Estimating degradation half-lives of pesticides from water-sediment studies with TOXSWA and PEST

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Problem

Estimation of degradation half-lives of pesticides from a water-sediment study is not straightforward. Fitted degradation rates often result in good visual correspondence between simulated and measured concentrations, but confidence limits are wide and PEST does not always find an unique solution.

Hypothesis

Degradation rates can only be estimated if degradation is a major process in the layer concerned. In more detail:

Hypothesis 1 (water):

If, at t=100 d: $\sum mass_{to\ sediment} < \sum mass_{degraded\ in\ water}$ then $DT_{50,water}$ can be well fitted.

Hypothesis 2 (sediment):

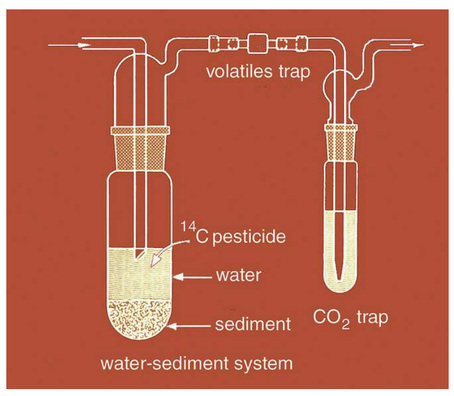
If, at t=100 d: $\sum mass_{back\ diffused} < \sum mass_{degraded\ in\ sediment}$ then $DT_{50,sediment}$ can be well fitted.

Method

1. Define theoretical compounds covering a range of degradation rates and sorption coefficients.

Theoretical compounds	Kom (L/kg)	$DT_{50,water}$ (d)	$DT_{50,sediment}$ (d)
	low sorption		
A	10	10	30
C	10	100	300
E	10	10	300
G	10	300	10
	high sorption		
B	1000	10	30
D	1000	100	300
F	1000	10	300
H	1000	300	10

2. Generate theoretical water-sediment studies for these compounds, including 'measured' concentration data with random error from 5 -10 %.



3. Parameterise the water-sediment systems for TOXSWA (all input known, except degradation rates in water and sediment).

TOXSWA

4. Let PEST optimize correspondence between simulated and 'measured' concentrations in water and sediment simultaneously by varying the degradation rates in water and sediment only.

PEST

Conclusions

1. Hypothesis 1 is confirmed for all 8 compounds and hypothesis 2 is confirmed for 7 out of 8 compounds.
2. In 5 of the 8 theoretical, so well-defined water-sediment studies PEST cannot fit degradation rates satisfactorily. The reason is that other processes (sorption and diffusion) determine the concentrations in the water and sediment layers, and so, PEST tries to fit insensitive parameters in those cases.
3. From a theoretical point of view, water-sediment studies are not suitable to determine degradation rates for a number of compounds.

Results

Water:

- for 5 compounds: $\sum mass_{to\ sediment} < \sum mass_{degraded\ in\ water}$ at t=100 d
  for 3 compounds: $\sum mass_{to\ sediment} > \sum mass_{degraded\ in\ water}$ at t=100 d
- PEST fitted $DT_{50,water}$ satisfactorily for the 5 compounds and failed for the 3 compounds.

Sediment:

- for 6 compounds: $\sum mass_{back\ diffused} < \sum mass_{degraded\ in\ sediment}$ at t=100 d
  for 2 compounds: $\sum mass_{back\ diffused} > \sum mass_{degraded\ in\ sediment}$ at t=100 d
- PEST fitted $DT_{50,sediment}$ satisfactorily for 5 of the 6 compounds and failed for 3 compounds.

