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)

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 $V_{0,c}$
  - Precise determination or underestimation of $V_{rec,m}$
  - Underestimation of $V_{rec,m}$ 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 $V_{res}$

Conclusion

- $A_p$ - value (soil/solution ratio * $K_F$) ≥ 0.3 (Boesten (1990)) can be achieved with $K_F$-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 ($r^2$)
  - Statistical assessment to investigate if $K_F$ values are different from zero at each concentration level
  - Calculation of 95% percentile to assess reliability of the $K_F$-values derived

References: