Effects of Seasonal Olive Mill Wastewater Application on soil: Field Experiment in Bait Reema village, Palestine

by

Nisreen Tamimi (M.Sc.)

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Thesis examiners:
Prof. Dr. Gabriele E. Schaumann, Universität Koblenz-Landau, Germany
Dr. Dörte Diehl, Universität Koblenz-Landau, Germany

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Declaration

I hereby declare that I autonomously conducted the work shown in this Ph.D. thesis entitled "Effects of Seasonal Olive Mill Wastewater Application on soil: Field Experiment in Bait Reema village, Palestine". 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.

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“On this earth is that which deserve life:
On this earth, there is the lady of the land,
the mother of beginnings,
and the mother of endings.
It used to be called Palestine,
it will be called Palestine.
My lady, I deserve,
because you are my lady,
I deserve life”

-Mahmoud Darwish-

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Abstract

The global problematic issue of the olive oil industry is in its generation of large amounts of olive mill wastewater (OMW). The direct discharge of OMW to the soil is very common which presents environmental problems for olive oil producing countries. Both, positive as well as negative effects on soil have been found in earlier studies. Therefore, the current study hypothesized that whether beneficial effects or negative effects dominate depends on the prevailing conditions before and after OMW discharge to soil. As such, a better understanding of the OMW-soil interaction mechanisms becomes essential for sustainable safe disposal of OMW on soil and sustainable soil quality.

A field experiment was carried out in an olive orchard in Palestine, over a period of 24 months, in which the OMW was applied to the soil as a single application of 14 L m^{-2} under four different environmental conditions: in winter (WI), spring (SP), and summer with and without irrigation (SU_{moist} and SU_{dry}). The current study investigated the effects of seasonal conditions on the olive mill wastewater (OMW) soil interaction in the short-term and the long-term. The degree and persistence of soil salinization, acidification, accumulation of phenolic compounds and soil water repellency were investigated as a function of soil depth and time elapsed after the OMW application. Moreover, the OMW impacts on soil organic matter SOM quality and quantity, total organic carbon (SOC), water-extractable soil organic carbon (DOC), as well as specific ultraviolet absorbance analysis ($SUVA_{254}$) were also investigated for each seasonal application in order to assess the degree of OMW-OM decomposition or accumulation in soil, and therefore, the persisting effects of OMW disposal to soil.

The results of the current study demonstrate that the degree and persistence of relevant effects due to OMW application on soil varied significantly between the different seasonal OMW applications both in the short-term and the long-term. The negative effects of the potentially hazardous OMW residuals in the soil were highly dependent on the dominant transport mechanisms and transformation mechanisms, triggered by the ambient soil moisture and temperature which either intensified or diminished negative effects of OMW in the soil during and after the application season. The negative effects of OMW disposal to the soil decreased by increasing the retention time of OMW in soil under conditions favoring biological activity. The moderate conditions of soil moisture and temperature allowed for a considerable amount of applied OMW to be biologically degraded, while the prolonged application time under dry conditions and high temperature resulted in a less degradable organic fraction of the OMW, causing the OMW constituents to accumulate and polymerize without being degraded. Further, the rainfall during winter season diminished negative effects of OMW in the soil; therefore, the risk of groundwater contamination by non-degraded constituents of OMW can be highly probable during the winter season.

Zusammenfassung

Der hohe Anfall von Olivenölmühlenabwasser (OMW) ist ein weltweites Problem in der Olivenölproduktion. Eine weit verbreitete Praxis ist die Entsorgung dieses Abwassers durch direktes Ausbringen auf den Boden die für Olivenöl produzierende Länder eine bisher nur wenig bekannte Umweltproblematik darstellt. Bisherige Untersuchungen ergaben sowohl positive als auch negative Effekte für den Boden. Daher wurde in der aktuellen Studie die Hypothese aufgestellt, dass, ob positive oder negative Effekte des OMW im Boden überwiegen, von den Bedingungen im Boden vor und nach der Ausbringung des OMW abhängt. Für eine nachhaltige und sichere Entsorgung von OMW bei gleichzeitiger Erhaltung der Bodenqualität ist außerdem ein besseres Verständnis der Mechanismen der Wechselwirkungen zwischen OMW und Boden unverzichtbar.

In einem 24 monatigen Feldexperiment in einem Olivenhain in Palästina wurde OMW in einer Einzeldosis von 14 L m^{-2} unter vier verschiedenen Umweltbedingungen im Winter, im Frühling, und im Sommer mit und ohne Bewässerung, auf den Boden ausgebracht. In der vorliegenden Arbeit wurde so der Einfluss von jahreszeitlichen Bedingungen auf die kurz- und langfristigen Wechselwirkungen zwischen OMW und Boden untersucht. Sowohl das Ausmaß als auch die Persistenz von Bodenversalzung, Bodenversauerung, die Anreicherung phenolischer Verbindungen und die Entwicklung von wasserabweisenden Eigenschaften wurden in Abhängigkeit von der Bodentiefe und von der Zeit nach der Abwasserausbringung bestimmt. Darüber hinaus wurden die Effekte des OMW auf die Qualität und Quantität der organischen Bodensubstanz (SOM), den gesamten organischer Kohlenstoff (SOC), den löslichen organischen Kohlenstoffs (DOC), sowie die spezifische UV-Absorption ($SUVA_{254}$) für alle jahreszeitlichen Bedingungen untersucht, um das Ausmaß an Abbau oder Anreicherung von OMW, und damit dessen Persistenz im Boden zu bewerten.

Die Ergebnisse der aktuellen Studie zeigen, dass das Ausmaß und die Persistenz der relevanten Effekte auf den Boden sich sowohl kurz- als auch langfristig deutlich zwischen den verschiedenen jahreszeitlichen Abwasserausbringungen unterscheiden. Die negativen Auswirkungen der potentiell gefährlichen OMW Rückstände im Boden hängen stark von den vorherrschenden Transport- und Transformationsmechanismen ab, die, gesteuert durch die Bodenfeuchte und –temperatur während und nach der Ausbringung, diese entweder verstärken oder verringern. Mit zunehmender Aufenthaltszeit des Abwassers unter günstigen Bedingungen für eine biologische

Aktivität treten weniger negative Effekte auf. Moderate Bodenfeuchte und –temperatur ermöglichen einen relevanten biologischen Abbau, während längere Kontaktzeiten unter heißen und trockenen Bedingungen dazu führen, dass sich abwasserbürtige organische Substanzen anreichern und durch Polymerisation in schwerer abbaubare Fraktionen umgewandelt werden. Die starken Niederschläge im Winter vermindern zwar die negativen Auswirkungen von Olivenölmühlenabwasser im Boden, was jedoch höchstwahrscheinlich zu Lasten eines erhöhten Risikos von Grundwasserkontamination durch nicht abgebaute abwasserbürtige Substanzen geht.

1 General Introduction

1.1 World olive production

The olive trees farming and olive oil production are major agricultural and economic activities for Mediterranean countries. More than 65 % of the world total cultivated areas of olive trees are located in Europe (Donoso-Bravo et al., 2016), and contribute to 72 % of the world olive production (Valta et al., 2015) as estimated in 2011/2012. The major producer countries worldwide are Spain, Italy, Greece (Tsagaraki et al., 2007), followed by, and to a lesser extent, Turkey, Morocco, Tunisia and Syria. Olive trees cultivation and olive production depend on many factors including soil fertility, irrigation availability and climatic conditions. The traditional or low-density cultivation system (50-150 tree ha^{-1}) is more common in areas of low soil fertility and lack of water resources which primarily depends on rainfall for irrigation. The intensive cultivation system (300-400 tree ha^{-1}) is common in irrigated high soil fertility regions.

In the Middle East countries such as Palestine, Jordan, and Lebanon, the olive production is for local consumption with only small amount of olives being exported abroad. In Palestine, the olive farming and olive oil carry both economic and social importance (Figure 1-1). According to the Palestinian Central Bureau of Statistics (2013), at least 52.5 % of the cultivated land, estimated at 881.9 km^2, is planted with olive trees; it accounts for 70 % of fruit production, contributes to 20% of agricultural income and more than 100,000 families depend on the olive trees for their livelihoods to some extent.

Figure 1-1: Traditional olive orchard in Palestine (left). Palestinian family during the olive harvesting season (right). (Source: Trilateral project "OLIVEOIL", Koblenz-Landau University).

1.2 Olive oil industry

Olive oil is considered as the cornerstone of the Mediterranean diet in traditional producer countries. However, the global consumption of olive oil has increased continuously in the last decades due to changes in the dietary style of the people over the world, and increase awareness of the health benefits associated with the consumption of olive oil and its vitality. This led to approximately 40 % increase in olive trees cultivation (Dermeche et al., 2013) in order to cover the global demand for olive oil.

Olive harvesting usually occurs during the autumn/winter season, mainly from October to February (Piotrowska et al., 2006; Moraetis et al., 2011). After harvesting the olive fruit, it is delivered to olive mills in order to extract the oil. Generally, the olive oil extraction is accomplished through a sequence of steps starting with washing of the olive seeds, followed by the grinding of olives together with their seeds and ending with milling and beating of the olive pulp. During the milling step, water is added to further break down the olives to create larger oil drops. For this purpose, salt is also added which aids the osmotic break down of cells in the olives and helps separate the oil and water from each other.

Different oil extraction technologies have advanced significantly during the past decades (Figure 1-2) and can be categorized into the traditional press, and continuous press as described below.

The traditional or discontinuous press: is the oldest and most widespread method for oil extraction (Dermeche et al., 2013). During the milling stage a small quantity of water approximately~ 0.03-0.05 m^3 ton^{-1} of olive seed is added (Tsagaraki et al., 2007). The byproducts of the traditional press are high-quality olive oil, the solid waste called pomace, and the liquid wastewater called olive mill wastewater (OMW).

The continuous press: is the modern method of olive oil extraction which uses an industrial decanter to separate oil from olive components by centrifugation. The press can be operated either by three-phase or two-phase decanter. The three-phase method produces better oil quality and requires small area for installation. However, during the milling step, a large quantity of water approximately ~ 0.6-1.3 m^3 ton^{-1} of olive seed is required (Alburquerque et al., 2004; Saadi et al., 2006; Hanifi, 2009). In addition to the olive oil, this technology produces a large amount of olive mill wastewater (Roig et al., 2006) and solid waste pomace. On the other hand, the two-phase decanter is a new centrifugation system, developed during the 1990s (Dermeche et al., 2013), which is similar to three-phase centrifugation system but modified to reduce the quantity of OMW generation. It has only two byproducts: the oil and humid solid waste. The advantage of this decanter over the three-phase one is in the limited quantity of water added during the milling step which in return minimizes the quantity of OMW produced by up to 80 % (Tsagaraki et al., 2007). Consequently, it is considered an "environmental friendly" method for olive oil production (Valta et al., 2015). Nevertheless, it produces a very humid solid waste, the disposal of which has not been fully resolved.

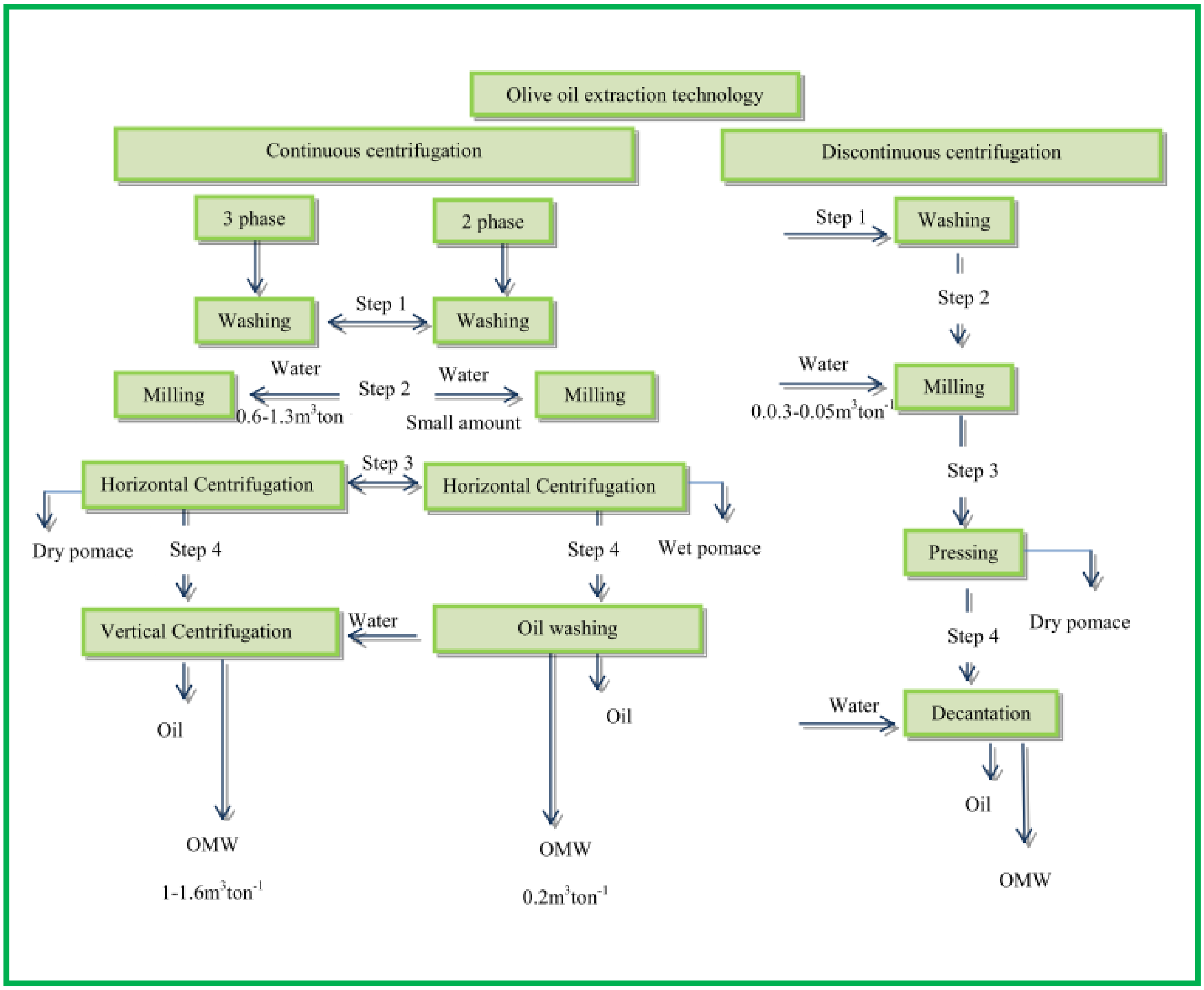

Figure 1-2: Key information of the olive oil extraction technologies. (Figure adapted from: Alburquerque et al., 2004; Dermeche et al., 2013; Valta et al., 2015).

1.3 Olive mill wastewater

1.3.1 Characteristic of olive mill wastewater

The global problematic issue of that olive oil industry is that it generates a high amount OMW (Figure 1-3), the disposal of which presents major social, economic and environmental problems for oil producing countries (Plaza et al., 2005; Di Serio et al., 2008). Despite the significant role the extraction technology plays in limiting the volume of OMW produced (Sierra et al., 2001; Kapellakis et al., 2008), the annual production of OMW in the Mediterranean countries exceeds $30x10^6m^3$ (Barbera et al., 2013) over a short period during the winter season (Chartzoulakis et al., 2010).

Figure 1-3: Olive oil produced by 3 phase extraction technology in Palestine (left). Olive mill wastewater produced during the oil extraction process (right). (Source: Trilateral project "OLIVEOIL", Koblenz-Landau University).

The OMW is a mixture of vegetation water, soft tissues of olive fruits and the water used in the milling process (Alburquerque et al., 2004). It is a turbid liquid, black to dark brown in color and smells of oil (Sierra et al., 2001; Dermeche et al., 2013). Its characteristics depend on many factors such as the extraction technology employed, the variety and maturity of the olives, the climatic conditions, the cultivation management and the storage time (Sierra et al., 2001; Aviani et al., 2012; Barbera et al., 2013; Dermeche et al., 2013; Tayoub et al., 2015; Valta et al., 2015). Nevertheless, the typical characteristics of OMW are: low pH ranges of 3-6 (Azbar et al., 2004; Niaounakis and Halvadakis, 2004), high biological and chemical oxygen demand (Arienzo and Capasso, 2000; Hanafi et al., 2013), high concentration of oils and greases of ranges 1-23 g L^{-1} (Sierra et al., 2001; Azbar et al., 2004; Amaral et al., 2008), high salinity (Roig et al., 2006), and the high content of phenolic compounds (De Marco et al., 2007; Hanifi and El Hadrami, 2008) responsible for the typical black color of OMW (Piotrowska et al., 2006).

1.3.2 Olive mill wastewater treatment and disposal options

The organic load in OMW is considered as one of the highest in all concentrated effluents, which is 100-150 times higher than the organic load of domestic wastewater (Khatib and Basheer, 2009). Furthermore, it was estimated that the load of phenolic compounds in OMW is 1000 times higher than in domestic wastewater (Niaounakis and Halvadakis, 2004). The seasonal large discharge of OMW with high pollution load of 30-150 g L^{-1} BOD and 40-200 g L^{-1} COD (Sierra et al., 2001; Azbar et al., 2004; Niaounakis and Halvadakis, 2004; Chartzoulakis et al., 2010) and its associated effects on sewerage corrosion and sediments build up (Tsagaraki et al., 2007) are the main reasons for the prohibition of OMW discharging into municipal sewerage system.

Evaporation in open lagoons and/or land disposal remain the most common practice for the OMW disposal (Azbar et al., 2004) 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 many Mediterranean countries such as Greece (Greco et al., 2006), Turkey, Israel (Laor et al., 2011), Syria (Tayoub et al., 2015) and Palestine (Khatib and Basheer, 2009) such OMW treatments are rare to non-existing due to the following factors: the high regional scattering of olive mills and their large variation in size and capacity, type of oil extraction press, the volume of OMW produced and the land availability. These factors limit the possibility of economic design with reasonable operational cost of such treatment options for OMW in these countries (Brunetti et al., 2007).

Consequently, OMW-land disposal has been the most common practice as a low-cost alternative. Currently, there is no unified legislation or regulations for OMW-land disposal quantities and the standards are left to individual countries to enforce. For example, the annual legal limit for controlled OMW disposal to soil in Portugal and Italy is 80 m^3 ha^{-1} (Giuffrida, 2010). While in Israel, it reaches up to 100 m^3 ha^{-1} (Laor et al., 2007; Saadi et al., 2007b). 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 (Chartzoulakis et al., 2010). But the problem in many of the Mediterranean countries lies in the uncontrolled OMW disposal into the open environment i.e. soil, streams, rivers and seas either because of the absence of legislation or the lack of OMW treatment alternatives.

In this context, Palestine is one example of such countries that generates a large amount of OMW annually. The quantity of olive oil produced in 2014 was 24,758.5 tons with an increase of 40.3 % compared to 2013 (PCBS, 2014) , an associated OMW is approximately 1.7 m^3ton^{-1} olive oil (Khatib and Basheer, 2009). This waste is generated from 265 olive presses, of which 241 utilize "three-phase technology" and only 24 are traditional presses. Due to the absence of legislation and treatment facilities for OMW in Palestine, the only disposal method available is the uncontrolled discharge to open fields and valleys which need to be regulated and standardized to limit potential pollution expected to soil and crop.

1.4 Environmental impacts of OMW-land disposal

The direct application of OMW to soil has been commonly used as a low-cost disposal method in the Mediterranean region until now. Its impacts on the soil physical, chemical, and biological properties have been extensively investigated during the last 20 years (Galoppini et al., 1994; Sierra et al., 2001; Barbera et al., 2013; Mekki et al., 2013; Peikert et al., 2015). Different findings and conclusions have not been conclusive on the environmental risk or benefit of OMW disposal in the agriculture system on the whole.

The Mediterranean region is characterized by arid and semi-arid climatic conditions. In addition to water deficiency in this region, the soil has a very low microbial activity and low nutrient availability (Garcia-Barrionuevo et al., 1993; Di Bene et al., 2013), therefore, many studies considered OMW disposal on soil as a fertilizer and organic amendment as well as an integrative water resource (Celano et al., 2010). In this perspective, the presence of organic matter (OM) and plant nutrients such as K, P, and Mg identifies the positive effect of OMW on soil fertility and productivity as an organic amendment (Paredes et al., 1999; Mekki et al., 2006a; Dermeche et al., 2013; Di Bene et al., 2013; Chaari et al., 2015).

OMW-land disposal was found to increase the soil organic matter (SOM) (Paredes et al., 1999; Casa et al., 2003; Chaari et al., 2014) up to 75 cm in depth (Kapellakis et al., 2015). Mohawesh et al. (2014) found that high organic matter content in OMW improved the soil water-holding capacity in two sites irrigated with OMW for 5 and 15 years respectively, despite significantly reducing the large pore (macro-pore) percentage. Further, the OMW application to soil encouraged microbiological activities in the soil (Buchmann et al., 2015; Saadi et al., 2007a; Tardioli et al.,

1997) in addition to herbicidal activity and ability of inhibiting soil–plant pathogens which were viewed as positive side effects of OMW disposal in soil (Kotsou et al., 2004).

On the other hand, the organic fraction of OMW contains greases, fatty acids, proteins, carbohydrates, polyalcohols, glucosides, tannins and polyphenols (Mulinacci et al., 2001; Diamantis et al., 2013). In this context, negative impacts and alteration on soil quality due to OMW disposal to soil were also investigated. The accumulation of OMW-OM in soil has been shown to decrease the saturated hydraulic conductivity and to enhance the soil water repellency (SWR) due to accumulation of hydrophobic constituents such as grease and oil in the topsoil (Gonzalez-Vila et al., 1995; Mahmoud et al., 2010; Steinmetz et al., 2015). Soil water repellency (SWR) could lead to non-equilibrium water flow in soils (Jarvis et al., 2008). Peikert et al. (2015) concluded that the hydrophobized effect on soil may accumulate with each new application of OMW. However, the degree of SWR is determined by the quality of organic matter in the soil rather than simply by its quantity (Doerr et al., 2000).

The OM brought by OMW in soil can result in an increase in soil organic carbon (SOC), and dissolved organic carbon (DOC) whether OMW was applied in single application or in repeated application over long period of time (Cox et al., 1997; Lopez-Pineiro et al., 2006; Brunetti et al., 2007; Piotrowska et al., 2006; Di Bene et al., 2013; Kurtz et al., 2015; Peikert et al., 2015). Thus, a modification in SOM qualitative properties can be expected as the response of OMW application (Schaumann et al., 2010). The dissolved organic matter in OMW can increase the mobilization of other organic and inorganic contaminants (Morillo et al., 2002) and, therefore, can also potentially influence microbial processes in downstream lakes and streams.

Further, numerous studies reported a decrease in soil pH, an increase in soil salinity and toxicity in response to OMW application (Zenjari and Nejmeddine, 2001; Di Serio et al., 2008; Chartzoulakis et al., 2010; Kavvadias et al., 2010; Moraetis et al., 2011; Di Bene et al., 2013). The phytotoxic effect was conclusively attributed to phenolic substances in OMW (Dalis et al., 1996; Buchmann et al., 2015). In this sense, the OMW disposal caused shift in soil microbial communities associated with abundant phenolic compounds as well as high salinity which negatively inhibited the bacterial growth (Mekki et al., 2006b; Wichern et al., 2006; Mohamed and Martiny, 2011; Barbera et al., 2013) and increased population ratio of fungi: bacteria (Mekki et al., 2006a; Mechri et al., 2007; Mechri et al., 2008; Di Bene et al., 2013).

However, the unwanted negative effects of OMW disposal on soil occurred shortly after discharge and decreased over time. No such long-term effects were observed when controlled doses of 50-100m^3ha^{-1} of OMW were utilized (Mekki et al., 2006a; Laor et al., 2011; Di Bene et al., 2013). This can be explained by either degradation of OM brought about by OMW or incorporation into soil organic matter or adsorption to soil particles or leaching.

Indeed, the OMW is generated during the winter season and its land disposal mostly occurs during this season. Not much is known about leaching in winter; nevertheless, a potential groundwater contamination has been reported by Azbar et al. (2004). Rainfall during the winter season help leach the salts and phenolic compounds accumulated in soil (Boukhoubza et al., 2008; Tzanakakis et al., 2011; Kapellakis et al., 2015). Some were found in deeper soil layers (up to 1.25m depth) and in the groundwater (Zenjari and Nejmeddine, 2001) during the winter season (Sierra et al., 2001).

Numerous studies related to a certain extent the environmental conditions during OMW disposal on soil (Zenjari and Nejmeddine, 2001, Mekki et al., 2009, Di Bene et al., 2013, Steinmetz et al., 2014), the soil properties, management practices (tillage) and the rate of OMW application to the beneficial or negative effects attributed to OMW. It is apparent that chemical, physical, and biological processes cause and influence the type and degree of relevant effects of OMW on soil, nevertheless, the actual OMW-soil interaction processes and mechanisms involved are still not clear. So far, little interest has been given to the study of the OMW-soil interaction mechanisms causing undesired changes in soil quality and whether they are reversible or irreversible in the long term.

1.5 Objectives and structure of the thesis

Understanding the OMW-soil interaction mechanisms which may lead to beneficial (increasing soil fertility) or negative effects (e.g. phytotoxicity and soil water repellency) is essential for sustainable safe disposal of OMW on soil and sustainable soil quality. This requires systematic studies based on comparative data from field experiments and incubation studies under laboratory conditions. The trilateral project “OLIVEOIL” (SCHA849/13) funded by German Research Foundation/Deutsche Forschungsgemeinschaf (DFG) has been devoted to this task. The overall aim of the project is to investigate the OMW-soil interaction mechanisms affecting the soil quality and their temporal dynamics in order to maximize the beneficial effects and minimize the negative effects of OMW disposal on soil and groundwater.

The current work presented in this thesis is part of the framework of this project. It includes an intensive systematic field study in a traditional olive orchard carried out in Palestine over a period of two years (2012-2014) (Figure 1-4). It is hypothesized that the environmental conditions such as temperature and soil moisture during and after the OMW disposal to soil can influence the overall effects in soil quality. During the winter season, low biological activities are expected under the cold and moist conditions which could delay the degradation of OM brought by OMW, and the frequent rainfalls could also promote leaching of soluble compounds into deeper layers. On the other hand, moderate conditions of moisture and temperature during the spring season are expected to allow for considerable biological degradation, and result in lower toxicity and repellency effects in soil. While in the summer season, under hot and dry conditions, organic compounds brought by OMW are expected to accumulate in soil due to low biological activities and may subsequently induce stronger negative effects. Combined hot and moist conditions, resulting from irrigation during the summer season, are expected to enhance the biological degradation of OM-OMW and thus to minimize its overall negative effects in soil.

To validate these hypotheses, four different scenarios of OMW application were performed in the study site, where OMW was applied to the soil as a single application of 14 L m^{-2}, to simulate an extreme situation under four different environmental conditions: in winter, spring and summer with and without irrigation (Figure 1-4). The study investigated and monitored the short-term and long-term effects of OMW application on soil properties in comparison to control plots administered with tap water at different depths under different environmental conditions to understand the OMW-soil transport and transformation mechanisms (Chapter 2). For each scenario, soil samples were collected one week prior to OMW or tap water application for the control plots, and 2 days, 3 weeks, 6 weeks, 3 months, 6 months, 9 months, and 12 to 18 months after OMW or tap water application. At each sampling event, samples were collected at five different depths of 0 - 5 cm, 5 - 10 cm, 10 - 15 cm, 15 - 25 cm, and 25 - 35 cm. The complete data set of the degree and persistence effects of soil salinity, acidity, the content of phenolic compounds as well as SWR were investigated for each scenario as a function of depth and time.

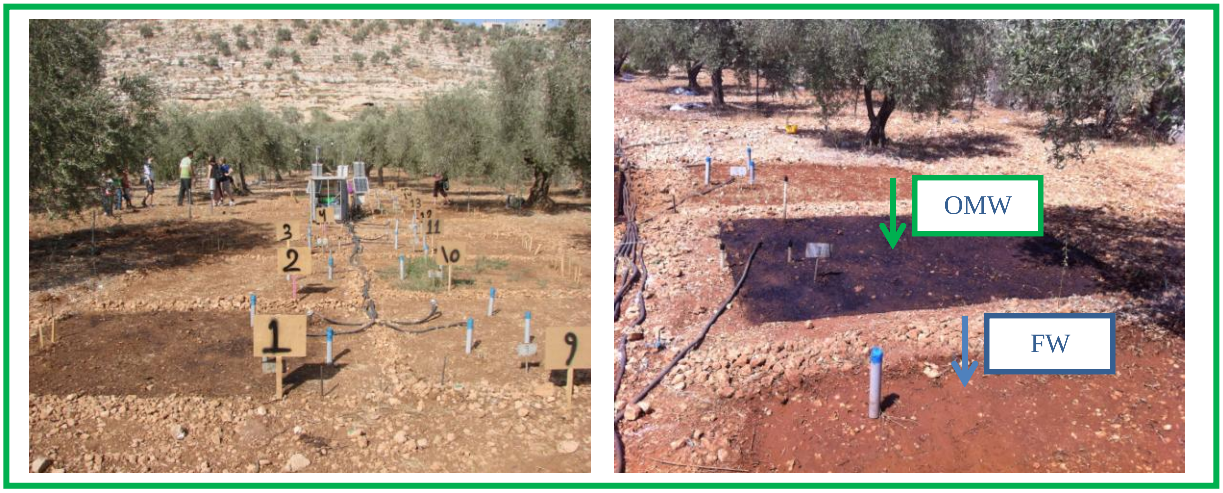

Figure 1-4: Experiment field study located in Beit Reema village-Palestine (left). An example of olive mill waste water treated plot (OMW) and control plot treated by tap water (FW) (right). (Source: Trilateral project “OLIVEOIL”, Koblenz-Landau University).

The second objective of the current study presented in this thesis is to investigate the qualitative and quantitative changes in native SOM after seasonal applications of OMW (spring, summer with and without irrigation and winter), and to investigate to which extent the environmental conditions may contribute to the persistence of such changes (Chapter 3). The OMW was beneficially assessed as it can increase OM content in soil. Nevertheless, the chemical composition of SOM can be influenced by the quality of OM inputs, the decomposition phase, and soil management practices (Baldock and Skjemstad, 2000). Thus, OMW-OM can induce such qualitative and quantitative changes in native SOM, but the degree to which these effects are reversible or irreversible is investigated. It is hypothesized that the OMW application to soil changes the native SOM quantitatively and qualitatively by increasing the labile fraction rather than the stable fraction. However, the degradation, transformation, and immobilization of OMW-OM in soil are expected to differ under different conditions of soil moisture and ambient temperature since the environmental conditions during and after OMW application to soil can influence the degree of OM degradation or stability. For this, SOM thermal properties of the top layers (0-10 cm depth) were investigated at two days and eighteen to twenty four months after each OMW application scenario, using thermogravimetry-differential scanning calorimetry (TG-DSC) coupled with mass spectrometry (MS). In addition to thermal analysis, the total and water-extractable soil organic carbon was quantified and specific ultra violet absorbance analysis was used to further characterize the quality of the dissolved organic carbon.

