Do Lab Derived K_{oc} Values of Pesticides Match K_{oc} Values Determined from Column and Field-Scale Experiments?
A critical Analysis of Relevant Literature.

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Introduction

- Sorption of pesticides to the soil matrix is an important process that is always considered when assessing the fate of pesticides in the environment.

- The equilibrium distribution coefficient of the substance between liquid and solid phase, *Kd*, is commonly used to quantify sorption.

- Batch sorption studies are used to determine *Kd* (OECD, 2000, 2004)

(Kd = Koc OC)

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Introduction

Problems with batch sorption studies and application of Kd derived from batch studies for the assessment of pesticide mobility:

- Drying, milling of soil --> change in soil properties?

- Optimized contact between solution and soil particles (large water:soil ratio, shaking) --> relevance for contact between solution and sorption sites in undisturbed soils?

- Limited duration (1 d) --> equilibrium?

- Do equilibrium conditions occur in soils (less optimal contact, range of flow rates in different pore sizes, other time scales, …)?

- Accuracy in the case of weakly sorbing substances?

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Introduction

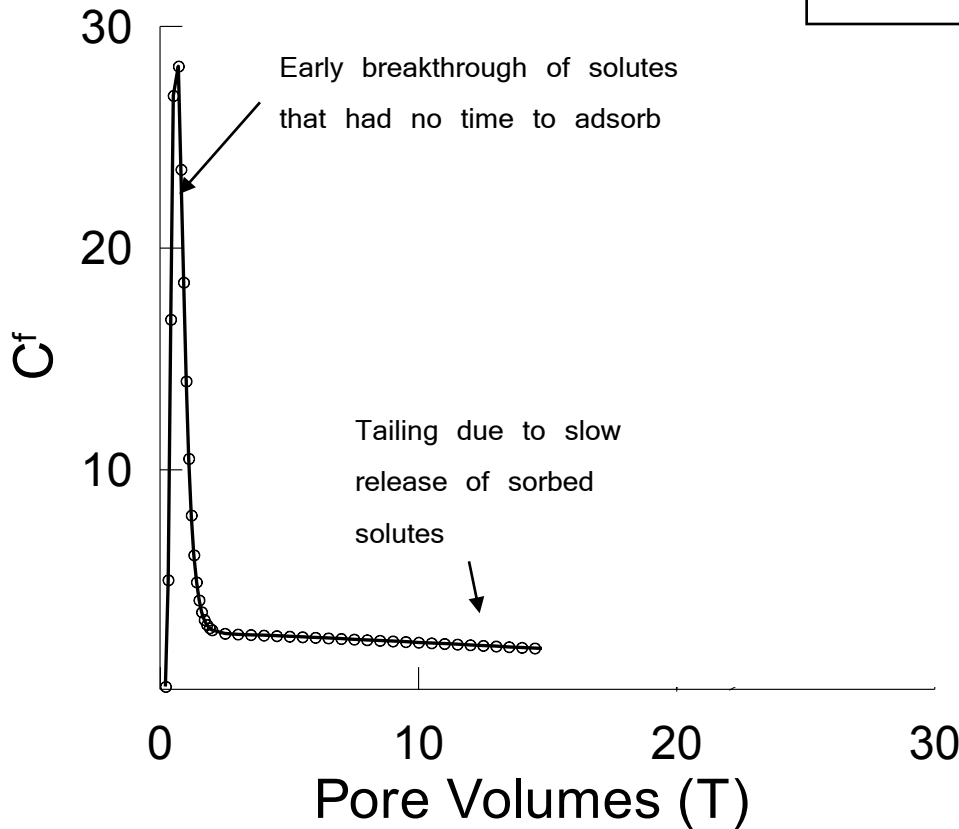Column and field studies to determine sorption parameters
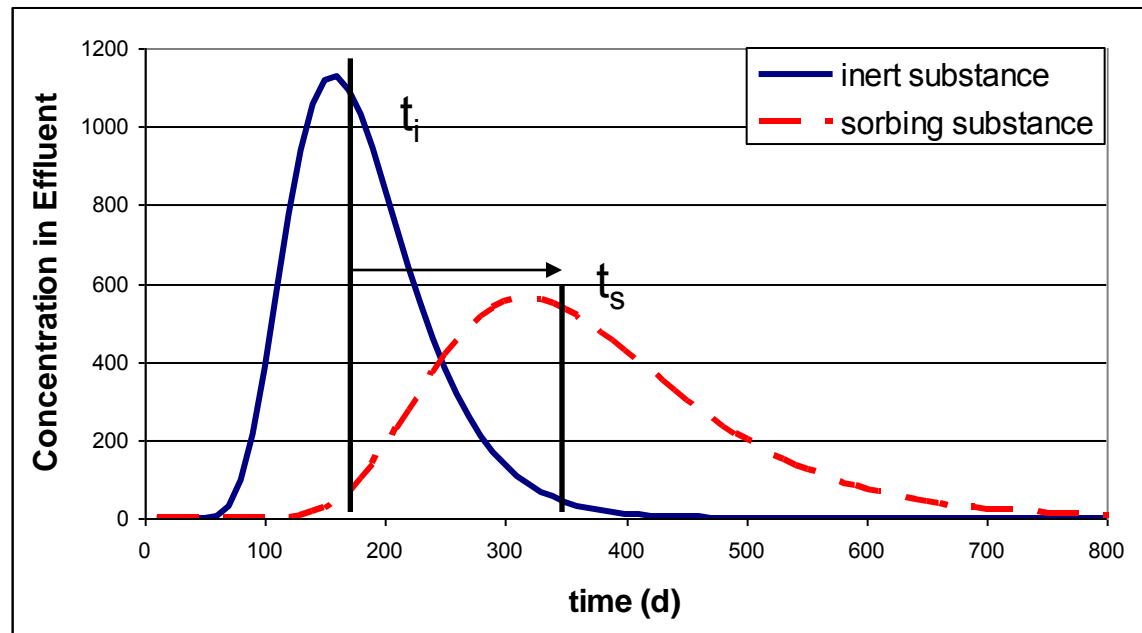
Retardation coefficient: $R = t_s / t_i$

