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Degradation and Isomerization of Haloxyfop Enantiomers in Soil

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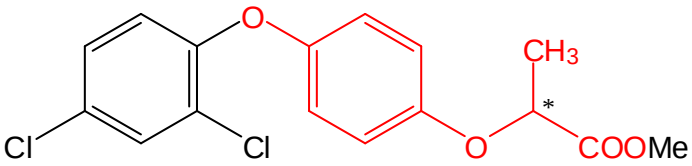
The aryloxyphenoxypropionic acids - „FOPs“

- family of herbicides developed in the 1980 to 1990s
- mostly post-emergent use in soybean, canola, vegetable growing….
- typical field rates around 100 - 200 g a.i. / ha
- interfere with the synthesis of fatty acids in susceptible grass weeds via inhibition of Acetyl-CoA-Carboxylase (ACCase)

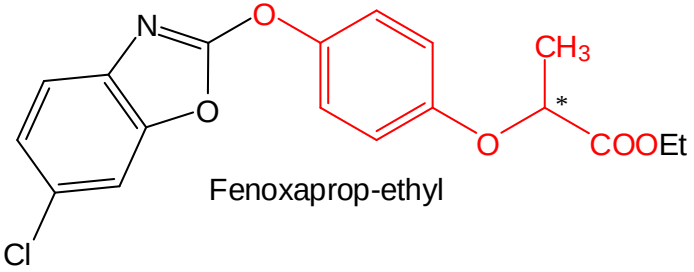
	Chemical family	Active ingredients
Inhibition of acetyl CoA carboxylase (ACCase)	Aryloxyphenoxy-propionate ‘FOPs’	haloxyfop-R-methyl clodinafop-propargyl
	Cyclohexanedione ‘DIMs’	clethodim cycloxydim

Selected aryloxyphenoxy propionate herbicides

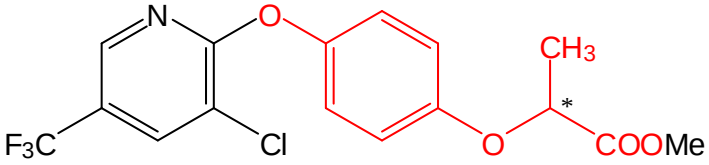
- applied as esters, after uptake in plants rapid hydrolysis to active acid
- optically active carbon atom, only *R*-isomers show herbicidal activity



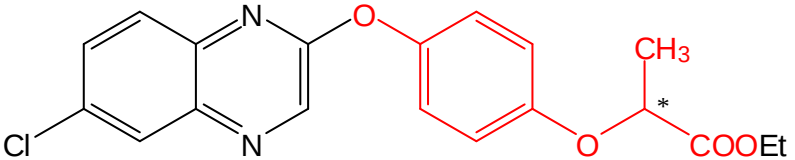
Diclofop-methyl



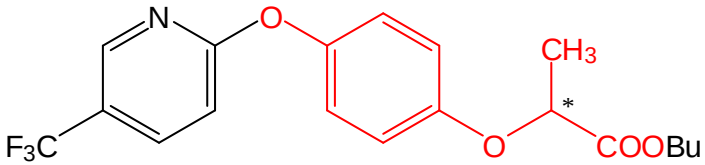
Fenoxaprop-ethyl



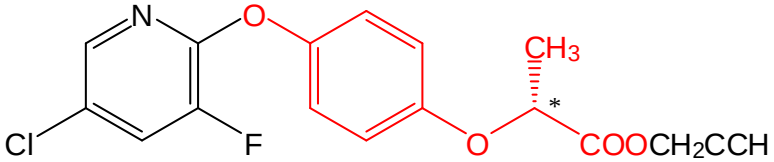
Haloxyfop-methyl



Quizalofop-ethyl

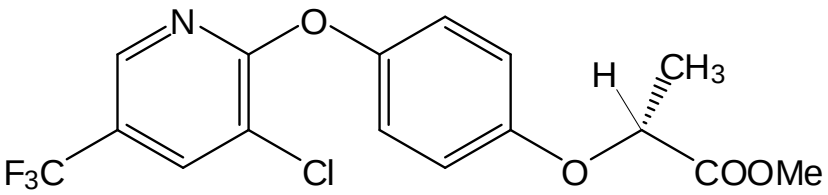


Fluazifop-butyl

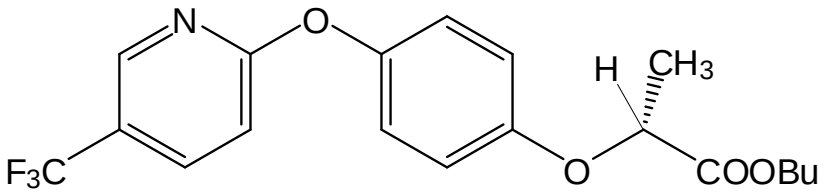


Clodinafop-propargyl

The enantioenriched FOPs: the „P“, e.g.

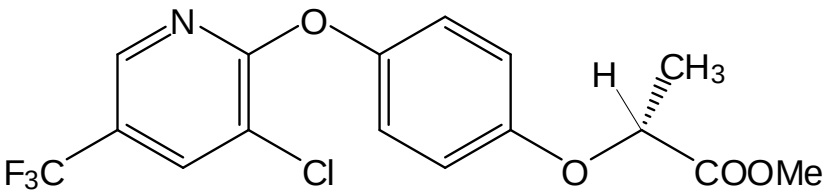


Haloxyfop-P-methyl

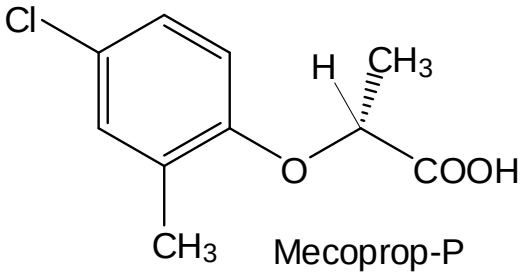


Fluazifop-P-butyl

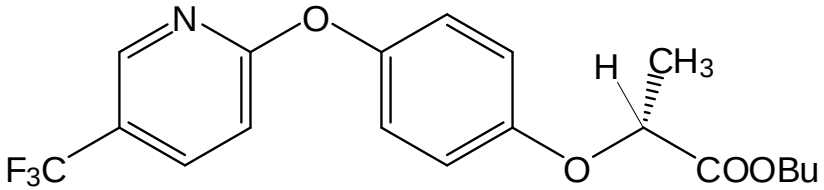
..... not to be confused with the „PROPs“



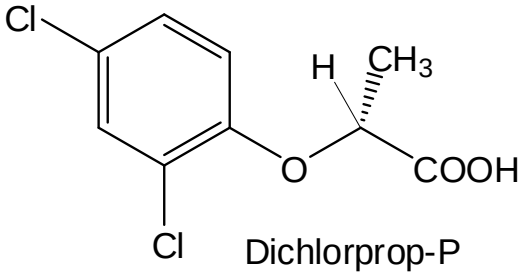
Haloxyfop-P-methyl



Mecoprop-P



Fluazifop-P-butyl



Dichlorprop-P

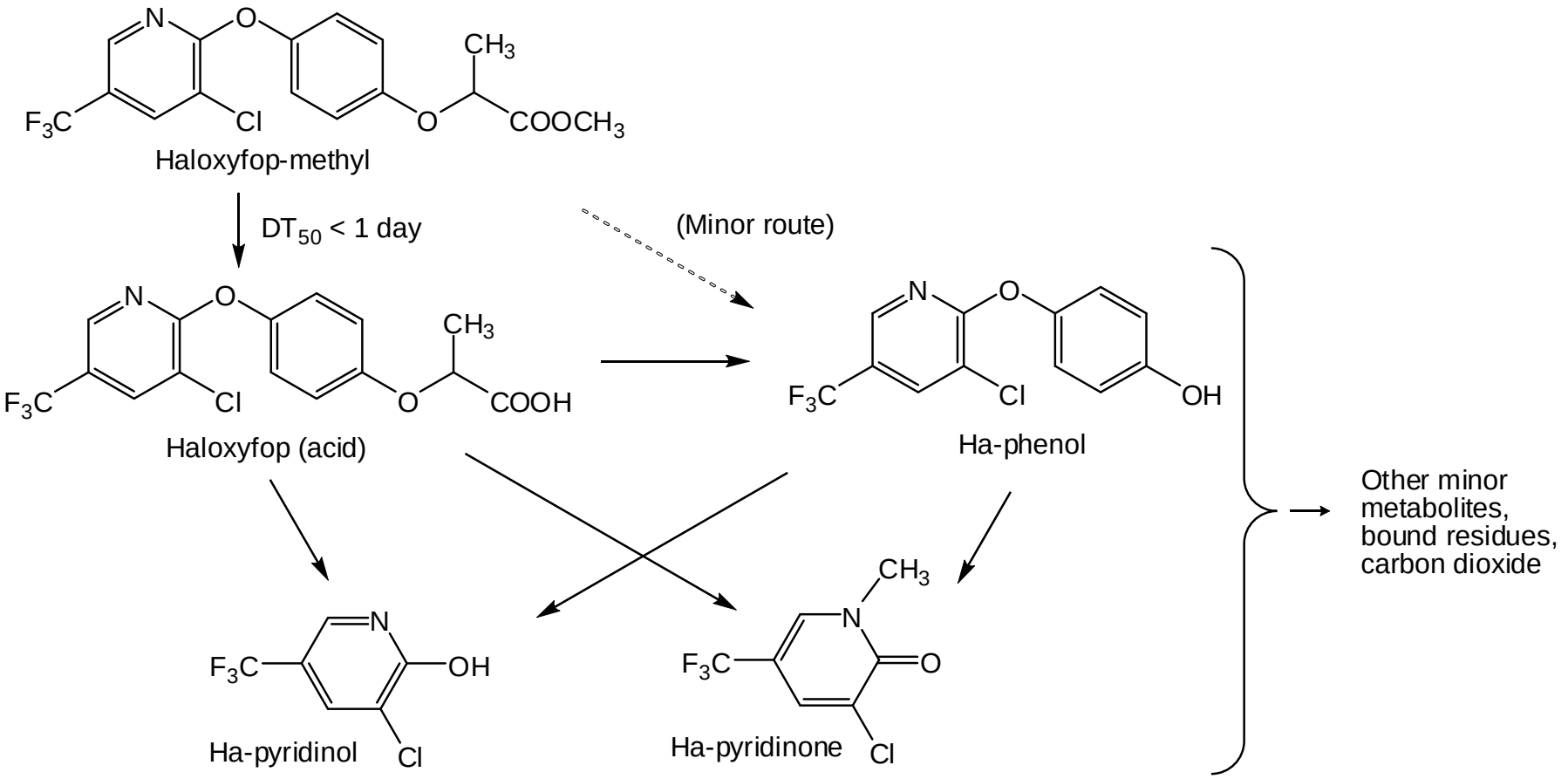
Aryloxypropionic acids:

- ACCase inhibitors
- grass weeds

Phenoxy acids:

- synthetic auxins (hormonal activity)
- broad leaved weeds

Degradation pathway of haloxyfop-methyl in soil



Source: Draft Assessment Report for the EU risk assessment of haloxyfop-P, (RMS Denmark, 2005)

Project scope

- investigate the
  - enantioselective degradation of haloxyfop in soil
  - chiral stability of haloxyfop enantiomers
- determine the influence of soil parameters (particularly pH) on enantioselectivity

Environ. Sci. Technol. **2003**, *37*, 2668−2674

Enantioselective Degradation of Metalaxyl in Soils: Chiral Preference Changes with Soil pH

