OECD/OCDE

106

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OECD GUIDELINE FOR THE TESTING OF CHEMICALS

Adsorption - Desorption Using a Batch Equilibrium Method

INTRODUCTION

1.   This Guideline is based on the proposal submitted by the European Commission in 1993 and takes into account the comments on that proposal submitted by the Member countries.   Several activities undertaken in the European Union bore on the development of an adsorption test.   These included an extensive investigation due to the collaboration of the German Umweltbundesamt (UBA), the University of Kiel, and the European Commission and its Joint Research Centre at Ispra, Italy (1)(2).   In 1988 UBA organised a ring-test in which 27 laboratories in EU Member States participated (3).   An OECD Workshop on Soil Selection was held at Belgirate, Italy, in 1995 (4).   The Workshop agreed on the main elements of the updated Test Guideline 106 for an adsorption/desorption test and, in particular, on the characterisation and selection of the soil types for use in the test.

2.   Other guidelines concerning adsorption/desorption exist only at national level and are mainly focused on pesticides testing (5)(6)(7)(8)(9)(10)(11).   These documents as well as an extensive relevant literature were considered when developing this Guideline.

SIGNIFICANCE AND USE

3.   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 our biosphere (12)(13)(14)(15)(16)(17)(18)(19)(20)(21).   They 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); and run-off from land surfaces into natural waters (18)(31)(32).   Adsorption data can also be used for comparative and modelling purposes (19)(33)(34)(35).

4.   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 Guideline. 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.

SCOPE

5.   This Guideline 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, 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.

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

7.   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 ionisable 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).

8.   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:

Tier1:   <u>Preliminary study</u> in order to determine:

-   the soil/solution ratio;
-   the equilibration 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:   <u>Screening test</u>: the adsorption is studied in five different soil types by means of adsorption kinetics at a single concentration and determination of distribution coefficients K_d and K_{oc}.

Tier 3:   <u>Determination of Freundlich adsorption isotherms</u> to determine the influence of concentration on the extent of adsorption on soils.
<u>Study of desorption by means of desorption kinetics/Freundlich desorption isotherms</u> (Annex 1).

DEFINITIONS AND UNITS

9.   Definitions and units are set out in the Data and Reporting section and Annex 2. The weight of soil samples as mentioned in the equations of the Guideline refer to the oven dry weight.

PRINCIPLE OF THE METHOD

10.   Known volumes of solutions of the test substance, non-labelled or radiolabelled, at known concentrations in 0.01 M $CaCl_2$ are added to soil samples of known dry weight which have been pre-equilibrated in 0.01 M $CaCl_2$. 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).

11.   As an option, the amount of the test substance adsorbed can also be directly determined by analysis of soil (direct method). Although this makes the analytical procedure more tedious, involving stepwise soil extraction with an appropriate solvent, it is recommended in cases where the difference in the solution concentration of the substance cannot be accurately determined. Examples of such cases are: adsorption of

the test substance on surfaces of the test vessels, instability of the test substance in the time scale of the experiment, weak adsorption giving only small concentration change in the solution; and strong adsorption yielding low concentration which cannot be accurately determined. If 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 the test chemical and its transformation products; therefore it should be used only if the test chemical is stable for the duration of the study.

INFORMATION ON THE TEST SUBSTANCE

12.   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.

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

(a)   solubility in water [OECD Guideline 105];
(b)   vapour pressure [OECD Guideline 104] or/and Henry's law constant;
(c)   abiotic hydrolysis as a function of pH [OECD Guideline 111];
(d)   n-octanol/water partition coefficient [OECD Guidelines 107 and 117];
(e)   ready biodegradability [OECD Guideline 301] or aerobic and anaerobic transformation in soil;
(f)   pKa of ionisable substances;
(g)   direct photolysis in water (i.e. UV-Vis absorption spectrum in water, quantum yield) and
         photodegradation on soil.

APPLICABILITY OF THE TEST

14.   The test is applicable to chemical substances for which an analytical method with sufficient accurancy is available. An important parameter that can influence the reliability of the results, especially when the indirect method is followed (see paragraph 10), is the stability of the test substance in the time scale 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.

