tamimi, 2016). Consequently, the combination of these factors, including the release of organic acids, pH modification, and ion exchange, collectively induces the observed acidity in the leachates.

In the current study, results showed that SPC slightly increased in the first and second week of WS1 causing acidity in all treated leachates so that a pH reduction was detected until the second week of simulation with a faster transport in OMW3 than in OMW1 and OMW2. Similarly, Achak et al., 2009 reported that the OMW acidity was due to the presence of phenolic and fatty acids, subsequently the application of OMW changed soil pH.

In the same context, Tamimi et al., 2016 showed that by oxidation of phenolic substances after OMW application, protons are released which explains the acidification.

During this experiment, pH kept on fluctuating and this may be attributed to dilution effects caused by artificial rainfall. Up to the third week of WS1, SPC decreased and this coincide with a reduction of acidity explained by a pH increase in all treated leachates. Such an observed increase in soil pH following OMW treatment is in accordance with the findings of other studies (Kurtz et al., 2021; Mekki et al., 2014). The low leaching amount of SPC as well as the pH increase indicated that the aromatic compounds responsible for acidity such as phenolic compounds, lignin and sterols were not degraded but tended to accumulate in soil and increased hydrophobicity (Tamimi, 2016). This could explain the water repellency observed in WS1 for OMW treated soils which was significantly higher than the control. The clear relation of SPC with the water drop penetration time (WDPT) supports our hypothesis of a relationship between OMW derived phenolic compounds and repellency effects on soil. Similar to our study, (Mahmoud et al. 2010 ; Kurtz et al. 2021) found persistent water repellency after repeated OMW applications in winter. Similarly, Mahmoud et al., (2010) observed that the WDPT was related to the soil organic carbon content derived from OMW with a significant correlation coefficient of $R = 0.98$. Also, they reported that the water repellency was generally higher at the soil surface, where OMW-organic matter had accumulated.

During spring simulation (SPS), OMW salts transport was faster in OMW2 than in OMW1 and OMW3 during first winter simulation (WS1). The increase in salinity in OMW treated soils during the SPS suggests an upward directed water flow within the soil profile due to evaporation at the surface layer (Magdich et al., 2013) by which OMW compounds migrated upward by capillary action (Steinmetz et al., 2015). In SPS, visible soil crusts were observed at the top. Most likely, crust formation visualized at the top treated soils due to the high evaporation level which affected the water balance inside the soil columns (Kurtz et al., 2021). This is in accordance with other studies which showed that fast drying could be responsible for the formation of biological soil crusts in OMW treated soils. These are known to positively affect the water balance in semi-arid ecosystems by modifying hydrological processes (Mahmoud et al., 2012; Chamizo et al., 2016; Kurtz et al., 2021). Therefore, during SPS, OMW-OM transport significantly decreased in all treated soils comparing with WS1. Consequently, acidity decreased in all treated soils leachates explained with higher pH ranges.

In SPS, salts and OMW-OM leaching particularly SPC was faster in OMW2 than OMW1 and OMW3. Since OMW2 deeper layer had the highest water content which favoured salts dilution and accumulation in the leachates of the treated soils. Observations of phenolic compounds rapidly reducing in concentration and degrading under environmental conditions favourable to biological activity have been reported by other researchers (Buchmann et al., 2015). They showed that the lower degradation rate of phenolic compounds derived from OMW was in agreement with their resistance to microbial degradation and their ability to form very stable and not easily degradable structures with minerals, proteins and other organic compounds. This suggest that the optimal soil moisture and temperature conditions in the spring simulation favored soil biological activity (Barbera et al., 2013) and enhanced microbial degradation of easily degradable OMW substances (Chaari et al., 2014). Therefore, during SPS, water repellency was observed for OMW treated soils however, it was significantly lower than in WS1. Most likely, degradation processes stimulated under spring reduced the occurrence of repellency (Steinmetz et al., 2015). The adjustment of matric potential during SPS caused drainage forces. Thus, a typical micro topography was developed at the topsoil. So that in the sinks, OMW accumulated and caused different scale of hydrophobicity. This enabled the grouping of soil spots to water repellent and wettable ones (Duncan et al., 2017). This aspect was also described by Kurtz et al., (2021). They found that the distance-dependent spatial distribution of water repellency is mainly due to the field micro topography which enhance the accumulation of OMW-derived organic compounds in low field areas causing high soil WDPT. Steinmetz et al., 2015 observed also a different WDPT spatial distribution in control as well as OMW-treated plots in the first 60 cm. Similarly, Harman et al., (2014) found that the micro topography strongly influences soil organic matter contents and soil hydraulic conductivity in semi-arid soil.

During WS2 salts transport was significantly higher than in WS1 and SPS. It was faster in OMW3 than OMW2 and OMW1. The increasing trend of conductivity can be caused by the fast leaching of the salts dissolved in OMW coupled with the effect of dilution caused by water (artificial rain events) that flowed through the porous soil matrix. Meanwhile, at the end of the second winter simulation (WS2), all investigated parameters for the treated soil leachates were at the same order of magnitude and a significant reduction of OMW effects was recorded. This is partly in accordance with our hypothesis since an increasing trend of conductivity was recorded as deduced previously. During the second winter simulation (WS2), WDPT significantly decreased comparing to the spring simulation but remain relatively high at the top soil and was coupled with a slight non-significant increase of soluble phenolic content in the leachates indicating that, part of phenolic becomes physically immobilized and temporarily less bioavailable.

The differences in the fate of OMW-organic substances between the WS1, SPS and WS2 led to the conclusion that besides the transport processes, there were also different transformation mechanisms that contributed to OMW-soil interactions (Tamimi, 2016). Notably, the water content distribution and the seasonal effects influenced the organic compounds transport and degradation inside the soil matrix, suggesting that soil water distribution under different seasonal effects is a major driver for spatio-temporal carbon mineralization reactions in soils (Bailey et al., 2017). Similarly, we found that changes in water content influenced the transport of organic matter in the soil matrix and consequently the amount of organic compounds reaching the leachates. This could explain that despite the same OMW application rate for OMW1, OMW2 and OMW3, OMW constituents reach the bottom of the soil columns with different amount and at different points of time.

2.6 CONCLUSION

Throughout all simulations phases, WDPT at the topsoil and EC in treated soil leachates were the only parameters that showed negative persistent effects of OMW exposure. Application of OMW under winter conditions favouring leaching led to outcoming concentrations of SPC that were negligible compared to the incoming concentrations. These results suggest that OMW application did not lead to significant amount of soluble phenolic compounds eventually reaching deeper soil layers through leachate.

However, application rates which exceed 50 m^3 ha^{-1} y^{-1} should be avoided since we detected high water repellency at the topsoil and we found indicators (EC, TOC and SUVA) for higher leaching risks after OMW disposal. The results confirmed that the degree of OMW-attributed negative impacts not only depend on the soil type or OMW amount since we observed different leaching trends for three similar OMW-treated soils. Carefully planned irrigation is recommended to avoid faster leaching and to give time for OMW-biodegradation, sorption and immobilization inside the soil. Further, investigations of the soil matrix itself after dismantling would help to understand the persistence of soil hydrophobicity, the low degree of SPC leaching and the underlying mechanisms responsible for OMW distribution in soil. Consequently, OMW application should take place only with a scheduled leaching survey and in a way that the soil can recover between consecutive application.

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3 OLIVE MILL WASTEWATERS HYDROPHOBIC EFFECT ON SOIL VERTICAL DEGRADATION - A LYSIMETER STUDY

3.1 ABSTRACT

The use of olive mill wastewaters (OMW) in irrigation is highly discussed since it could serve as agricultural fertilizer and substitute water especially in water scarce region. However, its high phenolic content ought to increase soil water repellency and disturb soil water retention capacity. Questions remain on the mechanisms for soluble phenolic compounds distribution inside the soil profile since they are controlled by leaching and soil contact time. To investigate these issues, a lysimeter study was conducted, in which OMW was applied to non-treated sandy-loam soils for an overall incubation time of 18 weeks including 4 seasonal simulation phases (two winter, one spring and one summer) under semi-arid climate Tunisian conditions. At the end of the incubation, phenolic compounds and soil pore-size distribution in the soil were determined by Folin-Ciocalteu (FC) method and ^{1}H-NMR relaxometry respectively. OMW application significantly increased soil water repellency and pore sizes in the treated OMW-soils. The results showed that OMW affected the soil in the upper 5 cm with most of the OMW-derived phenols immobilized.

