# Optimisation of the experimental conduct to accurately determined $K_d$ / $K_F$ values of low adsorbing compounds

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## Introduction

The determination of accurate adsorption parameters is a key parameter for the assessment of the leaching behaviour of mobile, low adsorbing compounds through soils down to groundwater.
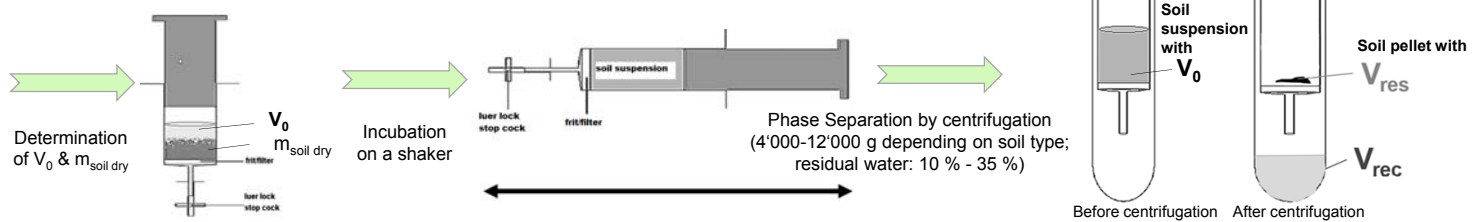
Applying the classical batch equilibrium method, the amount of residual liquid phase in the soil pellet after phase separation by centrifugation can still be so high that no meaningful K-values can be determined, even if the direct method (analysing both phases), is applied.

An optimised experimental approach is presented on how the amount of liquid phase in the soil after phase separation can be reduced to a solid/solution of greater than 3 (kg soil per L water) before soil extraction.

The impact of random and systematic errors has been taken into consideration when developing the experimental approach.

## Experimental Set-up

➢ Commercially available equipment used for set-up
➢ Optimised separation of soil and liquid by *centrifugation through* a filter/frit system (advanced centrifugation technique)



Determination of $V_0$ & $m_{soil\ dry}$

$V_0$
$m_{soil\ dry}$

Incubation on a shaker

luer lock stop cock

frit/filter

Phase Separation by centrifugation (4'000-12'000 g depending on soil type; residual water: 10 % - 35 %)

Soil suspension with $V_0$

Soil pellet with $V_{res}$

$V_{rec}$

Before centrifugation    After centrifugation

## Consideration of Random & Systematic Errors

### Random Error
➢ Is minimized by higher number of replicates and assessed in a statistical evaluation

### Systematic Error
➢ The experimental parameters that possibly lead to errors are analysed and found that they affect the resulting sorption value in a conservative way:

- Precise determination or overestimation of $V_0$, $c_{liquid}$
- Precise determination or underestimation of $V_{rec}$, $m_{extracted}$
- Underestimation of $V_{rec}$ results in overestimation of $V_{res}$

Examples:
- Particles / DOM (Dissolved Organic Matter) pass the frit system → Overestimation of $c_{liquid}$
- Loss at the determination of $V_{rec}$ → Underestimation of $V_{rec}$
- Underestimation of $V_{rec}$ → Overestimation of $V_{res}$

$$K_d = \left( \frac{m_s^{ads}(eq)}{m_{aq}^{ads}(eq)} \right) \times \left( \frac{V_0}{m_{soil}(dry)} \right)$$

