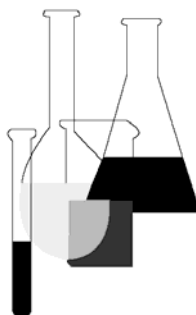




Fate, Transport and Transformation Test Guidelines

OPPTS 835.1230 Adsorption/Desorption (Batch Equilibrium)



INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances (OPPTS), United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data to meet the data requirements of the Agency under the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601), the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*), and section 408 of the Federal Food, Drug and Cosmetic (FFDCA) (21 U.S.C. 346a).

OPPTS developed this guideline through a process of harmonization of the testing guidance and requirements that existed for the Office of Pollution Prevention and Toxics (OPPT) in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) in publications of the National Technical Information Service (NTIS) and in the guidelines published by the Organization for Economic Cooperation and Development (OECD).

For additional information about OPPTS harmonized guidelines and to access this and other guidelines, please go to <http://www.epa.gov/oppts> and select "Test Methods & Guidelines" on the left side menu.

OPPTS 835.1230 Adsorption/desorption (batch equilibrium)

(a) **Scope—(1) Applicability.** This guideline is intended for use in meeting testing requirements of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C.136, *et seq.*) and for testing pursuant to the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601, *et seq.*) It describes procedures that, if followed, would result in data that would generally be of scientific merit for the purposes described in paragraph (b) of this guideline.

(2) **Background.** The source materials used in developing this harmonized OPPTS test guideline are OPP 163-1 Leaching and adsorption/desorption, EPA report 540/9-82-021, CFR 796.2750 Sediment and soil adsorption isotherm, OECD Guideline for Testing of Chemicals 106 Adsorption-Desorption Using a Batch Equilibrium Method (adopted January 2000), and OPPTS 5.1220 Sediment and Soil Adsorption/Desorption Isotherm.

(b) **Purpose** (1) Adsorption/desorption studies are used to estimate the adsorption/desorption behavior of a substance on soils. The goal is to obtain a sorption value which can be used to predict partitioning under a variety of environmental conditions; to this end, equilibrium adsorption coefficients for a chemical on various soils are determined as a function of soil characteristics (e.g., organic carbon content, clay content, soil texture, and pH). Different soil types have to be used in order to cover as widely as possible the interactions of a given substance with naturally occurring soils.

(2) Adsorption/desorption studies generate essential information on the mobility of chemicals and their distribution in the soil, water and air compartments of our biosphere. (see paragraphs (j)(1) through (j)(10) of this guideline). They can be used in the prediction or estimation, for example, of the availability of a chemical for degradation (see paragraphs (j)(11) and (j)(12) of this guideline), transformation and uptake by organisms (see paragraph (j)(13) of this guideline; leaching through the soil profile (see paragraphs (j)5), (j)(7), (j)(8), (j)(10) and (j)(14) through (j)(17) of this guideline), volatility from soil (see paragraphs (j)(10), (j)18) and (j)19) of this guideline); and run-off from land surfaces into natural waters (see paragraphs (j)(7), (j)(20) and (j)(21) of this guideline) as well as for comparative and modeling purposes (see paragraphs (j)(8) and (j)(22) through (j)(24) of this guideline).. The distribution of a chemical between soil and aqueous phases is a complex process depending on a number of different factors: the chemical nature of the substance (see paragraphs (j)(1) and (j)(25) through (j)(29) of this guideline), the characteristics of the soil (see paragraphs (j)(30), (j)(1) through ((j)3) and (j)(31) through (j)(39) of this guideline), and climatic factors such as rainfall, temperature, sunlight and wind.

(c) Definitions and symbols—(1) Definitions

Adsorption ratio, K_d is the amount of test chemical adsorbed by a sediment or soil (i.e., the solid phase) divided by the amount of test chemical in the solution phase, which is in equilibrium with the solid phase, at a fixed solid/solution ratio.

Cation exchange capacity (CEC) is the sum total of exchangeable cations that a sediment or soil can absorb. The CEC is expressed in milliequivalents of negative charge per 100 grams (meq/100g) or milliequivalents of negative charge per gram of soil or sediment.

Clay mineral analysis is the estimation or determination of the kinds of clay-size minerals and the amount present in a sediment or soil.

Organic matter is the organic fraction of the sediment or soil; it includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the microbial population.

Particle size analysis is the determination of the various amounts of the different particle sizes in a sample (i.e., sand, silt, clay), usually by sedimentation, sieving, micrometry, or combinations of these methods. The names and diameter range commonly used in the United States are shown in Table 1 following.

Table 1. Particle size distribution names and ranges used in the United States.

Name	Diameter range
Very coarse sand	2.0 to 1.0 mm
Coarse sand	1.0 to 0.5 mm
Medium sand	0.5 to 0.25 mm
Fine sand	0.25 to 0.125 mm
Very fine sand	0.125 to 0.05 mm
Silt	0.05 to 0.002 mm
Clay	< 0.002 mm

pH of a sediment or soil is the negative logarithm to the base ten of the hydrogen ion activity of the sediment or soil suspension. It is usually measured by a suitable sensing electrode coupled with a suitable reference electrode at a 1/1 solid/solution ratio by weight.

Sediment is the unconsolidated inorganic and organic material that is suspended in and being transported by surface water, or has settled out and has deposited into beds.

Soil is the unconsolidated mineral material on the immediate surface of the earth that serves as a natural medium for the growth of land plants. Its formation and properties are determined by various factors such as parent material, climate, macro- and microorganisms, topography, and time.

Soil aggregate is the combination or arrangement of soil separates (sand, silt, clay) into secondary units. These units may be arranged in the soil profile in a distinctive characteristic pattern that can be classified according to size, shape, and degree of distinctness into classes, types, and grades.

Soil classification is the systematic arrangement of soils into groups or categories. Broad groupings are based on general soil characteristics while subdivisions are based on more detailed differences in specific properties. The soil classification system used in this guideline and the one used today in the United States is the 7th Approximation-Comprehensive System. The ranking of subdivisions under this system is: Order, Suborder, Great group, Family, and Series.

Soil horizon is a layer of soil approximately parallel to the land surface. Adjacent layers differ in physical, chemical, and biological properties such as color, structure, texture, consistency, kinds and numbers of organisms present, and degree of acidity or alkalinity.

Soil Order is the broadest category of soil classification and is based on the general similarities of soil physical/chemical properties. The formation of soil by similar general genetic processes causes these similarities. The Soil Order found in the United States are: Alfisol, Aridisol, Entisol, Histosol, Inceptisol, Mollisol, Oxisol, Spodosol, Ultisol, and Vertisol.

Soil series is the basic unit of soil classification and is a subdivision of a family. A series consists of soils that were developed under comparable climatic and vegetational conditions. The soils comprising a series are essentially alike in all major profile characteristics except for the texture of the “A” horizon (i.e., the surface layer of soil).

Soil texture is a classification of soils that is based on the relative proportions of the various soil separates present. The soil textural classes are: clay, sandy clay, silty clay, clay loam, silty clay loam, sandy clay loam, loam, silt loam, silt, sandy loam, loamy sand, and sand.

(2) Symbols for equations. The weight of soil sample in the equations of this guideline refer to the oven dry weight.

Table 2. Symbols for equations used in this guideline

Symbol	Definition	Units
A_{t_i}	adsorption percentage at the time point t_i	%
A_{eq}	adsorption percentage at adsorption equilibrium	%
$m_s^{ads}(t_i)$	Mass of the test substance adsorbed on the soil at the time t_i	μg
$m_s^{ads}(\Delta t_i)$	mass of the test substance adsorbed on the soil during the time interval Δt_i	μg
$m_s^{ads}(eq)$	mass of the substance adsorbed on the soil at adsorption equilibrium	μg
m_0	mass of the test substance in the test tube, at the beginning of the adsorption test	μg
$m_m^{ads}(t_i)$	mass of the substance measured in an aliquot (v_a^A) at the time point t_i	μg
$m_{aq}^{ads}(eq)$	mass of the substance in the solution at adsorption equilibrium	μg
m_{soil}	quantity of the soil phase, expressed in dry mass of soil	g
C_{st}	Mass concentration of the stock solution of the substance	$\mu\text{g cm}^{-3}$
C_0	initial mass concentration of the test solution in contact with the soil	$\mu\text{g cm}^{-3}$
$C_{aq}^{ads}(t_i)$	mass concentration of the substance in the aqueous phase at the time t_i that the analysis is performed	$\mu\text{g cm}^{-3}$

Symbol	Definition	Units
$C_s^{ads} (eq)$	content of the test substance adsorbed on soil at adsorption equilibrium	$\mu\text{g g}^{-1}$
$C_{aq}^{ads} (eq)$	mass concentration of the substance in the aqueous phase at adsorption equilibrium	$\mu\text{g cm}^{-3}$
V_0	initial volume of the aqueous phase in contact with the soil during the adsorption test	cm^3
v_a^A	volume of the aliquot in which the test substance is measured	cm^3
K_d	distribution coefficient for adsorption	$\text{cm}^3 \text{g}^{-1}$
K_{oc}	organic carbon normalized adsorption coefficient	$\text{cm}^3 \text{g}^{-1}$
K_{om}	organic matter normalized distribution coefficient	$\text{cm}^3 \text{g}^{-1}$
K_F^{ads}	Freundlich adsorption coefficient	$\mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$
$1/n$	Freundlich exponent	
D_{t_i}	desorption percentage at a point time t_i	%
$D_{\Delta t_i}$	desorption percentage corresponding to a time interval Δt_i	%
K_{des}	apparent desorption coefficient	$\text{cm}^3 \text{g}^{-1}$
K_F^{des}	Freundlich desorption coefficient	$\mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$
$m_{aq}^{des} (t_i)$	Mass of the test substance desorbed from soil at the time t_i	μg
$m_{aq}^{des} (\Delta t_i)$	mass of the test substance desorbed from soil during the time Δt_i	μg
$m_m^{des} (eq)$	mass of substance determined analytically in the aqueous phase at desorption equilibrium	μg
$m_{aq}^{des} (eq)$	Total mass of test substance desorbed at desorption equilibrium	μg
$m_s^{des} (\Delta t_i)$	mass of the substance remaining adsorbed on the soil after the time interval Δt_i	μg
m_{aq}^A	mass of the test substance left over from the adsorption equilibrium due to incomplete volume replacement	μg
$C_s^{des} (eq)$	content of the test substance remaining adsorbed on the soil at desorption equilibrium	$\mu\text{g g}^{-1}$
$C_{aq}^{des} (eq)$	mass concentration of the substance in the aqueous phase at desorption equilibrium	$\mu\text{g cm}^{-3}$
V_T	total volume of the aqueous phase in contact with the soil during the desorption kinetics experiment performed with the serial method	cm^3
V_R	volume of the supernatant removed from the tube after the attainment of adsorption equilibrium and replaced by the same volume of a 0.01 M CaCl ₂ solution	cm^3

Symbol	Definition	Units
v_a^D	volume of the aliquot sampled for analytical purpose from the tube (i), during the desorption kinetics experiment performed with the serial method	cm ³
V_r^i	volume of the solution taken from the tube (i) for the measurement of the test substance, in desorption kinetics experiment (parallel method)	cm ³
V_r^F	volume of the solution taken from the tube for the measurement of the test substance, at desorption equilibrium	cm ³
MB	Mass balance	%
m_E	total mass of test substance extracted from the soil and walls of the test vessel in two steps	μg
V_{rec}	volume of the supernatant recovered after the adsorption equilibrium	cm ³
P_{ow}	octanol/water partition coefficient	
pK_a	dissociation constant	
S_w	water solubility	g l ⁻¹

(d) Principle of the test. (1) In this guideline, adsorption represents the process of the binding of a chemical to surfaces of soils; it does not distinguish between different adsorption processes (physical and chemical adsorption) and such processes as surface catalyzed degradation, bulk adsorption or chemical reaction. Adsorption that will occur on colloid particles (diameter < 0.2 μm) generated by the soils is not fully taken into account.

(2) Known volumes of solutions of the test substance, non-labeled or radiolabeled, at known concentrations in 0.01 M CaCl₂ are added to soil samples of known dry weight which have been pre-equilibrated in 0.01 M CaCl₂. The mixture is agitated for an appropriate time. The soil suspensions are then separated by centrifugation, which may also include filtration, with subsequent analysis of the aqueous phase. The amount of test substance adsorbed on the soil sample is calculated as the difference between the amount of test substance initially present in solution and the amount remaining at the end of the experiment (indirect method).