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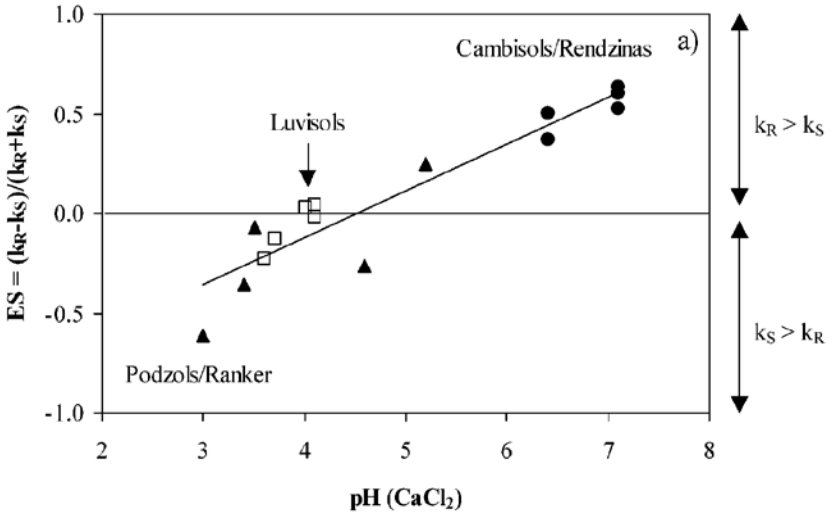
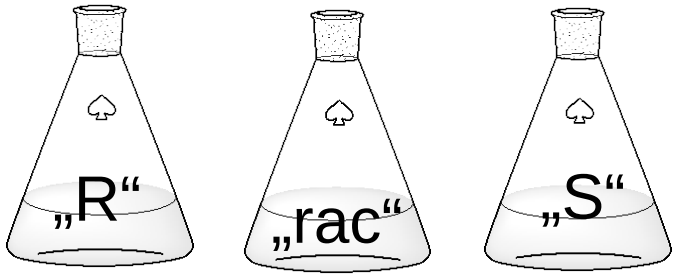


Incubation experiments

- 3 different soils

Soil	Site name	Altitude [m a.s.l.]	Land use	Soil type	pH ($CaCl_2$)	Organic carbon [%]
1	Realp	2120	Alpine pasture	Clay	4.0	18.1
2	Neualp	955	Fertilized pasture	-	5.5	4.2
3	Dübendorf	440	Arable land	-	7.2	1.9

- 1 sterile control
- 1 soil with ≈ 50% water replaced with D_2O
- separate experiments with (R)-, rac- and (S)-haloxyfop in each soil



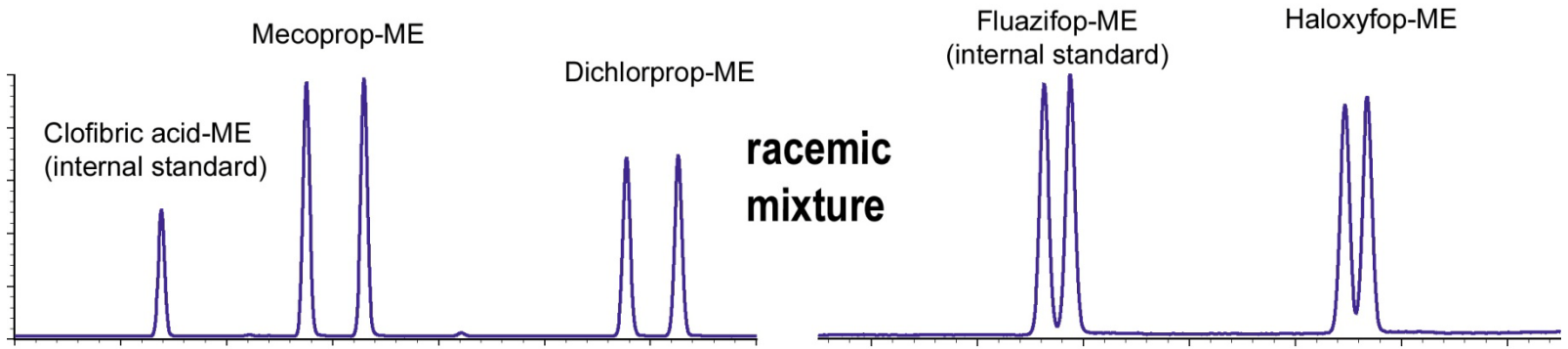
Sample preparation and analysis

- soil extraction with methanol
- rac-fluazifop added as internal standard
- acidified extract is partitioned with dichloromethane
- target compounds methylated with diazomethane
- analysis by enantioselective GC-MS

  (column: 0.25 mm i.D. x 20m x 0.15 µm film OV 1701 with 15% permethyl β-cyclodextrin)

Enantioselective GC-MS

Chromatograms of target compounds extracted from sterile soil :

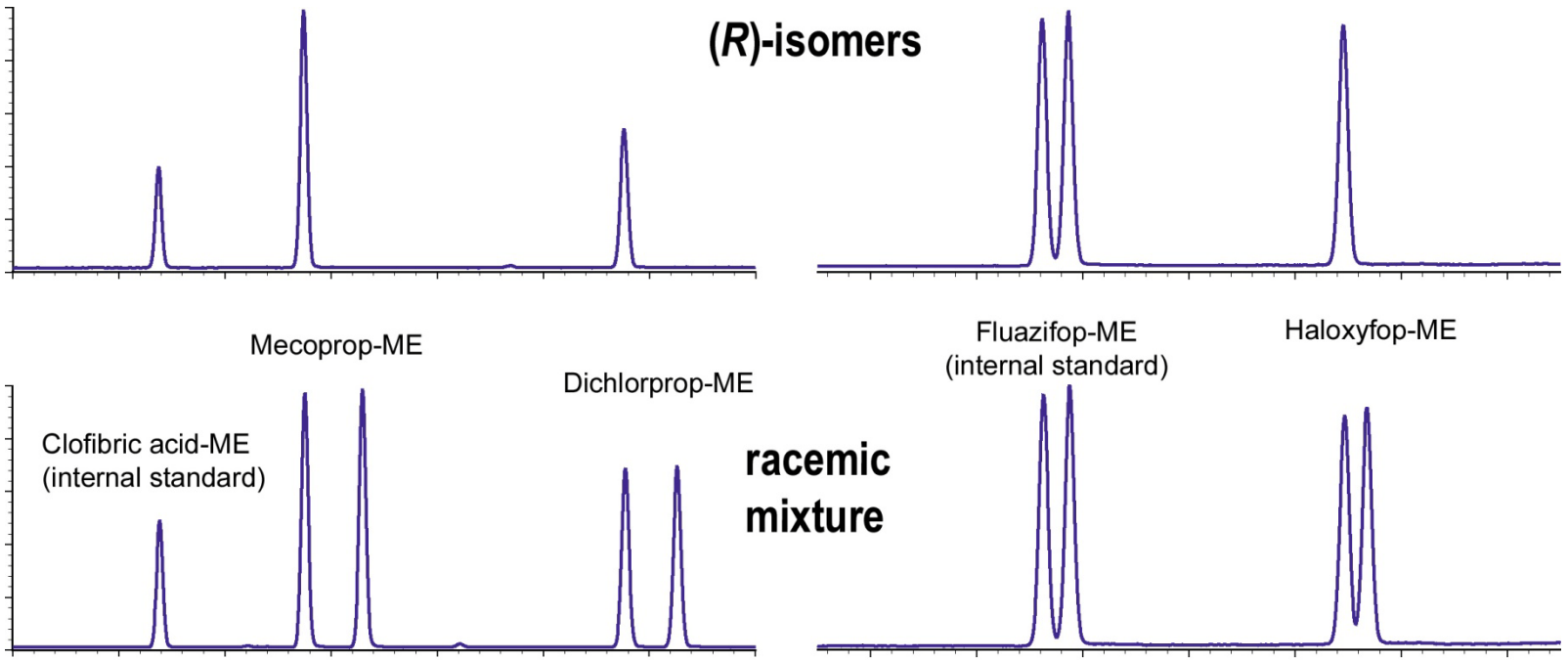


m/z 228 + 248

m/z 341 + 375

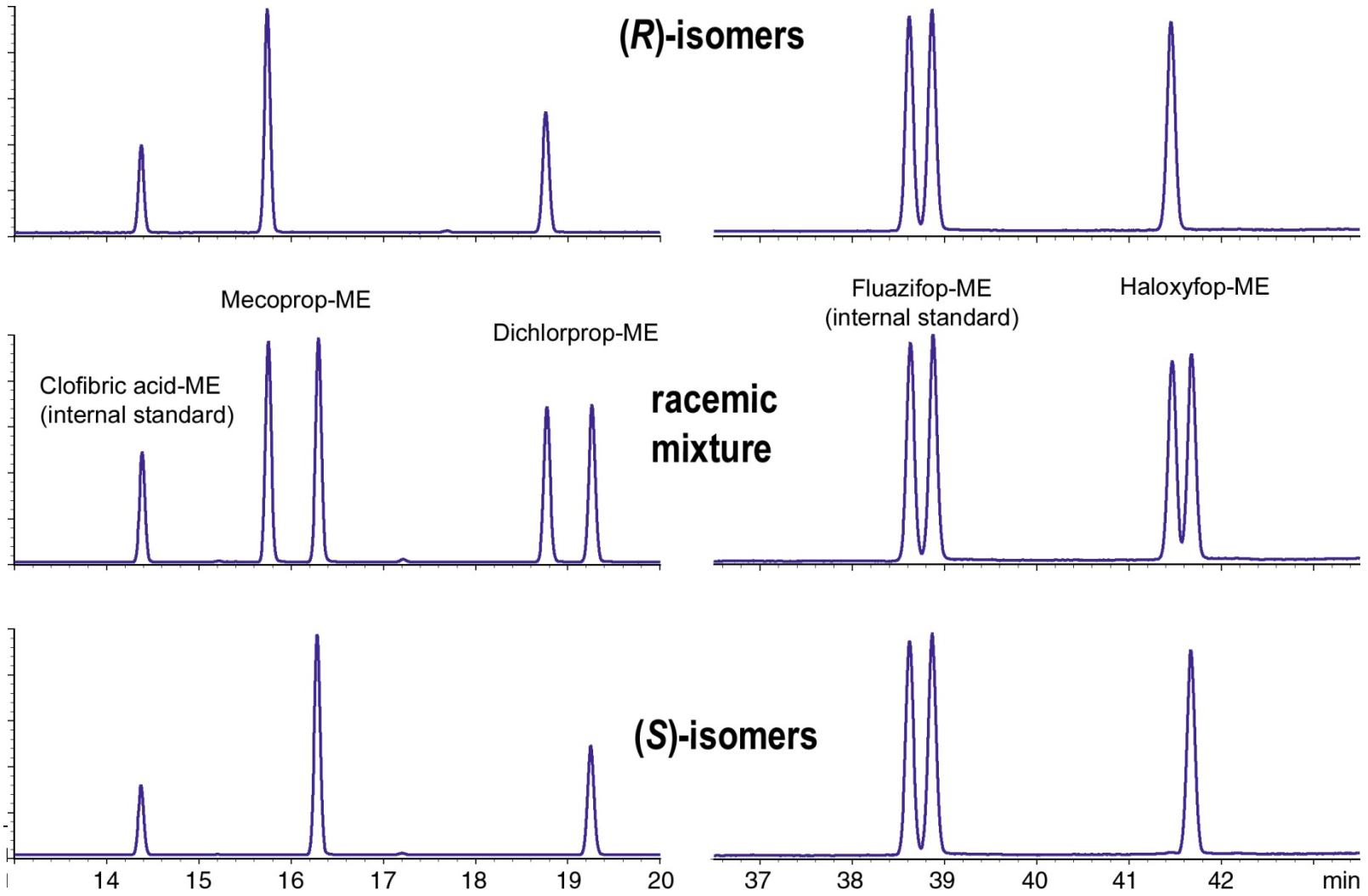
Enantioselective GC-MS

Chromatograms of target compounds extracted from sterile soil :



