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# Fast, simple and efficient supramolecular solvent-based microextraction of mecoprop and dichlorprop in soils prior to their enantioselective determination by liquid chromatography–tandem mass spectrometry

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## ABSTRACT

A simple, sensitive, rapid and economic method was developed for the quantification of enantiomers of chiral pesticides as mecoprop (MCP) and dichlorprop (DCP) in soil samples using supramolecular solvent-based microextraction (SUSME) combined with liquid chromatography coupled to mass spectrometry (LC–MS/MS). SUSME has been described for the extraction of chiral pesticides in water, but this is firstly applied to soil samples. MCP and DCP are herbicides widely used in agriculture that have two enantiomeric forms (R- and S-) differing in environmental fate and toxicity. Therefore, it is essential to have analytical methods for monitoring individual DCP and MCP enantiomers in environmental samples. MCP and DCP were extracted in a supramolecular solvent (SUPRAS) made up of dodecanoic acid aggregates, the extract was dried under a nitrogen stream, the two herbicides dissolved in acetate buffer and the aqueous extract directly injected in the LC–MS/MS system. The recoveries obtained were independent of soil composition and age of herbicide residues. The detection and quantitation limits of the developed method for the determination of R- and S-MCP and R- and S-DCP in soils were 0.03 and 0.1 ng g<sup>-1</sup>, respectively, and the precision, expressed as relative standard deviation ( $n=6$ ), for enantiomer concentrations of 5 and 100 ng g<sup>-1</sup> were in the ranges 4.1–6.1% and 2.9–4.1%. Recoveries for soil samples spiked with enantiomer concentrations within the interval 5–180 ng g<sup>-1</sup> and enantiomeric ratios (ERs) of 1, 3 and 9, ranged between 93 and 104% with standard deviations of the percent recovery varying between 0.3% and 6.0%. Because the SUPRAS can solubilize analytes through different type of interactions (dispersion, dipole–dipole and hydrogen bonds), it could be used to extract a great variety of pesticides (including both polar and non-polar) in soils.

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## 1. Introduction

Enantiospecificity of chiral pollutants is a key factor to consider when assessing their health and environmental risks. Pollutant enantiomers significantly differ in their environmental fate and toxicological effects [1]. They can suffer exclusive or preferential degradation and/or interconversion in the environment [2,3], and their toxicities can differ up to more than 30-fold [1,4]. Consequently, it is essential to have analytical methods able to reliably monitor individual enantiomers of chiral pollutants in the different environmental compartments.

Among chiral pollutants, pesticides are of special concern because of their widespread use and their toxicity, mutagenicity, carcinogenicity and/or endocrine disruption activity. Mecoprop (MCP) and dichlorprop (DCP) are chiral herbicides frequently

found in environmental waters and soils [5–8]. The half-life of these pesticides in soil is from a few days to several weeks, their concentrations ranging from micrograms to nanograms per gram of soil [8]. They have harmful effects on the biotic components of soils and reduce its fertility [9], and, owing to their high water solubility, they are amenable to transport to aquatic systems by run-off and leaching of herbicide-treated soils, and therefore, there is a high risk of contaminating rivers, aquifers and other drinking water sources [8–10].

The presence of a chiral carbon atom in the aliphatic side chain of MCP and DCP gives two enantiomeric forms (R- and S-). Although the R-form is the unique and responsible for their herbicidal activity [11], both MCP and DCP are frequently produced and applied as racemic mixtures. Different degradation rates [2,8,12] and toxicities [13,14] for the R- and S-enantiomers of both herbicides have been reported.

Methods for determining MCP and DCP enantiomers in soils are based on gas chromatography–mass spectrometry (GC–MS) [15,16], liquid chromatography–ultraviolet detection (LC–UV) [17]

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and capillary electrophoresis–ultraviolet detection (CE–UV) [18]. A major handicap associated with the use of MS with LC or CE is the incompatibility of the mobile phases and chiral selectors commonly used in LC and CE, respectively, for chiral resolution of MCPP and DCP. Analytes are extracted using methanol [13,27] or methanol/acetonitrile–water–acetic acid mixtures [16,18] with [17,18] or without [16,15] the assistance of ultrasounds, and extracts are cleaned-up by re-extraction in methylene chloride and concentrated by solvent evaporation. The extraction times and the volumes of organic solvent consumed for sample treatment vary within the intervals 1–2 h and 20–150 mL, respectively, and when GC–MS is used, diazomethane [15] or boron-trifluoride [16] are employed as derivatizing reagents. So, the development of simpler sample treatment methods to speed up sample throughput and save costs is of interest.

In this article, supramolecular solvents (SUPRASs) were firstly evaluated for the microextraction of chiral pollutants in soil samples prior to their enantiomer-specific quantitation by LC–MS. SUPRASs are nanostructured liquids made up of nanometer-sized aggregates produced through a self-assembly process [19]. They are produced from surfactant solutions by changing the temperature [20,21] or pH [22], or by addition of electrolytes [23], cosurfactants [24], amphiphilic counterions [25] or solvents [26,27]. Because of their high extraction efficiency and concentration capability, they have been largely used to extract organic compounds at low concentration levels in both liquid and solid samples [19]. In the environmental field, major applications focused on the analysis of aqueous samples [19], although methods for extracting pollutants such as polycyclic aromatic hydrocarbons (PAHs) [23,28] and surfactants [29] in soils [23,28], sediments [28] and sewage sludges [28,29] have also been reported. Recently, our group has described the use of SUPRAS for the extraction of chiral herbicides in environmental waters prior to LC–MS [30].