Finally, Chapter 4 includes the main conclusions and synthesis of the current thesis with an answer deduces OMW-soil interaction mechanism under different climatic conditions, and recommendations for best conditions of OMW disposal to soil in order to minimize negative effects in soil. Further, open questions and further research needs are presented in the outlook

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2 Effects of Olive Mill Wastewater disposal on Soil: Interaction Mechanisms during Different Seasons.

2.1 Abstract

Environmental conditions play a major role for effects of olive mill wastewater (OMW) application to soil. Choosing a different season for OMW application than the commonly practiced winter, may help avoid negative effects. However, understanding of the OMW-soil interaction during different seasons is still incomplete due to the lack of comparative data. In this study, an 18 months field experiment was carried out in an olive orchard in West Bank. Degree and persistence of soil salinization, acidification, accumulation of phenolic compounds and soil water repellency were investigated as a function of soil depth and time elapsed after OMW application, which was performed either in spring, summer (with and without irrigation) or winter. The persistence of negative effects increased with duration of the hot and dry period following the application due to accumulation and polymerization of OMW. On the other hand, leaching of OMW components to groundwater is favored during the rainy season and by formation of preferential flow paths before the rain season starts. The risks of groundwater contamination and persistent negative effects decrease with increasing time under conditions favoring biological activity. Therefore, OMW application in spring if improved by a careful irrigation is considered as the most suitable under semiarid conditions for clay loam soils.

2.2 Introduction

Olive mill wastewater (OMW) treatment and management pose major concerns for many Mediterranean countries due to the specific characteristics of OMW such as its high biological and chemical oxygen demand (Hanafi et al., 2013), high concentration of oils and greases (Amaral et al., 2008), high salinity (Roig et al., 2006) and content of phenolic compounds (De Marco et al., 2007; Hanifi and El Hadrami, 2008). Furthermore, decentralized olive oil production makes the treatment of OMW in municipal sewage systems difficult and unfeasible. Consequently, a common practice for OMW disposal has been its discharge into the soil, with varying level of control in order to limit its potential negative effects on the soil and groundwater.

Several Mediterranean countries enforce upper limits for OMW discharge into the soil (Buchmann et al., 2015) in order to avoid negative environmental impact associated with OMW disposal, but many do not control it. The West Bank of the Palestinian Territory is one case of the latter (Peikert et al., 2015) and is the focus of the current study. According to the Palestinian Central Bureau of Statistics (2013), at least, 52.5 % of the cultivated land in the West Bank, estimated at 881.9 km^2, is planted by olive trees. From 2010 to 2013, 275 olive mills, operated using the "three-phase technology", produced 67,459 tons of olive oil, and about 1.0 - 1.2 m^3 of OMW for each ton of olive oil (Saadi et al., 2007a; Hanifi, 2009); the resulting OMW was discharged in an uncontrolled manner into open fields and valleys.

The use of OMW for soil improvement has been proposed by several authors and comprehensively reviewed by Barbera et al. (2013). The high content of OMW organic matter and other nutrients, especially potassium (Roig et al., 2006), makes it valuable as a soil supplement (Mekki et al., 2006). However, the organic fraction of OMW contains sugars, polyphenols, tannins and lipids (Mulinacci et al., 2001) and is hardly biologically degradable due to the toxic effects of poly phenols (Saviozzi et al., 1991; Sobhi et al., 2008). It contains 0.5 - 24 g L^{-1} of phenolic compounds (Niaounakis and Halvadakis, 2006), and phytotoxic effects have been observed when it was directly used as an organic fertilizer (Ben Sassi et al., 2006). Many studies showed contradictory results about permanence and toxicity of phenolic compounds in soil which can be attributed to a) the different amounts of toxic organic compounds present in OMW (Piotrowska et al., 2006), b), different soil temperature and moisture during and after OMW application which can affect the biological decomposition process of organic matter constitutes (Steinmetz et al. 2015), or reduce the inhibition effect by dilution and leaching of toxic compound under the influence of irrigation (Kurtz et al., 2015) and c) the general status of soil (Saadi et al., 2007a). However, Buchmann et al. (2015) showed in an incubation study of soil treated by OMW under spring conditions, that its phytotoxicity was clearly attributed to phenolic substances. Other studies showed a rapid decrease in phenolic compounds (Di Serio et al., 2008) and degradation to almost 50 % of their initial concentration within the first 2 - 3 weeks following OMW application to soil (Saadi et al., 2007a; Sierra et al., 2007; Tsiknia et al., 2014). No such effect was observed when OMW was applied in the winter season (Steinmetz et al. 2015), not even in a depth of 2 m (Chartzoulakis et al., 2010) after one single OMW application during one year study. On the other hand, soluble phenolic compounds were observed in soil at 1.25 m depth during the winter season (Sierra et al., 2001) and phenolic monomers were detected at a depth of 1.2 m one year after OMW spreading on soil (Mekki et al., 2006). Furthermore, phenolic compounds have been found in groundwater (Zenjari and Nejmeddine, 2001), which was attributed to OMW leaching through the soil during the winter season (Boukhoubza et al., 2008), whereas lower concentrations of phenolic compounds in groundwater have been noted during the summer season (Spandre, 1996).

In addition to phenolic compounds, OMW contains considerable amounts of organic acids such as short chain fatty acids (C2-C8) from microbial metabolism of sugars and carbohydrates, and long chain fatty acids (C16-C18) from the residual oil (Diamantis et al., 2013). Hydrophobic organic compounds can induce soil water repellency (SWR) (Doerr et al., 2000), and fatty acids are the main components responsible for SWR (Graber et al., 2009). Therefore, OMW can induce soil water repellency as reported by Mahmoud et al. (2010) and lead to preferential flow and surface runoff that may induce or intensify soil erosion. Peikert et al. (2015) demonstrated that the hydrophobized effect of uncontrolled OMW disposal on soil may accumulate with each new application. The development and persistence of SWR is also influenced by variations in environmental conditions such as temperature (Diehl and Schaumann, 2007) and moisture content (Täumer et al., 2005) and has been correlated to soil properties including organic carbon content and pH (Lebron et al., 2012).

Many researchers indicated that ambient environmental conditions during OMW disposal on soil play a major role in favoring either beneficial or negative effects of OMW-soil interactions (e.g., Zenjari and Nejmeddine, 2001; Mekki et al., 2007; Barbera et al., 2013). The high temporal and spatial variability of ambient environmental conditions existent in the Mediterranean Basin, as well as the high variability of olive orchard types, may explain the partly contradictory results described above. However, systematic studies on the impact of different environmental conditions on the effects of OMW soil application are still scarce. In a field study comparing different cultivation managements in Israel and West Bank during the summer season, Kurtz et al. (2015) found that the OMW effect in SWR and phenolic compounds were lower in irrigated soil compared to non-irrigated soil due to dilution and leaching of toxic compounds as a subsequent impact of irrigation. Steinmetz et al. (2015) found in a field study after one year of OMW application under semi-arid conditions, that summer application revealed a higher SWR and higher concentrations of phenolic compounds than the winter application due to low biological activity, whereas Di Bene et al. (2013) found no long-term effects neither for OMW application in spring nor in autumn. Thus, understanding of the OMW-soil interactions mechanisms during different seasons or how these mechanisms may be influenced by the season of OMW application are still incomplete.

Therefore, the objectives of this study were to investigate the short and long-term effects of OMW application on soil properties at different depth under different seasons in order to understand the OMW - soil transport and interaction mechanisms.

For this, a field experiment was carried out in a traditional olive orchard under Mediterranean climate characterized by long hot dry summer, and short cool rainy winter in the West Bank over a period of 18 months. We hypothesized that the conditions of soil moisture and ambient temperature during and after OMW application to soil can influence the degree of its overall effects and their persistence. Application during cold and moist conditions (winter) may delay OMW degradation due to low biological activity, and frequent rainfalls may promote leaching of easily soluble compounds into deeper layers. On the other hand, moderate conditions of moisture and temperature (spring) are expected to allow for considerable biological degradation, and result in lower SWR and lower concentrations of phenolic compounds. In the summer, under hot and dry conditions, OMW organic compounds are expected to accumulate due to low biological activity and may consequently induce SWR. Hot and moist conditions (summer + irrigation) are expected to enhance the biological degradation of OMW organic matter and thus to minimize its hydrophobizing and toxic effect.

In order to test these hypotheses, four different OMW applications to soil were administered in a field experiment either in spring, in summer (with and without irrigation), or in winter. The persistence and degree of soil salinity, acidity, content of phenolic compounds as well as SWR have been investigated.

2.3 Material and Methods

2.3.1 Study site

The selected field site is typical for olive orchards in the West Bank in terms of soil type, texture and vegetation cover. It is located in the village Bait Reema, 40 km north of Ramallah city, and 500 m above sea level, perched on an intermediate saddle point. The terraced hill is covered with olive trees (almost 40 trees / ha) dating back to over 100 years under extensive use by local families. The soil is clay loam (37 % clay, 22 % sand, 41 % silt) and is classified as brown rendzina (Dan and Koyumdjisky, 1963). The field was tilled twice that year prior to the study. The Mediterranean climate is predominantly characterized by long hot dry summer and short cool rainy winter, with an average temperature of 24 °C and an average annual rainfall of 615 mm. Generally, 70 % of the annual rainfall occurs between November and March (Palestinian Meteorological Department, PMD, 2013).

2.3.2 Field experiment and equipment

2.3.2.1 Plots design and distribution

Due to the irregular distribution of olive trees in the field site and the suspected influence of a neighbored rock on subsurface water movement, we conducted a preliminary field characterization, in order to decide for an optimal arrangement of the test plots in the field. Soil pH and electric conductivity (EC) of samples taken from depths of 0 - 30 cm, and 30 - 60 cm in two transects in northeast-southwest and in east-west directions (Figure 2-1) revealed a small, but clear runoff-related gradient in the field perpendicular to the line of a large cliff located 100 m from the field edge (Figure S3 in Annex 1). To avoid potential influences of this gradient on our results, sixteen plots, each with dimensions of 2.5 m by 3 m were marked in two rows parallel to the cliff line. The distribution of the OMW treatments among the plots was chosen randomly (Figure 2-1).

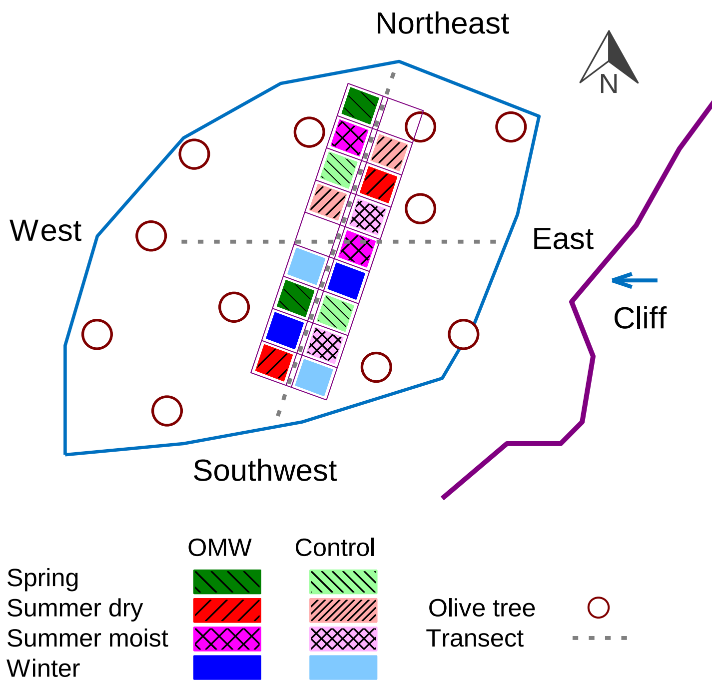


Figure 2-1: Location of transects for site exploration (gray dotted lines) and the plots for the different olive mill waste water (OMW) treatments and their respective control plots.

2.3.2.2 Field equipment for meteorological variables

A meteorological station (Umwelt-Geräte-Technik GmbH, Germany) was set up in the field which recorded air temperature, air humidity, rainfall, and wind direction. Further, eight temperature sensors (Umwelt-Geräte-Technik GmbH, Germany) have been installed distributed between treatment and control plots, and soil temperature was monitored hourly at five depths below the ground level (5, 8, 15, 50 and 70 cm). In each plot, volumetric soil moisture (vol %) was monitored on a weekly basis through three access tubes in 10, 20, 30, 50 and 90 cm depth using a portable PR2/6 moisture probe based on HH2 Moisture Meter Readout Unit (Delta-T Devices Ltd, United Kingdom).

2.3.3 OMW application to soil and soil sampling

Four different treatments of OMW application were performed; each conducted on two plots at a time as a single application of 14 L m^{-2} to simulate an extreme situation. Two corresponding control plots were treated with the same amount of tap water. For the spring treatment (SP), the OMW was applied to soil on 12 April 2012. The two summer treatments (dry and moist) were conducted on 13 August 2012. For the dry treatment (SU_{dry}), OMW was applied to non-irrigated soil, while for the moist treatment (SU_{moist}), OMW was applied to the soil which by irrigation had maintained a moisture content between 17 - 20 % for two weeks prior to application and during the following summer season. For the winter treatment (WI), the OMW was applied to soil on 14 January 2013.

For each plot, soil samples were collected one week prior to OMW application, and 2 days, 3 weeks, 6 weeks, 3 months, 6 months, 9 months, and 12 to 18 months after OMW or tap water application. At each sampling event, samples were collected at five different depths of 0 - 5 cm, 5 - 10 cm, 10 - 15 cm, 15 - 25 cm, and 25 - 35 cm. The samples taken from each depth were pooled from at least five sub-samples from five locations along one line across the plot under consideration (Figure S4 in Annex 1), and their soil chemical parameters were analyzed as described in section 2.3.4. For an overview of monitoring data and soil samples please refer to Table S1 (Annex 1).

2.3.4 Analysis of soil properties and OMW

2.3.4.1 General soil characteristics

Gravimetric water content (WC) was determined on a dry mass basis (38 h oven-drying at 105 °C). Sieved (< 2 mm) field moist soil samples were extracted with distilled water (1:5 w/v), shaken horizontally for 2 h. After paper filtration (Whatman, 150 mm), the chloride content was measured by precipitation titration with silver nitrate (Mohr's method) using potassium chromate as an indicator, and electrical conductivity (EC) and pH was measured according to DIN ISO 11265(1997) and DIN ISO 10390(2005), respectively.

In order to estimate the degree of soil acidification, a pH buffering curve for one representative soil sample pooled from all control plots was determined by measuring pH of an aqueous extract containing increasing amounts of NaOH and HCl, after an equilibration time of 2 h. Using the buffering curve, the proton (H^+) balance was deduced which is equivalent to the amount of H^+ that was added to the soil by OMW application to achieve the measured pH-difference between the treated and control soil plots (further details in Annex 1: the proton balance).

2.3.4.2 Soluble phenolic compounds

The total content of soluble phenolic compounds (SPC) was quantified in a soil water extract of air-dried soil samples (1:10 w/v, two hours horizontal shaking) by the Folin-Ciocalteu colorimetric method (Box, 1983). After 30 minutes of incubation, absorbance was measured at 700 nm using UV-1600/1800 Spectrophotometer (M.R.C., Israel). Tannic acid was used as a standard for calibration curve, and SPC is given in tannic acid equivalents.

2.3.4.3 Soil water repellency

In order to characterize the soil water repellency (SWR), water drop penetration time (WDPT) was measured twice for each sampling event. For the first test ($WDPT_{Field}$), fifty water drops of 100 µL were placed directly in the field randomly distributed on the undisturbed top soil and the time for complete penetration was determined. For the second test ($WDPT_{Lab}$), disturbed air-dried soil samples (< 1 mm) were measured as described by Diehl and Schaumann (2007). The soil was considered water repellent when the WDPT exceeded 5 seconds (Bisdom et al., 1993).

2.3.4.4 Pore size distribution and hydraulic potential gradient

In order to determine soil hydraulic properties of the experimental field and to estimate the direction of water transport at selected time points, proton nuclear magnetic resonance (^{1}H-NMR) relaxometry was performed for one representative pooled soil sample in triplicate 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 T2 and the corresponding relaxation rates of the water protons in the samples (Jaeger et al., 2009; Meiboom and Gill, 1958). Pore size distribution was determined following the procedure described in Meyer (2015). The pore size distribution was converted into a water retention curve (matric potential as a function of volumetric water content) using Young-LaPlace equation. From this curve, the respective matric potential could be obtained from measured volumetric water contents in the field. With these matric potentials, under consideration of the differences in gravimetric potential, the hydraulic potential gradients between the depths of water content measurement have been calculated for selected time points. This estimation assumed equal bulk density and texture for the whole profile. Further, hydrostatic pressure from water ponding on the soil surface during heavy rain events was not considered. Thus, this estimation is rather rough and might have led to underestimation of the matric potential gradients at high water contents and the data basis is not detailed enough for being able to account for hysteresis. However, it gives an overview of the water flow direction.

2.3.4.5 OMW characterization

OMW was obtained from an olive mill in Bait Reema. OMW used for SP, SU_{dry} and SU_{moist} treatments came from the olive harvesting seasons of 2011/2012, whereas the OMW which was used for WI application came from the olive harvesting season of 2012/2013. For all treatments, the OMW was stored in polyethylene containers underground in darkness until the time of application. The pH, EC, and SPC in OMW were determined as described above.

2.3.5 Statistical analysis

Soil chemical properties were determined in three replicate measurements for each pooled soil sample of each of the two replicate treated plots and control plots for the four OMW treatments. All results are depicted as a mean of six values with their respective standard error used as error bars. The average of pH and standard errors were calculated based on the H^+ concentrations and transferred back into pH values. The data sets were tested for normal distribution using the Shapiro–Wilk test ($\alpha = 0.05$) and visually checked by QQ-Plots using the statistical software R (R Core Team, 2014). Although normality of the most data sets could not be rejected with $p > 0.05$, we used the nonparametric Wilcoxon rank sum test (with holm p-value adjustment, using software R) for pair wise comparison of our data. Differences are supposed to be significant at $p < 0.05$.

The H^+ balance calculation required mean values from both treated and both control plots such that the results could not be related to the original 6 replicates and only one mean value remained which could not be tested with the described tests.

2.4 Results

2.4.1 Seasonal changes during the field experiment

The spring season 2012 (March-June) was characterized by a moderate increase in average air temperature (12 to 23 °C) and a mean monthly evaporation of 180 mm (PMD, 2013) causing a moderate soil temperature increase (15 to 25 °C) and moderate WC drop (15 to 12 %) in the top soil (Figure 2-2a-c). During this period, the pH in the control soil decreased from 8.3 to 7.7 (Figure 2-2d). During the summer season 2012 (June-October), the air temperature ranged between 24 and 27 °C with a mean monthly evaporation of 230 mm (PMD, 2013), causing a soil temperature rise from 25 to 35 °C and a WC drop from 8 to 2 % in the top soil (Figure 2-2a-c). The corresponding soil pH increased from 7.7 to 8.6 (Figure 2-2d). During the autumn season 2012 (October-November), the air temperature decreased from 24 to 17 °C with a mean monthly evaporation of 130 mm (PMD, 2013), causing a soil temperature drop to ~ 20 °C and a WC increase from 4 to 20 % due to the start of the rain season (Figure 2-2a-c). At the same time, the soil pH decreased from 8.6 to 8.0 (Figure 2-2d). The winter season was characterized by low air temperature in the range of 10 to 14 °C, high rainfall of 550 mm (Figure 2-2a), and low monthly evaporation between 60 to 110 mm (PMD, 2013). The corresponding soil temperature dropped to ~ 10 °C (Figure 2-2b). The rain fall replenished the porous structure of the soil profile to reach a WC of ~ 24 % (Figure 2-2c) and the pH level initially decreased to ~ 7.6 in January and then increased to ~ 8.2 in February (Figure 2-2d).

In comparison to 2012, 2013 witnessed higher rainfall in the spring season, a comparable summer, but a drier autumn. In the winter season 2013/2014, 86 % of the rainfall was concentrated in December 2013 (Figure 2-2a), resulting in a soil WC of 20 % in the top layer (Figure 2-2c). At the end of this season, the pH level remained between 8.0 and 8.5 (Figure 2-2d). These seasonal changes in soil temperature and soil moisture were also observed in the treatment plots in deeper soil layers, however, short-term fluctuations in air temperature and rain or irrigation events were reflected with decreasing degree with increasing soil depth (Figure S7 and S8 in Annex 1).

The observed seasonal changes in pH levels on the control soils indicate changing degree of proton releasing processes such as microbial and root activities, which tend to be higher in spring and autumn seasons, due to biologically favorable conditions i.e., soil moisture and temperature. However, the dryness of the summer months and the cold weather in winter, tend to reduce microbial and root activities and with this the proton releasing processes due to less biological favorable conditions in this season.

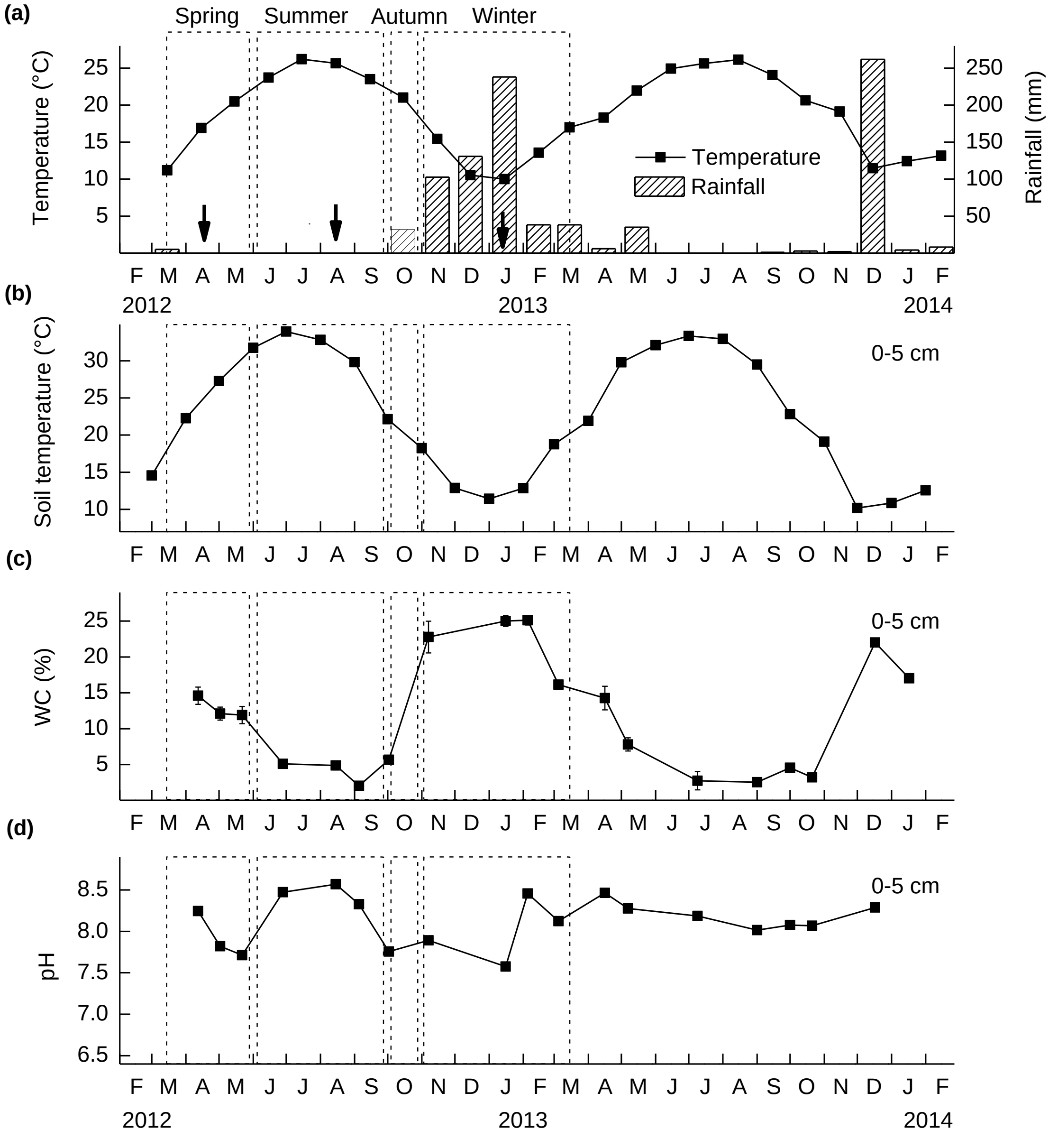


Figure 2-2: Monthly average of (a) air temperature and rainfall, (b) seasonal variations in soil temperature, (c) seasonal variations in gravimetric soil water content (WC), and (d) seasonal variation in soil pH in the field experiment during 18 months in 0 – 5 cm depth of control plots. Data points in (b) are the mean values of hourly measurements, in (c) and (d) are the mean of 18 values of 6 control plots except the irrigated plot with error bars representing standard error. The arrow (↓) indicates the date of olive mill waste water (OMW) application to soil.

2.4.2 Conditions before OMW application

2.4.2.1 Soil chemical properties

The spring treatment (SP) was performed, into relatively moist soil, with a WC of 15 % at the top layer, and an increasing WC up to ~ 35 % at 90 cm depth (Figure 2-3a), at moderate soil temperatures of ~ 18 °C down to 70 cm (Figure 2-3b). EC was low with 135 ± 6 µS cm^{-1} in the top layers dropping to 100 ± 6µS cm^{-1} at 35 cm depth (Figure 2-3c). The pH levels were of comparable with 8.3 ± 0.1 down to 35 cm depth (Figure 2-3d).

The two summer treatments were performed in August 2012, at a high air temperature of 27 °C. The corresponding soil temperature was 32 °C in the top layers, decreasing to 29 °C at 70 cm depth (Figure 2-3b). WC increased from 5 % in the top layer to 20 % at 90 cm depth in the non-irrigated plots (SU_{dry}), whereas the WC of the irrigated plots (SU_{moist}) was found to be almost uniform at ~ 20 % for the same soil depths (Figure 2-3a). For both the EC was comparable to that found in the SP plots (Figure 2-3c). The SU_{dry} plots also had pH values comparable to that of the SP plots (Figure 2-3d). In contrast, SU_{moist} plots showed increased pH values up to 8.7 ± 0.1, due to the daily administered irrigation for two weeks prior to OMW application (Figure 2-3d).

Winter treatment (WI) was performed in January 2013, at the highest monthly rainfall of 288 mm, and the lowest monthly average air temperature of 10 °C. The corresponding soil temperature was 8 °C at the top layers and 12 °C at 70 cm depth (Figure 2-3b). The WC was ~ 30 % at the top layers and ~ 35 % at 90 cm depth (Figure 2-3a). A strong seasonal effect was observed in the soil pH, which dropped to 7.4 ± 0.05 in winter (Figure 2-3d) and in the EC value which reduced to 90 ±5 μScm^{-1} in comparison to SU_{moist}, SU_{dry} and SP plots (Figure 2-3c).

The concentrations of SPC were uniform at 20 ± 5 mg kg^{-1} for the whole soil profile prior to OMW application, irrespective of the season, representing a natural background concentration. The soil was wettable before the OMW application, with a $WDPT_{Lab}$ and $WDPT_{Field}$ below 5 s throughout the whole soil profile, except for the top soil of WI plots, in which $WDPT_{Field}$ was ~ 20 s, indicating low infiltration rate due to pore saturation (Hillel, 2003).

One week before any application, the differences in temperature, WC, pH, EC and SPC between the two treatment plots and the two corresponding control plots, were within the range of the standard errors of replicates from each plot, and much smaller than the observed seasonal and depth dependent variations of these parameters (Figure 2-3a-d). Thus, treatment and control plots are comparable for these parameters, such that all observed differences after application to be presented in the following sections can be solely attributed to the effect of OMW.

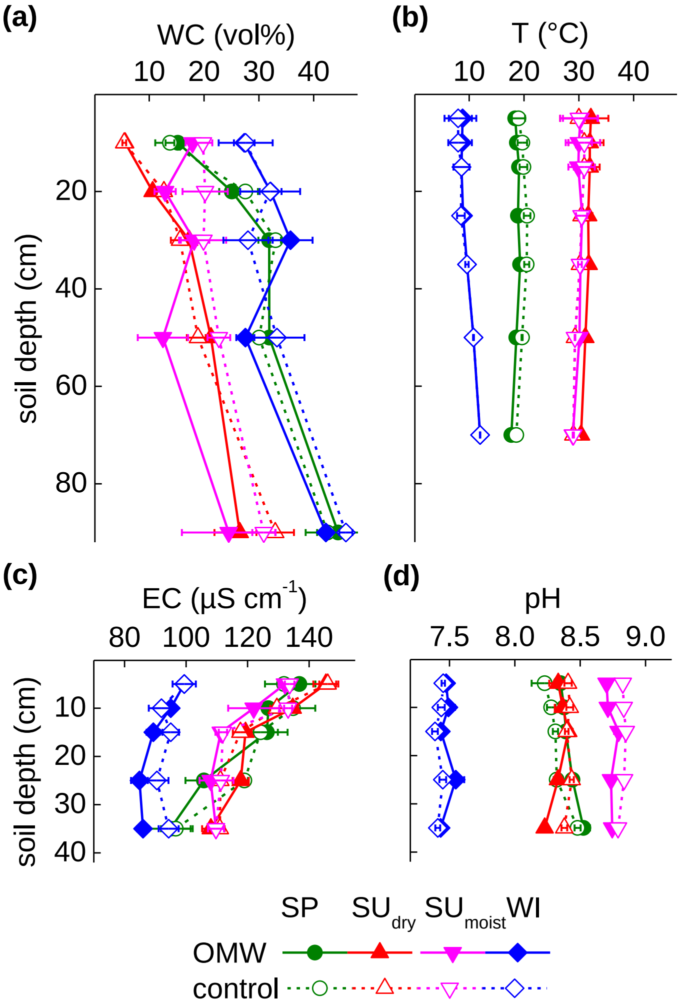


Figure 2-3: .Average of (a) volumetric soil water content (WC), (b) soil temperature (T), (c) electrical conductivity (EC), and (d) pH, measured one week prior to olive mill wastewater (OMW) or tap water application (control) for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation(SU_{moist}), winter (WI) treatment plots and the respective control plots as a function of soil depth. Data points are mean of six values of two plots for each treatment and two plots for each control with error bars representing standard error, except for b), where data points are means of hourly measurements over 24 h.

