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Effect of soil organic amendments on the behavior of bentazone and tricyclazole

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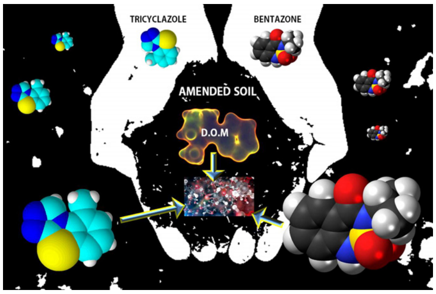
HIGHLIGHTS

- Dissolved organic matter can explain the different adsorption behavior observed for tricyclazole in the amended soils.
- Biochar increased tricyclazole adsorption due to the nature of its dissolved organic matter and high specific surface area.
- Delay of bentazone was observed in amended soils of lower dissolved organic matter content and higher specific surface area.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of soil amendment with different organic residues from olive oil production on the sorption and leaching of two pesticides used in rice crops (bentazone and tricyclazole) was compared in order to understand their behavior and to improve soil properties by recycling an abundant agricultural residue in Andalucía (S. Spain). A residue from olive oil production (AJ), the organic compost derived from this organic waste (CA) and a biochar (BA) made from CA were used. A soil devoted to rice cultivation, IFAPA (I), was amended at 2% (w/w) of each amendment individually (I + AJ, I + CA and I + BA). In order to evaluate the effect of dissolved organic matter (DOM) from these amendments on bentazone and tricyclazole behavior, the DOM from the amendments was extracted, quantified and characterized by fluorescence spectroscopy and FT-IR. The affinity of DOM for soil surfaces was evaluated with (I) soil and two other soils of different physicochemical properties, ARCO (A) and GUAD (G). These studies revealed differences in DOM quantity, quality and affinity for the used soils among amendments which can explain the different sorption behavior observed for tricyclazole in the amended soils. Leaching assays under saturated/unsaturated conditions revealed a slight delay of bentazone in I + CA and I + BA soils when compared to I + AJ, that can be related to the higher DOM content and much lower specific surface area of AJ. In contrast, tricyclazole was not detected in any of the leachates during the leaching assay. Extraction of tricyclazole residues from soil columns showed that the fungicide did not move below 5 cm in the higher sorptive systems (I + CA, I + BA). The sorption of DOM from amendments on soil during the transport process can decrease the mobility of the fungicide by changing the physicochemical properties of the soil surface whose behavior may be dominated by the adsorbed DOM.

Abbreviations: AJ, alperujo from Jaén; CA, compost of alperujo; BA, biochar of alperujo; I, IFAPA soil; A, ARCO soil; G, GUAD soil; I + AJ, IFAPA soil amended with alperujo from Jaén; I + CA, IFAPA soil amended with compost of alperujo; I + BA, IFAPA soil amended with biochar of alperujo; BTCs, breakthrough curves; OC, organic carbon; ON, organic nitrogen; OM, organic matter; DOM, dissolved organic matter; TOC, total organic carbon; C_e, equilibrium concentration; C_i, initial concentration; C_s, amount adsorbed of herbicide; K_f, sorption coefficient; n_f, Freundlich coefficient and linearity parameter; OAs, organic amendments; SSA, specific surface area; BET, Brunauer, Emmett, and Teller method; FT-IR, Fourier transform infrared spectroscopy; HIX, humification index; LOD, limit of detection; LOQ, limit of quantification.

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1. Introduction

In the last years, the use of organic wastes from different origins as soil amendment has increased in southern Spain. This land management is accepted as an ecological method for the disposal of organic wastes, maintaining or increasing soil fertility at the same time (Fernandes et al., 2006). Several studies have shown the benefits of using organic amendments (OAs) to prevent losses of pesticides from runoff or leaching due to an increase in pesticide adsorption or in pesticide persistence (Cox et al., 2000; Albarrán et al., 2004; Yu et al., 2011). Organic amendments, and their hydrosoluble fraction, induce an important impact on pesticide dissipation, affecting their adsorption and transport processes through various chemical interactions (Thevenot et al., 2009). Although in most cases addition of organic amendments increases sorption, leaching of the pesticides can be either reduced or promoted. Competition between pesticides and dissolved organic matter (DOM), from the amendments, molecules for sorption sites and pesticide–DOM interactions (cotransport) can both account for enhanced pesticide leaching (Cox et al., 2007; Müller et al., 2007; Barriuso et al., 2010). On the contrary, DOM might enhance the retardation of organic pollutants through different coating processes such as cumulative sorption or cosorption (Haham et al., 2012). Because of that, their effect on pesticide behavior must be assessed in order to optimize their use.

The first studies about the effect of organic amendments on pesticide behavior were done in the late 70s (Doyle et al., 1978). The most studied amendments are municipal solid waste compost (Vieublé-Gonod et al., 2009; Fagnano et al., 2011), straw wastes (Houot et al., 1998), sewage sludge (Roig et al., 2012) and wine distillery wastes (Andrades et al., 2004). In our lab, the use of different solid organic wastes as soil amendment has been previously studied. Diverse residues from the olive oil industry as the liquid waste called "alpechin" (Cox et al., 1997b) and the solid waste called "alperujo", have been applied to olive groves with very good results (Albarrán et al., 2004; Cabrera et al., 2009; Gámiz et al., 2012).

