



## Retention and transport of mecoprop on acid sandy-loam soils



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### ABSTRACT

Interaction with soil components is one of the key processes governing the fate of agrochemicals in the environment. In this work, we studied the adsorption / desorption and transport of mecoprop (methylchlorophenoxypropionic acid or MCP) in four acid sandy-loam soils with different organic matter contents. Kinetics of adsorption and adsorption/desorption at equilibrium were studied in batch experiments, whereas transport was studied in laboratory columns. Adsorption and desorption were found to be linear or nearly-linear. The kinetics of mecoprop adsorption were relatively fast in all cases (less than 24 h). Adsorption and desorption were adequately described by the linear and Freundlich models, with  $K_F$  values that ranged from 0.7 to 8.8 L<sup>n</sup> μmol<sup>1-n</sup> kg<sup>-1</sup> and  $K_D$  values from 0.3 to 3.6 L kg<sup>-1</sup>. The results of the transport experiments showed that the retention of mecoprop by soil was very low (less than 6.2%). The retention of mecoprop by the soils in all experiments increased with organic matter content. Overall, it was observed that mecoprop was weakly adsorbed by the soils, what would result in a high risk of leaching of this compound in the environment.

### 1. Introduction

Mecoprop [(RS)-2-(4-chloro-2-methylphenoxy)propionic acid] is a compound of the phenoxyalkanoic acid group, that includes several molecules used as herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2-(2,4-dichlorophenoxy)propanoic acid (dichlorprop). They are used mainly to control annual and perennial broadleaf weeds in cereals, grassland, orchards, and forestry and they represent the largest contribution to herbicide sales in the European Union (Paszko et al., 2016). Mecoprop has two stereoisomers, one of which, [2R]-2-[4-chloro-2-methylphenoxy] propionic acid, known as mecoprop-p, has herbicide properties and is widely used for agricultural, horticultural and domestic purposes (Buss et al., 2006). As happens with most pesticides, intensive use of mecoprop in agricultural land may result in adverse environmental effects, including potential pollution of water resources. In fact, mecoprop is among the most frequently found pesticides both in groundwater and in surface waters at several places in the world (Schipper et al., 2008; Glozier et al., 2012; Metcalfe et al., 2016; McManus et al., 2017). Mecoprop concentrations are higher in surface waters than in groundwater and they have been found to exceed frequently the European Union limit of 0.1 μg L<sup>-1</sup> for individual pesticide compounds (Buss et al., 2006; Glozier et al., 2012; McManus et al., 2017). Although the concentrations found in those studies are in general below the

predicted no-effect concentration of 5.5 μg L<sup>-1</sup> proposed by the British Environment Agency (Johnson et al., 2007), studies about the factors that influence and determine the environmental fate of this compound are necessary.

Mecoprop is a weak acid that exists in anionic form under most natural conditions, and it is relatively soluble in water compared to other organic compounds, which has important implications for the environmental risk associated. Relatively water-soluble herbicides are readily transported through soils and groundwater by advection, so their interaction with soil components in ways that reduce their movement can limit potential pollution. In this sense, adsorption processes play a key role in pesticide dynamics and environmental fate, reducing leaching and runoff, preventing their access into ground or surface water, as well as reducing bioavailability and potential detrimental effects on non-target organisms (Calvet et al., 2005). In the case of mecoprop, adsorption to soils is expected to be low because of the negative charge of the molecule at most normally occurring soil pH values (Buss et al., 2006) and indeed lower interaction with soil has been observed in comparison with other members of the phenoxyacetic family (Werner et al., 2013). However, some soil conditions could influence this low interaction: in addition to organic matter content, the presence of calcium (that could form bridges with the anionic form of mecoprop) and iron (hydr)oxides (that can be positively-charged and therefore present capacity for anion attraction) have been pointed out

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as components that control mecoprop retention (Clausen et al., 2001). In any case, compared with other phenoxyacetic herbicides, such as MCPA or 2,4-D, the study of mecoprop interactions with soils has received less attention. In this context, the study of mecoprop adsorption and transport in soil is necessary.

The properties of a great number of soils from the agricultural regions of the north-western area of the Iberian Peninsula have been studied previously. An important part of this area is covered with soils developed from granitic materials, characterized by moderate to strong acidity, coarse textures (sandy loam or coarser) and low clay contents (Fernández-Calviño et al., 2009). These features are a consequence of the weathering of granite that results in high quantities of sand-size quartz grains and relatively low clay amounts (Silva and Guitián, 1984; Mareschal et al., 2015). The coarse texture of these soils, in combination with climatic conditions where rainfall is higher than evapotranspiration, make them susceptible of low pesticide retention and a high risk of leaching. Under these conditions, the interaction of pesticides with soil becomes particularly important in order to limit their environmental risk, and consequently the study of the processes of retention and transport in these soils is necessary. Therefore, in this work we have studied the adsorption, desorption and transport of mecoprop in four acid coarse-textured soils from two vineyard regions in Spain and Portugal. The objective was to relate mecoprop retention and transport in soils developed on granites with a range of organic matter contents. It must be highlighted that, in a context where studies about the adsorption of mecoprop are not abundant in the literature, transport studies using soil columns or dealing simultaneously with mecoprop retention and transport are even more rare.

