

C.18. ADSORPTION/DES ORPTION USING A BATCH EQUILIBRIUM METHOD

1. METHOD

This method is a replicate of the OECD TG 106, for the Determination of Soil Adsorption/Desorption, using a Batch Equilibrium Method (2000).

1.1 INTRODUCTION

The method takes into account a ring test and a workshop for soil selection for the development of an adsorption test (1)(2)(3)(4) and also existing guidelines at national level (5)(6)(7)(8)(9)(10)(11).

Adsorption/desorption studies are useful for generating essential information on the mobility of chemicals and their distribution in the soil, water and air compartments of the biosphere (12)(13)(14)(15)(16)(17)(18)(19)(20)(21). The information can be used in the prediction or estimation, for example, of the availability of a chemical for degradation (22)(23), transformation and uptake by organisms (24); leaching through the soil profile (16)(18)(19)(21)(25)(26)(27)(28); volatility from soil (21)(29)(30); run-off from land surfaces into natural waters (18)(31)(32). Adsorption data can be used for comparative and modelling purposes (19)(33)(34)(35).

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 (12)(36)(37)(38)(39)(40), the characteristics of the soil (4)(12)(13)(14)(41)(42)(43)(44)(45)(46)(47)(48)(49), and climatic factors such as rainfall, temperature, sunlight and wind. Thus, the numerous phenomena and mechanisms involved in the process of adsorption of a chemical by soil cannot be completely defined by a simplified laboratory model such as the present method. However, even if this attempt cannot cover all the environmentally possible cases, it provides valuable information on the environmental relevance of the adsorption of a chemical.

See also General Introduction.

1.2 SCOPE

The method is aimed at estimating the adsorption/desorption behaviour 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 and 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.

In this method, 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 catalysed degradation, bulk adsorption or chemical reaction. Adsorption that will occur on colloids particles (diameter < 0.2 µm) generated by the soils is not taken into account.

The soil parameters that are believed most important for adsorption are: organic carbon content (3)(4)(12)(13)(14)(41)(43)(44)(45)(46)(47)(48); clay content and soil texture (3)(4)(41)(42)(43)(44)(45)(46) (47)(48) and pH for ionizable compounds (3)(4)(42). 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 aluminium oxides, particularly for volcanic and tropical soils (4), as well as the specific surface (49).

The test 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. It comprises three tiers:

Tier 1: Preliminary study in order to determine:

- the soil/solution ratio;
- the equilibrium time for adsorption and the amount of test substance adsorbed at equilibrium;
- the adsorption of the test substance on the surfaces of the test vessels and the stability of the test substance during the test period.

Tier 2: Screening test: the adsorption is studied in five different soil types by means of adsorption kinetics at a single concentration and determination of distribution coefficient K_d and K_{oc} .

Tier 3: 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 (Annex 1).

1.3

DEFINITIONS AND UNITS

Symbol	Definition	Units
A_{t_i}	adsorption percentage at the time 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 test 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 test 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	$\mu\text{g cm}^{-3}$

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

$C_S^{\text{ads}}(\text{eq})$	content of the substance adsorbed on soil at adsorption equilibrium an 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	$\mu\text{g cm}^{-3}$
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 normalised adsorption coefficient	$\text{cm}^3 \text{g}^{-1}$
K_{om}	organic matter normalised 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	$\mu\text{g}^{1-1/n} (\text{cm}^3)^{1/n} \text{g}^{-1}$
$m_{\text{aq}}^{\text{des}}(t_i)$	mass of the test substance desorbed from soil at the time t_i	μg
$m_{\text{aq}}^{\text{des}}(\Delta t_i)$	mass of the test substance desorbed from soil during the time Δt_i	μg
$m_m^{\text{des}}(\text{eq})$	mass of the substance determined analytically in the aqueous phase at desorption equilibrium	μg
$m_{\text{aq}}^{\text{des}}(\text{eq})$	total mass of the test substance desorbed at desorption equilibrium	μg
$m_s^{\text{des}}(\Delta t_i)$	mass of the substance remaining adsorbed on the soil after the time interval Δt_i	μg
m_{aq}^A	mass of the substance left over from the adsorption equilibrium due to incomplete volume replacement	μg
$C_S^{\text{des}}(\text{eq})$	content of the test substance remaining adsorbed on the soil at desorption equilibrium	$\mu\text{g g}^{-1}$
$C_{\text{aq}}^{\text{des}}(\text{eq})$	mass concentration of the test 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
v_a^D	volume of the aliquot sampled for analytical purpose from the time (i), during the desorption kinetics experiment performed with the serial method	cm^3
V_i^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_F^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 the test substance extracted from 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	
pKa	dissociation constant	
S_w	water solubility	g l ⁻¹

1.4 PRINCIPLE OF THE TEST METHOD

Known volumes of solutions of the test substance, non-labelled or radiolabelled, 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 and, if so wished, filtration and the aqueous phase is analysed. 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).

As an option, the amount of the test substance adsorbed can also be directly determined by analysis of soil (direct method). This procedure which involves stepwise soil extraction with appropriate solvent, 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 surface 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 radiolabelled substance is used, the soil extraction may be avoided by analysis of the soil phase by combustion and liquid scintillation counting. However, liquid scintillation counting is an unspecific technique which cannot differentiate between parental and transformation products; therefore it should be used only if the test chemical is stable for the duration of the study.

1.5 INFORMATION ON THE TEST SUBSTANCE

Chemical reagents should be of analytical grade. The use of non-labelled test substances with known composition and preferably at least 95% purity or of radiolabelled test substances with known composition and radio-purity, is recommended. In the case of short half-life tracers, decay corrections should be applied.

Before carrying out a test for adsorption-desorption, the following information about the test substance should be available:

- a) Water Solubility (A.6);
- b) Vapour Pressure (A.4) and/or Henry's Law Constant;
- c) Abiotic Degradation: Hydrolysis as a Function of pH (C.7);
- d) Partition Coefficient (A.8);
- e) Ready Biodegradability (C.4) or Aerobic and Anaerobic Transformation in Soil;
- f) pKa of Ionizable Substances;
- g) Direct Photolysis in Water (i.e. UV-Vis Absorption Spectrum in Water, Quantum Yield) and Photodegradation on Soil.

1.6 APPLICABILITY OF THE TEST

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, is the stability of the test substance in the timescale of the test. Thus, it is a prerequisite to check the stability in a preliminary study; if a transformation in the time scale of the test is observed, it is recommended that the main study be performed by analysing both soil and aqueous phases.

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 method.

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

1.7 DESCRIPTION OF THE METHOD

1.7.1 Apparatus and chemical reagents

Standard laboratory equipment, especially the following:

- a) Tubes or vessels to conduct the experiments. It is important that these tubes or vessels;
 - fit directly in the centrifuge apparatus in order to minimise handling and transfer errors;
 - be made of an inert material, which minimises adsorption of the test substance on its surface.
- b) Agitation device: overhead shaker or equivalent equipment; the agitation device should keep the soil in suspension during shaking.
- c) Centrifuge: preferably high-speed, e.g. centrifugation forces $> 3000g$, temperature controlled, capable of removing particles with a diameter greater than $0.2 \mu\text{m}$ from aqueous solution. The containers should be capped during agitation and centrifugation to avoid volatility and water losses; to minimise adsorption on them, deactivated caps such as teflon lined screw caps should be used.
- d) Optional: filtration device; filters of $0.2 \mu\text{m}$ porosity, sterile, single use. Special care should be taken in the choice of the filter material, to avoid any losses of the test substance on it; for poorly soluble test substances, organic filter material is not recommended.
- e) Analytical instrumentation, suitable for measuring the concentration of the test chemical.
- f) Laboratory oven, capable of maintaining a temperature of $103 \text{ }^\circ\text{C}$ to $110 \text{ }^\circ\text{C}$.

1.7.2 Characterization and selection of soils

The soils should be characterized by three parameters considered to be largely responsible for the adsorptive capacity: organic carbon, clay content and soil texture, and pH. As already mentioned (see Scope) 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.

The methods used for soil characterization are very important and can have a significant influence on the results. Therefore, it is recommended that 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 (ISO-10390-1). It is also recommended that the other relevant soil properties be determined according to standard methods (for example ISO "Handbook of Soil Analysis"); this permits the analysis 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 (50-52). For calibration of soil test methods, the use of reference soils is recommended.

Guidance for selection of soils for adsorption/desorption experiments is given in Table 1. The seven selected soils cover soil types encountered in temperate geographical zones. For ionizable test substances, the selected soils should cover a wide range of pH, in order to be able to evaluate the adsorption of the substance in its ionised and unionised forms. Guidance on how many different soils to use at the various stages of the test is given under "Performance of the test" 1.9.

If other soil types are preferred, they should be characterized by the same parameters and should have similar variation in properties to those described in Table 1, even if they do not match the criteria exactly.

Table 1: Guidance for selection of soil samples for adsorption-desorption

Soil Type	pH range (in 0.01 M CaCl ₂)	Organic carbon content (%)	Clay content (%)	Soil texture*
1	4.5 - 5.5	1.0 - 2.0	65 - 80	clay
2	> 7.5	3.5 - 5.0	20 - 40	clay loam
3	5.5 - 7.0	1.5 - 3.0	15 - 25	silt loam
4	4.0 - 5.5	3.0 - 4.0	15 - 30	loam
5	< 4.0 - 6.0 [§]	< 0.5 - 1.5 [‡]	< 10 - 15 [§]	loamy sand
6	> 7.0	< 0.5 - 1.0 [‡]	40 - 65	clay loam/ clay
7	< 4.5	> 10	< 10	sand/ loamy sand

* According to FAO and the US system (85).

§ The respective variables should preferably show values within the range given. If, however, difficulties in finding appropriate soil material occur, values below the indicated minimum are accepted.

‡ Soils with less than 0.3% organic carbon may disturb correlation between organic content and adsorption. Thus, it is recommended the use of soils with a minimum organic carbon content of 0.3%.

1.7.3 Collection and storage of soil samples

1.7.3.1 Collection

No specific sampling techniques or tools are recommended; the sampling technique depends on the purpose of the study (53)(54)(55)(56)(57)(58).

