Health and Safety Executive

An aid to consistent conduct, reporting and evaluation of adsorption / desorption studies that use a batch equilibrium method.

HSE

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Background

Introduction

OECD guideline 106[1] provides guidance on the conduct and interpretation of adsorption/desorption studies. These studies provide essential information on the mobility of chemicals and adsorption distribution coefficients that can be used to predict partitioning in soil under a variety of environmental conditions.

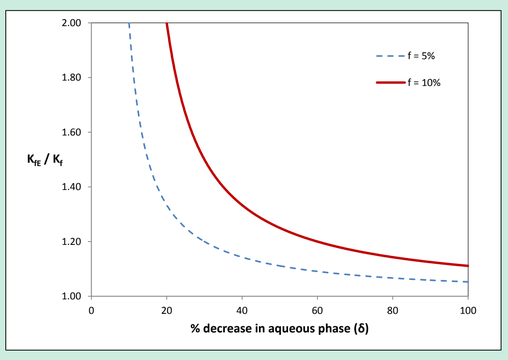
Principle of the adsorption test

Known volumes of solutions of the test substance are added to soil samples and the mixture agitated for an appropriate time. The soil suspensions are separated by centrifugation and the test substance in the aqueous phase analysed. The amount of test substance on the soil can be calculated by difference (indirect method) or measured separately (direct method). Most commonly, a Freundlich adsorption isotherm is plotted from the concentration of the test substance in each phase, and a Freundlich adsorption distribution coefficient and Freundlich exponent are determined.

The new OECD 106 checklist

This new OECD 106 checklist has been developed by Member State (MS) experts in collaboration with ECPA and EFSA, and provides supplementary information to aid consistency in the conduct, evaluation and reporting of batch adsorption/desorption studies. The checklist should be considered in support of OECD 106 studies to help to identify where deviations from the OECD guideline could lead to significant and systematic errors in fitted parameters as well as introducing some new supplementary quality checks. It should be emphasised that it is not intended to replace the basic quality checks outlined in the OECD guideline.

Quality criteria in the OECD 106 checklist

Quality check	Description	OECD criteria, OECD update, or supplementary check
(1) Analytical method	The reliability of the analytical method over the concentration range present in the study should be confirmed.	OECD
(2) Adsorbed percentage	Appropriate soil to solution ratios should be selected to ensure the adsorbed percentage (δ) is above 20% and preferably > 50%	OECD
(3) Soil to solution ratio	Accurate determination of the distribution coefficient, Kd, is best achieved via both the indirect and direct methods when the Kd * soil/solution ratio (g/cm³) is > 0.3 (based upon analytical and experimental error). If Kd * soil/solution ratio > 0.3 cannot be achieved the check for systematic errors can aid in consideration of these data or the direct method could be used.	OECD update
(4) Mass balance and test substance stability	Mass balance (percentage of test substance) should be > 90% for the indirect method to be used. If < 90%, it may be possible to carry out the study with the direct method.	OECD
(5) Check of the effect of systematic errors [2,3]	Systematic errors may still occur even if the quality checks 2 and 4 above are met. Errors can be assessed with the following equation: $\frac{K_{fE}}{K_f} = \frac{\delta}{\delta - f}$ Where: K_{fE} is the measured (experimental) Freundlich adsorption coefficient; K_f is the true Freundlich adsorption coefficient; δ is the adsorbed percentage or decrease in the concentration in the liquid phase (%); f is the percentage loss of test item during the study due to degradation or other loss processes (%). Where this ratio is greater than 1.2 these values should be treated with caution. The effect of the percentage decrease in the aqueous phase (δ) and the influence of the percentage loss (f) on the K_{fE}/K_f ratio are illustrated in the following figure: The graph shows that where there are greater losses (f value) more adsorption is required for this criteria to be met 	Supplementary
(6) Liquid entrained in soil pellet	Standard practice in data handling should be to include the volume of water entrained in the soil pellet after centrifugation in the calculation of the total mass of the compound in the aqueous phase.	Supplementary
(7) Quality criteria on the goodness of fit and parameter reliability	The following analysis should be included in a discussion of the suitability of the fits: • The standard linear regression plot and the corresponding plot of residuals. • The data should be supported by a high r^2 value (ideally above 0.975). • 95% confidence intervals of the K_f and 1/n parameters should be reported.	OECD / supplementary

Illustrative example

Test data

Data for two soils tested according to the indirect method outlined in OECD 106 was used to produce Freundlich adsorption plots.

