Dept Soil Science

University of Reading

Modelling the plant uptake of organic chemicals

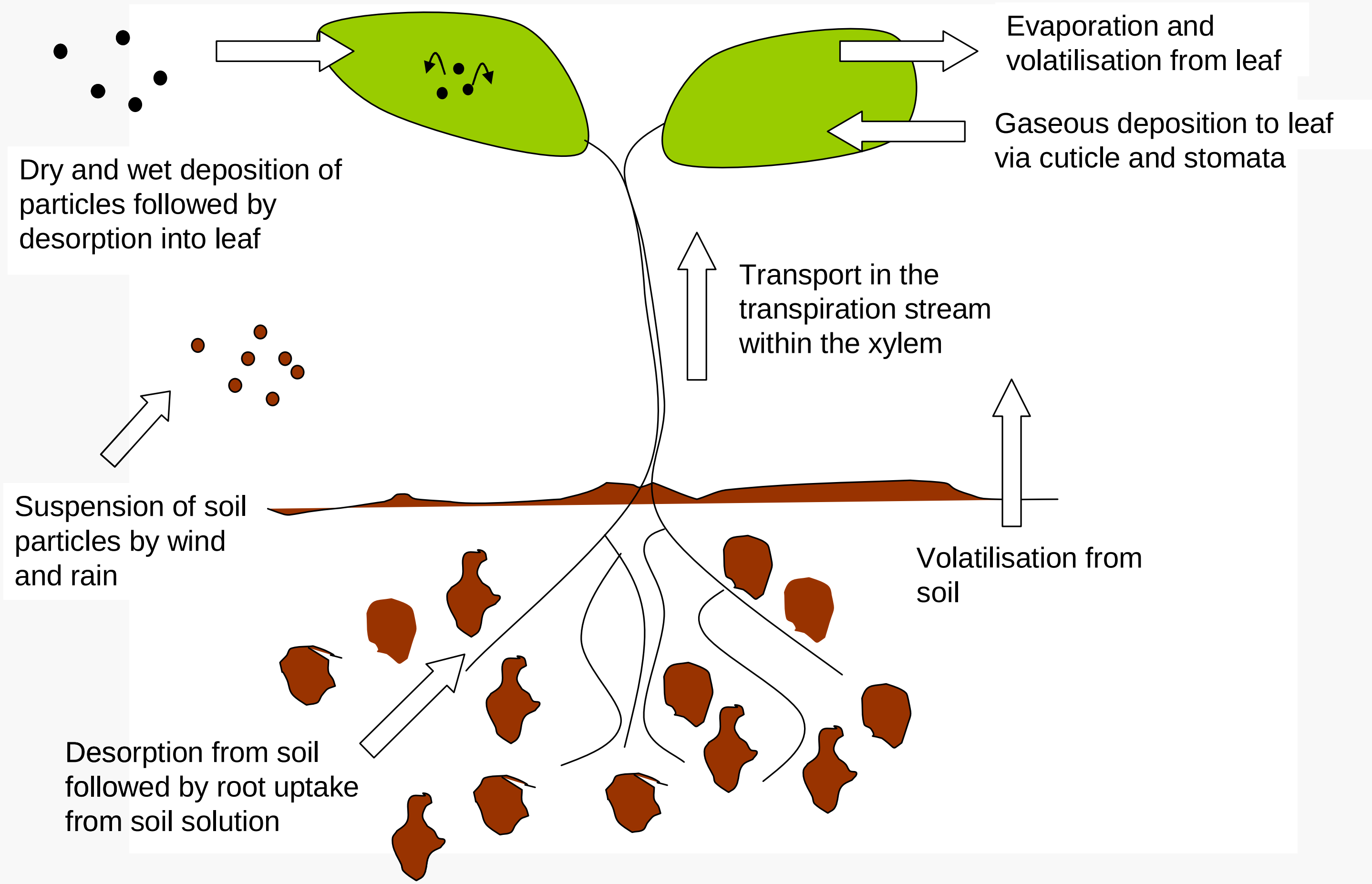
Chris Collins

Aim

- To give an overview of where we are, recent developments.
- Current models and their problems.
- The way forward.
- I am at the junction between modelling and experimentation
  - Jack of all trades master of none
  - We need the continuum

Current State

Uptake pathways

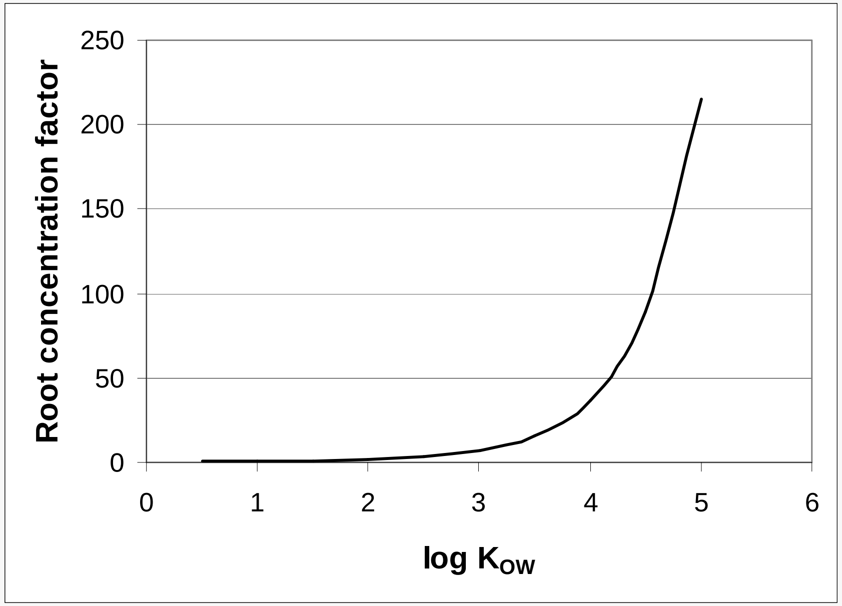


Plant uptake of organic pollutants

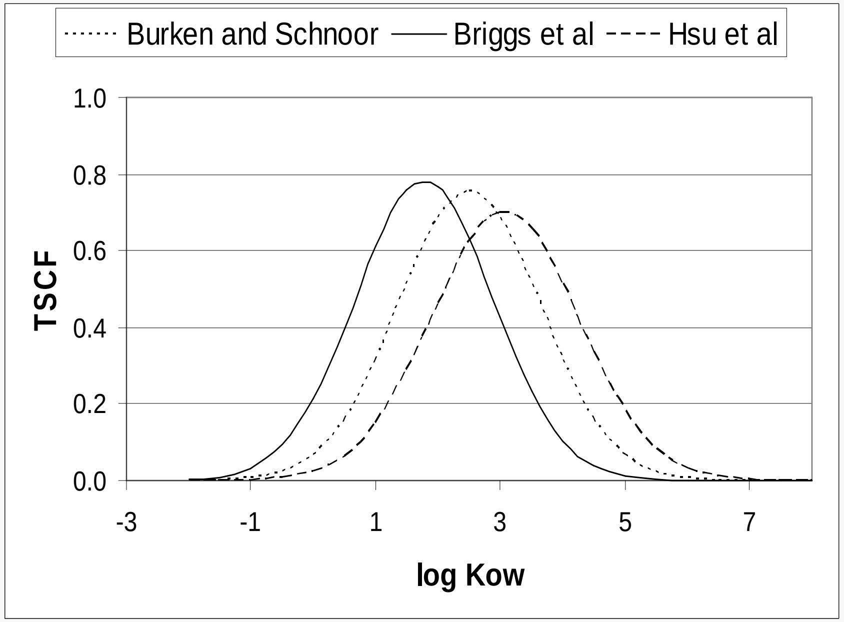
- We need to understand to model –
  - crop uptake of pollutants and pesticides
- We need to understand to remediate – plant uptake can be most important component of exposure.
- Many current models based on old research e.g. Briggs-Ryan (1983). These do not always provide the best prediction of the experimental data.

