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Characterization of topsoils subjected to poorly controlled olive oil mill wastewater pollution in West Bank and Israel

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ABSTRACT

Uncontrolled land disposal of olive mill waste water (OMW) can potentially result in soil pollution as a consequence of its high chemical and biochemical oxygen demand and high concentration of phytotoxic phenolic compounds. Although both positive and negative effects of OMW on soil quality have been reported, no clear consensus regarding its direct influence on soil hydrophobicity or soil organic matter (SOM) quality is apparent. An improved understanding of any changes in SOM quality would benefit from expanding current characterization approaches to include the determination of SOM stability and physico-chemical properties. In this screening study we investigated topsoils of sites in West Bank and Israel which have been subjected to a significant OMW disposal for several years. In most cases, amounts and disposal method are unknown. In addition to properties such as water repellency and sorption capacity, novel approaches that included carbon isotope ratio (δ^{13}C), thermostability index (TS) and contact angle tensiometry were tested. All polluted soils exhibited stronger water repellency and, in multiple cases, higher sorptive capacity for agrochemicals and were depleted in δ^{13}C. This coincided with higher organic carbon and water extractable organic matter contents with the magnitude of effects clearly stronger than those generally reported for controlled OMW disposal. Extractable organic matter of polluted soils contained higher amounts of non-aromatic compounds like fatty acids and sugars than their controls. Thermal analysis indicated a relative reduction of the recalcitrant OM compared to the controls although interestingly, individual calorific values were higher than those of the unpolluted controls. Water repellency correlated with the isotopic carbon ratio and with the calorific value of the recalcitrant OM, which are both useful indicators for the degree of decomposition of OMW organic matter. The calorific value of recalcitrant OM may also help describe the hydrophobic potential of OMW polluted soils.

1. Introduction

In 2011, over 3.4 million tons of olive oil were produced (FAOSTAT, 2012), mainly in Mediterranean countries. The newer two phase extraction technique generates a semi-solid byproduct containing solid residue and water, whereas in the continuous three-phase extraction process, water and crushed olives are put in a decanter separating the oil via centrifugation producing oil, pomace and olive mill wastewater (OMW). Especially in West Bank and Israel, the three phase technique is mainly used (Laor et al., 2011). During the milling season in winter, large amounts of OMW accrue in a rather short period of time. OMW is acidic, has a high concentration of organic material and is resisting to biodegradation due to toxic effects of some organic compounds, mainly polyphenols (Khatib et al., 2009). Compared to typical municipal sewage chemical and biological oxygen demand are about 200–400 times higher. For this reason, OMW cannot be discarded into the municipal sewage system. In Mediterranean countries, like Italy (Greco et al., 2006), West Bank, Gaza (Khatib et al., 2009) and Israel (Laor et al., 2011) proper treatment options are rare. Thus, in Israel the controlled application of OMW in the field is

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recommended by the ministry of environmental protection at doses between 50 and 100 $m^3\,ha^{-1}\,a^{-1}$, except in highly hydrological sensitive areas.

OMW pollution can affect soil quality. E.g., after repeated uncontrolled OMW disposal, soil next to an OMW evaporation pond showed an increase of organic matter (OM) as well as an increase in electrical conductivity and phenolic compounds (S'habou et al., 2009). Additionally, OMW infiltration to a depth of 6 m was observed whereas the pollution with phenolic substances even reached the groundwater (S'habou et al., 2009). At a location which has been subjected to uncontrolled OMW disposal for over 10 years, a thick horizon of organic matter developed, which was enriched by nutrients, e.g., nitrogen, phosphorus and potassium leading to an enhanced biological activity at all horizons (Sierra et al., 2001). In the same study, an increase in salinity and soluble phenolic substances was found. This increase was also observed at 110–125 cm depth.