2.4.2.2 Hydraulic properties

One important aspect of which is subject to significant seasonal variations, as shown above, is the distribution of water and its transport within the soil profile. Therefore, we estimated the gradient of the hydraulic potential for the WC measurements above (Figure S5 in Annex 1). Negative hydraulic gradients indicate an upward directed matric driven water flow, whereas positive gradients indicate a downward directed gravitation driven water flow. For both SU_{dry} and SP plots the hydraulic gradient indicates that during spring and summer seasons, down to at least 20 cm depth, an upward transport by capillary rise is a highly relevant process (Figure S5 in Annex 1). This is further underlined by the high evaporation rates in these periods, which range from 180 mm in April to 250 mm in August, resulting in daily evaporation rates of 6 - 8 mm. In contrast to that, irrigation in summer induced a more complicated hydraulic pattern. The hydraulic gradient in SU_{moist} profile indicates a downward movement of water towards 20 cm whereas from the depth of 30 cm both, an upward movement towards 20 cm and a downward movement of water towards 50 cm are expected. The WI plots reveal no significant positive or negative hydraulic gradients within the whole profile down to 90 cm which indicates an equilibrium state due to the water saturation from rain water. This is further supported by the low infiltration rate leading to the elevated $WDPT_{Field}$ on these plots.

2.4.3 OMW quality

OMW pH and EC for the season 2011/2012 were comparable to that in the season 2012/2013 with EC values of ~ 10.8 ± 0.2 mS cm^{-1} and a pH of 4.6 ± 0.1.The longer the storage period of the OMW before its application to the soil, the more significant are the changes expected in its quality (Saadi et al., 2007b). Therefore, the OMW quality in term of SPC concentration was closely monitored during storage. The SPC concentrations in OMW at the time of SP application (4 months storage), SU_{dry} and SU_{wet} application (8 months storage), and WI application (2 months storage) of 5.3 ± 0.2, 5.7 ± 0.2and 5.4 ± 0.2 g L^{-1}, respectively, differed only in the range of the standard error of measurement. Consequently, it can be inferred that the change in the quality of OMW during storage with respect to SPC was negligible and the observed differences after OMW application are unlikely to have been influenced by the age and/or quality of the OMW applied.

2.4.4 Short-term effects two days after OMW application to soil

Generally, the OMW application to soil increased EC, SPC, and $WDPT_{Lab}$ and reduced soil pH with respect to control plots (Figure 2-4). These observed short-term effects are in agreement with other studies and can be related to the acidic nature of OMW (Di Serio et al., 2008; Kavvadias et al., 2010; Di Bene et al., 2013), its high salinity (Sierra et al., 2007; Mekki et al., 2009; Moraetis et al., 2011), and its high content of phenolic compounds (Zenjari and Nejmeddine, 2001; Chartzoulakis et al., 2010). Nevertheless, the extent of these effects and their reach with respect to depth varied among the four OMW treatments and among the parameters (Table S2 in Annex 1).

The increase in EC in the top layer was higher after SP, SU_{dry} and WI treatments with comparable EC values of 638 ± 12 µS cm^{-1} than after SU_{moist} treatment with EC values of 250 ± 10 µS cm^{-1} (Figure 2-4a). The EC differences between treated and control plots were significant ($p < 0.01$) after SP and SU_{dry} treatments down to at least 35 cm depth with 172 ±5 µS cm^{-1} and 154 ±7 µS cm^{-1}, respectively. In contrast, significant salinization effects ($p < 0.01$) were observed only down to 15 cm after WI and SU_{moist} treatments with EC values of 115 ±10 µS cm^{-1} and 121 ±2 µS cm^{-1}, respectively. The highest short-term effect on pH in the top layer with respect to control plots was found after SP treatment with a pH reduction by 0.7 ± 0.06 units, followed by WI treatment with a pH reduction by 0.6 ± 0.01 units, whereas SU_{dry} and SU_{moist} treatments caused a lower short-term pH reduction by 0.4 ± 0.01 and 0.3 ± 0.01 units, respectively (Figure 2-4b). A significant pH reduction ($p < 0.01$) reached deeper soil layers to a depth of at least 35 cm after SU_{dry} and WI treatments, whereas it reached only a depth of 10 cm for SP ($p < 0.05$), and 25 cm for SU_{moist} treatments ($p < 0.01$). Because pH is a decimal logarithmic value, pH differences are indicative for the factor between two H^+ concentrations. Furthermore, in different pH ranges, different soil buffer systems will influence the reaction on acidification. A better picture of the acidification effect of OMW application separately from natural pH dynamics caused by seasonal effects (as indicated in the control soils in section 2.4.1) and under consideration of the buffer systems in the respective pH range, is given by the proton balance (for details see the proton balance in Annex 1). A comparably strong short-term acidification effect in the top soil layer was observed after WI and SP treatments with H^+ surplus of 0.15 ± 0.03 mol kg^{-1} which reached down to 35 cm depth, whereas no such effect was detectable after SU_{moist} and SU_{dry} treatments (Figure 2-4c).

The highest SPC concentration in the top soil layer was found after WI and SU_{dry} treatments (Figure 2-4d) with concentrations of 370 ± 10 and 260 ± 13 mg kg^{-1}, respectively, whereas it was lower after SP and SU_{moist} treatments, with values of 135 ± 3 mg $kg^{-1}$and 60 ±7 mg kg^{-1}, respectively. The differences between treated and control plots were significant ($p < 0.05$) after all treatments down to at least 35 cm depth. Nevertheless, after SU_{dry}, SU_{moist} and SP treatments, SPC concentrations continuously decreased with depth to 43 ± 5, 38 ± 5 and 34 ±5 mg kg^{-1}, respectively, at 35 cm. In contrast, SPC concentration after WI treatment only decreased from 5 to 10 cm depth and remained nearly constant in the range of 10 -35 cm depths with 166 ± 10 mg kg^{-1} (Figure 2-4d). The SPC mass balance evaluation showed that, depending on the treatment, only a part of the SPC applied with the OMW was still located in the upper 35 cm: Only for the winter treatment ~ 100 % of the SPC was still located in the upper 35 cm, whereas for the SU_{dry} treatment, the recovery in the upper 35 cm was ~ 60 %, and for SP and SU_{moist}, it was only 27 % and 20 %, respectively.

The water drop penetration times were elevated after SU_{moist}, SU_{dry} and WI treatment to $WDPT_{Lab}$ values of 20 ± 5 s, 38 ± 3 s and 120 ± 5 s, respectively, which suggests that the OMW application induced moderate water repellency in all treatments except the SP treatment which revealed with 0 s the same $WDPT_{Lab}$ as all control plots (Figure 2-4e). Water repellency in 10 cm depth was only detected after SU_{dry} treatment with a $WDPT_{Lab}$ of 13 ± 2 s. Thus, the top soil of the WI plots exhibited the highest short-term $WDPT_{Lab}$ and SPC among all treatments. The $WDPT_{Lab}$ probably increased due to the accumulation of hydrophobic substances from OMW application at the surface as indicated, for example, by the increased SPC.

The SPC mass balance suggests a significant loss of OMW-derived compounds already during the first two days of OMW-soil contact from the top 35 cm. This raises questions on the mechanisms for OMW distribution within the soil profile and the influence, if any, of ambient conditions on this distribution. In order to separate the transport effect from effects of sorption and degradation, the chloride (Cl^-) present in OMW was considered as an indicator for water movement respective the position of the water at the time of sampling (Figure 2-4f). The highest Cl^- concentration in the top layer was found after SU_{dry} treatment (760 ± 13 mg kg^{-1}), whereas the lowest concentration was found after SU_{moist} treatment (280 ± 15 mg kg^{-1}). The Cl^- concentrations after SP and WI treatments were 360 ± 40 and 390 ±8 mg kg^{-1}, respectively. Differences in Cl^- concentration between treated and control plots were significant ($p < 0.05$) until depths of 35 cm after SP and SU_{dry} treatments, but only to depths of 10 cm for SU_{moist} and 15 cm for WI treatments. This would suggest that at the time of sampling the aqueous phase of the OMW was located only in the top 15 cm for SU_{moist} and WI treatments, whereas it distributed to at least 35 cm depth for SP and SU_{dry} treatments. Unfortunately the calculated mass balances with respect to Cl^- (under consideration of the Cl^- content in the controls) would indicate that far more than 100 % of the OMW-derived Cl^- is located in the top 35 cm layer. These differences are most probably due to overlay with soil-inherent Cl^- and render a reliable mass balance assessment for OMW derived Cl^- with respect to control values impossible.

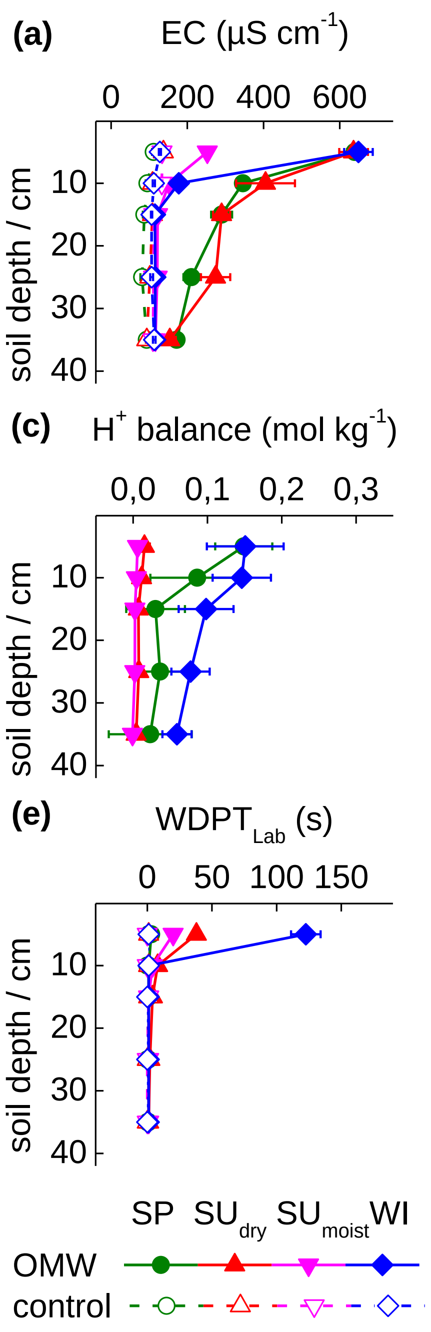


Figure 2-4: Average of (a) electrical conductivity (EC), (b) pH, (c) H^+ balance between control and treated soil, (d) concentration of water soluble phenolic compounds (SPC), (e) water drop penetration time of disturbed samples ($WDPT_{Lab}$), and (f) chloride concentration for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation(SU_{moist}), and winter (WI) olive mill waste water (OMW) treatment plots and the respective control plots as a function of soil depth. Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard error.

2.4.5 Long-term effects of OMW application in soil under different seasons

The strongest long-term changes in soil properties following OMW application were observed in the upper soil layer (0 - 5 cm depth). The extent of effects generally decreased with increasing soil depth and after the first rain season following the application (Figure S9 to S14 in Annex 1). Therefore, in this chapter, we will focus on the time-dependent variations of EC, SPC, $\mathrm{WDPT_{Field}}$, and H^+ balance in the top 5 cm.

Generally, the extent of effects of OMW application to soil decreased during the spring season (SP treatment) and increased during the summer season (SP, $\mathrm{SU_{dry}}$ and $\mathrm{SU_{moist}}$), but almost completely disappeared in all OMW-treated plots after the following rainy winter season (Figure 2-5).

EC and SPC in SP treated plots significantly decreased (p < 0.05) to 50 % within six weeks during spring season 2012 (Figure 2-5a-c, Table S3 in Annex 1). A secondary significant increase ($p < 0.05$) in EC, interpreted as an increase in salinity, was observed in both SP and $\mathrm{SU_{dry}}$ treated plots during the summer season 2012 (Figure 2-5a and Table S3 in Annex 1) This resulted in maximum EC values of 770 ± 20 $\mu S\ cm^{-1}$ in the SP plots, and 830 ± 40 $\mu S\ cm^{-1}$ in the $\mathrm{SU_{dry}}$ plots at the end of same summer season. Also, the SPC significantly increased ($p < 0.05$) in these plots (Figure 2-5b Table S3 in Annex 1). However, the increase was less pronounced in SP than in $\mathrm{SU_{dry}}$ treated plots with a maximal concentration of 123 ± 14 and 332 ± 17 $mg\ kg^{-1}$, respectively. In contrast, the EC slightly increased in $\mathrm{SU_{moist}}$ treated plots up to 350 ± 50 $\mu S\ cm^{-1}$ during the summer (Figure 2-5a), while the SPC gradually decreased ($p < 0.05$, Table S3 in Annex 1) to values similar to control plots within six weeks (Figure 2-5b). During the same period, the H^+ balance increased in the SP, $\mathrm{SU_{dry}}$ and $\mathrm{SU_{moist}}$ treated plots, which indicates a secondary acidification effect of the OMW application, albeit at varying degrees of severity depending on the time of application (Figure 2-5c). The strongest secondary acidification was observed in the $\mathrm{SU_{dry}}$ treated plots with a maximum additional H^+ generation of 0.32 ± 0.06 $mol\ kg^{-1}$, while less, but longer lasting surplus H^+ were found in $\mathrm{SU_{moist}}$ and SP treated plots with peak values of 0.15 ± 0.08 and 0.11 ± 0.02 $mol\ kg^{-1}$ in November 2012 and January 2013, respectively.

The $\mathrm{WDPT_{Field}}$ also increased in both $\mathrm{SU_{dry}}$ and SP treated plots during the summer season, where it reached the maximum values of 13 ± 2 s and 9 ± 2 s, respectively (Figure 2-5d), however the difference was only in $\mathrm{SU_{dry}}$ treated plots significant ($p < 0.01$, Table S3 in Annex 1). This trend was also observed for the $\mathrm{WDPT_{Lab}}$ of 46 ±2 s and 10±2 s for the $\mathrm{SU_{dry}}$ and SP plots, respectively.

However, in the SU_{moist} treated plots, $WDPT_{Field}$ significantly decreased ($p < 0.01$, Table S3 in Annex 1) during the summer season 2012.

During the winter season, the SPC values significantly decreased ($p < 0.05$) in SP, SU_{dry} and WI treated plots to minimal concentrations of 27 ± 2, 72 ± 11, and 75 ± 6 mg kg^{-1} respectively, in January and February 2013 (Figure 2-5b, Table S3 in Annex 1). The soil in SU_{moist} treated plots was already completely wettable before the winter season 2012/2013, whereas the $WDPT_{Field}$ for SU_{dry} and SP plots disappeared in the end of winter 2013 (Figure 2-5d, Table S3 in Annex 1). Also, for the WI plots, which exhibited the highest short-term $WDPT_{Field}$, values, significantly decreased ($p < 0.01$, Table S3 in Annex 1) during the winter season 2012/2013.

In SU_{dry} treated plots, the secondary acidification effect disappeared at the beginning of the winter season 2012/2013, while in the SU_{moist}, SP and WI treated plots, it decreased and disappeared ($p > 0.05$, Table S3 in Annex 1) in spring 2013 (Figure 2-5c). Also, the EC differences between treated and control plots ($p > 0.05$, Table S4 in Annex 1) disappeared for SP (Figure 2-5a), while in SU_{dry}, SU_{moist} and WI plots EC values of the upper soil layers (10 - 15 cm depth) were slightly higher than in the control plots.

In the following summer season 2013, no repellency was found in any of the treated plots, whereas a significant ($p < 0.05$) secondary salinization effect was re-observed in the top soil in WI and SU_{dry} plots with EC value of 200 ± 20 µS cm^{-1} (Figure 2-5a and Table S4 in Annex 1). Furthermore, also SPC remained significantly elevated with respect to control in all treated plots in nearly all depths (Table S4 in Annex 1). However, SPC mass balance (down to 35 cm) at this time showed, that the highest percentage of SPC applied with the OMW was found in SU_{dry} plots with 28%, followed by WI plots with 21%, whereas in SP and SU_{moist} plots only 18% and 13% of SPC, respectively. Although at the end of the experiment in winter 2013/14, EC and SPC were still significantly higher than in the respective control plots (Table S4 in Annex 1), these differences were with 3-15 µS cm^{-1} and 21-38 mg kg^{-1} negligible with respect to the seasonal fluctuations of these parameters on the control plots.

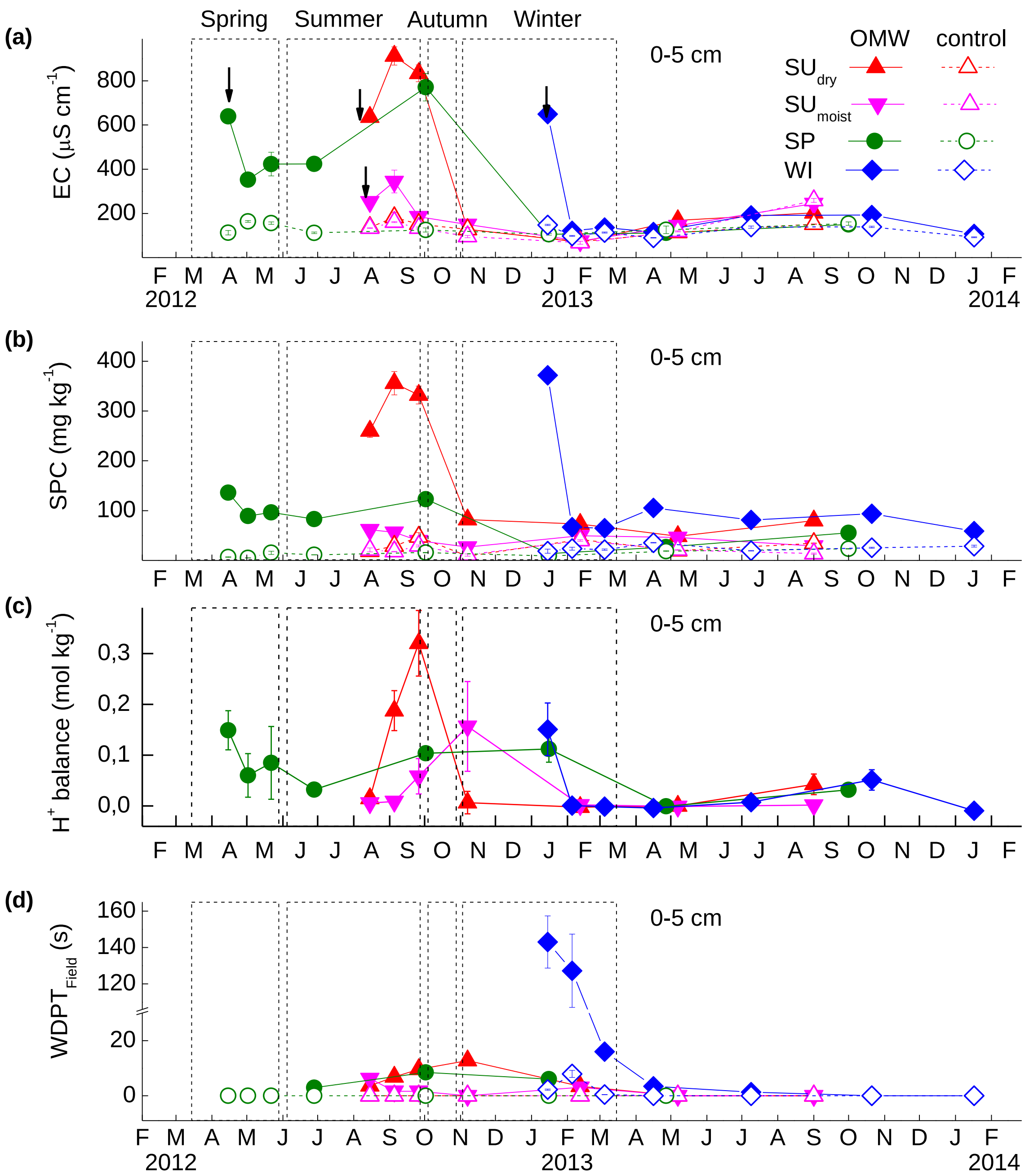


Figure 2-5: Average of (a) electrical conductivity (EC), (b) concentration of water soluble phenolic compounds (SPC), (c) H^+ balance between control and treated soil, and (d) water drop penetration time in field ($WDPT_{Field}$), for the top soil (0 - 5 cm) as a function of time for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}) and winter (WI) treatment plots. First results are obtained 2 days after olive mill waste water (OMW) application to soil (↓). Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard errors.

2.5 Discussion

2.5.1 Short-term OMW-soil interaction and transport mechanisms

The results above clearly show that the OMW has reached much deeper depths than expected from the applied amount of 14 L m^{-2}. This indicates that preferential flow is effective in all treatments and it cannot be excluded that part of OMW may have reached depths even below 35 cm. The SPC mass balances suggest that preferential flow might be most effective in the SP and SU_{moist} treatments, followed by SU_{dry} and then WI treatments. This is especially surprising for SU_{dry} treatments because the highest preferential flow would be expected in the driest soil (Hillel, 2003). Therefore, it cannot be excluded that the differences in SPC mass balance between SP/SU_{moist} and SU_{dry} are caused by an enhanced microbial degradation of OMW due to favorable moisture and temperature conditions (Chaari et al., 2014). Buchmann et al. (2015) found a reduction of ~ 40 % for total phenolic compounds within two days during an incubation experiment of OMW treated soil (14 L m^{-2}, 23 % WC, 15 C) which suggests that comparable microbial process may explain the difference of 30 % in the SPC recovery between SP/SU_{moist} and SU_{dry} in the field experiment.

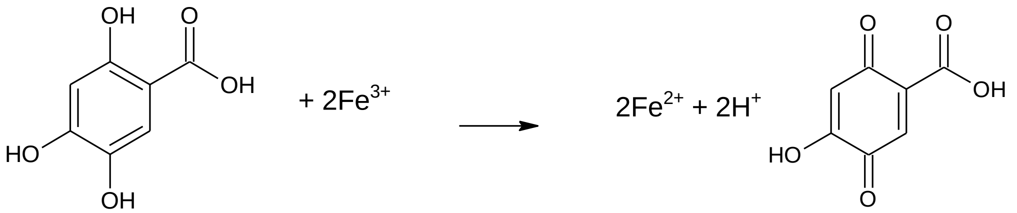
The deeper penetration depths of SPC, than of EC and Cl^- for SU_{moist} and WI points to an enhanced gravitation driven downward transport due to irrigation or rain water because the downward transport of the liquid part of OMW must have been slow enough to allow organic substances like SPC to interact with the soil leading to their retardation but still fast enough to leach inert ions like Cl^- from the observed horizons (Chaari et al., 2014). The higher short-term effects on most soil parameters in WI plots with respect to SU_{moist} plots suggest that during winter, the leaching is less effective than during irrigation in summer. This is further supported by the elevated $WDPT_{Field}$ of ~ 20 s of the WI plots already before application which points to a reduced infiltration rate of the OMW with respect to the other treatments due to the higher degree of water saturation (Hillel, 2003) and which did probably not indicate repellency. This is in line with the positive hydraulic gradients in the SU_{moist} profile. Further, the nearly constant SPC concentration in the soil profile below 10 cm depth in the WI plots suggests that the OMW organic matter which accumulated at the soil surface due to the lower infiltration rate may have been continuously releasing SPC into the soil solution which was slowly transported downward.

In contrast to SU_{moist} and WI, comparably negative hydraulic gradients in the upper 20 cm for SP and SU_{dry} indicate that capillary rise dominates the water movement in these horizons. This is further supported by the comparably elevated EC depth profiles with respect to SU_{moist}.

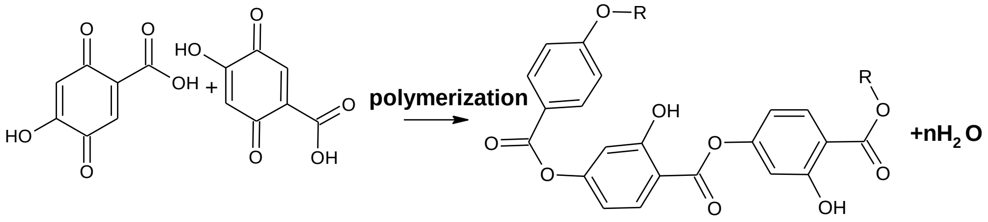
2.5.2 Long-term OMW-soil interaction and transport mechanisms

The secondary increase in salinity and SPC in SP and SU_{dry} plots during the summer season 2012 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). This matches with the clearly upward directed hydraulic gradient down to 50 cm depth in these plots (Figure S4 in Annex 1). The comparable salinization effect in SP and SU_{dry} treated plots suggests that the applied salt content was almost completely restored at the soil surface whereas a large part of the applied SPC from the SP plots disappeared. Loss of SPC in SP plots during the summer months due to leaching can be excluded due to the negative hydraulic gradients in the upper 50 cm, such that so the phenomenon could be explained by either incomplete biotic degradation of phenol OMW constitute in the first weeks following the OMW application (Kurtz et al., 2015) and/or incorporation into the organic matter (Saadi et al., 2007b; Sierra et al., 2007) or by sorption to soil particles and reduced mobility allowing part of the SPC to remain in deeper soil layers after the initial transport through preferential flow. However, the current results as they stand cannot distinguish between these feasible processes. Further investigations focusing on the binding mechanism of the phenolic compounds to soil and laboratory incubation studies for the degradation of phenolic compounds (Buchmann et al., 2015) will be required to obtain further evidence for transport, retardation and degradation mechanisms. For example Buchmann et al. (2015) found that during the initial phase of OMW-soil contact under spring conditions, degradation overbalances, whereas, after ~ 30 days, part of phenolic compounds becomes physically immobilized and temporarily less bioavailable.

In addition to the dryness, salt accumulation in the soil can reduce microbial activity (Mekki et al., 2009) which may offer an explanation for the persistence of phenolic substances observed in the upper layers in the SU_{dry} plots during summer. The highest acidification out of all treated plots was found in SU_{dry} plots between August and October 2012 with very low WC and consequently, could not be related to microbial activity and moisture content as in the SU_{moist} plots. An alternative explanation for the observed acidification is indicated by the reduced wettability and the deep brown-dark color in the top layers of SU_{dry} treated plots during this period. The major components of the colored fraction in OMW are substances of polymeric nature (Kachouri et al., 2005; Hanafi et al., 2011) that are often attributed to oxidation and polymerization products of tannins and have a strong toxic effect on microorganisms (Bhat et al., 1996). It can be deduced that abiotic phenol oxidation and polymerization rather than biotic degradation are at play as shown by Equation (1) and (2).



(1)



(2)

By oxidation of phenolic substances, oxidants (e.g. iron or manganese oxides) are reduced and protons are released (Eq. 1) which explains the acidification. This is underlined by the observation made by Peikert (2015) that Mn^{2+} concentration increased during an incubation experiment with OMW treated soil. Due to the polymerization of phenolic substances (Eq. 2), larger and more hydrophobic compounds are expected to be formed which could explain the reduced wettability in SU_{dry} plots.

The lower extent of secondary salinization and the decrease of SPC during the summer in SU_{moist} plots compared to SU_{dry} plots suggest that large parts of the soluble OMW substances which were removed from the observed profile during the first two days were not transported back to the surface via capillary rise. This indicates that the intermittent irrigation leached OMW constituents downwards (Kurtz et al., 2015) and prevented their accumulation at the surface. When looking at the depth profile of the hydraulic gradient (Figure S4 in Annex 1) it becomes clear that these compounds must have largely accumulated in ~ 50 cm depth, i.e. in the region of minimum water content, as throughout the year the hydraulic gradient in 50-90 cm depth was directed upwards, suggesting continuous capillary rise in the deeper layers throughout the year. This consequence should be tested in further investigations exploring the SPC-depth distribution up to at least 1 m depth.

The decrease of the SPC in the SU_{moist} plots during summer might be caused either by biological degradation, supported by the concomitant acidification and a decrease of SWR (Figure 2-5c-d), or by successive downward transport into the deeper layers, with the consequence of accumulation at ~ 50 cm as discussed above. Due to the biologically favourable conditions, at least, partial degradation is, however, highly probable. Observations of phenolic compounds rapidly reducing in concentration (Di Serio et al., 2008) and degrading (Sierra et al., 2007) under environmental conditions favourable to biological activity have been reported by other researchers (Barbera et al., 2013). However, other fixation mechanisms like sorption which is enhanced in hydrated soil with respect to dry soil (Ochsner et al., 2006) and which have been found by Buchmann et al. (2015), cannot be excluded.

The rapid decrease in EC, SPC and acidification during the rainy winter season in SP, SU_{dry} and WI plots is clearly related to leaching, because it occurred simultaneously for Cl^- and at all soil depths (Figure S14 in Annex 1). SWR in SP and SU_{dry} plots totally disappeared during the following winter which could be related to hydrolysis reactions mobilizing the polymerized compounds and consequently enabling their leaching. In contrast, the SWR in WI plots could not be related to polymerization but rather to the accumulation of hydrophobic OMW constituents in the top soil layers (Gonzalez-Vila et al., 1995). The latter could not leach out as fast as the most soluble compounds like SPC and Cl^- until conditions for microbial degradation of organic constituents improved in spring 2013.

The slight increase of EC and SPC during summer 2013 in SU_{dry} and WI plots could be attributed to capillary rise and shows that not 100% of the OMW constituents were immobilized, degraded or leached to the groundwater during the previous seasons. Steinmetz et al. (2015) found comparable results, i.e., no leaching or degradation, but only when OMW was applied during the hot season. In the SU_{moist} plots, only elevated EC values but no concomitant elevated SPC contents reappeared in summer 2013. This suggests that part of the organic compounds must have been immobilized or degraded during the previous seasons such that they could not be rise to the surface by capillary action as inorganic salts did in summer 2013.

2.6 Conclusions

The field experiment clearly demonstrates that each OMW treatment to the soil is dominated by different transport and transformation processes, triggered by the ambient soil moisture and temperature during and after the application. In all seasons, short-term OMW–soil interaction is dominated by preferential flow. However, in spring and summer season subsequent capillary rise is a highly relevant process.

Under the moderate ambient conditions of spring season, biotic degradation of OMW organic compounds is highly probable. However, also, incorporation into the organic matter cannot be excluded. In contrast, high temperature and low soil moisture in the summer season impede biotic degradation and any leaching so the OMW organic compounds rising to the soil surface by capillary action accumulate and polymerize. Irrigation during the summer season may cause leaching of soluble OMW constituents, part of which can intermittently rose back by capillary action to the upper soil layers where biotic degradation is enhanced by favorable moisture conditions. Finally, the winter season is dominated by leaching since the low temperature and high water content in the soil eliminates the biotic degradation of OMW constituents. This shifting in the dominating mechanisms across the different treatment conditions is depicted in Figure 2-6 which combines our main findings described above.