(3) The amount of test substance adsorbed can also be directly determined by analysis of soil. Although this makes the analytical procedure more tedious, involving stepwise soil extraction with an appropriate solvent, it is recommended in cases where the difference in the solution concentration of the substance cannot be accurately determined. Examples of such cases are: adsorption of the test substance on surfaces of the test vessels; instability of the test substance in the time scale of the experiment; weak adsorption giving only small concentration change in the solution; and strong adsorption yielding low concentration which cannot be accurately determined. If a radiolabeled substance is used, soil extraction may be avoided by analysis of the soil phase by combustion and liquid scintillation counting. However, liquid scintillation counting is a nonspecific technique which cannot differentiate between the test chemical and its transformation products; therefore it should be used only if the test chemical is stable for the duration of the study.

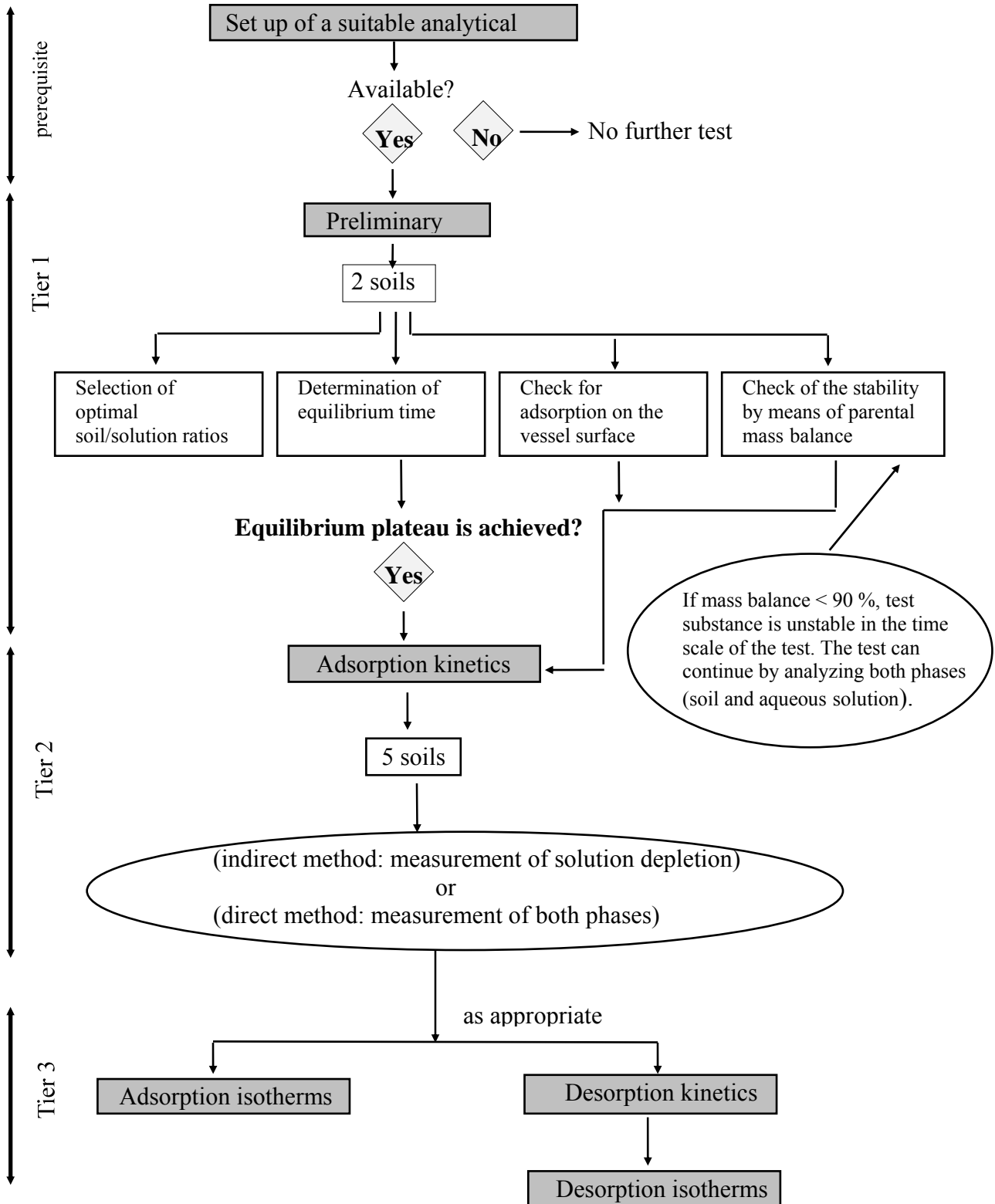
(4) Testing is designed to evaluate the adsorption of a chemical on different soil types with a varying range of organic carbon content, clay content and soil texture, and pH. Methods for the preliminary study and the main study are generally the same, exceptions are mentioned where relevant. It comprises three tiers. The tiers are as follows:

(i) Preliminary study. In order to determine the soil/solution ratio, the equilibration time for adsorption and the amount of test substance adsorbed at equilibrium and the adsorption of the test substance on the surfaces of the test vessels and the stability of the test substance during the test period.

(ii) Screening test. The adsorption is studied in five different soil types by means of adsorption kinetics at a single concentration and determination of distribution coefficients for adsorption (K_d) and organic carbon normalized adsorption distribution coefficient (K_{oc}).

(iii) Main study: Determination of Freundlich adsorption isotherms to determine the influence of concentration on the extent of adsorption on soils. Study of desorption by means of desorption kinetics/Freundlich desorption isotherms is shown in the following Figure 1.

Fig. 1.--Testing scheme.



(e) **General considerations**—(1) The soil parameters that are believed most important for adsorption are: organic carbon content (see paragraphs (j)(30) and (j)(40), (j)(1) through (j)(3), (j)(31) and (j)(33) through (j)(38) of this guideline); clay content and soil texture (see paragraphs (j)(30) and (j)(40), and (j)(32) through (j)(38) of this guideline); and pH for ionizable compounds (see paragraphs (j)(30), (j)(32) and (j)(40) of this guideline). Other soil parameters which may have an impact on the adsorption/desorption of a particular substance are the effective cation exchange capacity (ECEC), the content of amorphous iron and aluminum oxides, particularly for volcanic and tropical soils (see paragraph (j)(30) of this guideline), as well as the specific surface (see paragraph (j)(39) of this guideline).

(2) Influence of analytical method. The key parameters that can influence the accuracy of sorption measurements include the accuracy of the analytical method in analysis of both the solution and adsorbed phases, the stability and purity of the test substance, the attainment of sorption equilibrium, the magnitude of the solution concentration change, the soil/solution ratio, and changes in the soil structure during the equilibration process (see Table 3). The reliability of the analytical method used should be checked at the concentration range which is likely to occur during the test. The experimenter should feel free to develop an appropriate method with appropriate accuracy, precision, reproducibility, detection limits and recovery.

(3) From the following (see reference in paragraph (j)(41)) it becomes obvious that when the difference between the initial mass ($m_0 = 110 \mu\text{g}$) and equilibrium concentration ($m_{\text{aq}}^{\text{ads}}(\text{eq}) = 100 \mu\text{g}$) of the test substance in the solution is very small, an error of 5% in the measurement of equilibrium concentration results in an error of 50% in the calculation of the mass of the substance adsorbed in soil ($m_s^{\text{ads}}(\text{eq})$) and of 52.4% in the calculation of the K_d .

$$\text{Amount of soil } m_{\text{soil}} = 10 \text{ g}$$

$$\text{Volume of solution } V_0 = 100 \text{ cm}^3$$

Table 3. Influence of accuracy of analytical method and concentration change on accuracy of adsorption results ($m_0 = 110 \mu\text{g}$ or $C_0 = 1.100 \mu\text{g}/\text{cm}^3$)

	$m_{\text{aq}}^{\text{ads}}$ (eq) (μg)	$C_{\text{aq}}^{\text{ads}}$ (eq) ($\mu\text{g cm}^{-3}$)	R	$m_{\text{s}}^{\text{ads}}$ (eq)* (μg)	$C_{\text{s}}^{\text{ads}}$ (eq) *($\mu\text{g g}^{-1}$)	R^{\ddagger}	K_{d}^*	R^{\ddagger}	
$m_0 = 110 \mu\text{g}$ or $C_0 = 1.100 \mu\text{g}/\text{cm}^3$	For A = 9%								
	100	1.000	true value	10	1.00	true value	1		
	101	1.010	1%	9	0.90	10%	0.891	10.9%	
	105	1.050	5%	5	0.50	50%	0.476	52.4%	
	109	1.090	9%	1	0.10	90%	0.092	90.8%	
	For A = 55%								
	50.0	0.500	true value	60.0	6.00	true value	12.00		
	50.5	0.505	1%	59.5	5.95	0.8%	11.78	1.8%	
	52.5	0.525	5%	57.5	5.75	4.0%	10.95	8.8%	
	55.0	0.550	10%	55.0	5.50	8.3%	10.00	16.7%	
	For A = 99%								
	1.100	0.011	true value	108.9	10.89	true value	990		
	1.111	0.01111	1%	108.889	10.88	0.01%	980	1.0%	
	1.155	0.01155	5%	108.845	10.8845	0.05%	942	4.8%	
	1.21	0.0121	10%	108.790	10.8790	0.10%	899	9.2%	

$$* \quad m_{\text{s}}^{\text{ads}}(\text{eq}) = m_0 - m_{\text{aq}}^{\text{ads}}(\text{eq}), \quad C_{\text{s}}^{\text{ads}}(\text{eq}) = \frac{[C_0 - C_{\text{aq}}^{\text{ads}}(\text{eq})] V_0}{m_{\text{soil}}}, \quad K_{\text{d}} = \frac{m_{\text{s}}^{\text{ads}}(\text{eq})}{m_{\text{aq}}^{\text{ads}}(\text{eq})} \frac{V_0}{m_{\text{soil}}}$$

$m_{\text{s}}^{\text{ads}}(\text{eq})$ = mass of the test substance in the soil phase at equilibrium, μg ;

$m_{\text{aq}}^{\text{ads}}(\text{eq})$ = mass of the test substance in the aqueous phase at equilibrium, μg ;

$C_{\text{s}}^{\text{ads}}(\text{eq})$ = content of the test substance in the soil phase at equilibrium, $\mu\text{g g}^{-1}$;

$C_{\text{aq}}^{\text{ads}}(\text{eq})$ = mass concentration of the test substance in the aqueous phase at equilibrium, $\mu\text{g cm}^{-3}$.

R = analytical error in the determination of the $m_{\text{aq}}^{\text{ads}}(\text{eq})$;

R^{\ddagger} = calculated error due to the analytical error R.

(4) The test is applicable to chemical substances for which an analytical method with sufficient accuracy is available. An important parameter that can influence the reliability of the results, especially when the indirect method is followed (see paragraph (d)(2) of this guideline), is the stability of the test substance in the time scale of the test. The stability of the test substance should be determined in a preliminary study; if a transformation in the time scale of

the test is observed, the main study should be performed by analyzing both soil and aqueous phases.

(5) Difficulties may arise in conducting this test for test substances with low water solubility ($S_w < 10^{-4} \text{ g l}^{-1}$), as well as for highly charged substances, due to the fact that the concentration in the aqueous phase cannot be measured analytically with sufficient accuracy. In these cases, additional steps have to be taken. Guidance on how to deal with these problems is given in the relevant sections of this Guideline.

(6) When testing volatile substances, care should be taken to avoid losses during the study.

(7) The following information on the test substance should be available: solubility in water, vapor pressure and Henry's law constant; abiotic hydrolysis as a function of pH; n-octanol/water partition coefficient; ready biodegradability or aerobic and anaerobic transformation in soil; pKa of ionizable substances; and direct photolysis in water (i.e., UV-Vis absorption spectrum in water, quantum yield) and photodegradation on soil.

(f) **Test method**—(1) **Test substance**. The test substance may be radiolabeled with known composition and radiopurity or, if unlabelled substance is used, it should be of known composition and at least 95% purity.

(2) **Test conditions**. (i) All experiments are done at laboratory ambient temperature and, if possible, at a constant temperature between 20 °C and 25 °C.