Soluble phenolic compounds concentration was higher in clear soil spots with higher proportions of coarser pores than in the darker spots with higher proportions of fine pores, OMW-organic carbon seems to control soil depth-dependent hydrophobicity and therefore OMW transport mechanisms within the soil matrix. Our results suggest that repeated cycles of wetting and drying of OMW-treated soils may be accompanied by repeated cycles of increased carbon fluxes that are driven by i) leaching during rainy phases ii) evaporation and capillary rise mechanisms during dry phases. More experiments that target the sorption capacity of the soil during and after OMW application throughout an incubated soil matrix are needed to explore leaching effect on SPC stability in soils.

3.2 INTRODUCTION

Olive oil production is an important industry for Mediterranean countries such as Italy, Spain, Greece, Turkey and Tunisia (Khoufi et al., 2009). Thus, the generated amount of olive mill wastewater (OMW), the liquid by-product of oil production, reached 30 million cubic meters and 800000 cubic meters only in Tunisia (Mekki et al., 2013). Valorization of OMW via cost-effective treatments is difficult because it is complex to handle this particular hazardous wastes (Sáez et al., 2021). OMW contains an enormous supply of organic matter (OM) and has an high chemical oxygen demand (COD) between 40 and 210 g l^{-1} and biological oxygen demand (BOD_5) between 10 and 150 g l^{-1} (Mekki et al., 2009). This underscores the magnitude of the challenge posed by the management of OMW in the environment. The recently and most frequently method is the direct application to agricultural soils as organic fertilizers (Magdich et al., 2012). Agricultural irrigation with wastewater effluents has become a common practice in arid and semi-arid regions, where it has been used as a readily available and inexpensive option compared to fresh water (Mekki et al., 2012). However, to avoid its uncontrolled disposal on soil, OMW application is limited in several Mediterranean regions (Buchmann et al., 2015). For example, Tunisian laws permit an annual spreading of 50 m^3 ha^{-1} y^{-1}. In spite of the restricted OMW disposal on soil, an uncontrolled disposal at even higher quantities than recommended must be assumed (Kavvadias et al., 2014).

Some characteristics of OMW are favorable for agriculture since it is rich in organic matter (OM), N, P, K and Mg (Rinaldi et al., 2003) and therefore can have positive effects on soil structure e.g. increased aggregate stability and reduced run-off (Buchmann et al., 2015). Among the most expected risks threatening soil fertility and resulting from OMW use, pH and EC modifications are of severe concern (Zenjari & Nejmeddine, 2001). In addition, OMW cause phytotoxic effects on crops and change of sorptive capacity of soil for organic pollutants on a long-term scale (Jarvis et al., 2008; Achak et al., 2009; Buchmann et al., 2015). Further, OMW induced soil water repellency (SWR) on the soil surface in field experiment. SWR prevented the development of a homogeneous infiltration front and enhanced non-equilibrium flow by reducing hydraulic conductivity and infiltration rate (Jarvis et al., 2008; Mahmoud et al., 2010). This reduction is related to the clogging of soil pores and the sealing of the soil surface (N. Jarvis et al., 2008). The development and persistence of SWR is influenced by variations in environmental conditions such as temperature, moisture content, organic carbon content and pH (Zenjari & Nejmeddine, 2001; Boukhoubza et al., 2008; Kapellakis et al., 2015). Most of the studies were typically performed in the field to assess the impact of direct OMW application on groundwater contamination (Zenjari & Nejmeddine, 2001; Boukhoubza et al., 2008; Kapellakis et al., 2015). Still, only a few studies trace such effects with a particular focus on small-scale spatial resolutions. Results at a lab scale indicate that the application of OMW in the soil may in a longer term influence the infiltration capacity of soil, with possible negative effects on groundwater quality (Zenjari & Nejmeddine, 2001). In the lab, lysimeter are a promising tool, which favorite time dependent leaching quality monitoring (Chapter 2). They were also typically used to evaluate how the leaching of OMW and olive waste compost may reach the groundwater level (Caputo et al., 2013). Additionally, they were used to investigate the impact of OMW land spreading on both soil properties and mature olive plant performance (Chartzoulakis et al., 2010). Furthermore, to determine the flux density of the water through potassium bromide (KBr) applied as a nonreactive tracer in the soil column experiments (Mohawesh et al., 2014). Existing data on effects of OMW on soil properties is in several cases contradictory and mostly refer to bare soil application. Moreover, effects on leachates and soil composition have not been assessed through short-term studies in lab, where OMW doses were applied under different moisture and temperature conditions. This lack of knowledge was the main motivation for performing the current work. Aims of the present study were: i) To understand the mechanisms of OMW-soil interactions and their role for soil quality: This through the investigation of the depth-dependent OMW availability after the sequence of temperature and moisture conditions. ii) to Investigate the effects of hydrophobic OMW components into depth-dependent degradation processes of OMW in soil. In this context the changes of SWR with depth as commonly measured by optical contact angle (OCA) coupled with soil porosity measurement (^{1}H-NMR relaxometry) were performed. So that we will be able to describe spatial distribution patterns, which has been identified as the major OMW transport pathways within the soil body.

We hypothesized that depth-dependent degradation of phenolic compounds and OMW-derived organic carbon (OMW-OC) in general should come along with a reduction of SWR in the soil layers (from 0 to 40cm depth) since most of the hydrophobic components should be immobilized in the upper layer. It has already been shown that both single and repeated OMW applications increased dissolved organic carbon (Piotrowska et al., 2006; Brunetti et al., 2007; Di Bene et al., 2013; Kurtz et al., 2015) as characterized by a higher ratio of aliphatic: aromatic compounds than in untreated control soils (Peikert et al., 2015). Since OMW-OM is complex and contains greases, proteins, carbohydrates, organic acids, polyalcohols, glucosides, tannins and polyphenols (Mulinacci et al., 2001; Diamantis et al., 2013), it is likely that these compounds are partly responsible for the observed negative effects on soil quality. For example, phenolic compounds inhibit biodegradation of OMW-OM (Buchmann et al., 2015). Further, the input of hydrophobic OMW constitutes in soil, such as grease and oil, may cause the unwanted development of soil water repellency (Gonzalez-Vila et al., 1995; Mahmoud et al., 2010; Steinmetz et al., 2015; Tamimi et al., 2016). This hydrophobic effect on soil may further increase and remain with each additional application of OMW (Peikert et al., 2015). Since SWR is a surface phenomenon that strongly depends on the surface areas coated and governed by the strength of mineral-organic interactions, a better understanding of the mechanisms that define the fate of OMW-OM in soil is needed to reduce these and other potential negative effects. By combining the time-dependent leachate information of our first study (Chapter 2) with the information gained from depth-dependent soil analysis after completion of the experiments, we will be able to estimate the relevance of leaching of OMW constituents and their potential for upward movement via capillary rise. By bringing these together with soil wettability and porosity investigation results (WDPT, OCA and ^{1}H-NMR), we further be able to deduce the fate of OMW hydrophobicity on the water path flows in the soil.

3.3 MATERIALS AND METHODS

3.3.1 DISMANTLING DESIGN AND SAMPLING STRATEGY

To provide additional insights into the changes in soil leachates quality (Chapter 2), the lysimeters were dismantled to obtain a depth dependent OMW degradation profile helping to assess the persistent effects of OMW on the soil core. The soil was collected slice-wise for totally eight depths: soil crust, 0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-25 cm, 25-30 cm, 30-35 cm,35-40 cm. The samples were taken based on three water populations which were identified at the soil surface with different WDPT and colour (Figure 3-1).

