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Sorption interactions of organic compounds with soils affected by agricultural olive mill wastewater

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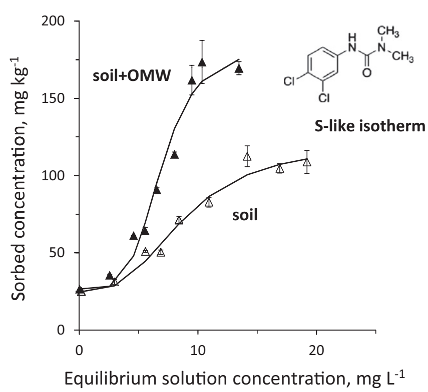
HIGHLIGHTS

- Soil application of olive mill wastewater (OMW) enhances soil–pesticide interactions.
- The OMW effect on pesticide sorption is not explained by soil OC content changes.
- Wastewater has different effects on pesticide–soil sorption mechanisms.
- Cooperative pesticide–soil interactions are suggested.
- Sigmoidal soil sorption isotherms are explained by the Hill model.

GRAPHICAL ABSTRACT



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ABSTRACT

The organic compound–soil interactions may be strongly influenced by changes in soil organic matter (OM) which affects the environmental fate of multiple organic pollutants. The soil OM changes may be caused by land disposal of various OM-containing wastes. One unique type of OM-rich waste is olive mill-related wastewater (OMW) characterized by high levels of OM, the presence of fatty aliphatics and polyphenolic aromatics. The systematic data on effects of the land-applied OMW on organic compound–soil interactions is lacking. Therefore, aqueous sorption of simazine and diuron, two herbicides, was examined in batch experiments onto three soils, including untreated and OMW-affected samples. Typically, the organic compound–soil interactions increased following the prior land application of OMW. This increase is associated with the changes in sorption mechanisms and cannot be attributed solely to the increase in soil organic carbon content. A novel observation is that the OMW application changes the soil–sorbent matrix in such a way that the solute uptake may become cooperative or the existing ability of a soil sorbent to cooperatively sorb organic molecules from water may become characterized by a larger affinity. The remarkable finding of this study was that in some cases a cooperative uptake of organic molecules by soils makes itself evident in distinct sigmoidal sorption isotherms rarely observed in soil sorption of non-ionized organic compounds; the cooperative herbicide-soil interactions may be characterized by the Hill model coefficients. However, no single trend was found for the effect of applied OMW on the mechanisms of organic compound–soil interactions.

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1. Introduction

Changes in the composition and content of soil organic matter (OM), due to various natural and anthropogenic processes, may influence interactions of organic compounds with soils and, therefore, the environmental fate of contaminants (Yang and Xing, 2012). The anthropogenic processes include land disposal of organic wastes. Important types of OM-rich wastes are associated with olive oil production. The production of olive oil via various extraction methods results in the release of solid and liquid OM-rich wastes (Azbar et al., 2004). The liquid waste formed in the three-phase-extraction method is known as olive mill wastewater (OMW). OMW is typically characterized by acidity (pH 4–5), high chemical and biological oxygen demands (i.e., about 220 and 100 g L^{-1}, respectively; Sabbah et al., 2004), high concentrations of organic carbon (OC; 47–62 g L^{-1}; Roig et al., 2006) and moreover it contains polyphenols and fatty acids, among many other substances (Azbar et al., 2004; Mulinacci et al., 2001). In many olive oil-producing countries, e.g., Greece, Portugal, Cyprus, Italy, Malta, Israel, the three-phase-extraction technology dominates in producing olive oil, and, therefore, the OMW disposal is a significant environmental problem (Roig et al., 2006; Rincon et al., 2012).

Despite the numerous methods that have been proposed for the disposal of OMW (Azbar et al., 2004; Roig et al., 2006), the spreading of OMW in orchards or on unpaved ways is very common (Saadi et al., 2007; Moraetis et al., 2011; Barbera et al., 2013). Hence, it is of importance to examine the sorption of organic compounds onto the soils affected by OMW. Such a study will contribute to our understanding of the physic-chemical and biological processes occurring with participation of natural and anthropogenically derived organic compounds (including agrochemicals, e.g., pesticides) in various and, specifically, OMW-affected soil environments. At present, little work has been done regarding the sorption of organic compounds onto soils affected by OMW (Cox et al., 1997; Schaumann et al., 2011). Recently, OMW-induced increases in soil sorption of simazine and diuron were demonstrated (Peikert et al., 2015), but that study did not include detailed examination of the sorption isotherms. As followed from a recent review by Barbera et al. (2013), data concerning the effects of OMW on soil sorption of agrochemicals and other organic compounds are generally lacking.