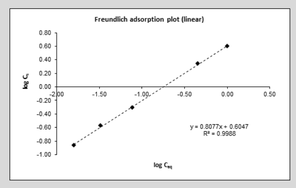
Concentration of test solution (µg/mL)	Aqueous phase (C_{aq}; µg/mL)	Soil (C_s; µg/g)	Log C_{aq}	Log C_s
Soil A (pH = 7.9; organic carbon = 4.9%, soil/solution ratio = 1:4)				
0.05	0.0159	0.1364	-1.799	-0.865
0.10	0.0325	0.2700	-1.488	-0.569
0.20	0.0773	0.4908	-1.112	-0.309
1.00	0.4510	2.1960	-0.346	0.342
2.00	1.0120	3.9520	0.005	0.597
Soil B (pH = 6.2, organic carbon = 1.5%, soil/solution ratio = 1:20)				
0.05	0.0440	0.120	-1.357	-0.921
0.10	0.0891	0.218	-1.050	-0.662
0.20	0.1810	0.380	-0.742	-0.420
1.00	0.9480	1.040	-0.023	0.017
2.00	1.9450	1.100	0.289	0.041

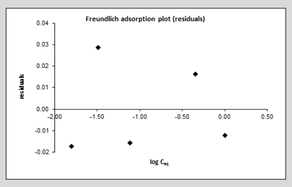
Initial examination

An initial examination of the plots would indicate that soil A is acceptable. The Freundlich linear adsorption plot is visually very good; K_{FOC} value = 82.1 mL/g. The Freundlich linear isotherm plot for soil B is visually relatively poor; the resulting K_{FOC} value is 60.3 mL/g.

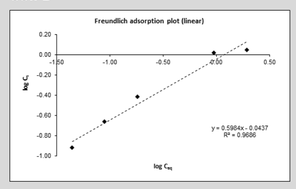
Should the plot for soil B and the K_{FOC} value be accepted?

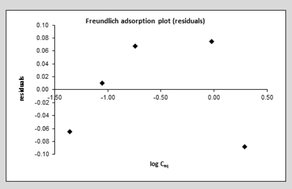
Soil A





Soil B





Use of the OECD checklist

A summary of the quality criteria as applied to soil A and soil B are presented in the following table:

Quality criteria	Soil A	Soil B
1	Analytical method reliable	Analytical method reliable
2	δ = **49.4 to 68.2%**	δ = **2.75 to 12.0%**
3	Kd * soil/solution ratio = **0.98 to 2.14**	Kd * soil/solution ratio = **0.03 to 0.14**
4	Percentage loss (f) = **4.5%**	Percentage loss (f) = **1.2%**
5	$\frac{K_{fE}}{K_f} = \mathbf{1.10}$	$\frac{K_{fE}}{K_f} = \mathbf{1.77}$
6	Liquid entrained included	Liquid entrained included
7	Goodness of fit: R^2 = **0.9985** Residuals: small, randomly distributed 95% confidence intervals: K_f: 4.024; interval: 3.510 – 4.613 1/n: 0.808; interval: 0.757 – 0.859	Goodness of fit: R^2 = **0.9686** Residuals: large, possible systematic deviation 95% confidence intervals: K_f: 0.904; interval: 0.615 – 1.330 1/n: 0.598; interval: 0.400 – 0.796

Discussion of quality criteria

The qualitative and quantitative criteria for soil A are all met. The residuals are small and randomly distributed and confidence intervals for K_f and 1/n are both relatively narrow.

Four of the five quantitative criteria for soil B are not met. The residuals were large with indications of systematic deviation and the confidence intervals were much wider than soil A for both K_f and 1/n. The relatively low adsorption levels (< 20%) and Kd * soil/solution ratio (< 0.3) indicates that either a more appropriate soil/solution ratio should have been selected or the direct method could have been used. The study with this soil could therefore be repeated with the aim of meeting these criteria. Alternatively if removal of this soil from the dataset is proposed then the impact of this on the robustness of the overall data set must be considered.

Considering the context of the results

Several of the criteria become more difficult to meet when adsorption is lower and therefore it is necessary to take care that excluding results does not lead to bias towards the selection of soils where adsorption is greater. Therefore, based upon the data available from other soils it may not be appropriate to exclude soil B from the overall dataset.

Conclusions

This new checklist highlights the importance of existing criteria within the OECD 106 guideline and introduces some new supplementary criteria to help decide on the acceptability of studies. Further consideration is required when quality criteria are not met to ensure best use of available data and that a representative data set is considered in establishing these critical and highly sensitive input parameters for regulatory modelling.

References

1. OECD guideline 106: Adsorption – desorption using a batch equilibrium method. 21 January 2000.
2. 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.
3. 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.