

Aging reduces bioaccessibility and explains persistence of triazol-fungicides accumulated in agricultural topsoil

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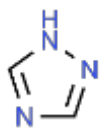
Geological Survey of Denmark and Greenland



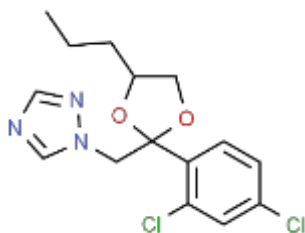
Objectives

1. Determine the fate of triazole fungicides in agricultural fields.
2. Determine how the bioaccessibility of triazole fungicides changes over time.

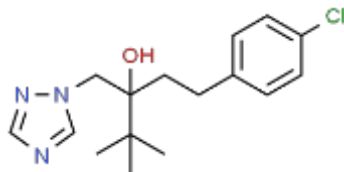
Danish Pesticide Leaching Assessment Programme (PLAP): 1,2,4-triazole was found in drainage- and groundwater before spraying PLAP fields with triazole fungicides.



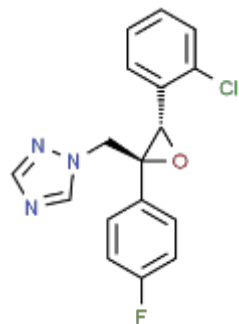
1,2,4-triazole



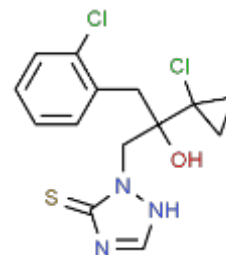
Propiconazole



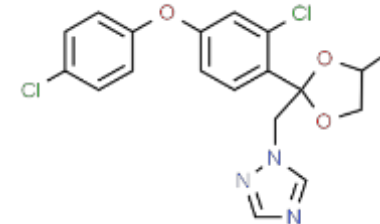
Tebuconazole



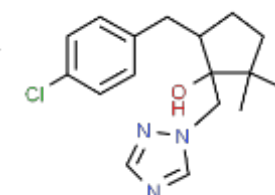
Epoxiconazole



Prothioconazole



Difenoconazole



Metconazole

Experimental design

Fields: 4 fields from the Danish Pesticide Leaching Assessment Programme with conventional agriculture.

Known history of spray applications (3 fields).

Sampling of plough layer for two years.

Analyses: Aged sorption (CaCl_2 extraction)

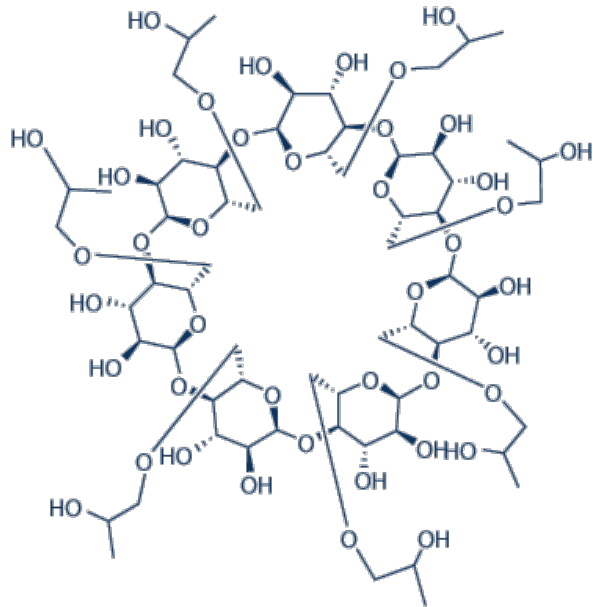
Bioaccessible concentration (HPCD extraction),

Total concentration (acetonitrile extraction).

Bioaccessible concentration, HPCD extraction

Complexation with hydroxypropyl-beta-cyclodextrin (HPCD) mechanistically mimics microbial uptake of hydrophobic compounds.

