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Effect of synthetic clay and biochar addition on dissipation and enantioselectivity of tebuconazole and metalaxyl in an agricultural soil: Laboratory and field experiments

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ABSTRACT

Laboratory and field experiments were conducted to assess how the addition of oleate-modified hydrotalcite (clay) and biochar (BC) to an agricultural soil affected the sorption, leaching, persistence, and enantiomeric composition of soil residues of two chiral fungicides, tebuconazole and metalaxyl. Laboratory experiments showed that the sorption of both fungicides ranked as follows: unamended soil < BC-amended soil < clay-amended soil. The addition of clay at a rate of 1% increased metalaxyl soil sorption coefficient (K_d) from 0.34 to 3.14 L kg^{-1} and that of tebuconazole from 2.4 to 47.4 L kg^{-1}. In our experimental set-up, field plots were either unamended or amended with clay (2 t ha^{-1}) or BC (4 t ha^{-1}), and subsequently treated with a mixture of tebuconazole and metalaxyl at 3 and 6 kg ha^{-1}, respectively. The leaching, persistence, and enantiomer composition of fungicides residues were monitored by sampling at different soil depths (0–5, 5–10, 10–20 cm) for 98 days. No significant changes in the scarce mobility and long persistence of tebuconazole upon amending the soil with clay or BC were observed. In contrast, sorption to clay and BC particles reduced the leaching and degradation of metalaxyl and the clay increased its persistence in the topsoil compared to the unamended soil. The enantioselective analysis of tebuconazole and metalaxyl soil residues indicated that tebuconazole remained mostly racemic along the experiment, whereas for metalaxyl the concentration of *S*-enantiomer was greater than the concentration of *R*-enantiomer, more so at longer experimental times and deeper horizons. Nevertheless, for the top 0–5 cm soil layer metalaxyl remained more racemic in clay- and BC-amended soil than in unamended soil. Our results show that addition of amendments with high sorptive capacities can be beneficial in reducing leaching and degradation losses of chiral pesticide enantiomers from the topsoil, and that sorption by the amendments can influence the final enantiomeric composition of pesticide residues.

1. Introduction

Modern agriculture relies on the use of pesticides to face the growing global demand for food. It is undeniable that the contribution of pesticides has increased the agricultural production over the past decades, but along with its advantages, there are environmental problems associated with pesticide use (Lefebvre et al., 2015; Pimentel et al., 2005; Waterfield and Zilberman, 2012). These problems are often a consequence of the movement of these chemicals to unwanted zones, which represents a potential risk for non-target organisms including human beings (Rice et al., 2007). In this regard, a number of recent monitoring studies have shown the presence of pesticides in soil, sediments, and surface and ground waters. This is indeed the case of the fungicides tebuconazole and metalaxyl, revealing the importance of controlling their presence in the environment (Li et al., 2015; Masiá et al., 2015; Pose-Juan et al., 2015; Robles-Molina et al., 2014).

Tebuconazole and metalaxyl are both systemic fungicides with protective and curative actions (Tomlin, 2006), but they diverge in their physico-chemical properties, as a result of which they show different behavior in soils. Tebuconazole has a water solubility of 36 mg L^{-1} and an octanol-water partition coefficient (log P) of 3.7 (Tomlin, 2006). Accordingly, it is strongly sorbed by soil organic matter and slightly mobile in soil (Aldana et al., 2011; Čadková et al., 2013; Herrero-Hernández et al., 2011; Vallée et al., 2013). Metalaxyl has a water solubility of 8400 mg L^{-1} and a log P of 1.75 (Tomlin, 2006). It is highly polar and mobile in soils and besides

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organic matter, certain soil clay minerals may play an important role in its sorption (Bermúdez-Couso et al., 2011; Fernandes et al., 2003; Gondar et al., 2013; Sharma and Awasthi, 1997). The addition of organic amendments and modified clay minerals has been shown to enhance the retention of tebuconazole and/or metalaxyl in soils (Fenoll et al., 2011; Fernandes et al., 2006; Herrero-Hernández et al., 2011; Marín-Benito et al., 2012; Rodríguez-Cruz et al., 2007).

Tebuconazole and metalaxyl are both chiral compounds. They contain an asymmetrically substituted C-atom in their structure (Fig. S1) and consist of a pair of enantiomers. Chiral pesticide enantiomers exhibit almost the same physico-chemical properties, but they usually differ in their biological efficacy, toxicity to non-target organisms, and biodegradation rates (Celis et al., 2013; Garrison, 2006; Liu et al., 2005; Poiger et al., 2015). In fact, the antifungal activity of metalaxyl has been mainly attributed to the *R*-enantiomer (Buerge et al., 2003; Buser et al., 2002; Marucchini and Zadra, 2002; Monkiedje et al., 2007; Nuninger et al., 1996) and that of tebuconazole has also been shown to be enantiomer-dependent (Stehmann and de Waard, 1995; Yang et al., 2002). In addition, as biologically-mediated processes are important in the degradation of tebuconazole and metalaxyl in soil (Buerge et al., 2003; Potter et al., 2005; Sehnem et al., 2010; Sukul and Spiteller, 2001, 2000; Sukul, 2006), the soil degradation rates for the individual *R* and *S* enantiomers can differ and be differently affected by agricultural practices such as the application of organic amendments, repeated pesticide treatments, or the type of formulation applied. This is because these agricultural practices can influence the enantiomers availability as well as the nature and activity of the soil microbial population (Celis et al., 2015, 2013; Gámiz et al., 2016, 2013; Lewis et al., 1999).

