

# Chiral Pesticides: Enantioselective Degradation and Interconversion of Enantiomers in Soil

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## Introduction

Enantiomers commonly differ with respect to biological properties. This may concern a desired biological activity, but also undesired, human or environmental toxicological effects.

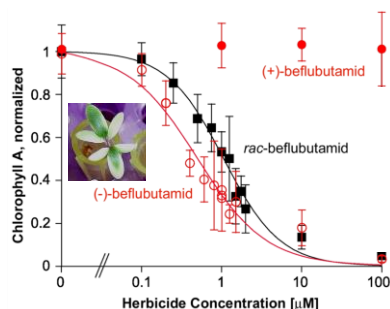


Fig 1: Herbicidal activity of (-), rac-, and (+)-bifluthutamid in miniaturized biotests with garden cress

Most chiral pesticides are applied as racemic mixtures. According to EU-Reg. 1107/2009, pesticides are classified as candidates for substitution if they contain a significant proportion of non-active isomers. However, there is currently no guidance on what additional studies are required for registration.

## Enantioselective Analytical Methods

Enantiomer separation is often achieved with chiral GC, but methods are limited to volatile compounds. Derivatization of less volatile compounds may make them amenable to GC, e.g., ethylation of metalaxyl-acid to an ethyl ester, which allows distinction from metalaxyl (a methyl ester, Fig 3, right).

For polar compounds, LC is suited, but enantiomer separation is typically achieved with normal-phase chromatography. However, solvents such as hexane and isopropanol are not suited for coupling with MS. Nevertheless, certain chiral LC phases are compatible with reversed-phase solvents as shown below:

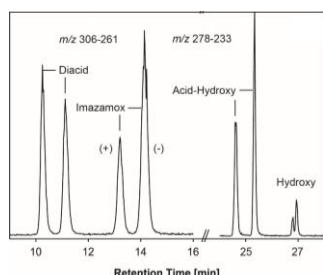


Fig 2: Enantiomer separation of imazamox and three metabolites with reversed-phase, chiral LC-MS/MS. Chromatogram after 10 d incubation in a soil with pH 6.7

## Enantioselective Degradation in Soil

Microbial degradation of pesticides may be enantioselective. For example, in certain soils, *R*-metalaxyl was degraded more than 3x faster than *S*-metalaxyl:

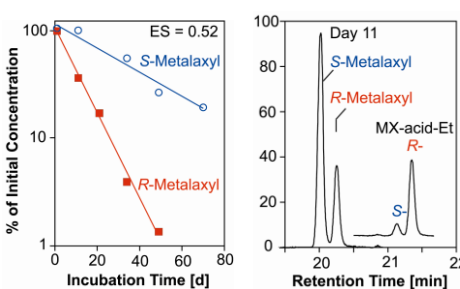


Fig 3: Preferential degradation of *R*-metalaxyl in a soil with pH 7.1 (left) and composition of residues from day 11 enriched with *S*-metalaxyl and the major metabolite *R*-metalaxyl-acid (right)

However, such findings can usually not be extrapolated to other soils. In strongly acidic soils, the enantioselectivity was just reversed:

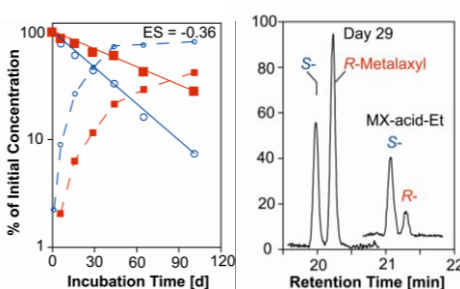


Fig 4: Preferential degradation of *S*-metalaxyl in a soil with pH 3.6 (left) and composition of residues from day 29 enriched with *R*-metalaxyl and the major metabolite *S*-metalaxyl-acid (right)

Enantioselectivity was linked to soil pH (Fig 5). Similar correlations were found for dichlorprop, mecoprop, or epoxiconazole, but the underlying mechanism is unknown.