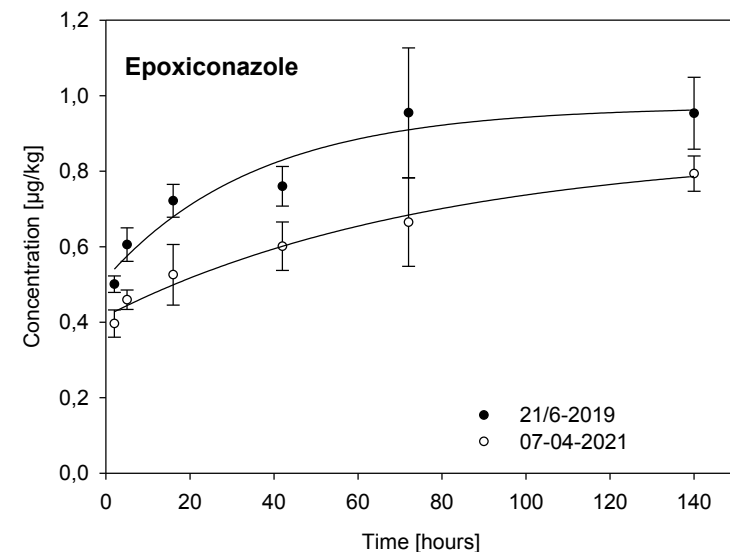
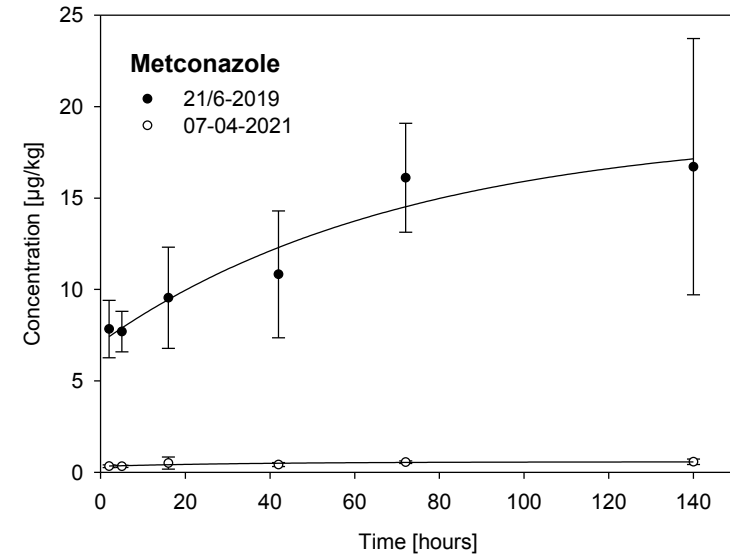
Immediately bioavailable + potentially accessible over time



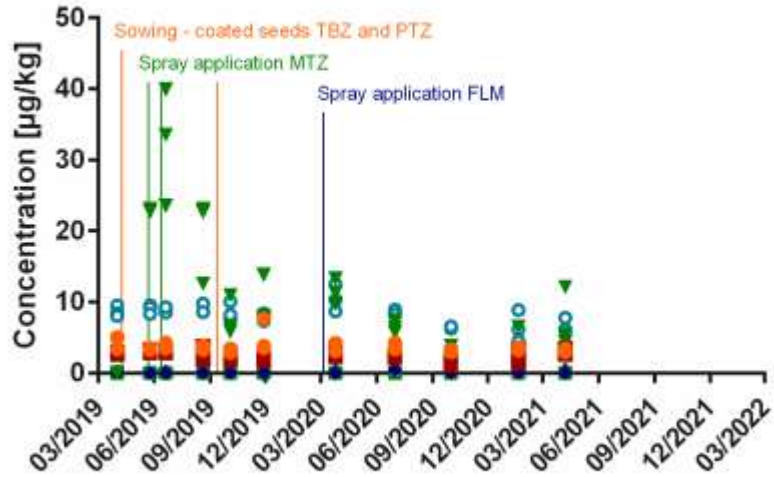
Reid et al, 2000. Environ Sci Technol 34: 3174-3179