Graphs

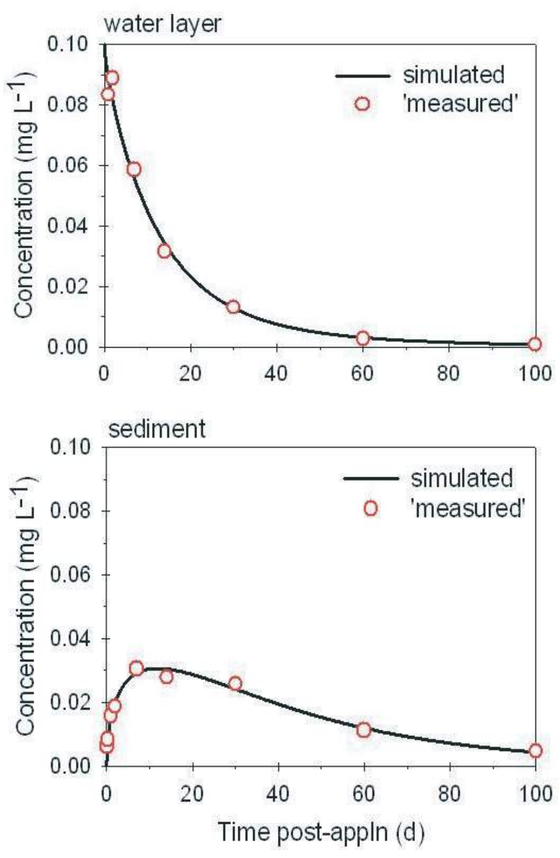
Example of fit of the degradation half-lives for compound E where:

- A good visual correspondence between simulated and 'measured' concentrations is found.
- $DT_{50,sediment}$ could not be fitted because back diffusion instead of degradation determines the concentration in the sediment.
- $DT_{50,water}$ is fitted satisfactorily because degradation determines the concentration in the water layer and not the processes transporting compound to the sediment (diffusion and sorption).

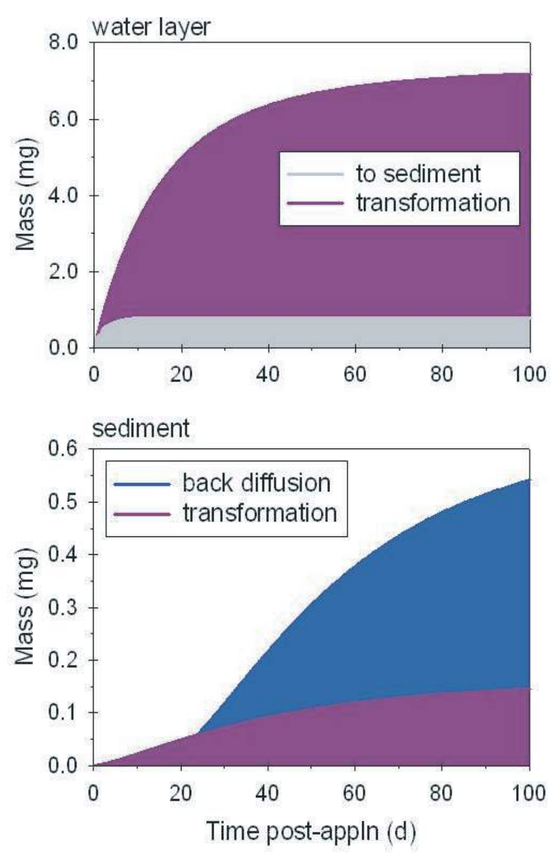
$DT_{50,water}$		$DT_{50,sediment}$	
fitted value	95% confidence limits	fitted value	95% confidence limits
10.4	8.5 - 12.2	194.1	-208.6 - 668.8
deviation from value theoretical compound			
4%	-15% - 22%	- 35%	-170% - 123%

Example: compound E

Concentration profiles



Fitted mass balances



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Most important criteria for a good fit in PEST

- *deviation fitted value from value theoretical compound < 20%*
- *deviation 95% confidence limits from value theoretical compound < 50%*
- *both $DT_{50,water}$ and $DT_{50,sediment}$ should be fitted well*