Briggs and Bromilow relationships

Roots



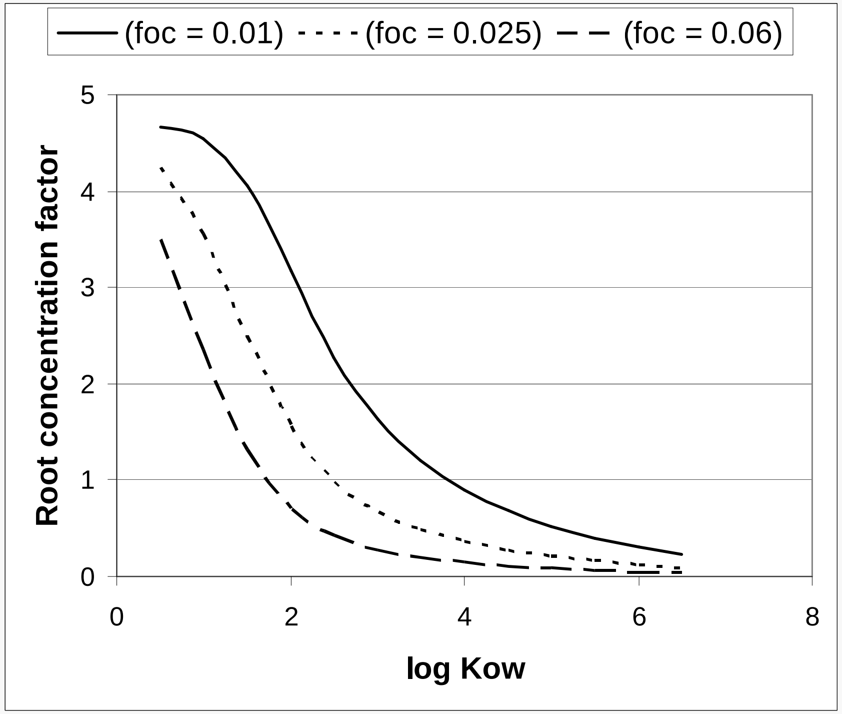
Shoots



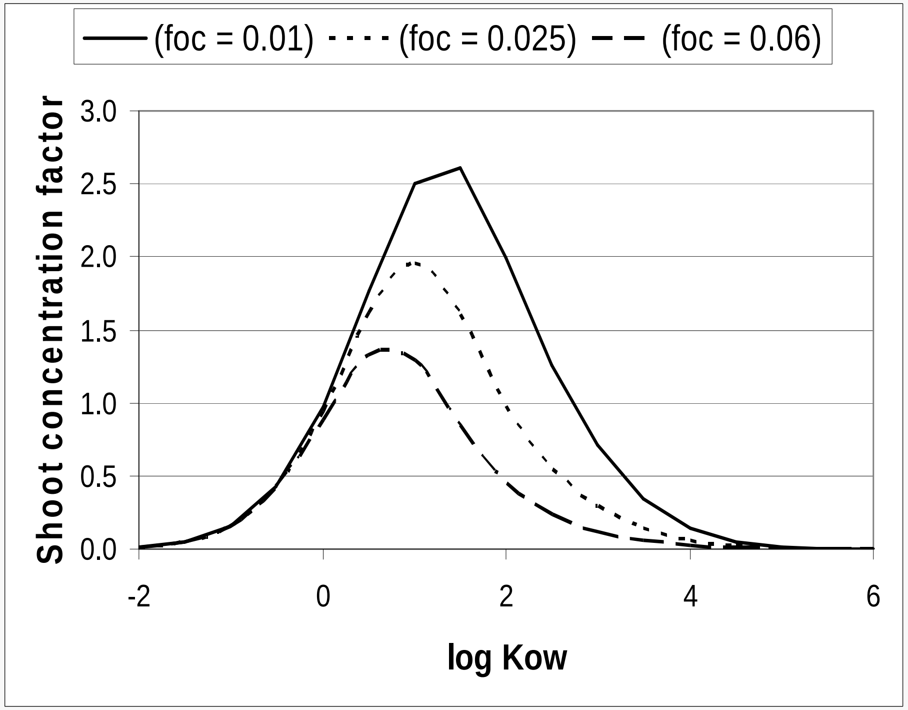
N.B. Solution culture experiments, limited number of chemicals, limited range of experiments.