Cuyper et al., 2002. Chemosphere 46: 1235-1245

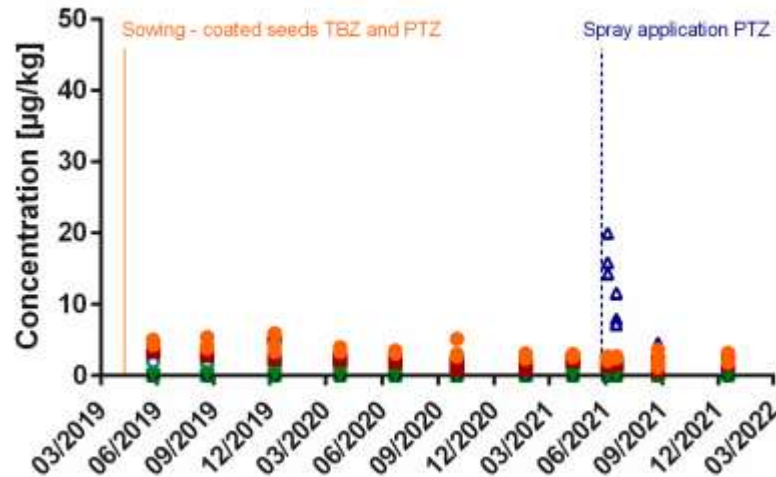
Papadopoulos et al., 2007. J Environ Monit 9:516-522



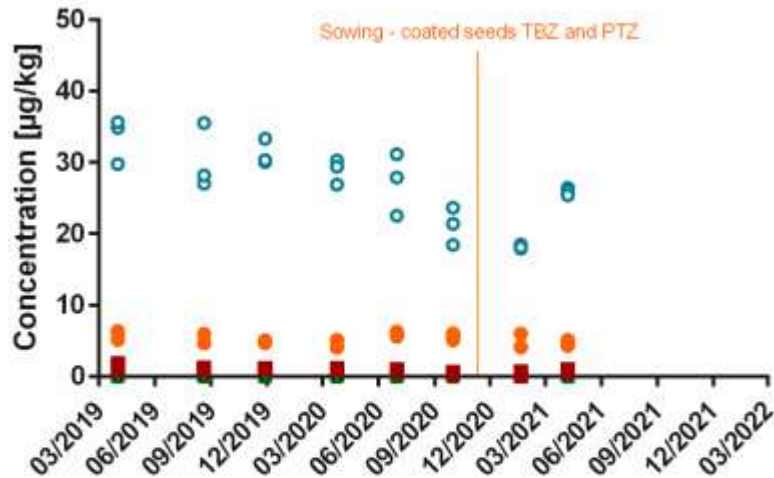
Estrup



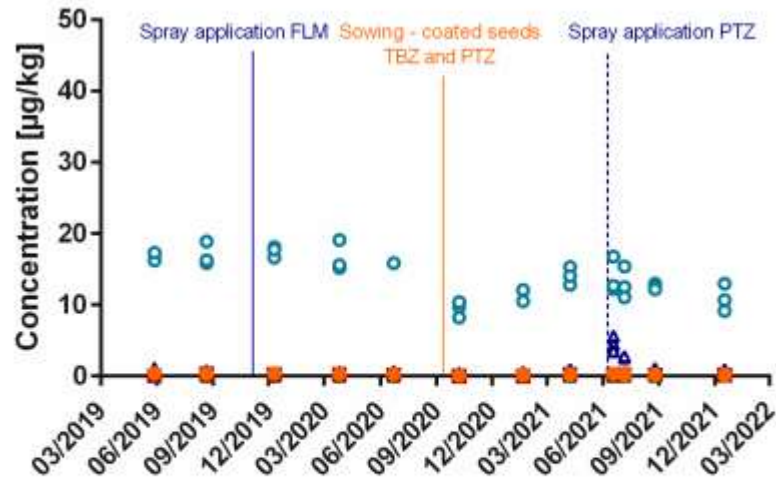
Fårdrup



Jyndeved



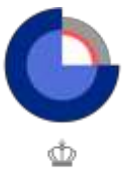
Lund



Changes over time in the concentration of triazole fungicides in the plough layer of four conventional PLAP fields.