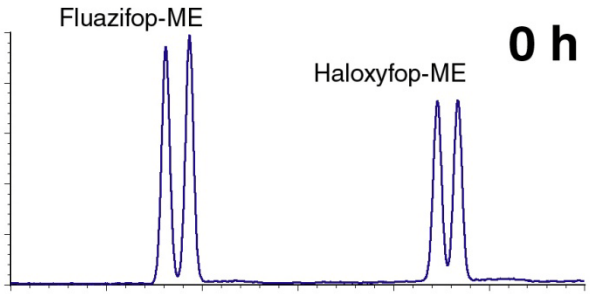
Enantioselective GC-MS

Chromatograms of target compounds extracted from sterile soil :

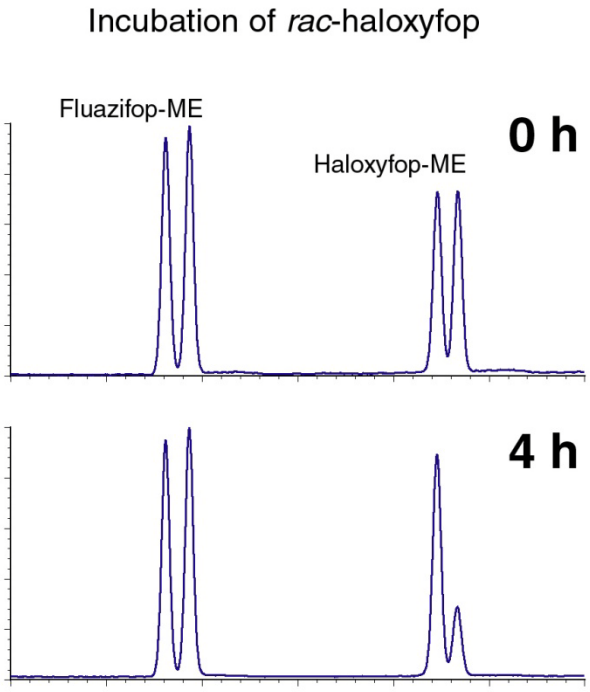


Rapid isomerization of haloxyfop enantiomers in soil

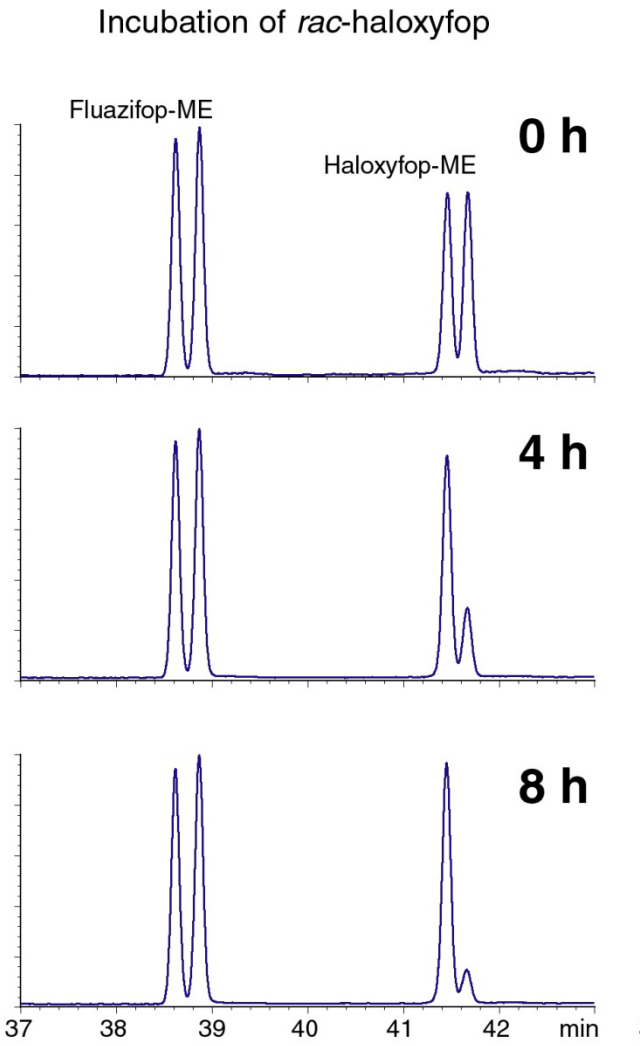
Incubation of *rac*-haloxyfop



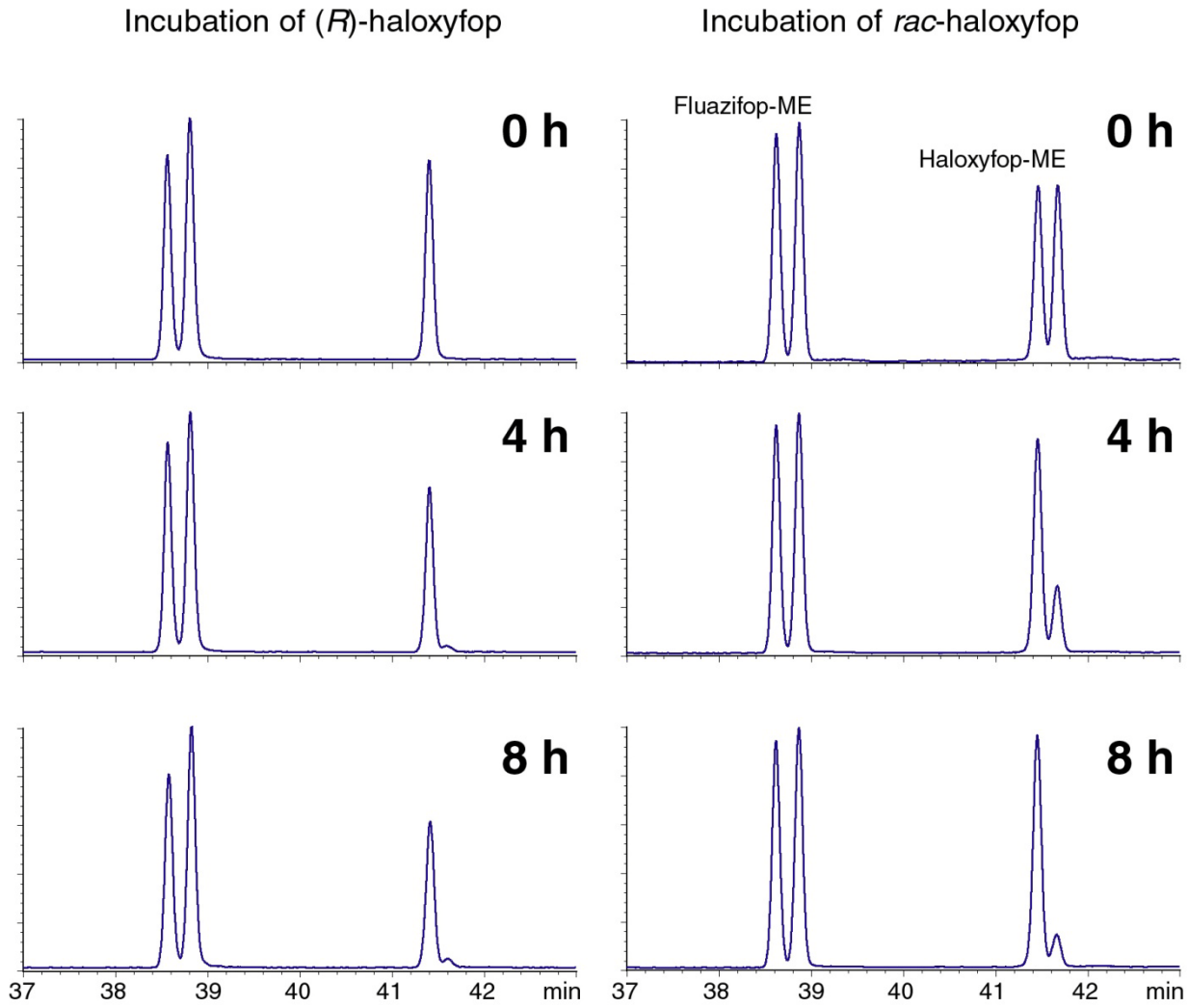
Rapid isomerization of haloxyfop enantiomers in soil