(ii) Centrifugation conditions should allow the removal of particles larger than 0.2 µm from the solution. This value triggers the smallest sized particle that is considered as a solid particle, and is the limit between solid and colloid particles. Correct centrifugation conditions can be determined by referring to the equipment manufacturer's instructions. If the centrifugation facilities cannot ensure that particles larger than 0.2 µm are removed, a combination of centrifugation and filtration with 0.2 µm filters could be used. These filters should be made of a suitable inert material to avoid any losses of the test substance on them. In any case, it should be demonstrated that no losses of the test substance occur during filtration.

(3) **Soils**—(i) The soils should be characterized by parameters considered to be largely responsible for the adsorptive capacity: organic carbon, clay content, pH, textural composition (percent sand, silt, and clay), and textural class. Other physico-chemical properties of the soil may have an impact on the adsorption/desorption of a particular substance and should be considered in such cases.

(ii) The methods used for soil characterization are very important and can have a significant influence on the results. Soil pH should be measured in a solution of 0.01 M CaCl₂ (that is the solution used in adsorption/desorption testing) according to the corresponding ISO method (as referenced in (j)(42) of this guideline). The other relevant soil properties should also be determined according to standard methods to permit the analyses of sorption data to be based on globally standardized soil parameters. Some guidance for existing standard methods of soil

analysis and characterization is given in references (j)(43) through (j)(45) of this guideline. or calibration of soil test methods, the use of reference soils may be considered.

(iii) Studies should be conducted with soils that are representative of agricultural areas where the pesticide will be used. Soils should be characterized according to the USDA classification system. At least one of the soils selected should have an organic matter content less than or equal to one percent (sand or sandy loam preferred).

(iv) Soil from foreign sources may be used, providing the foreign soil will have the same characteristics as soil in the United States common to the proposed use area. Additional information on use of foreign soils may be obtained from the document “Guidance for Determining the Acceptability of Environmental Fate Studies Conducted with Foreign Soils,” at the U.S. Environmental Protection Agency’s Environmental Fate and Effects Division, Office of Pesticides (see paragraph (j)(46). If the pesticide is intended for an aquatic use or for an aquatic impact use involving direct discharges of treated water into outdoor aquatic sites, an aquatic sediment obtained from or representative of the proposed use should be included.

(4) **Soil collection.** The sampling site should be exactly defined by UTM (Universal Transversal Mercator-Projection/European Horizontal Datum) or geographical coordinates in order to allow re-collection of a particular soil in the future or could help in defining soil under various classification systems used in different countries. Only the A horizon up to a maximum depth of 20 cm should be collected.

(5) **Soil transportation.** The soil samples should be transported using containers and under temperature conditions which guarantee that the initial soil properties are not significantly altered.

(6) **Soil storage.** The use of soils freshly taken from the field is preferred. If this is not possible, soil can be stored at ambient temperatures and should be kept air-dried. No limit on the storage time is recommended, but soils stored for more than three years should be re-analyzed prior to the use with respect to their organic carbon content, pH and CEC.

(7) **Soil preparation**—(i) Soils are to be air-dried at ambient temperature (preferably between 20-25 °C). Disaggregation should be performed with minimal force, so that the original texture of the soil will be changed as little as possible. The soils are sieved to a particle size ≤ 2 mm; recommendations of the ISO standard on soil sampling (see paragraph (j)(42) of this guideline) should be followed with respect to the sieving process. Careful homogenization is recommended, as this enhances the reproducibility of the results.

(ii) Moisture content of each soil is determined on three aliquots with heating at 105 °C until there is no significant change in weight (approx. 12h). For all calculations the mass of soil refers to oven dry mass, i.e., the weight of soil corrected for moisture content.

(8) **Test substance preparation.** (i) The test substance is dissolved in a 0.01 M solution of calcium chloride (CaCl_2) in distilled or de-ionized water; the CaCl_2 solution is used as the aqueous solvent phase to improve centrifugation and minimize cation exchange. The concentration of the

stock solution should preferably be three orders of magnitude higher than the detection limit of the analytical method used. The stock solution concentration should be below water solubility of the test substance. The stock solution should be prepared just before application to soil samples and should be kept closed in the dark at 4 °C. Storage time depends on the stability of the test substance and its concentration in the solution.

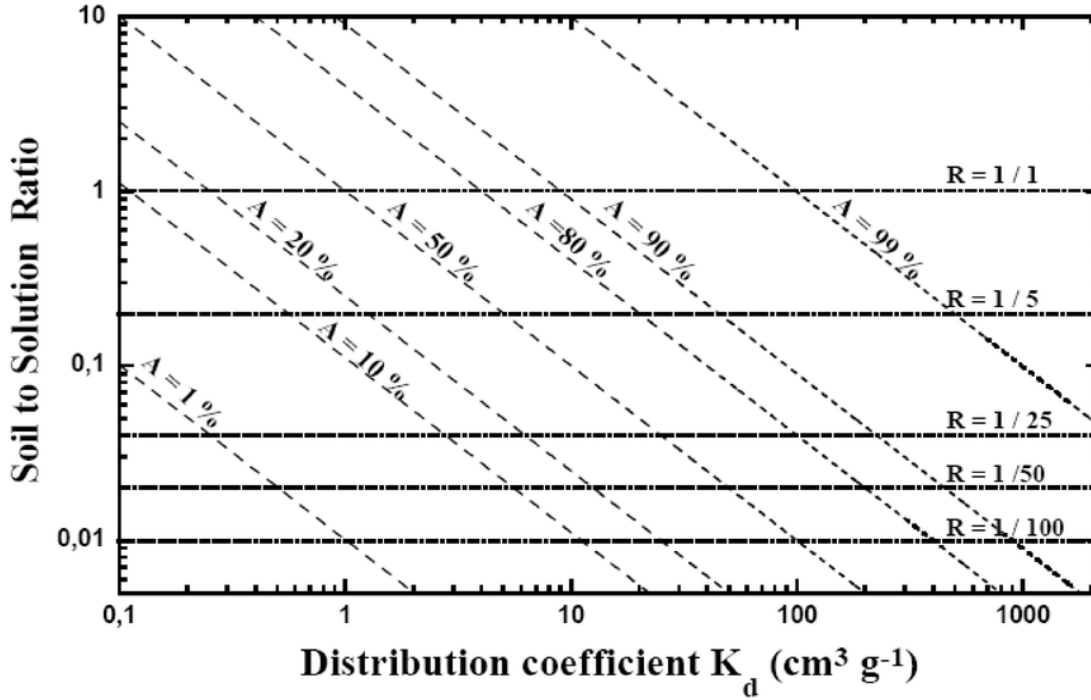
(ii) For poorly soluble substances ($S_w < 10^{-4} \text{ g L}^{-1}$), an appropriate solubilizing agent should be used when it is difficult to dissolve the test substance. This solubilizing agent should be miscible with water, such as methanol or acetonitrile. Its concentration should not exceed 1% of the total volume of the stock solution and should constitute less than that in the solution of the test substance which will come in contact with the soil (preferably less than 0.1%). The solubilizing agent should not be a surfactant or undergo solvolytic reactions with the test chemical

(iii) Another alternative for poorly soluble substances is to add the test substance to the test system by spiking: the test substance is dissolved in an organic solvent, an aliquot of which is added to the system of soil and 0.01 M solution of CaCl_2 in distilled or de-ionized water. The content of organic solvent in the aqueous phase should be kept as low as possible, normally not exceeding 0.1%. However, spiking from an organic solution may suffer from volume changes, leading to an additional error as the test substance and co-solvent concentration would not be exactly the same in all tests.

(9) **Soil/solution ratios.** (i) Selection of appropriate soil to solution ratios for sorption studies depends on the distribution coefficient K_d and the relative degree of adsorption desired. The change of substance concentration in the solution determines the statistical accuracy of the measurement based on the form of adsorption equation and the limit of the analytical methodology, in detecting the concentration of the chemical in solution. Therefore, in general practice it is useful to settle on a few fixed ratios, for which the percentage adsorbed is above 20%, and preferably >50% (see reference in paragraph (j)(47), while care should be taken to keep the test substance concentration in the aqueous phase high enough to be measured accurately. This is particularly important in the case of high adsorption percentages.

(ii) A convenient approach to selecting the appropriate soil/water ratios is based on an estimate of the K_d value either by preliminary studies or by established estimation techniques (see paragraph (h)(1) of this guideline. Selection of an appropriate ratio can then be made based on a plot of soil/solution ratio versus K_d for fixed percentages of adsorption (see the following Figure 2).

Figure 2.—Relationship between soil to solution ratios and K_d at various percentages of adsorbed test substance.



(A) In this plot it is assumed that the adsorption equation is linear (according to equation 1).

Equation 1

$$C_s^{\text{ads}}(\text{eq}) = K_d \cdot C_{\text{aq}}^{\text{ads}}(\text{eq})$$

(B) The applicable relationship is obtained by rearranging equation (4) of the K_d in the form of equation 2.

Equation 2

$$\frac{V_0}{m_{\text{soil}}} = \left(\frac{m_0}{m_s^{\text{ads}}(\text{eq})} - 1 \right) K_d$$

or in its logarithmic form assuming that

Equation 3

$$R = m_{\text{soil}}/V_0 \text{ and } A_{\text{eq}}\%/100 = \frac{m_s^{\text{ads}}(\text{eq})}{m_0} :$$

then

Equation 4

$$\log R = -\log K_d + \log \left[\frac{(A_{eq}\%/100)}{(1-A_{eq}\%/100)} \right]$$

(iii) Figure 2 shows soil/solution ratios as a function of K_d for different levels of adsorption. For example, with a soil/solution ratio of 1:5 and a K_d of 20, approximately 80% adsorption would occur. To obtain 50% adsorption for the same K_d , a 1:25 ratio should be used. This approach to selecting the appropriate soil/solution ratios gives the investigator the flexibility to meet experimental needs.

(iv) Where low adsorption of test substance occurs, a 1:1 soil/solution ratio is recommended, although for some very organic soil types smaller ratios may be necessary to obtain a slurry. In any case, care should be taken with the analytical methodology to measure small changes in solution concentration; otherwise the adsorption measurement will be inaccurate. On the other hand, at very high distribution coefficients K_d , one can go up to a 1:100 soil/solution ratio in order to leave a significant amount of chemical in solution. However, care should be taken to ensure good mixing, and adequate time should be allowed for the system to equilibrate. An alternative approach to deal with these extreme cases when adequate analytical methodology is missing, is to predict the K_d value applying estimation techniques based, for example, on P_{ow} values (see paragraph (h)(1) of this guideline). This could be useful especially for low adsorbed/polar chemicals with $P_{ow} < 20$ and for lipophilic/highly sorptive chemicals with $P_{ow} > 10^4$.

(10) **Analytical method.** (i) An appropriate volume of 0.01 M CaCl_2 , e.g., 100 cm^3 , is agitated during 4 h with a weight of soil, e.g., 20 g, of high adsorbability, i.e. with high organic carbon and clay content; these weights and volumes may vary depending on analytical needs, but a soil/solution ratio of 1:5 is a convenient starting point. The mixture is centrifuged and the aqueous phase may be filtrated. A certain volume of the test substance stock solution is added to the latter to reach a nominal concentration within the concentration range which is likely to occur during the test. This volume should not exceed 10% of the final volume of the aqueous phase, in order to change as little as possible the nature of the pre-equilibration solution. The solution is analyzed.

(ii) One blank run consisting of the system soil + CaCl_2 solution (without test substance) is included, in order to check for artifacts in the analytical method and for matrix effects caused by the soil.

(iii) Analytical methods which can be used for sorption measurements include gas-liquid chromatography (GLC), high-performance liquid chromatography (HPLC), spectrometry (e.g., GC/mass spectrometry, HPLC/mass spectrometry) and liquid scintillation counting (for radiolabeled substances). Independent of the analytical method used, recoveries should be between 90% and 110% of the nominal value. In order to allow for detection and evaluation after

partitioning has taken place, the detection limits of the analytical method should be at least two orders of magnitude below the nominal concentration.

(iv) The characteristics and detection limits of the analytical method available for carrying out adsorption studies play an important role in defining the test conditions and the whole experimental performance of the test. This guideline provides recommendations and guidance for alternative solutions where the analytical method and laboratory facilities may impose limitations.