- Tebuconazole
- Propiconazole
- Metconazole
- Flurasulam

- Epoxiconazole
- Prothioconazole-desthio
- Difenconazole

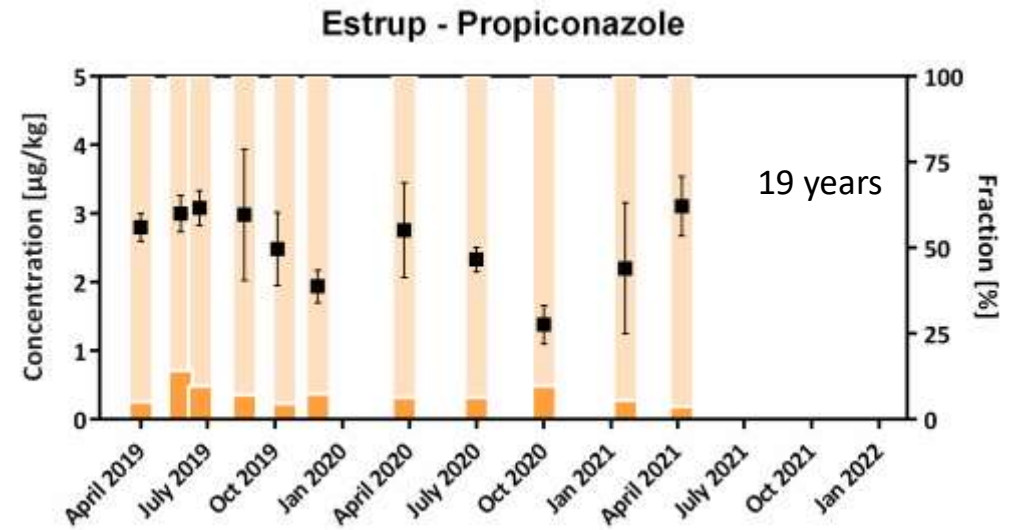
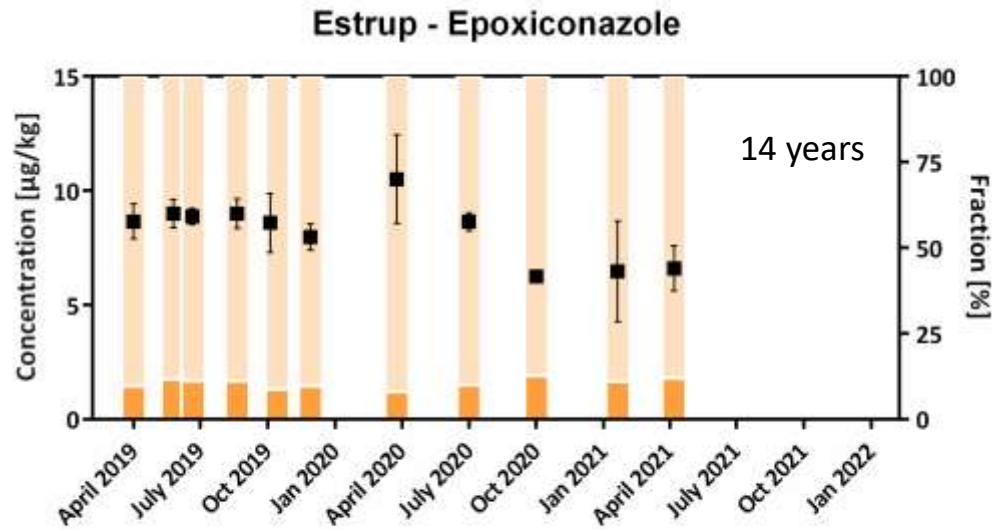
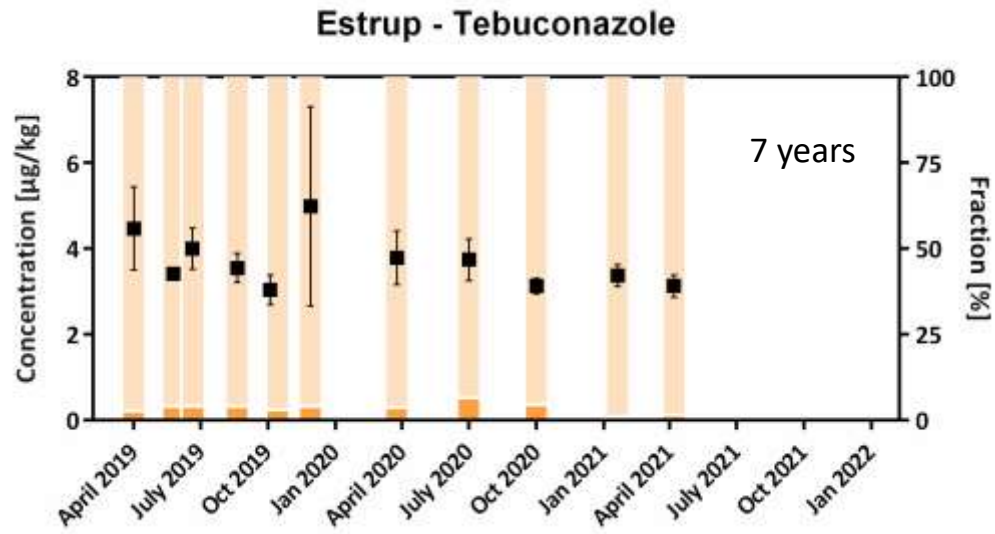