The results confirm that the degree of negative effects attributed to salinization, secondary acidification, SPC accumulation and appearance of SWR in soil depends primarily on the time of OMW application to soil and the dominant mode of OMW-soil interaction mechanisms. The most severe effects have to be expected in the hot dry summer and the cold wet winter seasons. Moderate negative effects are expected in the spring season, whereas low negative effects are expected in moist summer season (e.g., irrigation). The persistence of negative effects in the soil with time is more significant the longer the hot and dry conditions last following the OMW application, causing the OMW constituents to accumulate and polymerize without being degraded. Moreover, the composition and concentration of the potentially hazardous OMW residuals in the soil are highly dependent on the time span between the OMW application and the following rain season which leads to leaching of non-degraded constituents of OMW into the deeper soil layers and contamination of groundwater aquifers. Therefore, our findings suggest that summer and winter seasons should be avoided in OMW application to soil due to the high probability of groundwater contamination. This is in agreement with Steinmetz et al. (2015). Although Di Bene et al. (2013) concluded that OMW application in spring and autumn caused no long-term effect, the authors found strong indications for significant leaching, however, their study was limited to 20 cm depth. In accordance to Barbera et al. (2013), our results confirm that the spring season is the most suitable time for OMW application, especially, if improved by carefully planned irrigation events so as to avoid undesirable leaching of OMW constituents into deeper layers (Kurtz et al, 2015) through preferential flow paths but maintain sufficient moisture to ensure biological degradation activities. In addition, application in spring offers the longest period before the inevitable leaching occurs during the rainy winter season.

However, further studies involving deeper soil layers and groundwater are required to understand how deep the impact of preferential flow reaches and how leaching is triggered by irrigation and precipitation. Further, amount and quality of soil organic matter after OMW application should be investigated in order to understand the mechanisms of biotic degradation under different conditions of OMW application to soil.

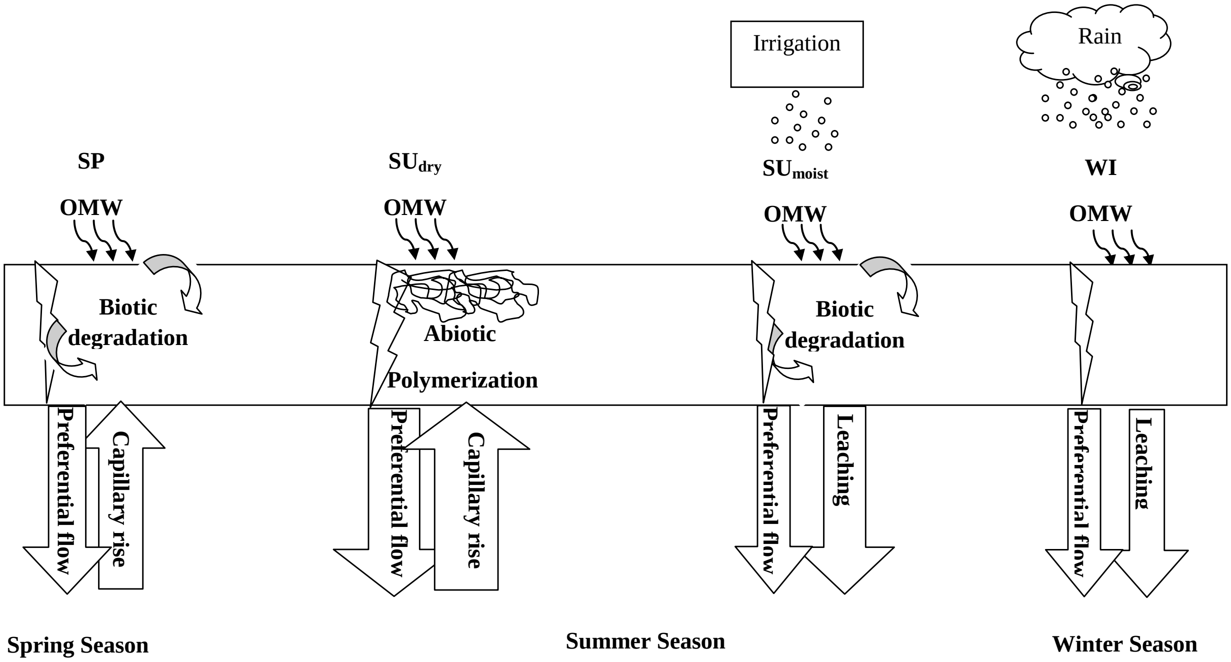


Figure 2-6: Combination of our findings on dominant olive mill waste water (OMW) - soil interaction and transport mechanisms for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}) and winter (WI) treatment across the different seasons.

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3 The fate of organic matter brought into soil by olive mill wastewater application at different seasons

Application of olive mill wastewater (OMW) to soil may cause positive or negative effects. The present study aims at a better understanding of the fate of organic matter brought into soil by OMW application under different environmental conditions. Single OMW application to soil was conducted in spring, dry summer, summer with irrigation, and in winter. Two days and 18 - 24 months after the application, soil samples from two depths were analyzed for thermal soil organic matter (SOM) properties, total organic carbon, water-extractable dissolved soil organic carbon and its specific ultraviolet absorbance at 254 nm. After winter and irrigated summer treatment, OMW was largely leached from the upper horizon within two days. Application in spring and summer dry initially increased the thermo-labile fraction and the calorific value of SOM, however, in a different degree due to different transport, transformation and immobilization mechanisms. At the long term, SOM content was still elevated after summer dry treatment. The reduction of the thermo-stable fraction in spring treatment indicates a priming effect of the labile OMW constituents. Application in winter or with irrigation cannot be recommended for the investigated site. Under hot and dry conditions, SOM content increased most persistently due to stronger mineral-organic interactions. Favorable conditions for biodegradation during OMW application in spring reduced the effects on SOM quantity in the long term. However, a possible priming effect and the persistence of changes in thermal properties need to be further investigated for repeated applications

3.1 Introduction

Soil organic matter (SOM) is regarded as “a key attribute of soil quality” (Gregorich et al. 1994). Thus, SOM management is considered crucial for the enhancement of long-term soil performance because SOM improves among others, soil water storage, nutrient availability, and biological activity. Organic wastes of different origins and nature are used as amendments to increase SOM content and to enhance crop productivity (Mekki et al. 2006a).

Several studies proposed the use of olive mill wastewater (OMW) as an organic fertilizer (Belaid et al. 2013; Chaari et al. 2014a; Kallel et al. 2009). OMW contains considerable amounts of plant nutrient, such as K, P, and Mg, and OM (Chaari et al. 2015; Di Bene et al. 2013; Mekki et al. 2006b) and can be directly applied to the agricultural soils as an organic supplement (Chaari et al. 2014a; Di Bene et al., 2013; Rozzi and Malpei 1996). Many researchers already demonstrated the enhancement of SOM content after OMW was disposed to the soil (Casa et al. 2003; Chaari et al. 2014a; Paredes et al. 1999). Chaari et al. (2015) found a positive correlation between the SOM content and the OMW application rate. Thereby, the resulting organic carbon concentration in soil depends on the olive oil extraction technology (Barbera et al. 2013) and the resulting OM concentration of the wastewater.

In addition to an increase in SOM content, OMW application is also expected to modify SOM properties (Schaumann et al. 2010). Single or repeated OMW applications increased dissolved organic carbon (Brunetti et al. 2007; Piotrowska et al. 2006; Di Bene et al. 2013; Kurtz et al., 2015) which was characterized by a higher ratio of aliphatic : aromatic compounds than in untreated control soils (Peikert et al. 2015). The composition of SOM is influenced by the quality of organic matter (OM) inputs (Baldock and Skjemstad 2000). The organic fraction of OMW is complex. It contains greases, proteins, carbohydrates, organic acids, polyalcohols, glucosides, tannins and polyphenols (Diamantis et al. 2013; Mulinacci et al. 2001). Some of these compounds may be also responsible for negative effects on soil quality. For example, phenolic compounds may render the soil highly phytotoxic for several weeks (Piotrowska et al. 2006; Piotrowska et al. 2011) and inhibit biodegradation of OMW-OM (Buchmann et al. 2015; Sierra et al. 2007). Further, the input of hydrophobic OMW constitutes in soil, such as grease and oil (Gonzalez-Vila et al. 1995), may cause the unwanted development of soil water repellency (Mahmoud et al. 2010; Steinmetz et al. 2015; Tamimi et al. 2016). This hydrophobizing effect on soil may further accumulate with each new application of OMW (Peikert et al. 2015). Soil water repellency is a surface phenomenon and strongly depends on the surface areas coated by organic matter. Because this is governed by the strength of mineral-organic interactions, a better understanding of the mechanisms that govern the fate of OMW-OM in soil is needed in order to reduce these and other potential negative effects.

Beside the quality of the applied OMW, also the environmental conditions during the application have an influence on the fate of the newly added OM. For example, the total organic carbon content increased when OMW was applied to soil during summer season, but not when it was applied during winter (Steinmetz et al. 2015), even though in this specific field experiment, the amount of accumulated application of OMW in the winter treatment was higher than in the summer treatment. Tamimi et al. (2016) showed that the degree of soil water repellency (SWR) due to single OMW application to soil depends primarily on the season of application and the dominant initial mode of OMW-soil interaction mechanisms. This shows that the season of application has a direct effect on the fate of OMW-OM in soil. Processes which are expected to control the fate of OMW-OM in soil, like immobilization, transport or biological degradation, strongly depend on soil moisture regime and temperature. Lab experiments suggest that environmental conditions during the first weeks of OMW-soil contact should favor biological activity in order to reach a sufficient degree of detoxification (Buchmann et al. 2015) and that the most favorable OMW biodegradation conditions are the combination of warm temperature and high moisture content (Saadi et al. 2013). Numerous field experiments have been carried out in order to analyze the effect of OMW application to soil on various parameters, like inorganic nutrients and salinization (e.g., Chaari et al. 2015; 2014b), plant growth and yield quality (e.g., Ben Brahim et al. 2016, Lopez-Pineiro et al. 2008), soil organic matter content and resulting soil properties like bulk density, porosity (e.g., Mohawesh et al. 2014), and soil water repellency (e.g., Mahmoud et al. 2010). However, the influence of the environmental conditions during the OMW application on the fate of OMW-OM has not been investigated yet systematically in a field experiment.

SOM is an undefined natural substance which makes its chemical characterization difficult without changing its properties by extractions or other separation techniques. Thermo-analytical techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC) are increasingly used in soil science for SOM characterizations (e.g., Dell'Abate et al., 2000; Lopez-Capel et al. 2005; Siewert 2004; Manning et al. 2005) because they captures the “complete quality continuum” of SOM (Fernández et al. 2011). However, except from Peikert et al. (2015), these promising techniques have not been used yet to assess effects of OMW application to soil, despite its high potential. By TG measurements the weight loss caused by thermal degradation during a defined temperature program is obtained for specific temperature ranges (~200 - ~500 °C for SOM) while with DSC the energy released from these processes is registered. Coupling with evolved gas analysis (EGA e.g., infrared spectroscopy or mass spectrometry) allows analyzing the gases evolved from these processes. Often, weight loss and energy release due to SOM oxidation occurs in two or more steps such that the total weight loss may be divided into fractions with different thermal stability. The thermal stability of a sample is then defined by the relative amount of organic matter that oxidizes at higher temperatures (thermo-stable fraction) with respect to the total weight loss. The calorific value (energy density) is the energy related to the weight loss of the fraction.

In their review, Plante et al (2009b) listed different approaches for the interpretation of thermal stability of SOM, like the degree of humification (e.g., Dell'Abate et al. 2000), chemical properties like the binding strength (e.g., Leinweber and Schulten 1992), or stability against biological degradation (e.g., Plante et al. 2011) However, also the physical state of the SOM within the whole matrix has a strong influence on the oxidative thermal stability, e.g., mineral-organic interactions (e.g., Feng et al. 2015), amount of organic matter (Peltre et al. 2013) or the pure mixing effect of organic and mineral phases (Rovira and Vallejo 2000). Further, grain size and packing density as well as available surfaces govern the heat and air flux through the samples and control the oxidative processes (Plante et al. 2009b; Fernández et al. 2011). But thermal decomposition of labile organic carbon may also cause artifacts by the formation of thermally more stable intermediate products during the measurement (Gélinas et al. 2001, Simpson and Hatcher 2004), especially, when oxygen consumption is not fully compensated by the oxygen supply (Cebulak and Langier-Kuzniarowa 1997). This may occur especially when SOM content is high (Fernández et al. 2011) and its distribution is very heterogenic such that oxygen consumption is concentrated in hot spots during the measurement. This shows that TGA-DSC of oxidative SOM decomposition is sensitive to changes in the physical state of SOM, like mineral-organic interactions and small scale SOM distribution within the bulk soil. The combination of TGA-DSC with evolved gas analysis (EGA) may provide further information to improve the characterization of SOM (Fernandez et al. 2012). This can help to distinguish changes in thermal stability and energy density due to chemical changes from those due to changes in the physical states of organic matter, i.e, a mineral-associated or a free particulate state of organic matter. For instance, as lower the molar H:C ratio of a specific fraction (which can be obtained from H_2O and CO_2 evolved during the respective temperature range) as more chemically condensed the original structure was (Dell'Abate et al. 2003, Peikert et al. 2015). In the absence of any effects of the physical state of SOM, a lower H:C ratio should go along with a lower energy density (Licursi et al. 2015; Trif-Tordai and Ionel 2011).

The objective of this study was to investigate the changes in SOM thermal stability and energy density after application of OMW to soil in a field experiment in order to understand how the environmental conditions during OMW disposal may influence the fate of the added OMW-OM.

Peikert et al. (2015) found a larger thermo-labile fraction and a higher calorific value for SOM from sites exposed to uncontrolled OMW disposal than for SOM from non-polluted control sites. Therefore, we hypothesized that the OMW application to soil initially changes the native SOM quantitatively and qualitatively by increasing the labile fraction stronger than the stable fraction and increasing the calorific value. However, the physical state of OMW-OM is expected to differ after application at different seasons because the environmental conditions during and after OMW application to soil can influence the degree of OMW-OM immobilization, mobilization or transport.

Mineral interactions will be enhanced under dry conditions when OMW can directly interact with the mineral surface. Under moist conditions water films on mineral surfaces may reduce these interactions. Biodegradation is expected to reduce preferentially the labile fraction and is favored under moist and warm conditions. Leaching is expected to be highest when mineral interactions are low. At the long term, we expect strongest reduction of the OMW effects on quality and quantity of SOM for winter application due to fastest leaching. In contrast, we expect the lowest reduction of the OMW effects for application in dry summer due to the strongest mineral interactions and resulting strongest immobilization of the OMW-OM. For the application in spring and summer with irrigation, we expect a moderate reduction of the OMW effects on quality and quantity of SOM. Environmental conditions during spring and summer with irrigation will favor biodegradation and only moderate mineral interactions and moderate leaching. Further, biodegradation is expected to reduce OMW effects stronger in the labile than in the stable fraction.

In order to test these hypotheses, a field experiment was conducted in an olive orchard. OMW was applied to soil in a single dose under four different seasonal scenarios (Tamimi et al. 2016). Two days and 18 - 24 months after OMW application, soil samples were collected from OMW treated and tap water treated control plots. These samples were analyzed with respect to SOM quantity and thermal properties. In addition, total and water-extractable soil organic carbon was quantified and the latter characterized by specific ultraviolet absorbance analysis in order to further characterize the quality of the dissolved organic carbon. Differences between control and treated plots were compared with expectations for a pure mixing effect of soil and OMW and interpreted with respect to our hypotheses.

3.2 Material and Methods

3.2.1 Study site and field experiment

The study site, described recently (Tamimi et al. 2016), is located in Bait Reema village in the West Bank of the Palestinian Authority. The soil is clay loam (37 % clay, 22 % sand, 41 % silt). The predominantly Mediterranean climate is characterized by a long, hot and dry summer (June - October) with an average air temperature ranging between 24 and 27 °C, a short cool and rainy winter (November - February) with low air temperature in the range of 10 to 14 °C, and an average annual rainfall of 615 mm.

One single application of olive mill wastewater (OMW) to soil (14 L m^{-2}) was conducted in four different treatments. For each treatment, the OMW application was conducted on two plots. In addition, two corresponding control plots were treated with the same amount of tap water. For the spring treatment (SP), the OMW was applied to soil in mid-April 2012 into soil with a water content of 15 % and a temperature of ~ 18 °C in the top layer. Two different summer treatments were performed in mid-August 2012 at a soil temperature of ~ 32 °C in the top layer. For the summer dry treatment (SU_{dry}), OMW was applied to soil with a water content of ~ 5 % in the top layer. For the summer moist treatment (SU_{moist}), OMW was applied to regularly irrigated soil which ensured water content between ~ 17 – 20 %. Irrigation started already two weeks prior the OMW application and continued during the following summer season. For the winter treatment (WI), OMW was applied to soil in mid-January 2013 at the highest monthly rainfall of 288 mm. At this time, the soil top layer had a water content of ~ 24 % and a soil temperature of 8 °C. The OMW used in this field experiment was obtained from an olive mill in Bait Reema. For all treatments, the OMW was stored in polyethylene containers in the underground in darkness until the time of application. The applied OMW is characterized by a dry mass of 53 ± 1 mg g^{-1}, a concentration of total organic carbon (TOC) of 35 ± 0.3 g L^{-1} with an elemental H:C mass ratio (H:Cmass) of 0.15, and a concentration of dissolved organic carbon (DOC) of 26 ± 2 g L^{-1}, with a specific UV absorbance at 254 nm ($SUVA_{254}$) of 0.68 - 0.07 L (mg C $m)^{-1}$ (Peikert et al. 2015).

3.2.2 Soil sampling and general soil characteristics

From each plot, pooled soil samples from at least five subsamples were collected at two depths in 0 - 5 and 5 – 10 cm two days and up to 18 - 24 months after OMW or tap water application. The dissolved organic carbon (DOC) was determined in water extracts (1:5 w/v). Therefore, sieved (< 2 mm) air-dried soil samples were horizontally shaken for 2 hours, centrifuged, and filtered (Whatmann, 0.45 μm). Organic carbon was determined by the difference of total carbon and total inorganic carbon concentrations obtained by Multi N/C Analyser 2100/2100S (Analytik Jena, Germany). For the same extracts, UV-absorption was measured at 254 nm using Specord (Analytik Jena, Germany). The UV-absorption was divided by the DOC concentrations to determine the specific UV absorbance ($SUVA_{254nm}$). The total carbon and hydrogen was determined by the elemental analyzer Vario Micro Cube (Elementar Analyzensysteme GmbH, Germany). In order to calculate the amount of soil organic carbon (SOC) the difference between total carbon measured by the elemental analyzer and inorganic carbon measured by thermal analysis (as described below) was calculated for each soil sample.

3.2.3 Advanced organic matter characterization by thermal analysis

Thermal analyses were performed using the Simultaneous TG-DTA/DSC Apparatus STA 449 F3 Jupiter® (NETZSCH, Germany) coupled with the mass spectrometer MS 403 Aëolos II® (NETZSCH, Germany). Soil samples were air dried, gently manually ground in a mortar to destroy larger aggregates, and sieved (< 1 mm). Between 20 to 30 mg of soil samples in aluminum oxides crucible were heated from 26 °C to 1000 °C at a heating rate of 10 K min^{-1} under dynamic reaction gas atmosphere of synthetic air with a flow rate of 50 ml min^{-1}. The differential scanning calorimetry (DSC) was calibrated using In, Sn, Bi, Zn, Al, Ag, and Au standards. An identical empty crucible was used as a reference for the DSC curve. A heat run from the empty reference crucible was stored in a correction file and used for baseline correction of the thermogravimetric (TG) curve. In order to monitor the correct device performance, one sample of calcium oxalate monohydrate was measured after each set of eight soil samples. From each heating run, TG, DSC, and ion current (IC) curves (from the coupled mass spectrometer) as a function of temperature were exported and further evaluated using Netzsch Proteous Software 5.2.1 (NETZSCH, Germany).

For soil samples, in general, three thermal events were distinguished by the combined evaluation of IC curves for released H_2O and CO_2 (mass to charge ratio 18 and 44, respectively), the sample mass loss by TG curve and the energy flows out from or into the sample by DSC curve. 1) The temperature region for water evaporation was identified by a mass loss going along with energy consumption (endothermic DSC signal) and the evolution of H_2O in the absence of evolved CO_2. 2) The temperature region for SOM combustion was identified by a mass loss going along with energy released (exothermic DSC signal) and the evolution of both H_2O and CO_2. 3) The temperature region for thermal decomposition of carbonates was identified by a mass loss going along with energy consumption (endothermic DSC signal) and the evolution of CO_2 in the absence of evolved H_2O. The second region was further split into two in order to distinguish the amount of thermo-labile from thermo-stable SOM fractions. Therefore, the borders of the temperature region for a separate thermal event were set at temperatures where local maxima of the first derivative of the TG curves (DTG) coincide with local minima of the DSC curve and the IC curves of H_2O and CO_2.

Thermo-labile and thermo-stable fractions of SOM (LOI_{labile}, LOI_{stable}) were calculated from the respective mass loss related to the mineral mass, i.e., the mass after SOM combustion before carbonate decomposition started, and total SOM content as loss on ignition (LOI) was calculated as the sum of mass losses of thermo-labile and thermo-stable fractions. Further, the thermal stability index (TS) for each soil sample was calculated as the percentage of mass loss of the stable fraction with respect to LOI (Peikert et al. 2015). The inorganic carbon content was calculated from the mass loss of the last temperature region and related to dry mass.

The calorific value (CV) i.e., the energy released or consumed during the heating process, was determined by the integration of the peaks in the DSC curve over the temperature of the respective region and related to the mass loss in this temperature region.

In order to further characterize qualitative differences in the SOM composition, the H:C atomic ratio was assessed from the amount of evolved H_2O and CO_2, the primary products of SOM decomposition in oxidizing atmosphere (Plante et al. 2009b). Therefore, peaks appearing in the IC curve of mass to charge ratio 18 and 44 were integrated over the respective temperature regions, the first divided by the second and multiplied with two in order to transform the ratio of H_2O to CO_2 ratio into the H:C atomic ratio.

Some samples with low SOM content revealed 100 to 1000 fold higher values of H_2O to CO_2 ratios compared to that of others. Therefore, all H_2O and CO_2 IC peaks with their frequencies were plotted in a histogram. For H_2O, all data points followed the normal distribution, while for CO_2, although most data points were normally distributed, a set of data points with values below $1 \cdot 10^{-10}$ µVs mg^{-1} appeared in higher frequency and strongly deviated from the normal distribution. All these data points belonged to the 5 – 10 cm soil depth with lower SOM content, thus these signals from the evolved CO_2 were probably too small to be measured accurately. Consequently, these data points were considered as below limit of determination and were excluded from further evaluation as outliers. Furthermore, MS-data from the end of SU_{dry}, SU_{moist}, and WI experiment were measured in the MS scan mode in which resolution and sensitivity do not allow a quantitative evaluation.

In the same manner as described for the soil samples, thermal properties of freeze dried OMW samples were analyzed by TGA-DSC-MS.

3.2.4 Statistical analysis

All thermal measurements were determined in three replicates and DOC, $SUVA_{254}$ and SOC were determined in two replicates for each pooled soil sample of each of the two treated plots and corresponding control plots for the four OMW treatments. All results are depicted as a mean of six or four values, respectively, with their respective standard errors used as error bars. The data sets were tested for normal distribution using the Shapiro–Wilk test ($\alpha = 0.05$) and visually checked by QQ-Plots using the statistical software R (R Core Team, 2014). Although normality of most data sets could not be rejected with $p > 0.05$, the nonparametric Wilcoxon rank sum test (with holm *p*-value adjustment, using software R) was used for pairwise comparison of the data. Differences were considered significant at $p < 0.05$ and highly significant at $p < 0.01$.

3.3 Results

3.3.1 Total and dissolved soil organic carbon content

The changes in soil organic carbon (SOC), as well as the mass ratio of hydrogen to organic carbon ($H:C_{mass}$) after the olive mill wastewater (OMW) application to soil, are depicted in Figure 3-1. After the spring treatment (SP), the initial SOC was by ~ 0.6 % dry mass significantly higher in the treated than in the respective control soils down to 10 cm depth (Figure 3-1a, b). The same trend was observed after the summer dry treatment (SU_{dry}) with a total increase by ~ 0.8 % dry mass with respect to the control soil. However, this increase was more pronounced and significant ($p < 0.05$) only in 5 - 10 cm depth (Figure 3-1a, b). Also after winter treatment (WI), an initial increase in SOC with respect to control was found in 0-5 cm depth ($p < 0.05$) by ~ 0.5 % dry mass. In contrast to this, no initial effect on SOC was observed after the summer treatment with irrigation (SU_{moist}). The increase in SOC due to OMW application goes along with a decrease of the respective H:C_{mass} ratios for SP, SU_{dry} and WI treatments which were significant ($p < 0.05$) in 0 - 5 cm depth of the SP and in 5 – 10 cm depth of SP and SU_{dry} treated soil (Figure 3-1c, d). At the end of the experiment, SOC in the top 5 cm of the SU_{dry} treated soil was in average still higher than in the control soils, which was reflected by a significantly ($p < 0.05$) reduced H:C_{mass} ratio. However, for all other treatments no significant persisting effects were detectable, (Figure 3-1a)

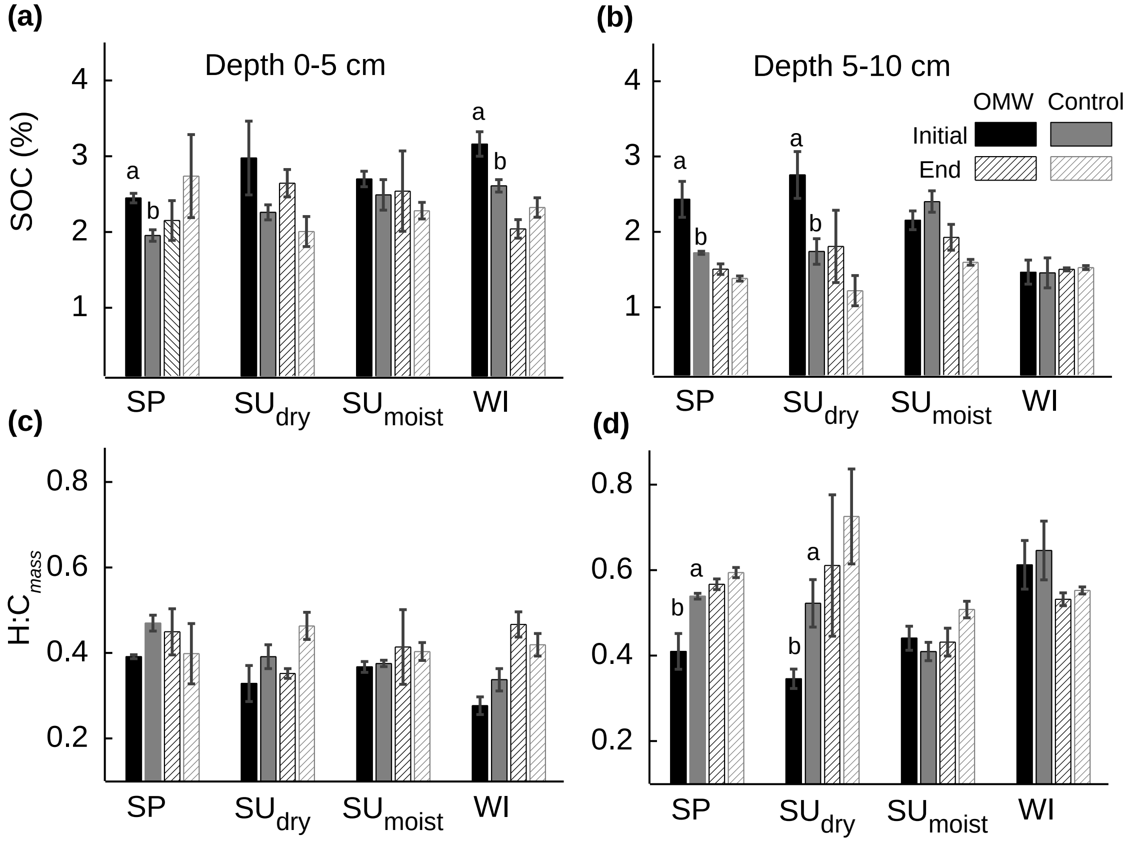

Figure 3-1: Soil organic carbon content (SOC) (a) from 0-5 cm and (b) 5-10 cm depth, mass ratio of hydrogen to organic carbon content (H:C_{mass}) (c) from 0-5 cm and (d) 5-10 cm depth for spring (SP), and summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) olive mill wastewater (OMW) application and the respective tap water treated control plots, two days after application (initial) and 18-24 months after application at the end of the field experiment (end). Data points are means of four values of two plots for each treatment and two plots for each control with error bars representing standard errors.

Figure 3-2 summarizes the initial and the persisting effect of OMW application on the amount of water extractable dissolved organic carbon (DOC) and the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) of these extracts for the top 5 cm. After all OMW treatments the initial concentration of DOC was with 1 - 3 g kg^{-1} significantly higher in the treated than in the respective control plots with < 0.2 g kg^{-1} (Figure 3-2a). For all treatments, the initial $SUVA_{254}$ was significantly reduced to 0.8 - 1.0 L (mg C $m)^{-1}$ with respect to the corresponding control plots with 1.5 - 2.3 L (mg C $m)^{-1}$ (Figure 3-2b). At the end of the field experiment, the effect of OMW on $SUVA_{254}$ disappeared in all treated soils (Figure 3-2b), whereas for SU_{dry} and SP treated soils the effect on DOC persisted significantly with 0.7 and 0.5 g kg^{-1}, respectively (Figure 3-2a).

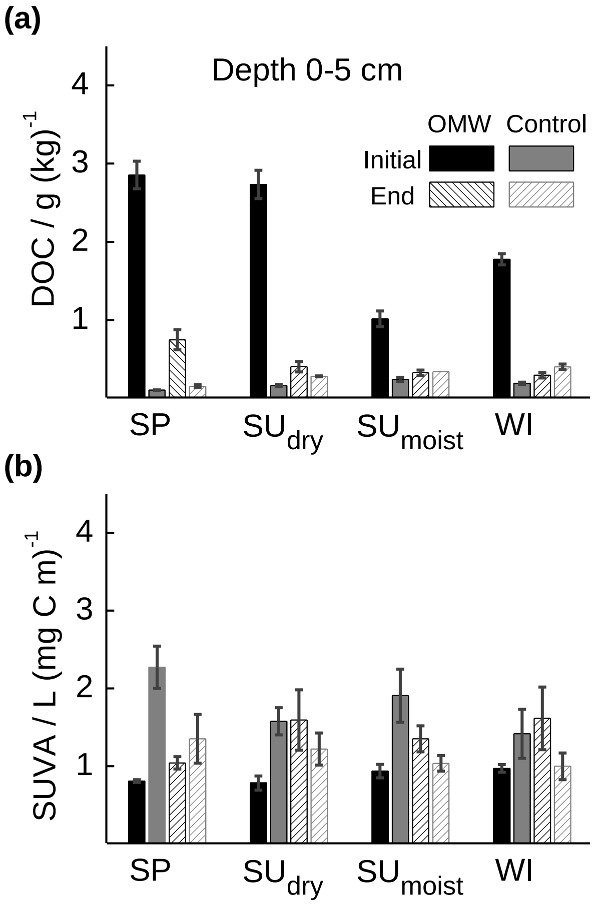

Figure 3-2: (a) Dissolved organic carbon content (DOC) from 0-5 cm, and (b) $SUVA_{254}$ from 0-5 cm depth for spring (SP), and summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) olive mill wastewater (OMW) application and the respective tap water treated control plots, two days after application (initial) and 18-24 months after application at the end of the field experiment (end). Data points are means of four values of two plots for each treatment and two plots for each control with error bars representing standard errors.

