Pesticide sorption and diffusion in natural clay loam aggregates

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Time-dependent sorption

- Time-dependent sorption: sorption increases with time
  - diffusion into aggregates
  - intra-particle diffusion into organic matter
  - irreversible chemical binding
- If controlled by diffusion only then sorption is fully reversible

Questions

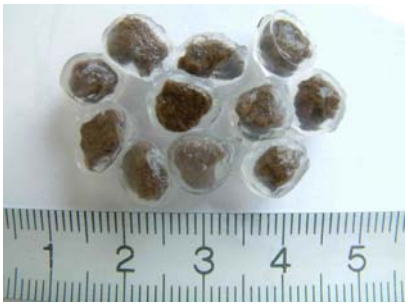
- Can we describe time-dependent adsorption in aggregates with a diffusion model?
- Can we predict desorption from the aggregates with the same diffusion model?

Overview

- Adsorption experiments
- Diffusion model fitted for adsorption
- Desorption experiments
- Model predictions for desorption

Gel-coated aggregates

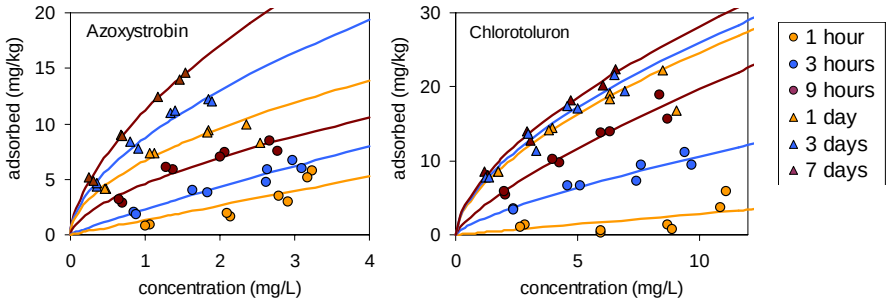
- clay loam aggregates
  - 24% clay, 2.3% OC
  - diameter 5 mm
  - density 1.37 g/cm^3
  - porosity 0.47
- alginate gel coating
  - open structure, >98% water
  - fast diffusion (not rate-limiting)
  - no interaction with pesticides



Sorption experiments

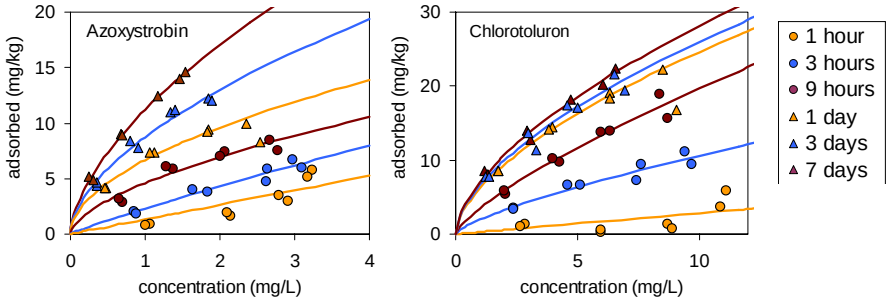
- 11 aggregates per batch (1 gram soil)
- added 4 ml pesticide solution
- azoxystrobin, chlorotoluron, cyanazine
- gently shaken for 1, 3, 9 hours, 1, 3, 7 days
- measure concentration in solution
- measure total pesticide by solvent extraction

Adsorption in soil aggregates



- adsorption increases with time

Adsorption in soil aggregates

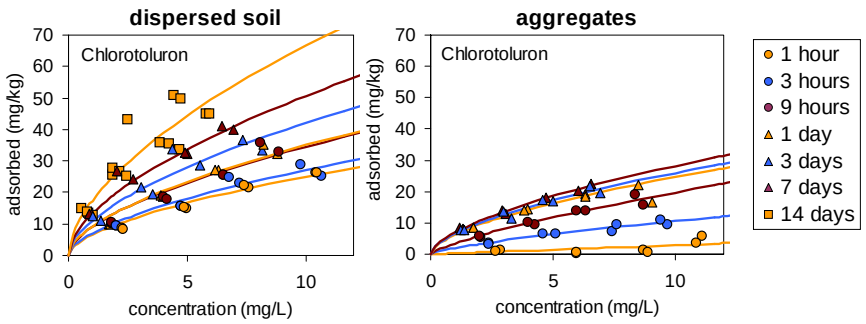


- no equilibrium reached for azoxystrobin
- more sorption takes longer to reach equilibrium

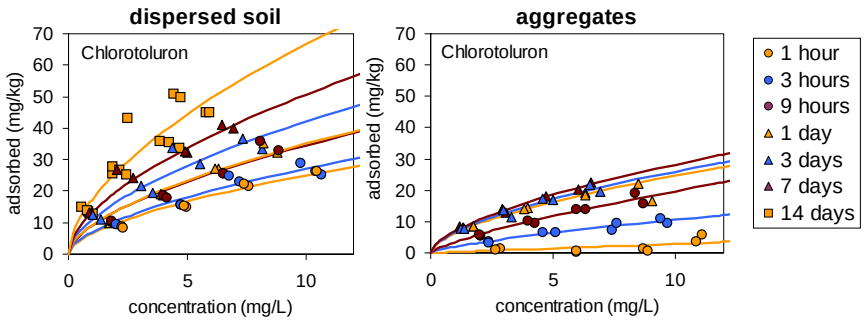
Dispersed soil versus soil aggregates

- Equilibrium sorption measured in batch experiments with soil particles in suspension?
- Parallel experiment: soil kept in suspension on orbital shaker