Accumulation of parent compounds

| Field | Compound | Concentration ± 1 standard deviation [$\mu\text{g}/\text{kg}$] | Years since spraying |
|----------|--------------------------|--|-------------------------|
| Estrup | Tebuconazole* | 3,1 \pm 0,2 | 7 |
| | Propiconazole | 3,1 \pm0,4 | 19 |
| | Metconazole | 7,3 \pm 3,4 | 2 |
| | Epoxiconazole | 6,6 \pm0,8 | 14 |
| | Prothioconazole-desthio* | 0,5 \pm 0,1 | No spraying |
| Fårdrup | Tebuconazole* | 2,4 \pm 0,6 | 7 |
| | Propiconazole | 1,7 \pm 0,2 | 4 |
| | Epoxiconazole | 0,9 \pm0,1 | 15 |
| | Prothioconazole-desthio* | 0,8 \pm 0,0 | 6 |
| Jyndevad | Tebuconazole* | 4,6 \pm 0,3 | 6 |
| | Propiconazole | 0,8 \pm 0,1 | 5 |
| | Epoxiconazole | 26,0 \pm0,4 | 6 |
| | Prothioconazole-desthio* | 0,6 \pm 0,0 | 6 |

*Also used for seed dressing

Bioaccessibility of aged epoxiconazole, tebuconazole and propiconazole.

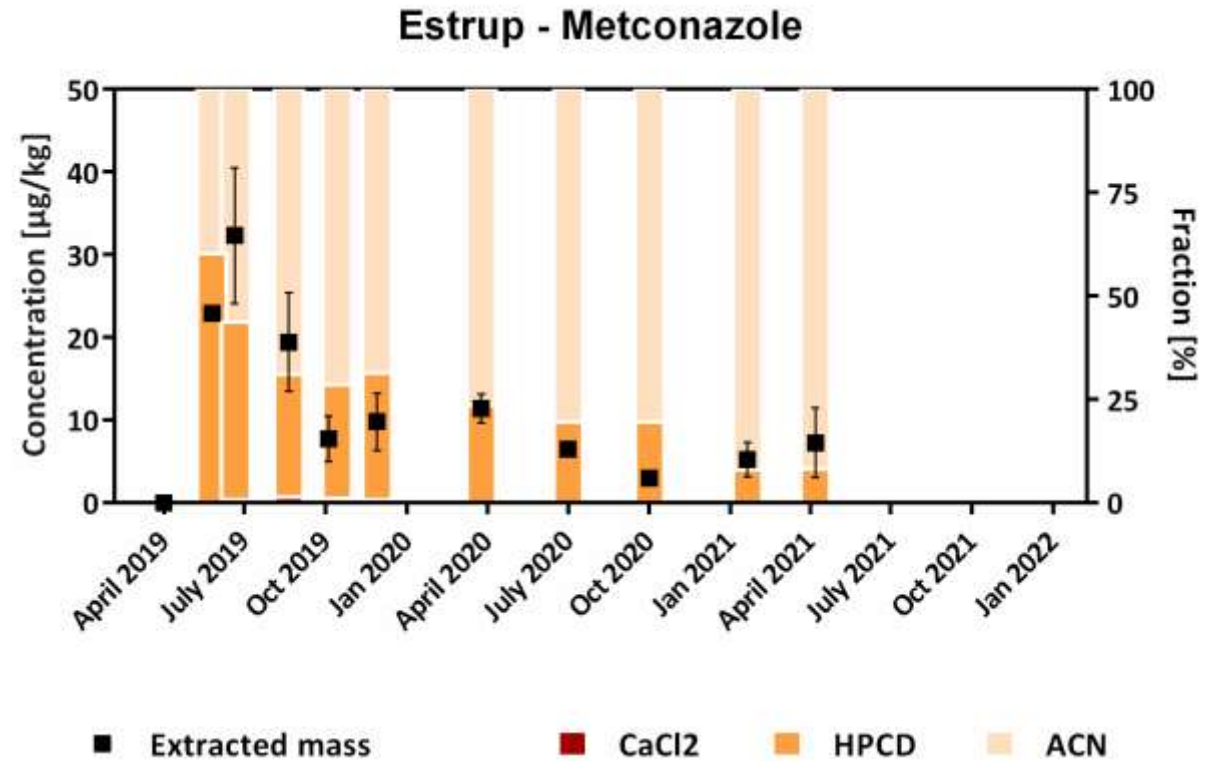
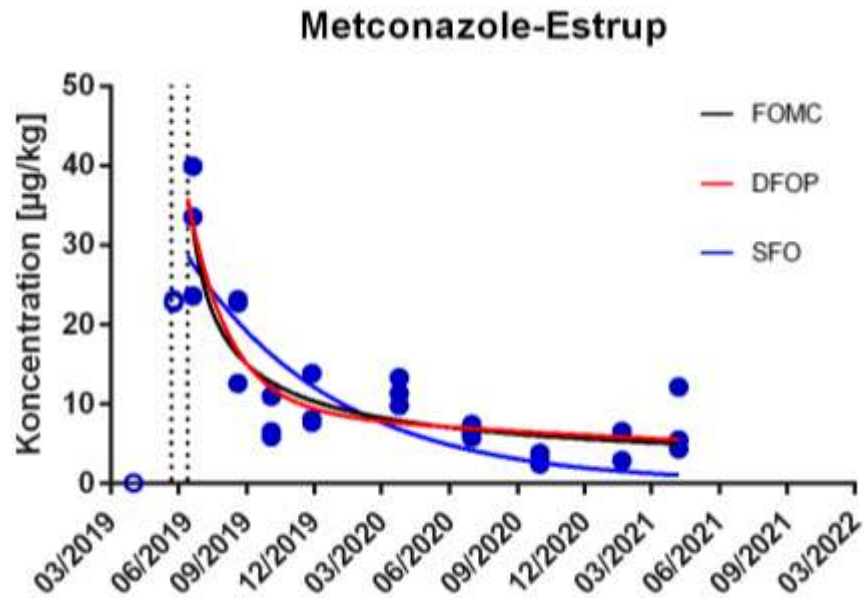