Briggs-Ryan raltionships - soil properties

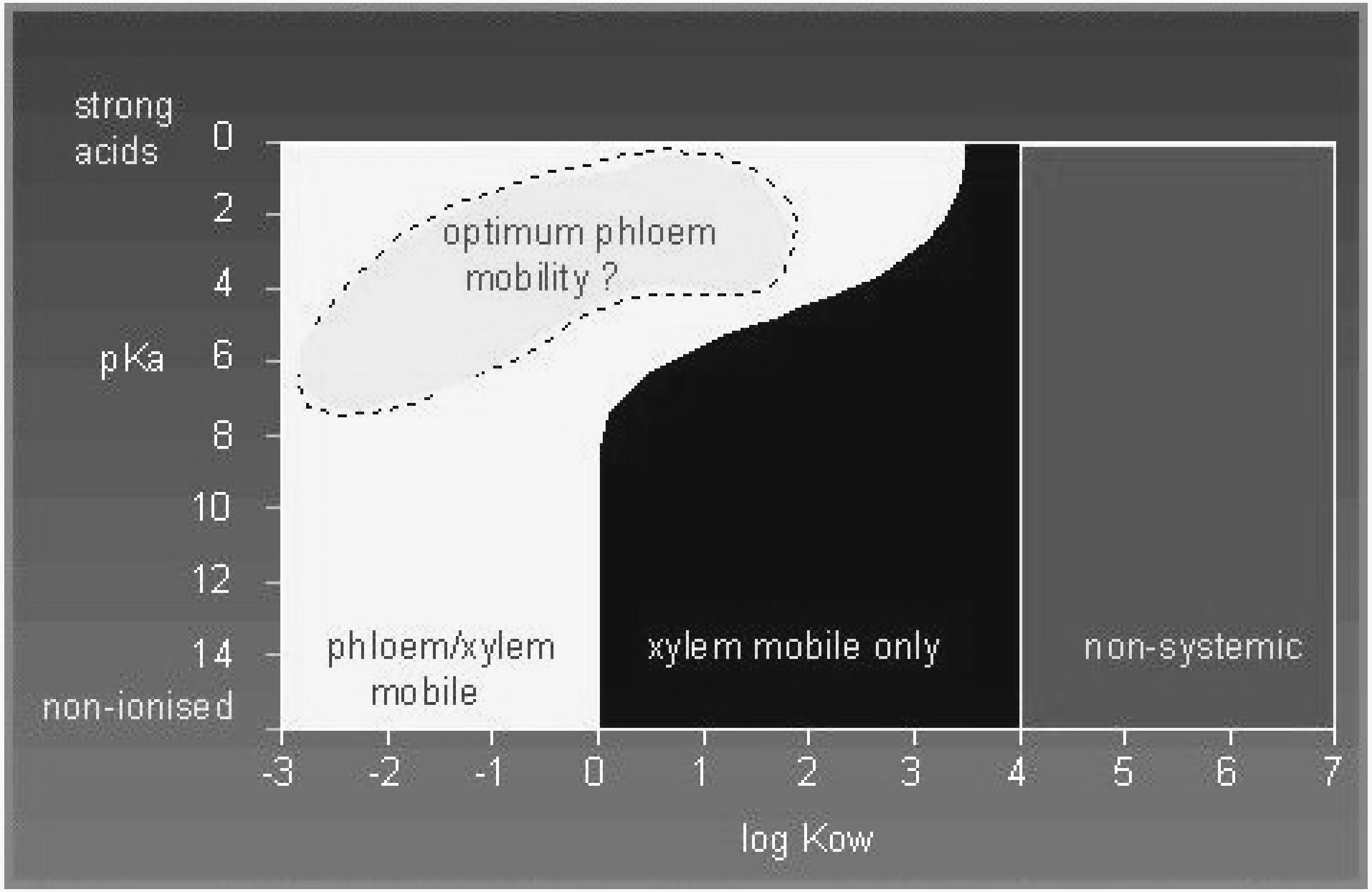
Root



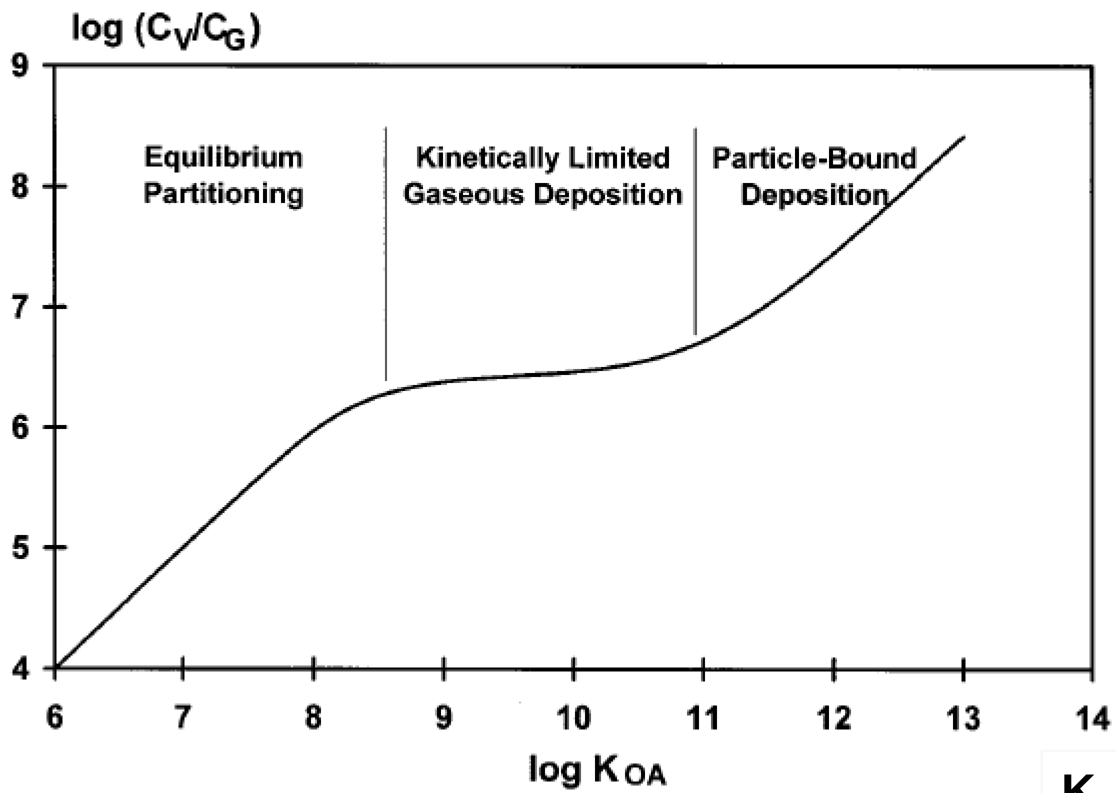
Shoot



Hydrophobicity and polarity



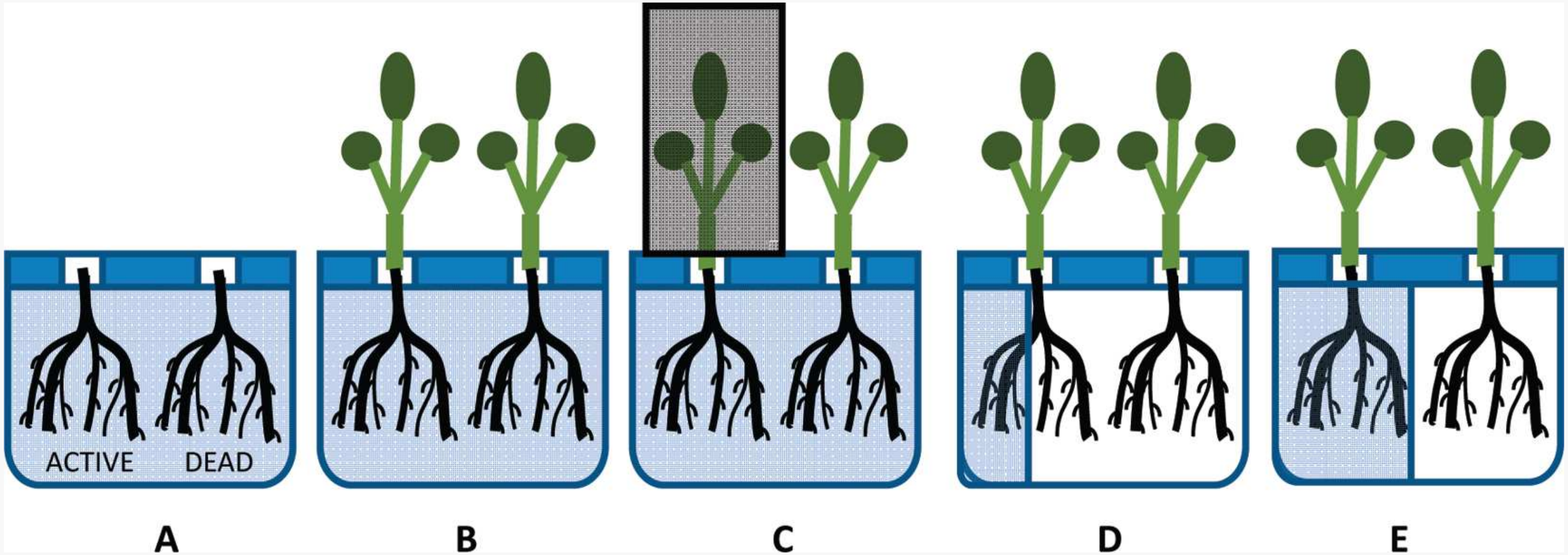
Aerial deposition – background source



$$K_{OA} = \frac{K_{OW}}{K_{AW}}$$

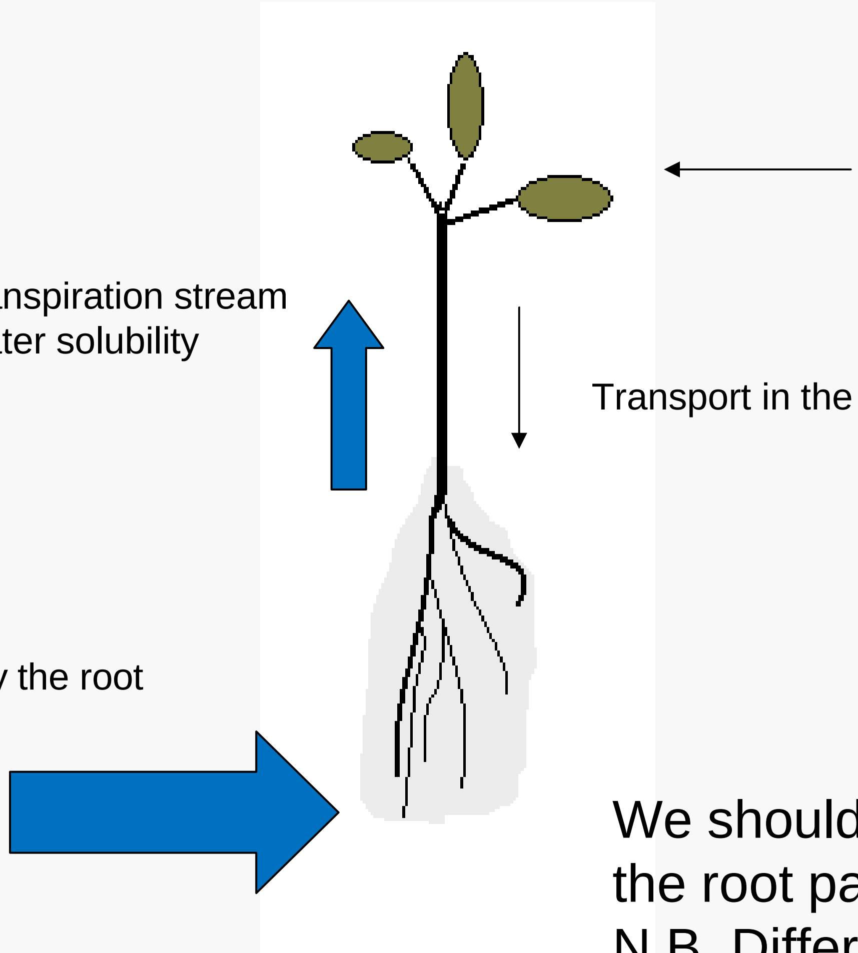
Predominant pathways

Predominant uptake pathways



Blue coloring indicates PAH spiked solution.
A: Bare roots in spiked solution; A_{ACTIVE} – shoot removed at start of the experimental period, A_{DEAD} root killed by acid treatment.
B: Plants grown in spiked solution with different PAH concentrations.
C: Plants grown in spiked solution, plant shoots in the light C_{LIGHT} and half darkness C_{DARK}.
D: Half plants grown in clean solution D_{CLEAN}; others have half of their roots in spiked solution and half in clean solution D_{POLL}; all the plants sharing the same air conditions.
E: Half plants grown in spiked E_{POLL} and half in clean E_{CLEAN} solution; all the plants sharing the same air conditions.