$R = 1 + \rho_b \, Kd/\theta$

Introduction

Effect of non-equilbrium sorption on transport

$$\left\{ \theta\left(1+f\,\frac{\rho_b}{\theta}\,\frac{dF(C_l)}{dC_l}\right)\frac{\partial C_l}{\partial t} = \frac{\partial}{\partial z}\left(\theta D_e\,\frac{\partial C_l}{\partial z}\right) - Jw\frac{\partial C_l}{\partial z} - \alpha\rho_b\left(-f\,F(C_l)-C_{a2}\right) \right.$$

$$\frac{\partial C_{a2}}{\partial t} = \alpha\left(-f\,F(C_l)-C_{a2}\right)$$

α = mass exchange coefficient

Early breakthrough of solutes that had no time to adsorb

Tailing due to slow release of sorbed solutes

C^f

Pore Volumes (T)

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Literature Review

- Peer reviewed articles in scientific journals (ISI listed)
- Kd/Koc derived from:
  - both batch and column studies for the same pesticide and soil. (139 Kd values; 31 substances)
  - both batch and field studies for the same pesticide and soil. (24 Kd values)
- α derived from column studies

- Additional parameters:
  - pore water velocity: v
  - solute residence time in column/field experiment: $T_{res} = z*R/v$

- Data subsets:
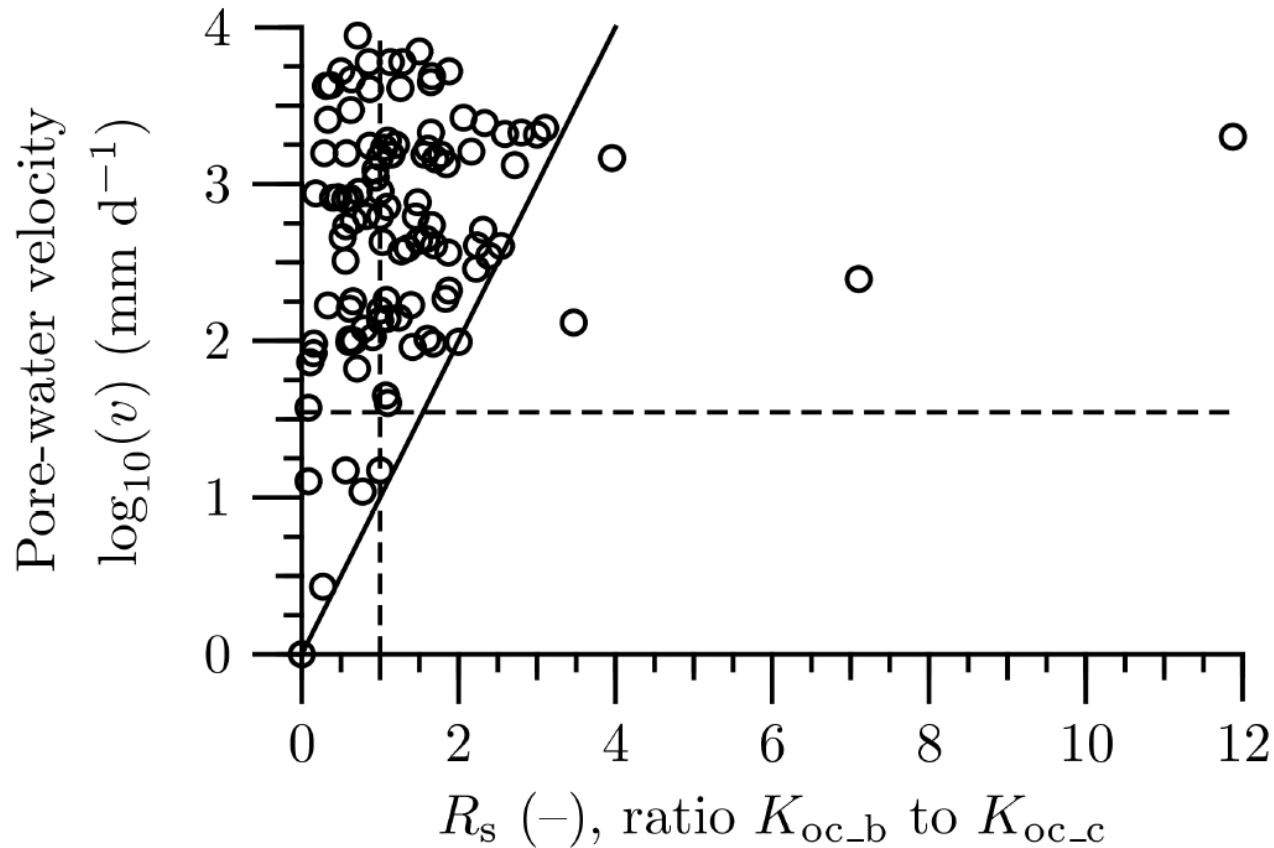 - saturated (S) vs. unsaturated (Us)
  - undisturbed (Ud) vs. packed (P)