■ Extracted mass ■ CaCl2 ■ HPCD ■ ACN

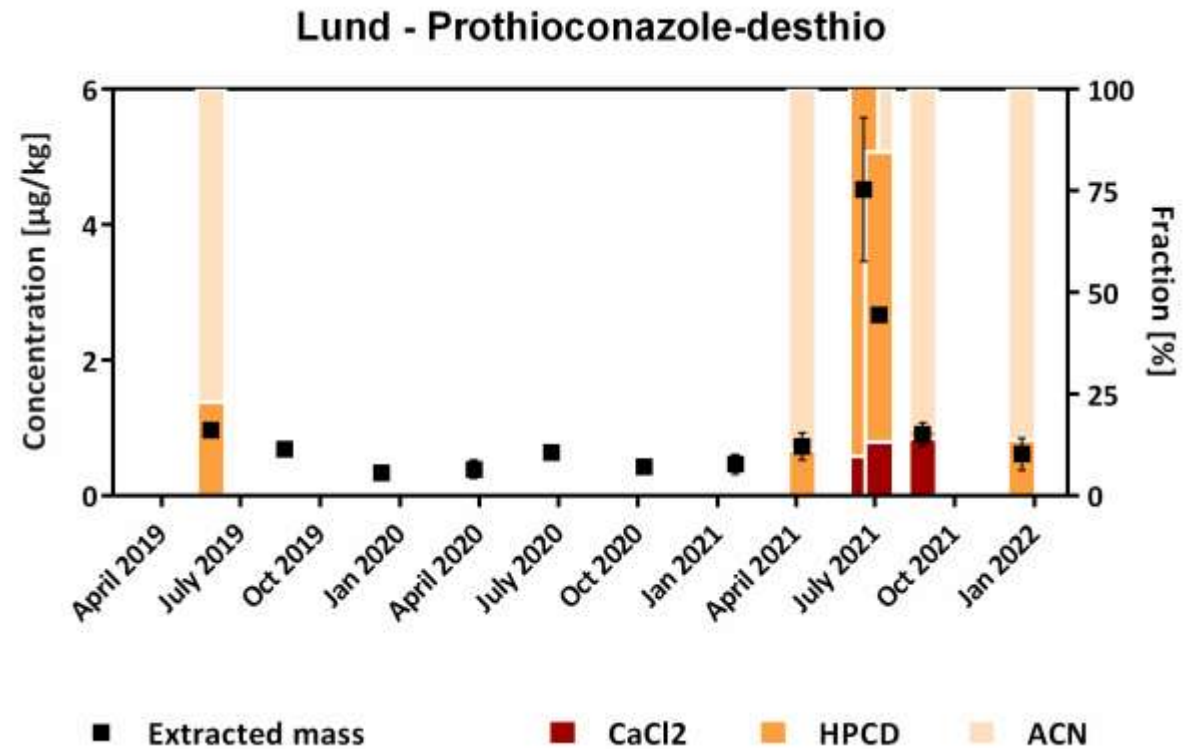
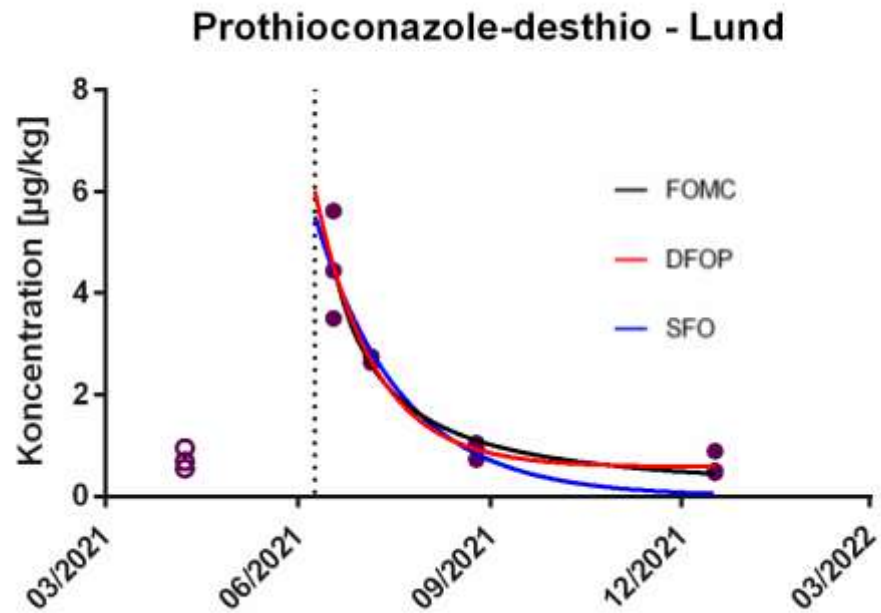


GEUS

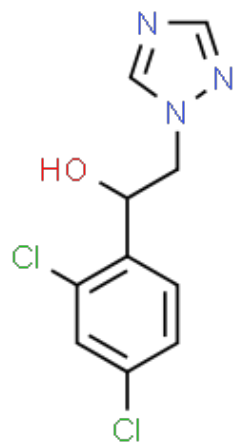
Metconazole in plough layer after spraying



Prothioconazole-desthio in plough layer after spraying