Rapid isomerization of haloxyfop enantiomers in soil

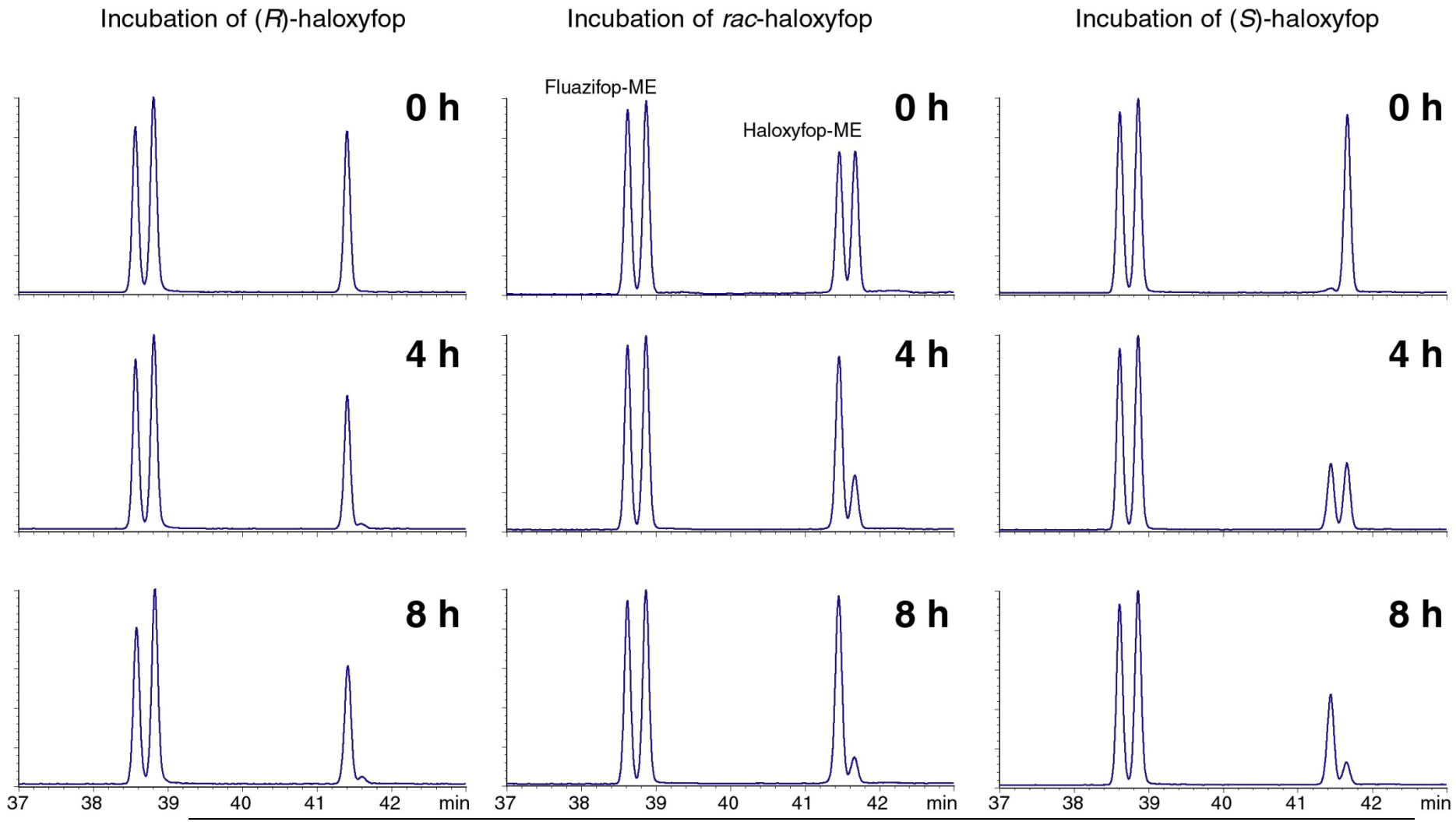


Rapid isomerization of haloxyfop enantiomers in soil



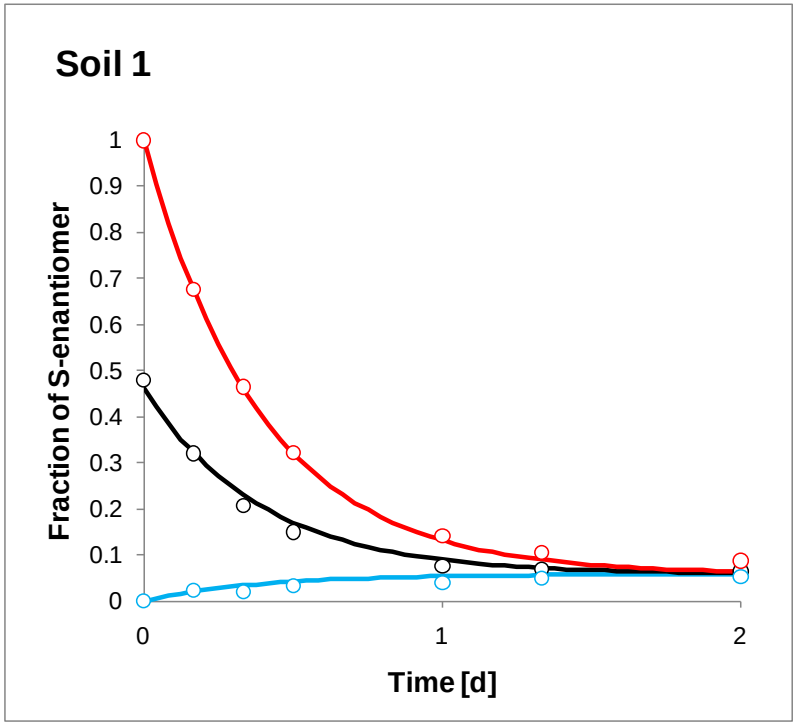
Degradation and racemization of haloxyfop enantiomers in soil
M.D. Müller, June 2010

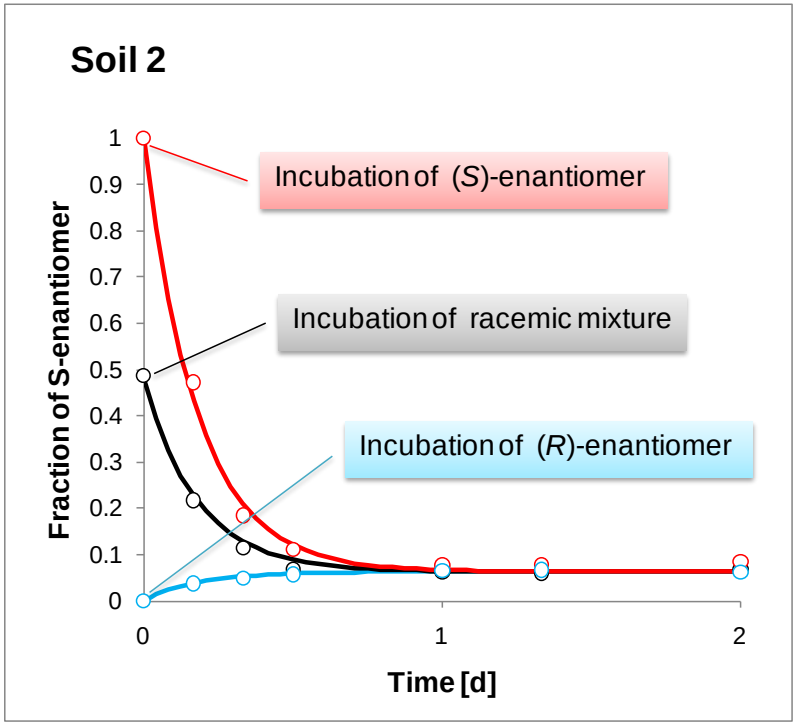
Rapid isomerization of haloxyfop enantiomers in soil



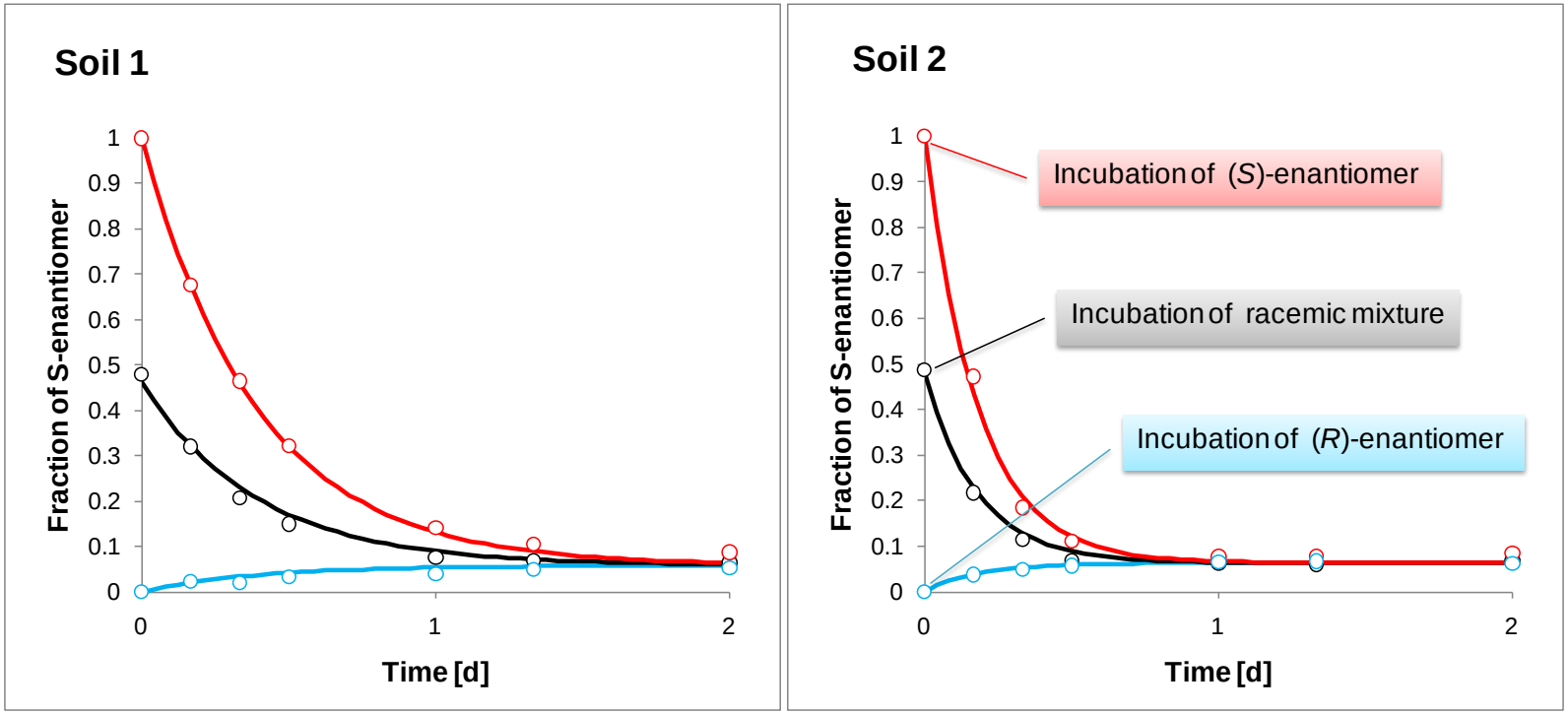
Degradation and racemization of haloxyfop enantiomers in soil
M.D. Müller, June 2010

Haloxyfop isomerization kinetics in soil
Enantiomeric fraction



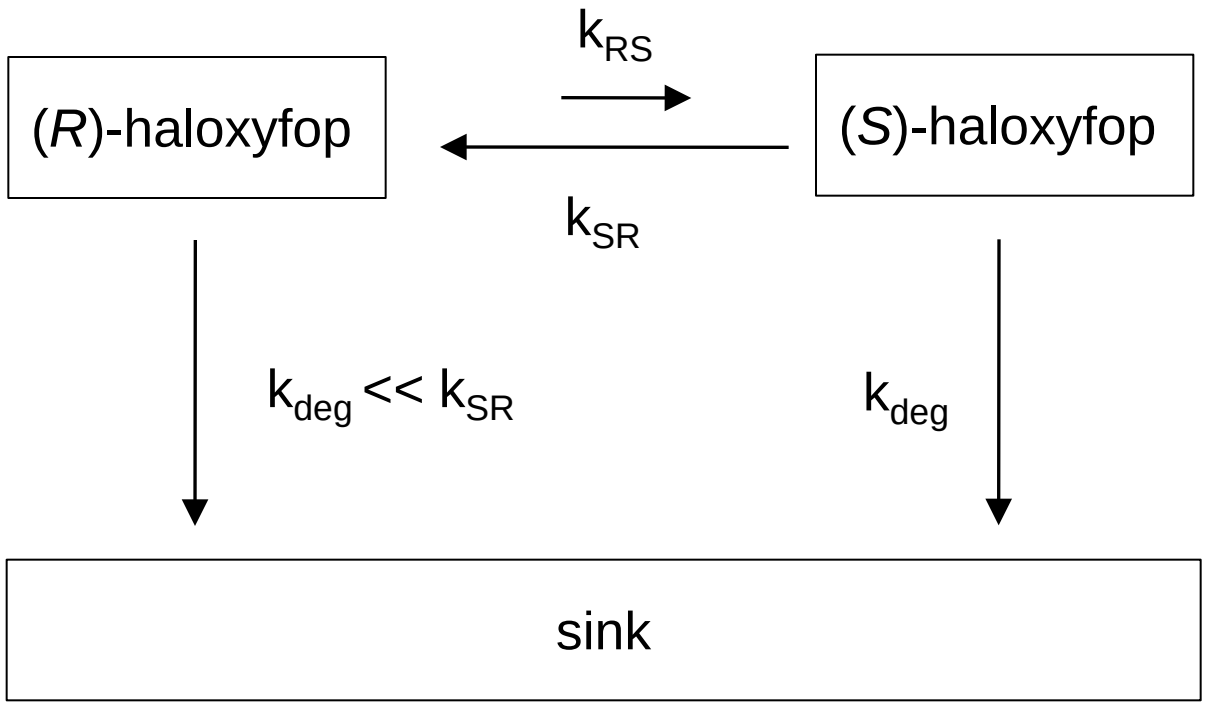


Haloxyfop isomerization kinetics in soil

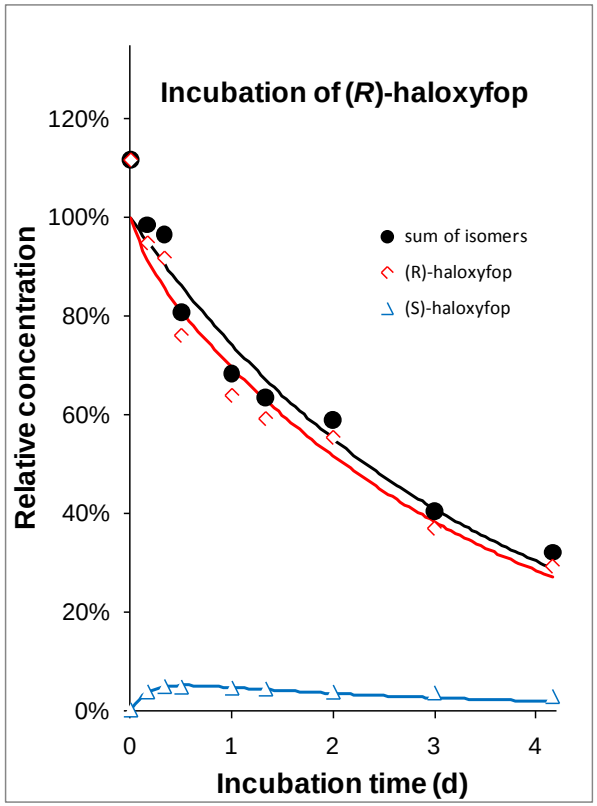


➢ no isomerization in sterile soil !