3.3.2 General pattern of thermal analysis for olive mill wastewater and soil

Explanatory examples for the evaluation of thermal analyses of OMW and soil samples are depicted in Figure 3-3. The thermogravimetric (TG) and the respective derivative (DTG) curves show the sample mass and the changes in sample mass, respectively, as a function of temperature, while the differential scanning calorimetry (DSC) curves depict the heat flux out of the sample during the heating run. Thereby, "negative" DSC peaks are caused by endothermic processes and "positive" DSC peaks are caused by exothermic processes during the thermal combustion (Lopez-Capel et al. 2005; Plante et al. 2009b). The IC curves show the amount of evolved H_2O and CO_2 as primary products which are reliable indicators for organic matter thermal decomposition in an oxidizing atmosphere (Plante et al. 2009b).

The comparison of TG/DTG, DSC, H_2O and CO_2 IC curves obtained for freeze dried OMW samples indicate four temperature regions with specific thermal events. The first thermal event in the temperature region ≤ 200°C (Figure 3-3a) resulted in a mass loss of 7 ± 0.4 % dry mass. However, peaks appeared neither for the DSC curve (Figure 3-3a) nor for H_2O and CO_2 IC curves in the same temperature region (Figure 3-3b). Therefore, the mass loss is probably associated with volatilization of compounds other than H_2O present in the OMW. Between 200°C and 775°C, the concurrent appearance of evolved H_2O and CO_2 (Figure 3-3b) together with positive peaks of the DSC curve (Figure 3-3a) clearly indicate that the mass loss of 95±2% dry mass and the total calorific value (CV) of 9 ± 0.75 kJ g^{-1} are caused by exothermic reactions of organic constituents in the OMW. Three distinguishable peaks in the DTG, DSC and in both IC curves further indicate that thermal degradation in this region can be divided into three different fractions of organic matter with increasing thermal stability: a) Between 200 and 400 °C, the largest part of the OMW dry mass ~ 60 ± 1.5 % degraded. This OM fraction with relatively low thermal stability is characterized by a CV value of ~ 3.7 ± 0.2 kJ g^{-1} and a molar H:C ratio of 10.6 ± 0.6. b) Between 400 and 560 °C, a thermally more stable OM fraction with 23 ± 1 % of dry mass degraded revealing a slightly higher CV value of ~ 5 ± 0.2 kJ g^{-1} and a smaller molar H: C ratio of 7.4 ± 0.01 compared with the first fraction. c) Between 560 and 775 °C, degradation of the thermally most stable OM fraction with a mass loss of ~ 12 ± 0.1 % revealed the highest CV value of ~ 22 ± 2 kJ g^{-1} and with 0.7 ± 0.1 the lowest molar H: C ratio of all OM fractions.

These results show that the freeze dried OMW sample contained > 95 % OM with a large thermally labile fraction. Further, the high H:C ratio of labile fraction of OMW indicates a high amount of substances with aliphatic structure (Dell'Abate et al. 2003; Peikert et al. 2015) and can be related to the high content of organic acids such as short chain fatty acids (C2-C8) from microbial metabolism of sugars and carbohydrates, and long chain fatty acids (C16-C18) from the residual oil in the OMW (Diamantis et al. 2013). The third fraction of OMW-OM which appeared in the heat run between ~ 600 and 800 °C was the smallest with respect to mass loss. However, it caused the strongest exothermic reaction, suggesting an exceptionally low O:C or high H:C atomic ratio because the calorific value of a substance increases with decreasing O:C and increasing H:C atomic ratio (Trif-Tordai and Ionel 2011). However, the third fraction is characterized by an exceptionally low H:C atomic ratio. Because with increasing degree of condensation both O:C and H:C atomic ratio decrease (Harvey et al. 2012) a very condensed aromatic carbon structure can be assumed for the third fraction of the OMW-OM. This is further supported from the peak temperature ~ 750 °C which was reported for soot-like black carbons (Harvey et al. 2012). The OMW does probably not contain charred carbonaceous substances, thus it is more likely that this fraction was formed during the combustion process. Therefore, in some regions within the OMW-OM, oxygen supply was probably not sufficient for complete oxidation during the TGA heat run, such that pyrolysis reactions occurred in these regions. As a result, a small amount of charred carbonaceous material may have been formed, being responsible for the observed high exothermic reaction. Char formation during thermal decomposition of fresh plant material has been already recognized in earlier studies (Kaloustian et al. 2001; Lopez-Capel et al. 2005).

The thermal analyses of the soil sample, as depicted in (Figure 3-3c and d) also reveal four temperature regions. However, they differ from that of the OMW. In the first temperature region ≤ 200°C, an endothermic peak in the DSC curve (Figure 3-3c) and a H_2O peak in the IC curve (Figure 3-3d) indicate that the respective mass loss is probably associated with dehydration and the removal of hygroscopic water (Dell'Abate et al. 2003; Lopez-Capel et al. 2005; Plante et al. 2009b). In the temperature region between ~ 200 - ~ 600 °C exothermic peaks in the DSC curve (Figure 3-3c) and the appearance of both H_2O and CO_2 peaks in the IC curves (Figure 3-3d), as described earlier by other authors (Lopez-Capel et al. 2005; Plante et al. 2009b), clearly indicate that the mass loss of this region is associated with thermal oxidation of SOM. Further, from the local maximum in the DTG curve and the local minimum in DSC curve and in both IC curves at ~ 400 °C, two SOM fractions of different thermal stability can be distinguished: a) The mass loss between 200 – 400 °C is associated with the thermo-labile fraction and b) the mass loss between

400 – 600 °C is associated with the thermo-stable fraction (Peikert et al. 2015). In the fourth temperature region between 600 – 800 °C (Figure 3-3c and d), an endothermic DSC peak and the only appearance of a CO_2 peak in the absence of any H_2O peak in the IC curves indicate that the mass loss of this region is associated with carbonate decomposition and can be easily quantified (Fernandez et al. 2012; Lopez-Capel et al. 2005; Plante et al. 2009b). Thus, the organic carbon content could be calculated from the total carbon content measured by the elemental analyzer and the carbonate content from the TGA measurements. In the following section, we will focus on the thermal results of the temperature region between 200 – 600 °C in order to investigate the changes in quantity and quality of native SOM due to OMW application.

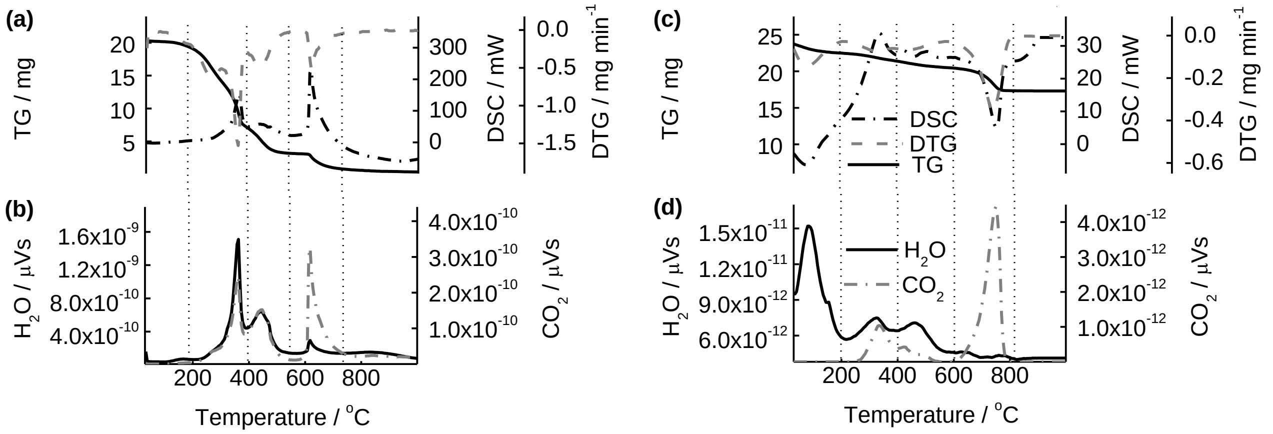

Figure 3-3: Explanatory examples for the evaluation of thermal analysis of (a+b) freeze-dried olive mill wastewater and (c+d) air-dried soil samples using TGA-DSC-MS. (a+c) Sample mass (Thermogravimetric curve, TG), change in sample mass (derivative thermogravimetric curve, DTG) and heat flow from the sample (differential scanning calorimetric curve, DSC) as a function of temperature and (b+d) ion current (IC) from mass spectrometer for mass to charge ratio 18 and 44 (evolved H_2O and CO_2, respectively) as a function of temperature obtained from a heat run with 10 K min^{-1} under synthetic air with 50 mL min^{-1}.

3.3.3 Changes in thermal SOM properties after OMW application

3.3.3.1 Total soil organic matter fraction

The changes in SOM properties after application of OMW in spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}) and winter (WI) treatments are depicted in Figure 3-4. As an initial effect (two days after OMW application), both SP and SU_{dry} treatments in average increased the SOM content determined as loss on ignition (LOI) with respect to the corresponding control soil (down to 10 cm) as shown in Figure 3-4a and b. For 0 - 10 cm depths in total, the SOM increased in average by ~ 1.2 % and ~ 2 % mineral mass for SP and SU_{dry}, respectively. Nevertheless, the extent of this effect was highly significant ($p < 0.01$) only in 5 – 10 cm depth of the SU_{dry} soil (Figure 3-4b), but not significant in the top 5 cm. SOM also changed qualitatively for both treatments. Down to 10 cm depth, the initial thermal stability index (TS) of SOM was with 49 ± 1.3 % and 53 ± 2.1 % for SP and SU_{dry} treated soils, respectively, significantly lower ($p < 0.05$) than for the counterpart control soils with 53 ± 2 % and 57 ± 2 % (Figure 3-4c, d). On the other hand, the initial calorific value of SOM (CV_{LOI}) in 0 – 10 cm depth of the SP application was by ~ 1.2 ± 0.1 kJ (g mass loss)$^{-1}$ significantly higher ($p < 0.01$) in the treated than in the corresponding control soil (Figure 3-4e, f). An increase in CV_{LOI} was also observed for SU_{dry} treated soils, particularly in the top 5 cm, although it was statistically not significant (Figure 3-4e, f). Surprisingly, none of the previously described initial effects were detectable for the SU_{moist} and WI treatments.

At the end of the field experiment (18 - 24 months after OMW application), the effect of OMW on LOI clearly disappeared in the SP-treated soil. However, down to 10 cm depth, SOM content of the SU_{dry} treated soil remained in average by ~ 1 % of mineral mass elevated, although statistically not significant (Figure 3-4a, b). In contrast to the quantitative changes, the OMW effects on SOM thermal quality were more persistent. Interestingly, for SP treatment, long-term effects on TS and CV_{LOI} clearly disappeared in 0 - 5 cm depth (Figure 3-4c, e) but significantly persisted ($p < 0.01$) in 5 – 10 cm depth (Figure 3-4d,f), whereas for SU_{dry} treatment, effects on TS and CV_{LOI} clearly disappeared in 5 – 10 cm depth (Figure 3-4d, f) but persisted in 0 – 5 cm depth (Figure 3-4c, e), although being significant ($p < 0.05$) only for TS. In accordance with the non-detectable initial effects, no long-term effects were detectable for SU_{moist} and WI treatments.

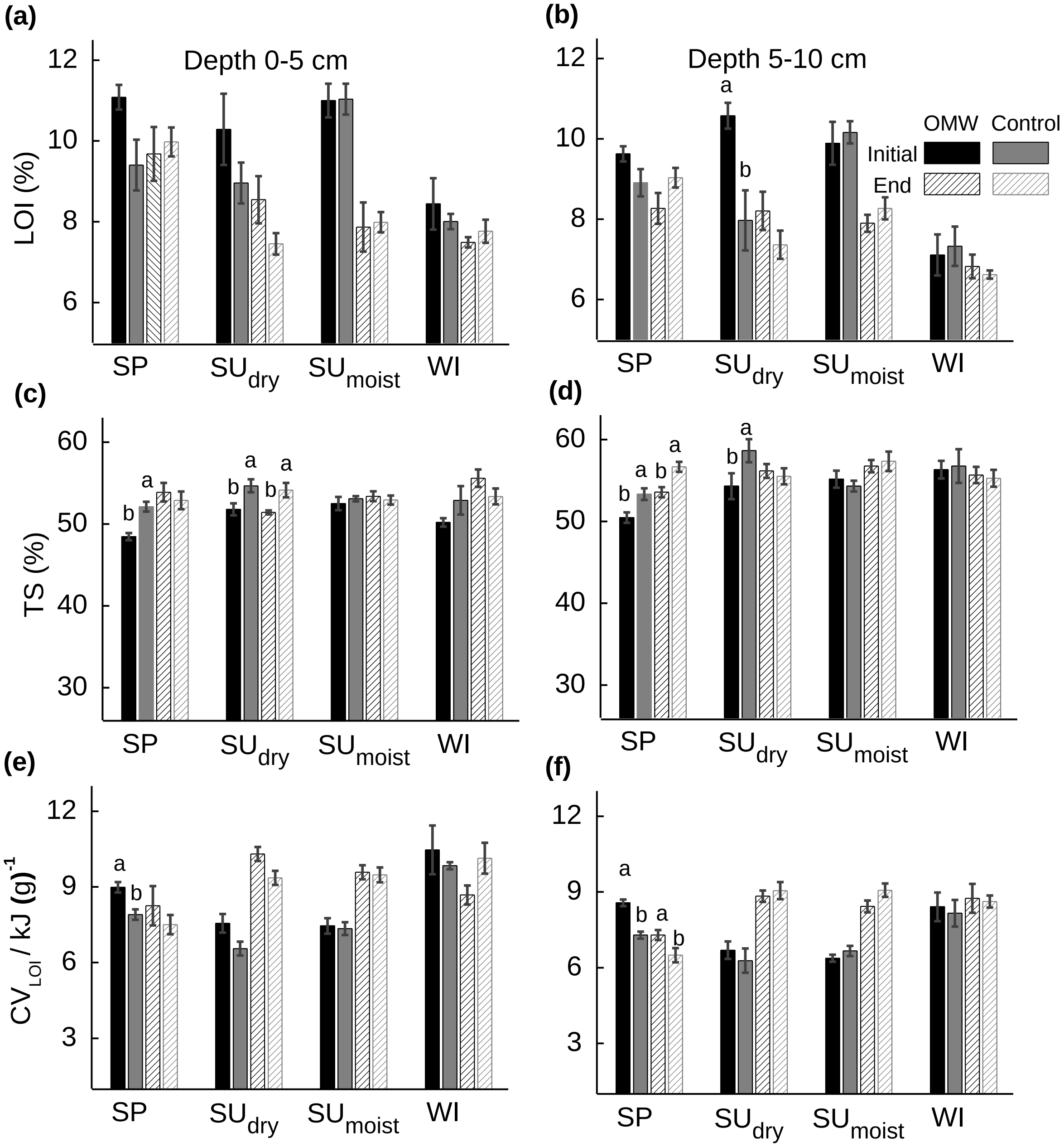

Figure 3-4: Results of thermal analysis of soil samples in 0-5 cm (a, c, e) and 5-10 cm depth (b, d, f) for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) olive mill wastewater (OMW) application and the respective tap water treated control plots, two days after application (initial) and 18-24 months after application at the end of the field experiment (end). (a+b) Total soil organic matter content determined as loss on ignition (LOI) as % mass loss between 200-580°C related to mineral mass, (c+d) thermal stability index (TS) as % mass loss between 400-580°C related to LOI, and (e+f) calorific value of the total soil organic matter obtained from 200-580°C (CV_{LOI}) Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard error.

3.3.3.2 Thermo-labile and thermo-stable fractions

For a more detailed picture of the thermal SOM properties, Figure 3-5a-d demonstrates how the initial and persisting effects observed after SP and SU_{dry} treatments are distributed between the thermo-labile and thermo-stable SOM fractions. After SP treatment, the quantity of thermo-labile fraction initially increased with respect to the control for both investigated depths, although this was significant ($p < 0.05$) only in the top 5 cm (Figure 3-5a, b). In contrast, no initial effects on the quantity of the thermo-stable fraction at any of the investigated depths could be detected for SP (Figure 3-5c, d). Also after SU_{dry} treatment, the quantity of the thermo-labile fraction initially increased with respect to control, however, significantly ($p < 0.05$) only in 5 – 10 cm depth (Figure 3-5a, b). Additionally, a significant increase ($p < 0.05$) in the quantity of the thermo-stable fraction was detected in the 5 – 10 cm depth, however, to a smaller degree than the increase in the thermo-labile fraction (Figure 3-5d).

At the end of the field experiment, for the SP treated plots all initial OMW effects on the quantity of labile SOM fraction disappeared (Figure 3-5a). Nevertheless, a significant decrease in the quantity of stable fraction was found in SP treated soil at 5 – 10 cm depth (Figure 3-5d). In contrast, for the SU_{dry} treated plots, the quantity of thermo-labile and thermo-stable SOM fractions were in average still elevated with respect to the control at the end of the experiment, although with $p < 0.1$ only for the thermo-labile fraction in the top 5 cm (Figure 3-5a). For SU_{moist} and WI treatments, no OMW effects on the quantity of any fraction neither in the short term nor in the long term were detected (data not shown).

As qualitative property, the CV of the thermo-labile fraction initially increased after SP treatment with respect to the control soil, although this increase appeared significant ($p < 0.01$) only in the 5 – 10 cm depth (Figure 3-5e, f). In contrast, the initial CV of the respective thermo-stable fraction was significantly higher ($p < 0.01$) than control in both depths (Figure 3-5g, h). After SU_{dry} treatment, only in the top 5 cm the initial CV of the thermo-labile fraction increased significantly ($p < 0.05$) with respect to control (Figure 3-5e), while the initial CV of the thermo-stable fraction increased in average in both depths, however, in none of them significantly.

At the end of the field experiment, significant OMW effects on the CV of the thermo-labile fraction disappeared for all treatments in both depths (Figure 3-5e, f). Only for the SP treatment, differences in the CV of the thermo-stable fraction disappeared in 0 - 5 cm depth (Figure 3-5g) but significantly persisted ($p < 0.05$) in 5 - 10 cm depth (Figure 3-5h). For the SU_{dry} treatment, CV of the thermo-stable fraction remained in average higher than in control in 0 - 5 cm although not significantly noted ($p < 0.065$), while this was not observed in 5 - 10 cm depth (Figure 3-5g, h). After SU_{moist} and WI treatments, no initial OMW effects on the CV of both thermal fractions were detectable down to 10 cm depth. However, in the long-term, the CV of both thermal fractions were in average higher for SU_{moist} than for the respective control in 5 - 10 cm depth, although significantly only for the thermo-stable fraction (data not shown). For WI treatment, CV of both fractions was in average lower than those of the control in the top 5 cm, although not significantly. While in 5 - 10 cm depth no such effects were detectable (data not shown).

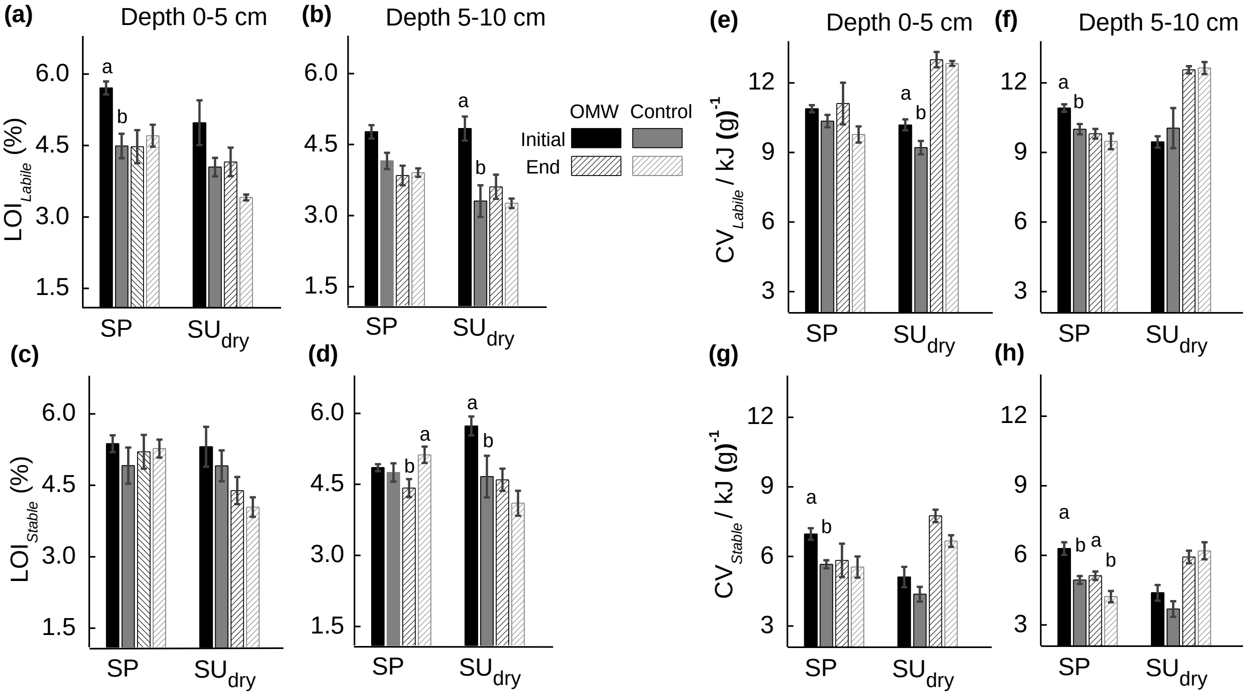

Figure 3-5: (a-d) Mass loss on ignition between 200-400°C (LOI_{labile}) (a) from 0-5 cm and (b) 5-10 cm depth, mass loss on ignition between 400-580°C (LOI_{stable}) (c) from 0-5 cm and (d) 5-10 cm depth and (e-h) Calorific value obtained from 200-400°C (CV_{labile}) (e) from 0-5 cm and (f) 5-10 cm depth and CV obtained from 400-580°C (CV_{stable}) (g) from 0-5 cm and (h) 5-10 cm depth for spring (SP) and summer without irrigation (SU_{dry}) olive mill wastewater (OMW) application and the respective tap water treated control plots, two days after application (initial) and 18-24 months after application at the end of the field experiment (end). Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard errors.

3.3.3.3 Composition of evolved gases

Further qualitative changes in SOM after OMW application may be reflected by the H:C atomic ratio of the gaseous reaction products H_2O and CO_2 formed during the thermal degradation process, and by how they are distributed between the thermo-labile and stable fractions. Figure 3-6 illustrates the H:C atomic ratios of different SOM fractions for SP and SU_{dry} treatments. The H:C atomic ratio of the total SOM was not significantly affected by OMW in 0 - 5 cm after SP treatment, neither initially with 5 - 6 nor in the long-term with 7 - 8. Whereas, in 5 - 10 cm depth, an initial effect of reduced H:C molar ratio of 6 with respect to the control of 8 was found, although this effect was with $p < 0.13$ not significant (Figure 3-6a, b). After the SU_{dry} treatment, the initial H:C atomic ratio of the total SOM was significantly decreased from 16 to 11 by OMW application ($p < 0.05$) only at 5 - 10 cm depth (Figure 3-6a, b). Unfortunately, long-term effects on H:C atomic ratio for SU_{dry} cannot be evaluated with the present dataset (see the end of section 2.3). However, already the initial H:C molar ratio of the thermo-labile fraction was for both treatments not significantly affected by OMW application (Figure 3-6c, d). In contrast to this, the H:C atomic ratio of the thermo-stable fraction was from 9 to 6 stronger reduced after SP than after SU_{dry} treatment were it was reduced from 13 to 11 in 0-5 cm depth. In 5 - 10 cm depth, it was stronger reduced from 38 to 23 for SU_{dry} ($p < 0.1$) than for SP treatment were it was reduced from 16 to 11, however, in none of the cases significantly (Figure 3-6e, f). At the end of the experiment, a reduced H:C atomic ratio from 36 to 24 of the thermo-stable fraction was found in 5 – 10 cm of SP treatment with $p < 0.01$ (Figure 3-6e, f).

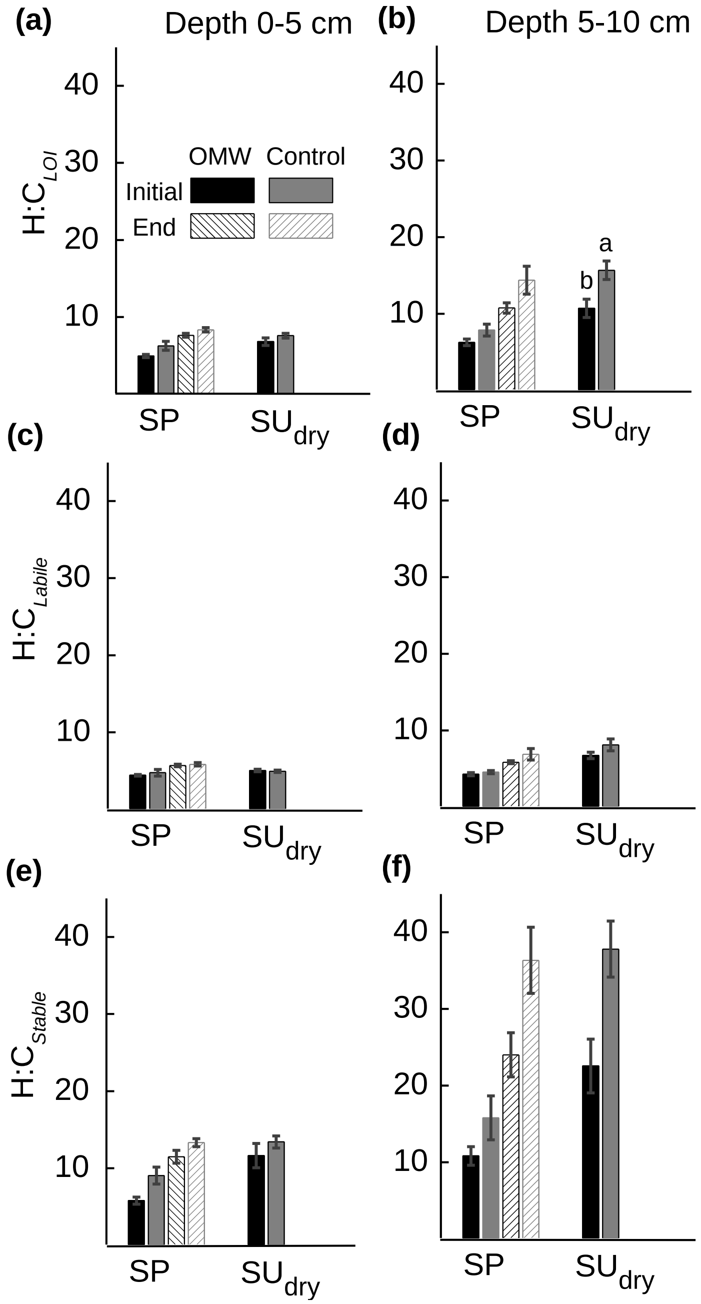

Figure 3-6: Atomic ratio of the mass spectrometric ion currency peak area caused by H_2O to that of CO_2 evolved from thermal degradation of total soil organic matter content at 200-600°C ($H:C_{LOI}$) (a) from 0-5 cm and (b) 5-10 cm depth, atomic ratio of H_2O to that of CO_2 evolved from thermal degradation between 200 400°C ($H:C_{labile}$) (c) from 0-5 cm and (d) 5-10 cm depth, and atomic ratio of H_2O to that of CO_2 evolved from thermal degradation at 400-600C ($H:C_{stable}$) (e) from 0-5 cm and (f) 5-10 cm depth for spring (SP), summer without irrigation (SU_{dry}), olive mill wastewater (OMW) application and the respective tap water treated control plots, two days after application (initial) and 18-24 months after application at the end of the field experiment (end). Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard errors.

3.4 Discussion

3.4.1 Initial OMW soil interactions causing quantitative SOM changes

Despite the same amount of OMW application, significant quantitative OMW effects were detected only for spring (SP) and summer dry (SU_{dry}) treatments but not for winter (WI) and irrigated summer (SU_{moist}) treatment. This suggests that different environmental conditions at the season of OMW application must have affected the initial distribution of the OMW within the profile by different degrees of transport, transformation and retention mechanisms. The added OMW-OM after WI and SU_{moist} treatments was probably largely removed from the top 10 cm already two days after the application. Preferential flow paths might have enhanced the downward transport of OMW-OM within the soil profile. This is in accordance to earlier studies (Tamimi et al. 2016) who found preferential flow as a relevant transport mechanism on the same field experiment. Since these treatments had the highest water content (WC) at the time of application, retention mechanisms due to OMW-mineral interactions were probably low. Therefore, leaching due to irrigation of the SU_{moist} plots and leaching or surface runoff due to rainfall during the WI application might explain the observed results.

The total SOM and SOC content in the upper 10 cm were increased stronger after the SU_{dry} than after the SP treatment. Nevertheless, a larger change in SOM quantity appeared in 0 - 5 than 5 - 10 cm for SP treatment, whereas for SU_{dry} a larger change in SOM appeared in 5 - 10 than 0 - 5 cm depth. This suggests that the distribution of OMW in soil varied among SP and SU_{dry} treatment. At the time of SU_{dry} treatment, the soil water content was with ~ 5 % significantly lower than at the time of SP treatment with ~ 15 %. Thus, OMW probably infiltrated slower after SP treatment such that OMW-OM could be retarded. Like in a filter bed, OMW-OM became stronger accumulated in the 0 - 5 than 5 - 10 cm of the SP treated soils. In contrast, the OMW probably infiltrated fast into deeper layers after SU_{dry} treatment due to dry conditions and the presence of preferential flow paths. Nevertheless, high temperature after SU_{dry} treatment may have soon stopped this downward transport due to evaporation and capillary rise before more OMW-OM could be leached into deeper horizons. Thus, a larger part of OMW-OM could be stronger accumulated in 5 - 10 cm than in 0 – 5 cm depth of SU_{dry} treated soils. These different OMW transport mechanisms agree with the findings of Tamimi et al. (2016). However, it seems contradictory that the slower transport in

SP treatment resulted in lower SOM content than the faster transport in SU_{dry} treatment. The most probable explanation for this would be biological degradation of parts of the added OMW-OM within the first two days after SP treatment. Buchmann et al. (2015) found in an incubation study of soil treated by OMW under spring conditions (14 L m^{-2}, 23 % WC, 15 ^{o}C) a strong stimulation of soil respiration and a significant reduction in SOM within 5 days after OMW application. This suggests that a comparable microbial activity cannot be excluded also in our field experiment for the SP treatment.

3.4.2 Theoretical pure mixing effects of OMW application on thermal SOM properties

The thermal analysis of OMW-OM showed different patterns than native SOM of control soils. By comparison of these patterns, a pure OMW-soil mixing effect can be distinguished from changes in OMW-OM thermal properties as a consequence of OMW-soil interactions.