(g) **Test sequence—(1) Preliminary study—Tier 1** (i) Selection of optimal soil/solution ratios. (A) Two soil types and three soil/solution ratios (six experiments) are used. One soil type has high organic carbon and low clay content, and the other low organic carbon and high clay content. The following soil to solution ratios are suggested. However, the absolute mass of soil and volume of aqueous solution corresponding to these ratios can be different with respect to laboratory facilities:

- (1) 50 g soil and 50 cm³ aqueous solution of the test substance (ratio 1/1).
- (2) 10 g soil and 50 cm³ aqueous solution of the test substance (ratio 1/5).
- (3) 2 g soil and 50 cm³ aqueous solution of the test substance (ratio 1/25).

(B) The minimum amount of soil on which the experiment can be carried out depends on the laboratory facilities and the performance of analytical method used. However, it is recommended to use at least 1 g, and preferably 2 g, in order to obtain reliable results from the test.

(C) One control sample with only the test substance in 0.01 M CaCl₂ solution (no soil) is subjected to precisely the same steps as the test systems, in order to check the stability of the test substance in CaCl₂ solution and its possible adsorption on the surfaces of the test vessels.

(D) A blank run per soil with the same amount of soil and total volume of 50 cm³ 0.01 M CaCl₂ solution (without test substance) is subjected to the same test procedure. This serves as a background control during the analysis to detect interfering compounds or contaminated soils.

(E) All experiments, including controls and blanks, should be performed at least in duplicate. The total number of the samples which should be prepared for the study can be calculated with respect to the methodology which will be followed (see paragraph (g)(1)(i)(J) of this guideline).

(F) The air-dried soil samples are equilibrated by shaking with a minimum volume of 45 cm³ of 0.01 M CaCl₂ overnight (12 h) before the day of the experiment. Afterwards, a certain volume of the stock solution of the test substance is added in order to adjust the final volume to 50 cm³. This volume of the stock solution added: (a) should not exceed 10% of the final 50 cm³ volume of the aqueous phase in order to change as little as possible the nature of the pre-equilibration solution; and (b) should preferably result in an initial concentration of the test substance being in contact with the soil (C₀) at least two orders of magnitude higher than the detection limit of the analytical method. This threshold safeguards the ability to perform accurate measurements even when strong adsorption occurs (> 90%) and to determine later the adsorption isotherms. It is also recommended, if possible, that the initial substance concentration (C₀) not exceed half of its solubility limit.

(G) An example of how to calculate the concentration of the stock solution (C_{st}) is as follows: a detection limit of $0.01 \mu\text{g cm}^{-3}$ and 90% adsorption are assumed; thus, the initial concentration of the test substance in contact with the soil should preferably be $1 \mu\text{g cm}^{-3}$ (two orders of magnitude higher than the detection limit). Supposing that the maximum recommended volume of the stock solution is added, i.e. 5 to 45 cm^3 0.01 M CaCl_2 equilibration solution (= 10% of the stock solution to 50 cm^3 total volume of aqueous phase), the concentration of the stock solution should be $10 \mu\text{g cm}^{-3}$; this is three orders of magnitude higher than the detection limit of the analytical method.

(H) The pH of the aqueous phase should be measured before and after contact with the soil since it plays an important role in the whole adsorption process, especially for ionizable substances.

(I) The mixture is shaken until adsorption equilibrium is reached. The equilibrium time in soils is highly variable, depending on the chemical and the soil; a period of 24 h is generally sufficient (see paragraph (j)(48) in this guideline). In the preliminary study, samples may be collected sequentially over a 48 h period of mixing (for example at 4, 8, 24, 48 h). However, times of analysis should be considered with flexibility of the work schedule of the laboratory.

(J) There are two options for the analysis of the test substance in the aqueous solution: the parallel method and the serial method. Although the parallel method is experimentally more tedious, the mathematical treatment of the results is simpler (see paragraph (h)(2) of this guideline).

(1) *Parallel method.* Sufficient samples with the same soil/solution ratio are prepared to accommodate designated time intervals to study the adsorption kinetics. After centrifugation or filtration, the aqueous phase of the first tube is recovered as completely as possible and is measured after, for example, 4 h, that of the second tube after 8 h, that of the third after 24 h, etc.

(2) *Serial method.* A duplicate sample is prepared for each soil/solution ratio. At defined time intervals the mixture is centrifuged to separate the phases. A small aliquot of the aqueous phase is immediately analyzed for the test substance; then the experiment continues with the original mixture. If filtration is applied after centrifugation, the laboratory should have facilities to handle filtration of small aqueous aliquots. It is recommended that the total volume of the aliquots taken not exceed 1% of the total volume of the solution, in order not to change significantly the soil/solution ratio or decrease the mass of solute available for adsorption during the test.

(K) The percentage adsorption A_{t_i} is calculated at each time point (t_i) on the basis of the nominal initial concentration and the measured concentration at the sampling time (t_i), corrected for the value of the blank. Plots of the A_{t_i} versus time (see Fig. 4 of paragraph (h)(2)(ii)(A)(3) of this guideline) are generated in order to estimate the achievement of equilibrium plateau. Plots of the concentration of the test substance in the aqueous phase (C_{aq}^{ads}) versus time could also be used to estimate the achievement of the equilibrium plateau (see Fig. 5 of paragraph (h)(2)(ii)(A)(3) of this guideline). The K_d value at equilibrium is also calculated. Based on this

K_d value, appropriate soil/solution ratios are selected from Fig. 4 in paragraph (h)(2)(ii)(A)(3) of this guideline, so that percent adsorption is greater than 20% and preferably greater than 50% (see reference in paragraph (j)(49) of this guideline). All applicable equations and principles of plotting are given in paragraphs (h)(1-7 inclusive) of this guideline).

(ii) Determination of adsorption equilibration time and of the amount of test substance adsorbed at equilibrium. (A) As mentioned in paragraph (g)(1)(i)(K) of this guideline, plots of A_t or C_{aq}^{ads} versus time permit estimation of the achievement of the adsorption equilibrium and the amount of test substance adsorbed at equilibrium. Figures 4 and 5 in paragraph (h)(2) of this guideline show examples of such plots. Equilibration time is the time the system needs to reach a plateau.

(B) If, with a particular soil, no plateau but a steady increase is found, this may be due to complicating factors such as biodegradation or slow diffusion. Biodegradation can be shown by repeating the experiment with a sterilized sample of the soil. If no plateau is achieved even in this case, the experimenter should search for other phenomena that could be involved. This could be done with appropriate modifications of the experimental conditions (temperature, shaking times, soil/solution ratios). The experimenter may decide whether to continue the test procedure in spite of a possible failure to achieve equilibrium.

(iii) Adsorption on the surface of the test vessel and stability of the test substance. (A) Some information on the adsorption of the test substance on the surface of test vessels, as well as its stability, can be derived by analyzing the control samples. If a depletion exceeding the standard error of the analytical method is observed, abiotic degradation and/or adsorption on the surface of the test vessel could be involved. Distinction between these two phenomena could be achieved by thoroughly washing the walls of the vessel with a known volume of an appropriate solvent and subjecting the wash solution to analysis for the test substance. If no adsorption on the surface of the test vessels is observed, the depletion demonstrates abiotic instability of the test substance. If adsorption is found, changing the material of the test vessels is necessary. However, data on the adsorption on the surface of the test vessels gained from this experiment cannot be directly extrapolated to soil/solution experiment. The presence of soil will generally reduce this adsorption.

(B) Additional information on the stability of the test substance can be derived by determination of the parental mass balance over time. This means that the aqueous phase and extracts of the soil and test vessel walls are analyzed for the test substance. The difference between the mass of the test chemical added and the sum of the test chemical masses in the aqueous phase and extracts of the soil and test vessel walls is equal to the mass degraded and volatilized and not extracted. In order to perform a mass balance determination, the adsorption equilibrium should have been reached within the time period of the experiment.

(C) The mass balance is conducted on both soils and for one soil/solution ratio per soil that gives a depletion greater than 20% and preferably greater than 50% at equilibrium. When the ratio-finding experiment is completed with the analysis of the last sample of the aqueous phase after 48 h, the phases are separated by centrifugation and, if so wished, filtration. The aqueous phase is recovered as much as possible, and a suitable extraction solvent (extraction coefficient of

at least 95%) is added to the soil to extract the test substance. At least two successive extractions are recommended. The amount of test substance in the soil and test vessel extracts is determined and the mass balance is calculated (see equation 10, Data and Reporting section in paragraph (h)(2)(ii)(B)(1) of this guideline). If it is less than 90%, the test substance is considered to be unstable in the time scale of the test. However, studies could still be continued, taking into account the instability of the test substance. In this case, both phases in the main study should be analyzed.

(2) **Adsorption kinetics at one concentration. Tier 2.** (i) Five soils are used using the guidance given in Table 1. There is an advantage to including some or all of the soils used in the preliminary study among these five soils. In this case, Tier 2 does not have to be repeated for soils used in the preliminary study.

(ii) The equilibration time, the soil/solution ratio, the weight of the soil sample, the volume of the aqueous phase in contact with the soil and the concentration of the test substance in the solution are chosen based on preliminary study results. Analysis should be initiated after about 2, 4, 6, 8 (possibly also 10) and 24 h contact time; the agitation time may be extended to a maximum of 48 h in case a chemical takes longer to equilibrate with respect to ratio-finding results; however, times of analysis could be considered with flexibility.

(iii) Each experiment (one soil and one solution) is done at least in duplicate to allow estimation of the variance of the results. In every experiment one blank is run. It consists of the soil and 0.01 M CaCl₂ solution, without test substance, and of weight and volume, respectively, identical to those of the experiment. A control sample with only the test substance in 0.01 M CaCl₂ solution (without soil) is subjected to the same test procedure, serving to safeguard against the unexpected. The test runs are described in paragraphs (g)(1)(i)(F) through (g)(1)(i)(K) of this guideline.

(iv) The percentage adsorption is calculated at each time point A_{t_i} and/or time interval $A_{\Delta t_i}$ (according to the needs of the study) and is plotted over time. The distribution coefficient K_d at equilibrium, as well as the organic carbon normalized adsorption coefficient K_{oc} (for non-polar organic chemicals), are also calculated.

(v) Results and discussion of the adsorption kinetics test.

(A) The linear K_d value is generally accurate to describe sorptive behavior in soil (see paragraphs (j)(24) and (j)(50) of this guideline) and represents an expression of inherent mobility of chemicals in soil. For example, in general chemicals with $K_d \leq 1 \text{ cm}^3 \text{ g}^{-1}$ are considered to be qualitatively mobile. Similarly, a mobility classification scheme based on K_{oc} values has been developed by McCall *et al.* (j)(5). Additionally, leaching classification schemes exist based on a relationship between K_{oc} and the degradation time for 50% of the test substance (DT-50) (see paragraphs (j)(20) and (j)(21) of this guideline).

(B) According to error analysis studies referenced in (j)(49), K_d values below $0.3 \text{ cm}^3 \text{ g}^{-1}$ cannot be estimated accurately from a decrease in concentration in the aqueous phase, even when the most favorable (from point of view of accuracy) soil/solution ratio is applied, i.e. 1:1. In this case analysis of both phases, soil and solution, is recommended.

(C) With respect to the above remarks, it is recommended that the study of adsorptive behavior of a chemical in soil and its potential mobility be continued by determining Freundlich adsorption isotherms for these systems, for which an accurate determination of K_d is possible with the experimental protocol followed in this guideline.

(3) Adsorption isotherms and desorption kinetics/desorption isotherms—Tier 3. (i) Adsorption isotherms. (A) Five test substance concentrations are used, covering preferably two orders of magnitude; in the choice of these concentrations the water solubility and the resulting aqueous equilibrium concentrations should be taken into account. The same soil/solution ratio per soil should be kept along the study. With one exception, the adsorption test is performed as described in paragraphs (g)(1)(i)(B) through (g)(1)(i)(J) of this guideline. The exception is the aqueous phase is analyzed only once at the time necessary to reach equilibrium as determined in Tier 2. The equilibrium concentrations in the solution are determined and the amount adsorbed is calculated from the depletion of the test substance in the solution or with the direct method. The adsorbed mass per unit mass of soil is plotted as a function of the equilibrium concentration of the test substance.