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Results: K_{oc} batch (K_{oc_b}) versus K_{oc} column (K_{oc_c})
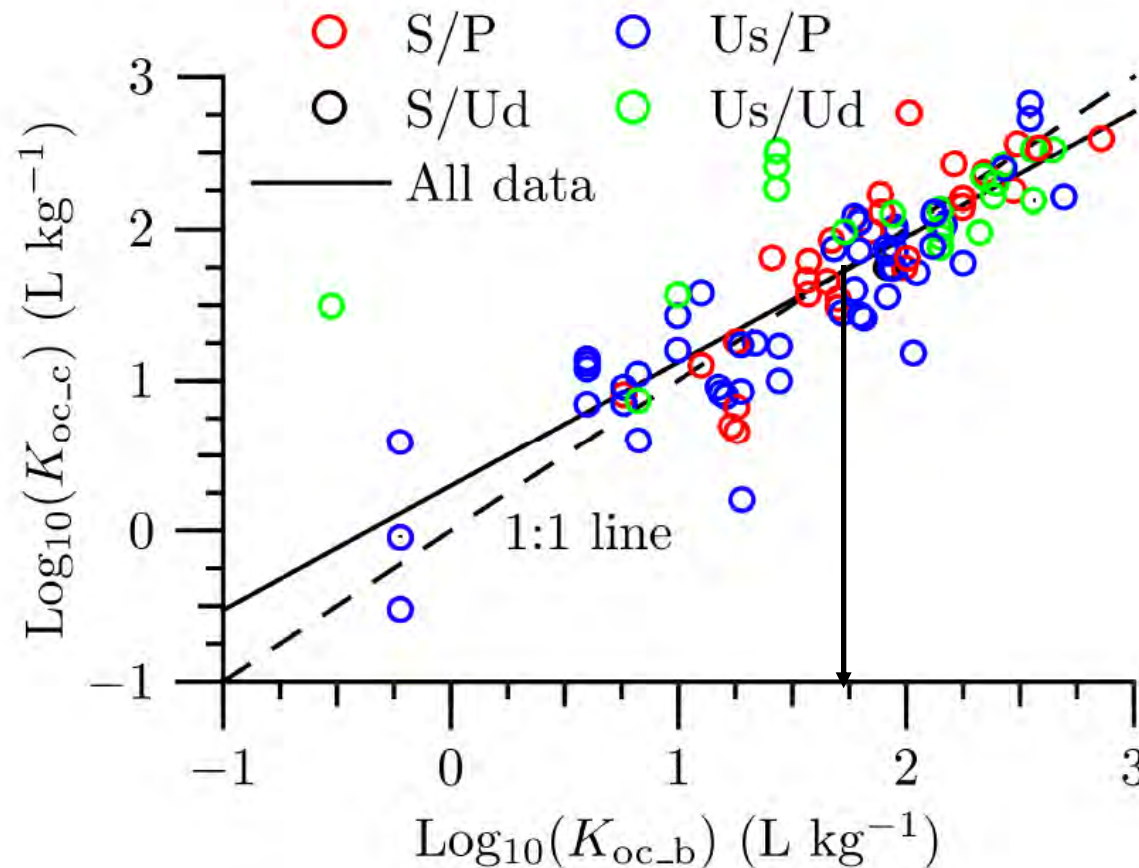
For $K_{oc} < 41.5$ l kg^{-1} : $K_{oc\_c} > K_{oc\_b}$

For Unsaturated/undisturbed column experiments, $K_{oc\_c} > K_{oc\_b}$

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Results: Effect of pore water velocity on ratio K_{oc_b}/K_{oc_c}

For v < 35 mm /d: K_{oc_b} < K_{oc_c} (R_s = K_{oc_b}/K_{oc_c} <1)
(only experiments in unsaturated and undisturbed soil columns)