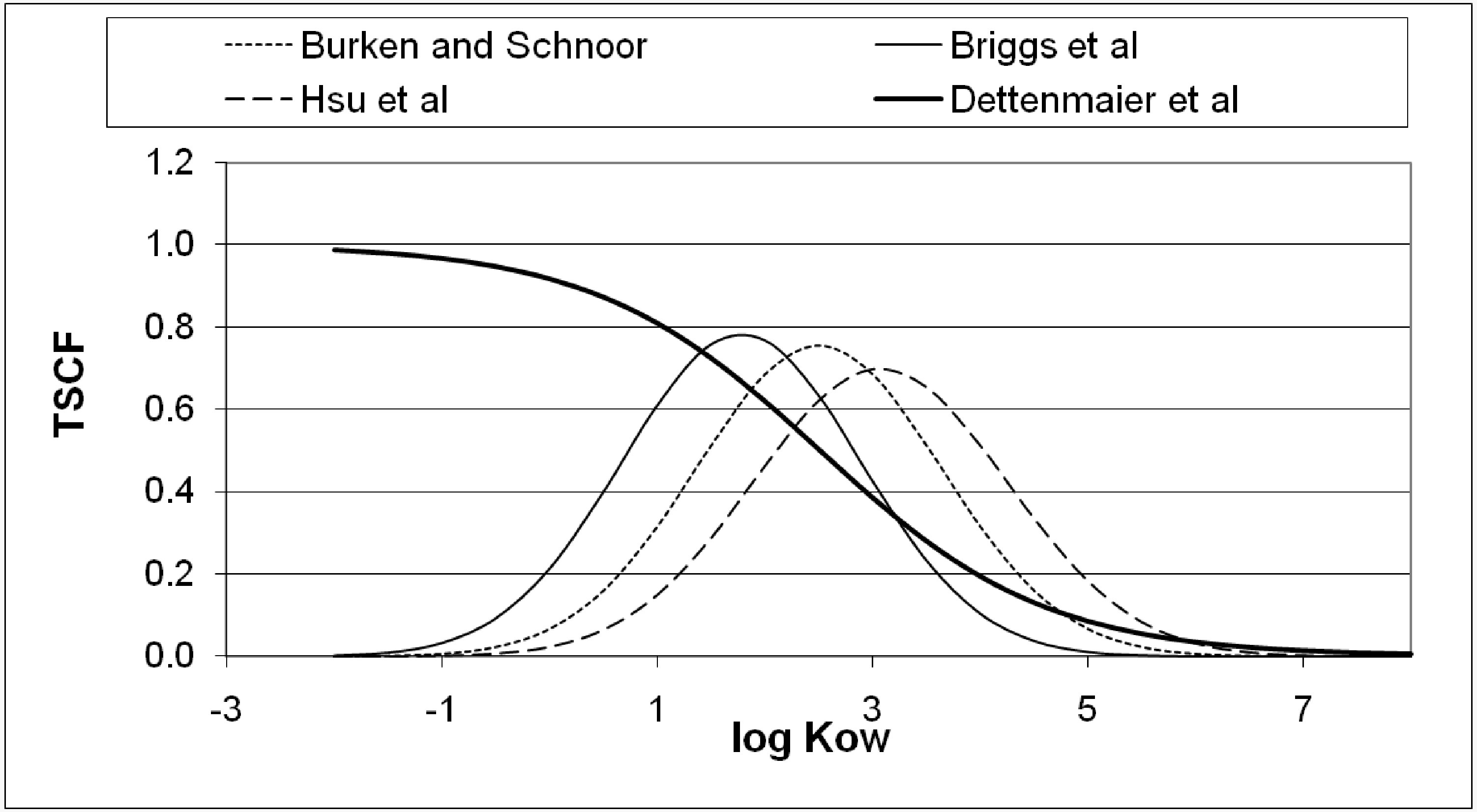
Significant pathways



We should focus research on the root pathway for PAH.
N.B. Different for other chemicals

Recent findings

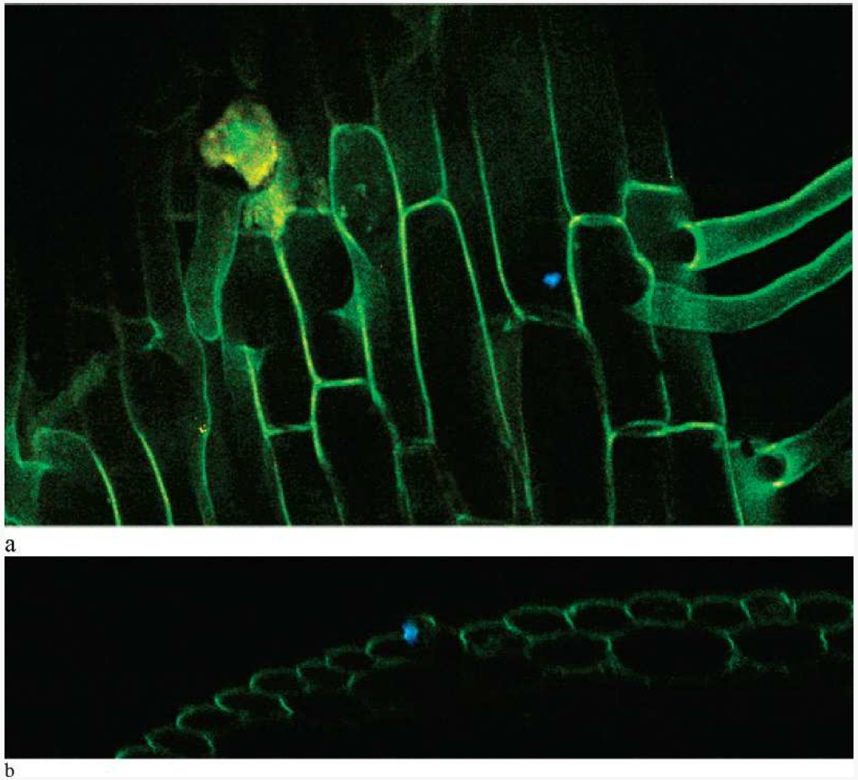
New work TSCF



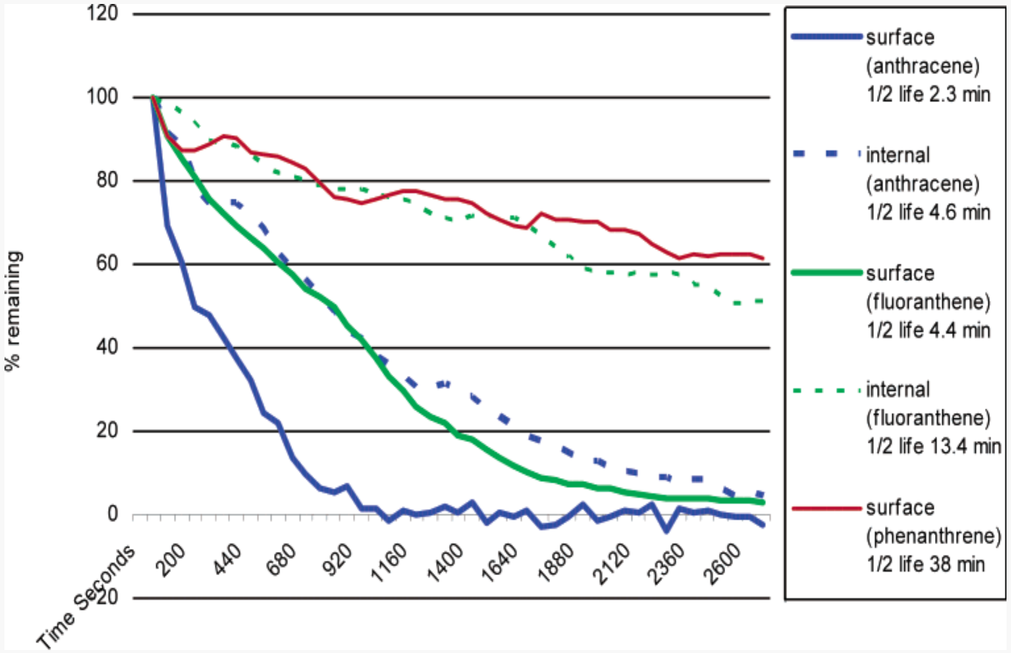
Dettenmaier study 100s of measurements and much wider range of chemicals, others 4-8