Much more studies have investigated the effects of OMW disposal to soil under controlled conditions (e.g., Chartzoulakis et al., 2010; Magdich et al., 2013). For instance, application of OMW with an annual rate of 420 $m^3\,ha^{-1}$ during a field experiment in Greece increased soil fertility, but did not induce negative effects (Chartzoulakis et al., 2010). After a greenhouse experiment applying OMW in steps of 5 t from 0 to 40 $t\,ha^{-1}$, an increase in non-humified organic matter (OM) was found (Lopez-Pineiro et al., 2006). Chartzoulakis et al. (2010) noted a rapid decomposition of phenols and no change in the composition of drainage water at a soil depth of 2 m. Furthermore, OMW disposal increased soil salinity, reduced soil pH (Zenjari and Nejmeddine, 2001) and negatively affected plant growth (Saadi et al., 2007). After adding pure OMW to cress seeds put on a filter paper, the germination was strongly reduced and even dilutions of <0.25% OMW affected seed germination negatively (Saadi et al., 2007). Although there is not yet a final consensus about the active toxicants (Aviani et al., 2009), phenolic compounds are largely claimed to be responsible for the phytotoxicity of OMW (Magdich et al., 2012). Even more important effects are soil water repellency and reduced hydraulic conductivity. During a field experiment in Syria, where OMW has been applied for up to 15 years, soil hydraulic conductivity was reduced and the infiltration rate decreased compared to the control (Mahmoud et al., 2010). The authors concluded that OMW pollution increases soil water repellency, which can in turn lead to preferential flow and surface runoff that induces or intensifies soil erosion (Mahmoud et al., 2010). Similarly, application of treated wastewater can lead to at least transient soil water repellency (Tarchitzky et al., 2007). It is yet unclear, which substances are responsible for water repellency. Gonzalez-Vila et al. (1995) reported that some hydrophobic components, e.g., lipids, accumulate in the upper soil layer after land treatment with OMW. Increased soil hydrophobicity after long-term OMW pollution may be caused by such substances forming a coating on soil particles. Wastewater constituents may also bind organic compounds in solution. Other researchers concluded that various pesticides can form complexes with DOM (Madhun et al., 1986). Organic matter quality, e.g., polarity and aromaticity (Madhun et al., 1986) and its hydrophobic fractions (Ilani et al., 2005) are claimed to be responsible for the extent of interactions within these complexes. In summary, OMW application can have both positive (OM, nutrients, watering) and unwanted effects on soil (salinization, water repellency, sorption of agrochemicals, phytotoxicity) (Barbera et al., 2013).

Investigating controlled OMW spreading will help to derive recommendations for suitable application rates. Such studies will, however, not help to understand and assess the current environmental situation on sites subjected to uncontrolled pollution, which is often more severe than that of controlled field studies. Therefore, both is necessary: research under well-known circumstances and the investigation of locations polluted under poorly controlled conditions. Numerous olive mills are confronted with large amounts of OMW every year. Although official numbers are not available, it is well-known that many olive mills discard their OMW on neighbored fields in uncontrolled manner and unknown amount (Cabrera et al., 1996). Analyzing such polluted soils is a challenge, but it would enable us to better understand possible mutual relations between added and original organic matter. Especially, knowledge of SOM stability and degradation parameters would be helpful to obtain more information on the degree or extent of unknown OMW pollution and potentially on its age. Furthermore, former studies predominantly addressed single locations and standard soil and OMW parameters for characterization of the polluted soils. With regard to the high number of hotspots of OMW pollution, more knowledge about the present environmental pollution is required. It is important to know (1) to what extent effects of OMW pollution are related to general properties of OMW and (2) how OMW polluted soils can be characterized in order to be able to judge the degree of OMW pollution despite unknown pollution history and variable OMW composition.

Up to now, no single analytical method has been able to describe SOM quality completely. Thermogravimetric analysis (TGA) is a versatile technique that has the potential to serve as an indicator of the distribution between biogeochemically labile and recalcitrant SOM (Dell'Abate et al., 2003; Plante et al., 2005) and to determine the degree of degradation of organic matter (Lopez-Capel et al., 2005). Sample preparation is fast and data is obtained relatively rapidly making it a favorable method for analyzing SOM quality (Plante et al., 2009). Further combination of TGA with differential scanning calorimetry (DSC) will provide additional information on the composition of OM and their calorific value, which indicates their energy content. Especially the calorific value of labile and recalcitrant OM is highly promising, but has up to now not been evaluated with respect to SOM quality. Another promising technique is carbon isotope ratio mass spectrometry. Substances undergoing different types of degradation processes are characterized by shifts in their ratio of ^{12}C–^{13}C (Elsner, 2010). So far it has not been used to characterize OMW polluted soils. Together with the specific UV absorption (SUVA), TGA and isotope ratio mass spectrometry are promising methods to characterize OM quality in polluted soils. Combining these methods with the results of soil water repellency analyses, sorption experiments and general soil parameters, will enable us to determine changes in soil organic matter quality which may be responsible for negative effects, e.g., hydrophobicity, of an uncontrolled OMW pollution. This extensive and promising set of measurements has not been applied to OMW polluted soils earlier.

The objective of this study was to characterize topsoils polluted with OMW due to uncontrolled but repeated OMW disposal in West Bank and Israel with respect to water repellency, adsorption of agrochemicals, fertility and organic matter quality. Using the e.g., of topsoils of five locations in West Bank and one location in Israel we aimed to investigate the relations between general soil characteristics, thermal stability, carbon isotope ratio and soil water repellency and to find out whether SOM quality parameters can be useful to estimate the extent of OMW pollution and the degree of degradation of the OMW OM.

2. Materials, sites and methods

2.1. Study assumptions and limitations

A screening study of locations polluted under poorly known conditions generally comes along with some open questions including frequency, extent and duration of the pollution as well as knowledge of potential additional pollution sources and the