Results: Effect of solute residence time on ratio K_{oc_b}/K_{oc_c}
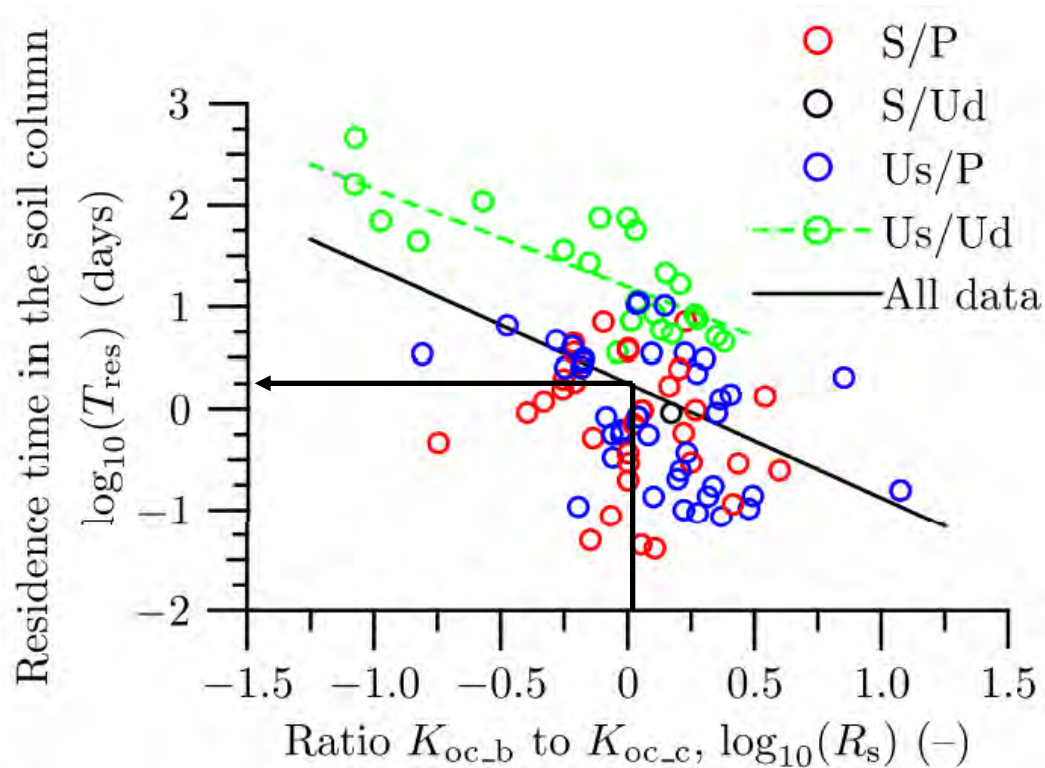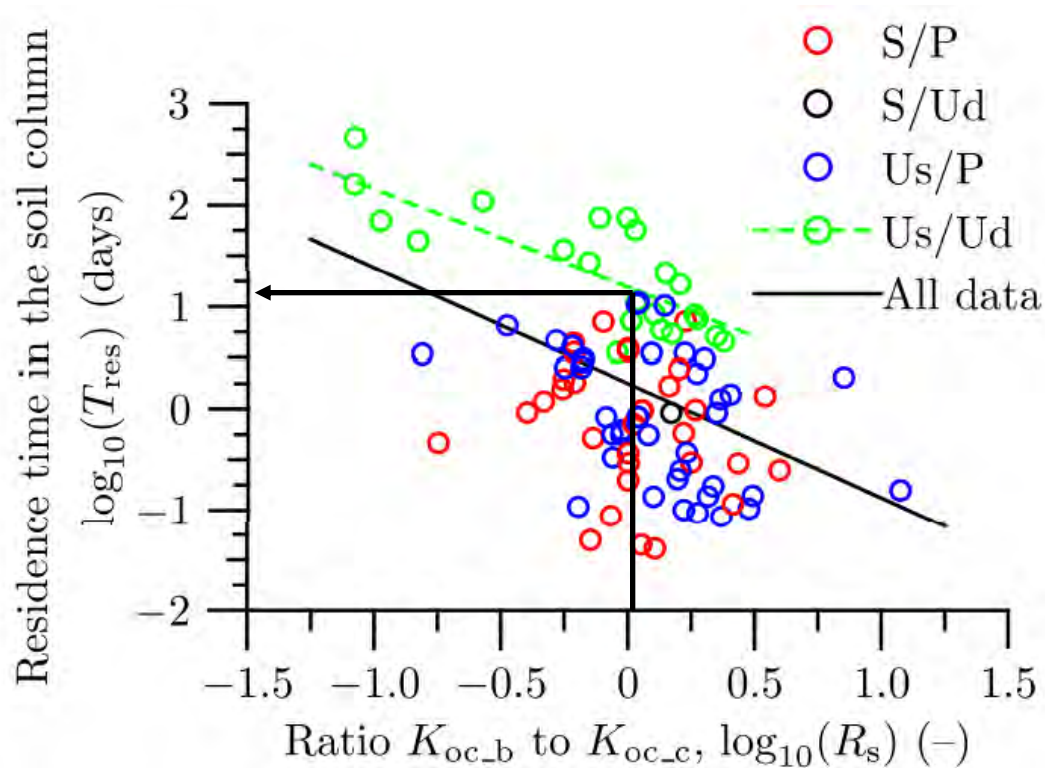

All data: $K_{oc\_b} < K_{oc\_c}$ when residence time $T_{res} > 1.8$ days

Batch experiments (with typical equilibration time of 1 d) underestimate Koc in column experiments with a residence time larger than 1.8 days.

