ISOMER-SELECTIVE BEHAVIOR OF METALAXYL IN ORGANICALLY-AMENDED SOIL

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Synergy in Science: Partnering for Solutions
ASA•CSSA•SSSA 2015 MEETING
November 15-18
Minneapolis, MN

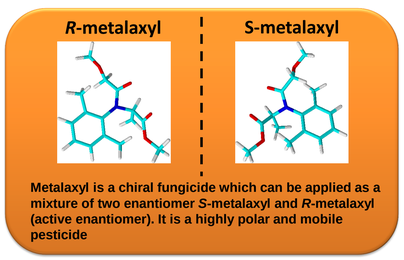
Introduction

Increasing knowledge of the factors controlling the environmental fate of chiral pesticide enantiomers is a recent matter of concern because a large number of pesticides are chiral and reach the environment as mixtures of optical isomers or enantiomers.

Use of organic amendments is a common agricultural practice to increase fertility of soils, 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. This is the case of the composted Olive-Mill Waste (OMWc), composted residue from olive oil production, and biochar (BC), the solid residue remaining after pyrolysis of biomass.

In this work, we investigated how amending a sandy loam agricultural soil with composted olive mill waste (OMWc) or its biochar (BC) at a rate of 2% (w:w) affected the enantioselectivity of the sorption, dissipation, and leaching processes of the fungicide metalaxyl.

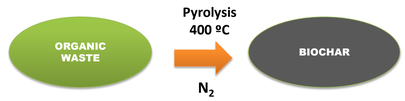
Chiral pesticide



Metalaxyl is a chiral fungicide which can be applied as a mixture of two enantiomer *S*-metalaxyl and *R*-metalaxyl (active enantiomer). It is a highly polar and mobile pesticide

Soil characteristics

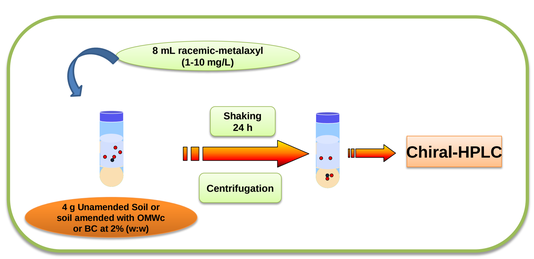
Texture	% OC	pH (H_2O)	% Sand	% Silt	% Clay	Crop
Sandy loam	0.68	7.22	73	7	19	olive

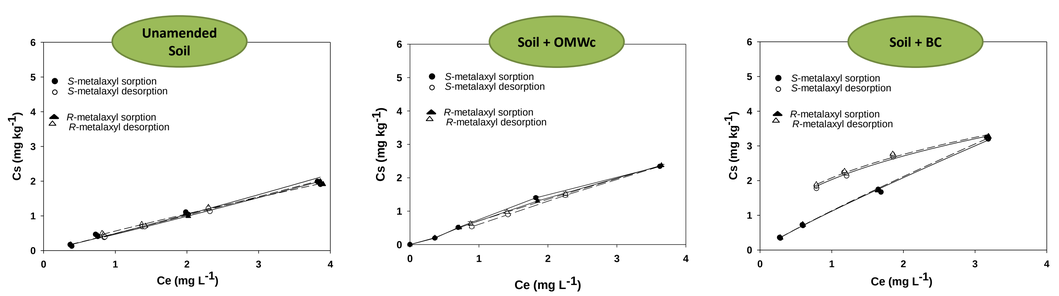


Organic amendment characteristics

Amendment	%C	%N	S_{BET} (m^2 g^{-1})	pH (H_2O)
OMWc	28	1.3	1.2	8.6
BC	30	1.8	0.3	9.8