with

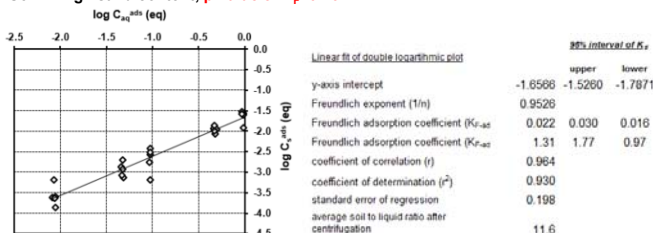$$m_{aq}^{ads} = c_{liquid} * V_0$$

$$m_s^{ads} = m_{extracted} - V_{res} * c_{liquid}$$

$$V_{res} = V_0 - V_{rec}$$

with
$m_s^{ads}$   mass of test substance adsorbed to soil [µg]
$m_{aq}^{ads}$   mass of test substance in aqueous phase [µg]
$m_{extracted}$   mass of test item extracted from soil and test vessel [µg]
$c_{liquid} = c_{aq}^{ads}$   concentration of test substance in aqueous phase [µg/cm³]
$V_0$   total volume of the aqueous phase in contact with the soil during the adsorption test [cm³]
$V_{rec}$   volume of supernatant recovered from the tube [µg/cm³]
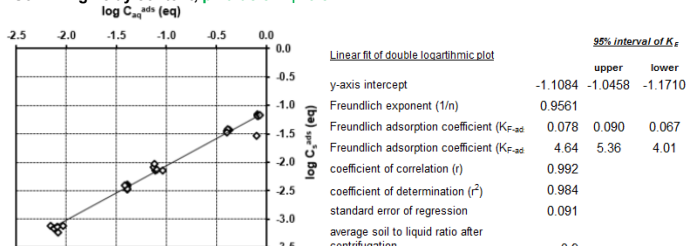$V_{res}$   residual volume of aqueous phase entrained in the soil pellet after phase separation [cm³]

## Example   Adsorption of a fungicide metabolite in two different soils at very low rates ($K_d$ of 0.007 L/kg - 0.12 L/kg)

Soil 1: high sand content; p-value of $K_F$=0.26



| Linear fit of double logartihmic plot | | 95% interval of $K_F$ | |
|---|---|---|---|
| | | upper | lower |
| y-axis intercept | -1.6566 | -1.5260 | -1.7871 |
| Freundlich exponent (1/n) | 0.9526 | | |
| Freundlich adsorption coefficient ($K_{F-ad}$) | 0.022 | 0.030 | 0.016 |
| Freundlich adsorption coefficient ($K_{F-ad}$) | 1.31 | 1.77 | 0.97 |
| coefficient of correlation (r) | 0.964 | | |
| coefficient of determination (r²) | 0.930 | | |
| standard error of regression | 0.198 | | |
| average soil to liquid ratio after centrifugation | 11.6 | | |

Soil 2: high clay content; p-value of $K_F$=0.3



| Linear fit of double logartihmic plot | | 95% interval of $K_F$ | |
|---|---|---|---|
| | | upper | lower |
| y-axis intercept | -1.1084 | -1.0458 | -1.1710 |
| Freundlich exponent (1/n) | 0.9561 | | |
| Freundlich adsorption coefficient ($K_{F-ad}$) | 0.078 | 0.090 | 0.067 |
| Freundlich adsorption coefficient ($K_{F-ad}$) | 4.64 | 5.36 | 4.01 |
| coefficient of correlation (r) | 0.992 | | |
| coefficient of determination (r²) | 0.984 | | |
| standard error of regression | 0.091 | | |
| average soil to liquid ratio after centrifugation | 3.9 | | |

**Statistical evaluation: t-test of $k_d$: all $K_d$ values ≠ 0 with 95% probability**

## Conclusion

➢ A „p - value (soil/solution ratio * $K_d$) ≥ 0.3" (Boesten (1990)) can be achieved with $K_d$-values <0.1 L/kg using the optimised experimental design

➢ Determination of reliable K-values when p < 0.3 is feasible under consideration of following measurements
- Sufficient number of experiments to handle random error (>2 replicates)
- Appropriate experimental settings to ensure that potential systematic errors lead to conservative estimate of the K-value
- Reliable regression needs to be achieved in the isotherms experiment (r²)
- Statistical assessment to investigate if $K_d$ values are different from zero at each concentration level
- Calculation of 95% percentile to assess reliability of the $K_F$-values derived

**References**: - OECD 106; Adsorption-desorption Using a Batch Equilibrium Method; Adopted 21.01.2000; - J.J.T.I. Boesten (1990) Influence of solid/liquid ratio on the experimental error of sorption coefficients in pesticide/soil systems. Pestic. Sci. 30, 31-41; - J.J.T.I. Boesten (2015). Effects of random and systematic errors on Freundlich parameters for pesticide sorption. Soil Sci. Soc. AM. J. 79:1306-1318; - Unpublished Document: OECD 106: Evaluators checklist – a guidance note developed by MS experts.