



Research article

Evaluation of an organo-layered double hydroxide and two organic residues as amendments to immobilize metalaxyl enantiomers in soils: A comparative study



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ABSTRACT

Many pollutants released into the environment as a result of human activities are chiral. Pollution control strategies generally consider chiral compounds as if they were achiral and rarely consider enantiomers separately. We compared the performance of three different materials, an organically-modified anionic clay (HT-ELA) and two organic agro-food residues (ALP and ALPc), as amendments to immobilize the chiral fungicide metalaxyl in two soils with different textures, addressing the effects of the amendments on the sorption, persistence, and leaching of each of the two enantiomers of metalaxyl (*R*-metalaxyl and *S*-metalaxyl) separately. The effects of the amendments were both soil- and amendment-dependent, as well as enantiomer-selective. The organo-clay (HT-ELA) was much more efficient in increasing the sorption capacity of the soils for the two enantiomers of metalaxyl than the agro-food residues (ALP and ALPc), even when applied at a reduced application rate. The enhanced sorption in HT-ELA-amended soils reduced the bioavailability of metalaxyl enantiomers and their leaching in the soils, mitigating the particularly high leaching potential of the more persistent *S* enantiomer. The immobilizing capacity of the agro-food residues was more variable, mainly because their addition did not greatly ameliorate the sorption capacity of the soils and had variable effects on the enantiomers degradation rates. HT-ELA showed potential to reduce the bioavailability and mobility of metalaxyl enantiomers in soil and to mitigate the contamination problems particularly associated with the higher leaching potential of the more persistent enantiomer.

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1. Introduction

Chiral pesticides have become a very important group of emerging pollutants. The use of this group of agrochemicals has spread in the last decades; currently, more than 25% of the registered pesticides are chiral (Garrison, 2011; Ulrich et al., 2012). Chiral pesticides consist of one (or more) pair of enantiomers that present practically identical physico-chemical properties; however, enantiomers can display significant differences in their behavior in soil and in their toxicity towards target and non-target organisms. In the majority of cases, only one of the enantiomers is active against the target pest, and the fate of the non-active enantiomer is largely unknown. Sometimes, the inactive enantiomer can affect non-target species or act on the effectivity of the active enantiomer

(Magrans et al., 2002). This is due to the fact that many reactions of pesticides in soil are enzymatic, and hence, enantioselective. For this reason, authorities have alarmed about the necessity to achieve a higher control of chiral agrochemicals and expressed the advantages of using active enantiomers separately (Magrans et al., 2002; Regulation (EC) N° 1107/2009). Nevertheless, because of economic reasons, chiral pesticides are yet often applied to soils as racemic mixtures rather than as pure active enantiomers, and this may pose serious environmental side-effects.

Metalaxyl is a phenylamide pesticide with an asymmetrical C in its structure, so that two different enantiomers can be identified: *S*-metalaxyl and *R*-metalaxyl (Fig. S1 of the Supplementary material). It is well known that the fungicidal activity of metalaxyl is due to *R*-metalaxyl mainly (Buerge et al., 2003; Chen and Liu, 2009). Previous studies on the sorption of racemic metalaxyl on soils and soil components have concluded that metalaxyl sorption is not enantioselective (Celis et al., 2013; Sukul et al., 2013), although recent findings have indicated that, when present in a non-racemic form,

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metalaxyl sorption can turn into enantioselective (Celis et al., 2015a).

The persistence of metalaxyl enantiomers in soil depends on several factors. One of the most important factors is the pH. Under aerobic conditions, the *R*-enantiomer degrades faster than the *S*-enantiomer in soils with pH > 5, whereas the *S*-enantiomer degrades faster than the *R*-enantiomer in acid soils (pH < 4) (Buerge et al., 2003). In sewage sludge, *S*-metalaxyl was preferentially degraded over *R*-metalaxyl both in aerobic and anaerobic conditions (Chen and Liu, 2009; Müller and Buser, 1995). Other factors influencing the behavior of metalaxyl enantiomers in soil are the amount and nature of mineral constituents and soil porosity. Celis et al. (2013) observed that a soil with high clay content had a high sorption capacity for metalaxyl and this appeared to reduce the availability of metalaxyl enantiomers to be biodegraded compared to soils with lower clay contents. Similarly, entrapment in small-size pores can protect this chiral pesticide from biodegradation in soil and prolong its presence in a racemic form (Celis et al., 2013). Some agricultural practices may also alter the behavior of metalaxyl enantiomers. For example, Gámiz et al. (2013, 2016) reported how adding fresh, composted, or pyrolyzed olive-mill waste (OMW) to sandy loam soil samples affected the sorption, persistence, and leaching of metalaxyl enantiomers.

Recently, the performance of layered double hydroxides (LDHs) as sorbents of pesticides has received considerable attention (Celis et al., 2014; Cornejo et al., 2008; Lagaly, 2001). LDHs, also known as hydrotalcites (HTs) or anionic clays, consist of Mg(OH)₂ brucite-type layers with isomorphous substitutions, which lead to positive charges in the layers that are balanced by exchangeable hydrated inorganic anions intercalated in the interlayer space (Cavani et al., 1991; Hou et al., 2003; Rives, 2001). The intercalated anion of LDHs can be exchanged by a specific anion with high affinity for a particular sorbate (Cornejo et al., 2008). Celis et al. (2014) prepared organo-LDHs consisting of nanohybrids of (3:1) Mg/Al layered double hydroxide (HT) with long-chain unsaturated fatty acid anions inserted in the interlayer space and evaluated them as pesticide sorbents. The study concluded that trans-unsaturated elaidate anion-modified hydrotalcite (HT-ELA) had a great sorption capacity for neutral pesticides.