The following should be considered:

- a) detailed information on the history of the field site is necessary; this includes location, vegetation cover, treatments with pesticides and/or fertilisers, biological additions or accidental contamination. Recommendations of the ISO standard on soil sampling (ISO 10381-6) should be followed with respect to the description of the sampling site;

- b) the sampling site has to be defined by UTM (Universal Transversal Mercator-Projection/European Horizontal Datum) or geographical co-ordinates; this could allow recollection of a particular soil in the future or could help in defining soil under various classification systems used in different countries. Also, only A horizon up to a maximum depth of 20 cm should be collected. Especially for the soil type n. 7 if a O_h horizon is present as part of the soil, it should be included in the sampling.

The soil samples should be transported using containers and under temperature conditions which guarantee that the initial soil properties are not significantly altered.

1.7.3.2 *Storage*

The use of soils freshly taken from the field is preferred. Only if this is not possible soil can be stored at ambient temperature 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-analysed prior to the use with respect to their organic carbon content, pH and CEC.

1.7.3.3 *Handling and preparation of soil samples for the test*

The soils are 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 (ISO 10381-6) should be followed with respect to the sieving process. Careful homogenization is recommended, as this enhances the reproducibility of the results. The 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.

1.7.4 **Preparation of the test substance for application to soil**

The test substance is dissolved in a solution of 0.01 M CaCl_2 in distilled or de-ionised water; the CaCl_2 solution is used as the aqueous solvent phase to improve centrifugation and minimise 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. This threshold safeguards accurate measurements with respect to the methodology followed in this method; additionally, the stock solution concentration should be below water solubility of the test substance.

The stock solution should preferably be prepared just before application to soil samples and should be kept closed in the dark at 4 °C. The storage time depends on the stability of the test substance and its concentration in the solution.

Only for poorly soluble substances ($S_w < 10^{-4} \text{ g l}^{-1}$), an appropriate solubilizing agent may be needed when it is difficult to dissolve the test substance. This solubilizing agent: (a) should be miscible with water such as methanol or acetonitrile; (b) 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%); and (c) should not be a surfactant or undergo solvolytic reactions with the test chemical. The use of a solubilising agent should be stipulated and justified in the reporting of the data.

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 CaCl₂ in distilled or de-ionised water. The content of organic solvent in the aqueous phase should be kept as low as possible, normally not exceeding 0.1%. Spiking from an organic solution may suffer from volume unreproducibility. Thus, an additional error may be introduced as the test substance and co-solvent concentration would not be the same in all tests.

1.8 PREREQUISITES FOR PERFORMING THE ADSORPTION/DESORPTION TEST

1.8.1 **The 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 (35)(59-62). Some examples bearing upon the accuracy issues are given in Annex 2.

The reliability of the analytical method used must 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, detect ion limits and recovery. Guidance on how to perform such a test is given by the experiment below.

An appropriate volume of 0.01 M CaCl₂, e.g. 100 cm³, 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 analysed.

One blank run consisting of the system soil + CaCl₂ solution (without test substance) must be included, in order to check for artefacts in the analytical method and for matrix effects caused by the soil.

The 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 radiolabelled substances). Independent of the analytical method used, it is considered suitable if the recoveries are 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.

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 method follows a general experimental path and provides recommendations and guidance for alternative solutions where the analytical method and laboratory facilities may impose limitations.

1.8.2

The selection of optimal soil/solution ratios

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 the 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% (62), 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.

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 (Annex 3). 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 (Fig.1). In this plot it is assumed that the adsorption equation is linear¹. The applicable relationship is obtained by rearranging equation (4) of the K_d in the form of equation (1):

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

or in its logarithmic form assuming that $R = m_{soil}/V_0$ and $A_{eq}/100 = \frac{m_s^{ads}(eq)}{m_0}$:

$$\log R = - \log K_d + \log \left[\frac{(A_{eq}/100)}{(1-A_{eq}/100)} \right] \tag{2}$$

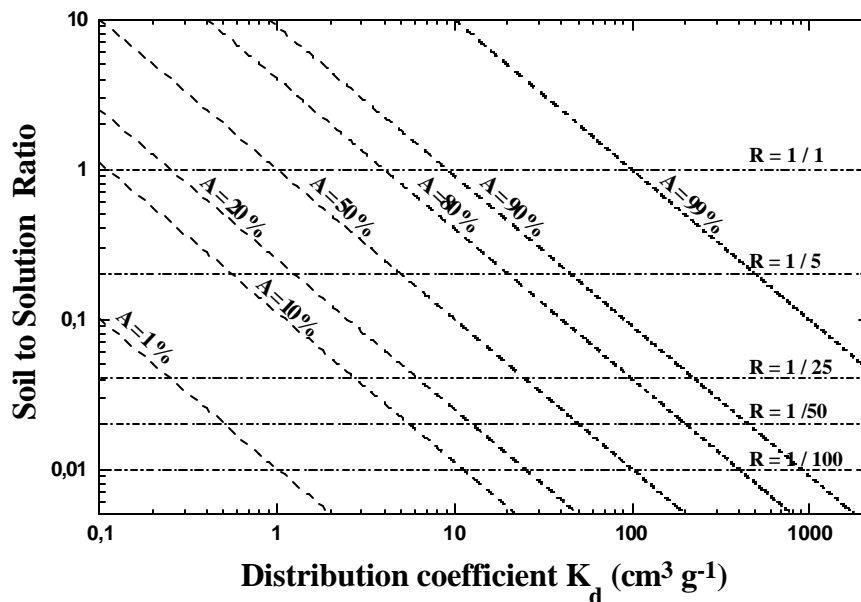


Fig. 1 Relationship between soil to solution ratios and K_d at various percentages of adsorbed test substance

¹ $C_s^{ads}(eq) = K_d \cdot C_{aq}^{ads}(eq)$

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L25 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

Fig. 1 shows soil/solution ratios required 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 must be used. This approach to selecting the appropriate soil/solution ratios gives the investigator the flexibility to meet experimental needs.

Areas which are more difficult to deal with are those where the chemical is highly or very slightly adsorbed. Where low adsorption 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. Care must 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 must be taken to ensure good mixing, and adequate time must 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 (Annex 3). This could be useful especially for low adsorbed/polar chemicals with $P_{ow} < 20$ and for lipophilic/highly sorptive chemicals with $P_{ow} > 10^4$.

1.9 PERFORMANCE OF THE TEST

1.9.1 Test conditions

All experiments are done at ambient temperature and, if possible, at a constant temperature between 20 °C and 25 °C.

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 colloidal particles. Guidance on how to determine the centrifugation conditions is given in Annex 4.

If the centrifugation facilities cannot guarantee the removal of particles larger than 0.2 µm, 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 proven that no losses of the test substance occur during filtration.

1.9.2 Tier 1- Preliminary study

The purpose of conducting a preliminary study has already been given in the Scope section. Guidance for setting up such a test is given with the experiment suggested below.

1.9.2.1 Selection of optimal soil/solution ratios

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:

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

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

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.

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 substances or contaminated soils.

All the experiments, included 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.

Methods for the preliminary study and the main study are generally the same, exceptions are mentioned where relevant.

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.

An example of how to calculate the concentration of the stock solution (C_s) is given below. A detection limit of 0.01 µg cm⁻³ and 90% adsorption are assumed; thus, the initial concentration of the test substance in contact with the soil should preferably be 1 µg 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 cm³ 0.01 M CaCl₂ equilibration solution (= 10% of the stock solution to 50 cm³ total volume of aqueous phase), the concentration of the stock solution should be 10 µg cm⁻³; this is three orders of magnitude higher than the detection limit of the analytical method.

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 ionisable substances.

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 (77). 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 with respect to the work schedule of the laboratory.

There are two options for the analysis of the test substance in the aqueous solution: (a) the parallel method and (b) the serial method. It should be stressed that, although the parallel method is experimentally more tedious, the mathematical treatment of the results is simpler (Annex 5). However, the choice of the methodology to be followed, is left to the experimenter who will need to consider the available laboratory facilities and resources.

(a) parallel method: samples with the same soil/solution ratio are prepared, as many as the time intervals at which it is desired to study the adsorption kinetics. After centrifugation and if so wished 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, etc.

(b) serial method: only 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 analysed 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 and to decrease the mass of solute available for adsorption during the test.

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 (Fig. 1 Annex 5) are generated in order to estimate the achievement of equilibrium plateau². The K_d value at equilibrium is also calculated. Based on this K_d value, appropriate soil/solution ratios are selected from Fig.1, so that the percentage adsorption reaches above 20% and preferably >50% (61). All the applicable equations and principles of plotting are given in section on Data and Reporting and in Annex 5.

1.9.2.2 *Determination of adsorption equilibration time and of the amount of test substance adsorbed at equilibrium*

As already mentioned, plots of A_{t_i} or C_{aq}^{ads} versus time permit estimation of the achievement of the adsorption equilibrium and the amount of test substance adsorbed at equilibrium. Figs. 1 and 2 in the Annex 5 show examples of such plots. Equilibration time is the system needs to reach a plateau.

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 sterilised sample of the soil. If no plateau is achieved even in this case, the experimenter should search for other phenomena that could be involved in his specific studies; this could be done with appropriate modifications of the experiment conditions (temperature, shaking times, soil/solution ratios). It is left to the experimenter to decide whether to continue the test procedure in spite of a possible failure to achieve an equilibrium.

1.9.2.3 *Adsorption on the surface of the test vessel and stability of the test substance*

Some information on the adsorption of the test substance on the surface of test vessels, as well as its stability, can be derived by analysing the control samples. If a depletion more than 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 affect this adsorption.

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, extracts of soil and test vessel walls are analysed 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, extracts of the soil and test vessel walls is equal to the mass degraded and/or volatilized and/or not extracted. In order to perform a mass balance determination, the adsorption equilibrium should have been reached within the period of the experiment.

² 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. 2 in Annex 5).