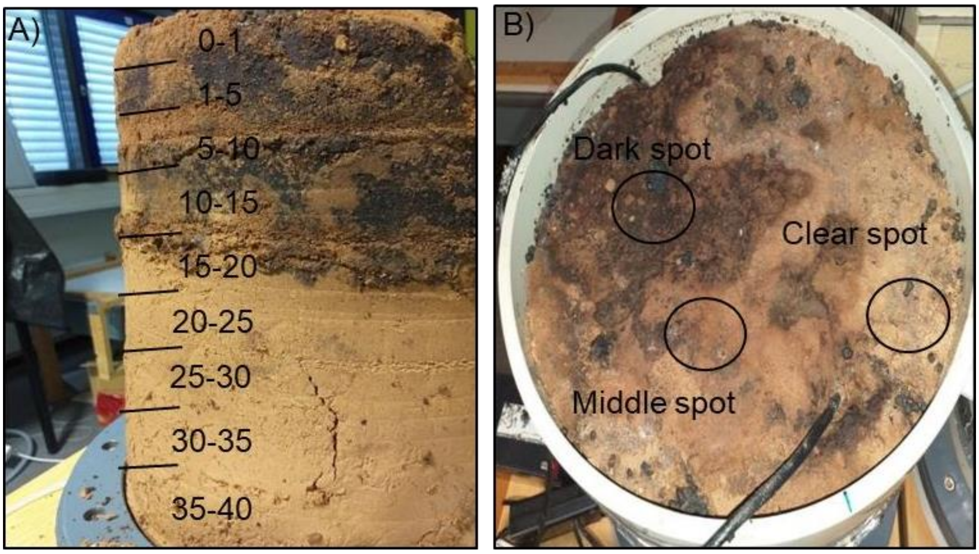

Figure 3-1 Lysimeter dismantling: A) is the core of the lysimeter OMW1 with the different sections of dismantling, B) is the surface of the soil at the end of the scenario. Three different soil colors representative soil spots, with different degree of repellency (clear spot, characterized with high SWR going to middle and dark spots characterized with lower SWR (own picture, Mesocosmos laboratory, Koblenz-Landau University).

After ^{1}H-NMR analysis to obtain the PSD, samples were homogenized and analyzed for pH, electrical conductivity (EC), total carbon (TOC), organic carbon (C_{org}), specific ultraviolet absorbance analysis to assess the degree of OMW organic matter decomposition and accumulation in soil ($SUVA_{254}$), soluble phenolic compounds (SPC) and optical contact angle (OCA) for soil water repellency.

3.3.2 DETERMINATION SOIL PHYSICO-CHEMICAL PROPERTIES

Aqueous soil extracts were prepared by shaking soil-water mixtures (1:5 w/v) for 24 h and centrifugating at 3720 g for 15 min using laboratotry centriguge (UNIVERSAL 320, Hettich, Germany). Soil extracts were filtered through a 0.45 µm filter (Whatmann) prior to measurements. Soil dry density was measured according to DIN ISO 11272 (2001), gravimetric water content (WC) was determined on a dry mass basis (38 h oven-drying at 105 °C). pH and electrical conductivity (EC) were determined according to DIN ISO 11265 (1997) and DIN ISO 38404–5 (2009), respectively. Total cation concentrations (K^+, Na^+) were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 720, Germany) in microwave-assisted reverse aqua regia ($HCl + 3HNO_3$) extraction at $pH < 2$. Chloride concentration was determined using an ion chromatograph (881 Compact IC pro, Metrohm, Switzerland). Organic carbon (C_{org}) was determined by the difference of total carbon (TC) and total inorganic carbon (TIC) concentrations obtained by Multi N/C Analyser 2100/2100S (Analytik Jena, Germany). Elemental analysis (carbon, hydrogen and nitrogen, DIN ISO 10694:1996-08, Vario micro cube, Elementar Analysensysteme GmbH, Germany). Soluble phenolic compounds (SPC) was determined by Folin-Ciocalteu (FC) method according to Box (1983) and Li et al. (2007): 300 µl of the concentrated OMW extract were added to 1.5 ml of 1:10 dH_2O-diluted Folin-Ciocalteu reagent. After 4 min, 1200 µl of saturated sodium carbonate solution (200 g l^{-1}) were added. Absorbance was measured after 1 h at 760 nm against a matrix blank using a Specord 50 UV/VIS spectrometer (Analytik Jena, Jena, Germany). To evaluate the photosensitivity of the FC reagent towards phenolis, a calibration curve with gallic acid (0 – 500 mg l^{-1}) was prepared. Results were presented in mg gallic acid units (GAU) per gram dry soil. $SUVA_{254}$ was investigated using a Specord 50 UV/VIS spectrometer (Analytik Jena, Germany) to assess the degree of OMW-OM decomposition or accumulation, and therefore, the persisting effects of OMW disposal to soil (Tamimi et al., 2016).

Under laboratory conditions, $SUVA_{254}$ is sufficiently sensitive to detect changes in the concentration of humified dissolved organic carbon (DOC) in soil amended with OMW, and likely to have a longer residence time in soil (Pittaway & Eberhard, 2014). Therfore, specific ultraviolet absorbance analysis ($SUVA_{254}$) were investigated to assess the degree of OMW organic matter (OMW-OM) decomposition or accumulation in soil and therefore, the persisting effects of OMW disposal to soil.

3.3.3 SOIL WATER REPELLENCY (SWR) AND SOIL PORE-SIZE DISTRIBUTION (PSD)

To characterize soil water repellency (SWR), contact angles were measured by sessile drop method using a video-based optical contact angle measuring device (OCA15Pro, DataPhysics, Filderstadt, Germany). Consecutively, 5 drops of 10 µl volume (MQ-water) were placed on each sample in distances of a few millimetres. The shape of each drop was captured in a video sequence of which the OCA after 2min was evaluated using the SCA20 software (DataPhysics). Pore size distribution (PSD) was measured using proton nuclear magnetic resonance (^{1}H-NMR) relaxometry. Three replicates were analyzed using a Bruker Minispec MQ (Bruker, Karlsruhe, Germany) at a magnetic field strength of 0.176 T (proton Larmor frequency of 7.5 MHz). To obtain T_2 and the corresponding relaxation rates of the water protons in the samples), a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence was used (Meiboom & Gill, 1958; Jaeger et al., 2009).
Then PSD was converted into a water retention curve (matric potential as a function of volumetric water content) (Meyer et al., 2018) using Young-LaPlace equation (Hartge et al., 2014). From the obtained curve, the respective matric potential could be determined after measuring the water content of the soil samples.

3.3.4 DATA ANALYSIS

The statistical analysis was performed using *R* (v3.1). Results were statistically analyzed using two-way analyses of variances (ANOVA) and Tukey's multiple comparison test at $p < 0.05$ to find significant differences between three OMW from each OMW-treated soil and untreated control samples. Statistical differences in the results section were presented with small letters only where the differences between the OMW-treated and control soils are significant (Tukey $p < 0.05$). To additionally resolve difference between three different spots of soil based on the color appearing at the soil surface at the end of the experiment, linear regression and correlation analysis (Pearson correlation) were performed to determine relationships between SPC and PSD.

3.4 RESULTS

3.4.1 pH AND EC

Untreated control soil was generally alkaline with a pH of 8.8. OMW application changed soil pH as well as EC as depicted in figure 3-2.

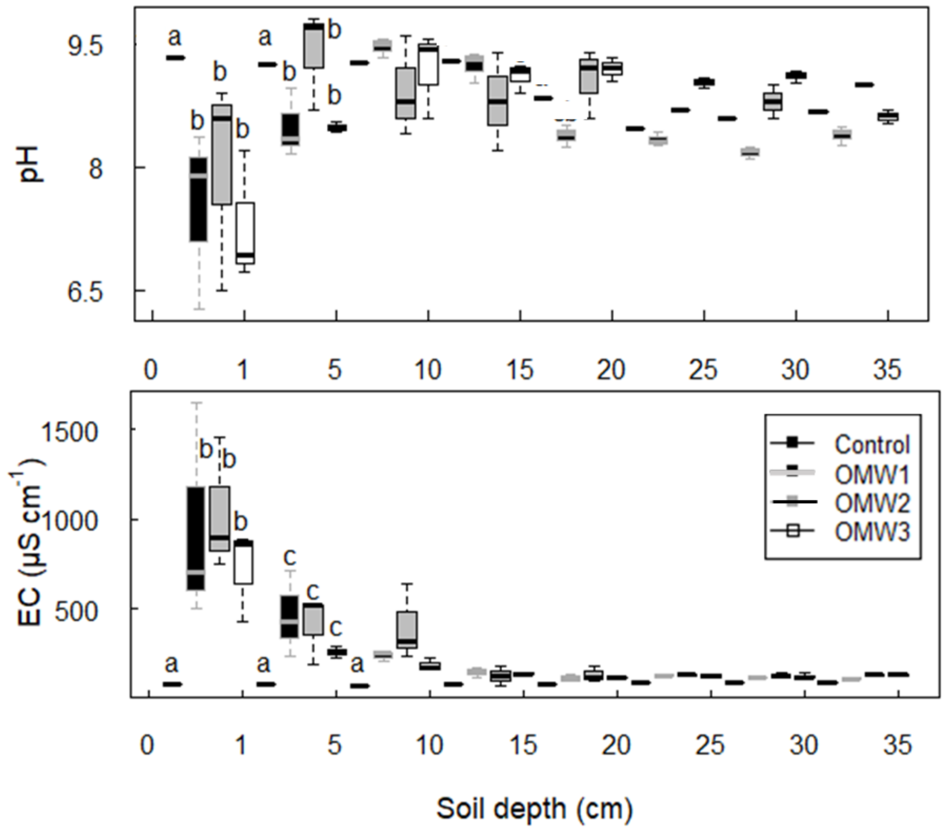

Figure 3-2 A) Electrical conductivity (EC) and B) pH related for 0 to 35 cm depth of OMW-treated soils (OMW 1-3) and control soil (Control). Box plots show median (straight line) values. Different small letters indicate significant differences between soils, as well difference between the three treated soils at different depths (Tukey: $p < 0.05$)