## 2. Materials and methods

### 2.1. Pesticide

A high-purity mecoprop (99.5% purity) standard [(RS)-2-(4-chloro-2-methylphenoxy) propionic acid], was obtained from Sigma-Aldrich (Steinheim, Germany). It was used as a racemic mixture (i.e. 50% of each enantiomer). The main physicochemical properties of mecoprop are given in Table S1 (Supplementary material).

### 2.2. Soils

Four vineyard soils developed from granite were used in this study. Soil sieved by a 2-mm mesh was used in all the experiments. The soils were selected from a previous sampling by Fernández-Calviño et al. (2009) in two wine regions in NW of the Iberian Peninsula: Monterrei and Vinhos Verdes. Regosols (IUSS Working Group WRB, 2014) are the predominant soil type in both areas. Eight to ten soil sub-samples (0–20 cm depth) were collected with a soil auger and subsequently mixed into a single composite soil sample, obtaining a total soil amount of about 2 kg from each vineyard. The soils were air-dried and stored in polypropylene containers in a dry area protected from the light. Further details about sampling procedure and soil analysis are given in the reference above. All the soils are acidic, with loamy-sand texture, organic carbon contents ranging from 3.1 to 48 g kg<sup>-1</sup> and total Cu contents from 25 to 107 mg kg<sup>-1</sup> (Table 1). Texture, pH and the range

organic matter contents of the soils selected are intended to be representative of the vineyard soils in the granitic areas of the region (Fernández-Calviño et al., 2009).

### 2.3. Batch experiments

#### 2.3.1. Kinetics of adsorption

Two grams of soil were weighed in polypropylene centrifuge tubes and suspended in 10 mL of a 50-μM mecoprop solution containing 0.01 M CaCl<sub>2</sub> as a background electrolyte. Suspensions were shaken for different times (1, 2, 4, 8, 16 and 24 h) at 60 rpm on a rotary shaker at room temperature (25 ± 1 °C), and centrifuged at 2665g for 10 min. Aliquots from the supernatant were immediately analyzed for mecoprop, as explained below (Section 2.5). The amount of mecoprop adsorbed was calculated as the difference between the amount added and the amount remaining in the solution. Blanks without soil were run in parallel in order to test pesticide sorption to the polypropylene tubes. The pH of the suspensions did not show significant variations with time during the kinetic studies (Fig. S1, Supplementary material).

Data for kinetics of adsorption were described by the pseudo-first order and pseudo-second order models, described by Eqs. (1) and (2), respectively:

$$q_a = q_e(1 - e^{-k_1 t}) \quad (1)$$

$$q_a = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where  $q_a$  (μmol kg<sup>-1</sup>) is the total amount of herbicide retained by the soil at a moment  $t$ ,  $q_e$  (μmol kg<sup>-1</sup>) is the amount of herbicide retained by the soil at equilibrium (this parameter has to be fitted by the model),  $k_1$  (h<sup>-1</sup>) is the pseudo-first-order rate constant for adsorption, and  $k_2$  (kg μmol<sup>-1</sup> h<sup>-1</sup>) is the pseudo-second-order rate constant.

#### 2.3.2. Adsorption/desorption at equilibrium

For the batch equilibrium experiments, two grams of each soil were weighed in polypropylene centrifuge tubes and suspended in 10 mL of solutions containing variable mecoprop concentrations (2.5–200 μM), using 0.01 M CaCl<sub>2</sub> as a background electrolyte. Suspensions were shaken on a rotary shaker at 60 rpm at room temperature (25 ± 1 °C) for 24 h and centrifuged at 2665g for 10 min. The supernatant was removed and immediately analyzed for mecoprop (or stored until analysis at 4 °C protected from light). The centrifuged residues were weighed to calculate the amount of pesticide solution entrapped in the soil and then resuspended in 10 mL of a 0.01 M CaCl<sub>2</sub> solution for the desorption experiments. Suspensions were shaken again and centrifuged as described previously and the supernatants were immediately analyzed for mecoprop (see Section 2.5). All the batch experiments were performed in duplicates. Blanks without soil were run in parallel in order to test pesticide sorption to the polypropylene tubes. The pH of the herbicide solutions after equilibration with soil in the batch experiments was in all cases close to 4.5 (Table S2, Supplementary material).

The amount of mecoprop adsorbed in batch experiments was calculated as the difference between the amount added and the amount remaining in the solution. Mecoprop desorption was expressed as

Table 1

Main properties of the four soils employed in the study. OC: total organic carbon; eCEC: effective cation exchange capacity.

	Sand	Silt	Clay	Texture	pH <sub>w</sub>	pH <sub>KCl</sub>	OC	N	eCEC
	g kg <sup>-1</sup>	g kg <sup>-1</sup>	g kg <sup>-1</sup>				g kg <sup>-1</sup>		cmol <sub>c</sub> kg <sup>-1</sup>
Soil 1	696	166	138	Sandy loam	4.6	3.4	3.1	0.4	3.31
Soil 2	621	194	185	Sandy loam	5.2	4.1	47.6	3.7	2.85
Soil 3	676	183	141	Sandy loam	4.8	4.3	37.3	3.3	3.73
Soil 4	735	176	89	Sandy loam	4.7	3.8	12.5	0.9	2.48

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