The mass balance is performed on both soils and for one soil/solution ratio per soil that gives a depletion above 20% and preferably >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 (equation 10, Data and Reporting). 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 it is recommended to analyse both phases in the main study.

1.9.2.4 Tier 2 - Adsorption kinetics at one concentration of the test substance

Five soils are used, selected from Table 1. There is an advantage to including some or all of the soils used in the preliminary study, if appropriate, among these five soils. In this case, Tier 2 has not to be repeated for the soils used in preliminary study.

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 concentration of the test substance in the solution are chosen based on the preliminary study results. Analysis should preferably be done approximately after 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 requires longer equilibration time with respect to ratio-finding results. However, times of analysis could be considered with flexibility.

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 percentage adsorption is calculated at each time point A_{t_1} and/or time interval $A_{\Delta t_1}$ (according to the need) and is plotted versus 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.

Results of the adsorption kinetics test

The linear K_d value is generally accurate to describe sorptive behaviour in soil (35)(78) 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 MacCall *et al.* (16). Additionally, leaching classification schemes exist based on a relationship between K_{oc} and DT-50³ (32)(79).

Also, according to error analysis studies (61), 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 favourable (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.

³ DT-50: degradation time for 50% of the test substance.

With respect to the above remarks, it is recommended that the study of the adsorptive behaviour 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 test method. Accurate determination is possible if the value which results by multiplying the K_d with the soil/solution ratio is >0.3 , when measurements are based on concentration decrease in the aqueous phase (indirect method), or > 0.1 , when both phases are analysed (direct method) (61).

1.9.2.5 Tier 3 - Adsorption isotherms and desorption kinetics/desorption isotherms

1.9.2.5.1 Adsorption isotherms

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. The adsorption test is performed as described above, with the only difference that the aqueous phase is analysed only once at the time necessary to reach equilibrium as determined before 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 (see Data and Reporting).

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 the references (41)(45)(80)(81)(82).

Note: 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 (83).

1.9.2.5.2 Desorption kinetics

The purpose of this experiment is to investigate whether a chemical is reversibly or irreversibly adsorbed on a soil. This information is important, since the desorption process also plays an important role in the behaviour of a chemical in field soil. Moreover, desorption data are useful inputs in the computer modelling of leaching and dissolved run-off simulation. If a desorption study is desired, it is recommended that the study described below be carried out on each system for which an accurate determination of K_d in the preceding adsorption kinetics experiment was possible.

Likewise with the adsorption kinetics study, there are two options to proceed with the desorption kinetics experiment: (a) the parallel method and (b) serial method. The choice of methodology to be followed, is left to the experimenter who will need to consider the available laboratory facilities and resources.

(a) parallel method: for each soil which is chosen to proceed with the desorption study, samples with the same soil/solution ratio are prepared, as many as the time intervals at which it is desired to study the 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 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 CaCl₂ 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. All the mixtures of the soil with the solution is agitating until to reach adsorption equilibrium (as determined before in Tier 2). Then, the phases are separated by centrifugation and the aqueous phases are 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.

(b) 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 analysed 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.

The percentage desorption is calculated at each time point (D_{t_1}) and/or time interval ($D_{\Delta t_1}$) (according to the needs of the study) and is plotted versus time. The desorption coefficient of K_{des} at equilibrium is also calculated. All applicable equations are given in Data and Reporting and Annex 5.

Results from desorption kinetics experiment

Common plots of the percentage desorption D_{t_1} and adsorption A_{t_1} 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.

1.9.2.5.3 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", with the only difference that the aqueous phase is analysed only 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 (see Data and Reporting and Annex 5).

2. DATA AND REPORTING

The analytical data are presented in tabular form (see Annex 6). Individual measurements and averages calculated are given. Graphical representations of adsorption isotherms are provided. The calculations are made as described below.

For the purpose of the test, it is considered that the weight of 1 cm³ of aqueous solution is 1g. The soil/solution ratio may be expressed in units of w/w or w/vol with the same figure.

2.1 ADSORPTION

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 the equation:

$$A_{t_i} = \frac{m_s^{\text{ads}}(t_i) \cdot 100}{m_0} \quad (\%) \quad (3)$$

where:

A_{t_i} = adsorption percentage at the time point t_i (%);

$m_s^{\text{ads}}(t_i)$ = mass of the test substance adsorbed on the soil at the time t_i (μg);

m_0 = mass of the test substance in the test tube, at the beginning of the test (μg).

Detailed information on how to calculate the percentage of adsorption A_{t_i} for the parallel and serial methods is given in Annex 5.

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.

$$K_d = \frac{C_s^{\text{ads}}(\text{eq})}{C_{\text{aq}}^{\text{ads}}(\text{eq})} = \frac{m_s^{\text{ads}}(\text{eq})}{m_{\text{aq}}^{\text{ads}}(\text{eq})} \cdot \frac{V_0}{m_{\text{soil}}} \quad (\text{cm}^3 \text{ g}^{-1}) \quad (4)$$

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 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);

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).

The relation between A_{eq} and K_d is given by:

$$K_d = \frac{A_{\text{eq}}}{100 - A_{\text{eq}}} \cdot \frac{V_0}{m_{\text{soil}}} \quad (\text{cm}^3 \text{ g}^{-1}) \quad (5)$$

where:

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

The organic carbon normalised adsorption coefficient K_{oc} relates the distribution coefficient K_d to the content of organic carbon of the soil sample:

$$K_{oc} = K_d \cdot \frac{100}{\%OC} \quad (\text{cm}^3 \text{ g}^{-1}) \quad (6)$$

where:

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

K_{oc} coefficient represents a single value which characterises the partitioning mainly of non-polar organic chemicals between organic carbon in the soil or sediment and water. The adsorption of these chemicals is correlated with the organic content of the sorbing solid (7); 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.

2.1.1

Adsorption isotherms

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 8).

The 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 ($C_s^{ads}(eq)$, elsewhere denoted as x/m) is calculated. It is assumed that equilibrium has been attained and that $C_s^{ads}(eq)$ represents the equilibrium value:

$$C_s^{ads}(eq) = \frac{m_s^{ads}(eq)}{m_{soil}} = \frac{[C_0 - C_{aq}^{ads}(eq)] \cdot V_0}{m_{soil}} \quad (\mu\text{g g}^{-1}) \quad (7)$$

The Freundlich adsorption equation is shown in (8):

$$C_s^{ads}(eq) = K_F^{ads} \cdot C_{aq}^{ads}(eq)^{1/n} \quad (\mu\text{g g}^{-1}) \quad (8)$$

or in the linear form:

$$\log C_s^{ads}(eq) = \log K_F^{ads} + 1/n \cdot \log C_{aq}^{ads}(eq) \quad (9)$$

where:

K_F^{ads} = Freundlich adsorption coefficient; its dimension is $cm^3 g^{-1}$ only if $1/n = 1$; in all other cases, the slope $1/n$ is introduced in the dimension of K_F^{ads} ($\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$);

n = regression constant; $1/n$ generally ranges between 0.7 - 1.0, indicating that sorption data is frequently slightly non-linear.

Equations (8) and (9) are plotted and the values of K_F^{ads} and $1/n$ are calculated by regression analysis using the equation 9. The correlation coefficient r^2 of the log equation is also calculated. An example of such plots is given in Fig.2.

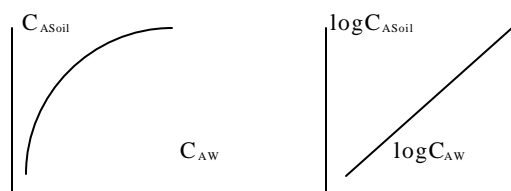


Fig. 2. Freundlich Adsorption Plot, normal and linearized

2.1.2

Mass balance

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.

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.

The mass balance MB for the adsorption is calculated as follows; 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:

$$MB = \frac{(V_{rec} \cdot C_{aq}^{ads} (eq) + m_E) \cdot 100}{V_0 \cdot C_0} \quad (\%) \quad (10)$$

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 ($\mu g cm^{-3}$);

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

2.2 DESORPTION

The desorption (D) is defined as the percentage of the test substance which is desorbed, related to the quantity of substance previously adsorbed, under the test conditions:

$$D_{t_i} = \frac{m_{aq}^{des}(t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%) \quad (11)$$

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).

Detailed information on how to calculate the percentage of desorption D_{t_i} for the parallel and serial methods is given in Annex 5.

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:

$$K_{des} = \frac{m_s^{ads}(eq) - m_{aq}^{des}(eq)}{m_{aq}^{des}(eq)} \frac{V_T}{m_{soil}} \quad (\text{cm}^3 \text{ g}^{-1}) \quad (12)$$

where:

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

$m_{aq}^{des}(eq)$ = 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).

Guidance for calculating the $m_{aq}^{des}(eq)$ is given in Annex 5 under the heading "Desorption".

Remark

If the adsorption test which was preceded, was performed with the parallel method the volume V_i in the equation (12) is considered to be equal to V_0 .

2.2.1 Desorption isotherms

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 (equation 16).

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

$$C_s^{des}(eq) = \frac{m_s^{ads}(eq) - m_{aq}^{des}(eq)}{m_{soil}} \quad (\mu\text{g g}^{-1}) \quad (13)$$

m_{aq}^{des} (eq) is defined as :

$$m_{aq}^{des} (eq) = m_m^{des} (eq) \cdot \frac{V_0}{V_F} - m_{aq}^A \quad (\mu g) \quad (14)$$

where:

C_s^{des} (eq) = content of the test substance remaining adsorbed on the soil at desorption equilibrium ($\mu g g^{-1}$);

m_m^{des} (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_{aq}^{des} (eq) = mass of the substance in the solution at adsorption equilibrium (μg);

$$m_{aq}^A = m_{aq}^{ads} (eq) \cdot \left(\frac{V_0 - V_R}{V_0} \right) \quad (15)$$

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);

The Freundlich desorption equation is shown in (16):

$$C_s^{des} (eq) = K_F^{des} \cdot C_{aq}^{des} (eq)^{1/n} \quad (\mu g g^{-1}) \quad (16)$$

or in the linear form:

$$\log C_s^{des} (eq) = \log K_F^{des} + 1/n \cdot \log C_{aq}^{des} (eq) \quad (17)$$

where:

K_F^{des} = Freundlich desorption coefficient;

n = regression constant;

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

The equations (16) and (17) can be plotted and the value of K_F^{des} and $1/n$ are calculated by regression analysis using the equation 17.