Dispersed soil versus soil aggregates



Dispersed soil versus soil aggregates

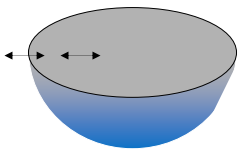


- not all sorbent available inside aggregates
- soil suspension cannot be used to measure equilibrium sorption in aggregates

Diffusion model

- Assume aggregates are homogeneous porous spheres
- Spherical diffusion

$$\theta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = \theta f D \left(\frac{\partial^2 C}{\partial r^2} - \frac{2}{r} \frac{\partial C}{\partial r} \right)$$

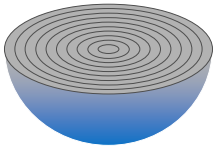


- Freundlich sorption

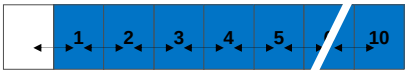
$$S = K_F C^n$$

Diffusion model

- Implemented in ORCHESTRA
- Numerical method
- Mass fluxes between concentric layers
- Equilibrium sorption in each layer

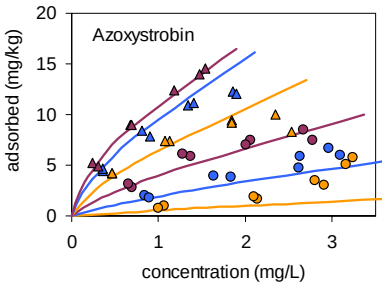


concentric layers

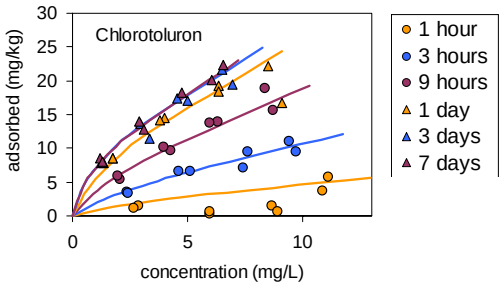


calculation cells

Simulation Results

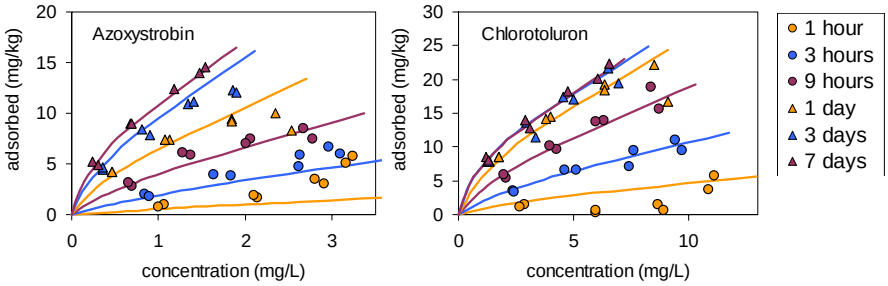


Azoxystrobin
K_F = 11.2 kg/L, n=0.61
$D_e = 0.7 \cdot 10^{-10}$ m²/s



Chlorotoluron
K_F = 7.0 kg/L, n=0.60
$D_e = 1 \cdot 10^{-10}$ m²/s

Simulation Results

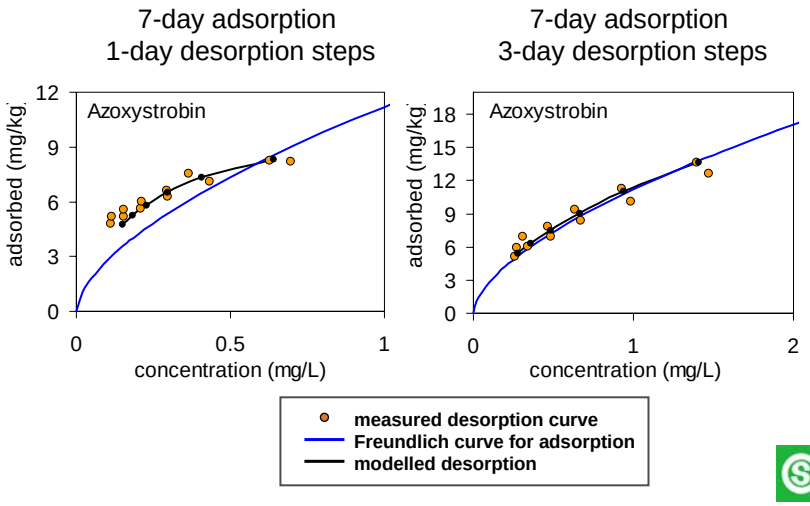


- Diffusion model describes time-dependent sorption in aggregates well
- Diffusion coefficient is similar to theoretical diffusion coefficient

Desorption experiments

- Replacement of external solution after 1, 3, or 7 days equilibration
- Stepwise desorption at 1 or 3-day intervals

Desorption results



Conclusions

- Time-dependent sorption in aggregates is controlled by diffusion into the aggregates only
- Sorption is reversible and adsorption and desorption follow the same mechanism
- Sorption in soil suspensions does not represent sorption in aggregates

Current research…