Biochar (BC), i.e. the solid residue remaining after pyrolysis of biomass, has attracted much attention over the last years as a soil amendment, because, among other benefits, it can improve the quality and fertility of soils and contribute to mitigate greenhouse gas emissions (Agegnehu et al., 2015; Genesio et al., 2015; Lehmann et al., 2011; Sohi, 2012). Likewise, the use of BC has been proposed as a strategy to attenuate the mobility of pesticides and mitigate contamination of soils and surface and ground waters (Gámiz et al., 2016; García-Jaramillo et al., 2014; Kookana, 2010; Mesa and Spokas, 2010). Another type of materials suggested as pesticide sorbents are layered double hydroxides (LDHs) or hydrotalcite (HT)-like compounds (anionic clays). These are minerals with high sorption capacity due to anion exchange properties, acid-base buffering capacity, reconstruction from their calcination products, and customization potential (Cavani et al., 1991; Celis et al., 2014, 1999; Cornejo et al., 2008; Forano et al., 2006). For example, Celis et al. (2014) showed that the intercalation of fatty acid anions into a Mg/Al (3:1) LDH resulted in organo-hydrotalcites with very high affinities for neutral (uncharged) pesticides. Amendment with organo-hydrotalcites has also been proposed as a strategy to reduce the mobility of pesticides and other organic pollutants in soils (Bruna et al., 2012; Cornejo et al., 2008).

This research was designed as a follow-up study of previous experiments conducted under well-controlled laboratory conditions indicating that olive mill waste (OMW)-derived biochars and organo-hydrotalcites could be useful as soil amendments to mitigate contamination by pesticides. The primary objective was to assess the effect of adding an oleate-modified hydrotalcite (clay) and an OMW-derived biochar (BC) to an agricultural soil on the sorption, persistence, and mobility of two widely used fungicides with contrasting physico-chemical properties (tebuconazole and metalaxyl) under real field conditions. Considering that the studied fungicides were chiral, we also intended to get insight into the effects of the addition of clay and BC on the enantiomeric composition of tebuconazole and metalaxyl soil residues. The information provided in this work should help in the design of real pollution control strategies based on the use of clays and biochars as soil amendments.

2. Materials and methods

2.1. Soil, amendments, and fungicides

The field experiment was conducted on a 4 × 4 m soil area of an experimental farm located in Sevilla, Spain (37°17′02″N, 6°03′58″W), devoted to field trials by IRNAS (CSIC). The soil was selected for being a typical low organic carbon content, Mediterranean agricultural soil susceptible to receive the studied fungicides. It was a sandy loam soil with 66% sand, 16% silt, 18% clay (16% smectites, 1% illite/mica, 1% kaolinite), 19% $CaCO_3$, 0.59% organic carbon, and had a pH of 7.3. It was similar to that used in a previous laboratory study (Gámiz et al., 2016), but with greater carbonate and smectite contents. For the laboratory sorption experiment, a sample of untreated soil was taken (0–20 cm), air dried, sieved to pass a 2 mm-aperture mesh, and used within one week after sampling.

The amendments used were oleate-modified hydrotalcite (clay) and biochar (BC). They were prepared under less strictly controlled conditions compared to similar sorbents used in previous laboratory experiments to simulate feasible, larger scale production procedures. Hydrotalcite and sodium oleate were both purchased from Sigma-Aldrich with a purity of 99% and 80%, respectively. The preparation of the oleate-intercalated hydrotalcite (clay) was carried out through the reconstruction method, following a procedure similar to that described in Celis et al. (2014). Briefly, 75 g of sodium oleate was stirred in 1.5 L of deionized water for 2 h at 60 °C until a clear, yellow solution was obtained. Simultaneously, 50 g of hydrotalcite was calcined at 500 °C for 2 h, and then added to the sodium oleate solution. The suspension was stirred for 24 h at 60 °C, filtered (pore size = 0.45 μm), and the resultant solid was dried at 60 °C to obtain the final oleate-modified hydrotalcite (clay) sample. The properties of the clay were: 17.8% Mg, 7.2% Al, 30.2% C, and a basal spacing value of 3.4 nm, which reflected the successful intercalation of the oleate anions in the interlayer space of the clay (Celis et al., 2014). Biochar (BC) was obtained from the same composted olive-mill waste (OMWc) as that used in Gámiz et al. (2016), but was prepared at higher pyrolysis temperature (550 °C) and under a less strictly controlled oxygen-restricted atmosphere by pyrolizing 10 kg of OMWc in an experimental, higher capacity pyrolysis furnace for 2 h. This resulted in a BC with a lower carbon content, but slightly greater nitrogen-specific surface area (S_{BET}) compared to that obtained in Gámiz et al. (2016). The properties of BC were: 24.2% C, 2.0% N, S_{BET} of 2.5 $m^2 g^{-1}$ and pH of 10.2.

Technical-grade (racemic) metalaxyl [methyl-*N*-(2-methoxyacetyl)-*N*-(2,6-xylyl)-DL-alaninate] (purity 97.7%) and tebuconazole [(*RS*)-1-*p*-chlorophenyl-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol)] with a purity >95% were used in laboratory and field experiments. High-purity (>99%) standards of (racemic) metalaxyl and tebuconazole purchased from Sigma-Aldrich (Spain) were used to prepare the external calibration curves for the analysis of the fungicides.

2.2. Laboratory sorption experiment

A preliminary laboratory batch sorption experiment was conducted in order to determine the effect of the amendments on the sorption capacity of the soil for the fungicides. For this purpose, triplicate 4 g samples of unsterilized soil, either unamended or amended with clay or BC at two different rates