But, …

Results: Effect of solute residence time on ratio K_{oc_b}/K_{oc_c}


Experiments in undisturbed columns for unsaturated conditions: $K_{oc\_b} < K_{oc\_c}$ when residence time $T_{res} > 15.5$ days

--> Sorption in undisturbed unsaturated columns is slower than in batch experiments (sorption sites are not so accessible under unsaturated conditions and in undisturbed columns)

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Results: Relation Between Mass Exchange Rate Coefficient α and Residence Time
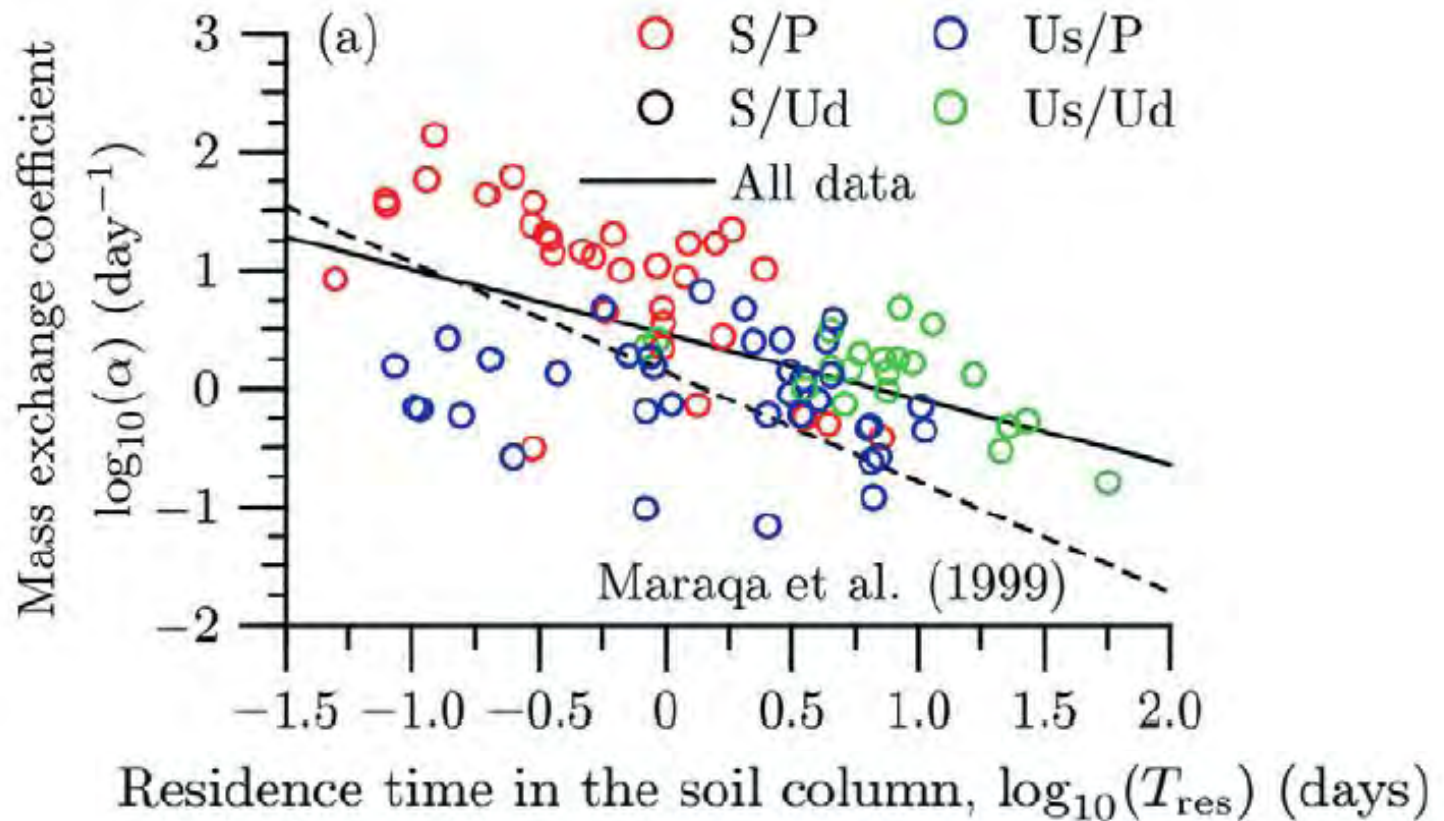
Results: K_{oc} batch (K_{oc_b}) versus K_{oc} field (K_{oc_f})
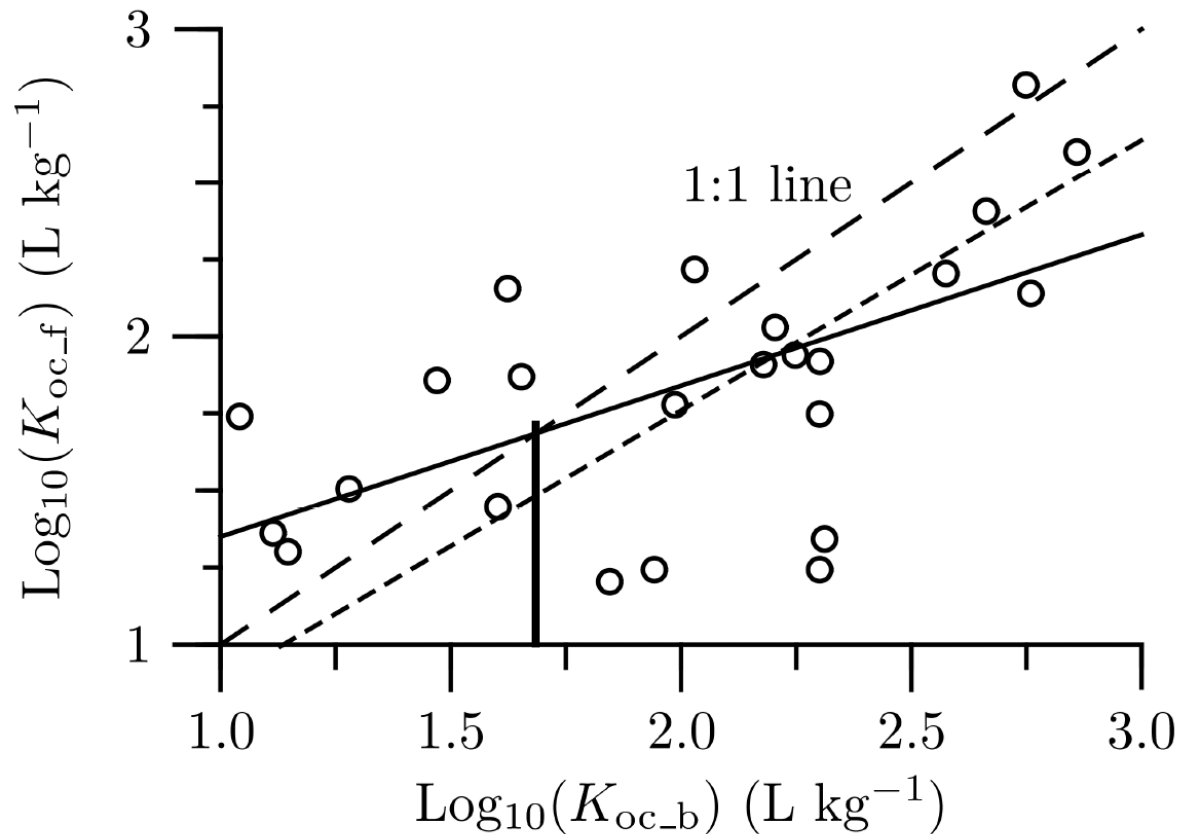
For $K_{oc\_b} > 48.5$ l kg^{-1}, $K_{oc\_b} > K_{oc\_f}$