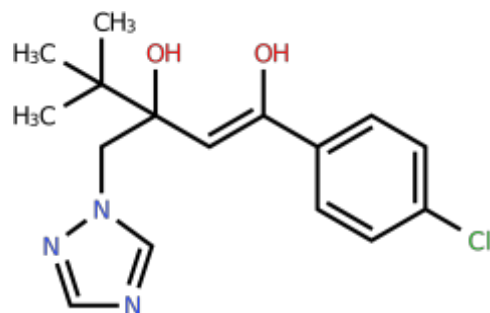


High-resolution MS suspect-screening



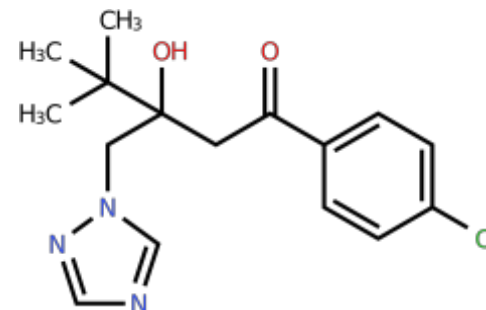
$C_{10}H_9Cl_2N_3O$
CGA 91305

Parent: Propiconazole



$C_{16}H_{20}O_2N_3Cl$
HWG 1608-5-enol (M09)

