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ENANTIOMER-ESPECIFIC DETERMINATION OF CHIRAL PESTICIDES IN NATURAL WATERS BY MICROEXTRACTION IN A SUPRAMOLECULAR SOLVENT AND LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Quantitation of individual enantiomers of chiral pesticides in aqueous environmental samples is a difficult task and only a few methods providing the selectivity and sensitivity (quantitation limits at the low ng L^{-1} level) required have been reported. These methods are based on the liquid-liquid or solid phase extraction (SPE) of the target pesticides, the clean-up and concentration of the extracts, and the chiral liquid (LC) or gas (GC) chromatographic separation and mass spectrometry (MS) detection of the enantiomers.

In this work, supramolecular solvent-based microextraction (SUSME) was used to simplify sample treatment in the enantiomer-specific determination of pesticides. A method for the simultaneous quantitation of the R- and S-enantiomers of mecoprop (MCCP) and dichlorprop (DCPP) in natural waters was developed. MCPP and DCPP are herbicides widely used that can easily reach natural waters owing to their high water-solubility and soil mobility. They are frequently employed as racemates, but in the environment, their enantiomeric ratio (ER, defined as the molar ratio of R to S enantiomers) is usually different from one as a result of differences in the degradation rates between the R- and S-enantiomers and the occurrence of interconversion reactions. Differential toxicological effects of the R- and S-enantiomers of MCPP and DCPP on aquatic organisms and plants have been also reported. Therefore, determination of individual enantiomers will provide a more adequate basis for assessing the risk of these chiral pollutants in the environment.

Reported method for the stereoselective determination of MCPP and DCPP in natural waters at concentrations at the low ng L^{-1} level are based on GC with MS detection. No methods based on LC-MS have been described so far. Analytes are extracted from samples by repetitive (n=3) liquid-liquid extraction with dichloromethane or solid phase extraction (SPE) on polymeric sorbents, the extracts are subjected to derivatization to obtain methyl or pentafluorobenzyl esters, cleaned-up by liquid-liquid back-extraction or SPE on silica, and concentrated by solvent evaporation.

SUSME and LC-MS were combined in this research to develop a simple a rapid method for the sensitive and selective determination of the R- and S-enantiomers of DCPP and MCPP in underground and river waters. The method involved the extraction of the herbicides in a supramolecular solvent made up of reverse aggregates of dodecanoic acid, analyte re-extraction in acetate buffer (pH = 5.0), separation of the target enantiomers on a chiral column of permethylated α-cyclodextrin under isocratic conditions, and detection of the daughter ions (m/z = 140.9 and 160.6 for MCPP and DCPP, respectively) using a triple quadrupole mass spectrometer equipped with a TurboIonSpray source operating in the negative ion mode. The quantitation limits were 1 ng L^{-1} for R- and S-MCPP, and 4 ng L^{-1} for R- and S-MCPP, and the precision, expressed as relative standard deviation (n=6) were lower than 3 % at concentrations at the low ng L^{-1} level.