The OMW-OM is characterized by a larger thermally labile fraction with a relatively higher H:C atomic ratio than in the control soils. The total calorific value (CV) is with 9 kJ (g mass loss)$^{-1}$ comparable to that of SOM of the control soils with ~ 6 - 10 kJ (g mass loss)$^{-1}$. However, thermal analysis of OMW-OM showed a third fraction which does not exist in the soil. This fraction the calculation of the pure OMW-soil mixing effect for thermal stability index (TS), CV or H:C atomic ratio separately for the thermally labile and stable fractions impossible because it did not occur in the OMW-treated soil samples. It is, thus, not clear to which of the two SOM fractions the third OMW-OM fraction could be related after soil application. As such, we estimated the expected theoretical pure OMW-SOM mixing effects for three extreme assumptions. i) The third OMW-OM fraction fully appears in the labile SOM fraction. ii) The third OMW-OM fraction fully appears in the stable SOM fraction. iii) The former labile and stable OMW fractions will be united into the labile SOM fraction and the stable SOM fraction is represented by the former third OMW fraction. All these three assumptions provided the same trend for pure OMW-SOM mixing effects except for two cases (CV_{labile}, CV_{stable}) in which one assumption suggested no effect (Table 1). This qualitative estimation shows that as a pure mixing effect, OMW application is expected to decrease the thermal stability due to the addition of a higher percentage of labile than of stable OM. For the total CV, only a small reduction or no reduction at all can be expected because total CV of OMW-OM is comparable to that of the control soils. For the labile fraction, a decrease in CV is expected because based on the first two assumptions the CV of the labile OMW is lower than the CV of the labile SOM fractions from the control soils. In contrast, the CV of the stable fraction is expected not to change based on the first assumption, but to increase due to OMW application based on the two other assumptions. In accordance to the total CV, also the total H:C ratio is expected not to change upon OMW application. However, an increase in the H:C ratio of SOM for the labile and a decrease for the stable fraction is expected as a pure soil OMW-OM mixing effect based on all assumptions. In the following, the expected theoretical effects are compared with the trends of the measured effects for SU$_{dry}$ and SP treated soils.

Table 3-1: Comparison of expected pure mixing effects from OMW application on quantitative and qualitative thermal SOM properties with actual trends of effects ($p < 0.3$) found two days and 18-24 months after OMW application (* Statistical significant effects with $p < 0.05$, $^{i)}$ no expected effect for assumption i, $^{iii)}$ no expected effect for assumption iii, for details, please refer to section 3.4.2).

Parameter	Expected pure mixing effects	Effects	after two days		after 18-24 months	
		Depth/cm	SP	SU$_{dry}$	SP	SU$_{dry}$
LOI$_{lab}$ / % mineral mass	>	0-5	>*	>	none	>
		5-10	>	>*	none	none
LOI$_{stab}$ / % mineral mass	>	0-5	>	>	none	none
		5-10	none	>*	<*	>
TS / %	<	0-5	<*	<*	<	<*
		5-10	<*	<*	<*	none
CV$_{lab}$ / kJ (g mass loss)$^{-1}$	< / none $^{iii)}$	0-5	>	>*	none	none
		5-10	>*	none	>	none
CV$_{stab}$ / kJ (g mass loss)$^{-1}$	none $^{i)}$ / >	0-5	>*	>	none	>
		5-10	>*	>	>*	none
H:C$_{mass}$	none	0-5	<*	<	none	<*
		5-10	<*	<*	<	none
H:C$_{lab}$	>	0-5	none	none	none	n.d.
		5-10	none	<	none	n.d.
H:C$_{stab}$	<	0-5	<	none	none	n.d.
		5-10	<	<	<	n.d.

3.4.3 Initial OMW-soil interactions causing changes in thermal SOM properties

In accordance with these expectations, the reduced TS two days following the OMW application in SP and SU_{dry} treatments is clearly caused by an increase of the thermo-labile fraction and not by a reduction of the thermo-stable fraction. The presence of high amounts of non-humidified, aliphatic, and more labile organic compounds in the OMW (Dell'Abate et al. 2003; Peikert et al. 2015) was already indicated by a high H:C ratio of the labile OMW fraction. This is further supported by the decreased $SUVA_{254}$ that indicates that also the ratio of aromatic:aliphatic compounds in the water extractable organic matter was reduced due to the OMW application. In accordance to the total SOM, also the amount of the thermo-labile fraction increased stronger in 0 - 5 than 5 - 10 cm depth after SP treatment and in 5 - 10 than 0 - 5 cm after SU_{dry} treatment. The CV of thermo-labile fraction did not decrease as expected from the pure mixing effects. In contrast, it increased and the increase was stronger where the amount of labile fraction was less affected, i.e., in 5 - 10 cm for SP and in 0 - 5 cm for SU_{dry} treated soil. Furthermore, no increase in the H:C atomic ratio reflected the increased thermo-labile fraction. This is in contrast to the expectations (Table 1) and indicates that the CV and H:C atomic ratio of the thermo-labile fraction of SP and SU_{dry} treated soil are not simply influenced by a pure mixing effect with OMW. Possible explanations for an increased CV may be an increase of the H:C ratio (Trif-Tordai and Ionel 2011) which can be excluded from our data. Probably, not the elemental composition of OMW-OM, but initial interaction mechanisms between the OMW-OM and soil increased the CV of the thermo-labile fraction. The lower the amount of OMW-OM in one horizon, the thinner will be a potential OMW-OM coating on soil particles and as stronger its thermal properties will deviate from that of the pure OMW. Mineral-organic interactions may influence thermal properties in both directions: monovalent cations bridges are reported to increase the decomposition temperature while bi- and trivalent cations are reported to decrease decomposition temperature (Buurman et al. 2002; Peltre et al. 2013; Schnitzer 1967). To our best knowledge, the only explanation for an increasing CV of OM due to mineral interactions would be a catalyzing effect of multivalent cations during the burning process (Aho et al. 1991). The reduced activation energy of burning probably shifted parts of the energy-rich thermally stable fraction of OMW-OM into the thermally labile fraction after interaction with mineral soil. A similar shift in CV from stable to labile fraction due to mineral-organic interactions was found by the comparison of DSC curves of OM alone and as coatings on mineral soil (Rovira and Vallejo 2000). This is in contrast to other studies which found the opposite effect, a lower CV for low-C soils with probably more mineral associated SOM than for high-C soils with probably lower mineral associated SOM (Peltre et al. 2013). Therefore, our explanation requires further experimental evidence. Especially the relation between thermal stability as well as calorific value and mineral-organic interaction need further investigation to be better understood (e.g., Plante et al. 2011).

Our explanation, however, would suggest that the slow infiltration in SP treatment lead to a filter effect for OMW-OM. By this, thicker organic coatings on mineral particles may have formed in the upper 5 cm than in the 5 - 10 cm depth. In contrast, the fast infiltration during the SU_{dry} treatment, most likely, allowed the formation of coatings only in the upper 5 cm, whereas OMW-OM reached 5 - 10 cm depth mainly through preferential flow paths. By this, OMW-OM aggregated and precipitated during the following fast drying in 5 - 10 cm depth forming rather particulate OMW-OM than coatings.

Furthermore, the thermo-stable fraction increased after SU_{dry} treatment only in 5 - 10 cm depth but was not significantly affected in the upper 5 cm of SU_{dry} and in both depth of the SP treated soil, although generally an increase was expected. This could be attributed to the heterogeneity of OMW distribution within the soil matrix under different moisture conditions as described above. We suggested higher mineral-organic interactions for the more homogeneously distributed OMW-OM in the upper 5 cm of SU_{dry} and in 5 - 10 cm depth of the SP treated soil. This would suggest that mineral-organic interactions would decrease the stabile fraction. This is in line with our interpretation of catalyzing effects of cation bridges from mineral surfaces. Probably, part of the stable fraction was decomposed at lower temperature due to reduced activation energy and thereby decreased the weight loss of the stable fraction during the burning process.

In line with our expectations from the pure mixing effects, CV of the stable fraction significantly increased and H:C ratio decreased after SP treatment in both depths and showed a comparable trend for the SU_{dry} treated plots in 5 - 10 cm. The absence of short-term effects on SOM quality after SU_{moist} and WI treatment provides further evidence for a rapid wash-out of the OMW-OM from the upper 10 cm soil layerPersisting effects in SOM properties.

3.4.4 Long-term fate of OMW-OM in soil

For SU_{moist} and WI treatments, no long term effects of OMW application to soil were detectable. In accordance with the non-detectable initial effects, this further supports that the added OMW was nearly completely leached out from the observed horizons within the first two days.

In 0 - 5 cm depth of the SP treatment, no significant persisting quantitative or qualitative effects were observed in the long term. This suggests that the added OMW-OM could be biologically degraded or leached from the upper 5 cm during the following seasons. However, in 5 - 10 cm of the SP treated soil, the total SOM content was reduced due to a significantly lower thermo-stable fraction with respect to the control soil. Further, the CV of the stable fraction remained significantly higher and the H:C ratio was lower than in the control soil as expected from a pure mixing effect of soil with OMW. One possible explanation could be that not the stable OMW-OM fraction which has a high CV but probably preferentially the native thermo-stable SOM fraction with a lower CV was degraded. This is surprising, because, microorganisms are thought preferring to degrade substances with higher energy content among substances of the same stability. However, to our best knowledge, this is the only explanation for a decreased amount of the stable fraction without a decrease in the CV in 5 - 10 cm depth of the SP treatment. A possible explanation for this unusual microbial behavior could be the so called priming effect. Priming effect is defined as an increased decomposition of recalcitrant SOM after the input of easily degradable exogenous substrate (Blagodatskaya and Kuzyakov 2008). Following the “co-metabolism” theory, the exogenous substrate serves as an energy source for microorganisms enabling the synthesis of extracellular enzymes capable of degrading recalcitrant SOM, whereas following the “N-mining” theory, soil microbial growth is stimulated causing nutrients limitation such that degradation of recalcitrant SOM which contains higher amount of N and other nutrients is needed (Wang et al. 2015). The initial effects showed that a considerable amount of labile organic matter was added to the soil by the OMW application. These probably easily degradable labile C and N can strongly stimulate the growth and activity of soil microorganisms (Piotrowska et al. 2006). During the first weeks following SP treatment, moisture and temperature conditions were optimal for microbial activity, especially in 5 - 10 cm depth, where the soil did not dried out as fast as in 0 - 5 cm. This would explain why the “priming” effect was only in SP treatment and only in 5 - 10 cm depth detectable.

In contrast to the SP treatment, no significant persisting quantitative or qualitative effects were observed in the 5 - 10 cm depth of the SU_{dry} treatment in the long term. The still significantly reduced TS and a tendency for a still elevated CV of the stable fraction in 0 - 5 cm of the SU_{dry} treatment indicate that OMW effects did not fully disappeared in the upper horizon two years after OMW application. This indicates that soil in 0 - 5 cm depth of the SU_{dry} treatment preserved the

OMW-OM effects longer than soil in 5 - 10 cm depth, although initially effects were stronger in 5 - 10 cm. The hot and dry conditions during the first weeks following the SU_{dry} treatment probably inhibited microbial activity and favored mineral-organic interactions. These mineral-organic interactions could probably not be fully reversed during the following rain seasons. In earlier studies, Tamimi et al. (2016) found that soil water repellency and secondary acidification effects significantly increased for SU_{dry} treated soil during the summer season. The authors ascribed these effects to abiotic polymerization and condensation of OMW-OM. The same mechanisms may have led to the persistence of quantitative and qualitative changes in thermal SOM properties in 0 - 5 cm depth of the SU_{dry} treated soil. The following rain season did probably not significantly affected the more hydrophobic OMW-OM coatings in 0 - 5 cm, while it enabled mobilization and degradation or leaching of the largest part of the less hydrophobic OMW-OM in 5 - 10 cm depth (Steinmetz et al. 2015).

3.5 Conclusions

Generally, the results of this study support our hypothesis that the environmental conditions prevailing at the time of OMW application strongly control the fate of OMW-OM in soil. As expected, OMW application to soil increased the thermo-labile fraction stronger than the thermo-stable fraction. Surprisingly, rain or irrigation water leached the OMW-OM already within two days from the upper 10 cm of winter and irrigated summer treatment plots. This fast leaching suggests that OMW application under these conditions might cause a severe risk for groundwater contamination. Therefore, future investigations on the fate of OMW-OM should include the observation of the groundwater quality in short and long term.

As hypothesized, moist and warm conditions during spring treatment favored biodegradation of OMW-OM and reduced hardly reversible immobilization mechanisms (e.g., mineral-organic interaction) especially in the 5 - 10 cm depth. However, in contrast to our expectations, biodegradation in the spring treatment plots did not only reduce the thermo-labile fraction of the OMW-OM but also the thermo-stable fraction of the native SOM at the long term. This was probably due to a priming effect caused by the applied easily degradable labile OMW-OM fraction.

OMW application under hot and dry conditions initially led to a heterogeneous distribution of the OMW-OM within the soil profile due to preferential flow paths. Thereby higher amounts of the

OMW-OM reached the deeper soil layer than remained in the upper. However, in accordance to our hypotheses, the persistence of OMW effects of the summer dry application were strongest in the upper layer where the hottest and driest conditions during summer favored mineral-organic interactions and abiotic polymerization and condensation reactions.

We conclude that for the investigated field (including soil texture and climatic conditions) application of OMW to soil in winter or combined with irrigation cannot be recommended as long as groundwater contamination cannot be excluded by additional investigations. Lower persisting OMW effects in SOM quantity were found after application in spring than after summer dry application. If the increase of SOM in soil is the essential aim of OMW application and changes in quality can be neglected, summer dry application would be the most recommended. However, the persistent OMW-OM in form of coatings on mineral particles in the top soil layer of SU_{dry} treated plots may accumulate with repeated applications and increase the risk of soil water repellency development. If instead the recovery of soil from the effects of OMW application is the essential aim of the OMW soil treatment, spring application would be the most recommended. However, both applications caused in long term changes in some thermal properties of the SOM. In order to judge which application is more favorable, long-term investigations with repeated applications are needed to detect potential negative or positive accumulated effects of these SOM properties, like toxicity and soil water repellency.

In future, the relation between thermal stability as well as calorific value and mineral-organic interactions needs further investigation to be better understood. Further, it is still not clear how thermal SOM properties like thermal stability and energy density as well as H:C ratio may affect soil fertility properties like cation exchange capacity, water holding capacity or microbial activity.

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3.6 References

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4 Synthesis and General Conclusions

4.1 Summary of the observations

The data of the current study demonstrates the effects of seasonal olive mill wastewater (OMW) disposal to soil where a single application of OMW (14 L m^{-2}) was applied to soil either in the spring (SP), summer with and without irrigation (SU$_{moist}$ and SU$_{dry}$) and winter (WI) season. The short-term and long-term effects were investigated for each seasonal application, in order to understand the OMW-soil interaction under different climatic conditions. The overall results of the current study demonstrate that several soil parameters changed due to the OMW application. These include increases in the soil salinity, the soil acidity, soluble phenolic compound (SPC), total soil organic matter (SOM), soil organic carbon (SOC), 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; Kurtz, et al. 2015; Mekki, et al. 2013; Peikert, et al. 2015; Steinmetz, et al. 2015).

Nevertheless, the degree and persistence of these relevant effects due to OMW application on soil varied significantly between the different seasonal OMW applications both in the short-term and the long-term. It was validated that the observed effects were caused by different transport and transformation processes taking place depending on the seasonal conditions, triggered by the ambient soil moisture and temperature which either intensified or diminished negative or positive effects of OMW in the soil during and after the application season.

The transport mechanisms were shown to be a combination of i) fast leaching of dissolved and solid colloidal OMW substances due to preferential flow, ii) slow downward transport of soluble substances due to matrix flow as well as iii) the upward transport of soluble substances due to capillary rise. Together with the environmental conditions, the interplay of these transport mechanisms determined which transformation processes could take place in the soil such as i) accumulation of OMW-OM, ii) abiotic condensation and polymerization or iii) biotic degradation.

These OMW- soil interaction mechanisms were identified based on the effects observed of OMW on soil at the time of its application, SP, SU$_{dry}$, SU$_{moist}$, or WI, during the time span of the application and the first winter season following the application and after one to two years after the application. The first winter season had a significant impact in reducing the negative effects observed in the soil, with respect to salinity, repellency, and soluble phenolic compounds as well as acidification irrespective of application time. Moreover, each of the four applications exhibited a different trend in the degree and persistence of OMW effects in the soil as discussed below.

4.2 Short-term OMW- soil interaction

The initial effects of OMW among the SP, SU_{dry}, SU_{moist}, and WI applications reached deeper depths than expected from the application amount of 14 L m^{-2} and it cannot be excluded that part of OMW may have reached depths well below the 35 cm depth investigated. Thus, preferential flow was identified as the major OMW transport pathway within the soil profile in all seasons. Additionally, capillary rise process was found highly relevant in both spring and summer seasons.

The highest degree of negative effects of OMW in term of soil water repellency and soluble phenolic compounds were observed after SU_{dry} and WI applications, with moderate effects after SP and quite minimal after SU_{moist}. However, the relevant effects of OMW application in SU_{moist} soon disappeared even before the advent of winter season. Further, initial SOM content showed no differences compared to the control soils for SU_{moist} application. This all indicates that capillary rise mechanism in the summer season was interrupted by the action of irrigation which led to a faster leaching of the OMW from the soil than in soil without irrigation.

Even for the WI application, relevant negative effects of OMW fast depleted and the SOM content showed no difference when compared to control plots even though the SOC was higher. This indicates that after WI application, the OMW also leached out due to rainfall, but the process was probably slower than the leaching by irrigation in SU_{moist}. During the winter season, the soil moisture reached values of water saturation and an increase in the undisturbed water drop penetration time ($WDPT_{Field}$) was also detected in the control plots. This indicates that matrix flow played an additional role in the OMW transport with low infiltration rate due to pore saturation and, therefore, leaching was probably slower than by irrigation in summer.

In comparison to the fast decline of the relevant effects of OMW after SU_{moist} and WI applications due to leaching at short-term, the SP and SU_{dry} applications showed longer lasting short-term effects. However, the thermal analysis showed that SOM as well as SOC had on average stronger accumulation after SU_{dry} application than after SP application. Furthermore, it had stronger accumulation in deeper soil layer than in the surface layer for the SU_{dry} application, while the opposite was observed for the SP application. This allocation of OMW-OM indicates that the initial preferential flow was more enhanced during the summer season due to the shrinkage of clay soils (Hillel 2012), particularly in the top layers. This led to a heterogeneous distribution of OMW in SU_{dry} soil and to a further penetration into the deeper layers where the particulate OMW-OM accumulated in aggregates when the OMW dried out as indicated by an increased thermal stability of OM due to physical protection in these aggregates. In contrast, the soil moisture during spring season was higher than summer season so in addition to preferential flow, matrix flow also occurred during SP application which promoted a more homogeneous distribution of OMW-OM after the SP application than after the SU_{dry} application due to slower infiltration rate which retarded the initial downward transport of OMW in the soil during SP application. Moreover, the capillary rise during the spring and summer seasons led to comparable salinity effects initially and in the short term for both, SU_{dry} and SP applications.

The extent of soil water repellency and the content of soluble phenolic compounds, as well as acidification increased more after SU_{dry} application than after SP application whether initially or during the period between OMW application and the winter season. The differences in the fate of organic substances between the two applications led to the conclusion that besides the transport processes, there were also different transformation mechanisms that contributed to OMW-soil interactions. The optimal soil moisture and temperature conditions in the spring season favored soil biological activity (Barbera, et al. 2013) and enhanced microbial degradation of easily degradable OMW substances (Chaari, et al. 2014) within two days after SP application. Buchmann, et al. (2015) found in an incubation experiment of OMW treated soil (14 L m^{-2}, 23 % *WC*, 15 °C) relevant OMW-OM degradation and a reduction of ~ 40 % for total phenolic compounds after two days. Similar degradation processes probably occurred in the field site which reduced the SPC and prevented the occurrence of repellency at least during the spring season. In contrast, high temperature and low soil moisture in the summer season impeded microbial degradation of OMW. Further, soluble organic constitutes of OMW raised to the soil surface by capillary action accumulated and dried. Under hot and dry conditions, condensation reactions of amphiphilic substances such as long chain fatty acids (C16-C18) from the residual oil (Diamantis, et al. 2013) induced and enhanced repellency in soil due to the accumulation of such hydrophobic compounds. Meanwhile, dry conditions also induced polymerization reactions of phenolic compounds into larger molecules which further induced abiotic acidification effects. In addition to the earlier mentioned physical protection in SOM aggregates, the condensation, and polymerization of OMW-OM may be an alternative explanation for the thermally more stable OM after SU_{dry} application. The repellency and acidification effects clearly disappeared during the first rain season and SPC significantly decreased in both SP and SU_{dry} applications which indicate that hydrolysis reactions mobilized the condensed and polymerized compounds and consequently enabled their leaching.

4.3 Long-term OMW-soil interaction

One year after each application, no repellency or acidification effects were observed but a slight increase in soil salinity during the following summer as well as 28% of SPC applied with the OMW was found for SU_{dry} application followed by WI application with 21%. This shows that not 100% of the OMW constituents were immobilized, degraded or leached during the first rain season but parts of them probably rose back to the surface by capillary action. However, after two years, persisting effects on SOM quantity and quality were only observed for the SU_{dry} application, which leads to the conclusion that part of the particulate OMW-OM in soil aggregates was still protected against decomposition by reduced access for the microorganisms (von Lützow, et al. 2006) or incomplete leaching during the following rain seasons due to the immobilization by physical occlusion within soil aggregates. In contrast, the persisting qualitative changes in SOM of SP applications in the absence of quantitative effects indicate that a significant part of the added OMW could be biologically degraded or leached after two years.

4.4 Recommendations for OMW application to soil

In areas where the OMW-land disposal is the only feasible solution, several factors should be considered prior to the OMW application to soil in order to minimize the negative environmental impact of OMW disposal either on the soil or the groundwater and to maximize its beneficial effects due to its content of OM and nutrients. As concluded earlier, negative effects of the potentially hazardous OMW residuals in the soil are highly dependent on the underlying transport mechanisms and transformation mechanisms favored by different conditions of soil moisture and temperature.

The hydrological knowledge about the application site is the primary factor to be considered prior to OMW application. Leaching of OMW cannot be avoided completely as it can be transported faster to deeper layers reaching groundwater aquifers through preferential pathways.

The risks of groundwater contamination, as well as negative effects of OMW on soil can be decreased with increasing the retention time of OMW in soil under conditions favoring biological activity. The moderate conditions of soil moisture and temperature will allow for a considerable amount of applied OMW to be biologically degraded. Therefore, OMW application in spring if accompanied by controlled irrigation can be considered as the most suitable in semiarid conditions for clay loam soils and offers the longest retention period before the inevitable leaching occurring during the following rainy winter season. The prolonged time under dry conditions and at high temperature allows OMW constituents to accumulate and polymerize without being degraded forming a less degradable organic fraction of the OMW . Further, the OMW disposal to soil should be avoided during the rainy winter season due to the short retention time of OMW in the soil. Therefore, the risk of groundwater contamination by non-degraded constituents of OMW can be highly probable during the winter season.

4.5 Outlook

In agreement with the study hypothesis, the current field study demonstrated clearly that prevailing environmental conditions during and after the OMW application to soil play a significant role in the degree of relevant negative effects of OMW disposal to soil. The current field experiment showed that OMW may have reached deeper depths than expected due to preferential flow, therefore, further studies are needed to investigate the phenolic compounds dynamics in deeper soil layers and in the groundwater aquifers. Moreover, it was not possible to verify whether SU_{moist} conditions are more favorable for OMW degradation due to fast leaching by irrigation. Thus, the SU_{moist} application remains questionable and further research is needed to distinguish leaching and biodegradation mechanisms under controlled conditions in laboratory scale.

The recommendations for OMW disposal to soil in the current study are based on a single application. Therefore, further research is needed to study the accumulated effect with repeated application of OMW under different climatic conditions in order to investigate the relationship between the degree of OMW-OM degradation or accumulation and the changes in soil quality. Furthermore, the tillage as a common agricultural practice should be considered in future work because of its main role in increasing the organic matter decomposition rate, and consequently may reduce the accumulated effects of repeated application of OMW.

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5 Annexes

5.1 Annex 1: Supporting information for chapter 2

The proton balance

In order to determine the proton balance, i.e., the amount of protons or hydroxyl ions needed to increase or decrease the pH of the control samples, one pooled soil sample (from all control plots) was extracted (1 : 5 wt / vol) with aqueous solutions of different concentrations of standard base NaOH and standard acetic acid HCl and. The pH was recorded after horizontal shaking for 2, 24 and 48 h and plotted vs. the molar concentration in mol kg^{-1} of base or acid supplied. The result of this plot is an "S" shaped curve (Figure S1).

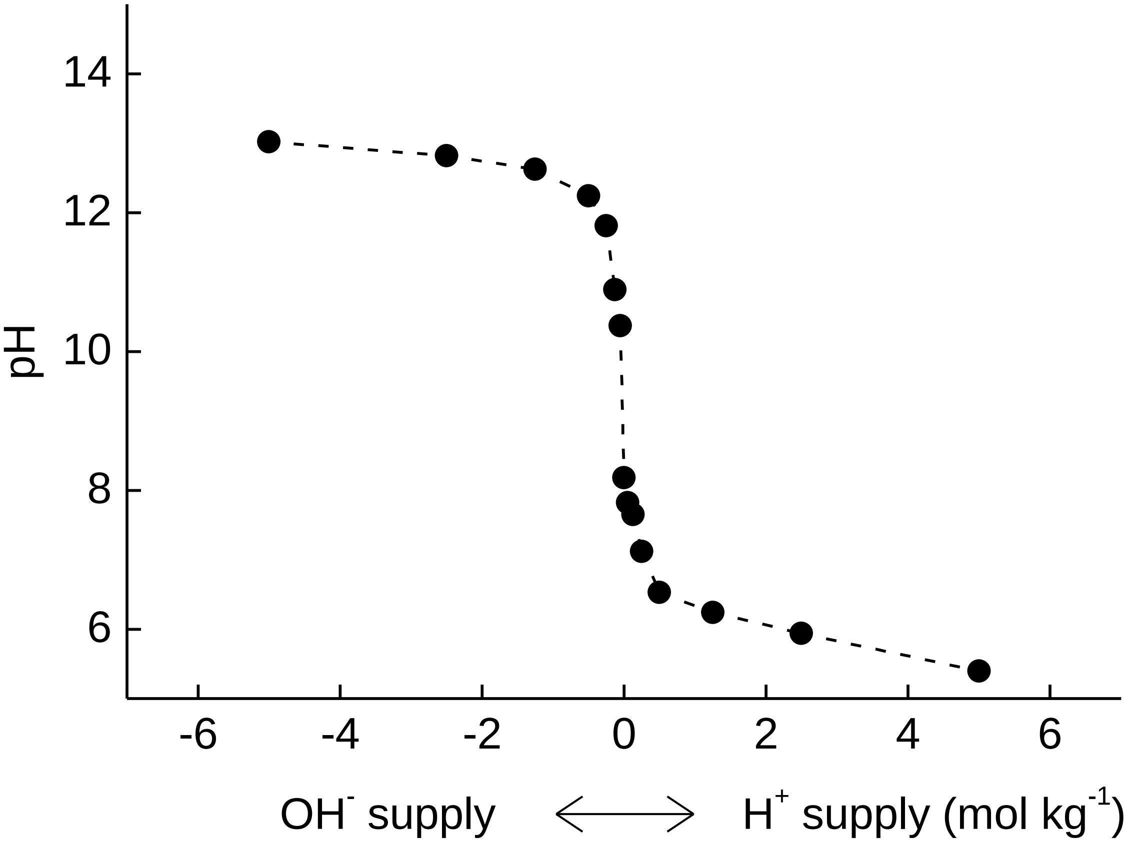

Figure S1: pH titration curve of one pooled soil sample (from all control plots).

Within the pH-range of all samples, we defined two regions which could be fitted linearly (Figure S2) with the slope *a* and the intercept *b*.