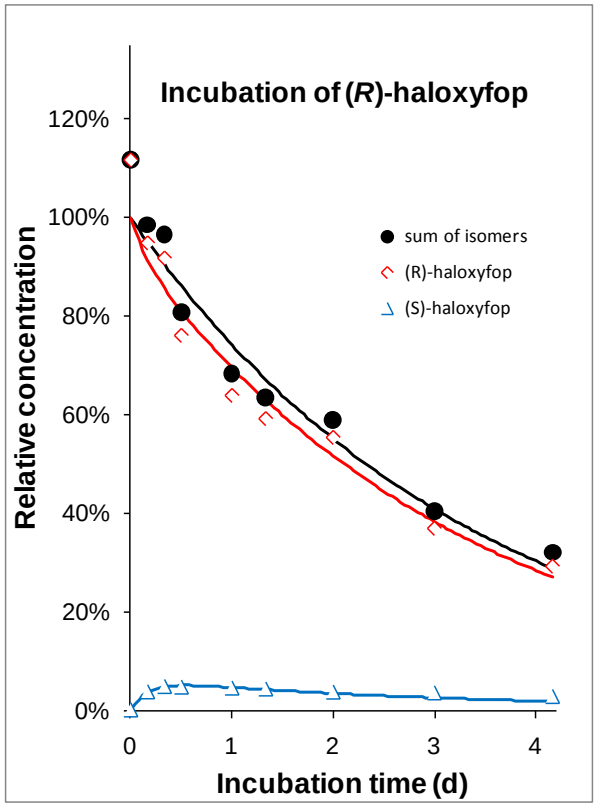
Conceptual model for curve fitting

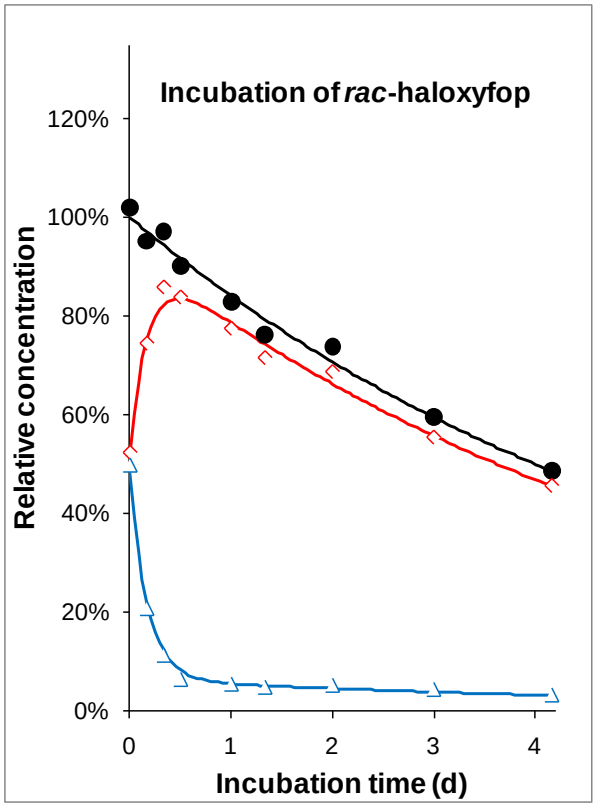


Degradation kinetics

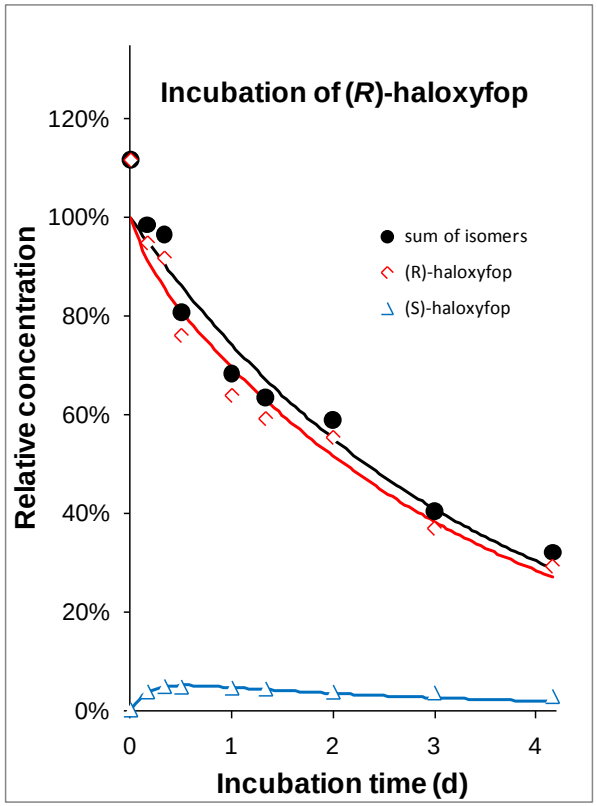


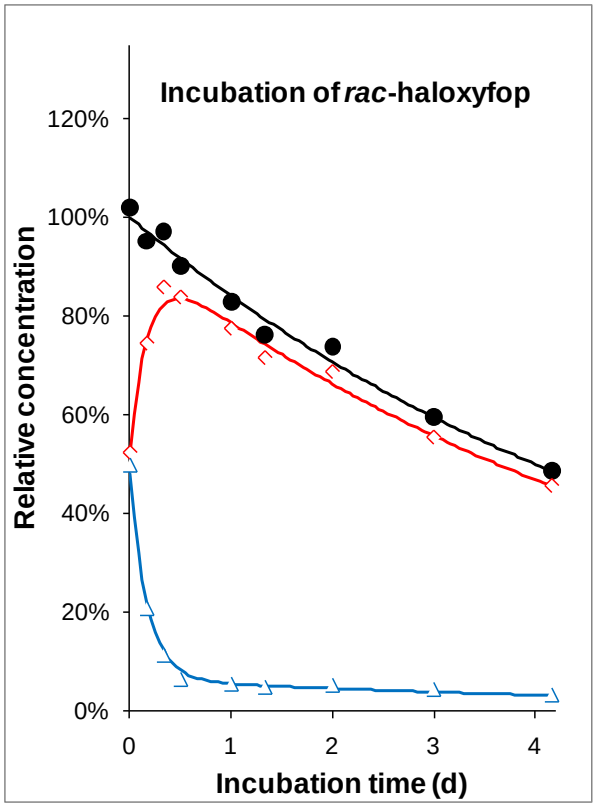
Degradation kinetics

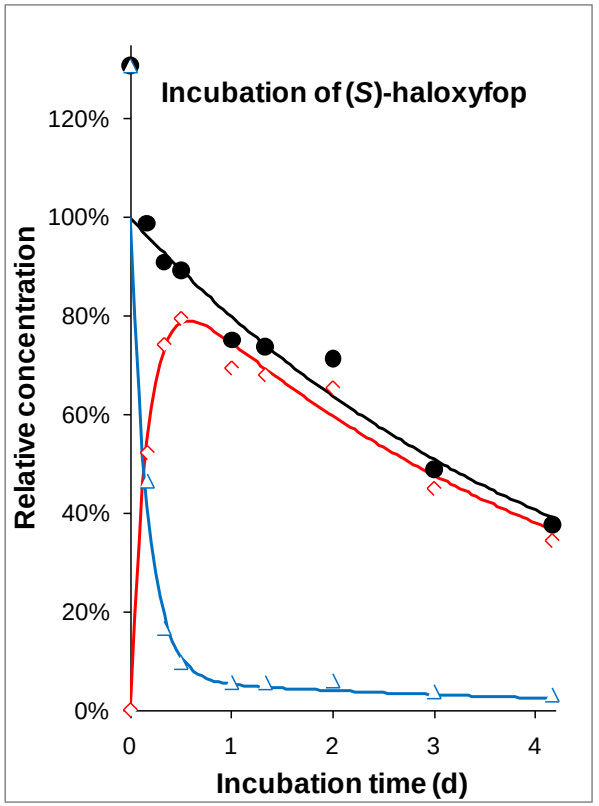




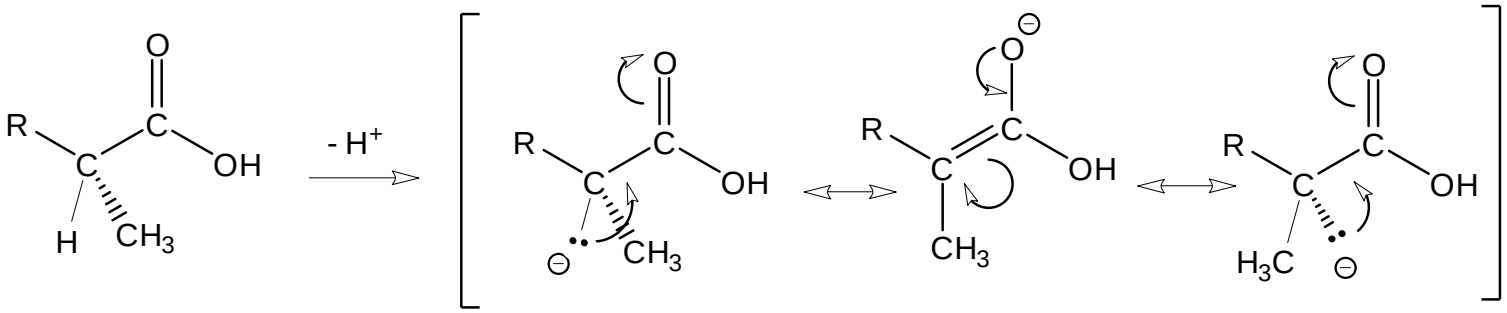
Degradation kinetics



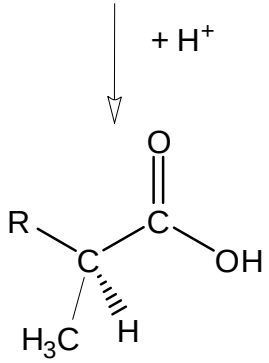




Mechanistic considerations

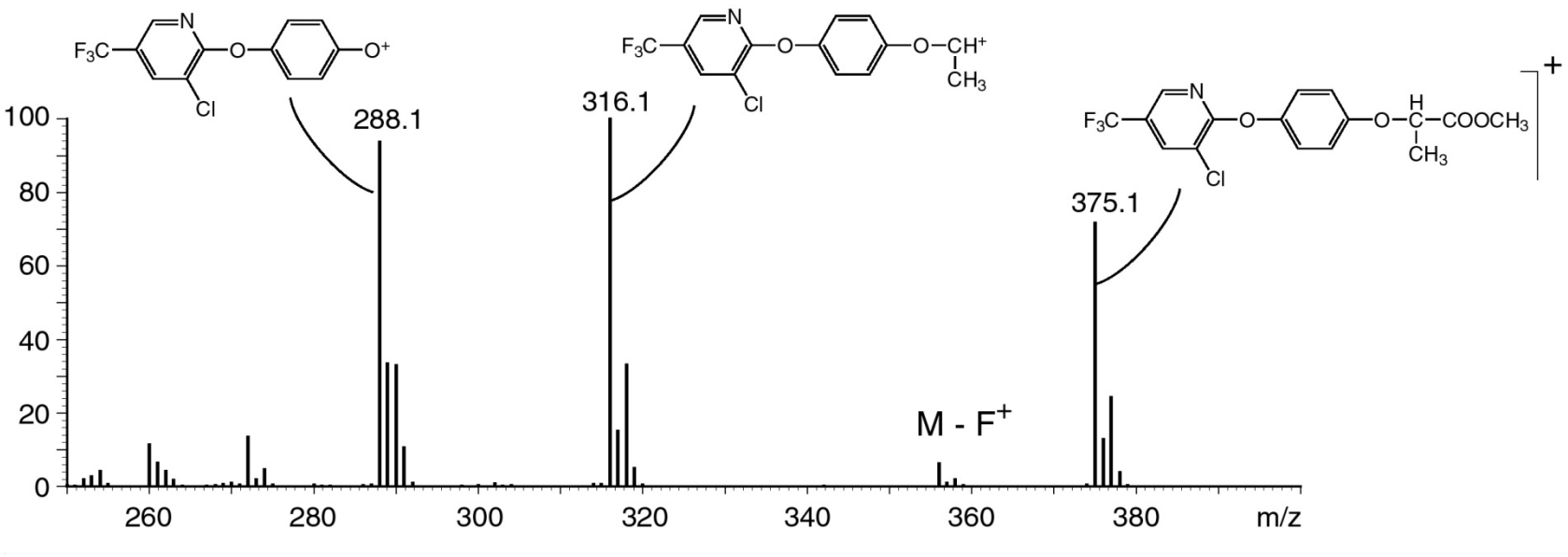


(*S*)-Haloxyfop (*S*)-carbanion planar anion (*R*)-carbanion