Soil pH decreased from initially 8.8 to finally 6.3, 6.5 and 6.7 for OMW1, OMW2 and OMW3, respectively, and was therefore lower than in the respective control. pH reduction was more pronounced and significant ($p < 0.05$) only in 0 - 5 cm depth. From 10 cm depth on, soil pH did not significantly differ anymore between OMW-treated and control soil. OMW-induced reduction of soil pH came along with an increased electrical conductivity (EC). EC increased in all soil depths compared to the control soil ($p < 0.05$). We found the highest EC at a depth of 5 cm 1700 ± 100 µS cm^{-1} in OMW1 while the lowest at a depth 35 cm 100 ± 100 µS cm^{-1} in OMW3.

3.4.2 OMW-OM AND CATIONS

OMW application resulted in a significant salinization of the top-soils. The concentration of Na^+ was significantly higher in the OMW-treated than in the control soil only until 5 cm depth. Moreover, the concentration of K^+ was significantly higher in OMW-treated than in the control soil, especially in the upper soil layer (0 –10 cm) (Figure 3-3).

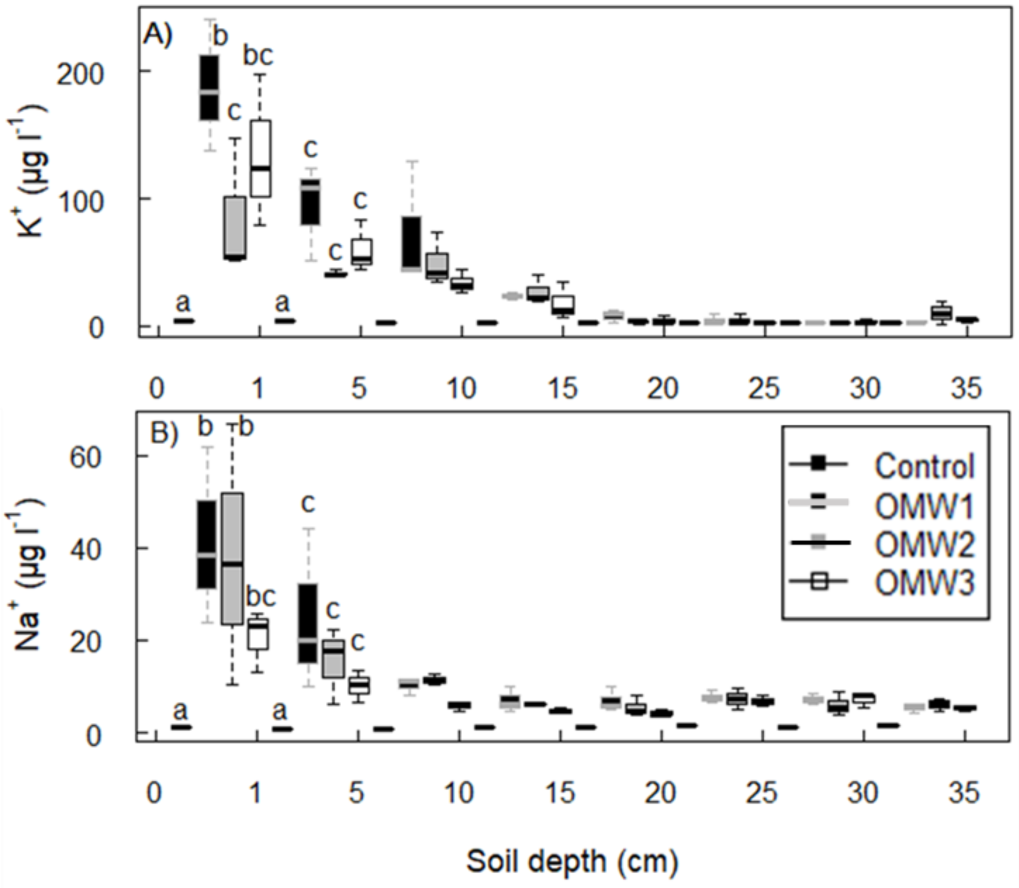

Figure 3-3 Evolution of sodium (Na^+) and potassium (K^+) level as function of soil depth (data determined 18 weeks after OMW spreading in lab with OMW1,-3 as treated soils in three incubated lysimeters). Different small letters indicate significant difference between treated and control soil as well difference between the three treated soils at different depths. (Tukey: $p < 0.05$)

For all treatments, $SUVA_{254}$ significantly increased until 5 cm depth with respect to the corresponding control plots (Figure 3-4).

