Science of the Total Environment 541 (2016) 776–783

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Environmental fate of the fungicide metalaxyl in soil amended with composted olive-mill waste and its biochar: An enantioselective study

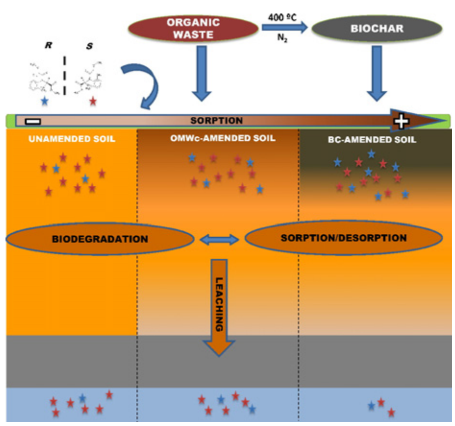
Beatriz Gámiz [a,*], Joseph J. Pignatello [b], Lucía Cox [a], María C. Hermosín [a], Rafael Celis [a]

[a] Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Avenida Reina Mercedes 10, P.O. Box 1052, 41080 Sevilla, Spain
[b] Department of Environmental Sciences, The Connecticut Agricultural Experiment Station, 123 Huntington St., P.O. Box 1106, New Haven, CT 06504-1106, United States

HIGHLIGHTS

- Solid waste-derived biochar (BC) was assayed as a sorbent of metalaxyl enantiomers.
- Sorption of metalaxyl enantiomers on BC was considerably higher than on its feedstock.
- BC affected the soil behavior of metalaxyl by reducing the enantiomers availability.
- Sorption to BC protected metalaxyl enantiomers from degradation and leaching in soil.
- BC shows potential as a sorbent for soil and water remediation and pollution control.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form 10 September 2015
Accepted 18 September 2015
Available online 2 October 2015

Editor: D. Barcelo

Keywords:
Chiral pesticides
Degradation
Leaching
Organic wastes
Soil amendments
Sorption

ABSTRACT

A large number of pesticides are chiral and reach the environment as mixtures of optical isomers or enantiomers. Agricultural practices can affect differently the environmental fate of the individual enantiomers. We investigated how amending an agricultural soil with composted olive-mill waste (OMWc) or its biochar (BC) at 2% (w:w) affected the sorption, degradation, and leaching of each of the two enantiomers of the chiral fungicide metalaxyl. Sorption of metalaxyl enantiomers was higher on BC ($K_d \approx 145$ L kg^{-1}) than on OMWc ($K_d \approx 22$ L kg^{-1}) and was not enantioselective in either case, and followed the order BC-amended > OMWc-amended > unamended soil. Both enantiomers showed greater resistance to desorption from BC-amended soil compared to unamended and OMWc-amended soil. Dissipation studies revealed that the degradation of metalaxyl was more enantioselective ($R > S$) in unamended and OMWc-amended soil than in BC-amended soil. The leaching of both *S*- and *R*-metalaxyl from soil columns was almost completely suppressed after amending the soil with BC and metalaxyl residues remaining in the soil columns were more racemic than those in soil column leachates. Our findings show that addition of BC affected the final enantioselective behavior of metalaxyl in soil indirectly by reducing its bioavailability through sorption, and to a greater extent than OMWc. BC showed high sorption capacity to remove metalaxyl enantiomers from water, immobilize metalaxyl enantiomers in soil, and mitigate the

* Corresponding author at: Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Avenida Reina Mercedes 10, Apartado 1052, 41080 Sevilla, Spain.
E-mail address: bgamiz@irnase.csic.es (B. Gámiz).

http://dx.doi.org/10.1016/j.scitotenv.2015.09.097
0048-9697/

groundwater contamination problems particularly associated with the high leaching potential of the more persistent enantiomer.

1. Introduction

Increasing knowledge of the factors controlling the environmental fate of chiral pesticide enantiomers is a recent matter of concern (Garrison, 2006; Petrie et al., 2015; Sekhon, 2009). Over 25% of pesticides currently in use are chiral, and in China up to 40% of the pesticides in use are classified as chiral compounds (Garrison, 2006; Ye et al., 2009). The presence of chirality in pesticides has received very little attention. Chiral pesticides are often treated and analyzed as if they were achiral compounds (Celis et al., 2013; Gámiz et al., 2013; Petrie et al., 2015; Ye et al., 2009). Although chiral pesticide enantiomers have almost identical physico-chemical properties (Liu et al., 2009; Pérez and Barceló, 2008), they can differ in their biological efficacy, toxicity, or dissipation (Buerge et al., 2003; Celis et al., 2013; Garrison, 2006; Müller and Buser, 1995; Poiger et al., 2015; Zhang et al., 2014). In recent years, new analytical approaches have facilitated characterization of the behavior of chiral pesticide enantiomers in the environment (Pérez and Barceló, 2008; Pérez-Fernández et al., 2011).