Two photon excitation microscopy

Root uptake

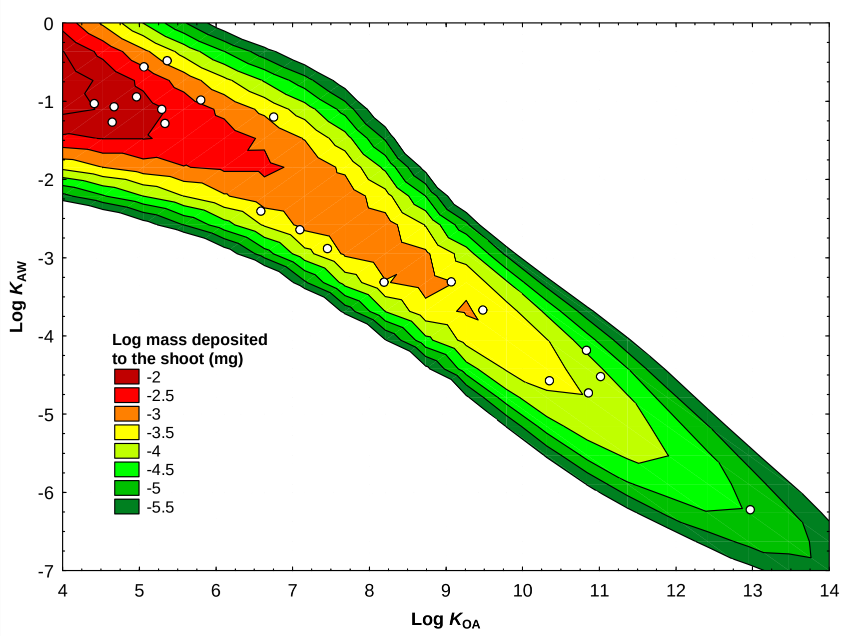

a
b

Calculated degradation

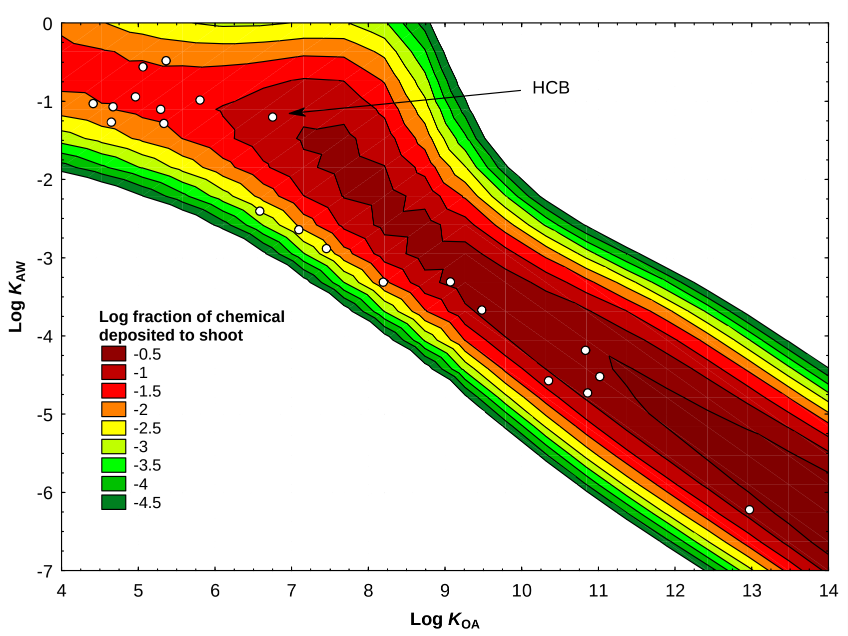


Combined root uptake and soil volatilisation model

Total uptake



Fractional uptake



Modelling

Model types

- Simple regression e.g. Travis and Arms

$$\log B_v \quad = \quad 1.588 - (0.578 \log K_{ow})$$

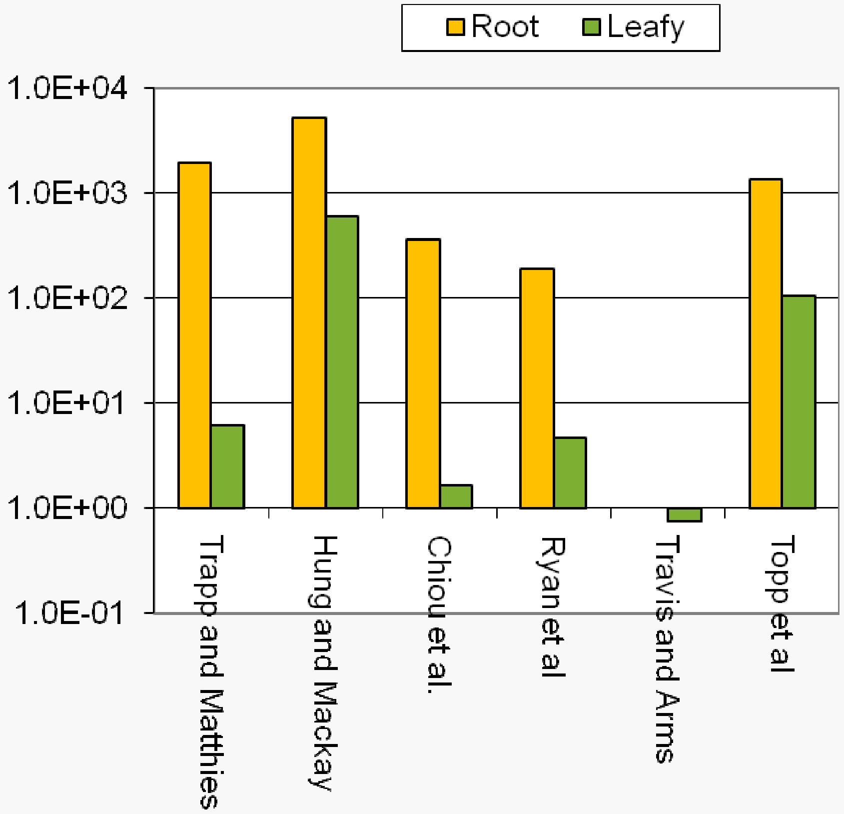
- Mechanistic models e.g. Trapp and Matthies
  - Growth dilution
  - Metabolism
  - Transpiration
- Fugacity models e.g. Hung and Mackay
  - Suite of partition coefficients between different environmental media and plant components.

Model types

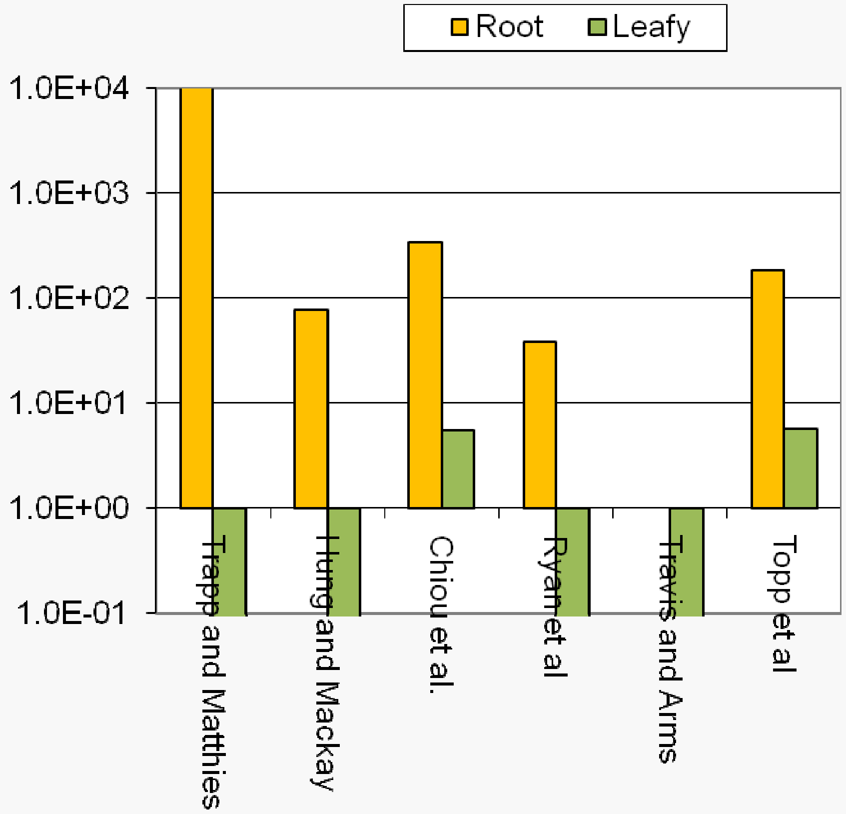
- A note about ionisable compounds – not my area of expertise.
- Separate compounds into neutral and ionic free fractions – e.g. Henderson-Hasselbach equation
- Subsequent uptake following soil to root partition and movement into stem via the transpiration stream as previously discussed.