The SUPRAS used in this work to extract MCPP and DCP enantiomers in soils consisted of three-dimensional aggregates of dodecanoic acid (DoA). The effect of experimental variables used for SUPRAS synthesis on the composition of the solvent was investigated, and the factors affecting the extraction efficiency of the target analytes and the cleanliness of extracts were optimized. The quality parameters of the developed method were assessed and both fresh and aged spiked samples of soils with variable organic matter content, pH and granulometric composition were analyzed.

## 2. Experimental

### 2.1. Chemicals

All chemical were of analytical reagent-grade and were used as supplied. Dodecanoic acid (DoA), racemic mecoprop (R/S-MCPP, 99.6% purity) and dichlorprop (R/S-DCPP, 99.9% purity), and the pure enantiomers R-MCPP (99.9% purity) and R-DCPP (99.9% purity) were purchased from Fluka (Buchs, Switzerland). Standard solutions (1 g L<sup>-1</sup>) of R/S-MCPP and R/S-DCPP were prepared in methanol and stored under dark conditions at 4 °C. They were stable for at least 2 months. Deuterated R/S-MCPP (D<sub>6</sub>, ring D<sub>3</sub>, methyl D<sub>3</sub>) and R/S-DCPP (D<sub>6</sub>, ring D<sub>3</sub>, 3,3,3-D<sub>3</sub>), used as internal standards (ISs), were supplied by Dr Ehrenstorfer (Augsburg, Germany) as racemic solutions of 100 mg L<sup>-1</sup> (D<sub>6</sub>-R/S-MCPP in acetonitrile and D<sub>6</sub>-R/S-DCPP in acetone; purity = 98.5%). Working solutions containing mixtures of the target analytes (0.5 mg L<sup>-1</sup> of each enantiomer) were prepared weekly in 100 mM acetate buffer at pH 5.0 and those containing mixtures of the ISs (0.1 mg L<sup>-1</sup> of each enantiomer) were prepared in both methanol and 100 mM acetate buffer at pH 5.0. Methanolic IS solutions were used to

spike soils before their analysis and the aqueous ones for preparing calibration standards. Tetrahydrofuran (THF), hydrochloric and acetic acid, ammonia, formic acid and sodium acetate were purchased from Panreac (Barcelona, Spain) and LC-grade methanol from Sigma-Aldrich (Steinheim, Germany). Ultra-high-quality water was obtained from a Milli-Q water purification system (Millipore, Madrid, Spain).

### 2.2. Apparatus

The LC–MS system used was a hybrid triple quadrupole/linear ion trap Applied Biosystems MSD Sciex 4000QTRAP (Applied Biosystems, Foster City, CA, USA) coupled to a liquid chromatograph Agilent HP 1200 Series (Agilent Technologies, Palo Alto, CA, USA) with a TurbolonSpray (TIS) interface. All data were acquired and processed using Analyst 1.5.1 Software. MCPP and DCP enantiomers were separated on a chiral column Nucleodex α-PM (alpha cyclodextrin permethylated stationary-phase, 200 mm × 4.0 mm, 5 μm) from Macherey-Nagel (Düren, Germany). A magnetic stirrer Basicmagmix from Ovan (Barcelona, Spain) and a digitally regulated centrifuge Mixtasel equipped with an angle rotor 4 × 100 mL from JP-Selecta (Abrera, Spain) were used for SUPRAS production. A multi-position magnetic stirrer RO 10 power IKAMAG<sup>®</sup> from IKA<sup>®</sup>-Werke GmbH & Co. KG. (Staufen, Germany), a vortex-shaker REAX Top equipped with an attachment for 10 microtubes from Heidolph (Schwabach, Germany) and a high speed brushless centrifuge MPW-350R equipped with an angle rotor 36 × 2.2/1.5 mL from MPW Med-Instruments (Warszawa, Poland), were used for sample treatment.

### 2.3. Extraction efficiency studies

The effect of experimental variables on the efficiency of the microextraction of the racemic herbicides from soil was assessed by extracting 200–1200 mg of a sandy loam soil containing 3.8% organic matter (sample A in Table 1) spiked with 100 ng g<sup>-1</sup> of racemic MCPP and DCP, and determining the recoveries and the method quantitation limits for the R- and S-enantiomers of both pesticides. Method quantitation limits (MQLs) were calculated from the equation  $MQL = (100/R) \text{ SSR BSR IQL}$ , where *R* is the recovery obtained in the SUPRAS-based microextraction, SSR the sample amount/SUPRAS volume ratio, BSR the acetate buffer volume/SUPRAS volume ratio used in the back-extraction step (see Section 2.4.3) and IQL the instrumental quantitation limit for the herbicides (0.05 ng mL<sup>-1</sup>). The variables investigated were composition and volume of SUPRAS, sample amount, temperature, time for vortex-shake and centrifugation and rotation rate. The influence of experimental variables on the amount of humic substances extracted in the SUPRAS as well as the effect of the time of contact between the analytes and the soil samples on

**Table 1**  
Physico-chemical properties of the soils tested.

Soil sample	Organic matter (%)	pH	Sand (%)	Silt (%)	Clay (%)	Textural class <sup>a</sup>
A	3.8	6.1	73	15	12	Sandy loam
B	1.3	7.9	58	13	29	Sandy clay loam
C	1.2	7.8	18	16	66	Clay
D	0.9	6.4	68	7	25	Sandy clay loam
E	0.8	7.9	10	44	46	Silty clay
F	0.5	7.0	80	6	14	Sandy loam

<sup>a</sup> USDA/FAO classification system [United States Department of Agriculture (USDA). Soil survey manual. U.S. Department. Agriculture Handbook No. 18 (1951) Washington, DC. Food and Agriculture Organization (FAO). Guidelines for soil description, 3rd edn. FAO/ISRIC (1990) Rome].

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