Metalaxyl is widely used as an acylanilide fungicide in the control of plant diseases caused by pathogens of the Oomycota division in several crops (Tomlin, 2006). Metalaxyl can be applied to fields as the optically pure biologically-active *R* stereoisomer or the racemic (1:1) mixture of *R* and *S* enantiomers (Buerge et al., 2003; Liu et al., 2009). Application of the racemate can generate an important source of contamination due to the presence of the non-active enantiomer (Buerge et al., 2003; Buser et al., 2002; Monkiedje et al., 2007; Pose-Juan et al., 2015; Wong, 2006). Metalaxyl undergoes enantioselective microbial degradation in soil and organic matrices depending on pH and redox conditions (Buerge et al., 2003; Buser et al., 2002; Celis et al., 2013; Monkiedje et al., 2003; Müller and Buser, 1995). Thus, *S*-metalaxyl is degraded faster than *R*-metalaxyl in soils under anaerobic conditions and in aerobic soils of pH < 4, whereas *R*-metalaxyl is degraded faster than *S*-metalaxyl in aerobic soils of pH > 5 (Buerge et al., 2003; Monkiedje et al., 2003). Interconversion of enantiomers in soil has been ruled out (Buerge et al., 2003; Buser et al., 2002). Although abiotic processes, such as sorption, appeared to be non-enantioselective (Celis et al., 2013; Sukul et al., 2013), it has been suggested that sorption and entrapment in small-size pores can protect metalaxyl from enantioselective biodegradation, prolonging its existence in racemic form (Celis et al., 2013). Furthermore, certain management practices, such as the addition of organic amendments, the repeated application of the fungicide, or the type of formulation applied, affect the enantioselective behavior of metalaxyl in soils (Celis et al., 2015; Gámiz et al., 2013).

Addition of organic amendments is a common agricultural practice to increase soil fertility, particularly in areas where soils are poor in organic matter, and can also be used to prevent and remediate soil and water contamination by pesticides and other organic pollutants by reducing their mobility (Gámiz et al., 2012; Marín-Benito et al., 2012a). For instance, the use of organic wastes from olive oil production or olive-mill wastes (OMWs) is considered as an "ecological" way of disposal of these wastes (Gámiz et al., 2012). Composting of OMW residues prior to application helps decrease the phenolic components which can be toxic to some organisms (Alburquerque et al., 2006). Due to its high organic matter content, composted OMW (OMWc) can affect the sorption, degradation, and mobility of pesticides in soil (Cabrera et al., 2007).

Recently, considerable research has focused on the application of biochar (BC) as a soil amendment (Mesa and Spokas, 2010). Biochar is the solid residue remaining after the thermochemical transformation (pyrolysis) of biomass. Reported attributes of biochar include higher stability compared to other organic wastes (Sohi, 2012), soil fertility improvement, enhancement of soil water retention capacity, carbon sequestration potential (Sohi, 2012) and augmentation of soil microbial activity (Lehmann and Joseph, 2015; Lehmann et al., 2011). The addition of BC and OMWc to soil has been shown to have various impacts on the fate of pesticides, including increased sorption capacity, modification of degradation behavior, and reduction in leaching potential (Cabrera et al., 2014; Cabrera et al., 2011; Fernandes et al., 2006; Gámiz et al., 2010; García-Jaramillo et al., 2014; Martin et al., 2012), but until now the effects of BC or OMWc amendment on the behavior of individual chiral pesticide enantiomers have been overlooked. The purpose of this study was to assess whether a particular OMWc and its BC can affect the enantioselectivity of sorption, degradation, and leaching of the chiral fungicide metalaxyl in soil, and to test their potential for the removal of metalaxyl enantiomers from water and their immobilization in soil.

2. Materials and methods

2.1. Fungicide and soil

Analytical grade racemic-metalaxyl [methyl-N-(2-methoxyacetyl)-N-(2,6-xylyl)-DL-alaninate] supplied by Sigma-Aldrich (Spain) with a purity of 99.6% was used in all experiments. Metalaxyl has a molecular mass of 279.3 g mol^{-1}, water solubility of 8.4 g L^{-1} (22 °C), and vapor pressure of 0.75 mPa (25 °C) (Tomlin, 2006). An agricultural soil was sampled from the top 0–20 cm soil layer of an olive orchard located in Seville (Spain), air-dried, sieved to pass a 2 mm mesh, and stored at 4 °C. It is a sandy loam soil and contains 73% sand, 7% silt, 19% clay (10% smectites, 4% illite/mica, 5% kaolinite), and 0.68% organic carbon. The pH of a 1:2 (*w*/*v*) soil/deionized water mixture was 7.7.

2.2. Organic amendment and biochar

A composted olive-mill waste (OMWc) from an olive-processing factory in Jaen (Spain) was used as organic soil amendment. Prior to use, the waste was air-dried and ground to pass a 2 mm-aperture sieve. Biochar (BC) obtained from OMWc was also used to amend the soil. BC production was carried out by heating OMWc at 400 °C for 4 h under a flow of N_2 at 1.5 L min^{-1}. The C and N contents of OMWc and BC were determined by the combustion, catalytic oxidation method using a total carbon analyzer with a total nitrogen unit Shimadzu TOC-V shc. Physisorption of N_2 at 77 K, using a Carlo Erba Sorptomatic 1900 gas adsorption analyzer (Fisons Instruments), was used to obtain the specific surface areas (S_{BET}) of OMWc and BC by applying the BET method. pH values were measured in 1:2 (*w*/*v*) amendment:deionized water mixtures. The air-dried OMWc had 28% C, 2.3% N, S_{BET} of 1.2 m^2 g^{-1}, a pH of 8.6, and 9.2% soluble organic carbon, as measured in a filtered supernatant of 1 g OMWc in 20 mL $CaCl_2$ (0.01 M). The properties of BC are: 30% C, 1.8% N, S_{BET} of 0.3 m^2 g^{-1}, a pH of 9.8, and 4.4% soluble organic carbon.

The collected soil was amended with OMWc and BC at 2% (*w*/*w*) by adding the corresponding amount of amendment to a pre-weighed amount of soil and then mixing with a stainless steel spatula to homogenize the mixture. The main characteristics of the soil amended with OMWc and BC are included in Table S1 of the Supplementary information.