Plant uptake modelling – model inter-comparison

DCB from sludge

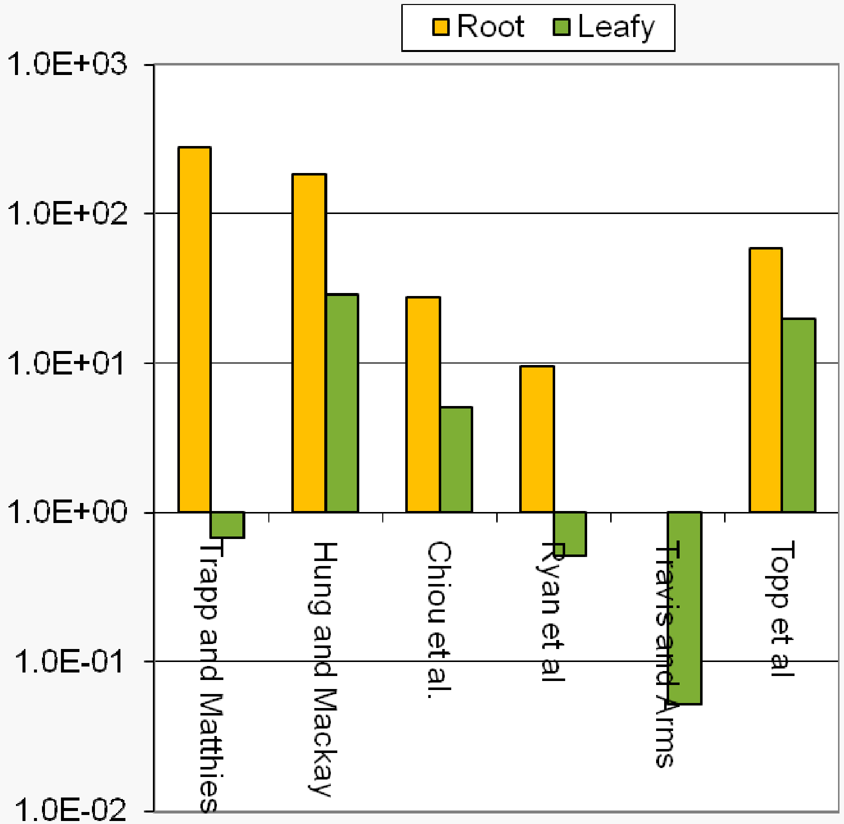


HCB from sludge

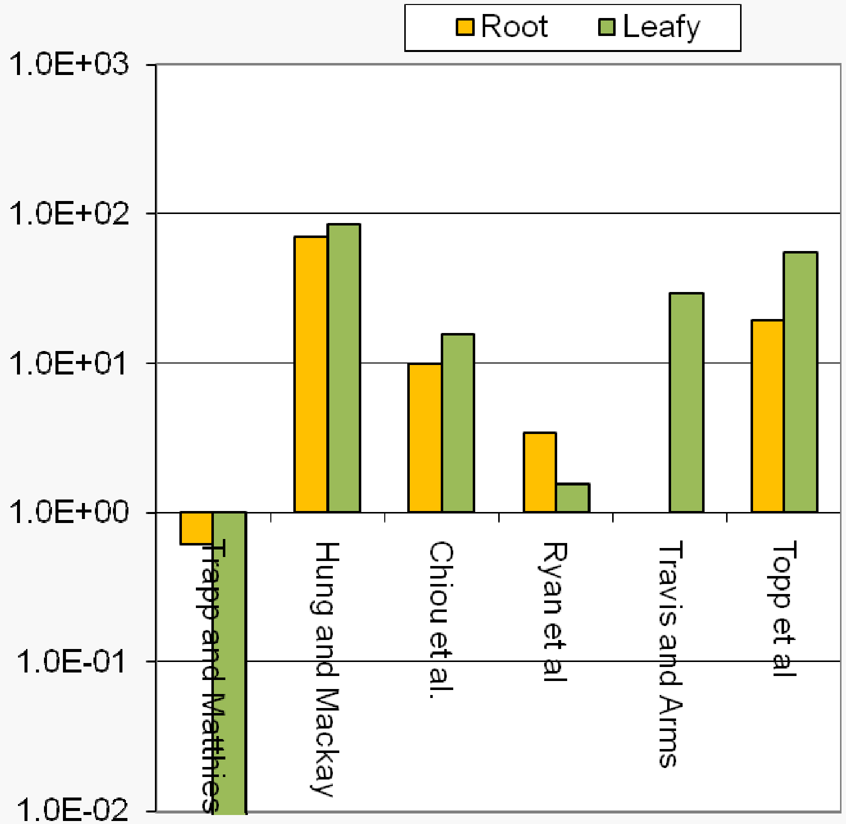


Plant uptake modelling – model inter-comparison

TCB sludge - aged



TCB spiked - fresh

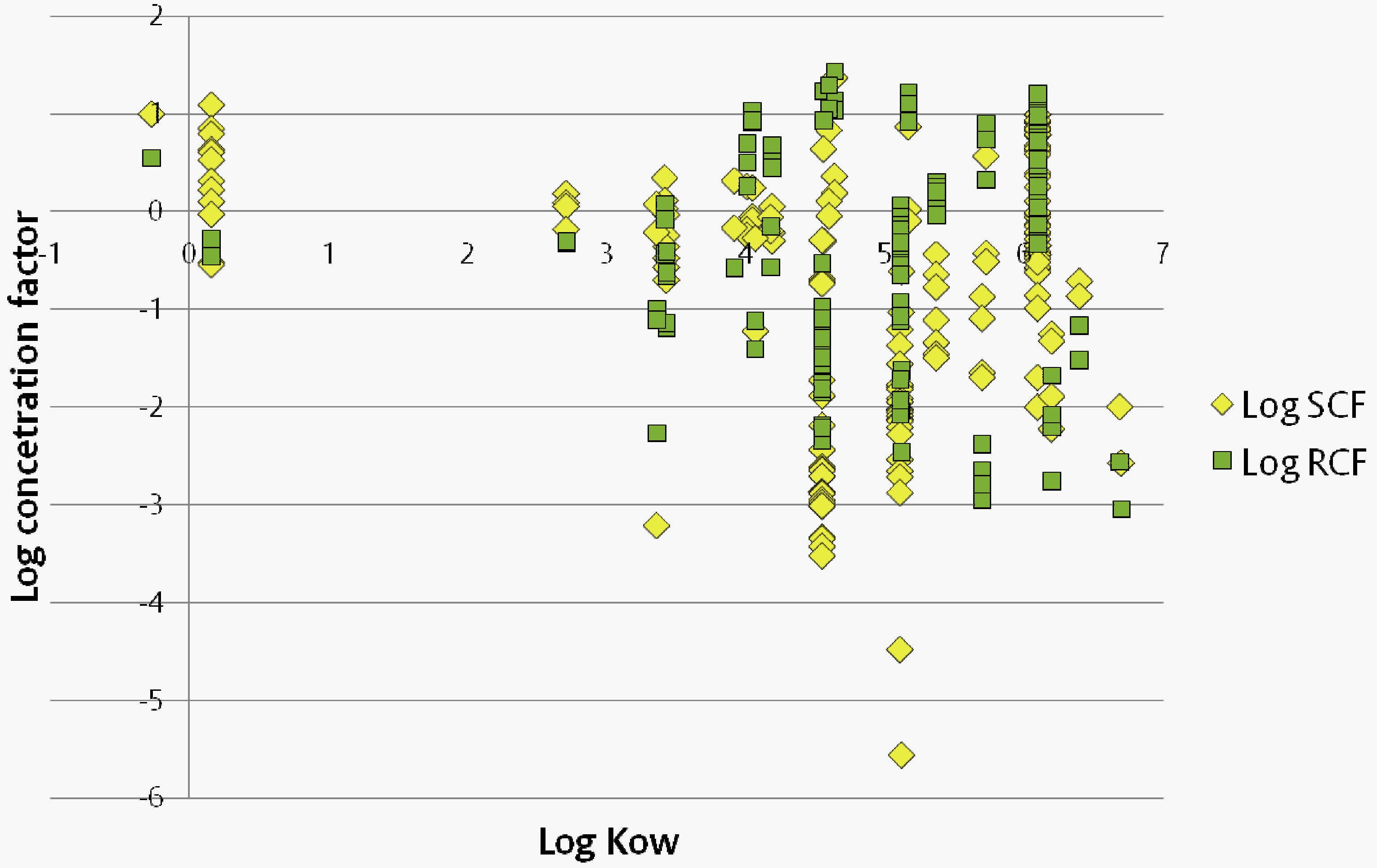


Model Intercomparison

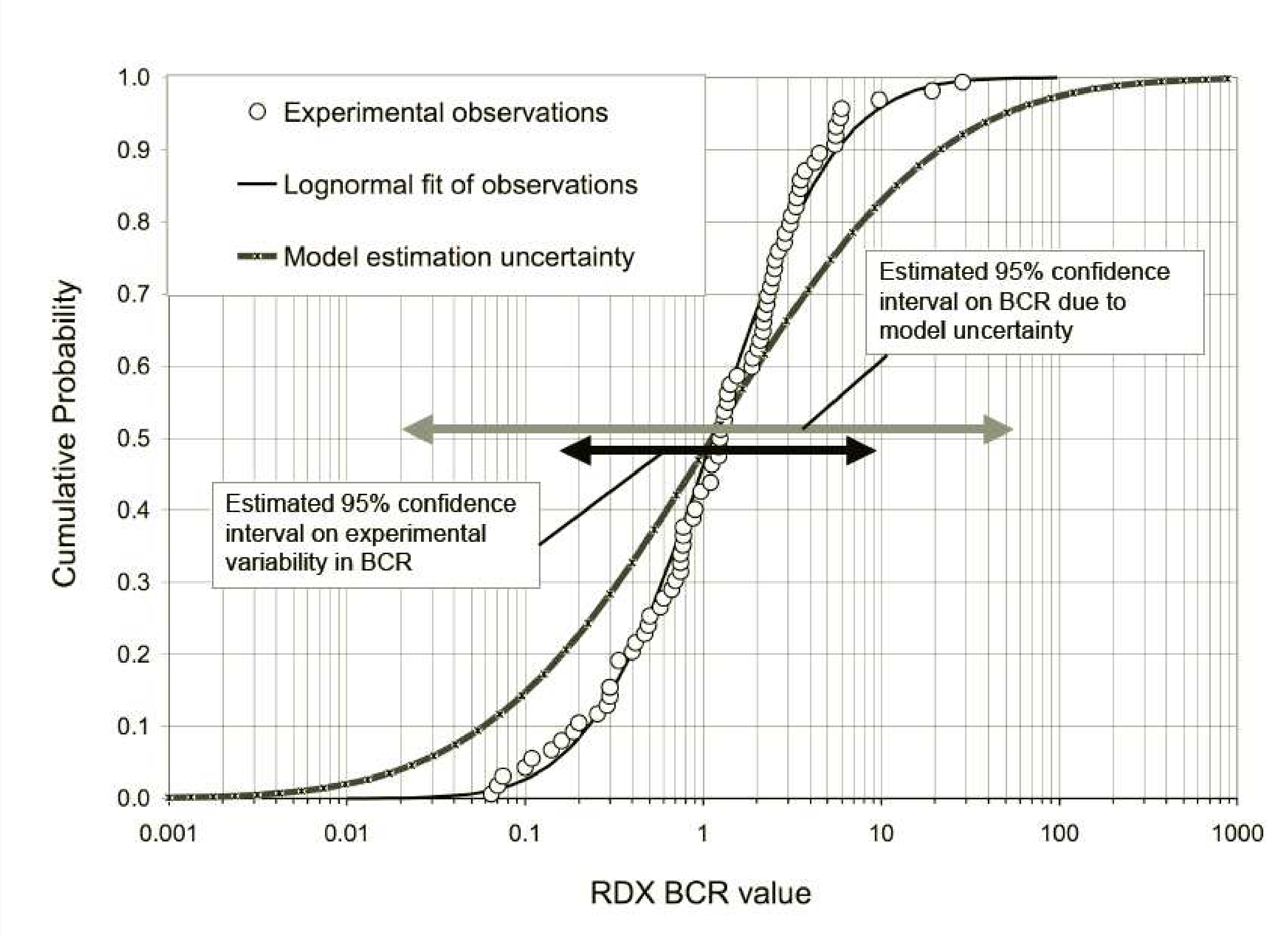
	Shoot vegetables		Root vegetable s	
Travis and Arms	2.2	Trapp and Matthies	1.6	
Ryan et al.	1.9	Ryan et al.	1.1	
Topp et al	0.9	Hung and Mackay	0.9	
Hung and Mackay	0.7	Chiou et al	0.6	
Chiou et al	0.6	Topp et al	0.6	
Trapp and Matthies	0.5			

