Fate Model to Predict the Dynamics of Bioavailability in Soil

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SPME fibers as tools for bioavailability

SPME fibers are promising tools to determine bioavailability of organic contaminants in environmental media. However, application to soil presents unique difficulties due to the low water content. Headspace analysis provides a possible solution but the dynamics of contaminant transfer is more complicated, involving not only desorption from soil and uptake into the fiber, but also soil-air transport. To facilitate test design and analysis, we developed a dynamic model for soil test systems.

Model definition

The model consists of a small-scale multi-media fate model of the Mackay type (Fig. 1). SPME fibers can be positioned in the soil headspace or in a soil slurry. All model parameters can be estimated from physico-chemical properties (diffusion and partition coefficients) or derived from estimated diffusion path lengths (rate constants), see table.

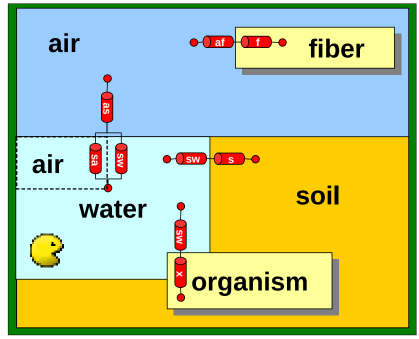


Fig. 1. Schematic representation of the model. Red cylinders represent diffusion resistances.

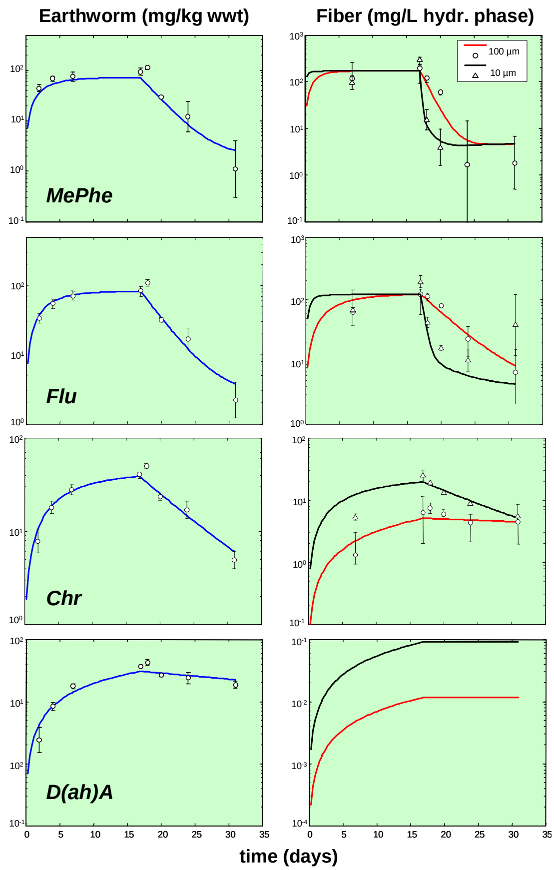


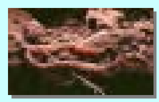
Fig. 2. Measured and predicted concentrations for four PAHs.

Test data for PAHs

Closed systems (0.5 L jars) with 100 g wet soil, 3 earthworms (*Eisenia fetida*), and fibers (10 and 100 µm) in the headspace. Jars were opened every 3-4 d to provide fresh air for the worms (included in the model).

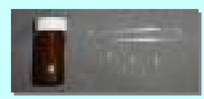
After 17 days, worms and fibers were transferred to jars with clean soil to eliminate for 14 days. At day 17, soil samples (3 g) were put in 4 ml jars with 3 ml water (poisoned with $HgCl_2$) and 10 µm fibers. This slurry was shaken for 7 days to ensure equilibrium.

At several time points, jars were sacrificed and worms and fibers analyzed for PAHs. Fibers were analyzed by automated thermal desorption (ATD) coupled directly to a GC-MS system, operated in single ion recording (SIR) mode.



adult Eisenia fetida

disposable 4 cm PDMS fibers



Model fitting

There are too many model parameters to fit simultaneously to worm and fiber data. Therefore, for calibration only four parameters were adjusted (see table). To simplify calibration, mass transport in soil is assumed to be rapid (due to bioturbation of worms), and equilibrium between soil OM and water is assumed. All modeling is performed in MatLab®.

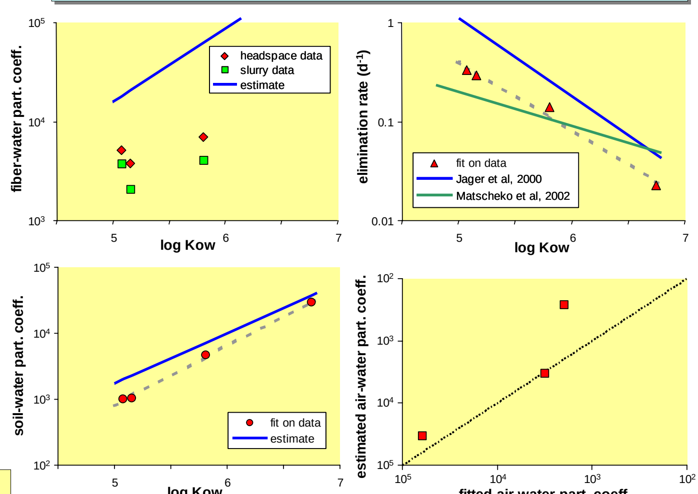


Fig. 3. Fitted and estimated parameter values.

	Default estimation	Fit?
Partition coefficients		
Soil OC-water	QSAR from Gerstl (1990)	✓
Fiber-Water	Calculated from data Ter Laak *et al* (2005)	✓
Air-Water	Calculated from VP and solubility	✓
Air-Fiber	Calculated from fiber-water and air-water	
Worm-Water	QSAR from Jager (1998)	
Diffusion coefficients		
PDMS fibers	$1.7 \cdot 10^{-5}$ m²/d (Mayer *et al*, 2000)	
Air	From molwt. (Schwarzenbach *et al*, 1993)	
Effective diff. soil	∞ (due to bioturbation)	
Diffusion path length		
Fiber-Air, fiber side	Thickness of fiber coating	
Fiber-Air, air side	200 µm (based on Ter Laak *et al*, 2005)	
Soil-Air, air side	9 mm (based on Brandes *et al*, 1996)	
Rate constants		
Desorption in soil	∞ (generally insensitive parameter)	
Elimination in earthworms	QSAR Jager *et al* (2000)	✓

Conclusions

- The model is able to describe the time course of PAHs in headspace fibers and earthworms.
- For these PAHs, air-side of fiber-air interface is limiting transport.
- Fitted parameters are consistent with model estimates, with exception of the fiber-water partition coefficient (lower than predicted from *Kow*). Reason needs to be explored further.
- Next step will be to model aliphatic hydrocarbons using the same model definition.

References

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