Transformations of triazole fungicides

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Introduction

- Triazole fungicides are a group of widely used pesticides. In 2013, their market share in Germany was 18.5%, making them the most commonly used organic fungicides.[1]
- Difenoconazole and propiconazole (Fig. 1) are non-polar fungicides generally perceived as persistent.[2] This results in a high potential for soil contamination. Polluted soils may then lead to water body pollution.

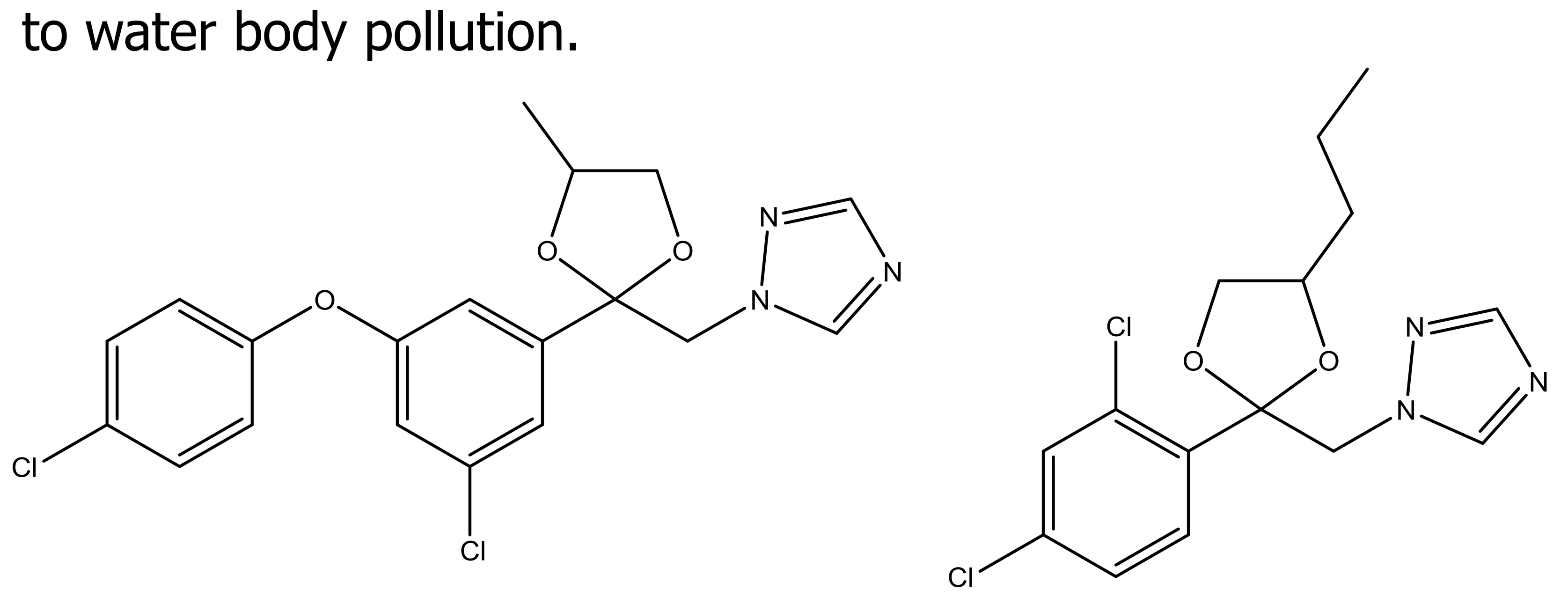

Fig. 1: Difenoconazole (left) and Propiconazole (right).

- Fungicides are subject to transformation processes in the environmental compartments soil and water, as well as in waste water treatment plants (WWTP).
- Transformation products may be readily soluble in water and more toxic.

Objective

Investigation of degradation of difenoconazole and propiconazole under environmental and technical conditions. Identification of transformation products formed during these processes.

Theoretical Background

- Pesticides can be transformed by various mechanisms in the environment and under technical conditions. Selected processes will be investigated (Fig. 2).

Compartment		*Induced transformation process*
Surface water		• Global radiation • Bacterial metabolism • Influence of humic substances
Soil	Humus	• Global radiation • Bacterial metabolism
Soil	Humus rich topsoil	• Bacterial metabolism • Fenton reaction (soil remediation) • Mobility • Soil aging
Soil	Mineral subsoil	
Soil	Parent material	
Ground water		• Bacterial metabolism • Influence of humic substances
Water purification plant		• Chlorination • Ozonation • Energy-rich UV radiation • Advanced oxidation processes (TiO_2)

Fig. 2: Compartments and selected transformation conditions.

Experimental

- Ruggedness test study for determination of effective solid-liquid-extraction of pesticides using model soils of different total carbon content (Fig. 3).

Fig. 3: Model soils *Arm*, *Mittel*, *Reich*, and *Super* (Tab. 1) generated from blank compost, blank RefeSol 01-A, and spiked compost. Increasing total carbon content (L-R).

Tab. 1: Total carbon content (C [%]) of the model soils.