Remark:

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 non-linear and the adsorption and desorption constants will vary along the isotherms.

2.2.2

TEST REPORT

The test report should include the following information:

- Complete identification of the soil samples used including:
 - geographical reference of the site (latitude, longitude);
 - date of sampling;
 - use pattern (e.g. agricultural soil, forest, etc.);
 - depth of sampling;
 - sand/silt/clay content;
 - pH values (in 0.01 M CaCl_2);
 - organic carbon content;
 - organic matter content;
 - nitrogen content;
 - C/N ratio;
 - Cation Exchange Capacity (mmol/kg);
 - all information relating to the collection and storage of soil samples;
 - where appropriate, all relevant information for the interpretation of the adsorption - desorption of the test substance;
 - reference of the methods used for the determination of each parameter.
- information on the test substance as appropriate;
- temperature of the experiments;
- centrifugation conditions;
- analytical procedure used to analyse the test substance;
- justification for any use of solubilising agent for the preparation of the stock solution of the test substance;
- explanations of corrections made in the calculations, if relevant;
- data according to the form sheet (Annex 6) and graphical presentations;
- all information and observations helpful for the interpretation of the test results.

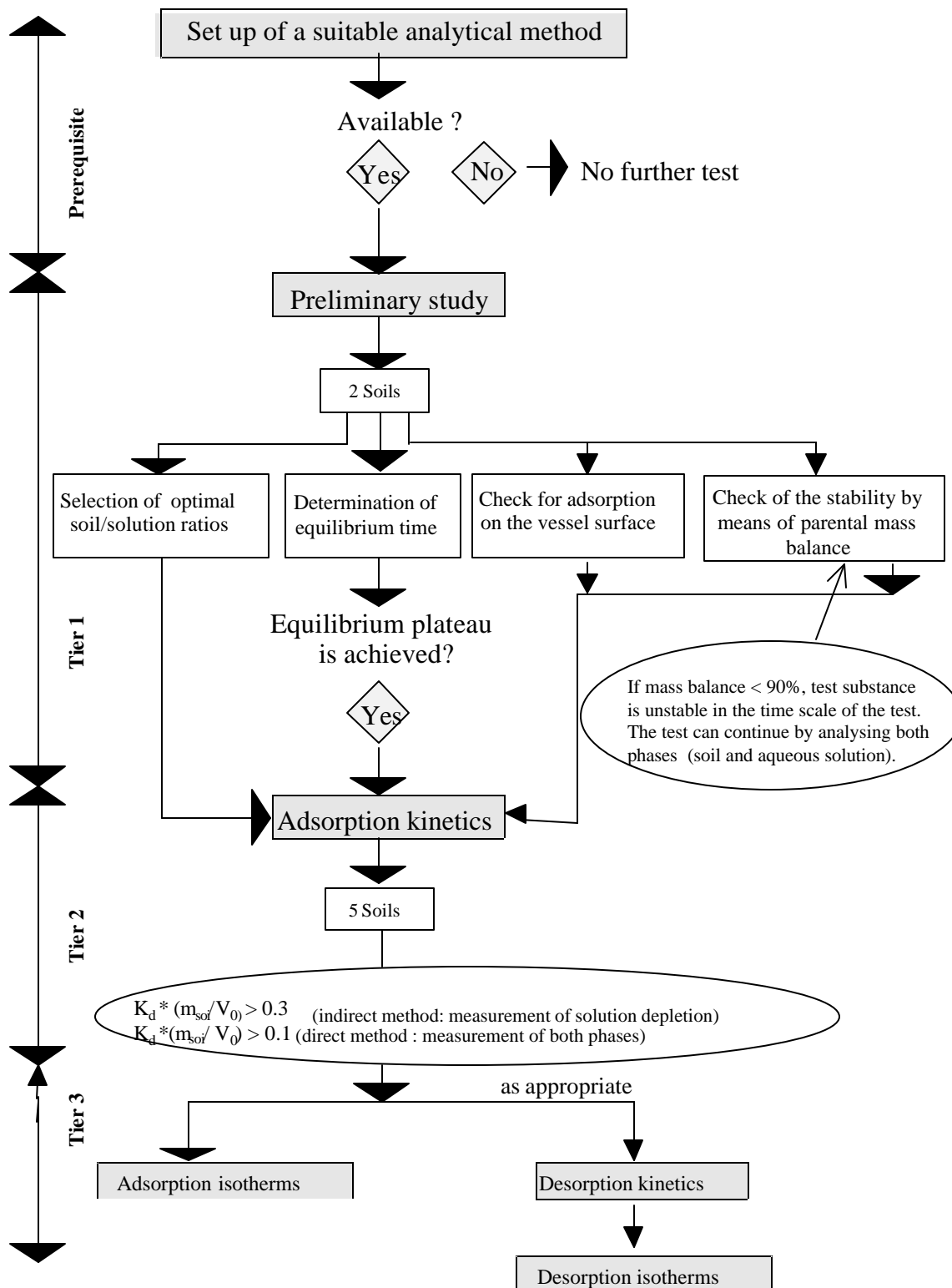
1. Kukowski H. and Brümmer G., (1987). Investigations on the Adsorption and Desorption of Selected Chemicals in Soils. UBA Report 106 02 045, Part II.
2. Fränzle O., Kuhnt G. and Vetter L., (1987). Selection of Representative Soils in the EC-Territory. UBA Report 106 02 045, Part I.
3. Kuhnt G. and Muntau H. (Eds.) EURO-Soils: Identification, Collection, Treatment, Characterisation. Special Publication no. 1.94.60, Joint Research Centre. European Commission, ISPRA, December 1994.
4. OECD Test Guidelines Programme, Final Report of the OECD Workshop on Selection of Soils/Sediments, Belgirate, Italy, 18-20 January 1995 (June 1995).
5. US-Environment Protection Agency: Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Series 163-1, Leaching and Adsorption/Desorption Studies, Addendum 6 on Data Reporting, 540/09-88-096, Date: 1/1988.
6. US-Environment Protection Agency: Prevention, Pesticides and Toxic Substances, OPPTS Harmonized Test Guidelines, Series 835-Fate, Transport and Transformation Test Guidelines, OPPTS No: 835.1220 Sediment and Soil Adsorption/Desorption Isotherm. EPA No: 712-C-96-048, April 1996.
7. ASTM Standards, E 1195-85, Standard Test Method for Determining a Sorption Constant (K_{oc}) for an Organic Chemical in Soil and Sediments.
8. Agriculture Canada: Environmental Chemistry and Fate. Guidelines for registration of pesticides in Canada, 15 July 1987.
9. Netherlands Commission Registration Pesticides (1995): Application for registration of a pesticide. Section G. Behaviour of the product and its metabolites in soil, water and air.
10. Danish National Agency of Environmental Protection (October 1988): Criteria for registration of pesticides as especially dangerous to health or especially harmful to the environment.
11. BBA (1990), Guidelines for the Official Testing of Plant Protection Products, Biological Research Centre for Agriculture and Forestry, Braunschweig, Germany.
12. Calvet R., (1989), "Evaluation of adsorption coefficients and the prediction of the mobilities of pesticides in soils", in Methodological Aspects of the Study of Pesticide Behaviour in Soil (ed. P. Jamet), INRA, Paris, (Review).
13. Calvet R., (1980) "Adsorption-Desorption Phenomena" in Interactions between herbicides and the soil. (R.J. Hance ed.), Academic Press, London, pp. 83-122.
14. Hasset J.J., and Banwart W.L., (1989), "The sorption of nonpolar organics by soils and sediments" in Reactions and Movement of Organic Chemicals in Soils. Soil Science Society of America (S.S.S.A), Special Publication no. 22, pp 31-44.
15. van Genuchten M. Th., Davidson J.M., and Wierenga P.J., (1974), "An evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media". Soil Sci. Soc. Am. Proc., Vol. 38(1), 29-35.
16. McCall P.J., Laskowski D.A., Swann R.L., and Dishburger H.J., (1981), "Measurement of sorption coefficients of organic chemicals and their use, in environmental fate analysis", in Test Protocols for Environmental Fate and Movement of Toxicants. Proceedings of AOAC Symposium, AOAC, Washington DC.
17. Lambert S.M., Porter P.E., and Schieferrstein R.H., (1965), "Movement and sorption of chemicals applied to the soil". Weeds, 13, 185-190.
18. Rhodes R.C., Belasco I.J., and Pease H.L., (1970) "Determination of mobility and adsorption of agrochemicals in soils". J.Agric.Food Chem., 18, 524-528.
19. Russell M.H., (1995), "Recommended approaches to assess pesticide mobility in soil" in Environmental Behavior of Agrochemicals (ed. T.R. Roberts and P.C. Kearney). John Wiley & Sons Ltd.
20. Esser H.O., Hemingway R.J., Klein W., Sharp D.B., Vonk J.W. and Holland P.T., (1988), "Recommended approach to the evaluation of the environmental behavior of pesticides", IUPAC Reports on Pesticides (24). Pure Appl. Chem., 60, 901-932.

