Factors controlling the behaviour of ionisable pesticides in soils

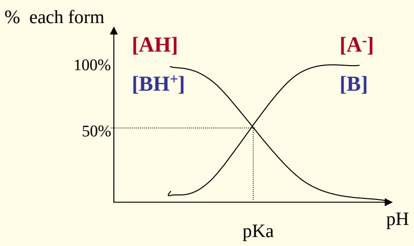
Mélanie KAH
March 2006

Central Science Laboratory THE UNIVERSITY of York

Ionisable pesticides

- weak acids : $HA + H_2O = A^- + H_3O^+$
  weak bases : $B + H_2O = BH^+ + OH^-$

→ lower sorption at pH > pKa



- Important contaminants of ground and surface water : 2,4-D, atrazine, mecoprop etc…

Ionisable pesticides

- Literature : influence of OM content and pH

⇒ conflicting results

⇒ no modelling approach

M. Kah and C.D. Brown, 2006 (*in press*)

Project aim

Influence of **soil/molecular properties** on

the **adsorption and degradation** of

ionisable pesticides

Screening experiment

- Adsorption and degradation parameters
- 10 ionisable compounds x 9 soils

Adsorption by batch

OECD guidelines n°106

- Soil suspensions in 0.01M $CaCl_2$ **(4°C, dark)**
- single concentration : 2 $mg.kg^{-1}$

  (1 $mg.kg^{-1}$ for sulfonylureas)

  → shaken 72 h → pseudo-equilibrium

  → **Kd**

- Centrifugation technique : realistic soil/solution ratio

  Kd after 1 and 7 days equilibrium

Degradation experiments

OECD guidelines n°307

- Incubation : -33 kPa, 15°C, dark
- Duration: 40 - 115 days
- Initial concentration: 2 $mg.kg^{-1}$

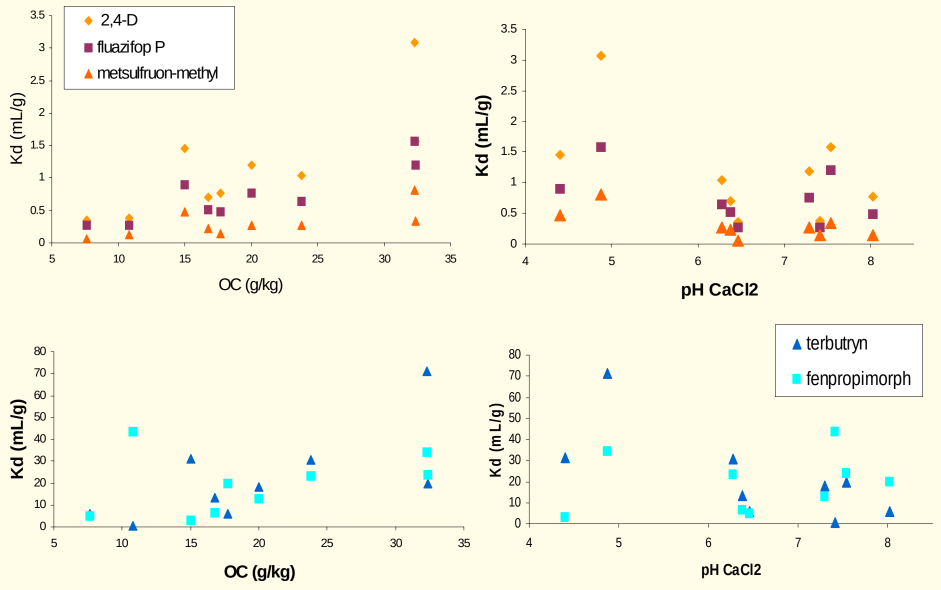
(1 $mg.kg^{-1}$ for sulfonylureas)