(*R*)-Haloxyfop

Mass spectra showing rapid H-D exchange



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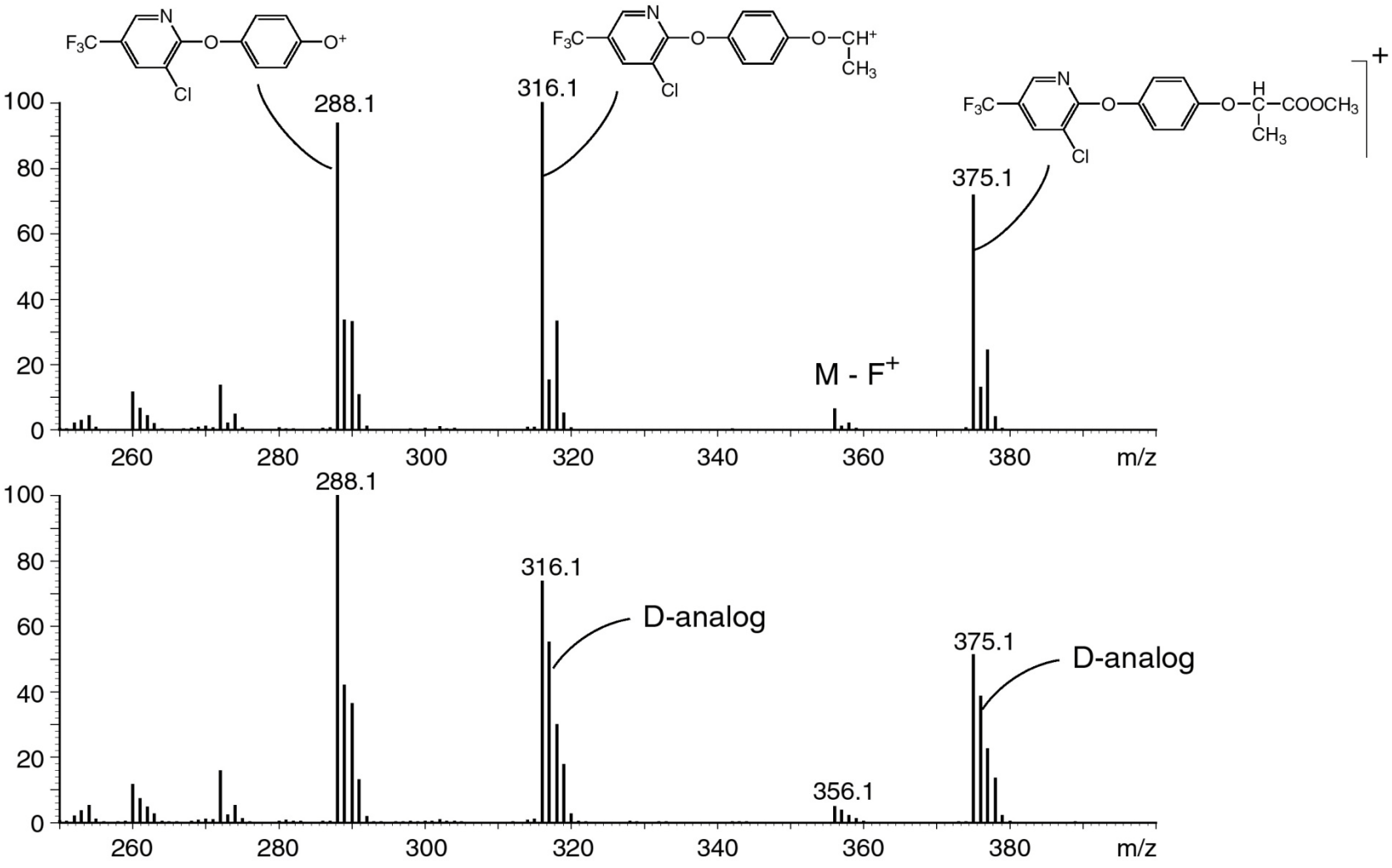
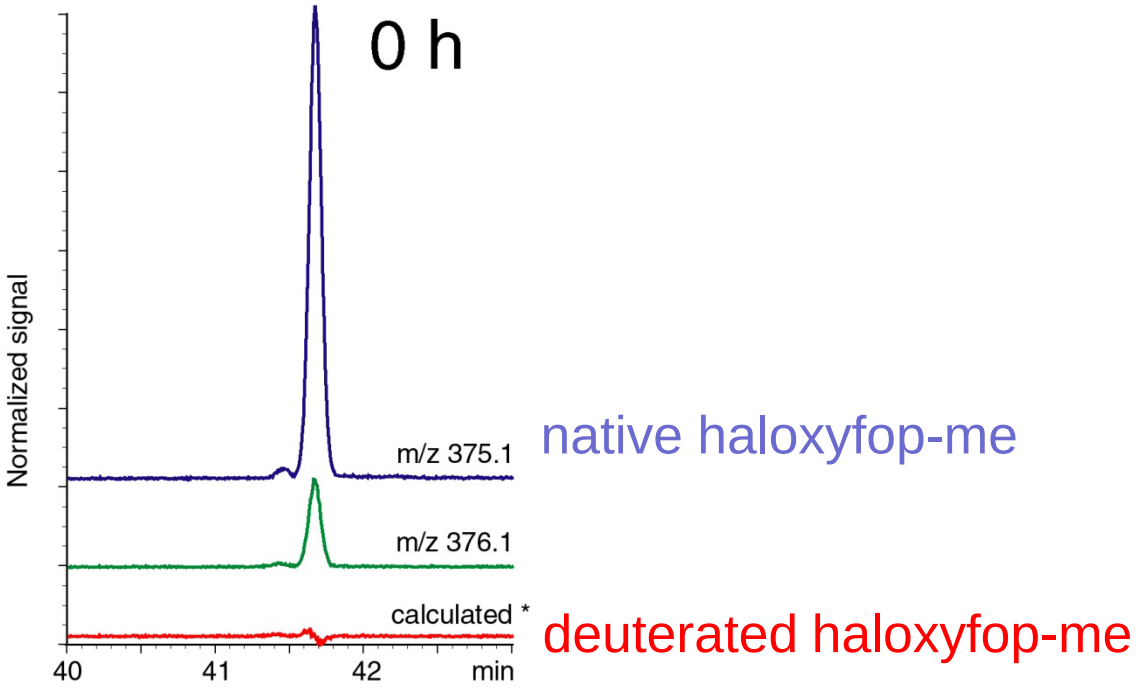
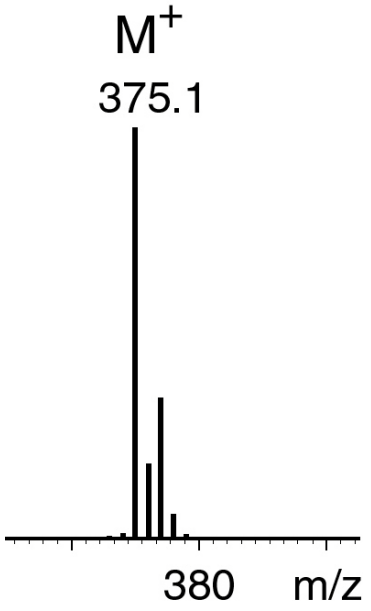


Incubation of *S*-haloxyfop in D_2O containing soil

Chromatograms showing formation of deuterated haloxyfop:





* calculated trace: theoretical signal for ^{13}C (18.5% of m/z 375.1) subtracted from m/z 376.1

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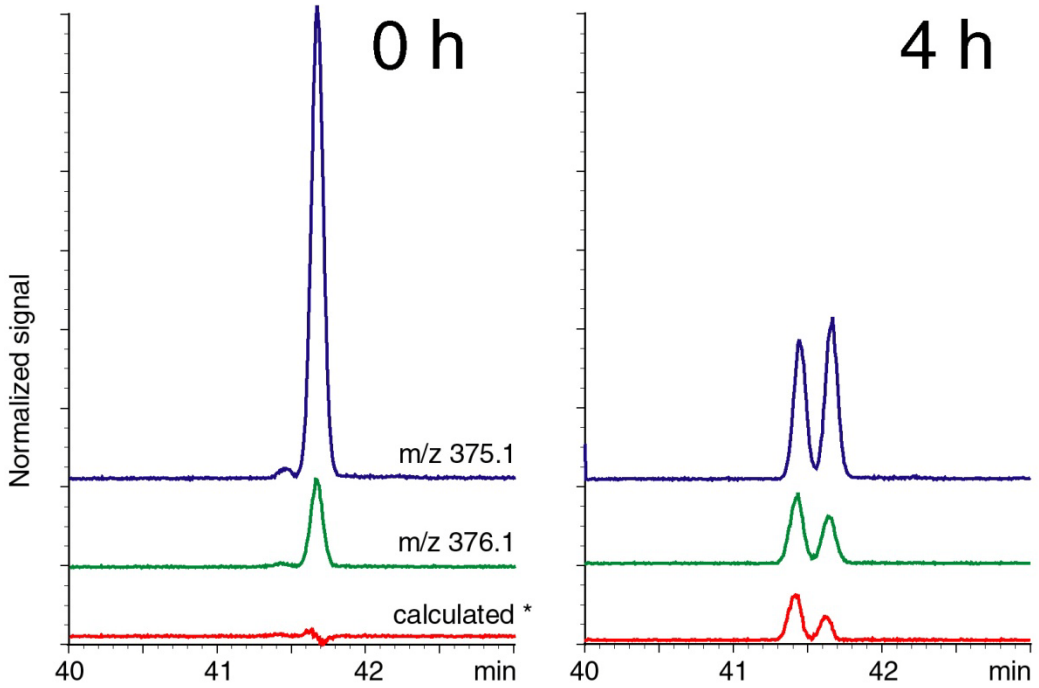