21. Guth J.A., Burkhard N., and D.O. Eberle, (1976), "Experimental models for studying the persistence of pesticides in soils". Proc. BCPC Symposium: Persistence of Insecticides and Herbicides, pp 137-157, BCPC, Surrey, UK.
22. Fumming C.G.L., and Osgerby J.M., (1967), "Persistence of herbicides in soil". J. Sci. Fd Agric., 18, 269-273.
23. Burkhard N., and Guth J.A., (1981), "Chemical hydrolysis of 2-Chloro-4,6-bis(alkylamino)-1,3,5-triazine herbicides and their breakdown in soil under the influence of adsorption". Pestic. Sci. 12, 45-52.
24. Guth J.A., Gerber H.R., and Schlaepfer T., (1977). "Effect of adsorption, movement and persistence on the biological availability of soil-applied pesticides". Proc. Br. Crop Prot. Conf., 3, 961-971.
25. Osgerby J.M., (1973), "Process affecting herbicide action in soil". Pestic. Sci., 4, 247-258.
26. Guth J.A., (1972), "Adsorptions- und Einwascheverhalten von Pflanzenschutzmitteln in Böden". Schr. Reihe Ver. Wass. -Boden-Lufthyg. Berlin-Dahlem, Heft 37, 143-154.
27. Hamaker J.W., (1975), "The interpretation of soil leaching experiments", in Environmental Dynamics of Pesticides (eds R. Haque and V.H. Freed), pp. 135-172, Plenum Press, NY.
28. Helling C.S., (1971), "Pesticide mobility in soils". Soil Sci. Soc. Amer. Proc., 35, 732-210.
29. Hamaker J.W., (1972), "Diffusion and volatilization" in Organic chemicals in the soil environment (C.A.I. Goring and J.W. Hamaker eds), Vol. I, 49-143.
30. Burkhard N. and Guth J.A., (1981), "Rate of volatilisation of pesticides from soil surfaces; Comparison of calculated results with those determined in a laboratory model system". Pestic. Sci. 12, 37-44.
31. Cohen S.Z., Creeger S.M., Carsel R.F., and Enfield C.G., (1984), "Potential pesticide contamination of groundwater from agricultural uses", in Treatment and Disposal of Pesticide Wastes, pp. 297-325, Acs Symp. Ser. 259, American Chemical Society, Washington, DC.
32. Gustafson D.I., (1989), "Groundwater ubiquity score: a simple method for assessing pesticide leachability". J. Environ. Toxic. Chem., 8(4), 339-357.
33. Leistra M., and Dekkers W.A., (1976). "Computed effects of adsorption kinetics on pesticide movement in soils". J. of Soil Sci., 28, 340-350.
34. Bromilov R.H., and Leistra M., (1980), "Measured and simulated behavior of aldicarb and its oxydation products in fallow soils". Pest. Sci., 11, 389-395.
35. Green R.E., and Karickhoff S.W., (1990), "Sorption estimates for modeling", in Pesticides in the Soil Environment: Process, Impacts and Modeling (ed. H.H. Cheng). Soil Sci. Soc. Am., Book Series no. 2, pp.80-101,
36. Lambert S.M., (1967), "Functional relationship between sorption in soil and chemical structure". J. Agri. Food Chem., 15, 572-576.
37. Hance R.J., (1969), "An empirical relationship between chemical structure and the sorption of some herbicides by soils". J. Agri. Food Chem., 17, 667-668.
38. Briggs G.G. (1969), "Molecular structure of herbicides and their sorption by soils". Nature, 223, 1288.
39. Briggs G.G. (1981). "Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor". J. Agric. Food Chem., 29, 1050-1059.
40. Sabljic A., (1984), "Predictions of the nature and strength of soil sorption of organic polutance by molecular topology". J. Agric. Food Chem., 32, 243-246.
41. Bailey G.W., and White J.L., (1970), "Factors influencing the adsorption, desorption, and movement of pesticides in soil". Residue Rev., 32, 29-92.
42. Bailey G.W., J.L. White and Y. Rothberg., (1968), "Adsorption of organic herbicides by montomorillonite: Role of pH and chemical character of adsorbate". Soil Sci. Soc. Amer. Proc. 32:222-234.
43. Karickhoff S.W., (1981) "Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils". Chemosphere 10, 833-846.
44. Paya-Perez A., Riaz M. and Larsen B., (1989), "Soil Sorption of 6 Chlorobenzenes and 20 PCB Congeners". Environ. Toxicol. Safety 21, 1-17.

45. Hamaker J.W., and Thompson J.M., (1972). "Adsorption in organic chemicals" in Organic Chemicals in the Soil Environment (Goring C.A.I. and Hamaker J.W., eds), Vol I and II, Marcel Dekker, Inc., New York, NY, 1972, pp. 49-143.
46. Deli J., and Warren G.F., 1971, "Adsorption, desorption and leaching of diphenamid in soils". Weed Sci. 19:67-69.
47. Chu-Huang Wu, Buehring N., Davinson J.M. and Santelmann, (1975), "Napropamide Adsorption, desorption and Movement in soils". Weed Science, Vol. 23, 454-457.
48. Haues M.H.B., Stacey M., and Thompson J.M., (1968) "Adsorption of s-triazine herbicides by soil organic preparations" in Isotopes and Radiation in Soil Organic Studies, p.75, International Atomic Energy Agency, Vienna.
49. Pionke H.B., and Deangelis R.J., (1980), "Methods for distributing pesticide loss in field run-off between the solution and adsorbed phase", CREAMS, in A Field Scale Model for Chemicals, Run-off and Erosion from Agricultural Management Systems, Chapter 19, Vol. III: Supporting Documentation, USDA Conservation Research report.
50. ISO Standard Compendium Environment: Soil Quality - General aspects; chemical and physical methods of analysis; biological methods of analysis. First Edition (1994).
51. Scheffer F., and Schachtschabel, Lehrbuch der Bodenkunde, F. Enke Verlag, Stuttgart (1982), 11th edition.
52. Black, Evans D.D., White J.L., Ensminger L.E., and Clark F.E., eds. "Methods of Soil Analysis", Vol 1 and 2, American Society of Agronomy, Madison, WI, 1982.
53. ISO/DIS 10381-1 Soil Quality -- Sampling -- Part 1: Guidance on the design of sampling programmes.
54. ISO/DIS 10381-2 Soil Quality -- Sampling -- Part 2: Guidance on sampling techniques.
55. ISO/DIS 10381-3 Soil Quality -- Sampling -- Part 3: Guidance on safety of sampling.
56. ISO/DIS 10381-4 Soil Quality -- Sampling -- Part 4: Guidance on the investigation of natural and cultivated soils.
57. ISO/DIS 10381-5 Soil Quality -- Sampling -- Part 5: Guidance on the investigation of soil contamination of urban and industrial sites.
58. ISO 10381-6, 1993: Soil Quality - Sampling - Part 6: Guidance on the collection, handling and storage of soil for the assessment of aerobic microbial processes in the laboratory.
59. Green R.E., and Yamane V.K., (1970) "Precision in pesticide adsorption measurements". Soil Sci. Am. Proc., 34, 353-354.
60. Grover R., and Hance R.J. (1970), "Effect of ratio of soil to water on adsorption of linuron and atrazine". Soil Sci., 109-138.
61. Boesten, J.J.T.I., "Influence of soil/liquid ratio on the experimental error of sorption coefficients in pesticide/soil system". Pest. Sci. 1990, 30, 31-41.
62. Boesten, J.J.T.I. "Influence of soil/liquid ratio on the experimental error of sorption coefficients in relation to OECD guideline 106" Proceedings of 5th international workshop on environmental behaviour of pesticides and regulatory aspects, Brussels, 26-29 April 1994.
63. Bastide J., Cantier J.M., et Coste C., (1980), "Comportement de substances herbicides dans le sol en fonction de leur structure chimique". Weed Res. 21, 227-231.
64. Brown D.S., and Flagg E.W., (1981), "Empirical prediction of organic pollutants sorption in natural sediments". J. Environ.Qual., 10(3), 382-386.
65. Chiou C.T., Porter P.E., and Schmedding D.W., (1983), "Partition equilibria of non-ionic organic compounds between soil organic matter and water". Environ. Sci. Technol., 17(4), 227-231.
66. Gerstl Z., and Mingelgrin U., (1984), "Sorption of organic substances by soils and sediments". J. Environm. Sci. Health, B19 (3), 297-312.
67. Vowles P.D., and Mantoura R.F.C., (1987), "Sediment-water partition coefficient and HPLC retention factors of aromatic hydrocarbons". Chemosphere, 16(1), 109-116.
68. Lyman W.J., Reehl W.F. and Rosenblatt D.H. (1990). Handbook of Chemical Property Estimation Methods. Environmental Behaviour of Organic Compounds. American Chemical Society, Washington DC.

69. Keniga E.E., and Goring, C.A.I. (1980). "Relationship between water solubility, soil sorption, octanol-water partitioning and concentration of chemicals in the biota" in Aquatic Toxicology (eds J.G. Eaton, et al.), pp.78-115, ASTM STP 707, Philadelphia.
70. Chiou C.T., Peters L.J., and Freed V.H., (1979), "A physical concept of soil-water equilibria for non-ionic organic compounds". Science, Vol. 206, 831-832.
71. Hassett J.J., Banwart W.I., Wood S.G., and Means J.C., (1981), "Sorption of *p*-Naptol: implications concerning the limits of hydrophobic sorption". Soil Sci. Soc. Am. J. 45, 38-42.
72. Karickhoff S.W., (1981), "Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils". Chemosphere, Vol. 10(8), 833-846.
73. Moreale A., van Bladel R., (1981), "Adsorption de 13 herbicides et insecticides par le sol. Relation solubilité - réactivité. Revue de l'Agric., 34 (4), 319-322.
74. Müller M., Kördel W. (1996), "Comparison of screening methods for the determination/estimation of adsorption coefficients on soil". Chemosphere, 32(12), 2493-2504.
75. Kördel W., Kotthoff G., Müller M. (1995), "HPLC - screening method for the determination of the adsorption coefficient on soil - results of a ring test". Chemosphere 30 (7), 1373-1384.
76. Kördel W., Stutte J., Kotthoff G. (1993), "HPLC - screening method for the determination of the adsorption coefficient on soil - comparison of different stationary phases. Chemosphere 27 (12), 2341-2352.
77. Hance, R.J., (1967), "The speed of Attainment of Sorption Equilibria in Some Systems Involving Herbicides". Weed Research, Vol. 7, pp. 29-36.
78. Koskinen W.C., and Harper S.S., (1990), "The retention processes: mechanisms" in Pesticides in the Soil Environment: Processes, Impacts and Modelling (ed. H.H. Cheng). Soil Sci. Soc. Am. Book Series, No. 2, Madison, Wisconsin.
79. Cohen S.Z., Creeger S.M., Carsel R.F., and Enfield C.G. (1984), "Potential pesticide contamination of groundwater from agricultural uses", in Treatment and Disposal of Pesticide Wastes, pp.297-325, ACS Symp. Ser. 259, American Chemical Society, Washington, DC.
80. Giles C.H., (1970), "Interpretation and use of sorption isotherms" in Sorption and Transport Processes in Soils. S.C.I. Monograph No. 37, 14-32.
81. Giles, C.H.; McEwan J.H.; Nakhwa, S.N. and Smith, D. (1960), "Studies in adsorption: XI. A system of classification of solution adsorption isotherms and its use in the diagnosis of adsorption mechanisms and in measurements of pesticides surface areas of soils". J. Chem. Soc., 3973-93.
82. Calvet R., Tercé M., and Arvien J.C., (1980), "Adsorption des pesticides par les sols et leurs constituants: 3. Caractéristiques générales de l'adsorption". Ann. Agron. 31: 239-251.
83. Bedbur E., (1996), "Anomalies in the Freundlich equation", Proc. COST 66 Workshop, Pesticides in soil and the environment, 13-15 May 1996, Stratford-upon-Avon, U.K.
84. Guth, J.A., (1985), "Adsorption/desorption", in Joint International Symposium, Physicochemical Properties and their Role in Environmental Hazard Assessment, July 1-3, Canterbury, UK.
85. Soil Texture Classification (US and FAO systems): Weed Science, 33, Suppl. 1 (1985) and Soil Sci. Soc. Amer. Proc. 26:305 (1962).