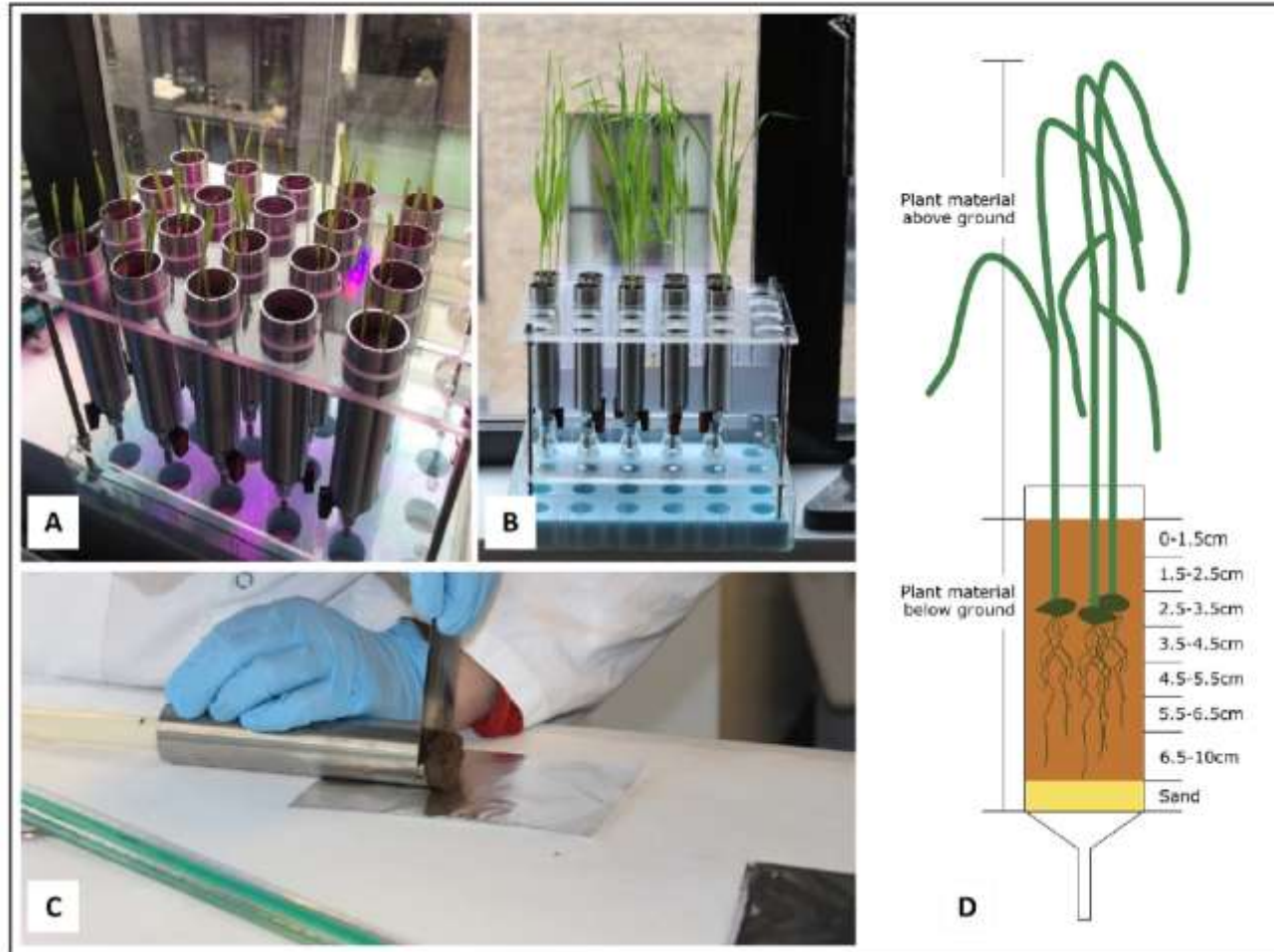
Parent: Tebuconazole



$C_{16}H_{20}O_2N_3Cl$
HWG 1608-5-keto (M08)

Parent: Tebuconazole

P-10 Seed dressing with triazole fungicides – an additional source of 1,2,4-triazole?



Conclusions

- Some triazole-fungicides were detectable 7-19 years after the last spraying.
- Concentrations were almost constant over time for aged triazole fungicides.
- After metconazole spraying, soil concentrations levelled off at a constant concentration instead of approaching zero.
- Due to sorption and low bioaccessibility, a fraction of triazole-fungicides may persist in the topsoil and may accumulate after repeated spraying.