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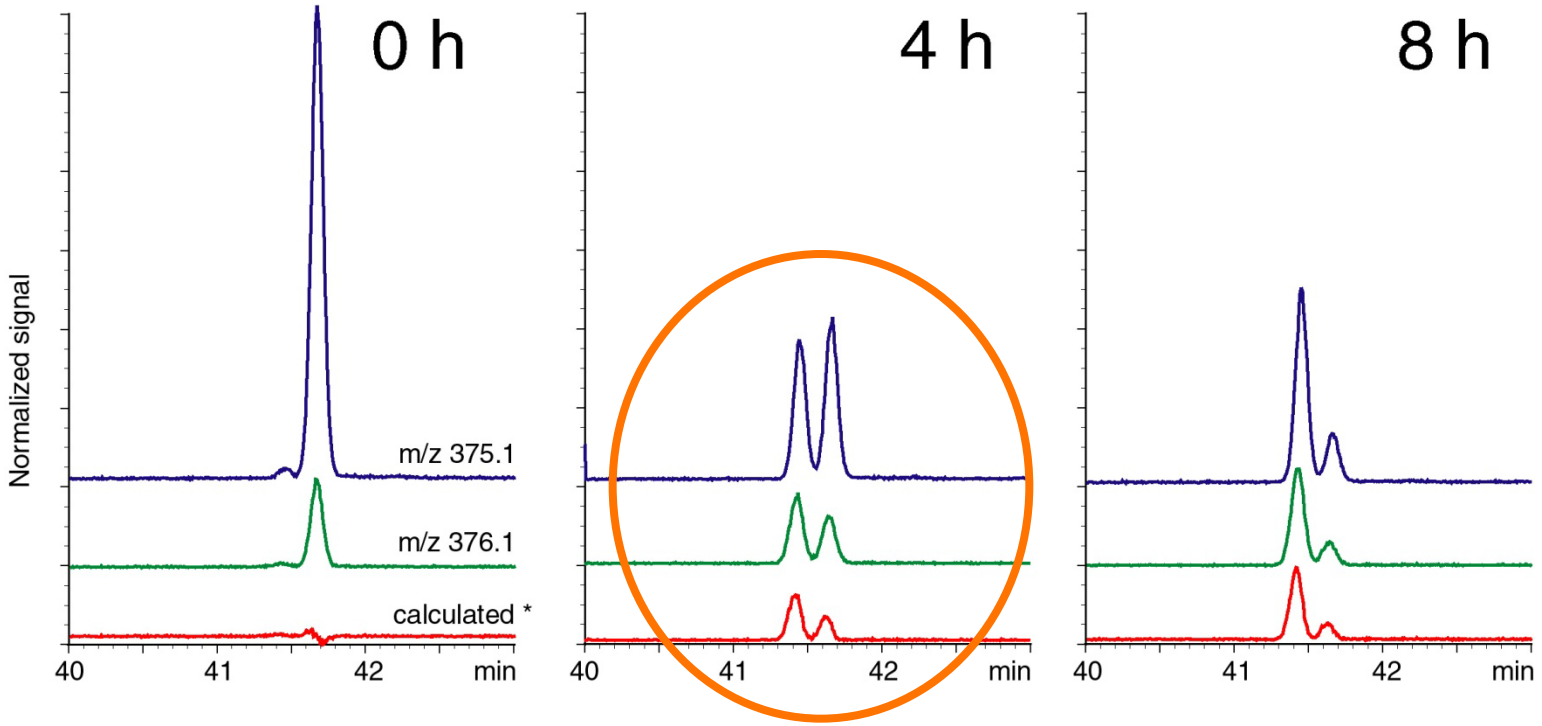

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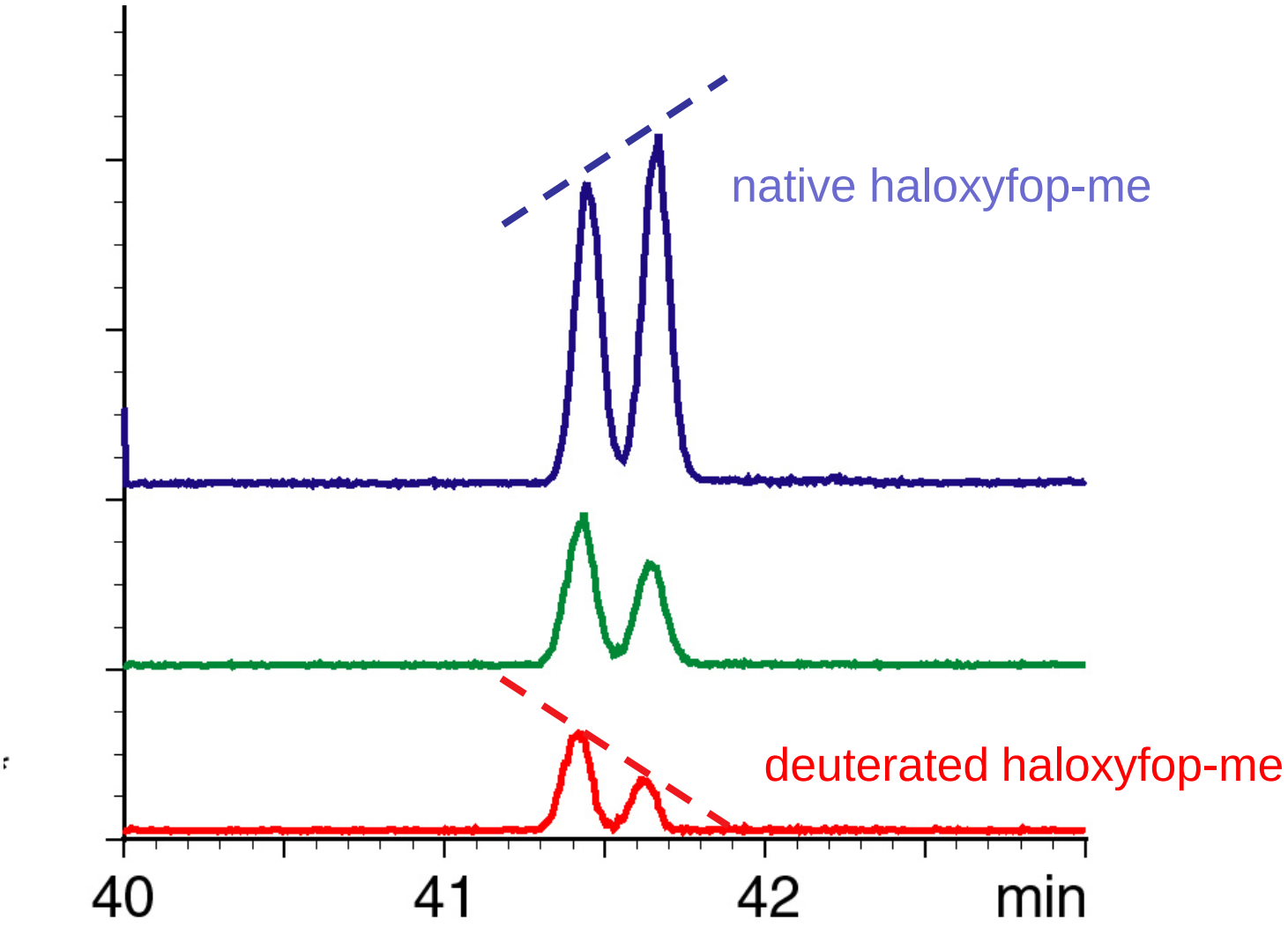
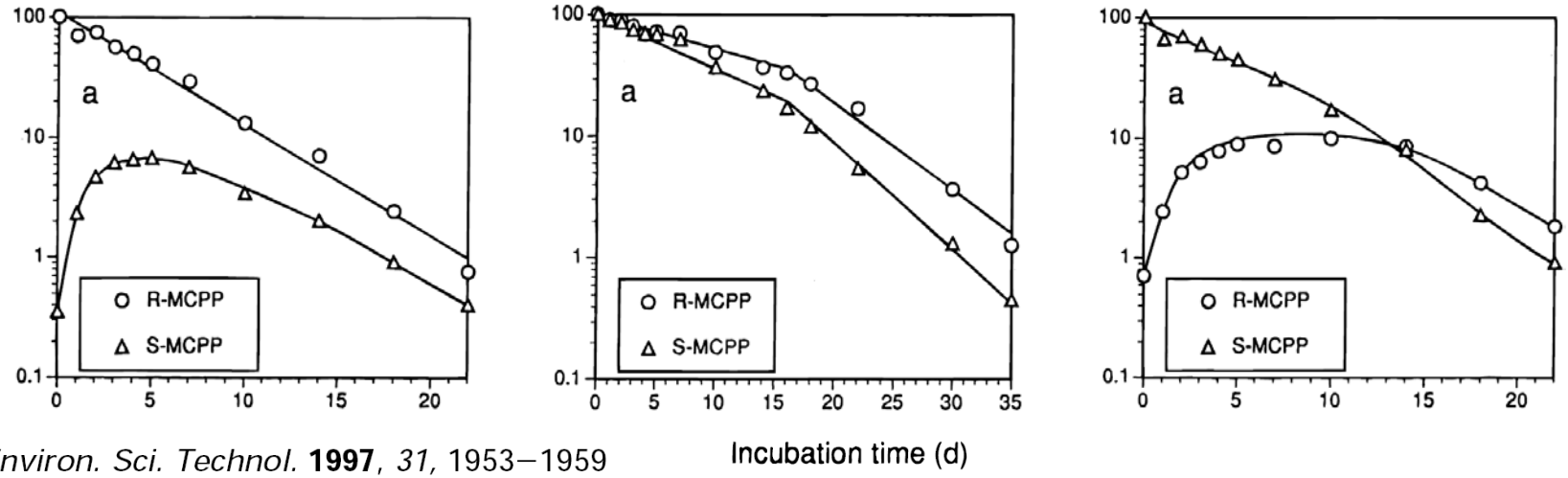


Comparison to previous results with mecoprop



Environ. Sci. Technol. **1997**, *31*, 1953−1959

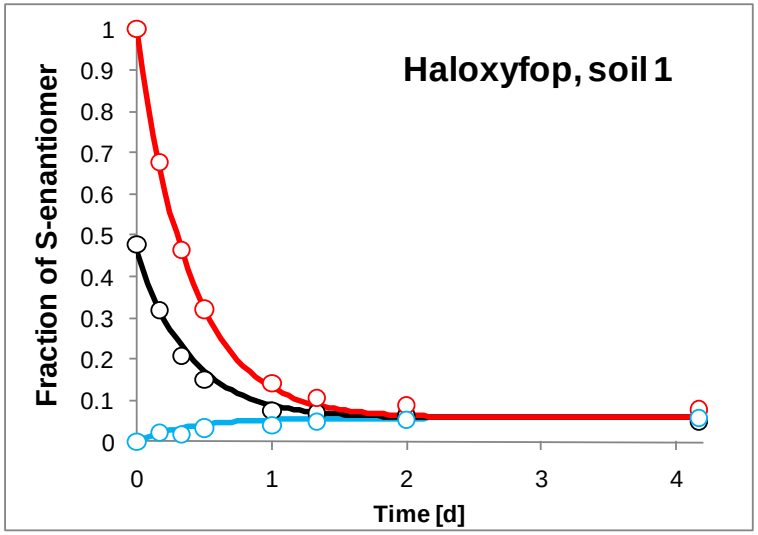
Same behavior as haloxyfop

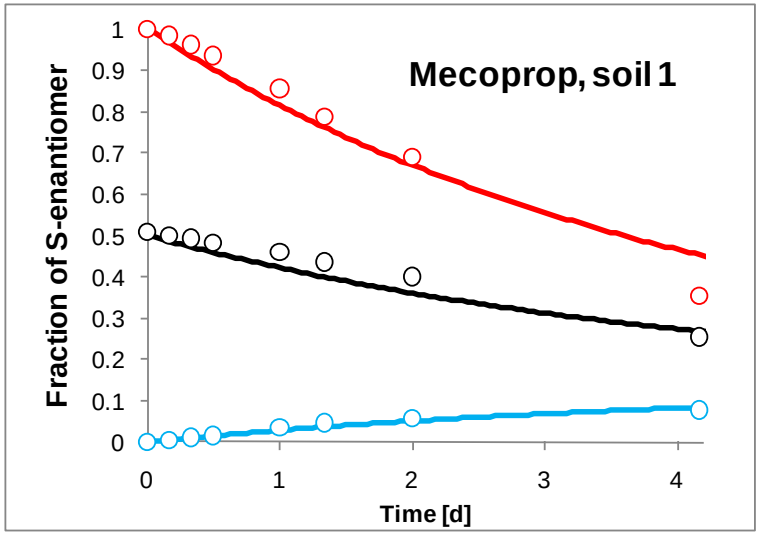
- biologically mediated isomerization of mecoprop (MCPP) in soil
- preference for R-isomer (although reversed in alkaline soils)