ANNEX 1
Testing Scheme



Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L25 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

ANNEX 2

INFLUENCE OF ACCURACY OF ANALYTICAL METHOD AND CONCENTRATION CHANGE
ON ACCURACY OF ADSORPTION RESULTS

From the following table (84) it becomes obvious that when the difference between the initial mass ($m_0=110 \mu\text{g}$) and equilibrium mass ($m_{\text{aq}}^{\text{ads}}(\text{eq})=100 \mu\text{g}$) 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 .

$$\begin{aligned} \text{Amount of soil} \quad m_{\text{soil}} &= 10 \text{ g} \\ \text{Volume of solution} \quad V_0 &= 100 \text{ cm}^3 \end{aligned}$$

	$m_{\text{aq}}^{\text{ads}}(\text{eq})$ (μg)	$C_{\text{aq}}^{\text{ads}}(\text{eq})$ ($\mu\text{g cm}^{-3}$)	R	$m_s^{\text{ads}}(\text{eq})^*$ (μg)	$C_s^{\text{ads}}(\text{eq})^*$ ($\mu\text{g g}^{-1}$)	R_d^\dagger	K_d^*	R_d^\ddagger
$m_0 = 110 \mu\text{g}$ or $C_0 = 1.100 \mu\text{g/cm}^3$	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%
$m_0 = 110 \mu\text{g}$ or $C_0 = 1.100 \mu\text{g/cm}^3$	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%
$m_0 = 110 \mu\text{g}$ or $C_0 = 1.100 \mu\text{g/cm}^3$	FOR A = 99%							
	1.100	0.011	true value	108.9	10.89	true value	990	
	1.111	0.01111	1%	108.889	10.8889	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%

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal.

This method can be found in Dir 2001/59/EC (O.J. L225 2001).

A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

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

$m_s^{\text{ads}}(\text{eq})$ = 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 ;

$C_s^{\text{ads}}(\text{eq})$ = 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.

ANNEX 3

ESTIMATION TECHNIQUES FOR K_d

1. Estimation techniques permit prediction of K_d based on correlations with, for example, P_{ow} values (12)(39)(63-68), water solubility data (12)(19)(21)(39)(68-73), or polarity data derived by application of HPLC on reversed phase (74-76). As shown in Tables 1 and 2, is the K_{oc} or K_{om} that are calculated from these equations and then, indirectly, the K_d from the equations:

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

2. The concept of these correlations is based on two assumptions: (1) It is the organic matter of the soil that mainly influences the adsorption of a substance; and (2) The interactions involved are mainly non-polar. As a result, these correlations: (1) are not, or are only to some extent, applicable to polar substances, and (2) are not applicable in cases where the organic matter content of the soil is very small (12). In addition, although satisfactory correlations have been found between P_{ow} and adsorption (19), the same cannot be said for the relationship between water solubility and extent of adsorption (19)(21); so far the studies are very contradictory.

3. Some examples of correlations between the adsorption coefficient and the octanol-water partition coefficient, as well as water solubility are given in Tables 1 and 2, respectively.

Table 1. Examples of correlations between the adsorption distribution coefficient and the octanol-water partition coefficient; for further examples (12) (68).

Substances	Correlations	Authors
Substituted ureas	$\log K_{om} = 0.69 + 0.52 \log P_{ow}$	Briggs (1981) (39)
Aromatic chlorinated	$\log K_{oc} = -0.779 + 0.904 \log P_{ow}$	Chiou <i>et al.</i> (1983) (65)
Various pesticides	$\log K_{om} = 4.4 + 0.72 \log P_{ow}$	Gerstl and Mingelgrin (1984) (66)
Aromatic hydrocarbons	$\log K_{oc} = -2.53 + 1.15 \log P_{ow}$	Vowles and Mantoura (1987) (67)

Table 2. Examples of correlations between the adsorption distribution coefficient and water solubility; for further examples see (68) (69).

Compounds	Correlations	Authors
Various pesticides	$\log K_{om} = 3.8 - 0.561 \log S_w$	Gerstl and Mingelgrin (1984) (66)
Aliphatic, aromatic chlorinated substances	$\log K_{om} = (4.040 \pm 0.038) - (0.557 \pm 0.012) \log S_w$	Chiou <i>et al.</i> (1979) (70)
α -naphthol	$\log K_{oc} = 4.273 - 0.686 \log S_w$	Hasset <i>et al.</i> (1981) (71)
Cyclic, aliphatic aromatic substances	$\log K_{oc} = -1.405 - 0.921 \log S_w - 0.00953 (\text{mp}-25)$	Karickhoff (1981) (72)
Various compounds	$\log K_{om} = 2.75 - 0.45 \log S_w$	Moreale van Blade (1982) (73)

ANNEX 4

CALCULATIONS FOR DEFINING THE CENTRIFUGATION CONDITIONS

1. The centrifugation time is given by the following formula, assuming spherical particles:

$$t = \frac{9}{2} \left[\frac{h}{w^2 r_p^2 (r_s - r_{aq})} \right] \ln \left(\frac{R_b}{R_t} \right) \quad (1)$$

For simplification purposes, all parameters are described in non-SI units (g, cm).

where:

- ω = rotational speed ($=2 \pi \text{ rpm}/60$), rad s^{-1} ;
- rpm = revolutions per minute;
- η = viscosity of solution, $\text{g s}^{-1} \text{ cm}^{-1}$;
- r_p = particle radius, cm;
- ρ_s = soil density, g cm^{-3} ;
- ρ_{aq} = solution density, g cm^{-3} ;
- R_t = distance from the centre of centrifuge rotor to top of solution in centrifuge tube, cm;
- R_b = distance from the centre of centrifuge rotor to bottom in centrifuge tube, cm;
- $R_b - R_t$ = length of the soil/solution mixture in the centrifuge tube, cm.

In general practice, double the calculated times is used to ensure complete separation.

2. The equation (1) can be simplified further if we consider the viscosity (η) and the density (ρ_{aq}) of the solution as equal to the viscosity and density of water at 25 °C; thus, $\eta = 8.95 \times 10^{-3} \text{ g s}^{-1} \text{ cm}^{-1}$ and $\rho_{aq} = 1.0 \text{ g.cm}^{-3}$.

Then, the centrifugation time is given by the equation (2):

$$t = \frac{3.7}{(\text{rpm})^2 \cdot \eta^2 (r_s - 1)} \ln \frac{R_b}{R_t} \quad (2)$$

3. From the equation (2) it becomes apparent that two parameters are important in defining the centrifugation condition, i.e. time (t) and speed (rpm), in order to achieve separation of particles with a specific size (in our case 0.1 μm radius): (1) the density of the soil and (2) the length of the mixture in the centrifuge tube ($R_b - R_t$), i.e. the distance which a soil particle covers from the top of the solution to the bottom of the tube; obviously, for a fixed volume the length of the mixture in the tube will depend on the square of the radius of the tube.

4. Fig. 1 presents variations in the centrifugation time (t) versus centrifugation speed (rpm) for different soil densities (ρ_s) (Fig.1a) and different lengths of the mixture in the centrifuge tubes (Fig.2a). From Fig.1a the influence of the soil density appears obvious; for example, for a classical centrifugation of 3000 rpm the centrifugation time is approx. 240 min for 1.2 g cm^{-3} soil density, while it is only 50 min for 2.0 g cm^{-3} . Similarly, from Fig 1b, for a classical centrifugation of 3000 rpm the centrifugation time is approx. 50 min for a length of the mixture of 10 cm and only 7 min for a length of 1 cm. However, it is important to find an optimal relation between centrifugation which requires the less length possible and easy handling for the experimenter in separating the phases after centrifugation.

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

5. Moreover, when defining the experimental conditions for the separation of soil/solution phases, it is important to consider the possible existence of a third “pseudo-phase”, the colloids. These particles, with a size less than 0.2 μm , can have an important impact on the whole adsorption mechanism of a substance in a soil suspension. When centrifugation is performed as described above, colloids remain in the aqueous phase and are subjected to analysis together with the aqueous phase. Thus, the information about their impact is lost.

If the conducting laboratory has ultracentrifugation or ultrafiltration facilities, the adsorption/desorption of a substance in soil could be studied more in depth, including information on the adsorption of the substance on the colloids. In this case, an ultracentrifugation at 60,000 rpm/min or an ultrafiltration with filter porosity of 100,000 Daltons should be applied in order to separate the three phases soil, colloids, solution. The test protocol should also be modified accordingly, in order all three phases to be subjected to substance analysis.