Model soil	*C [%]*
Arm	0.84 ± 0.14
Mittel	3.08 ± 0.27
Reich	6.58 ± 0.80
Super	10.61 ± 0.81

- Generation of transformation products in water and soil using model reactions (Fig. 4).

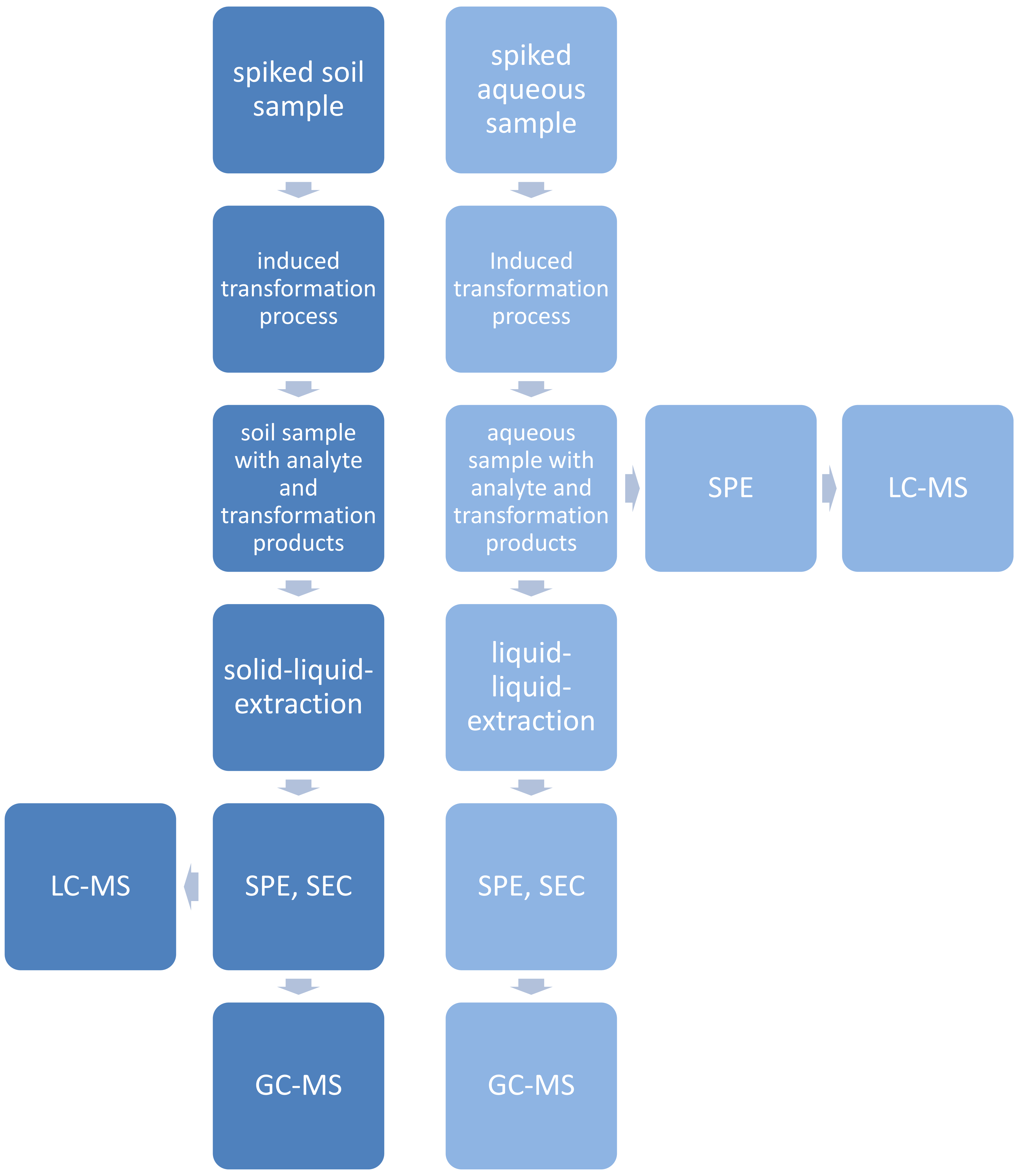

Fig. 4: Sample generation, preparation, and analysis.

- Identification of transformation products:
  - EI-MS-spectra
  - HR-MS-spectra
  - Isolation of substances and NMR measurements
  - Synthesis of proposed transformation products and comparison of retention times and spectra
- Instrumentation: GC-MS (Agilent GC 7890 & Agilent MSD 5975)
  UPLC-ESI-TOF-MS (Waters Acquity UPLC & Waters Micromass QTOF Ultima)

Outlook

- Identification of transformation products generated during Fenton reaction
- Treatment of fungicides with iron-oxidising bacteria

References

[1] BVL (2014), Absatz an Pflanzenschutzmitteln in der Bundesrepublik Deutschland 2013
[2] Pesticide Properties DataBase, University of Hertfordshire, http://sitem.herts.ac.uk/aeru/ppdb/index.htm

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