Data variability

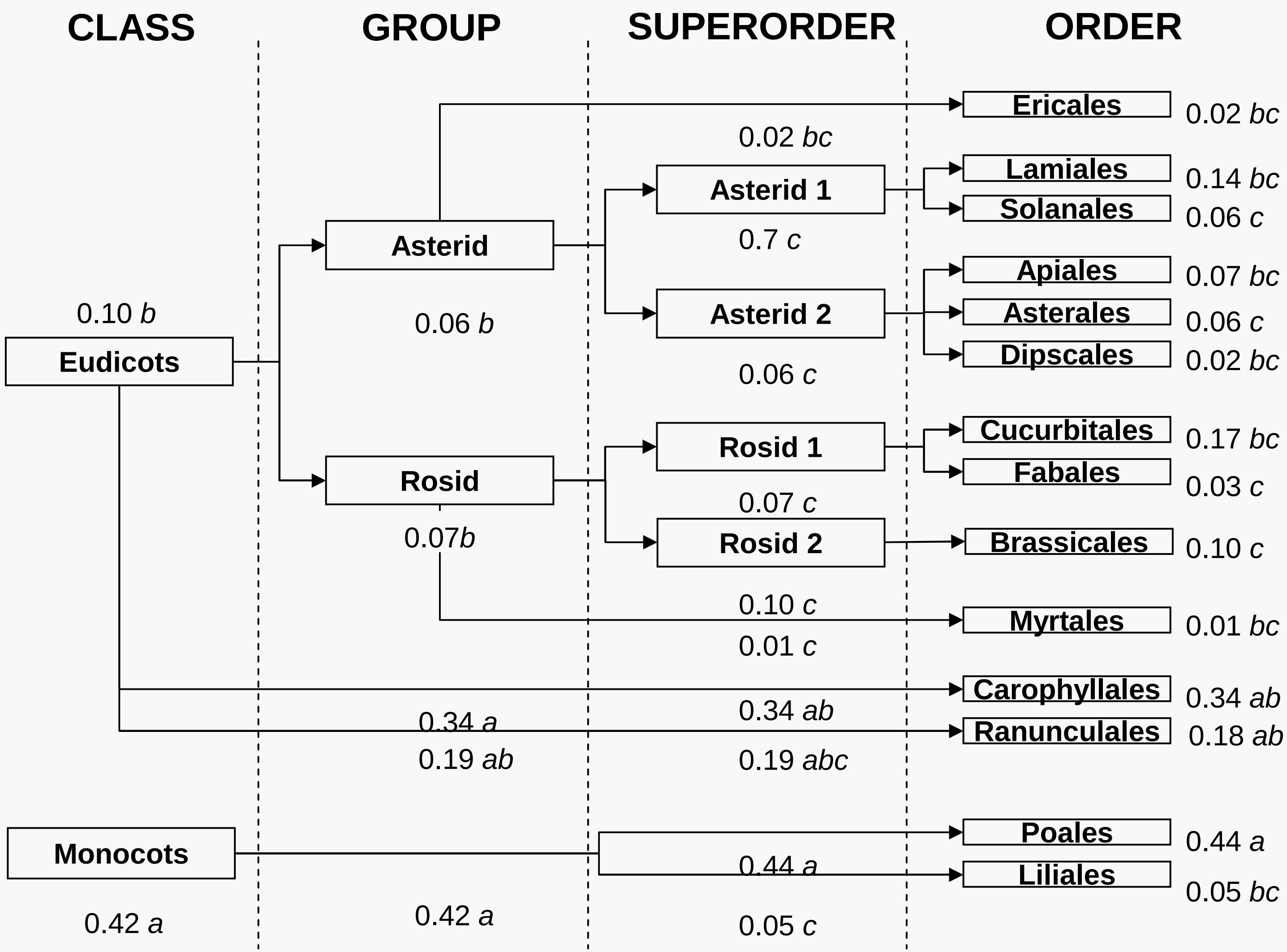
Data variability



Plants Experimental variability -1



Plants experimental variability – species



RSC, Contaminated Land Meeting, 2010

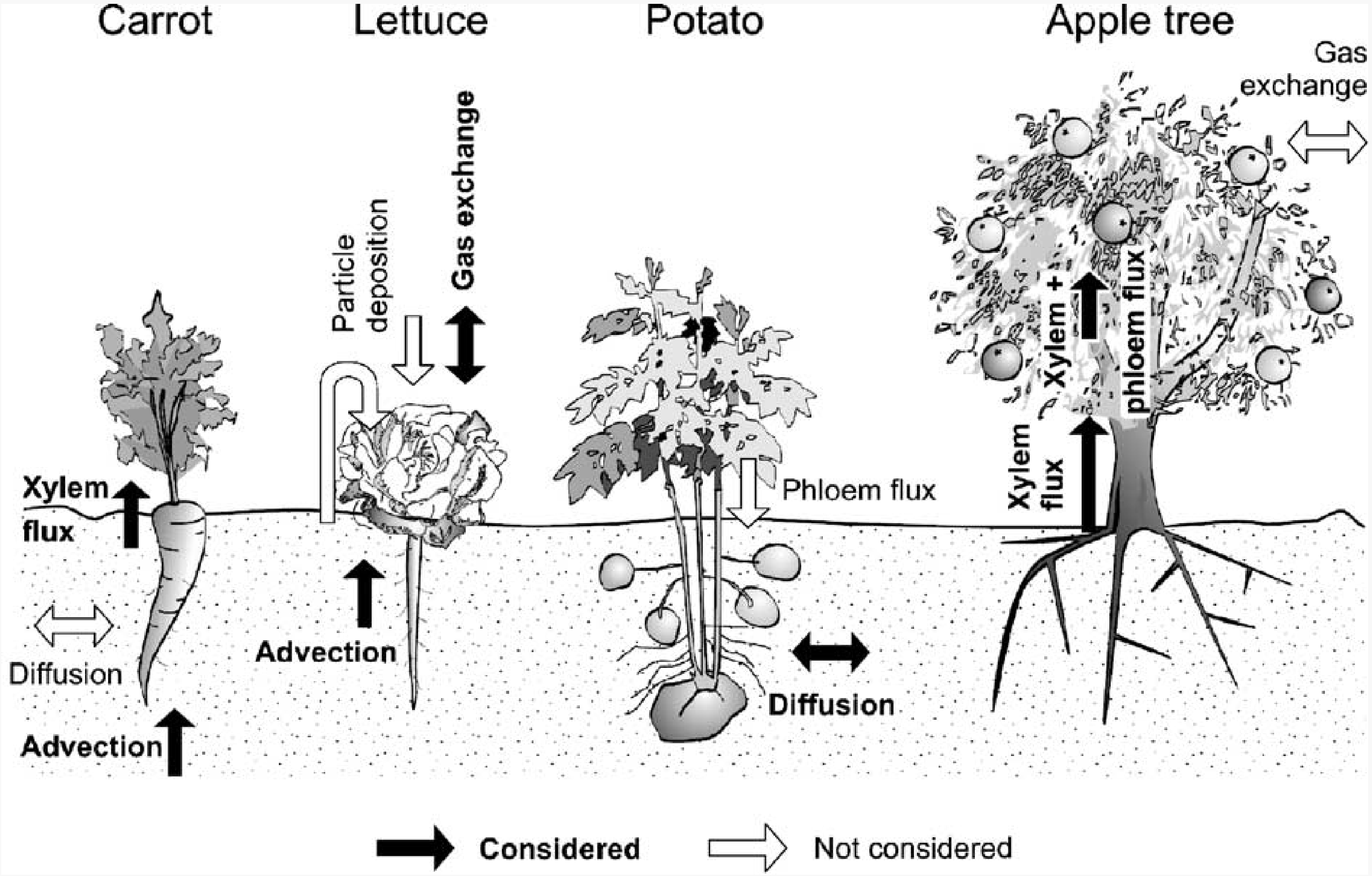
Do we have the data we need?

Chemical	Plant component	Range	Mean	Data	Most sensitive parameters (% of variation)
DCB	Leaf	2.1×1^{-5} – 1.51×1^{-3}	2.0×10^{-4}	1.3	bL^2 (84)
	Root	0.04 – 1.1	0.15	0.1 (core) 0.1 (peel)	bR^2 (53) f.o.c. (22)
TCB	Leaf	2.6×1^{-6} – 1.92×1^{-4}	2.0×10^{-5}	8.3	bL (81)
	Root	0.06 – 2.40	0.30	2.8 (core) 5.5 (peel)	bR (54) f.o.c. (23)
HCB	Leaf	2.1×1^{-6} – 1.51×1^{-4}	1.8×10^{-5}	4.4	bL (80.6)
	Root	4.6×1^{-5} – 2.2×1^{-2}	1.2×10^{-3}	0.08 (core) 9.5 (peel)	bR (91.3)

Models do not account for differences between core and peel

The way forward

Crop specific models



Crop specific models

Step 1: Dissolved concentration in soil

Chemical concentration in soil C_{Soil} is 1 mg MTBE per kg soil (wet weight). The $\log K_{OC}$ is $0.81 \log K_{OW} + 0.1 = 1.0234$, giving $K_{OC} = 10.55$. The concentration in the soil pore water C_W is

$$\frac{C_W}{C_{Ssoil}} = \frac{\rho_{wet}}{OC \times K_{OC} \times \rho_{dry} + P_W + K_{AW} \times P_A}$$

$$= \frac{1.95}{0.02 \times 10.55 \times 1.6 + 0.35 + 0.0175 \times 0.1} = 2.83$$

OC = organic carbon content of soil

K_{OC} = soil water to organic carbon partition coefficien

ρ_{wet} = soil wet density

ρ_{dry} = soil dry density

K_{AW} = air to water partition coefficient

P_A = volume fraction soil air

P_W = volume fraction soil water

Crop specific models

Step 2: Concentration in stem

Basic equation:

$$C_{\text{Stem}}(t=\infty) = \frac{C_{\text{Xy}} \times \frac{Q}{M}}{\frac{Q}{M \times K_{\text{Wood}}} + k_{\text{E}} + k_{\text{G}}}$$

$$\log K_{\text{Wood}} = -0.266 + 0.632 \log K_{\text{OW}}$$

$$C_{\text{Xy}} = \text{TSCF} \times C_{\text{W}} = \text{TSCF} \times 2.83 \times C_{\text{Soil}}$$

$$\text{TSCF} = 0.756 \times \exp\left\{\frac{-(\log K_{\text{OW}} - 2.50)^2}{2.58}\right\} = 0.37$$

$$\frac{C_{\text{Stem}}}{C_{\text{Soil}}} = \frac{2.83 \times 0.37 \times \frac{3000}{100}}{\frac{3000}{100 \times 2.85} + (0.01 + 0.692)} = 2.80 \frac{\text{mg/kg fresh plant}}{\text{mg/kg wet soil}}$$