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Results: Effect of pore water velocity on ratio K_{oc_b}/K_{oc_c}
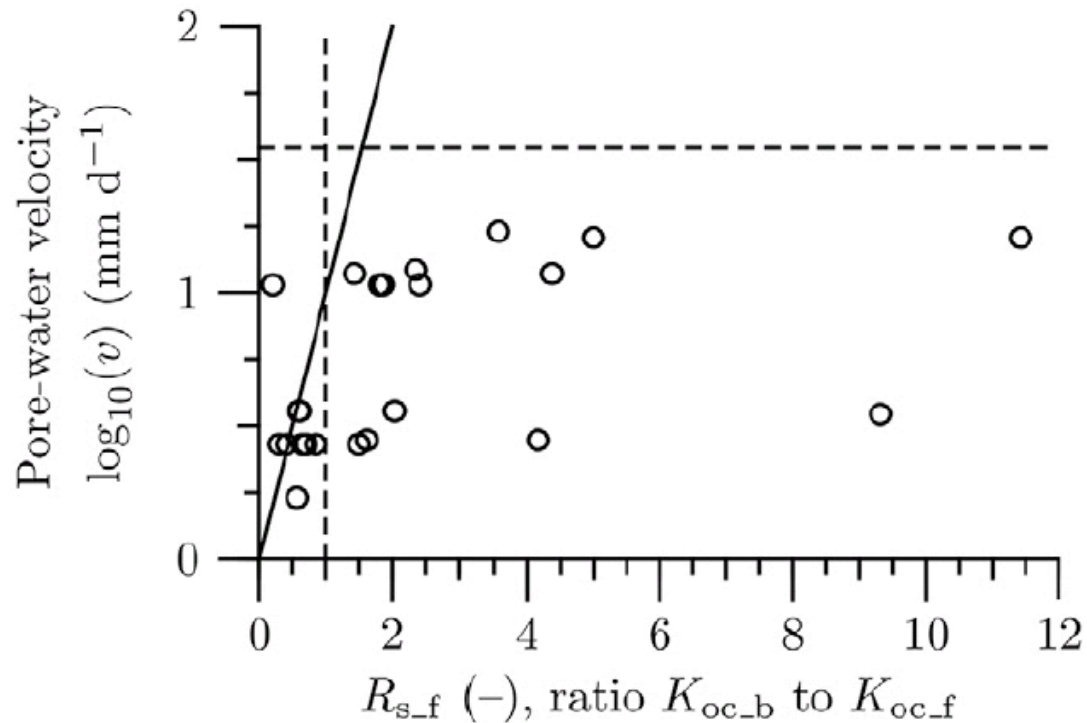
Pore water velocities are much smaller than in column studies.

In column studies, $K_{oc\_c} > K_{oc\_b}$ for these pore water velocities.

$K_{oc\_f} < K_{oc\_b}$ for a considerable number of experiments.

(--> uncertainty of inversely estimated parameters from field experiments, effect of degradation and irreversible sorption, effect of spatial variability, …)

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Conclusions

- For low pore water velocities $K_{oc\_c} > K_{oc\_b}$ (unsaturated and undisturbed columns).

- With increasing residence time ratio K_{oc_b}/K_{oc_c} decreases

- --> Equilibrium conditions reached in batch experiments of 1 d?

- For undisturbed and unsaturated column experiments, residence time should be considerably larger than the duration of the batch experiments to obtain the same Koc

- --> sorption rates in these columns are slower

- Flow velocities in field experiments are generally much lower than in column experiments.

- Nevertheless, $K_{oc\_f} < K_{oc\_b}$ in many cases

- --> uncertainty

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