(B) Results from the adsorption isotherms experiment. Among the mathematical adsorption models proposed so far, the Freundlich isotherm is the one most frequently used to describe adsorption processes. More detailed information on the interpretation and importance of adsorption models is provided in references (j)(31), (j)(35), and (j)(51) through (j)(53) of this guideline). It should be mentioned that a comparison of K_F (Freundlich adsorption coefficient) values for different substances is only possible if these K_F values are expressed in the same units (j)(54).

(ii) Desorption kinetics. (A) The purpose of this experiment is to determine if a chemical is reversibly or irreversibly adsorbed on a soil. This information is important, since the desorption process is key in the behavior of a chemical in field soil. Moreover, desorption data are useful inputs in the computer modeling of leaching and dissolved run-off simulation. If a desorption study is desired, it is recommended that the study described below be conducted on each system for which an accurate determination of K_d in the preceding adsorption kinetics experiment was possible.

(B) As with the adsorption kinetics study, there are two options for the desorption kinetics experiment: the parallel method and the serial method. The choice of the methodology is left to the experimenter who should consider the available laboratory facilities and recourses, and remarks made in paragraph (g)(1)(i)(J) of this guideline.

(1) Parallel method: For each soil chosen for the desorption study, sufficient samples with the same soil/solution ratio are prepared, to accommodate the time intervals desired to study desorption kinetics. Preferably, the same time intervals as in the adsorption kinetics experiment should be used; however, the total time may be extended as appropriate in order for the system to reach desorption equilibrium. In every experiment (one soil, one solution) one blank is run. It consists of the soil and 0.01 M CaCl_2 solution, without test substance, and of weight and volume, respectively, identical to those of the experiment. As a control sample the test substance in 0.01 M

CaCl₂ solution (without soil) is subjected to the same test procedure. Each mixture of soil with solution is agitated until adsorption equilibrium is reached (as determined in Tier 2). Then, the phases are separated by centrifugation and the aqueous phases removed as much as possible. The volume of solution removed is replaced by an equal volume of 0.01 M CaCl₂ without test substance and the new mixtures are agitated again. The aqueous phase of the first tube is recovered as completely as possible and is measured after, for example, 2 h, that of the second tube after 4 h, that of the third after 6 h, etc until the desorption equilibrium is reached.

(2) *Serial method*: After the adsorption kinetics experiment, the mixture is centrifuged and the aqueous phase is removed as much as possible. The volume of solution removed is replaced by an equal volume of 0.01 M CaCl₂ without test substance. The new mixture is agitated until the desorption equilibrium is reached. During this time period, at defined time intervals, the mixture is centrifuged to separate the phases. A small aliquot of the aqueous phase is immediately analyzed for the test substance; then, the experiment continues with the original mixture. The volume of each individual aliquot should be less than 1% of the total volume. The same quantity of fresh 0.01 M CaCl₂ solution is added to the mixture to maintain the soil to solution ratio, and the agitation continues until the next time interval.

(C) The percentage desorption is calculated at each time point D_{t_i} and/or time interval $D_{\Delta t_i}$ (according to the needs of the study) and is plotted over time. The desorption coefficient K_{des} at equilibrium is also calculated. All applicable equations are given in sections (h)(3) through (h)(8) inclusive.

(D) Results from desorption kinetics experiment. Common plots of the percentage desorption D_{t_i} and adsorption A_{t_i} versus time, allow estimation of the reversibility of the adsorption process. If the desorption equilibrium is attained even within twice the time of the adsorption equilibrium, and the total desorption is more than 75% of the amount adsorbed, the adsorption is considered to be reversible.

(E) Desorption isotherms. Freundlich desorption isotherms are determined on the soils used in the adsorption isotherms experiment. The desorption test is performed as described in the section “Desorption kinetics” (see paragraphs (g)(3)(ii)(B)(1) or (g)(3)(ii)(B)(2) of this guideline) with the only difference being that the aqueous phase is analyzed but once, at desorption equilibrium. The amount of the test substance desorbed is calculated. The content of test substance remaining adsorbed on soil at desorption equilibrium is plotted as a function of the equilibrium concentration of the test substance in solution

(h) **Considerations for data reporting**—(1) **Estimation techniques for K_d** . (i) Estimation techniques permit prediction of K_d based on correlations with, for example, P_{ow} values (see paragraphs (j)(1), (j)(28) and, (j)(55) through (j)(60) in this guideline), water solubility data (see paragraphs (j)(1), (j)(10), (j)(8), (j)(28), (j)(33) and (j)(60) through (j)(64) of this guideline), or polarity data derived by application of HPLC on reversed phase (see paragraphs (j)(65) through (j)(67) of this guideline). (See also Draft OECD Test Guideline “Estimation of Adsorption Coefficient (K_{oc}) on Soil and on Sewage Sludge using High Performance Liquid Chromatography (HPLC)”, July 1997 (j)(68)). As shown in Table 4 and

Table 5 in paragraph (h)(1)(iii) of this guideline, is the K_{oc} or K_{om} that are calculated from these equations and then, indirectly, the K_d from the equations:

Equation 5

$$K_{oc} = K_d \cdot \frac{100}{\%oc} \quad (\text{cm}^3 \text{g}^{-1})$$

and

Equation 6

$$K_{om} = \frac{K_d}{1.724} \cdot \frac{100}{\%oc} \quad (\text{cm}^3 \text{g}^{-1})$$

(ii) The concept of these correlations is based on two assumptions: It is the organic matter of the soil that mainly influences the adsorption of a substance and the interactions involved are mainly non-polar. As a result, these correlations are not, or are only to some extent, applicable to polar substances, and are not applicable in cases where the organic matter content of the soil is very small (j)(1). In addition, although satisfactory correlations have been found between P_{ow} and adsorption (j)(8), the same cannot be said for the relationship between water solubility and extent of adsorption (j)(8) and (j)(10); so far the studies are contradictory.

(iii) Some examples of correlations between the adsorption coefficient and the octanol-water partition coefficient, as well as water solubility are given in Tables 5 and 6, respectively.

Table 4. Examples of correlations between the adsorption distribution coefficient and the octanol-water partition coefficient

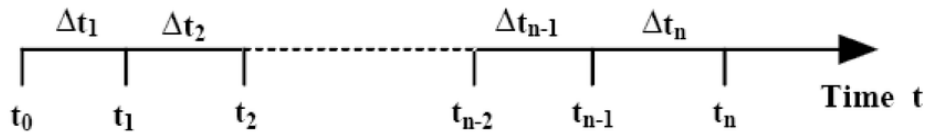
Compounds	Correlations	Authors
Substituted ureas	$K_{om} = 0.69 + 0.52 \log P_{ow}$	Briggs (reference (j)(28))
Aromatic chlorinated	$K_{oc} = -0.779 + 0.904 \log P_{ow}$	Chiou <i>et al.</i> (reference (j)(57))
Various pesticides	$\log K_{om} = 4.4 + 0.72 \log P_{ow}$	Gerstl and Mingelgrin (reference (j)(58))
Aromatic hydrocarbons	$K_{oc} = -2.53 + 1.15 \log P_{ow}$	Vowles and Mantoura (reference (j)(59))

Table 5. Examples of correlations between the adsorption distribution coefficient and water solubility

Compounds	Correlations	Authors
Various pesticides	$\log K_{om} = 3.8 - 0.561 \log S_w$	Gerstl and Mingelgrin (j)(58)
Aliphatic, aromatic chlorinated substances	$K_{om} = (4.040 \pm 0.038) - (0.557 \pm 0.012) \log S_w$	Chiou <i>et al.</i> (j)(62)
a-naphtol	$\log K_{oc} = 4.273 - 0.686 \log S_w$	Hasset <i>et al.</i> (j)(63)
Cyclic, aliphatic aromatic substances	$\log K_{oc} = -1.405 - 0.921 \log S_w - 0.00953$ (mp-25)	Karickhoff (j)(33)
Various compounds	$K_{om} = 2.75 - 0.45 \log S_w$	Moreale van Blade (j)(64)

(2) Calculation of adsorption A(%) and desorption D(%). (i) Time scheme. The time scheme of the procedure is shown in Figure 3:

Fig. 3.—Time Scheme for calculation of adsorption A(%) and desorption D(%).



(Note. For all the calculations it is assumed that the test substance is stable and does not adsorb significantly to the container walls.)

(ii) Adsorption A(%). (A) Parallel method. (1) The percentage adsorption is calculated for each test tube (i) at each time point (t_i), according to the equation:

Equation 7

$$A_{t_i} = \frac{m_s^{\text{ads}}(t_i) \cdot 100}{m_0} (\%)$$

(2) The terms of this equation may be calculated as follows:

Equation 7A

$$m_0 = C_0 \cdot V_0 (\mu\text{g})$$

$$m_s^{\text{ads}}(t_i) = m_0 - C_{\text{aq}}^{\text{ads}}(t_i) \cdot V_0 (\mu\text{g})$$

where:

- A_{t_i} = adsorption percentage (%) at the time point t_i ;
 $m_s^{\text{ads}}(t_i)$ = mass of test substance on soil at the time t_i that the analysis is performed (μg);
 M_0 = mass of test substance in the test tube, at the beginning of the test (μg);
 C_0 = initial mass concentration of the test solution in contact with the soil ($\mu\text{g cm}^{-3}$);
 $C_{\text{aq}}^{\text{ads}}(t_i)$ = mass concentration of the substance in the aqueous phase at the time t_i that the analysis is performed ($\mu\text{g cm}^{-3}$); this concentration is analytically determined taking into account the values given by the blanks.
 V_0 = initial volume of the test solution in contact with the soil (cm^3).

(3) The values of the adsorption percentage A_{t_i} or $C_{\text{aq}}^{\text{ads}}(t_i)$ are plotted versus time and the time after which the sorption equilibrium is attained is determined. Examples of such plots are given in Figures 4 and 5, respectively.

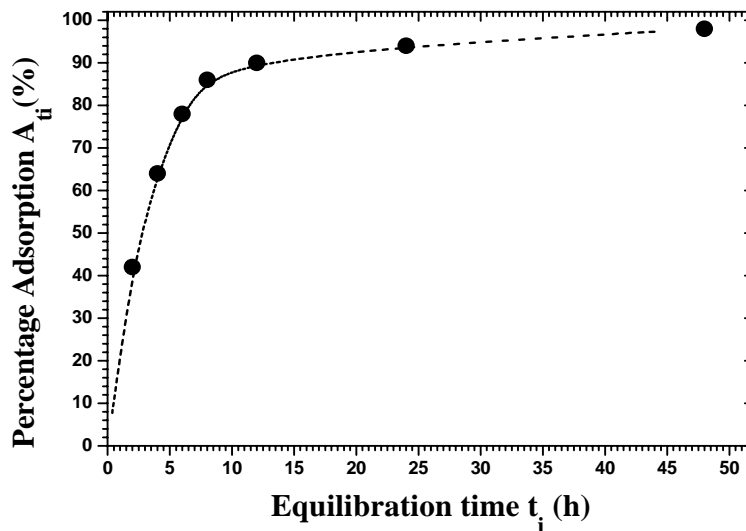


Fig. 4 Adsorption Equilibrium Plot

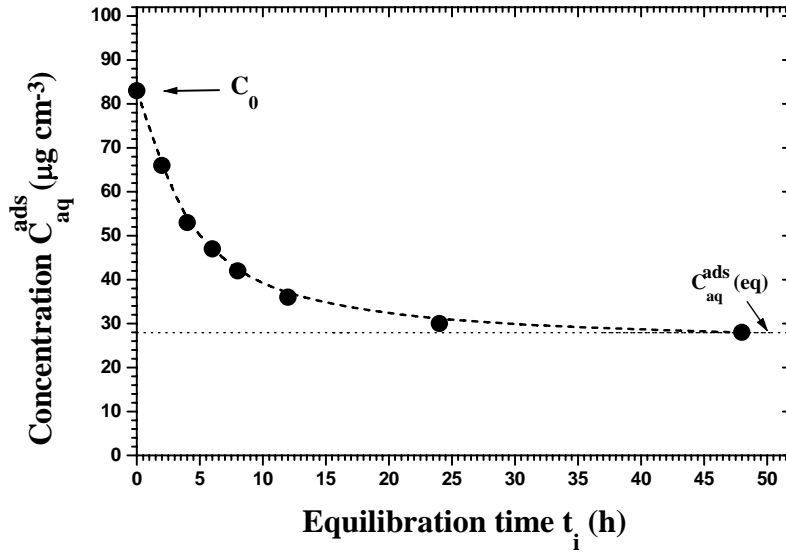


Fig. 5 Mass concentration of the test substance in the aqueous phase (C_{aq}) versus time

(B) Serial method. (1) The following equations take into account that the adsorption procedure is carried out by measurements of the test substance in small aliquots of the aqueous phase at specific time intervals.