As pesticide sorption can affect the dissipation of pesticides by reducing their availability to be biodegraded, as well as their transport to ground and surface water (Reichenberger et al., 2007; Rojas et al., 2013; Zipper et al., 1998), we hypothesized that increasing metalaxyl sorption in soil by using organo-LDHs as amendments could be used to control the enantioselective behavior of this chiral pesticide in soils and as a pollution control strategy. Studies on the potential application of organo-LDHs as amendments for pollutant immobilization in soils are very scarce (Bruna et al., 2012), and to our knowledge, there are no published reports addressing their possible enantiomer-selective immobilizing effect for chiral pollutants.

Thus, the objective of this work was to assess under laboratory conditions whether the addition of HT-ELA could be used to increase the sorption of metalaxyl enantiomers in two soils with markedly different textures, a clay soil and a sandy clay loam soil. Subsequently, we evaluated the changes in the persistence and leaching of metalaxyl enantiomers due to the increase in sorption. For comparative purposes, the effects observed after the addition of two organic (OMW) residues to the tested soils are also reported.

2. Materials and methods

2.1. Fungicide

Metalaxyl [methyl-*N*-(2-methoxyacetyl)-*N*-(2,6-xylyl)-DL-

alaninate] is a phenylamide pesticide with a molecular mass of 279.3 g/mol, water solubility of 8.4 g/L (22 °C), and vapor pressure of 0.75 mPa (25 °C) (Tomlin, 2006). Analytical standard grade, racemic-metalaxyl (chemical purity >99.5%) provided by Sigma-Aldrich (Spain) was used in the experiments.

2.2. Soils

Two agricultural soils with different textures and clay mineralogy were used in this study. The soils were sampled (0–20 cm), air-dried, sieved to pass a 2 mm mesh, and stored at 4 °C until their characterization and use in the experiments. The most important physicochemical properties of the soils are summarized in Table 1.

2.3. Amendments

The two organic residues, fresh and composted olive-mill waste or “alperujo” (ALP and ALPc), were supplied by Spanish olive-processing factories. Alperujo (ALP) is the solid residue generated during the two-phase olive-oil extraction technology, which is currently widely used in Spain and other olive-oil producing countries. ALPc corresponded to the material resulting from composting fresh alperujo for about 5 months. Both ALP and ALPc were ground and sieved (2 mm), and stored at 4 °C until used. The main properties of the ALP and ALPc used in this work are summarized in Table S1 of the Supplementary material. The rate of ALP and ALPc applied in the soils (2% w/w) was equivalent to a typical agronomic dose of 50 t/ha, considering a soil bulk density of 1.3 g/cm³ and that the organic amendment is mixed with the top 0–20 cm soil layer. The third amendment used was a 3:1 Mg/Al LDH (hydrotalcite, HT) intercalated with elaidate anions (HT-ELA). It was prepared and characterized as described in Celis et al. (2014) and, on the basis of its high sorption capacity, was added to the soils at a rate of 1% (w/w). Its elemental composition was 12.2% Mg, 4.3% Al, and 39.1% C.

2.4. Sorption experiment

Sorption-desorption isotherms were measured by the batch equilibration technique. Triplicates of 1 g of unamended soils or soils amended with ALP (2% w/w), ALPc (2% w/w) or HT-ELA (1% w/w) were treated with 8 mL of aqueous solutions of *rac*-metalaxyl with concentrations (C_{ini}) ranging from 2 to 30 mg/L. After 24 h of shaking at 20 ± 2 °C, the suspensions were centrifuged (5000 rpm for 15 min) and 4 mL of the supernatant solutions were removed, filtered (0.45 μm pore size GHP membrane disk filters) and analyzed by chiral high-performance liquid chromatography (HPLC). The amount of *S*- and *R*-metalaxyl sorbed by the unamended and amended soil samples (C_s) was determined from the differences between the initial (C_{ini}) and equilibrium (C_e) solution concentrations of each enantiomer. Initial metalaxyl solutions without soil were also prepared and served as controls.

Desorption was measured immediately after sorption from the highest concentration point ($C_{ini} = 30$ mg/L) of the sorption isotherms. The 4 mL of supernatant used for the sorption analysis were replaced with 4 mL of distilled water and the soil suspensions

Table 1
Physicochemical properties of the soils.

Soil	Texture	Sand (%)	Silt (%)	Clay (M, I, K) ^a (%)	OC ^b (%)	pH ^c
Soil 1	Clay	6	26	68 (20, 38, 10)	0.49	8.6
Soil 2	Sandy clay loam	74	4	22 (12, 4, 6)	0.50	8.8

^a M: montmorillonite, I: illite/mica, K: kaolinite.

^b OC: organic carbon content measured by dichromate oxidation.

^c Measured in 1 g soil: 2.5 mL water suspension.

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