The use of biochar as soil amendment is being widely extended in the last years. Several articles have already reported benefits of biochar as soil amendment, from the standpoint of carbon sequestration, reduction in greenhouse gas emission and improvement of soil fertility (Xu et al., 2012; Beesley et al., 2011; Cross and Sohi, 2011; Atkinson et al., 2010). Biochar is also an interesting material because of its ability to bind agrochemicals and prevent losses of pesticides from runoff or leaching (Cabrera et al., 2011; Martin et al., 2012; Lü et al., 2012; Ippolito et al., 2012). On the contrary, negative impacts have also been associated with biochar amending, including the reduction in pesticide plant uptake when biochar is added to the soil (Yu et al., 2009), reduced biodegradation of pesticides (Zhang et al., 2004), formation and release of potential toxicants in biomass combustion (Chagger et al., 1998) and ecotoxicological effects on soil organisms (Liesch et al., 2010).

The aim of this study was to assess the effect of the addition of three different organic amendments on pesticide–soil behavior (adsorption–desorption and leaching) in a paddy soil. We also characterized the nature of the soluble organic matter added to the soil with the amendments in order to improve the understanding on how it can modify pesticide–soil interactions. The pesticides studied were bentazone and tricyclazole, which are used in rice crops at South Spain in paddy soils and their environmental behavior is of interest. Bentazone (3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide) is one of the most widely used herbicides in farming worldwide for controlling sedges and broad-leaf weeds in rice paddies and other intensive crops (Romero et al., 1996). Bentazone acts as a photosynthetic electron transfer inhibitor (EPA, 1994). It is a weak acid that can be found mainly in the anionic form. Most of the available reports state that bentazone exhibits little sorption in soil and has relatively high mobility (Li et al., 2003). Hence, its potential risk of leaching and ground water contamination is very high and it is commonly detected in ground and surface waters at concentrations above the European threshold for drinking water (Dousset et al., 2004). In fact, slow release formulations have been proposed for decreasing the water potential contamination of this herbicide (Carrizosa et al., 2000). Tricyclazole (5-methyl-1,2,4-triazolo [3,4-*b*] benzo-thiazole) is a systemic fungicide, effective against *Pyricularia oryzae* and other fungus, applied during the transplant and direct sowing in rice crops. The potential environmental risk of this pesticide is very high because of its high persistence in the soil–water system (Padovani et al., 2006; Pareja et al., 2012). Its half life goes from 4 to 17 months in laboratory assays, and approximately 6 months in the field. Also, it does not readily hydrolyze in the environment and it is stable at 51 °C without volatilization. Furthermore, a considerable percentage of the active substance is expected to be bound to soil due to its high adsorption (Tomlin, 2006).

2. Materials and methods

2.1. Pesticides

Analytical grade bentazone (≥97% purity) was supplied by BASF (Limburgerhof, Germany). Water solubility was 570 mg l^{-1} (20 °C), $pK_a = 2.3$, and molecular mass 240.3 g mol^{-1}. Tricyclazole (≥97% purity) was provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany). Water solubility was 596 mg l^{-1} (20 °C), and molecular mass 189.24 g mol^{-1}. These compounds were used to prepare the initial pesticide solutions used as external standards for pesticide analysis and to carry out all the experimental assays.

2.2. Soils and organic amendments

Soils used were sampled from three different locations. IFAPA and GUAD are soils from Guadalquivir valley devoted to rice crop. ARCO soil, which comes also from the same valley, was chosen because of its remarkable physicochemical differences (sandy soil). Three organic amendments were selected for this study, all of them proceeding from the olive oil industry: alperujo (AJ), composted alperujo (CA) and a biochar made of the composted alperujo (BA) obtained through pyrolysis at 550 °C in a restricted oxygen atmosphere. Alperujo, obtained by a two-phase centrifugation process in the olive oil production, and composted alperujo (mixed with sheep manure) was produced in IFAPA Centro Venta del Llano, Jaén (Spain). Soils, air-dried and sieved through a 2 mm mesh, were amended at a rate of 2% (w/w) with the different amendments.

2.3. Physicochemical analysis of soils and amendments

Soil texture was determined by sedimentation using the pipette method and clay mineralogy by X-ray diffraction on oriented specimens (Jackson, 1975). Soil pH were measured in a 1:2 (w/w) soil/deionized water mixture and the organic carbon content was determined by dichromate oxidation (Nelson and Sommers, 1996). Physicochemical properties of the soils and amendments are given in Table 1. The specific surface area (SSA) of the amendments was measured by nitrogen surface sorption, using a Carlo Erba Sorptomatic 1900 (Fisons Instruments) and the Brunauer, Emmett, and Teller (BET) method on 0.2 g of a sample previously degassed at 80 °C during 24 h (Table 1).

2.4. Characterization of DOM and interaction with soils

For DOM extraction, soils and amendments were treated with a solution of 0.01 M $CaCl_2$ (1:20 w/v), and shaken for 15 min at room temperature. The samples were then centrifuged at 8000 rpm for 10 min and filtered with polycarbonate filters (0.45 μm pore diameter). All the extracts were diluted 5 times to avoid organic matter precipitation. The samples were stored at 4 °C until use. The samples were measured with a Shimadzu 5050 Total Carbon Analyzer and their absorption