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

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

DESCRIPTION OF THE METHOD

Apparatus and chemical reagents

17.   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 μm 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 PTFE (Teflon®) lined screw caps should be used.

(d)   Optional: filtration device; filters of 0.2 μm 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 ° to 110 °C.

Characterisation and selection of soils

18.   The soils should be characterised by three parameters considered to be largely responsible for the adsorptive capacity: organic carbon, clay content and soil texture, and pH. As already mentioned in paragraph 7, 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.

19.   The methods used for soil characterisation 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 $CaCl_2$ (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 analyses of sorption data to be based on globally standardised soil parameters. Some guidance for existing standard methods of soil analysis and characterisation is given in references 50-52. For calibration of soil test methods, the use of reference soils might be considered.

20.   Guidance for selection of soils for adsorption/desorption experiments is given in Table 1. The seven selected soils cover soil types typically encountered in temperate geographical zones. For ionisable test substances, the selected soils should cover a wide range of pH, in order 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 the heading "Performance of the test".

21.   Other soil types may sometimes be necessary to represent cooler, temperate and tropical regions within the OECD Countries. Therefore, if other soil types are preferred, they should be characterised by the same parameters and should have similar variations 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,)	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%.

Collection and storage of soil samples

Collection

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

23.   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 exactly defined by UTM (Universal Transversal Mercator-Projection/European Horizontal Datum) or geographical co-ordinates; this could allow re-collection 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 no. 7, if a O_h horizon is present as part of the soil, it should be included in the sampling.

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

Storage

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

Handling and preparation of soil samples for the test

26.   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 homogenisation is recommended, as this enhances the reproducibility of the results.

27.   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.

Preparation of the test substance for application to soil

28.   The test substance is dissolved in a 0.01 M solution of calcium chloride ($CaCl_2$) 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 Guideline (paragraphs 52-58); additionally, the stock solution concentration should be below water solubility of the test substance.

29.   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.

30.   Only for poorly soluble substances ($S_w < 10^{-4}$ g l^{-1}), an appropriate solubilising agent may be needed when it is difficult to dissolve the test substance. This solubilising 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.

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

PREREQUISITES FOR PERFORMING THE ADSORPTION/DESORPTION TEST

The analytical method

32.   The key parameters that can influence the accurancy 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 3.33.

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, detection limits and recovery. Some guidance on how to perform such a test is given by the experiment below.

34.   An appropriate volume of 0.01 M CaCl$_2$, e.g. 100 cm^3, is agitated during 4 h with a weight of soil, e.g. 20 g, of high adsorbability, i.e. with high organic carbon and clay content; these weights and volumes may vary depending on analytical needs, but a soil/solution ratio of 1:5 is a convenient starting point. The mixture is centrifuged and the aqueous phase may be filtrated. A certain volume of the test substance stock solution is added to the latter to reach a nominal concentration within the concentration range which is likely to occur during the test. This volume should not exceed 10% of the final volume of the aqueous phase, in order to change as little as possible the nature of the pre-equilibration solution. The solution is analysed.

35.   One blank run consisting of the system soil + CaCl$_2$ solution (without test substance) must be included, in order to check for artifacts in the analytical method and for matrix effects caused by the soil.

36.   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.

37.   The characteristics and detection limits of the analytical method available for carrying out adsorption studies play an important role in defining the test conditions and the whole experimental performance of the test. This Guideline follows a general experimental path and provides recommendations and guidance for alternative solutions where the analytical method and laboratory facilities may impose limitations.

The selection of optimal soil/solution ratios

38.   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.

