



Enantioselective stable isotope analysis (ESIA) of polar Herbicides

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The complexity of aquatic systems makes it challenging to assess the environmental fate of chiral micropollutants. As an example, chiral herbicides are frequently detected in the environment (Buser and Muller, 1998); however, hydrological data is needed to determine their degradability from concentration measurements. Otherwise declining concentrations cannot unequivocally be attributed to degradation, but could also be caused by dilution effects. In contrast, isotope ratios or enantiomeric ratios are elegant alternatives that are independent of dilution and can even deliver insights into reaction mechanisms. To combine the advantages of both approaches we developed an enantioselective stable isotope analysis (ESIA) method to investigate the fate of the chiral herbicides 4-CPP ((RS)-2-(4-chlorophenoxy)-propionic acid), mecoprop (2-(4-Chloro-2-methylphenoxy)-propionic acid) and dichlorprop (2-(2,4-Dichlorophenoxy)-propionic acid). After testing the applicable concentration range of the method, enantioselective isotope fractionation was investigated by microbial degradation using dichlorprop as a model compound.

The method uses enantioselective gas-chromatography (GC) to separate enantiomers. Subsequently samples are combusted online to CO₂ and carbon isotope ratios are determined for each enantiomer by isotope-ratio-mass-spectrometry (IRMS). Because the analytes contain a polar carboxyl-group, samples were derivatised prior to GC-IRMS analysis with methanolic BF₃ solution. Precise carbon isotope analysis ($2\sigma \leq 0.5\text{‰}$) was achieved with a high sensitivity of $\geq 7\text{ ng C}$ that is needed on column for one analysis.

Microbial degradation of the model compound dichlorprop was conducted with *Delftia acidovorans* MC1 and pronounced enantiomer fractionation, but no isotope fractionation was detected. The absence of isotope fractionation can be explained by two scenarios: either the degrading enzyme has no isotopic preference, or another step in the reaction without an isotopic preference was rate determining. Our findings are in contrast to previously reported results for the degradation of α -hexachlorocyclohexane (Badea et al., 2012), where isotope fractionation, but no enantiomeric fractionation was observed. Hence the two lines of evidence seem to be independent of each other. Enhanced insight maybe provided when both effects appear simultaneously, as shown downstream of a landfill site under anaerobic conditions for the chiral herbicide 4-CPP (Milosevic et al., 2013).

Buser HR, Muller MD (1998): Occurrence and transformation reactions of chiral and achiral phenoxyalkanoic acid herbicides in lakes and rivers in Switzerland. *Environmental Science & Technology* 32 (5):626-633.

Badea S-L, Vogt C, Gehre M, Fischer A, Danet A-F, Richnow H-H (2011): Development of an enantiomer-specific stable carbon isotope analysis (ESIA) method for assessing the fate of alpha-hexachlorocyclohexane in the environment. *Rapid Communications in Mass Spectrometry* 25 (10):1363-1372.

Milosevic N, Qiu S, Elsner M, Einsiedl F, Maier MP, Bensch HKV, Albrechtsen HJ, Bjerg PL (2013): Combined isotope and enantiomer analysis to assess the fate of phenoxy acids in a heterogeneous geologic setting at an old landfill. *Water Research* 47 (2): 637-649.