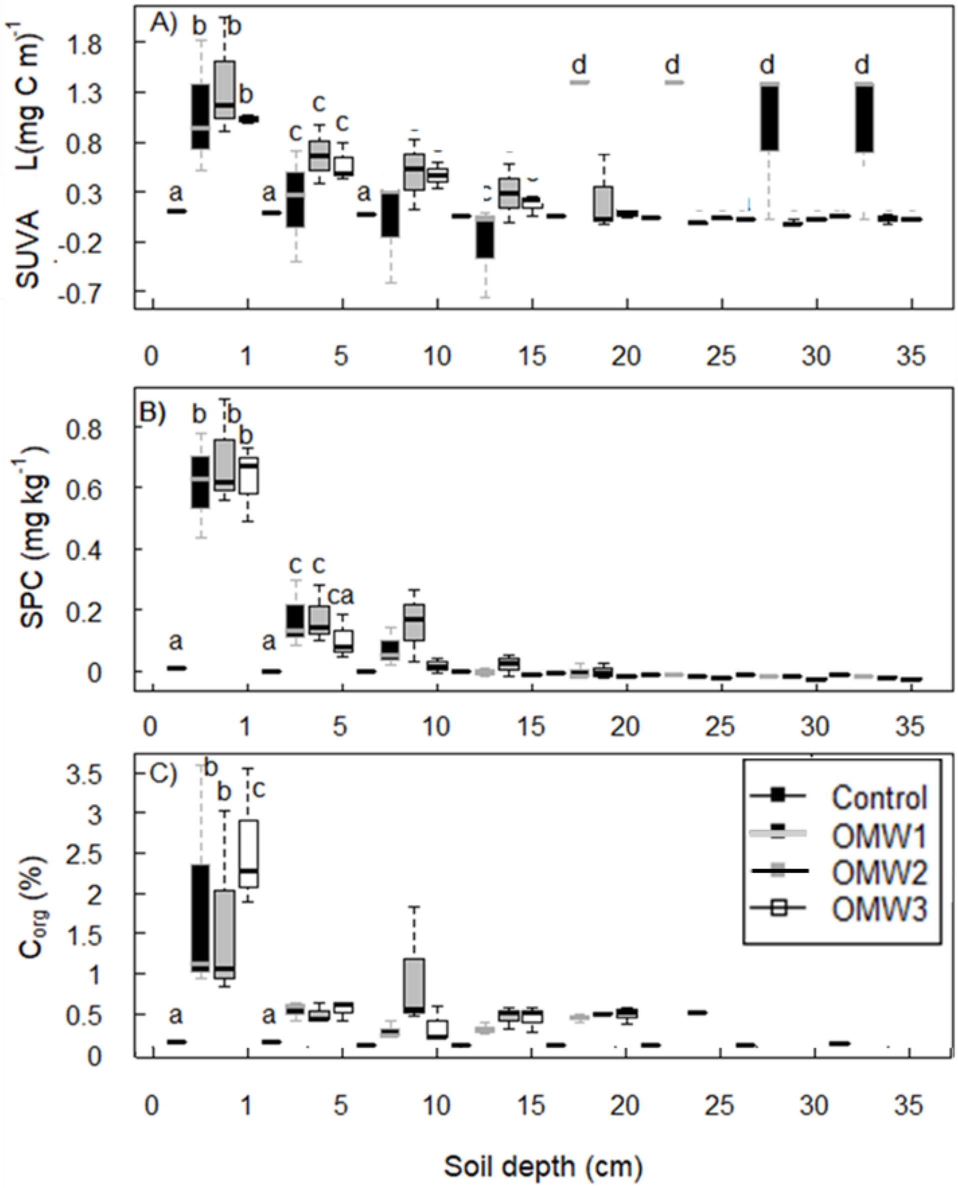

Figure 3-4 (A) Evolution of dissolved organic carbon (SUVA$_{254}$), (B) Soil soluble phenolic compounds (SPC) and (C) Organic carbon (C_{org}) as function of soil depth for OMW-treated (OMW 1-3) and untreated control soil. Different small letters indicate significant difference (p < 0.05) between OMW-treated and control soil as well difference between the three OMW-treated soils at different depths.

Up to 10 cm depth, the effect of OMW on SUVA$_{254}$ disappeared in OMW-treated soils expect OMW2. OMW application increased SPC and C_{org} only in the topsoil (0–10 cm) after the application of the winter scenario, whereby the increase was only significant for 0 to 5 cm depth (Fig.6). Within the first 5 cm, SPC sharply decreased until 10 cm and remained on a constant

level until 35 cm. The highest C_{org} (3-4 %) and SPC (0.8 – 1 mg kg^{-1}) were observed in the topsoil of OMW1, OMW2 and OMW3 (Fig.6), in which SPC was ten times and C_{org} was four times higher compared to control soil, which showed only low SPC and C_{org} concentration in all dephts (Tukey, $p < 0.001$). The difference between the OMW-treated soils and the untreated control soil are significant only until 5 cm depth ($p < 0.05$).

3.4.3 SOIL WATER REPELLENCY AND SOIL POROSITY DISTRIBUTION

NMR relaxometry was combined with optical contact angle measurements to assess the contribution of OMW on soil pore-size distribution and soil wettability. OMW application induced a significant increase of the OCA in all OMW-treated soils. The differences in the OCA between the OMW-treated soils and the untreated control soil was significant in all depths ($p < 0.05$) (Figure 3-5).

Under saturated conditions the relative proportion of coarse pores significantly increased in all OMW-treated soils compared with the control ($p < 0.05$). The increased proportion of soil coarse pores came along with the relative reduction of middle and fine pores (Figure 3-6).

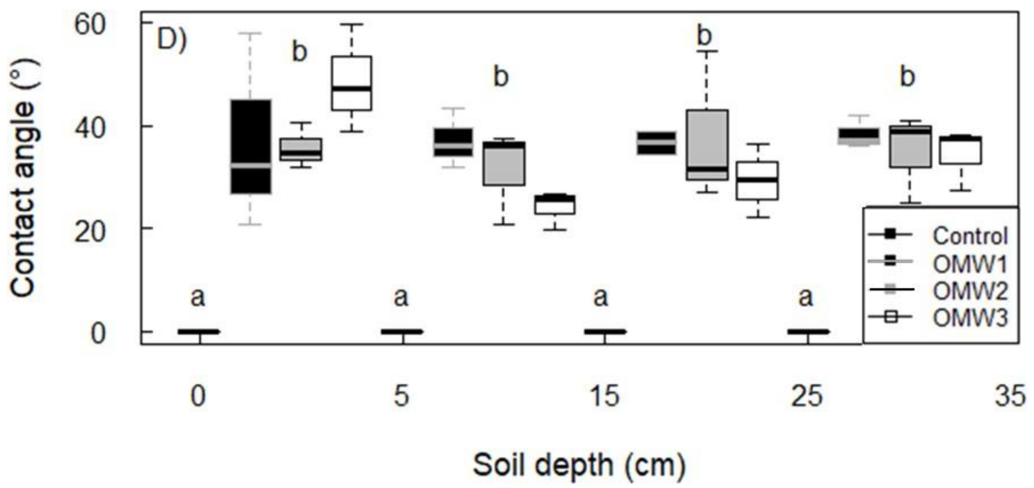

Figure 3-5 Optical contact angle measurements related for 0 to 35 cm depth of OMW-treated soils (OMW 1-3) and control soil (Control). Box plots show median (straight line) values. Different small letters indicate significant differences between soils, (Tukey: $p < 0.05$)

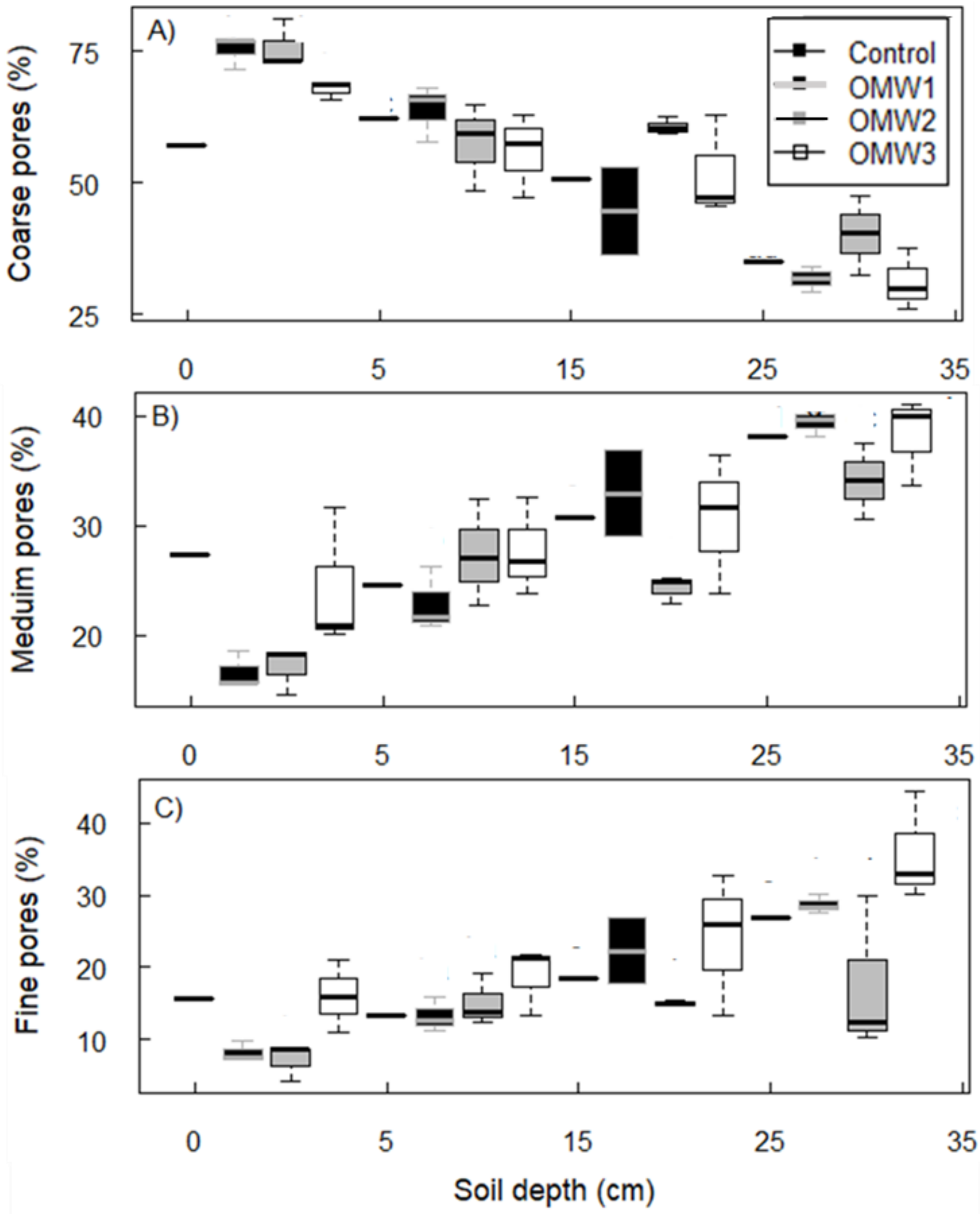

Figure 3-6 Pore size distribution (A) Coarse pore, (B) medium pores, (C) fine pores) based on the pore diameter 10μm-50μm, 0.2μm-10μm and <0.2μm for the coarse pore, medium pore and fine pore respectively for 0 to 35 cm depth of OMW-treated soils (OMW 1-3) and control soil (Control). Box plots show median (straight line) values.