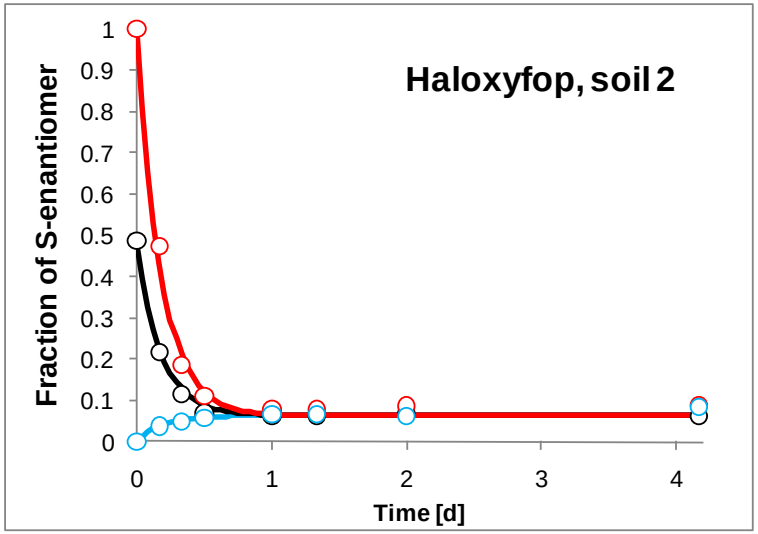
But:

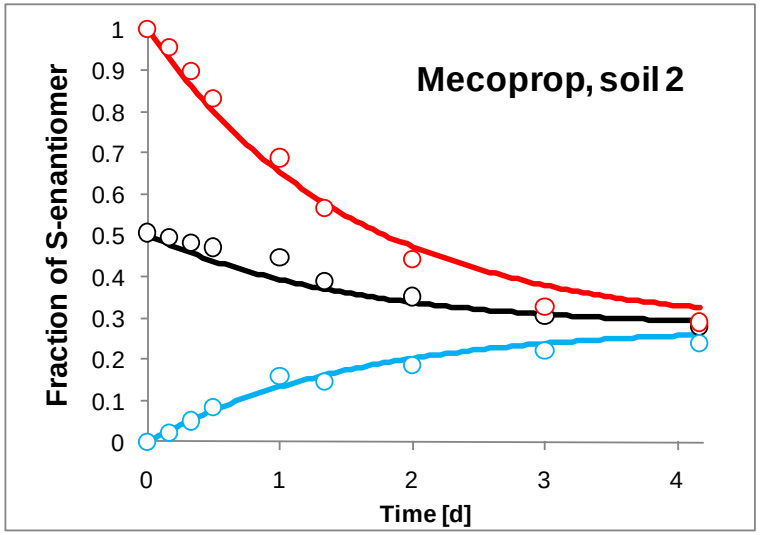
- isomerization is substantially slower

Comparison of isomerisation kinetics

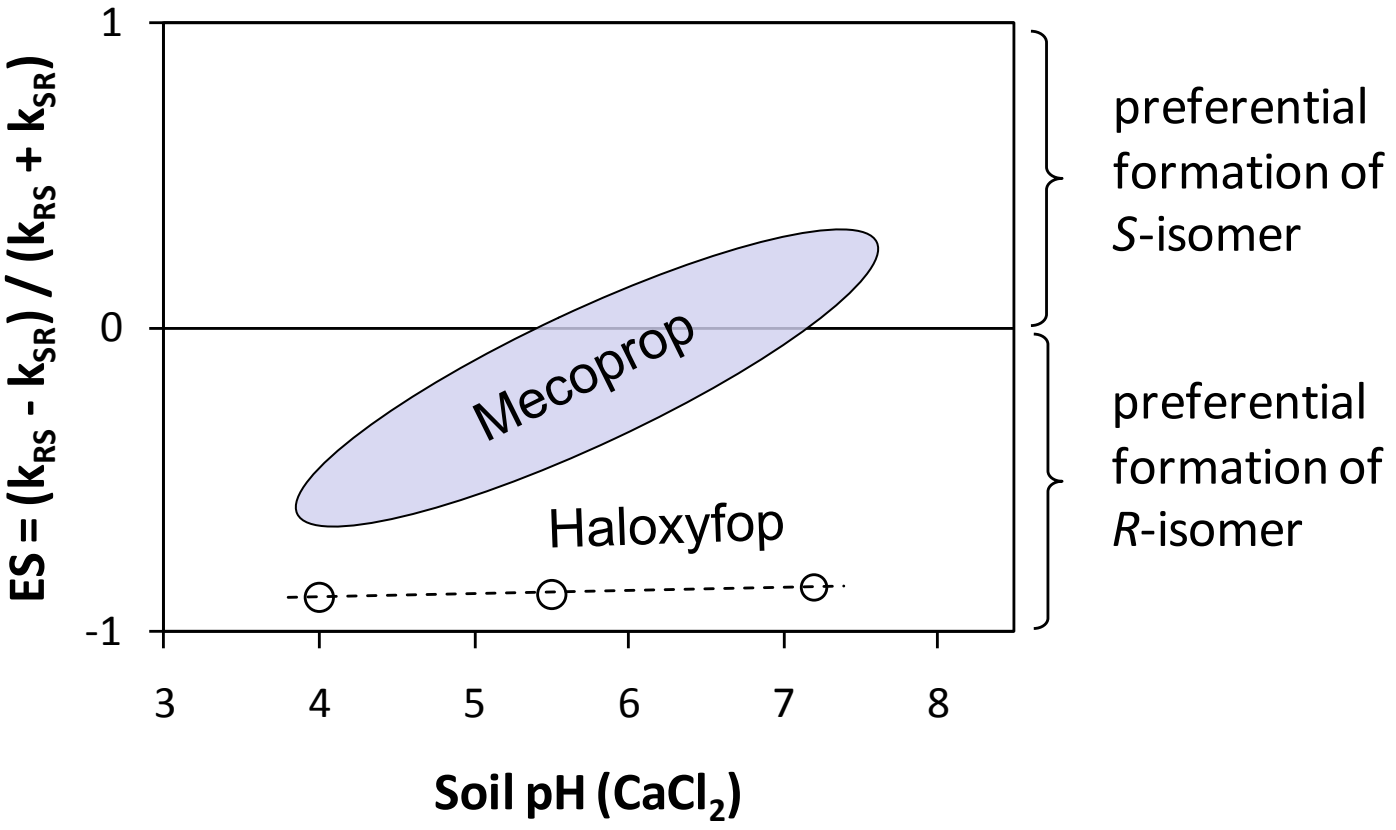








Influence of soil properties on isomerization



ES = enantioselectivity (of isomerization)

Similar behavior in soil as in mammalian metabolism

JMPR* evaluation of haloxyfop-methyl, 2006:

- Irrespective of whether haloxyfop or haloxyfop-R methyl ester was administered, haloxyfop was the only substance detected in the plasma.
- *S*-isomeric form(s) of haloxyfop underwent rapid and almost complete inversion to *R*-form(s) in rats, and it was assumed that this also occurred in other species

* JMPR: Joint FAO/WHO Meeting on Pesticide Residues

Conclusions

- rapid isomerization of haloxyfop enantiomers in soil (faster than previously observed with mecoprop)
- isomerization is biologically mediated
- predominant formation of herbicidally active R-enantiomer (same preference as with mecoprop, yet more pronounced)
- final isomer ratio is independent of soil properties in tested soils (in contrast to mecoprop, where reversed isomer ratios were observed in alkaline soils)

Thank you for your attention!

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Preemergence and Postemergence Activities of the (R) and (S) Enantiomers of Haloxyfop[1]

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Abstract. The relative activities of (R) and (S) enantiomers of the methyl ester of haloxyfop were determined on annual grasses. Samples enriched in the (S) enantiomer were markedly less active than the (R) in petri dish evaluations and foliar applications. The pure (S) enantiomer was estimated by regression to be 1000-fold or less active than the (R). The activity of the (S) enantiomer was found to be equivalent to that of the (R) following preemergence applications. Isolation and characterization of haloxyfop from soil treated with the methyl ester of haloxyfop indicated inversion of the (S) enantiomer to the (R) enantiomer within 7 days. Field trials confirmed the differential activity of enantiomers applied postemergence and their equivalence when applied preemergence. These findings indicate that inversion of the (S) enantiomer to the (R) occurs in soil following preemergence applications. Nomenclature: Haloxyfop, 2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid.

Additional index words. Optically active herbicides, (D) and (L) isomers.

While several of these studies have evaluated the (I tiomer against only a racemic mixture of the (R) enantiomers, the published data nevertheless indic the (S) enantiomer is virtually inactive within thi of herbicides (5, 6, 7).

In addition to foliar activity, several of the aryloxy propionate herbicides possess significant soil activity However, comparatively little information is avail the preemergence activity of enantiomers of thes cides. In one report the difference in activity betw enantiomers of diclofop was noted to be less follow emergence applications than postemergence (5).

Effective weed control has been demonstrated w emergence applications of haloxyfop[4]. Preemergence is also important in the suppression of later gen weeds following postemergence applications of ha (3). Because of the importance of both foliar and soil of haloxyfop, the objective of this research was to the comparative postemergence and preemergence a of the enantiomers of haloxyfop.

Previous report on enantioselective transformation of fluazifop-butyl

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Stereochemistry of Fluazifop-butyl Transformations in Soil

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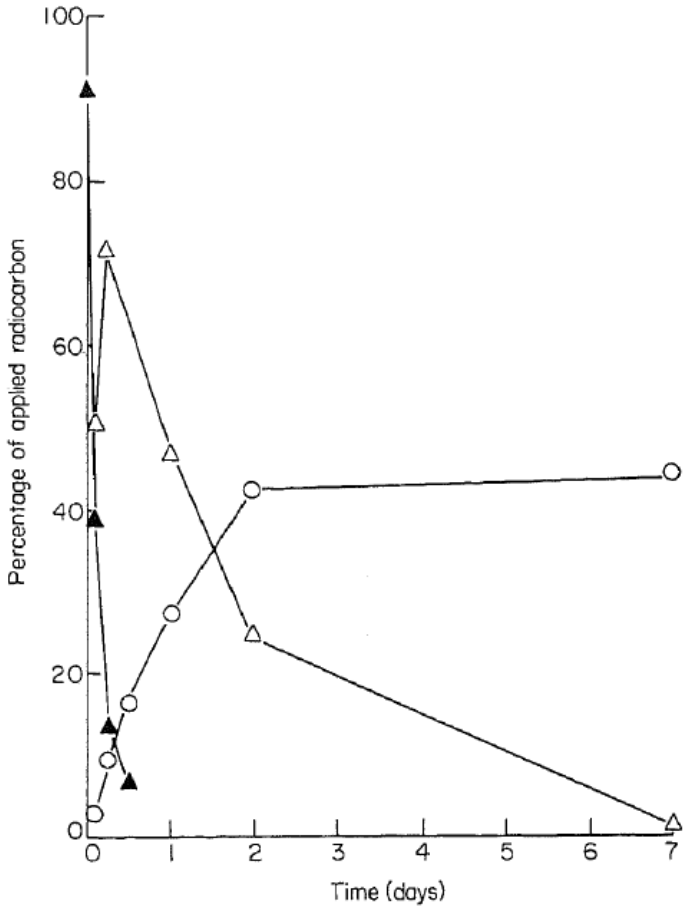

Figure 6. Transformation products of *S*-fluazifop-butyl in '18 Acres' soil: (▲), *S*, fluazifop-butyl; (△), *S*-fluazifop; (○), *R*-fluazifop.