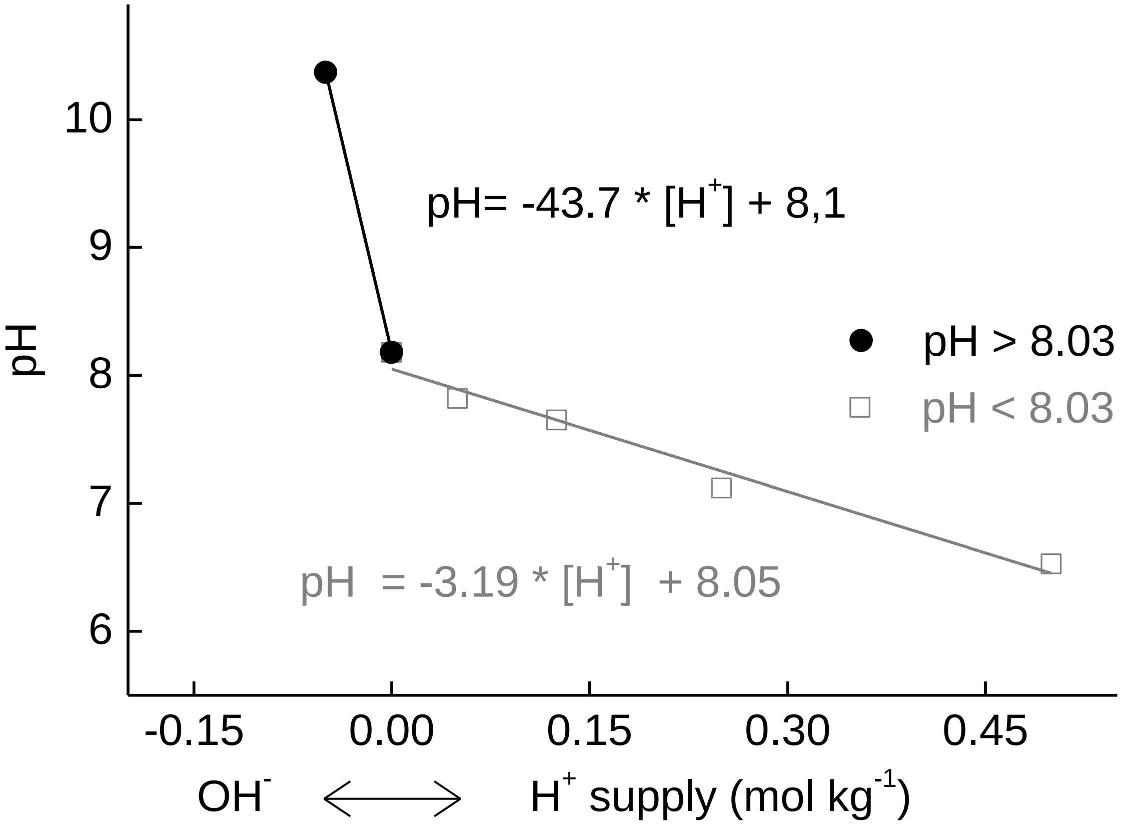

Figure S2: Linear fitting for *pH* range (6 to 11)

With the help of these linear functions, we calculated [H$^+$] concentration from pH of the sample using Eq. S.1 and S.2.

$$\left[\mathrm{H}^+\right]_{\mathrm{OMW}} = \frac{pH_{\mathrm{OMW}} - b}{a} \qquad \text{(S.1)}$$

$$\left[\mathrm{H}^+\right]_{\mathrm{control}} = \frac{pH_{\mathrm{control}} - b}{a} \qquad \text{(S.2)}$$

The H$^+$ supply by OMW treatment (Δ[H$^+$]) was calculated by the difference in [H$^+$] between treated and respective control samples (Eq. S.3)

$$\Delta\left[\mathrm{H}^+\right] = \left[\mathrm{H}^+\right]_{\mathrm{control}} - \left[\mathrm{H}^+\right]_{\mathrm{OMW}} \qquad \text{(S.3)}$$

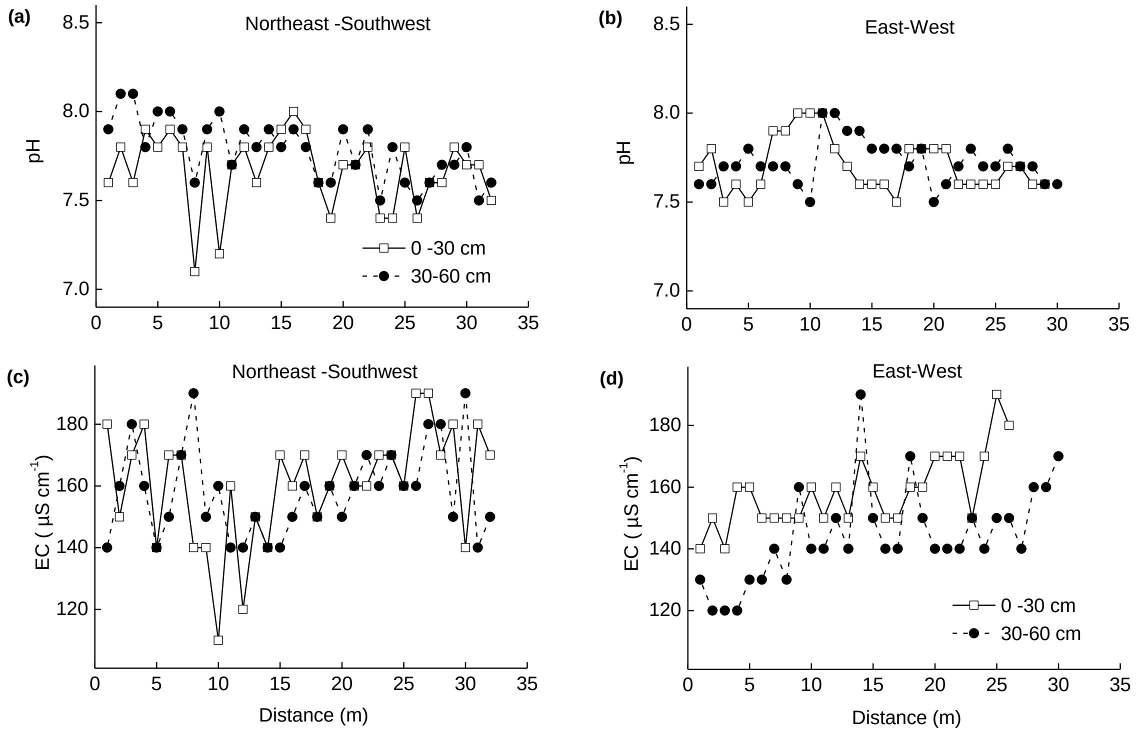

Figure S3: Spatial distribution of (a) pH in Southwest-Northeast transect, (b) pH in East- West transect, (c) Electrical conductivity (EC) Southwest-Northeast transect and (d) EC in East-West transect obtained for site exploration in July 2011 (see Figure2-1).

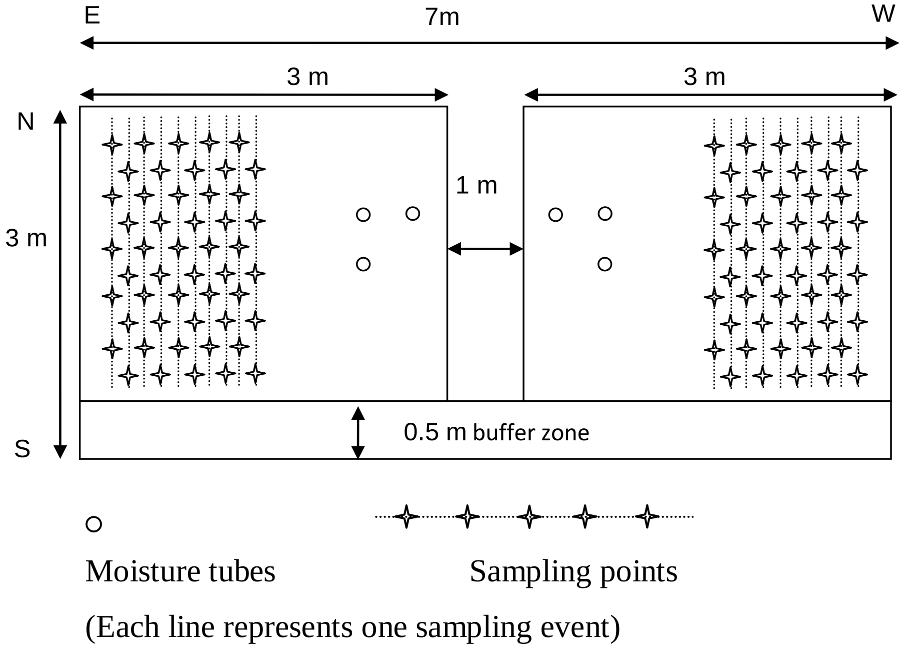

Figure S4: Overview of each two parallel plots located in the field and the sampling points for each event after olive mill waste water (OMW) application to soil.

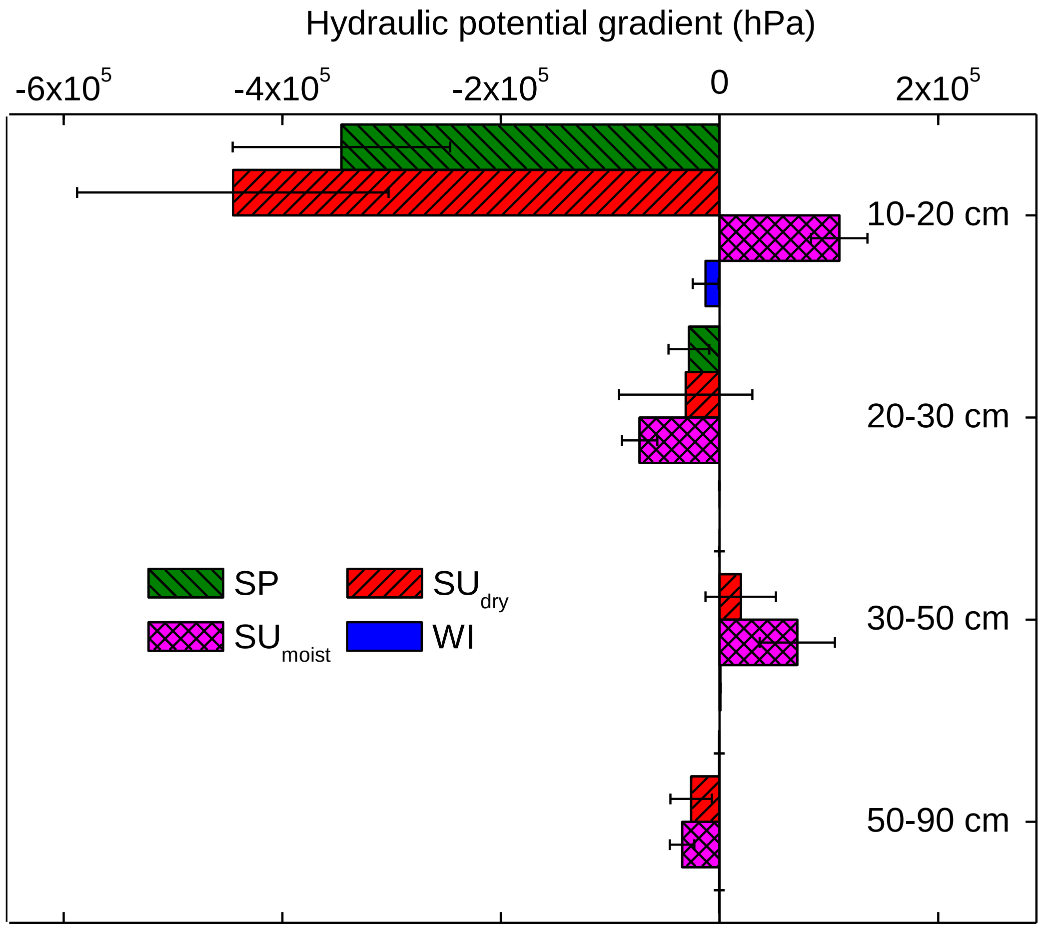

Figure S5: Average of estimated hydraulic potential gradient as a function of soil depth for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) treatment plots one week prior to olive mill waste water (OMW) application. Data points are mean of six values of two treated plots for each treatment with error bars representing standard errors.

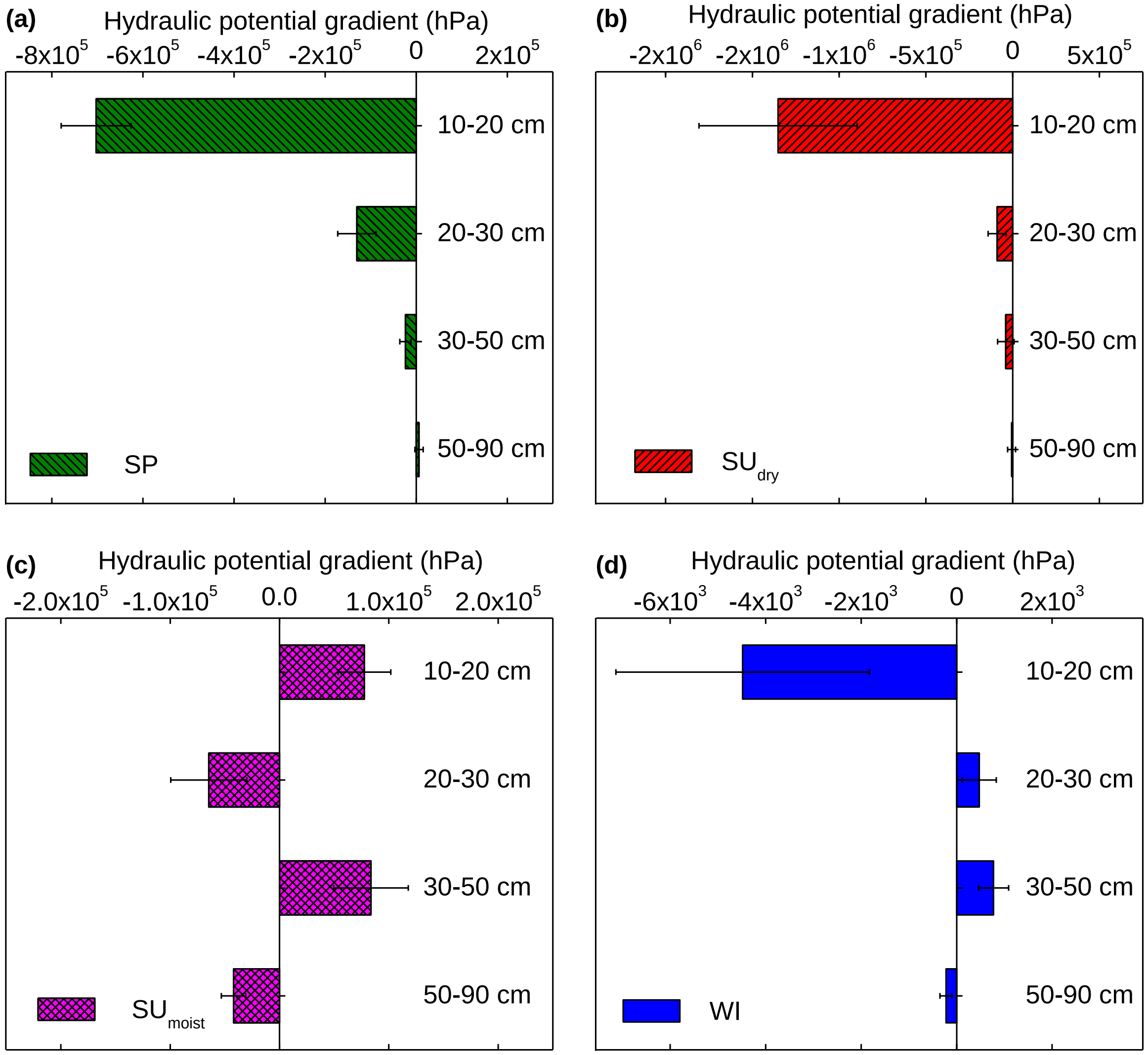

Figure S6: Average of estimated hydraulic potential gradient as a function of soil depth for (a) spring (SP), (b) summer without irrigation (SU$_{dry}$), (c) summer with irrigation (SU$_{moist}$) during the summer season 2012 and for (d) winter (WI) treatment plots during the winter season 2012/13. Data points are means of six values of two treated plots for each treatment with error bars representing standard errors.

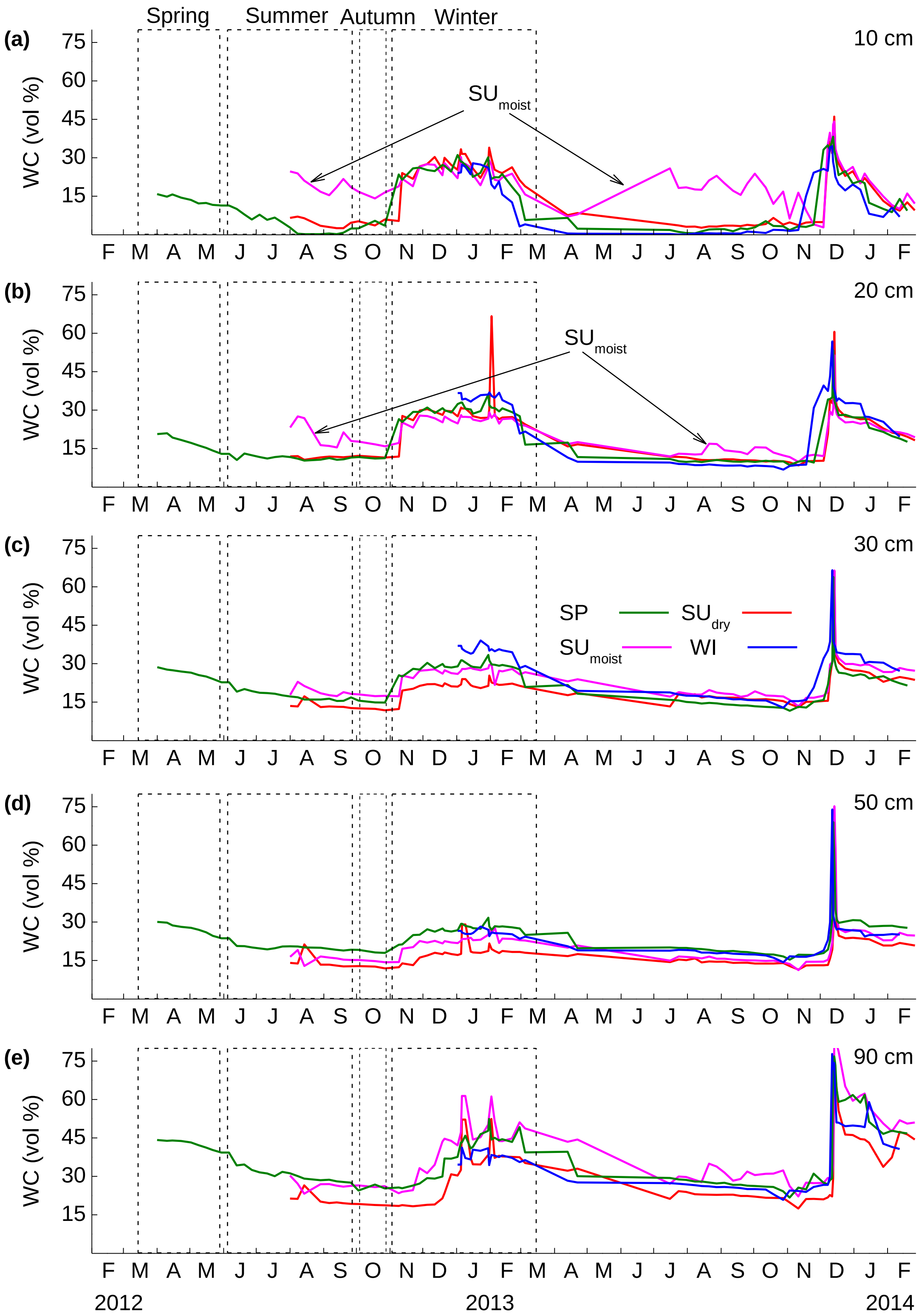

Figure S7: Average of weekly measurements of soil water content in field (vol. %) in (a) 0-10 cm, (b) 10-20 cm, (c) 20-30 cm, (d) 30-50 cm, (e) 50-90 cm depth for spring (SP), summer without irrigation (SU$_{dry}$), summer with irrigation (SU$_{moist}$), and winter (WI) treatment plots as a function of time. Data points are means of six values of two treated plots for each treatment with a standard deviation of 5%.

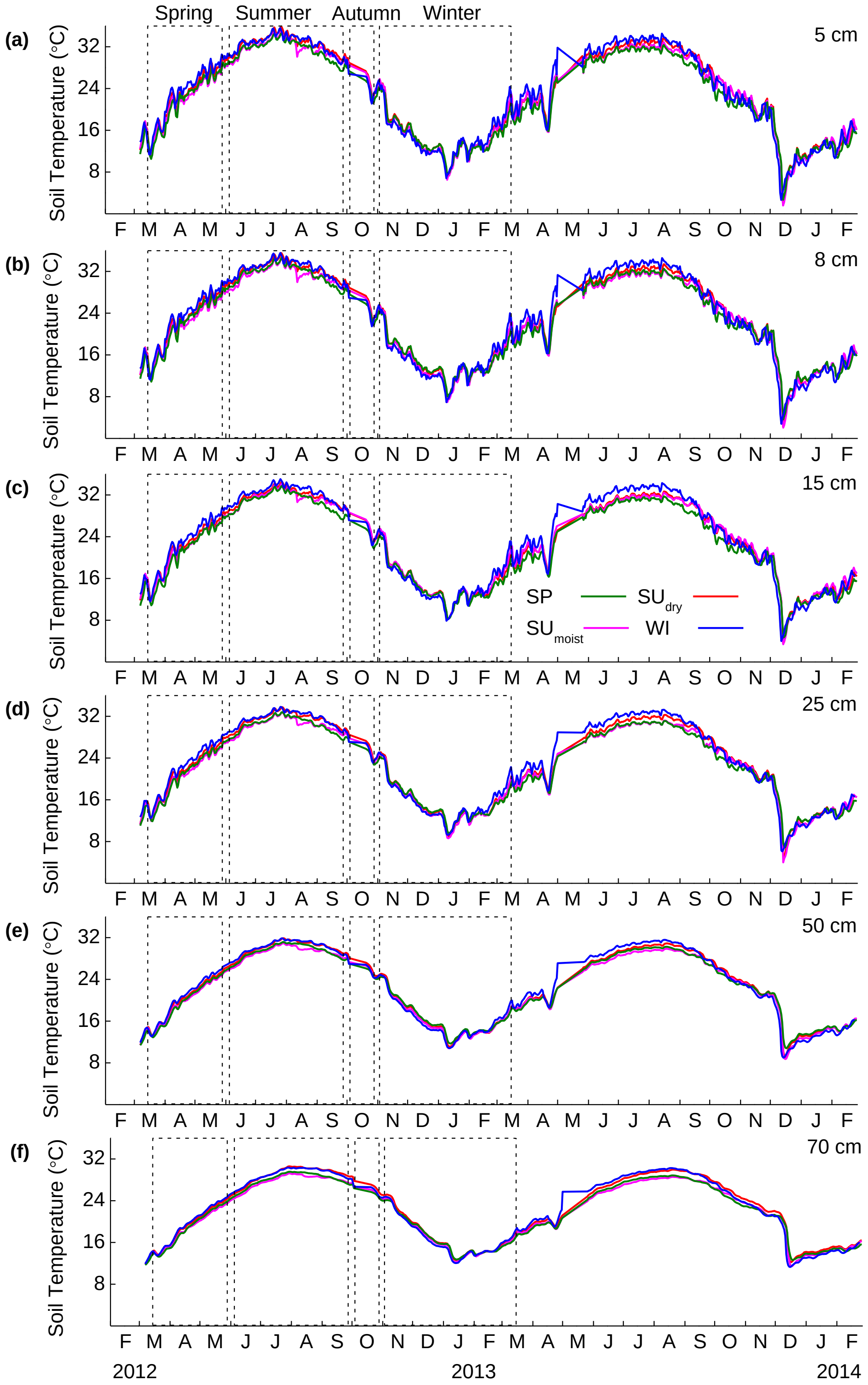

Figure S8: Daily average of soil temperature (°C) in (a) 0-5 cm , (b) 5-8 cm, (c) 8-15 cm, (d) 15-25 cm, (e) 25-50 cm, (f) 50-70 cm depth for spring (SP), summer without irrigation (SU$_{dry}$), summer with irrigation (SU$_{moist}$), and winter (WI) treatment plots as a function of time. Data points are means of hourly measurements over 24 h for one probe for each treatment.

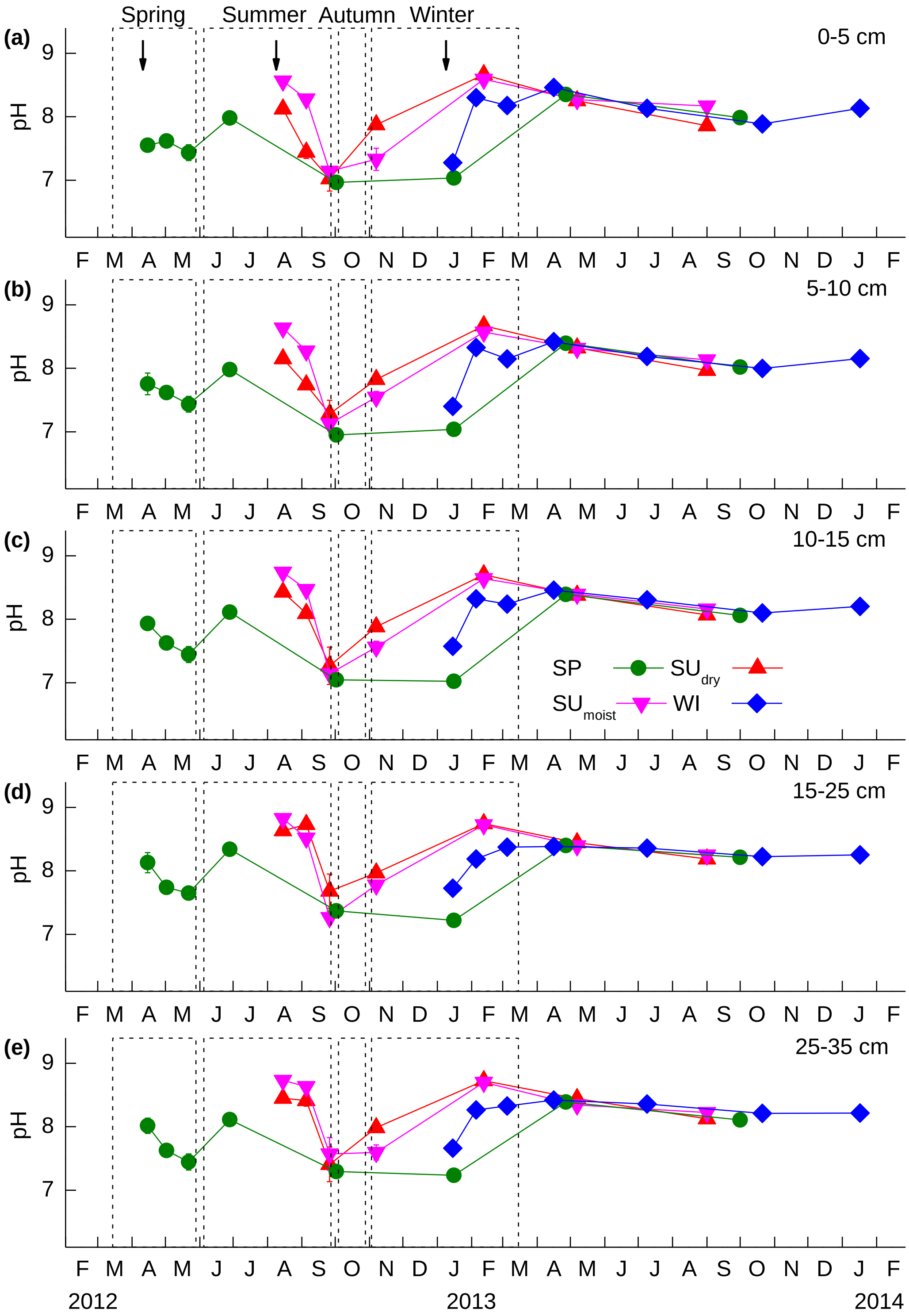

Figure S9: Average of pH of olive mill waste water (OMW) treated plots in (a) 0-5 cm , (b) 5-10 cm, (c) 10-15 cm, (d) 15-25 cm and (e) 25-35 cm depth for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) application as a function of time. First results obtained 2 days after OMW application to soil. Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard error.

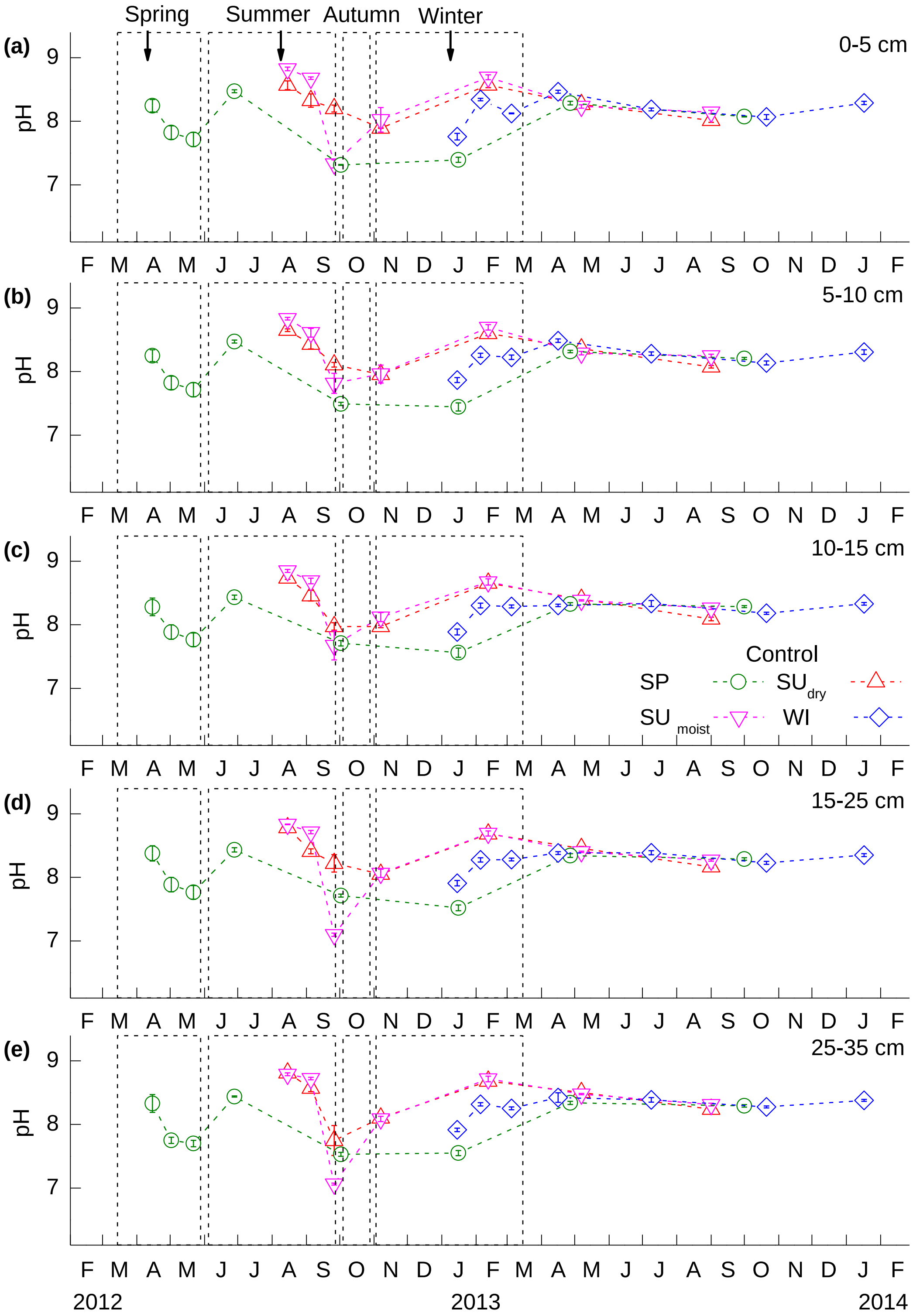

Figure S10: Average of pH of control plots in (a) 0-5 cm, (b) 5-10 cm, (c) 10-15 cm, (d) 15-25 cm and (e) 25-35 cm depth for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) application as a function of time. First results obtained 2 days after tap water application to soil. Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard errors.