3.4.4 EFFECTS OF SPC ON SOIL POROSITY DISTRIBUTION AND SOIL WETTABILITY

Most of phenols were immobilized in the upper soil layer. This can be explicated by the high correlation between SPC of the soil spots and the soil macro pores (Pearson correlation, *r* = 0.63). The clear soil spots have more coarse pore (Figure 3-7), higher SPC and contact angle (Figure 3-8) than the middle and dark spots.

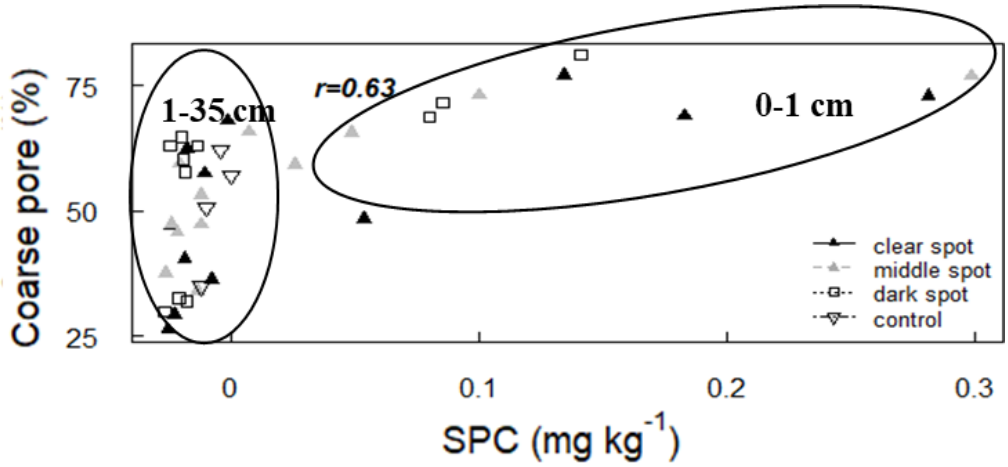

Figure 3-7 Pearson correlation between soluble phenolic compounds (SPC) and coarser pore in three OMW-treated soil spots colors and one untreated control. The difference between the treated soils and the control are significant *Tukey *p*< 0.05 (only at the soil depth 1cm).

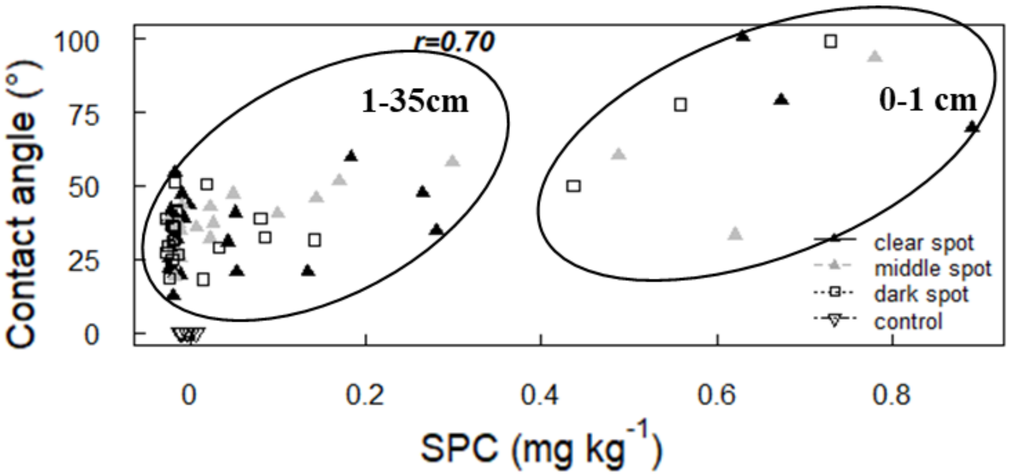

Figure 3-8 Pearson correlation between soluble phenolic compounds (SPC) and optical contact angle in three OMW-treated soil spots colors and one untreated control. The difference between the treated soils and the control are significant *Tukey p< 0.05 (only at the soil depth 1cm)

3.5 DISCUSSION

In the first part of this study (Chapter 2), a lysimeter experiment was conducted to assess the fate of OMW on the soil leaching quality on a small scale. We used the leachates information described previously to get insights about the transport mechanisms of the OMW and the percentages of OMW-constituents leaving the top 40 cm. Through comparison with the expected water transport based on conventional assumptions in the first work, we were able to evaluate the potential relevance of preferential flow effects during and after OMW application. However, as the transport experiment was not designed in a way allowing for traditional breakthrough curve analysis, this evaluation was semi-quantitative. A characterization of the transport regime in the lysimeters was not planned due to its expected influence on the soil properties and biological activity if performed before the experiment and on the retention profile if performed during the experiment. This turns out that such a characterization is necessary. Therefore, a slicewise dismantling was performed to obtain an idea on the relevance of preferential flow pathways derived through hydrophobic OMW constituents on the transport mechanisms responsible for leachates contamination.

At the end of the incubation phase, the soil surface was largely wettable with 15% WC and more than 20% of the WDPT were >60s. During the incubation phase, spatial heterogeneity has been observed in soil WDPT and color. The soil spots characterized with light color revealed higher WDPT than the dark soil spot. Therefore, OMW-treated and untreated control soil were dismantled slice wise following 8 depths considering three different soil WDPT scale. The chemical nature of the organic fraction and the different pore size domains in water pooled samples were also a key characteristic needed to differentiate physical and chemical OMW transport mechanisms in the soil core.

Results showed that OMW application changed the soil properties and resulted in chemical and physical heterogeneity in the soil core. These mechanisms were most effective in the first 10 cm. The clear soil spots were dominated with soil pores larger than 12µm in diameter. They were rich in phenols, K^+ and C_{org} and have a contact angle near to 100°. This is in accordance with Negassa et al., (2015) and Bailey et al., (2017) which revealed higher microbial transformations involving polyphenols observed in coarse pore domains. In the current study, a significant depth dependent reduction of coarse soil pores in OMW-treated soils because of the high OM and salt content of OMW, which can clog soil pores especially in the upper layers (Mahmoud et al., 2010). In fact, a strong effect of OMW application was found for soil EC. The high EC could result from the main ionic species, sodium chloride and sulphate, coming from OMW. This is in line with previous finding (Sierra et al., 2001). Hence, in long-term applications, replacement of the soil Ca by Na, K and Mg could lead to the degradation of the soil structure and the formation of saline soils as was suggested earlier by Zenjari & Nejmeddine, 2001. The increase of the salinity in soil due to OMW application can change soil physical properties by causing fine particles to bind together into aggregates (Warrence et al., 2002; Ayoub et al., 2014). This could be explained by the high correlation between Na^+ ions and contact angle data (cor.test OCA, Na r=0.71).

Contrarily to clear soil spots, the dark soil spots were dominated with the finer less accessible pores. They were characterized with lower OCA and contained relatively low proportions of SPC, C_{org}. This is in accordance with Yang et al., (2015) who found that finer pores are subject to spatial isolation under conditions of partial saturation than in coarser, better connected pores in which local hydration varies more regularly. The repartition of the soluble carbon in the different pores could be due to the chemical effects of wetting (winter simulation) and drying (summer simulation) of OM-OMW during the incubation phase. Similar observations were detected by (Bailey et al., 2017). They showed that the mineral components of the soil pores sorb OMW-organic compounds under drier soil conditions that are thus at higher local ionic strengths. Then when water tension decreases, and the soil pores fill with water for example under moist winter conditions, ionic strength decreases and patterns of sorption-desorption associated with different chemical forms of C change (Aubry et al., 2013). This phenomenon would be more significant in affecting carbon mineralization, in finer pores than in coarser, better connected pores in which local hydration varies more regularly (Yang et al., 2015).