(2) During each time interval the amount of the substance adsorbed on the soil is calculated as follows:

-for the first time interval $\Delta t_1 = t_1 - t_0$

Equation 8

$$m_s^{ads}(\Delta t_1) = m_0 - m_m^{ads}(t_1) \cdot \left(\frac{V_0}{V_a^A} \right)$$

- for the second time interval $\Delta t_2 = t_2 - t_1$

Equation 9

$$m_s^{ads}(\Delta t_2) = m_m^{ads}(t_1) \cdot \left(\frac{V_0}{V_a^A} \right) - m_m^{ads}(t_2) \cdot \left(\frac{V_0 - V_a^A}{V_a^A} \right)$$

- for the third time interval $\Delta t_3 = t_3 - t_2$

Equation 10

$$m_s^{\text{ads}}(\Delta t_3) = m_m^{\text{ads}}(t_2) \cdot \left(\frac{V_0 - v_a^\Lambda}{v_a^\Lambda} \right) - m_m^{\text{ads}}(t_3) \cdot \left(\frac{V_0 - 2 \cdot v_a^\Lambda}{v_a^\Lambda} \right)$$

- for the n^{th} time interval $\Delta t_n = t_n - t_{n-1}$

Equation 11

$$m_s^{\text{ads}}(\Delta t_n) = m_m^{\text{ads}}(t_{n-1}) \cdot \left(\frac{V_0 - (n-2) \cdot v_a^\Lambda}{v_a^\Lambda} \right) - m_m^{\text{ads}}(t_n) \cdot \left(\frac{V_0 - (n-1) \cdot v_a^\Lambda}{v_a^\Lambda} \right)$$

(3) The percentage of adsorption at each time interval, $A_{\Delta t_i}$, is calculated using the following equation:

Equation 12

(This equation is applicable to both direct and indirect methods. All other equations are applicable only to indirect method.)

$$A_{\Delta t_i} = \frac{m_s^{\text{ads}}(\Delta t_i)}{m_0} \cdot 100 \quad (\%)$$

while the percentage of adsorption (A_{t_i}) at a time point t_i is given by equation 13.

Equation 13

(This equation applicable to both direct and indirect methods. All other equations are applicable only to indirect method.)

$$A_{t_i} = \frac{\sum_{j=\Delta t_1}^{\Delta t_i} m_s^{\text{ads}}(j)}{m_0} \cdot 100 \quad (\%)$$

(4) The values of the adsorption A_{t_i} or $A_{\Delta t_i}$ (with respect to the needs of the study) are plotted versus time and the time after which the sorption equilibrium is attained is determined.

(5) At the equilibration time t_{eq} :

- the mass of the test substance adsorbed on the soil is shown as equation 14:

Equation 14

(This equation is applicable to both direct and indirect methods. All other equations are applicable only to indirect method.)

$$m_s^{ads}(eq) = \sum_{\Delta t_i=1}^n m_s^{ads}(\Delta t_i)$$

- the mass of the test substance in the solution is shown as equation 15.

Equation 15

(This equation applicable to both direct and indirect methods. All other equations are applicable only to indirect method.)

$$m_{aq}^{ads}(eq) = m_0 - \sum_{\Delta t_i=1}^n m_s^{ads}(\Delta t_i)$$

- and the percentage of adsorption at equilibrium is shown as equation 16:

Equation 16

(This equation is applicable to both direct and indirect methods. All other equations are applicable only to indirect method.)

$$A_{eq} = \frac{m_s^{ads}(eq)}{m_0} \cdot 100 (\%)$$

- The parameters used above are defined as :

$m_s^{\text{ads}}(\Delta t_1), m_s^{\text{ads}}(\Delta t_2), \dots, m_s^{\text{ads}}(\Delta t_n)$	=	Mass of the substance adsorbed on the soil during the time intervals $\Delta t_1, \Delta t_2, \dots, \Delta t_n$ respectively (μg);
$m_m^{\text{ads}}(t_1), m_m^{\text{ads}}(t_2), \dots, m_m^{\text{ads}}(t_n)$	=	Mass of the substance measured in an aliquot (v_a^A) at the time points t_1, t_2, \dots, t_n respectively (μg);
$m_s^{\text{ads}}(\text{eq})$	=	Mass of the substance adsorbed on the soil at adsorption equilibrium (μg);
$m_{\text{aq}}^{\text{ads}}(\text{eq})$	=	mass of the substance in the solution at adsorption equilibrium (μg);
v_a^A	=	volume of the aliquot in which the test substance is measured (cm^3);
$A_{\Delta t_i}$	=	percentage of adsorption corresponding at a time interval Δt_i (%);
A_{eq}	=	percentage of adsorption at adsorption equilibrium (%).

(iii) Desorption D(%). The time t_0 that the desorption kinetics experiment begins, is considered as the moment that the maximal recovered volume of the test substance solution (after that the adsorption equilibrium is attained) is replaced by an equal volume of 0.01 M CaCl_2 solution.

(A) **Parallel method.** (1) At a time point t_i , the mass of the test substance is measured in the aqueous phase taken from the tube i (V_r^i), and the mass desorbed is calculated according to equation 17.

Equation 17

$$m_{\text{aq}}^{\text{des}}(t_i) = m_m^{\text{des}}(t_i) \cdot \left(\frac{V_0}{V_r^i} \right) - m_{\text{aq}}^A$$

At desorption equilibrium $t_i = t_{\text{eq}}$ and therefore $m_{\text{aq}}^{\text{des}}(t_i) = m_{\text{aq}}^{\text{des}}(\text{eq})$.

The mass of the test substance desorbed during a time interval (Δt_i) is given by equation 18.

Equation 18

$$m_{\text{aq}}^{\text{des}}(\Delta t_i) = m_{\text{aq}}^{\text{des}}(t_i) - \sum_{j=1}^{i-1} m_{\text{aq}}^{\text{des}}(j)$$

(2) The percentage of desorption is calculated:

- at a time point t_i from equation 19.

Equation 19

$$D_{t_i} = \frac{m_{\text{aq}}^{\text{des}}(t_i)}{m_{\text{s}}^{\text{ads}}(\text{eq})} \cdot 100 \quad (\%)$$

- and during a time interval (Δt_i) from equation 20:

Equation 20

$$D_{\Delta t_i} = \frac{m_{\text{aq}}^{\text{des}}(\Delta t_i)}{m_{\text{s}}^{\text{ads}}(\text{eq})} \cdot 100 \quad (\%)$$

where:

- D_{t_i} = desorption percentage at a time point t_i (%);
- $D_{\Delta t_i}$ = desorption percentage corresponding to a time interval Δt_i (%);
- $m_{\text{aq}}^{\text{des}}(t_i)$ = mass of the test substance desorbed at a time point t_i (μg);
- $m_{\text{aq}}^{\text{des}}(\Delta t_i)$ = mass of the test substance desorbed during a time intervals Δt_i (μg);
- $m_{\text{m}}^{\text{des}}(t_i)$ = mass of the test substance analytically measured at a time t_i in a solution volume V_{r}^i , which is taken for the analysis (μg);
- m_{aq}^{A} = mass of the test substance left over from the adsorption equilibrium due to incomplete volume replacement (μg) is shown as equation 21;

Equation 21

$$m_{\text{aq}}^{\text{A}} = m_{\text{aq}}^{\text{ads}}(\text{eq}) \cdot \left(\frac{V_0 - V_{\text{R}}}{V_0} \right)$$

- $m_{\text{aq}}^{\text{ads}}(\text{eq})$ = mass of the test substance in the solution at adsorption equilibrium (μg);
- V_{R} = volume of the supernatant removed from the tube after the attainment of adsorption equilibrium and replaced by the same volume of a 0.01 M CaCl_2 solution (cm^3);
- V_{r}^i = volume of the solution taken from the tube (i) for the measurement of the test substance, in desorption kinetics experiment (cm^3).

The values of the desorption D_{t_i} or $D_{\Delta t_i}$ (according to the needs of the study) are plotted versus time and the time after which the desorption equilibrium is attained is determined.

(B) Serial method. (1) The following equations take into account that the adsorption procedure, which was preceded, was carried out by measurements of the test substance in small

aliquots (v_a^A) of the aqueous phase. It is assumed that: a) the volume of the supernatant removed from the tube after the adsorption kinetics experiment was replaced by the same volume of 0.01 M CaCl_2 solution (V_R) and b) the total volume of the aqueous phase in contact with the soil (V_T) during the desorption kinetics experiment remains constant and is given by equation 22.

Equation 22

$$V_T = V_o - \sum_{i=1}^n v_a^A(i)$$

(2) At a time point t_i :

- the mass of the test substance is measured in a small aliquot (v_a^D) and the mass desorbed is calculated, according to equation 23:

Equation 23

$$m_{aq}^{des}(t_i) = m_m^{des}(t_i) \cdot \left(\frac{V_T}{v_a^D} \right) - m_{aq}^A \cdot \left(\frac{(V_T - (i-1) \cdot v_a^D)}{V_T} \right)$$

- At desorption equilibrium $t_i = t_{eq}$ and therefore $m_{aq}^{des}(t_i) = m_{aq}^{des}(eq)$.

- The percentage of desorption D_{t_i} is calculated, from equation 24:

Equation 24

$$D_{t_i} = \frac{m_{aq}^{des}(t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%)$$

(3) At a time interval (Δt_i):

- During each time interval the amount of the substance desorbed is calculated as follows:

- for the first time interval $\Delta t_1 = t_1 - t_0$

Equation 25

$$m_{aq}^{des}(\Delta t_1) = m_m^{des}(t_1) \cdot \left(\frac{V_T}{v_a^D} \right) - m_{aq}^A$$

and

Equation 26

$$m_s^{des}(t_1) = m_s^{aq}(eq) - m_{aq}^{des}(\Delta t_1)$$

- for the second time interval $\Delta t_2 = t_2 - t_1$, shown in equation 27:

Equation 27

$$m_{\text{aq}}^{\text{des}}(\Delta t_2) = m_{\text{m}}^{\text{des}}(t_2) \cdot \left(\frac{V_{\text{T}}}{v_{\text{a}}^{\text{D}}} \right) - m_{\text{aq}}^{\text{des}}(\Delta t_1) \cdot \left(\frac{(V_{\text{T}} - v_{\text{a}}^{\text{D}})}{V_{\text{T}}} \right) - m_{\text{aq}}^{\text{A}} \cdot \left(\frac{(V_{\text{T}} - v_{\text{a}}^{\text{D}})}{V_{\text{T}}} \right)$$

and equation 28

Equation 28

$$m_{\text{s}}^{\text{des}}(t_2) = m_{\text{s}}^{\text{ads}}(\text{eq}) - \left[m_{\text{aq}}^{\text{des}}(\Delta t_1) + m_{\text{aq}}^{\text{des}}(\Delta t_2) \right]$$

- for the n^{th} time interval $\Delta t_n = t_n - t_{n-1}$ (equation 29)

Equation 29

$$m_{\text{aq}}^{\text{des}}(\Delta t_n) = \left[m_{\text{m}}^{\text{des}}(t_n) \cdot \left(\frac{V_{\text{T}}}{v_{\text{a}}^{\text{D}}} \right) - m_{\text{aq}}^{\text{A}} \cdot \left(\frac{(V_{\text{T}} - (n-1) \cdot v_{\text{a}}^{\text{D}})}{V_{\text{T}}} \right) - \sum_{i=1, n \neq 1}^{n-1} \left(\frac{(V_{\text{T}} - (n-i) \cdot v_{\text{a}}^{\text{D}})}{V_{\text{T}}} \cdot m_{\text{aq}}^{\text{des}}(\Delta t_i) \right) \right]$$

and equation 30

Equation 30

$$m_{\text{s}}^{\text{des}}(t_n) = m_{\text{s}}^{\text{ads}}(\text{eq}) - \sum_{i=1, n \neq 1}^n m_{\text{aq}}^{\text{des}}(\Delta t_i)$$

- Finally, the percentage of desorption at each time interval, $D_{\Delta t_i}$ is calculated using equation 31:

Equation 31

$$D_{\Delta t_i} = \frac{m_{\text{aq}}^{\text{des}}(\Delta t_i)}{m_{\text{s}}^{\text{ads}}(\text{eq})} \cdot 100 \quad (\%)$$

while the percentage of desorption D_{t_i} at a time point t_i is given by equation 32:

Equation 32

$$D_{t_i} = \frac{\sum_{j=\Delta t_1}^{\Delta t_i} m_{\text{aq}}^{\text{des}}(j)}{m_{\text{s}}^{\text{ads}}(\text{eq})} \cdot 100 = \frac{m_{\text{aq}}^{\text{des}}(t_i)}{m_{\text{s}}^{\text{ads}}(\text{eq})} \cdot 100 \quad (\%)$$

where the above used parameters are defined as:

$m_{\text{s}}^{\text{des}}(\Delta t_1), m_{\text{s}}^{\text{des}}(\Delta t_2), \dots, m_{\text{s}}^{\text{des}}(\Delta t_n)$ = mass of the substance remaining adsorbed on the soil after the time intervals $\Delta t_1, \Delta t_2, \dots, \Delta t_n$ respectively (μg);

$m_{\text{aq}}^{\text{des}}(\Delta t_1), m_{\text{aq}}^{\text{des}}(\Delta t_2), \dots, m_{\text{aq}}^{\text{des}}(\Delta t_n)$ = mass of the test substance desorbed during the time intervals $\Delta t_1, \Delta t_2, \dots, \Delta t_n$ respectively (μg);

$m_{\text{m}}^{\text{des}}(t_1), m_{\text{m}}^{\text{des}}(t_2), \dots, m_{\text{m}}^{\text{des}}(t_n)$ = mass of the substance measured in an aliquot (v_{a}^{D}) at time points t_1, t_2, \dots, t_n , respectively (μg);

V_{T} = total volume of the aqueous phase in contact with the soil during the desorption kinetics experiment performed with the serial method (cm^3);

m_{aq}^{A} = mass of the test substance left over from the adsorption equilibrium due to incomplete volume replacement (μg) (equation 33)

Equation 33

$$m_{\text{aq}}^{\text{A}} = \left(\frac{\left(V_0 - \sum_{i=1}^n v_{\text{a}}^{\text{A}}(i) \right) - V_{\text{R}}}{\left(V_0 - \sum_{i=1}^n v_{\text{a}}^{\text{A}}(i) \right)} \right) \cdot m_{\text{aq}}^{\text{ads}}(\text{eq})$$

V_{R} = volume of the supernatant removed from the tube after the attainment of adsorption equilibrium and replaced by the same volume of a 0.01 M CaCl_2 solution (cm^3);

V_a^D = volume of the aliquot sampled for analytical purpose from the tube (i), during the desorption kinetics experiment performed with the serial method (cm^3);
 $v_a^D \leq 0.02 \cdot V_T$

(3) **Adsorption** (i) The adsorption A_{t_i} is defined as the percentage of substance adsorbed on the soil related to the quantity present at the beginning of the test, under the test conditions. If the test substance is stable and does not adsorb significantly to the container wall, A_{t_i} is calculated at each time point t_i , according to equation 34.

Equation 34

$$A_{t_i} = \frac{m_s^{\text{ads}}(t_i) \cdot 100}{m_0} \quad (\%)$$

where:

A_{t_i} = Adsorption percentage at the time point t_i (%);
 $m_s^{\text{ads}}(t_i)$ = mass of test substance adsorbed on the soil at the time t_i (μg);
 M_0 = mass of test substance in the test tube, at the beginning of the test (μg).

Detailed information how to calculate the percentage of adsorption A_{t_i} for the parallel and serial methods is given in paragraph (h)(2) of this guideline.

(ii). The distribution coefficient K_d is the ratio between the content of the substance in the soil phase and the mass concentration of the substance in the aqueous solution, under the test conditions, when adsorption equilibrium is reached, as shown in equation 35:

Equation 35

$$K_d = \frac{C_s^{\text{ads}}(\text{eq})}{C_{\text{aq}}^{\text{ads}}(\text{eq})} = \frac{m_s^{\text{ads}}(\text{eq})}{m_{\text{aq}}^{\text{ads}}(\text{eq})} \frac{V_0}{m_{\text{soil}}} \quad (\text{cm}^3 \text{ g}^{-1})$$

where:

$C_s^{\text{ads}}(\text{eq})$ = content of the substance adsorbed on the soil at adsorption equilibrium ($\mu\text{g g}^{-1}$);
 $C_{\text{aq}}^{\text{ads}}(\text{eq})$ = mass concentration of the substance in the aqueous phase at adsorption equilibrium ($\mu\text{g cm}^{-3}$); this concentration is analytically determined taking into account the values given by the blanks.
 $m_s^{\text{ads}}(\text{eq})$ = mass of the test substance adsorbed on the soil at adsorption equilibrium (μg);

$m_{\text{aq}}^{\text{ads}}(\text{eq})$ = mass of the test substance in the solution at adsorption equilibrium (μg);
 m_{soil} = quantity of the soil phase, expressed in dry mass of soil (g);
 V_0 = initial volume of the aqueous phase in contact with the soil (cm^3).

(iii) The relation between A_{eq} and K_d is given by equation 36.

Equation 36

$$K_d = \frac{A_{\text{eq}}}{100 - A_{\text{eq}}} \cdot \frac{V_0}{m_{\text{soil}}} \quad (\text{cm}^3 \text{g}^{-1})$$

where:

A_{eq} = percentage of adsorption at adsorption equilibrium, %.

(iv) The organic carbon normalized adsorption coefficient K_{oc} relates the distribution coefficient K_d to the content of organic carbon of the soil sample is shown in equation 37.

Equation 37

$$K_{\text{oc}} = K_d \cdot \frac{100}{\% \text{OC}} \quad (\text{cm}^3 \text{g}^{-1})$$

where:

$\% \text{OC}$ = percentage of organic carbon in the soil sample (g g^{-1}).

(v) K_{oc} coefficient represents a single value which characterizes the partitioning mainly of non-polar organic chemicals between the organic carbon in the soil or sediment and water. The adsorption of these compounds is correlated with the organic content of the sorbing solid (see paragraph (j)(69) of this guideline); thus, K_{oc} values depend on the specific characteristics of the humic fractions which differ considerably in sorption capacity, due to differences in origin, genesis, etc.

(4) Adsorption isotherms. (i) The Freundlich adsorption isotherms equation relates the amount of the test substance adsorbed to the concentration of the test substance in solution at equilibrium (equation 38).

These data are treated as under "Adsorption" and, for each test tube, the content of the test substance adsorbed on the soil after the adsorption test ($C_s^{\text{ads}}(\text{eq})$, elsewhere denoted as x/m) is calculated. It is assumed that equilibrium has been attained and that $C_s^{\text{ads}}(\text{eq})$ represents the equilibrium value:

Equation 38

$$C_s^{\text{ads}}(\text{eq}) = \frac{m_s^{\text{ads}}(\text{eq})}{m_{\text{soil}}} = \frac{[C_0 - C_{\text{aq}}^{\text{ads}}(\text{eq})] \cdot V_0}{m_{\text{soil}}} (\mu\text{g g}^{-1})$$

(ii) The Freundlich adsorption equation is shown in equation 39:

Equation 39

$$C_s^{\text{ads}}(\text{eq}) = K_F^{\text{ads}} \cdot C_{\text{aq}}^{\text{ads}}(\text{eq})^{1/n} (\mu\text{g g}^{-1})$$

- or in the linear form (equation 40):

Equation 40

$$\log C_s^{\text{ads}}(\text{eq}) = \log K_F^{\text{ads}} + 1/n \cdot \log C_{\text{aq}}^{\text{ads}}(\text{eq})$$

where:

- K_F^{ads} = Freundlich adsorption coefficient; its dimension is $\text{cm}^3 \text{g}^{-1}$ only if $1/n = 1$; in all other cases, the slope $1/n$ is introduced in the dimension of K_F^{ads} ($\mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$);
- N = Regression constant; $1/n$ generally ranges between 0.7-1.0, indicating that sorption data is frequently slightly nonlinear.

(iii) Equations (39) and (40) are plotted and the values of K_F^{ads} and $1/n$ are calculated by regression analysis using the equation 40. The correlation coefficient r^2 of the log equation is also calculated. An example of such plots is given in Fig. 6.

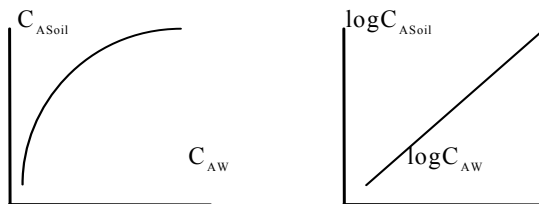


Fig. 6 Freundlich Adsorption Plot, normal (left) and linearized

(5) **Mass balance.** (i) The mass balance (MB) is defined as the percentage of substance which can be analytically recovered after an adsorption test versus the nominal amount of substance at the beginning of the test.

(ii) The treatment of data will differ if the solvent is completely miscible with water. In the case of water-miscible solvent, the treatment of data described under "Desorption" may be applied to determine the amount of substance recovered by solvent extraction. If the solvent is less miscible with water, the determination of the amount recovered has to be made.

(iii) The mass balance MB for the adsorption is calculated in equation 41. It is assumed that the term (m_E) corresponds to the sum of the test chemical masses extracted from the soil and surface of the test vessel with an organic solvent:

Equation 41

$$MB = \frac{(V_{rec} \cdot C_{aq}^{ads}(eq) + m_E) \cdot 100}{V_0 \cdot C_0} \quad (\%)$$

where:

MB = mass balance (%);

m_E = total mass of test substance extracted from the soil and walls of the test vessel in two steps (μg);

C_0 = initial mass concentration of the test solution in contact with the soil ($\mu\text{g cm}^{-3}$);

V_{rec} = volume of the supernatant recovered after the adsorption equilibrium (cm^3).

(6) **Desorption.** (i) The desorption is defined as the percentage of the test substance which is desorbed, related to the quantity of substance previously adsorbed, under the test conditions (equation 42). Detailed information on how to calculate the percentage of desorption D_{t_i} for the parallel and serial methods is given in paragraph (h)(2) of this guideline.

Equation 42

$$D_{t_i} = \frac{m_{aq}^{des}(t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%)$$

where:

D_{t_i} = Desorption percentage at a time point t_i (%);

$m_{aq}^{des}(t_i)$ = mass of the test substance desorbed from soil at a time point t_i (μg);

$m_s^{ads}(eq)$ = mass of the test substance adsorbed on soil at adsorption equilibrium (μg).

(ii) The apparent desorption coefficient (K_{des}) is, under the test conditions, the ratio between the content of the substance remaining in the soil phase and the mass concentration of the desorbed substance in the aqueous solution, when desorption equilibrium is reached (see equation 43).

Equation 43

$$K_{\text{des}} = \frac{m_s^{\text{ads}}(\text{eq}) - m_{\text{aq}}^{\text{des}}(\text{eq})}{m_{\text{aq}}^{\text{des}}(\text{eq})} \frac{V_T}{m_{\text{soil}}} \quad (\text{cm}^3 \text{ g}^{-1})$$

where:

K_{des} = Desorption coefficient ($\text{cm}^3 \text{ g}^{-1}$);

$m_{\text{aq}}^{\text{des}}(\text{eq})$ = total mass of the test substance desorbed from soil at desorption equilibrium (μg);

V_T = total volume of the aqueous phase in contact with the soil during the desorption kinetics test (cm^3).

(iii) Guidance for calculating the $m_{\text{aq}}^{\text{des}}(\text{eq})$ is given in paragraph (h)(2)(iii) of this guideline under the heading “Desorption”.

Note: If the adsorption test which was preceded, was performed with the parallel method the volume V_T in equation 43 is considered to be equal to V_0 .

(7) **Desorption isotherms.** (i) The Freundlich desorption isotherms equation relates the content of the test substance remaining adsorbed on the soil to the concentration of the test substance in solution at desorption equilibrium (equations 44, 45 and 46).