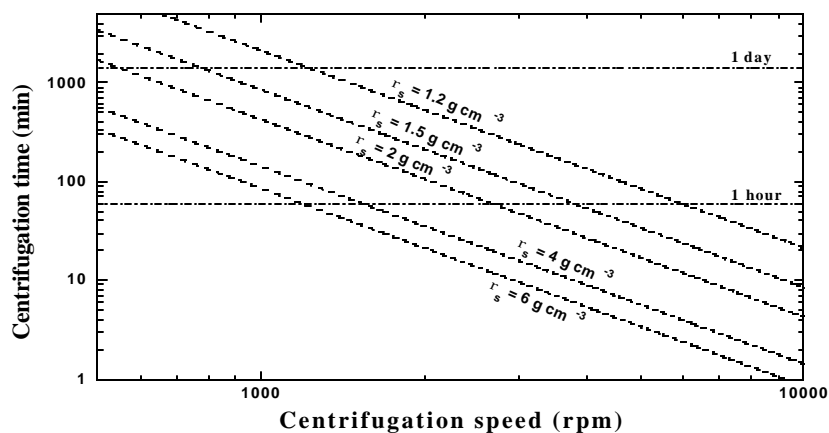


Fig. 1a. Variations of centrifugation time (t) versus centrifugation speed (rpm) for different soil densities (ρ_s). $R_t = 10$ cm, $R_b - R_t = 10$ cm, $\eta = 8.95 \times 10^{-3} \text{ g s}^{-1} \text{ cm}^{-1}$ and $\rho_{\text{aq}} = 1.0 \text{ g cm}^{-3}$ at 25 °C.

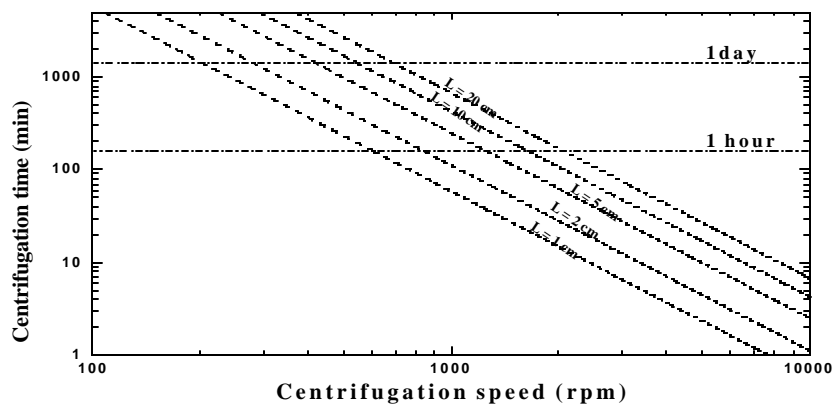
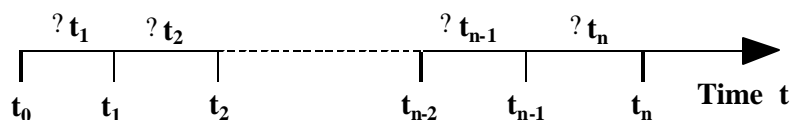


Fig. 1b. Variations of centrifugation time (t) versus centrifugation speed (rpm) for different lengths of the mixture in the centrifuge tube ($R_b - R_t = L$); $R_t = 10$ cm, $\eta = 8.95 \times 10^{-3} \text{ g s}^{-1} \text{ cm}^{-1}$, $\rho_{\text{aq}} = 1.0 \text{ g cm}^{-3}$ at 25 °C and $\rho_s = 2.0 \text{ g cm}^{-3}$.

ANNEX 5

CALCULATION OF ADSORPTION A (%) AND DESORPTION D (%)

The time scheme of the procedure is:



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

ADSORPTION A (A%)

a) Parallel method

The percentage adsorption is calculated for each test tube (i) at each time point (t_i), according to the equation:

$$A_{t_i} = \frac{m_s^{\text{ads}}(t_i) \cdot 100}{m_0} \quad (\%) \quad (1)^4$$

The terms of this equation may be calculated as follows:

$$m_0 = C_0 \cdot V_0 \quad (\mu\text{g}) \quad (2)$$

$$m_s^{\text{ads}}(t_i) = m_0 - C_{\text{aq}}^{\text{ads}}(t_i) \cdot V_0 \quad (\mu\text{g}) \quad (3)$$

where:

A_{t_i} = adsorption percentage (%) at the time point t_i ;

$m_s^{\text{ads}}(t_i)$ = mass of the 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).

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 Fig.1 and Fig.2 respectively.

⁴ Equation applicable to both direct and indirect methods. All the other equations are applicable only to indirect method.

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

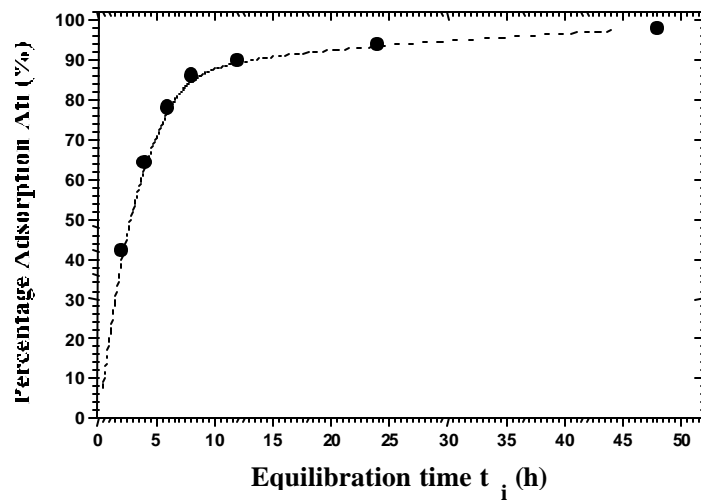


Fig. 1. Adsorption Equilibrium Plot

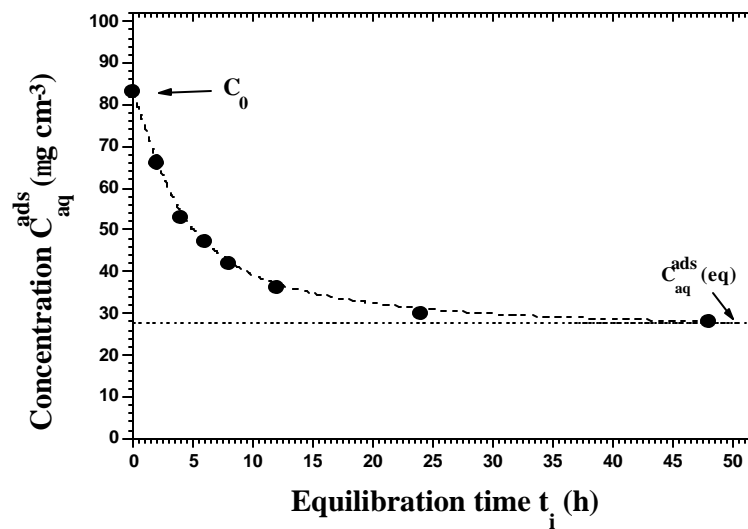


Fig.2. Mass concentration of the test substance in the aqueous phase (C_{aq}) versus time

b) Serial method

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.

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

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

$$m_s^{\text{ads}}(\Delta t_1) = m_0 - m_m^{\text{ads}}(t_1) \cdot \left(\frac{V_0}{v_a^A} \right) \quad (4)$$

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

$$m_s^{\text{ads}}(\Delta t_2) = m_m^{\text{ads}}(t_1) \cdot \left(\frac{V_0}{v_a^A} \right) - m_m^{\text{ads}}(t_2) \cdot \left(\frac{V_0 - v_a^A}{v_a^A} \right) \quad (5)$$

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

$$m_s^{\text{ads}}(\Delta t_3) = m_m^{\text{ads}}(t_2) \cdot \left(\frac{V_0 - v_a^A}{v_a^A} \right) - m_m^{\text{ads}}(t_3) \cdot \left(\frac{V_0 - 2 \cdot v_a^A}{v_a^A} \right) \quad (6)$$

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

$$m_s^{\text{ads}}(\Delta t_n) = m_m^{\text{ads}}(t_{n-1}) \cdot \left(\frac{V_0 - (n-2) \cdot v_a^A}{v_a^A} \right) - m_m^{\text{ads}}(t_n) \cdot \left(\frac{V_0 - (n-1) \cdot v_a^A}{v_a^A} \right) \quad (7)$$

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

$$A_{\Delta t_i} = \frac{m_s^{\text{ads}}(\Delta t_i)}{m_0} \cdot 100 \quad (\%) \quad (8)^5$$

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

$$A_{t_i} = \frac{\sum_{j=\Delta t_1}^{\Delta t_i} m_s^{\text{ads}}(j)}{m_0} \cdot 100 \quad (\%) \quad (9)^5$$

⁵ Equations applicable to both direct and indirect methods. All the other equations are applicable only to indirect method.

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.