Much more work has been done earlier regarding the effect of other OM-rich olive mill-originating amendments (such as the solid or semi-solid byproducts formed during two-phase extraction and their composted derivatives) on soil interactions with organic compounds, mostly pesticides (Morillo et al., 2002; Albarran et al., 2004; Delgado-Moreno et al., 2007; Cabrera et al., 2008). However, the OMW differs from other olive mill byproducts in a number of ways, including OM content, C:N ratio, elemental composition and the concentrations of various components (e.g., phenols, carbohydrates, oil, lipids and oil residues) (Lopez et al., 2001; Azbar et al., 2004; Prosodol Project, 2012). Two-phase olive mill waste may contain between 60% and 98% of OM including lignin, cellulose, hemicelluloses which is much higher than the OM content in OMW (Roig et al., 2006; Ouzounidou et al., 2010). Furthermore, two-phase olive mill waste contains multiple water-insoluble organic substances not present in OMW.

Although the studies on effects of solid olive mill wastes and their derivatives on organic compound sorption by soils are continued (e.g., Gamiz et al., 2013; López-Piñeiro et al., 2013; Pena et al., 2013; Rojas et al., 2013), they do not necessary shed light on the potential effects of OMW on organic compound–soil interactions. Due to the significant differences between OMW and other olive mill wastes in OM load, its composition and the way of waste disposal (or application) in the field, the effect of OMW on organic compound–soil interactions cannot be directly deduced from soil sorption studies that involved OM-concentrated solid or semi-solid olive mill-borne (or other OM-containing) amendments. Thus, there is novelty in the examination of the interactions of organic compounds with various soils that have been affected by the OMW (obtained in the three-phase-extraction method) under field conditions, as distinct from the soil sorption studies on effects of solid olive mill wastes. Hence, the general objectives of this study were (1) to determine the sorption isotherms of selected organic compounds in a series of agricultural soils affected by the land disposal of OMW, and (2) to examine the possible effects of OMW on the mechanisms of interactions of organic compounds with these soils. Simazine and diuron were used as suitable organic model sorbates. Both compounds represent two families of herbicides (i.e., triazines and phenylureas, respectively) used in many countries in the world and have been widely examined in numerous soil sorption studies (Sheng et al., 2001; Albarran et al., 2004; Cabrera et al., 2008; Smernik and Kookana, 2015).

2. Materials and methods

2.1. Soil sorbents

For the soil sorption experiments, three types of soils that varied in terms of texture, OC content and the rate of the OMW application were sampled from olive orchards in the Negev (southern Israel): a sandy clay loam from Gilat, a silt loam from Negba and a sandy clay loam from Revivim. In each case, soil was sampled in triplicate from the 0–3 cm top layer in the area affected by the local OMW disposal and in a control area which were selected to minimize differences except OMW application. The 0–3 cm layer was selected following the work by Peikert et al. (2015) since there the major effects of OMW application on soil properties including water infiltration and repellence are expected. The OMW disposal was carried out once per year for 4 years in Revivim and one time in Negba and Gilat. The soil sampling was carried out about 3–5 months after the latest OMW application. The soil samples were air-dried and sieved through 2-mm mesh. The examined soils and the OMW application rates are listed in Table 1. The particle size distribution in each soil was characterized using the Bouyoucos hydrometer method (Gee and Bauder, 1986). The OC contents of the soils were determined with a Thermo-Finnigan C, N analyzer (after pretreatment of the soil samples with 0.2 M HCl to remove carbonates). All of the analyses were carried out in triplicate. The particle size distributions, OC contents and pH values of soil extracts determined by Chen et al. (1991) are also listed in Table 1.

2.2. Chemicals

Simazine (6-chloro-N,N′-diethyl-1,3,5-triazine-2,4-diamine; CAS number 122-34-9; >97% purity) was kindly provided by Agan Chemical Manufacturers, Ltd (Israel). Diuron (N-(3, 4-dichlorophenyl)-N,N-dimethylurea; CAS number 330-54-1; >98% purity) was purchased from Sigma–Aldrich (Israel). Acetonitrile (HPLC supra-gradient) and methanol (absolute) were obtained from Merck (Darmstadt, Germany). Water (ULC/MS) was purchased from Biolab Chemicals (Jerusalem, Israel).

2.3. Sorption experiments

Batch experiments to examine sorption from aqueous solutions were carried out according to a protocol similar to that published previously (Borisover and Graber, 2003; Borisover et al., 2011). In