(ii) For each test tube, the content of the substance remaining adsorbed on the soil at desorption equilibrium is calculated as follows:

Equation 44

$$C_s^{\text{des}}(\text{eq}) = \frac{m_s^{\text{ads}}(\text{eq}) - m_{\text{aq}}^{\text{des}}(\text{eq})}{m_{\text{soil}}} \quad (\mu\text{g g}^{-1})$$

where $m_{\text{aq}}^{\text{des}}(\text{eq})$ is defined as:

Equation 45

$$m_{\text{aq}}^{\text{des}}(\text{eq}) = m_m^{\text{des}}(\text{eq}) \cdot \frac{V_0}{V_r} - m_{\text{aq}}^{\text{A}} \quad (\mu\text{g})$$

where:

- $C_s^{\text{des}}(\text{eq})$ = content of the test substance remaining adsorbed on the soil at desorption equilibrium ($\mu\text{g g}^{-1}$);
 $m_m^{\text{des}}(\text{eq})$ = mass of substance determined analytically in the aqueous phase at desorption equilibrium (μg);
 m_{aq}^{A} = mass of the test substance left over from the adsorption equilibrium due to incomplete volume replacement (μg);
 $m_{\text{aq}}^{\text{ads}}(\text{eq})$ = mass of the substance in the solution at adsorption equilibrium (μg);

Eq. 46

$$m_{\text{aq}}^{\text{A}} = m_{\text{aq}}^{\text{ads}}(\text{eq}) \cdot \left(\frac{V_0 - V_{\text{R}}}{V_0} \right)$$

- V_{r}^{F} = volume of the solution taken from the tube for the measurement of the test substance, at desorption equilibrium (cm^3);
 V_{R} = volume of the supernatant removed from the tube after the attainment of adsorption equilibrium and replaced by the same volume of a 0.01 M CaCl_2 solution (cm^3);

(iii) The Freundlich desorption equation is shown in Equation 47:

Equation 47

$$C_s^{\text{des}}(\text{eq}) = K_{\text{F}}^{\text{des}} \cdot C_{\text{aq}}^{\text{des}}(\text{eq})^{1/n} \quad (\mu\text{g g}^{-1})$$

- or in the linear form as equation 48:

Equation 48

$$\log C_s^{\text{des}}(\text{eq}) = \log K_{\text{F}}^{\text{des}} + 1/n \cdot \log C_{\text{aq}}^{\text{des}}(\text{eq})$$

where:

- $K_{\text{F}}^{\text{des}}$ = Freundlich desorption coefficient;
 N = regression constant;

C_{aq}^{des} (eq) = mass concentration of the substance in the aqueous phase at desorption equilibrium ($\mu\text{g cm}^{-3}$).

(iv) Equations 47 and 48 can be plotted and the value of K_F^{des} and $1/n$ are calculated by regression analysis using equation 48.

Note: If the Freundlich adsorption or desorption exponent $1/n$ is equal to 1, the Freundlich adsorption or desorption binding constant (K_F^{ads} and K_F^{des}) will be equal to the adsorption or desorption equilibrium constants (K_d and K_{des}) respectively, and plots of C_s vs C_{aq} will be linear. If the exponents are not equal to 1, plots of C_s vs C_{aq} will be nonlinear and the adsorption and desorption constants will vary along the isotherms.

(8) Additional data reporting considerations. (i) Methods for the preliminary study and the main study are generally the same, exceptions are mentioned where relevant in this guideline.

(ii) For the purpose of the test, it is considered that the weight of 1 cm^3 of aqueous solution is 1g. The soil/solution ratio may be expressed in units of w/w or w/vol with the same figure.

(iii) The weight of soil samples in the equations of the guideline refer to the oven dry weight.

(i) **Test report** (1) Detailed information on the history of the field site including; location, vegetation cover, treatments with pesticides and/or fertilizers, biological additions or accidental contamination. Recommendations of the ISO standard on soil sampling (j)(42) should be followed with respect to the description of the sampling site.

(2) Complete identification of the soil samples used including:

(i) Geographical reference of the site (latitude, longitude).

(ii) Date of sampling.

(iii) Use pattern (e.g., agricultural soil, forest, etc.).

(iv) Depth of sampling.

(v) Sand/silt/clay content.

(vi) pH values (in 0.01 M CaCl_2).

(vii) Organic carbon content.

(viii) Organic matter content.

(ix) Nitrogen content.

(x) C/N ratio.

- (xi) Cation Exchange Capacity (meq/100 g).
- (xii) All information relating to the collection and storage of soil samples.
- (xiii) Where appropriate, all relevant information for the interpretation of the adsorption/desorption of the test substance.
- (xiv) Reference of the methods used for the determination of each parameter.
- (3) Information on the test substance as appropriate.
- (4) Temperature of the experiments.
- (5) Centrifugation conditions.
- (6) Analytical procedure used to analyze the test substance.
- (7) Justification for any use of solubilizing agent for the preparation of the stock solution of the test substance.
- (8) Explanations of corrections made in the calculations, if relevant.
- (9) All information and observations helpful for the interpretation of the test results.
- (10) Data according to the following suggested form sheets and graphical presentations:

Adsorption-Desorption in Soils: Data Reporting Sheets

Substance tested: _____

Soil tested: _____

Dry mass content of the soil (105 °C, 12 h): _____ %

Temperature: _____ °C

Table 6. Suitability of the analytical method

Weighed soil	g	
Soil: dry mass	g	
Volume of CaCl ₂ sol.	cm ³	
Nominal conc. final sol.	µg cm ⁻³	
Analytical conc. Final sol.	µg cm ⁻³	

Principle of the analytical method used: _____

Calibration of the analytical method: _____

Substance tested: _____

Soil tested: _____

Dry mass content of the soil (105 °C, 12 h): ____%

Temperature: ____°C

Analytical methodology followed:

- Indirect
- Direct
- Parallel
- Serial

Table 7 Adsorption test: test samples

	Symbol	Units	Equilibration Time	Equilibration Time	Equilibration Time	Equilibration Time	Equilibration Time	Equilibration Time	Equilibration Time
Tube No.									
Weighed soil	-	g							
Soil: dry mass	m_{soil}	g							
Water vol. in weighed soil (calculated)	V_{WS}	cm^3							
Vol. 0.01 M CaCl_2 to equilibrate soil		cm^3							
Vol. stock solution		cm^3							
Total volume of aq. phase in contact with soil	V_0	cm^3							
Initial concentration Test solution	C_0	$\mu\text{g cm}^{-3}$							
Mass test subst. at beginning of test	M_0	μg							
After agitation and centrifugation									
Indirect Method									
Parallel method									
Conc. test subst. aq. phase Blank correction included	$C_{\text{aq}}^{\text{ads}}(t_i)$	$\mu\text{g cm}^{-3}$							
Serial method									
Measured mass test subst. in aliquot v_a^A	$m_m^{\text{ads}}(t_i)$	μg							
Direct method									
Mass test substance adsorbed on soil	$m_s^{\text{ads}}(t_i)$	μg							
Calculation of adsorption									
Adsorption	A_{t_i}	%							
	$A_{\Delta t_i}$	%							
Means									
Adsorption coefficient	K_d	$\text{cm}^3 \text{g}^{-1}$							
Means									
Adsorption coefficient	K_{oc}	$\text{cm}^3 \text{g}^{-1}$							

Means						
-------	--	--	--	--	--	--

Substance tested: _____

Soil tested: _____

Dry mass content of the soil (105 °C, 12 h): ____%

Temperature: ____°C

Table 8. Adsorption test: blanks and control

	Symbol	Units	Blank		Blank		Control	
Tube No.								
Weighed soil		g					0	0
Water amount in weighed soil (calculated)		cm ³					-	-
Volume of 0.01 M CaCl ₂ solution added		cm ³						
Volume of the stock solution of the test substance added		cm ³	0	0				
Total volume of aq. phase (calculated)		cm ³					-	-
Initial concentration of the test substance in aqueous phase		µg cm ⁻³						
After agitation and centrifugation								
Concentration in aqueous phase		µg cm ⁻³						

Remark: Add columns if necessary

Substance tested: _____

Soil tested: _____

Dry mass Content of the soil (105 °C, 12 h): ____%

Temperature: ____°C

Table 9. Mass balance

	Symbol	Units				
Tube No.						
Weighed soil	-	g				
Soil: dry mass	m_{soil}	g				
Water volume in weighed soil (calculated)	V_{WS}	ml				
Vol. 0.01 M CaCl ₂ sol. to equilibrate soil		ml				
Volume of stock solution		cm ³				
Total vol. of aq. phase in contact with soil	V_0	cm ³				
Initial concentration test solution	C_0	μg cm ⁻³				
Equilibration time	-	h				
After agitation and centrifugation						
Conc. test subst. aq. phase at adsorption equilibrium blank correction included	$C_{\text{aq}}^{\text{ads}} (\text{eq})$	μg cm ⁻³				
Equilibration time	t_{eq}	h				
Removed volume aq. phase	V_{rec}	cm ³				
Added volume of solvent	ΔV	cm ³				
1st extraction with solvent						
Signal analyzer in solvent	S_{E1}	var.				
Conc. test substance in solvent	C_{E1}	μg cm ⁻³				
Mass subst. extracted from soil & vessel walls	m_{E1}	μg				
2nd dilution with solvent						
Removed volume of solvent	ΔV_s	cm ³				
Added volume of solvent	$\Delta V'$	cm ³				
2nd extraction with solvent						
Signal analyzer solvent phase	S_{E2}	var.				

	Symbol	Units				
Conc. test subst. in solvent	C_{E2}	$\mu\text{g cm}^{-3}$				
Mass subst. extracted from soil & vessel walls	m_{E2}	μg				
Total mass test subst. extracted in two steps	m_E	μg				
Mass balance	MB	%				

Substance tested: _____

Soil tested: _____

Dry mass content of the soil (105 °C, 12 h): ____%

Temperature: ____°C

Table 10. Adsorption isotherms

	Symbol	Units								
Tube No.										
Weighed soil	-	g								
Soil: dry mass	m_{soil}	g								
Water volume in weighed soil (calculated)	V_{WS}	cm^3								
Volume 0.01 M CaCl_2 sol. to equilibrate the soil		cm^3								
Volume of stock solution added		cm^3								
Total volume of aq. phase in contact with soil (calculated)	V_0	cm^3								
Concentration solution	C_0	$\mu\text{g cm}^{-3}$								
Equilibration time	-	h								
After agitation and centrifugation										
Conc. Test substance in aqueous phase, blank correction included	$C_{\text{aq}}^{\text{ads}}(\text{eq})$	$\mu\text{g cm}^{-3}$								
Temperature		°C								
Adsorbed mass per unit soil	$C_{\text{s}}^{\text{ads}}(\text{eq})$	$\mu\text{g g}^{-1}$								

Regression analysis: _____

value of K_F^{ads} : _____

value of $1/n$: _____

regression coefficient r^2 : _____

Substance tested: _____

Soil tested: _____

Dry mass content of the soil (105°C, 12 h): ____%

Temperature: ____°C

Analytical methodology followed:

- Indirect
- Parallel
- Serial

Table 11. Desorption test

	Symbol	Units	Time interval	Time interval	Time interval	Time interval
Tube No. coming from adsorption step						
Mass of substance adsorbed on soil at adsorption equilibrium	$m_s^{ads} (eq)$	μg				
Removed volume aq. phase, replaced by 0.01 M $CaCl_2$	V_R	cm^3				
Total volume of aq. phase in contact with soil	PM	V_0	cm^3			
	SM	V_T	cm^3			
Mass test subst. left over the adsorption equilibrium due to incomplete volume replacement	m_{aq}^A	μg				

	Symbol	Units	Time interval	Time interval	Time interval	Time interval
Desorption kinetics						
Measured mass of substance desorbed from soil at time t_i	$m_m^{\text{des}}(t_i)$	μg				
Volume of solution taken from the tube (i) for the measurement of the test substance	PM	V_r^i	cm^3			
	SM	V_a^D	cm^3			
Mass of substance desorbed from soil at time t_i (calculated)	$m_{\text{aq}}^{\text{des}}(t_i)$	μg				
Mass of substance desorbed from soil during time interval Δt_i (calculated)	$m_{\text{aq}}^{\text{des}}(\Delta t_i)$	μg				
Desorption percentage						
Desorption at time t_i	D_{t_i}	%				
Desorption at time interval Δt_i	$D_{\Delta t_i}$	%				
Apparent desorption coefficient	K_{des}					

PM: Parallel method SM: Serial method

(j) **References.** The following references should be consulted for additional background information on this guideline.

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