39.   With respect to the above remarks, 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 4). 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 linear[1]. The applicable relationship is obtained by rearranging equation (4) of the K_d in the form of equation (1):
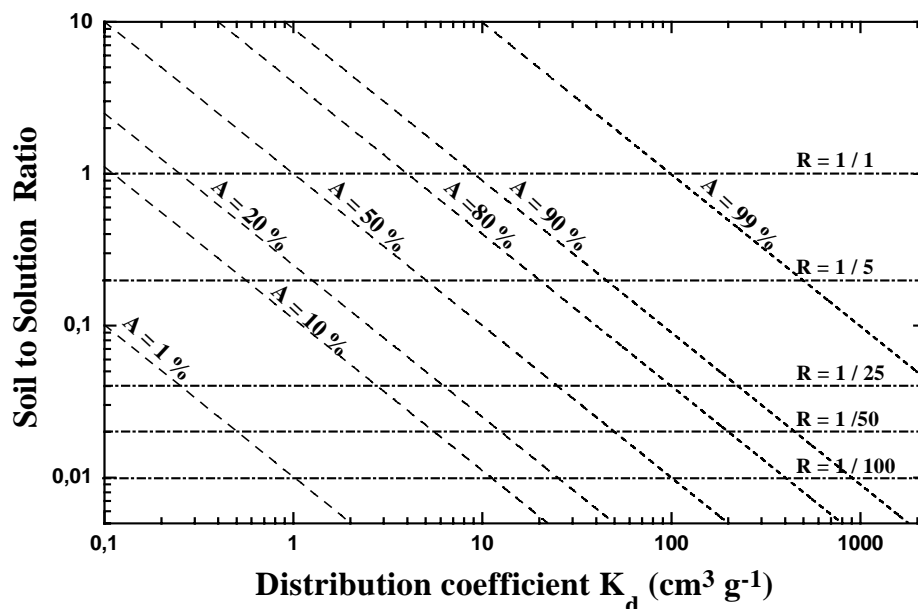
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[1] $C_s^{ads} (eq) = K_d \cdot C_{aq}^{ads} (eq)$

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

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

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

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

40.   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.

41.   Areas which are more difficult to deal with are those where the chemical is very slightly or highly 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. In any case, 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 4). This could be useful especially for low adsorbed/polar chemicals with $P_{ow} < 20$ and for lipophilic/highly sorptive chemicals with $P_{ow} > 10^4$.

PERFORMANCE OF THE TEST

Test conditions

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

43.   Centrifugation conditions should allow the removal of particles larger than 0.2 μm from the solution. This value triggers the smallest sized particle that is considered as a solid particle, and is the limit between solid and colloid particles. Guidance on how to determine the centrifugation conditions is given in Annex 5.

44.   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.

Tier 1- Preliminary study

45.   The purpose of conducting a preliminary study has already been given in paragraph 8 in the Scope section. Guidance for setting up such a test is given with the experiment suggested below.

Selection of optimal soil/solution ratios

46.   Two soil types and three soil/solution ratios (six experiments) are used. One soil type has high organic carbon and low clay content, and the other low organic carbon and high clay content. The following soil to solution ratios are suggested. However, the absolute mass of soil and volume of aqueous solution corresponding to these ratios can be different with respect to laboratory facilities:

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

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

48.   One control sample with only the test substance in 0.01 M CaCl$_2$ 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 CaCl$_2$ solution and its possible adsorption on the surfaces of the test vessels.

49.   A blank run per soil with the same amount of soil and total volume of 50 cm^3 0.01 M CaCl$_2$ solution (without test substance) is subjected to the same test procedure. This serves as a background control during the analysis to detect interfering compounds or contaminated soils.

50.   All the experiments, including controls and blanks, should be performed at least in duplicate. The total number of the samples which should be prepared for the study can be calculated with respect to the methodology which will be followed (paragraphs 57-58).

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

52.   The air-dried soil samples are equilibrated by shaking with a minimum volume of 45 cm^3 of 0.01 M CaCl$_2$ 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 cm^3. This volume of the stock solution added: (a) should not exceed 10% of the final 50 cm^3 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 (C$_0$) 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 (C$_0$) not exceed half of its solubility limit.

53.   An example of how to calculate the concentration of the stock solution (C$_{st}$) 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 cm^3 0.01 M CaCl$_2$ equilibration solution (= 10% of the stock solution to 50 cm^3 total volume of aqueous phase), the concentration of the stock solution should be 10 µg cm^{-3}; this is three orders of magnitude higher than the detection limit of the analytical method.

54.   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.

55.   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.

56.   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 6). 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.

57.   (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 h, etc.

58.   (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.