C_{stem} = conc. in stem

C_{Xy} = conc. in xylem

Q = annual transpiration

M = mass of woody stem

K_{Wood} = water to wood partition coefficient

K_E = metabolic rate

K_G = growth rate

Crop specific models

Step 3: Concentration in apples

Water flux into apples:

$$Q_F = \mathrm{dw} \times 20 = 0.156 \times 20 = 3.12\,\mathrm{l/kg}$$

Concentration in fruit:

$$C_{\mathrm{Fruit}} = Q_F \times C_{\mathrm{Stem}} / K_{\mathrm{Wood}} = 3.12 \times 2.80/2.85 = 3.06 \times C_{\mathrm{Soil}}$$

Q_F = fruit annual transpiration
C_{fruit} = conc. in fruit
C_{stem} = conc. in stem
K_{Wood} = water to wood partition coefficient
C_{Soil} = conc. in soil

Crop specific models

TABLE II Calculated uptake of chemicals from soil into tree fruits and comparison to measured results

Chemical	*log K_{OW}*	*Fruit*	*BCF T&A*	*BCF_{Fruit} Fruit Tree Model*	*BCF_{Fruit} measured (std dev)*
MTBE	1.14	Apple	1.74	3	n.d.f.
Benzene	2.02	Apple	0.54	1.6	n.d.f.
Toluene	2.75	Apple	0.2	0.37	n.d.f.
Trichloroethene	3.03	Apple	0.14	0.17	n.d.f.
Naphthalene	3.36	Apple	0.09	0.06	n.d.f.
Fluoroanthene	5.13	Apple	0.009	2.36×10^{-5}	5.6×10^{-4} (8.8×10^{-4})[a]
Fluoroanthene		Pear	0.009	2.27×10^{-5}	8.4×10^{-5} (8.9×10^{-5})[a]
Fluoroanthene		Plum	0.009	2.39×10^{-5}	1.2×10^{-5} (5.4×10^{-6})[a]
Benzo[*a*]pyrene	6.13	Apple	0.003	7.80×10^{-8}	1.4×10^{-4} (1.1×10^{-4})[a]
Benzo[*a*]pyrene		Pear	0.003	7.50×10^{-8}	7.3×10^{-6} (4.7×10^{-6})[a]
Benzo[*a*]pyrene		Plum	0.003	7.90×10^{-8}	2.7×10^{-6} [a]
2,3,7,8-TCDD[c]	6.76	Apple	0.001	1.41×10^{-9}	"0" [b]
2,3,7,8-TCDD[c]		Pear	0.001	1.36×10^{-9}	"0" [b]
OCDD[c]	8.2	Apple	0.0001	4.58×10^{-14}	"0" [b]

No genuine sensitivity analysis
Pattern same as T and A
Comparison with one data set

What next?

- Focus on important pathways for chemical of interest.
- Emphasise *law of parsimony*
- Validation, validation, validation
- Good experimental protocols required to allow modellers to use all results.
  - Rapid measures of bioavailable fraction – SPME, silicone
  - Background air concentrations
  - Soil properties