- At the equilibration time t_{eq} :
- the mass of the test substance adsorbed on the soil is:

$$m_s^{ads}(eq) = \sum_{\Delta t_i=1}^n m_s^{ads}(\Delta t_i) \quad (10)^5$$

- the mass of the test substance in the solution is:

$$m_{aq}^{ads}(eq) = m_0 - \sum_{\Delta t_i=1}^n m_s^{ads}(\Delta t_i) \quad (11)^5$$

- and the percentage of adsorption at equilibrium is:

$$A_{eq} = \frac{m_s^{ads}(eq)}{m_0} \cdot 100 \quad (\%) \quad (12)^5$$

The parameters used above are defined as:

$m_s^{ads}(\Delta t_1), m_s^{ads}(\Delta t_2), \dots, m_s^{ads}(\Delta t_n)$ = mass of the substance adsorbed on the soil during the time intervals $\Delta t_1, \Delta t_2, \dots, \Delta t_n$ respectively (μg);

$m_m^{ads}(t_1), m_m^{ads}(t_2), \dots, m_m^{ads}(t_n)$ = mass of the substance measured in an aliquot v_a^A at the time points t_1, t_2, \dots, t_n respectively (μg);

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

$m_{aq}^{ads}(eq)$ = 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 to a time interval Δt_i ;

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

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

At a time point t_i , the mass of the test substance is measured in the aqueous phase taken from the tube i (V_i^1), and the mass desorbed is calculated according to the equation:

$$m_{aq}^{des}(t_i) = m_m^{des}(t_i) \cdot \left(\frac{V_0}{V_i^1} \right) - m_{aq}^A \quad (13)$$

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

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

$$m_{aq}^{des}(\Delta t_i) = m_{aq}^{des}(t_i) - \sum_{j=1}^{i-1} m_{aq}^{des}(j) \quad (14)$$

The percentage of desorption is calculated:

- at a time point t_i from the equation:

$$D_{t_i} = \frac{m_{aq}^{des}(t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%) \quad (15)$$

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

$$D_{\Delta t_i} = \frac{m_{aq}^{des}(\Delta t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%) \quad (16)$$

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 (%);

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

$m_{aq}^{des}(\Delta t_i)$ = mass of the test substance desorbed during a time interval Δt_i (μg);

$m_m^{des}(t_i)$ = mass of the test substance analytically measured at a time t_i in a solution volume V_i^1 , 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);

$$m_{\text{aq}}^{\text{A}} = m_{\text{aq}}^{\text{ads}} (\text{eq}) \cdot \left(\frac{V_0 - V_R}{V_0} \right) \quad (17)$$

$m_{\text{aq}}^{\text{ads}}(\text{eq})$ = 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_T^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 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

The following equations take into account that the adsorption procedure, which was preceded, was carried out by measurement of test substance in small aliquots (v_a^{A}) of the aqueous phase (serial method in "Performance of the test" 1.9). 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) and 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 the equation:

$$V_T = V_0 - \sum_{i=1}^n v_a^{\text{A}}(i) \quad (18)$$

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 the equation:

$$m_{\text{aq}}^{\text{des}}(t_i) = m_{\text{aq}}^{\text{des}}(t_i) \cdot \left(\frac{V_T}{v_a^{\text{D}}} \right) - m_{\text{aq}}^{\text{A}} \cdot \left(\frac{(V_T - (i-1) \cdot v_a^{\text{D}})}{V_T} \right) \quad (19)$$

- 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 percentage of desorption D_{t_i} is calculated, from the following equation:

$$D_{t_i} = \frac{m_{\text{aq}}^{\text{des}}(t_i)}{m_{\text{S}}^{\text{ads}}(\text{eq})} \cdot 100 \quad (\%) \quad (20)$$

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 $\Delta t_1 = t_1 - t_0$

$$m_{aq}^{des}(\Delta t_1) = m_m^{des}(t_1) \cdot \left(\frac{V_T}{v_a^D} \right) - m_{aq}^A \quad \text{and} \quad m_s^{des}(t_1) = m_s^{aq}(eq) - m_{aq}^{des}(\Delta t_1) \quad (21)$$

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

$$m_{aq}^{des}(\Delta t_2) = m_m^{des}(t_2) \cdot \left(\frac{V_T}{v_a^D} \right) - m_{aq}^{des}(\Delta t_1) \cdot \left(\frac{(V_T - v_a^D)}{V_T} \right) - m_{aq}^A \cdot \left(\frac{(V_T - v_a^D)}{V_T} \right) \quad \text{and}$$

$$m_s^{des}(t_2) = m_s^{ads}(eq) - [m_{aq}^{des}(\Delta t_1) + m_{aq}^{des}(\Delta t_2)] \quad (22)$$

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

$$m_{aq}^{des}(\Delta t_n) = \left[m_m^{des}(t_n) \cdot \left(\frac{V_T}{v_a^D} \right) - m_{aq}^A \cdot \left(\frac{(V_T - (n-1) \cdot v_a^D)}{V_T} \right) - \sum_{i=1, n \neq 1}^{n-1} \left(\frac{(V_T - (n-i) \cdot v_a^D)}{V_T} \right) \cdot m_{aq}^{des}(\Delta t_i) \right]$$

$$\text{and } m_s^{des}(t_n) = m_s^{ads}(eq) - \sum_{i=1, n \neq 1}^n m_{aq}^{des}(\Delta t_i) \quad (23)$$

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

$$D_{\Delta t_i} = \frac{m_{aq}^{des}(\Delta t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%) \quad (24)$$

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

$$D_{t_i} = \frac{\sum_{j=\Delta t_1}^{\Delta t_i} m_{aq}^{des}(j)}{m_s^{ads}(eq)} \cdot 100 = \frac{m_{aq}^{des}(t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%) \quad (25)$$

where the above used parameters are defined as:

$m_s^{des}(\Delta t_1), m_s^{des}(\Delta t_2), \dots, m_s^{des}(\Delta t_n)$ = 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);

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

$m_m^{des}(t_1), m_m^{des}(t_2), \dots, m_m^{des}(t_n)$ = 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);

$$m_{aq}^A = \left(\frac{\left(V_0 - \sum_{i=1}^n v_a^A(i) \right) - V_R}{\left(V_0 - \sum_{i=1}^n v_a^A(i) \right)} \right) \cdot m_{aq}^{ads}(eq) \quad (26)$$

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);

$$v_a^D \leq 0.02 \cdot V_T \quad (27)$$

ANNEX 6

ADSORPTION-DESORPTION IN SOILS: DATA REPORTING SHEETS

Substance tested:

Soil tested

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

Temperature:.....
.....°C

Suitability of the analytical method

Weighed soil	g	
Soil: dry mass	g	
Volume 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:

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

Substance tested:

Soil tested

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

Temperature:.....°C

Analytical methodology followed: Indirect Parallel Serial
Direct

Adsorption test: test samples

	Symbol	Units	Equilibration Time	Equilibration Time	Equilibration Time	Equilibration Time
Weighed soil	-	mg				
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		cm ³				
Total volume of aq. phase in contact with soil	V_0	cm ³				
Initial concentration Test solution	C_0	µg cm ⁻³				
Mass test subst. at the beginning of the test	m_0	µg				
After agitation and centrifugation						
Indirect Method						
Parallel method						
Concentration test subst. aq. phase Blank correction included	$C_{aq}^{ads}(t_i)$	µg cm ⁻³				
Serial method						
Measured mass test subst. in the aliquot V_a^A	$m_{fl}^{ads}(t_i)$	µg				
Direct method						
Mass test substance adsorbed on soil	$m_s^{ads}(t_i)$	µg				
Calculation of adsorption						
Adsorption	A_{t_i}	%				
	$A_{\Delta t_i}$	%				
Means						
Adsorption coefficient	K	cm ³ g ⁻¹				
Means						
Adsorption coefficient	K	cm ³ g ⁻¹				

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L25 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal.

This method can be found in Dir 2001/59/EC (O.J. L225 2001).

A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

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

Substance tested:

Soil tested:

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

Temperature:.....°C

Adsorption test: blanks and control

Symbol	Units	Blank		Blank		Control	
Tube N°							
Weighed soils	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

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

Substance tested:

Soil tested:

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

Temperature:.....
.....°C

Mass balance

	Symbol	Units				
Tube No.						
Weighed soil	-	g				
Soil: dry mass	m_{soil}	g				
Water volume in weighed soil (calculated)	V_{WS}	ml				
Volume 0.01 M CaCl ₂ sol. to equilibrate the soil		ml				
Volume of stock solution		cm ³				
Total volume 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						
Concentr. test subst. aq. phase at adsorption equilibrium blank correction included	$C_{aq}^{ads}(eq)$	µg cm ⁻³				
Equalibration time	t_{eq}	h				
1st dilution with solvent						
Removed volume aq. phase	V_{rec}	cm ³				
Added volume of solvent	ΔV	cm ³				
1st extraction with solvent						
Signal analyzed in solvent	S_{E1}	var.				
Conc. test subst. in solvent	C_{E1}	µg cm ⁻³				
Mass of substance extracted from soil and 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 analyzed in solvent phase	S_{E2}	var.				
Conc. test subst. in solvent	C_{E2}	µg cm ⁻³				
Mass of substance extracted from soil and vessel walls	m_{E2}	µg				
Total mass test subst. extracted in two steps	m_E	µg				
Mass balance	MB	%				

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

Substance tested:

Soil tested:

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

Temperature:.....°C

Adsorption isotherms

	Symbol	Units								
Tube No.										
Weighed soil	-	g								
Soil: dry mass	E	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	µg cm ⁻³								
Equilibration time	-	h								
After agitation and centrifugation										
Concentration subst. aq. phase, blank correction included	C_{aq}^{ads} (eq)	µg cm ⁻³								
Temperature		°C								
Adsorb. mass per unit soil	C_s^{ads} (eq)	µg g ⁻¹								

Regression analysis:

value of K_F^{ads} :

value of 1/n:

regression coefficient r^2 :

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.

Substance tested:

Soil tested:

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

Temperature:.....
.....°C

Analytical methodology followed: Indirect Parallel Serial

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				
Desorption kinetics						
Measured mass of substance desorbed from soil at time t_i	$m_m^{des}(t_i)$	µg				
Volume of the solution taken from the tube (i) for the measurement of the test substance	PM V_i^i	cm ³				
	SM v_a^D	cm ³				
Mass of substance desorbed from soil at time t_i (calculated)	$m_{aq}^{des}(t_i)$	µg				
Mass of substance desorbed from soil during time interval Δt_i (calculated)	$m_{aq}^{des}(\Delta t_i)$	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

Please notice that only European Community's legislation published in the paper editions of the Official Journal of the European Communities is deemed authentic. This text was prepared from the draft protocol sent for approval to the Member States. Minor editorial differences may exist between this version and the one published in the paper edition of the Official Journal. Care has been taken to ensure correctness of the text; nevertheless possibility of errors cannot be completely excluded. In case of doubt the reader is advised to consult the Official Journal. This method can be found in Dir 2001/59/EC (O.J. L225 2001). A complete list of Annex V Testing Methods and the corresponding OJ can be downloaded from a previous page in this site.