Sorption experiments



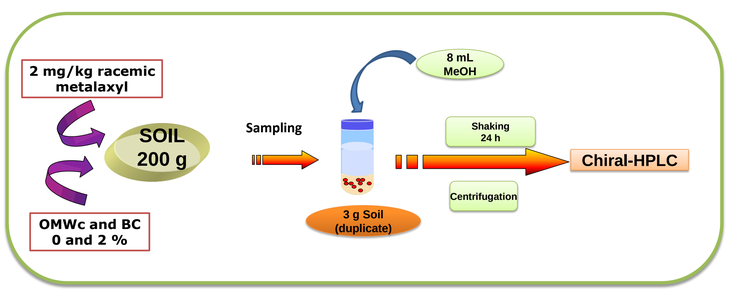


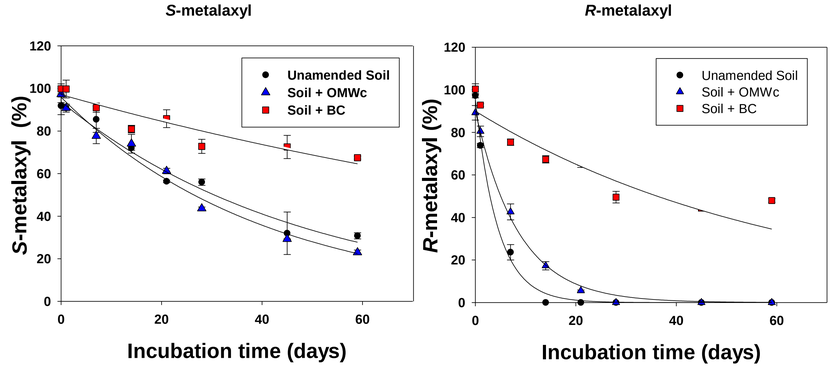
Sorption of metalaxyl enantiomers was non-enantioselective process. *S*- and *R*-metalaxyl were equally sorbed in each treatment, and followed the order:

Unamended Soil < OMWc –amended soil < BC-amended soil

Soil and OMWc-amended soil showed linearity and reversibility in sorption in contrast to BC-amended soil which displayed hysteresis.

Persistence experiments





Dissipation of metalaxyl in all cases was enantiomer-selective and treatment-dependent, with *R*- degrading faster than *S*-enantiomer.

The extent of enantioselectivity was altered after amending soil. OMWc accelerated the degradation of *S*-metalaxyl and retarded the degradation of *R*-metalaxyl compared to unamended soil.

In contrast, addition of BC resulted in higher persistence of both enantiomers in comparison to unamended soil.

Column leaching experiments

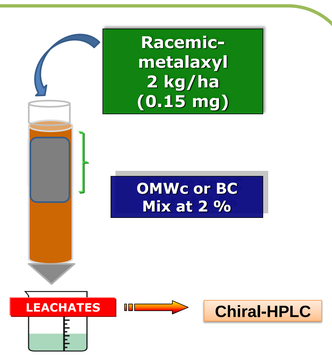
Leaching studies were performed in glass columns of length 30 cm and i.d. 3.1 cm, hand packed with 160 g of soil (20 cm).

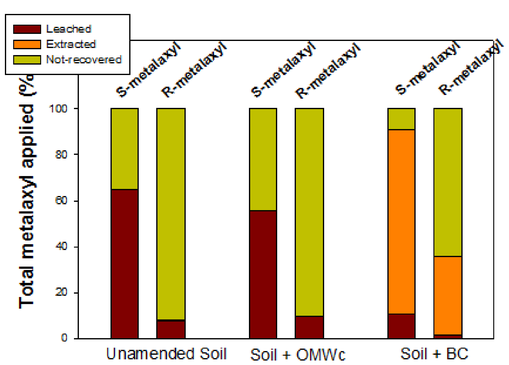
Amendment of soil was carried out mixing the soil with OMWc and BC at rate of 0 % and 2 %, unamended soil and amended soil, respectively, in triplicate experiments.

Racemic-metalaxyl was applied to the top in each column at rate of 2 kg/ha.

Daily, 15 mL of deionized water were added, the leachates were collected in which concentration of *S*-metalaxyl and *R*-metalaxyl were determined by Chiral-HPLC.

At the end of the leaching experiment, columns were extracted with MeOH to determine metalaxyl-enantiomer residues.





Leaching resulted in an enantioselective process, where *S*-metalaxyl leached in greater amounts than *R*-metalaxyl in all three cases, likely, due to *S*-enantiomer was degraded lower than *R*-metalaxyl.

The amount leached of both enantiomers was similar in OMWc-amended and unamended soil, whereas the addition of BC reduced the leaching of both enantiomers. Hence, BC could be used in soil to reduce the mobility of highly polar chiral pesticides

Conclusions

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 groundwater contamination problems particularly associated with the high leaching potential of the more persistent (*S*)-enantiomer.

Acknowledgment

This work has been financed by the Spanish Ministry of Economy and Competitiveness (MINECO Project AGL2014-51897-R) and Junta de Andalucía (Research Group AGR-264), cofinanced with European FEDER-FSE funds (Operative Program 2007-2013).