All in all, the pore-size distribution in dependence on soil texture mainly influence the OMW-mobility in soil with high sand content which is the case on this experiment. This typically results from the temporal redistribution of OMW from initially coarse pores directly after OMW application into smaller soil pores as a result of increasing pore wall hydrophobicity (Lourenço et al., 2012; Negassa et al., 2015; Bailey et al., 2017). Spatial distribution of hydrophobicity could be probably due to the i) OMW-spreading which was done manually and/or the distribution of water during artificial irrigation using the sprinkler ii) leaching during rainy phases iii) evaporation and capillary rise mechanisms during dry phases. This is in line with Täumer et al., 2005, Diehl & Schaumann, 2007, and Lebron et al., 2012 who found also that the development and persistence of SWR is influenced by variations in environmental conditions such as temperature, moisture content, organic carbon content and pH. Throughout all analysis, SPC was the only parameter that showed high correlation with both Contact angle and the amount of coarse pore. After OMW treatment all the parameters were comparable to the non-treated control up to 10 cm depth expect the contact angle and some SUVA indictors. Therefore, further investigations that target the sorption capacity of the soil during and after OMW application throughout an incubated soil are needed to explore leaching effect on SPC stability in soils.

3.6 CONCLUSION

OMW application under semi-arid conditions with sandy loam soils has positive effects (accumulation of K^+ and organic carbon, increased water retention capacity) but also negative consequences (accumulation of phenolic substances, increased soil hydrophobicity, and salinity). These effects are most substantial in the topsoil. The negative effects despite the low rate applied (50 m^3 ha^{-1} $y^{-}1$) underline the strategy to apply lower application rates of OMW in alternating locations and times to enhance a beat monitoring of equal leaching timing and quality. Especially leaching after OMW application needs to be further investigated as we found indicators for SUVA and OCA in deeper soil layers. The remaining hydrophobic effects even at deeper soil depths induce the importance to make regular tillage to enhance biological degradation and homogeneity inside the soil matrix. An annual control of the WDPT even at deeper depth is also recommended for a rough estimation of the degree of soil recovery to plan further OMW applications. The overall results of this study indicate that applying the recommended doses of 50 m^3 OMW ha^{-1} y^{-1} in a sandy-loam soil under semi-arid conditions pose no clear negative effects on soil chemical properties. The only measured negative effect is the remaining increase in soil surface hydrophobicity. Whether phenolic compounds increased hydrophobicity in deeper soil layers was not completely resolved and need further lab analysis and attention. Additional research focusing on the optimal OMW spreading method and treatment before application is needed.

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4 FINAL SYNTHESIS AND CONCLUSION

4.1 RESULTS OVERVIEW

The conducted lysimeter study enabled to identify the effects of OMW on soil and leachate quality by providing insights into the mechanisms of (poly-)phenol transport and the driving factors modulating their leaching. The overall results showed that OMW application increased several soil parameters, including soil salinity, acidity, soluble phenolic compounds (SPC), total organic carbon (TOC), pore size distribution (PSD) and soil water repellency (SWR). These observations agree with several conducted studies on the effect of OMW on soil characteristics (Kurtz et al., 2015, 2021; Peikert et al., 2015; Steinmetz et al., 2015; Tamimi, 2016). Nevertheless, the relevance of these effects varied significantly between i) the OMW-treated soil leachates determined at different time points during the incubation phase and ii) the subsequent dismantled OMW-treated soil at different selected depths at the end of the incubation phase.

During the incubation phase, OMW application had hydrophobic effect on the soil surface and significant effects on soil leachate quality. It resulted in increased EC and reduced pH in soil leachates as well as increased leaching of organic indicators such as TOC, SPC, and $SUVA_{254}$. The effects varied among the different simulated seasons due to the complex interplay of factors related to precipitation through artificial rainfall, temperature, evapotranspiration, soil properties, and microbial processes. These seasonal variations lead to differences in the mobility, retention, and transformation of OMW components within the soil, ultimately resulting in varying impacts on soil. Since, the retention of organic compounds by the soil column varied among similar treated soils and among the parameters. The percentage of retained compounds differed substantially, indicating differences in the leaching potential of different organic components following OMW treatment.

The transport mechanisms could be a combination of advection, dispersion, diffusion, and preferential flow pathways: Advection referred to the movement of polyphenols with the water flow inside the lysimeters, while dispersion occurred due to the mixing of polyphenols within the water phase. Diffusion involved the movement of polyphenols from areas of higher OMW concentration to lower OMW concentration. Preferential flow pathways, e.g., macro pores which facilitated the rapid transport of polyphenols through the soil, bypassing significant retention and transformation processes. These mechanisms were controlled by:

a. Seasonal Variations: different simulated seasons (WS1, SPS, SS, and WS2) influenced soil dynamics, affecting polyphenol leaching and retention. Factors such as artificial precipitation patterns, temperature, evapotranspiration rates varied across simulated seasons, influencing water movement and polyphenol transport (Tamimi, 2016). For example, in WS1 and WS2 phenolic compounds concentrations increased in soil leachates. This could be due to hydrolysis reactions that mobilized the condensed and polymerized compounds, enabling their leaching. During SPS and SS, light and drought induced polymerization processes that caused OMW-derived soluble organic constituents to accumulate and remain on the soil surface (Steinmetz et al., 2015). In addition to polymerization, other processes were suggested to contribute to the accumulation of OMW-derived soluble organic constituents on the soil surface. Adsorption onto clay minerals, induced by the clay-rich soil, can effectively remove phenols from the OMW and contribute to their depletion in the soil (Kapellakis et al., 2015). Overall, light or drought-induced polymerization processes, along with other factors such as adsorption, microbial degradation, and changes in the soil microbial community, could contribute to the accumulation and persistence of OMW-derived soluble organic constituents on the soil surface. These processes can have environmental implications and should be considered in the management of OMW to minimize pollution and protect ecosystems.

b. Soil specific factors: the differences in SPC leachates between the simulated seasons were not significant highlighting the impact of soil-specific factors (e.g. pH, texture, OM content, …) which influenced significantly the leaching of polyphenols (Tapia-Quirós et al., 2022). For example, after OMW application soils had higher clay due to the increase in organic matter content and tended to have a higher adsorption capacity for polyphenols, reducing their leaching potential e.g., during SPS (Kavvadias et al., 2015; Levy et al., 2018). Also, pH affected the dissociation and solubility of polyphenols, promoting again their mobility in the soil-water system, e.g., during WS1 (Nagar et al., 2021).

c. Hydraulic conditions: water content, hydraulic conductivity, and hydraulic gradient in the soil column played a vital role in polyphenol leaching (Comegna et al., 2021). High soil moisture content enhanced hydraulic conductivity. For example, artificial rainy events during WS1 and WS2 promoted faster water flow, potentially increasing polyphenol transport through hydrolysis reactions. However, capillary rise mechanisms during SS raised OMW-derived soluble organic constitutes to the soil surface. Overall, phenol leaching through the soil matrix was significantly lower than the amount retained in the soil showing that the soil matrix retained a considerable portion of these OMW-derived compounds especially at the topsoil which revealed significant water repellency. The repellency effects were most severe during the first winter simulation. The matrix flow played an additional role in the OMW transport with low infiltration rate due to pore saturation and, therefore, leaching was slower. However, WDPT persisted throughout the subsequent simulation, and this raises the question whether these effects predominated the whole soil matrix. Even the soil retained OMW contaminants like SPC, the leaching of salts was not avoided and were transported faster during the whole incubation phase indicating that OMW application influenced the ion composition and conductivity of soil leachates over time, potentially affecting soil fertility and nutrient balance. Therefore, this study also assessed the retention of OMW-derived organic compounds in the soil column, showing substantial differences among the treated soils and individual parameters. After soil dismantling, OMW effects on the various assessed soil parameters were most substantial in the topsoil (0-5cm).

The study's assessment of the retention of OMW-derived organic compounds in the soil column revealed important findings, showing the complex interplay between OMW and soil parameters, with particularly noteworthy effects observed in the topsoil (0-5cm). The application of OMW triggered several significant alterations in key soil characteristics. Firstly, there was a notable decrease in soil pH, especially in the uppermost soil layer, shifting from an alkaline state in the control soil to a more acidic condition in the treated soils. This change in pH could be attributed to the introduction of organic acids and phenolic compounds from OMW, impacting soil chemistry (Mohawesh et al., 2019).