→ **DT50**

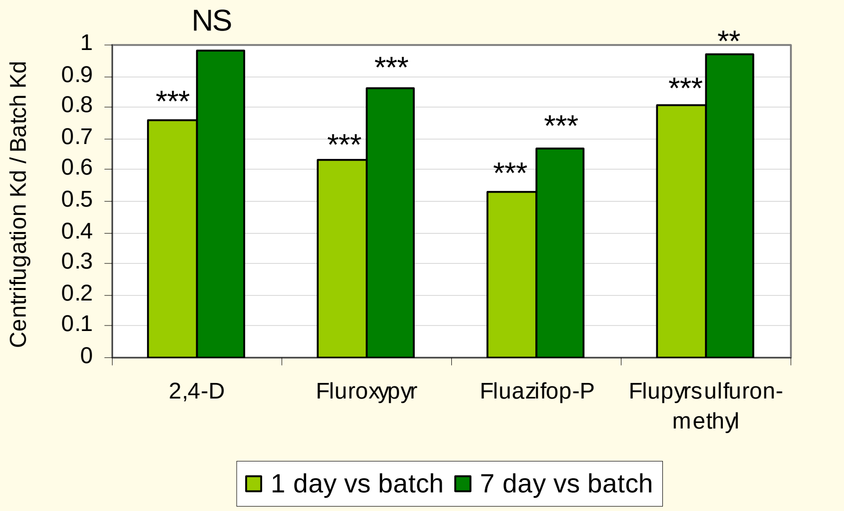
Pesticides	**pKa**	**Koc**	**DT50 (d)**	…
2,4-D	2.9	5 - 212	7	
dicamba	1.9	3.5 - 21	1 - 11	
fluroxypyr	2.9	5 - 81	3 - 55	
fluazifop P	2.9	39 - 84	2 - 9	
metsulfuron-methyl	3.7	4 - 60	14 - 51	
flupyrsulfuron-methyl	4.9	15 - 23	6 - 11	
metribuzin	1.0	9 - 95	6 - 377	
pirimicarb	4.4	290	7 - 234	
terbutryn	4.3	2000	15 - 93	
fenpropimorph	6.9	2770 - 5943	14 - 50	

Soils	Texture	pH_{CaCl2}	% OM	% clay	…
1	silty clay loam	8.0	3.1	38.5	
2	sandy clay loam	7.5	5.6	25.7	
3	sandy clay loam	7.4	1.9	27.5	
4	sandy clay loam	7.2	3.5	34.5	
5	sandy clay loam	6.3	4.1	19.9	
6	sandy	6.5	1.3	5.6	
7	loam	6.4	2.9	23.6	
8	clay	4.8	5.6	41.5	
9	sandy loam	4.4	2.6	13.5	

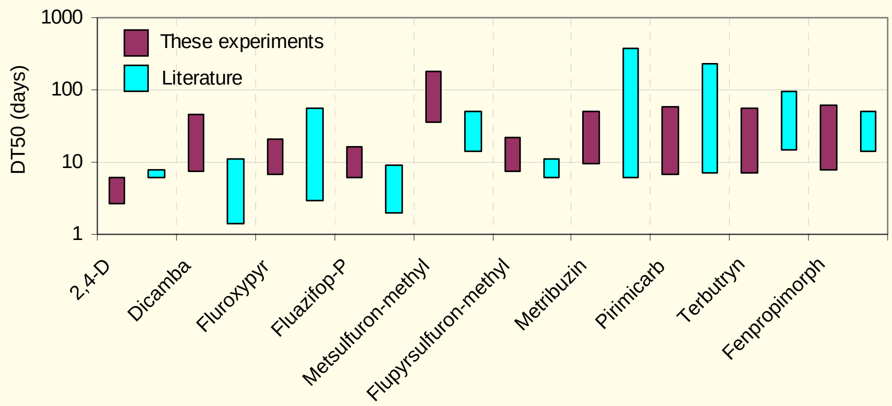
Results: adsorption by batch



Results: adsorption by centrifugation



Results : degradation



Statistical analysis

- Aim: identification of the strongest predictors of variability in Kd and DT50
- 2 software packages: Genstat and Mobydigs

30 soil prop.
n molecular prop. $\xrightarrow{\text{each pesticide, each soil}}$ 3 properties $\xrightarrow{\text{sift for common predictors}}$ 2 predictors

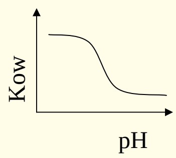
Results: adsorption vs. soil properties

- **Acids** : regression analysis

→ Kb = a.**OC%** + b. **log D** + c (0.72 < r^2 < 0.93; p<0.001)
→ Kb = a.OC% + b. pH_{CaCl2} + c (0.70 < r^2 < 0.90; p<0.001)

- Log D : lipophilicity (Kow) corrected to soil pH

Sorption of ionic form neglible in temperate soils



- **Bases** : regression analysis

→ Kb = a.**CEC** + b. $\mathbf{pH_{CaCl2}}$ + c (0.65 < r^2 < 0.84; p<0.001)
→ Kb = a.OC% + b. pH_{CaCl2} + c (0.53 < r^2 < 0.78; p<0.001)

fenpropimorph seems to behave differently

Results : degradation

- Regression analysis (2 software packages)

  soil properties and **molecular** descriptors

  → No obvious influence

- No obvious link with adsorption

Conclusion

- ADSORPTION : prediction with soil properties

  Acids : log D + OC %

  Bases : CEC + pH

- DEGRADATION : difficult to predict
- NO OBVIOUS LINK between adsorption and degradation
- More work on log D, entire dataset

Acknowledgement

for funding the project

for providing some of the pesticides