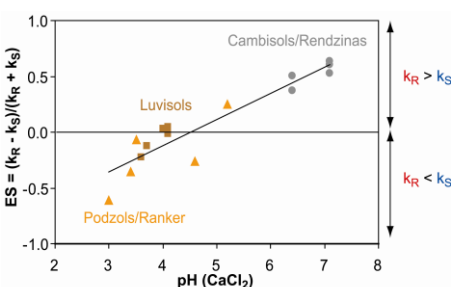


Fig 5: Preferential degradation of *R*-metalaxyl at pH>5, similar rates for both enantiomers at pH 4-5, and preferential degradation of *S*-metalaxyl at pH<4

## Interconversion of Enantiomers in Soil

The enantiomer composition may not only change due to preferential degradation of one enantiomer, but may also be affected by interconversion of enantiomers. Extremely fast conversion was observed for FOP-herbicides. This process is biologically mediated:

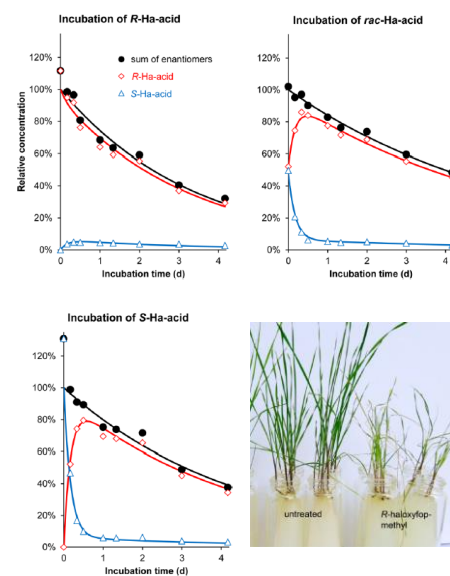


Fig 6: Rapid conversion of *S*-haloxyfop to *R*-haloxyfop in a soil with pH 5.5. No interconversion of enantiomers is observed in weeds, e.g., blackgrass.

## Conclusions

- The fate of individual stereoisomers can differ vastly in soils and may depend on soil properties such as pH.
- To adequately describe the degradation behavior, experiments with racemic mixtures and, additionally, with individual stereoisomers are required.
- If chiral metabolites are to be considered, direct incubation of metabolites (and their pure stereoisomers) may be necessary.

## References

- Buerge IJ, Poiger T, Müller MD, Buser HR, Enantioselective degradation of metalaxyl in soils: chiral preference changes with soil pH. *Environ. Sci. Technol.* 2003, 37, 2668-2674.
- Buerge IJ, Poiger T, Müller MD, Buser HR, Influence of pH on the stereoselective degradation of the fungicides epoxiconazole and cyproconazole in soils. *Environ. Sci. Technol.* 2006, 40, 5443-5450.
- Buerge IJ, Bächli A, De Jeuffrey JP, Müller MD, Poiger T, The chiral herbicide beflubutamid (I): isolation of pure enantiomers by HPLC, herbicidal activity of enantiomers, and analysis by enantioselective GC-MS. *Environ. Sci. Technol.* 2013, 47, 6806-6811.
- Poiger T, Müller MD, Buser HR, Buerge IJ, Environmental behavior of the chiral herbicide haloxyfop. 1. rapid and preferential interconversion of the enantiomers in soil. *J. Agric. Food Chem.* 2015, 63, 2583-2590.
- Buerge IJ, Bächli A, Heller WE, Keller M, Poiger T, Environmental behavior of the chiral herbicide haloxyfop. 2. unchanged enantiomer composition in blackgrass (*Alopecurus myosuroides*) and garden cress (*Lepidium sativum*). *J. Agric. Food Chem.* 2015, 63, 2591-2596.



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