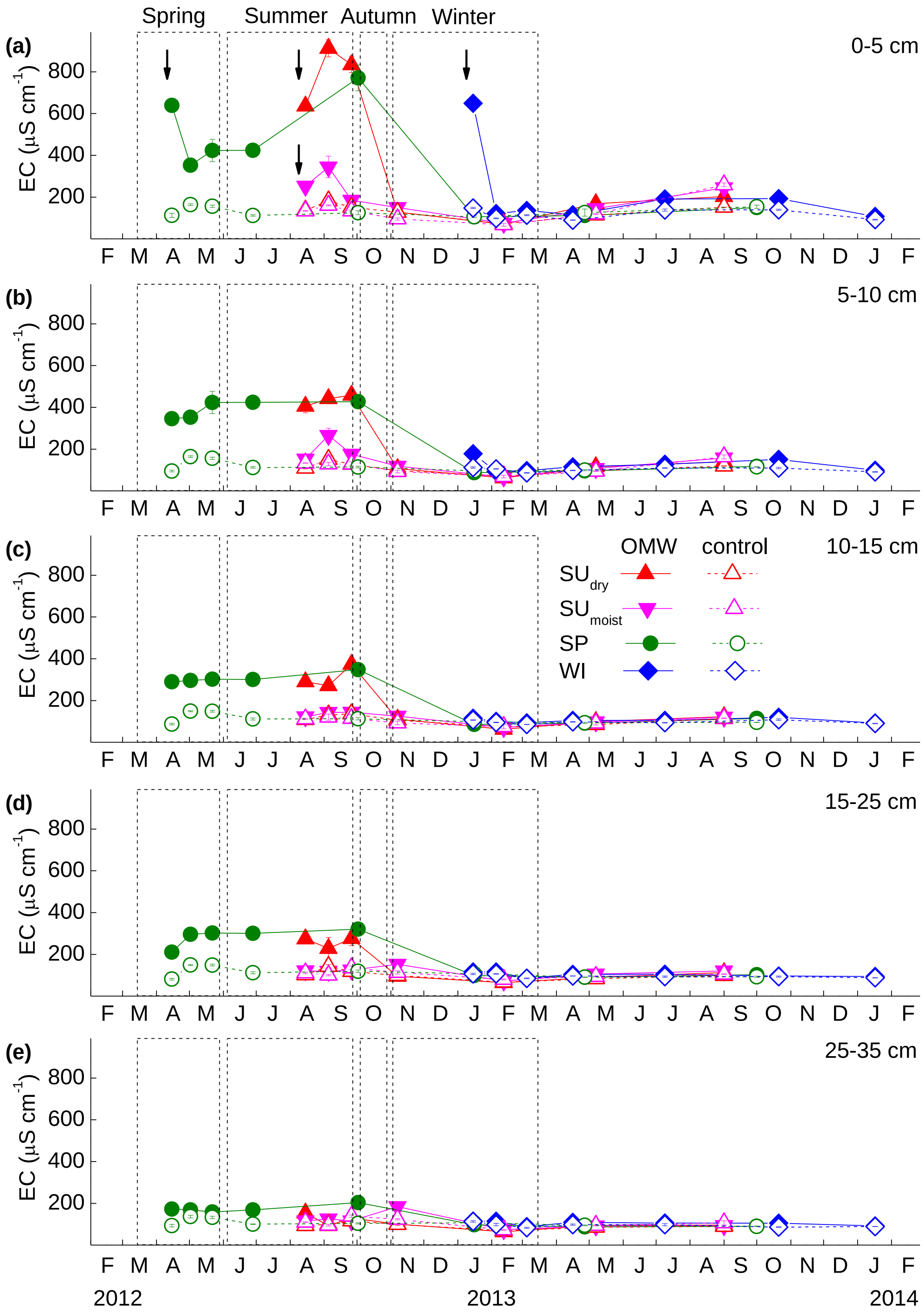

Figure S11: Average of electrical conductivity (*EC*) in (a) 0-5 cm, (b) 5-10 cm, (c) 10-15 cm, (d) 15-25 cm and (e) 25-35 cm depth for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) olive mill waste water (OMW) treated and the respective control plots as a function of time. First results obtained 2 days after application to soil (↓). Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard errors.

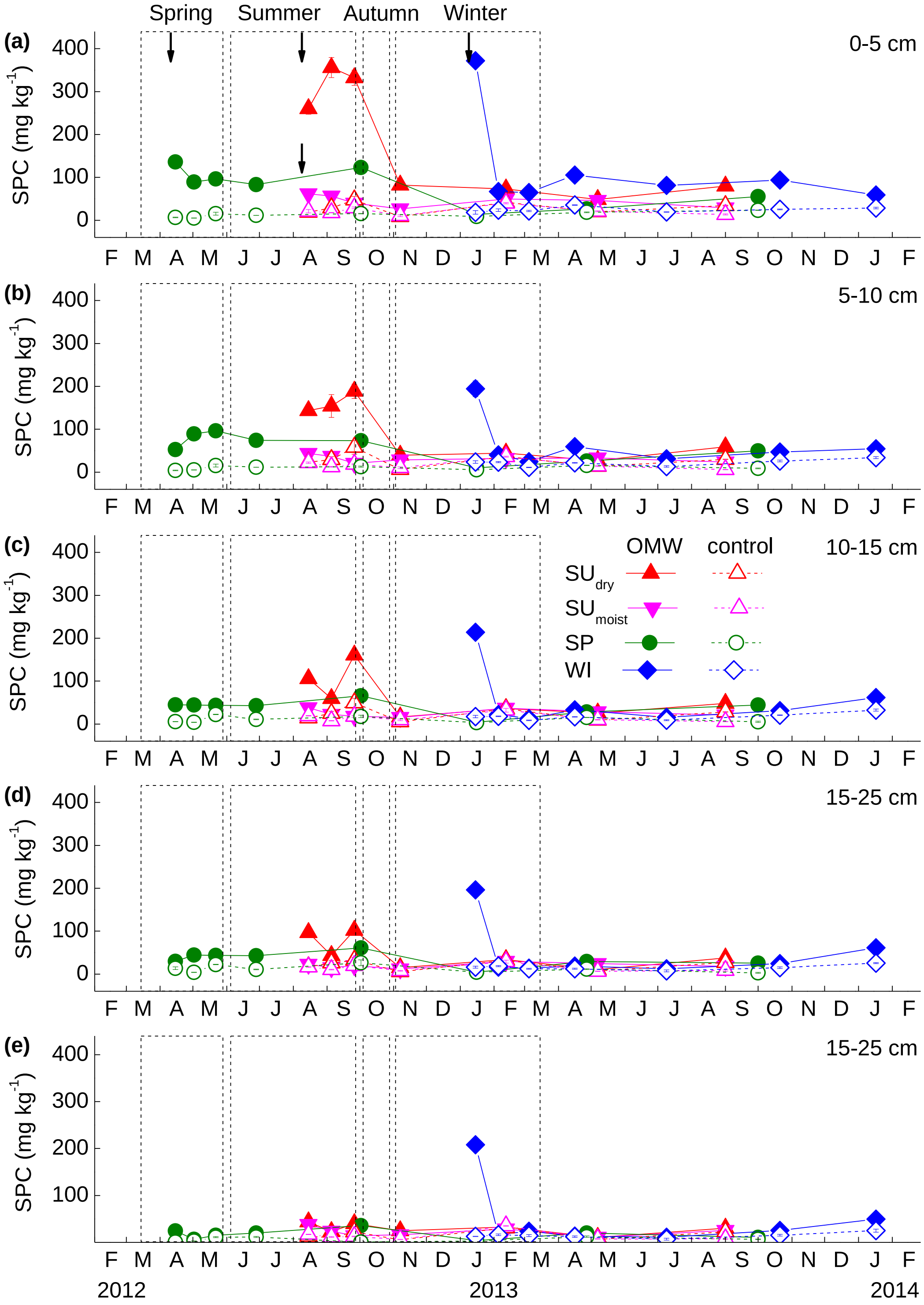

Figure S12: Average of soluble phenolic compounds content (SPC) in (a) 0-5 cm, (b) 5-10 cm, (c) 10-15 cm, (d) 15-25 cm and (e) 25-35 cm depth for spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) olive mill waste water (OMW) treated and the respective control plots as a function of time. First results obtained 2 days after OMW application to soil (↓). Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard errors.

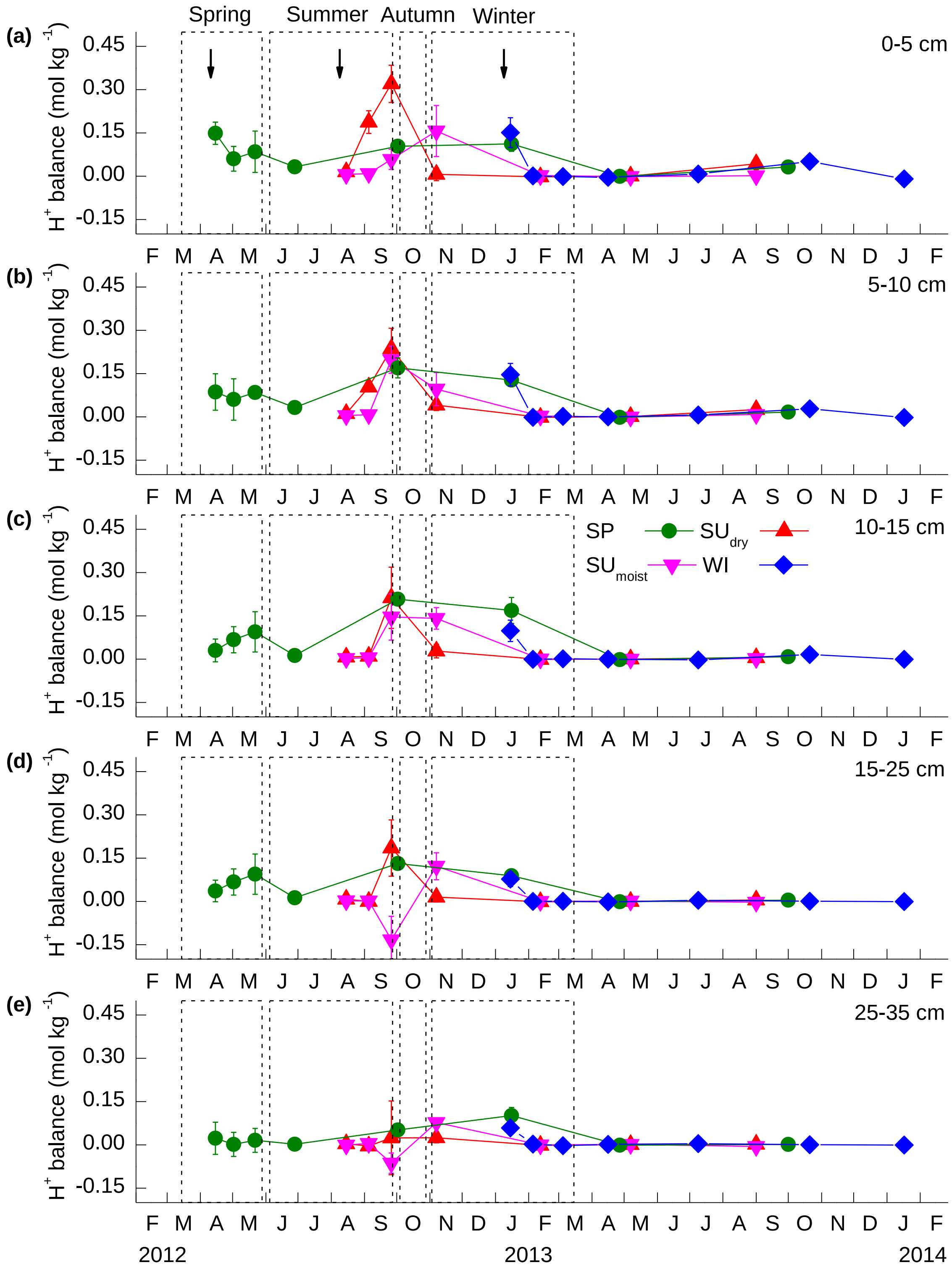

Figure S13: Average of H$^+$ balance (see text for explanation) (a) 0-5 cm, (b) 5-10 cm, (c) 10-15 cm, (d) 15-25 cm and (e) 25-35 cm depth for spring (SP), summer without irrigation (SU$_{dry}$), summer with irrigation (SU$_{moist}$), and winter (WI) treatment plots and the control plots as a function of time. Data points are means of six values of two plots for each treatment with error bars representing standard errors.

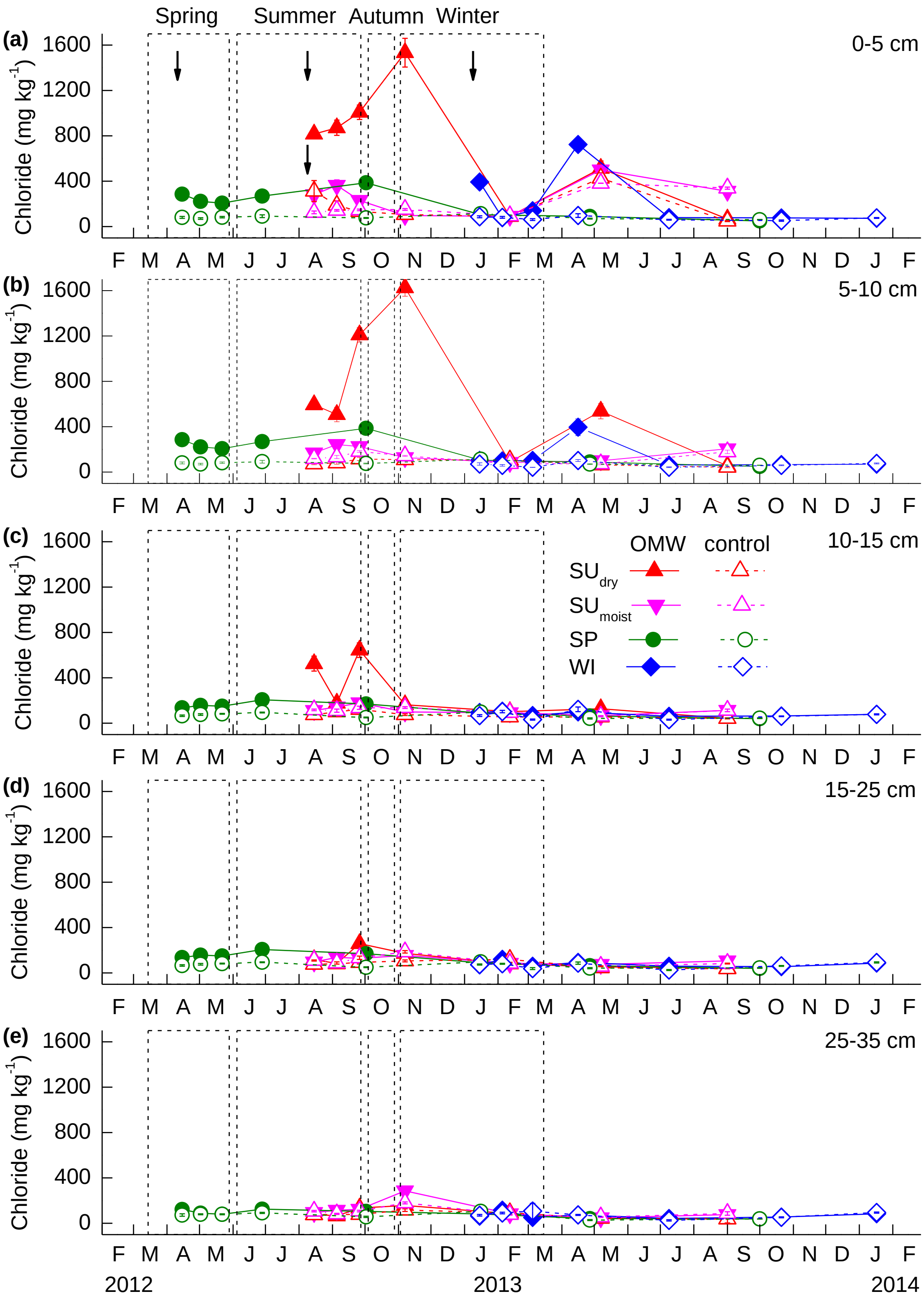

Figure S14: Average of chloride ion concentration (Cl^{-}) in (a) 0-5 cm, (b) 5-10 cm, (c) 10-15 cm, (d) 15-25 cm and € 25-35 cm depth for spring (SP), summer without irrigation (SU$_{dry}$), summer with irrigation (SU$_{moist}$), and winter (WI) treatment plots and the control plots as a function of time. First results obtained 2 days after OMW application to soil. Data points are means of six values of two plots for each treatment and two plots for each control with error bars representing standard errors.

Table S1: Overview of soil samples and the obtained parameter as well as the monitoring data during the field experiment.

Soil samples and obtained parameters					
Treatment		**No. of plots**	**Sampling time**	**Sampling depth**	**Parameters**
4 treatments		4 plots for each treatment	8 time points for each plot	5 depth (cm) for each time	640 samples (3 repl. each)
SP	Spring		1 week before		
	2012-04-12		2 days after	0 - 5	WC (grav.)
SU_{dry}	Summer (dry)	2 OMW	3 weeks after	5 - 10	pH
	2012-08-13	2 control	6 weeks after	10 - 15	EC
SU_{moist}	Summer (moist)		3 months after	15 - 25	Cl
	2012-08-13		6 months after	25 - 35	SPC
WI	Winter		9 months after		WDPT
	2013-01-14		12-18 months after treatment		

Monitoring data				
Parameter	**Method**	**No. of probes**	**depth / height m**	**Frequency**
Air temperature Air humidity Precipitation Wind direction	Meteorological station	1	2 m above ground	hourly
Soil temperature	Temperature sensors	8	5 depths 5, 8, 15, 50, 70 cm	hourly
Volumetric soil moisture	Moisture probes	48	5 depths: 10, 20, 30, 50, 90 cm	weekly

Table S2*:* Results of Wilcoxon rank sum test of data of the plots treated with olive mill waste water (OMW) in spring (SP), summer without irrigation (SU$_{\mathrm{dry}}$), summer with irrigation (SUmoist), and winter (WI) against the respective control plots 2 days after of OMW application (short-term effects). Listed are p-values (shaded in light red for $p < 0.05$ and dark red for $p < 0.01$) for each depth for the parameters pH and electrical conductivity (EC), soluble phenolic compounds (SPC) and chloride (Cl).

depth	(cm)	0-5	5-10	10-15	15-25	25-35
pH						
SP	2 days	0.005	0.0247	0.132	0.1797	0.1712
SU$_{\mathrm{dry}}$	2 days	0.0022	0.0022	0.0022	0.0022	0.0064
SU$_{\mathrm{moist}}$	2 days	0.0022	0.005	0.0646	0.0022	0.4848
WI	2 days	0.005	0.0022	0.0101	0.0124	0.0081
EC						
SP	2 days	0.005	0.0022	0.0022	0.0022	0.0022
SU$_{\mathrm{dry}}$	2 days	0.0022	0.0022	0.005	0.0022	0.0022
SU$_{\mathrm{moist}}$	2 days	0.005	0.005	0.0048	0.8182	0.0651
WI	2 days	0.005	0.0022	0.01	0.1986	0.6304
SPC						
SP	2 days	0.005	0.0022	0.0049	0.0022	0.005
SU$_{\mathrm{dry}}$	2 days	0.0022	0.0022	0.005	0.0049	0.005
SU$_{\mathrm{moist}}$	2 days	0.005	0.005	0.005	0.0298	0.005
WI	2 days	0.0022	0.0022	0.0022	0.0022	0.005
Cl						
SP	2 days	0.005	0.0048	0.0046	0.008	0.0423
SU$_{\mathrm{dry}}$	2 days	0.0043	0.0043	0.0048	0.0048	0.0043
SU$_{\mathrm{moist}}$	2 days	0.0049	0.0046	0.9354	0.3726	0.37
WI	2 days	0.0049	0.1269	0.0126	0.8089	0.0916

Table S3: Results of Wilcoxon rank sum test of data of the plots treated with olive mill waste water (OMW) in spring (SP), summer without irrigation ($\mathrm{SU}_{\mathrm{dry}}$), summer with irrigation ($\mathrm{SU}_{\mathrm{moist}}$), and winter (WI). Listed are *p*-values (shaded in red for values < 0.05) to test significant changes during spring, summer and winter 2012 and summer 2013 (long-term effects) for each depth for the parameters *pH*, electrical conductivity (*EC*) and soluble phenolic compounds (*SPC*). Water drop penetration time (*WDPT*) data are obtained in field only for the top layer.

		2012			**2012**				**2012/13**				**2013**		
	depth	**Spring season**			**Summer season**				**Winter season**				**Summer season**		
	(cm)	**pH**	**EC**	**SPC**	**WDPT**	**pH**	**EC**	**SPC**	**WDPT**	**pH**	**EC**	**SPC**	**pH**	**EC**	**SPC**
		2 days – 6 weeks			**6 weeks – 6 months**				**6 months – 12 months**				**12 months - 18 months**		
SP	0-5	1	0.032	0.013	0.223	0.026	0.032	0.013	6.63E-15	0.025	0.025	0.02	0.029	0.025	0.015
SP	5-10	0.123	0.67	0.013		0.123	0.67	0.18		0.02	0.03	0.013	0.025	0.108	0.013
SP	10-15	0.127	1	1		0.127	0.074	0.013		0.019	0.013	0.025	0.013	1	0.015
SP	15-25	0.03	0.052	0.013		0.485	0.937	0.013		0.026	0.025	0.015	0.03	0.941	0.024
SP	25-35	0.129	0.481	0.518		0.041	0.279	0.03		0.025	0.025	0.03	0.03	0.184	0.025
					2 days – 6 weeks				**6 weeks – 6 months**				**6 months - 12 months**		
$\mathrm{SU}_{\mathrm{dry}}$	0-5				5.90E-08	0.013	0.013	0.03	3.33E-19	0.025	0.013	0.02	0.025	0.013	0.297
$\mathrm{SU}_{\mathrm{dry}}$	5-10					0.013	0.31	0.359		0.013	0.013	0.013	0.013	0.013	0.359
$\mathrm{SU}_{\mathrm{dry}}$	10-15					0.013	0.02	0.02		0.013	0.013	0.02	0.013	0.013	1
$\mathrm{SU}_{\mathrm{dry}}$	15-25					0.015	1	1		0.015	0.013	0.013	0.013	0.013	1
$\mathrm{SU}_{\mathrm{dry}}$	25-35					0.024	1	1		0.024	0.03	1	0.024	0.03	1
					2 days – 6 weeks				**6 weeks – 6 months**				**6 months - 12 months**		
$\mathrm{SU}_{\mathrm{moist}}$	0-5				3.69E-11	0.013	0.025	0.04	3.31E-08	0.013	0.013	0.039	0.02	0.025	0.03
$\mathrm{SU}_{\mathrm{moist}}$	5-10					0.03	0.041	0.025		0.03	0.013	0.013	0.03	0.013	0.06
$\mathrm{SU}_{\mathrm{moist}}$	10-15					0.03	0.02	0.013		0.03	0.013	0.013	0.03	0.013	0.013
$\mathrm{SU}_{\mathrm{moist}}$	15-25					0.013	1	0.691		0.013	0.03	0.026	0.013	0.03	1
$\mathrm{SU}_{\mathrm{moist}}$	25-35					0.013	1	0.025		0.015	0.024	0.013	0.015	0.024	1
									2 days – 6 weeks				**6 weeks - 6 months**		
WI	0-5								4.30E-25	0.029	0.03	0.013	0.868	0.03	0.788
WI	5-10									0.04	0.026	0.026	1	0.031	0.095
WI	10-15									0.029	0.029	0.015	0.06	0.029	0.378
WI	15-25									0.013	0.03	0.013	0.422	0.03	0.699
WI	25-35									**0.007**	**0.007**	**0.006**	0.949	0.011	0.073

Table S4: Results of Wilcoxon rank sum test of data of the plots treated with olive mill waste water (OMW) in spring (SP), summer without irrigation (SU_{dry}), summer with irrigation (SU_{moist}), and winter (WI) against the respective control plots at different time points after the application (long-term effects). Listed are p-values (shaded in red for $p < 0.05$, in dark red for $p < 0.01$) for each depth and for the parameters pH, electrical conductivity (EC) and soluble phenolic compounds (SPC).

			2013			**2013**			**2013/14**	
	depth		**Spring season**			**Summer season**			**Winter season**	
	(cm)	**pH**	**EC**	**SPC**	**pH**	**EC**	**SPC**	**pH**	**EC**	**SPC**
			12 months			**18 months**				
SP	0-5	0.8089	0.810	0.010	0.072	0.310	**0.005**			
SP	5-10	0.1087	0.575	**0.005**	**0.005**	1.000	**0.002**			
SP	10-15	0.0771	0.935	**0.005**	**0.005**	1.000	**0.002**			
SP	15-25	0.2607	0.685	**0.005**	**0.005**	0.394	**0.005**			
SP	25-35	0.1994	0.029	**0.005**	**0.010**	0.810	0.025			
			9 months			**12 months**				
SU_{dry}	0-5	0.686	**0.002**	**0.005**	0.020	**0.005**	**0.002**			
SU_{dry}	5-10	0.295	0.013	0.026	0.573	1.000	0.013			
SU_{dry}	10-15	0.574	0.170	**0.005**	0.573	0.937	1.000			
SU_{dry}	15-25	0.748	0.106	0.065	0.310	0.818	**0.005**			
SUdry	25-35	0.228	0.054	0.520	0.126	0.240	**0.005**			
			9 months			**12 months**				
SU_{moist}	0-5	0.748	0.037	**0.005**	0.375	0.468	**0.005**			
SU_{moist}	5-10	0.627	0.010	0.077	0.016	0.810	**0.005**			
SU_{moist}	10-15	0.871	0.172	0.044	0.164	**0.006**	0.065			
SU_{moist}	15-25	0.378	0.394	**0.002**	0.126	0.937	**0.005**			
SU_{moist}	25-35	0.043	0.748	0.126	0.054	1.000	**0.005**			
			3 months			**9 months**			**12 months**	
WI	0-5	1.000	**0.005**	**0.005**	0.019	**0.002**	**0.005**	**0.008**	**0.006**	**0.005**
WI	5-10	0.458	0.012	**0.008**	0.045	**0.008**	**0.008**	0.074	0.034	**0.008**
WI	10-15	0.029	0.012	**0.002**	0.744	1.000	**0.002**	**0.005**	0.192	**0.002**
WI	15-25	0.468	0.419	0.078	0.808	0.873	**0.002**	**0.005**	0.016	**0.002**
WI	25-35	0.565	0.035	0.305	0.194	0.010	0.018	**0.002**	0.036	0.001

5.2 Annex 2: List of Abbreviations

EC	electrical conductivity	[µS cm^{-1}]
Cl$^-$	chloride	[mg kg^{-1}]
CV_{labile}	calorific value of thermos-labile fraction	[kJ g mass loss^{-1}]
CV_{LOI}	calorific value of total soil organic matter	[kJ g mass loss^{-1}]
CV_{stable}	calorific value of thermos-stable fraction	[kJ g mass loss^{-1}]
DOC	dissolved organic carbon	[g kg^{-1}]
DSC	differential scanning calorimetry	[-]
DTA	derivative thermogravimetry	[-]
Gravimetric WC	water content	[weight %]
$H:C_{labile}$	atomic ratio of spectrometric ion currency H_2O to CO_2 of thermos-labile fraction	[-]
$H:C_{LOI}$	atomic ratio of spectrometric ion currency H_2O to CO_2 of total soil organic matter	[-]
$H:C_{mass\ ratio}$	mass ratio of hydrogen to total organic carbon	[-]
$H:C_{stable}$	atomic ratio of spectrometric ion currency H_2O to CO_2 of thermos-stable fraction	[-]
H$^+$	proton	[mol kg^{-1}]
IC	Ion current	[µVs mg^{-1}]
LOI	loss on ignition	[mineral mass %]
LOI_{labile}	thermos-labile fraction	[mineral mass %]
LOI_{stable}	thermos-stable fraction	[mineral mass %]
MS	mass spectrometry	[-]
OM	organic matter	[weight %]
p	probability of error	[-]
SOC	total soil organic carbon	[weight %]]
SOM	total soil organic matter	[weight %]]
SPC	total content of soluble phenolic compounds	[mg kg^{-1}]
$SUVA_{254}$	specific ultraviolent absorbance	[L mg C m^{-1}]
SWR	soil water repellency	[-]
TG	thermogravimetry	[-]
TS	thermal stability index	[mineral mass %]
Volumetric WC	water content	[volume %]
WDP_{Field}	water drop penetration time for undisturbed soil	[second]
WDP_{Lab}	water drop penetration time for disturbed soil	[second]

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5.5 Annex 5: Curriculum vitae

Contact		**Personal Information**	
Name:	Nisreen Tamimi	Date of Birth:	24.04.1977
Email	tamimi@uni-landau.de	Nationality	Palestinian
	nesreenmansour@yahoo.com	Marital status	Married
Address	Godramsteiner st.1,76829-Landau-Germany		

Education

Date	2003-2006
Degree	M.Sc.
Principle Subject	Water science and technology
University	Birzeit University-Palestine
Date	1995-2000
Degree	B.Sc.
Principle Subject	Agriculture engineer for plant production and protection
University	Al-Najah National University-Palestine

Employment history

Date	March 2014- present
Occupation	Scientific researcher-OLIVEOIL SCHA849/13 DFG project
employer	University of Koblenz landau
Date	2012- March 2014
Occupation	Scientific researcher- OLIVEOIL SCHA849/13 DFG project
employer	Al-Quds University
Date	2000- end 2011
Occupation	Agriculture engineer- department of irrigation
employer	Ministry of Agriculture-Palestine

5.6 Annex 6: Publications

Peer-reviewed:

Tamimi, N., Diehl, D., Njoum, M., Marei Sawalha, A., Schaumann, G.E. *, 2016. Effects of Olive Mill Wastewater disposal on Soil: Interaction Mechanisms during Different Seasons. Journal of Hydrology and Hydromechanics 64(2), 176-195.

Tamimi, N., Schaumann, G.E., Diehl, D*, (under review) Changes in Soil Organic Matter Properties after Seasonal Application of Olive Mill Wastewater. Journal of Soils and Sediments.

Kurtz, M.P., Tamimi, N., Buchmann, C., Steinmetz, Z., Keren, Y., Peikert, B., Borisover, M., Diehl, D., Marei, A., Shoqeir Hasan, J., Zipori, I., Dag, A., Schaumann, G.E. *, (2016) Soil based wastewater treatment – Effective utilization of olive mill wastewater. Water Solutions, 82-86

Y. Keren, M. Borisover*, G.E. Schaumann, D. Diehl, N. Tamimi, N. Bukhanovsky., (under review) Land Disposal of Olive Mill Wastewater Enhances Soil Sorption of Diuron: Temporal Persistence and the Effects of Soil Depth and Application Season. Journal of Agriculture, Ecosystem, and Environment.

Oral Presentation

Tamimi, N., Marei Sawalha, A., Schaumann, G.E. Effect of Olive Mill Wastewater Spreading on Soil under Different Climatic Condition in a Semi Humid Area: A field study in Bait Reema – West Bank – Palestine. Workshop: “Olive mill wastes and low quality water in agriculture”. April. 2013. Landau –Germany.

Tamimi, N., Diehl, D., Schaumann, G.E. Changes in Soil Organic Matter Quality and Composition after seasonal Application of Olive Mill Wastewater. German Soil Science Society Annual Seminar. September. 2015. München, Germany.

Poster Presentation

Tamimi, N., Diehl, D., Marei Sawalha, A., Schaumann, G.E. Effect of Olive Mill Wastewater Spreading on Soil Wettability and Acidity under Different seasons in a Semi humid Area: A field study in Bait Reema -West Bank - Palestine “EGU –General assembly ” May.2014 Viena-Austria.

Tamimi, N., Diehl, D., Schaumann, G.E. Development of Phenol Content, Acidification and Soil Water Repellency after OMW Application in an Olive Orchard in Palestine: Influence of the OMW application season. “SETAC Europe 25th Annual meeting” May.2015. Barcelona-Spain.