Furthermore, electrical conductivity (EC) levels increased across all soil depths in OMW-treated soils compared to the control. This increase in EC indicates a rise in soil salinity, particularly pronounced in the upper soil layer. The higher concentrations of sodium (Na^+) and potassium (K^+) in the topsoil of OMW-treated soils confirmed this salinization effect. It suggests that the leaching of these ions from OMW contributed to changes in soil salinity dynamics. Additionally, the study examined the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) which increased up to a certain depth in OMW-treated soils compared to the control. The rise in $SUVA_{254}$ suggests an accumulation of OMW-derived organic matter in the soil, particularly in the upper soil layers, which may influence its organic carbon content.

Moreover, soluble phenolic compounds (SPC) exhibited significant differences, primarily in the 0-5 cm depth of the topsoil following OMW application, with the highest SPC concentrations detected in this layer. These findings underscore the influence of OMW on the distribution and accumulation of phenolic compounds in the uppermost soil horizon, potentially affecting soil health and plant interactions.

One important observation was the alteration of soil pore sizes, notably under saturated conditions. OMW-treated soils displayed a considerable increase in the proportion of coarse pores, coupled with a reduction in middle and fine pores when compared to the control soil. This phenomenon indicates that the presence of phenols from OMW led to the clogging of soil pores, particularly in soil spots with larger coarse pores exhibiting a high contact angle. In contrast, finer, less accessible pores in dark spots contained lower concentrations of SPC and OCA. This shift in pore size distribution has implications for various soil processes, particularly water infiltration and movement (N. J. Jarvis, 2020).

The impact of these changes in soil pore structure extends to water infiltration dynamics. Wetting and drying cycles during the incubation phase influenced the distribution of soluble carbon in different pore sizes, resulting in variations in carbon mineralization. Soil transport patterns were also affected by significant deviations from the original pore size distribution, leading to the reassembly of the soil's internal structure. This reconfiguration manifested as an overall increase in macro pores and a reduction in middle and fine pores. Consequently, this alteration in soil porosity can contribute to the formation of narrow pathways within treated soils, potentially limiting the transfer of water and OMW particles (Figure 4-1)

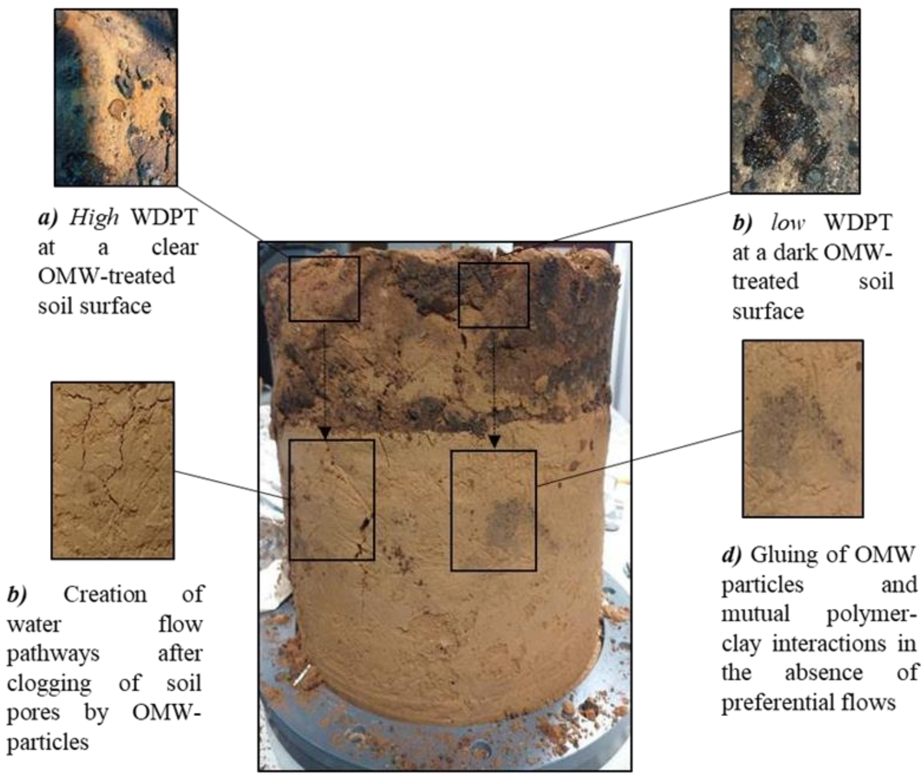

Figure 4-1 Schematic model for dismantled OMW- treated soil incubated in a lysimeter after the sequence of temperature and moisture conditions, (own figure)

All in all, the dismantling and analysis of the soil samples provided additional insights into the changes in pH, EC, SPC, C_{org}, OCA and soil porosity. OMW application led to salinization of the topsoil's and changes in the concentrations of Na^+ and K^+. The increase in $SUVA_{254}$ values indicated the persistence of OMW-derived effects in certain soil depths. The increase in SPC only in the topsoil highlighted the accumulation of these compounds in the topsoil after OMW application.

4.2 RECOMMENDATIONS AND OUTLOOK

To effectively manage the impact of OMW on soil and make informed irrigation decisions, several recommendations emerge from this study. Firstly, regular monitoring of soil moisture content and distribution is essential to gauge water availability for plant uptake and guide irrigation scheduling based on timing and quantity. Second, it's crucial to monitor soil electrical conductivity (EC) levels to manage soil salinity effectively. If OMW application increases EC, adjustments in irrigation practices should be made to maintain optimal soil salinity for plant growth, possibly involving drainage to mitigate salinization. Third, understanding the fate and leaching potential of OMW-derived organic compounds is crucial for environmental assessment and irrigation decision-making. Monitoring TOC, SPC, and SUVA parameters can offer insights into OMW organic matter transport dynamics. Lastly, when making irrigation decisions, considering the specific soil-plant system characteristics, including soil properties, crop type, and water requirements, and the effects of OMW application should be factored in for optimizing practices and ensuring sustainable crop production. Looking ahead, based on this study's findings, it is advisable to minimize OMW application due to high salinity levels in the leachates. Lower OMW application rates at different times and locations, coupled with regular tillage and monitoring, can be considered. Additionally, researching effective treatment methods for OMW and optimizing its disposal pre-application can help mitigate negative consequences, exploring advanced treatment technologies' effectiveness in improving soil and water quality. Long-term field-scale studies are essential to comprehend the real-world impact of OMW application, providing insights into OMW contaminant dynamics in the soil matrix and their transport through rainwater and irrigation. Future studies should employ continuous simulation systems with weighing lysimeters to accurately determine water content changes and capture a full range of hydrological and agricultural phenomena in the field. Regular leaching campaigns during OMW application are crucial to monitor contaminant movement and fate beyond the immediate soil environment, evaluating leachate composition and potential contamination risks. Lastly, to comprehensively assess OMW application's impact on land, research should extend beyond soil properties to include monitoring OMW constituents' leaching behavior, contamination potential, and long-term effects on soil health, water quality, and the overall ecosystem balance. In conclusion, implementing these recommendations and pursuing further research, as outlined in the outlook section, can contribute to better managing OMW application, minimizing its adverse effects on soil and water resources, and ensuring sustainable agricultural practices.

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5 ANNEX

5.1 LIST OF ABBREVIATIONS

OMW	olive mill wastewater
WC	water content
OM	organic matter
WS1	first winter simulation
WS2	second winter simulation
SPS	spring simulation
SS	summer simulation
SWR	soil water repellency
PSD	pore size distribution
TOC	total organic carbon
DOC	dissolved organic carbon
^1H-NMR	^1H proton nuclear magnetic resonance relaxometry
OCA	optical contact angle
EC	electrical conductivity
SPC	Soluble phenolic compounds
$SUVA_{254}$	Specific ultraviolet absorbance at 254 nm

5.2 LIST OF TABLES

5.3 LIST OF FIGURES

5.4 CURRICULUM VITAE

Education:

2009-2014	**Diploma Environmental Sciences** University of Sfax, FSS Main subject: Earth sciences Minor subjects: Environment and planning
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