59.   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 6) are generated in order to estimate the achievement of

equilibrium plateau[2]. 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 the Data and Reporting section and in Annex 6.

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

60.   As already mentioned in paragraph 59, 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 Annex 6 show examples of such plots. Equilibration time is the time the system needs to reach a plateau.

61.   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.

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

62.   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 generally reduce this adsorption.

63.   Additional information on the stability of the test substance can be derived by determination of the parental mass balance over time. This means that the aqueous phase and extracts of the soil and test vessel walls are 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 and 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 time period of the experiment.

64.   The mass balance is carried out 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 section). If it is less than

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[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 6).

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 unstability of the test substance; in this case it is recommended to analyse both phases in the main study.

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

65.   Five soils are used, selected using the guidance given in 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.

66.   The equilibration time, the soil/solution ratio, the weight of the soil sample, the volume of the aqueous phase in contact with the soil and the concentration of the test substance in the solution are chosen based on 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.

67.   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 CaCl$_2$ 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 CaCl$_2$ solution (without soil) is subjected to the same test procedure, serving to safeguard against the unexpected. The test runs as described in paragraphs 52-59.

68.   The percentage adsorption is calculated at each time point A_{t_i} and/or time interval $A_{\Delta t_i}$ (according to the needs of the study) and is plotted 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 and discussion of the adsorption kinetics test

69.   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 ≤ 1 cm^3 g^{-1} are considered to be qualitatively mobile. Similarly, a mobility classification scheme based on K_{oc} values has been developed by McCall *et al*. (16). Additionally, leaching classification schemes exist based on a relationship between K_{oc} and DT-50[3] (32)(79).

70.   Also, according to error analysis studies (61), K_d values below 0.3 cm^3 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 accurancy) soil/solution ratio is applied, i.e. 1:1. In this case analysis of both phases, soil and solution, is recommended.

71.   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 Guideline. 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).

Tier 3 - Adsorption isotherms and desorption kinetics/desorption isotherms

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

Adsorption isotherms

72.   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 in paragraphs 47-58, 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

73.   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).

Desorption kinetics

74.   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.

75.   Likewise with the adsorption kinetics study, there are two options to proceed with the desorption kinetics experiment: (a) the parallel method and (b) the serial method. The choice of the methodology to be followed, is left to the experimenter who will need to consider the available laboratory facilities and resourses, keeping in mind the remarks made in paragraph 56.

76.   (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 $CaCl_2$ solution, without test substance, and of weight and volume, respectively, identical to those of the experiment. As a control sample the test substance in 0.01 M $CaCl_2$ 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 $CaCl_2$ 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.

77.   (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 $CaCl_2$ 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 $CaCl_2$ solution is added to the mixture to maintain the soil to solution ratio, and the agitation continues until the next time interval.

78. The percentage desorption is calculated at each time point D_{t_i} and/or time interval $D_{\Delta t_i}$ (according to the needs of the study) and is plotted versus time. The desorption coefficient of K_{des} at equilibrium is also calculated. All applicable equations are given in Data and Reporting Section and Annex 6.

Results from desorption kinetics experiment

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

Desorption isotherms

80. 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" (paragraph 76 or 77), 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 6).

DATA AND REPORTING

81. The analytical data are presented in tabular form (see Annex 7). Individual measurements and averages calculated are given. Graphical representations of adsorption isotherms are provided. The calculations are made as described in paragraphs 83-86.

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

Adsorption

83. 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:

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

(3)

where:

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

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

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

Detailed information how to calculate the percentage of adsorption A_{t_i} for the parallel and serial methods is given in Annex 6.

84.   The <u>distribution coefficient</u> 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.

$$(4)$$

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

where:

$C_s^{ads}(eq)$ =   content of the substance adsorbed on the soil at adsorption equilibrium ($\mu g \, g^{-1}$);

$C_{aq}^{ads}(eq)$ =   mass concentration of the substance in the aqueous phase at adsorption equilibrium ($\mu g \, cm^{-3}$); this concentration is analytically determined taking into account the values given by the blanks.

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

$m_{aq}^{ads}(eq)$ =   mass of the test substance in the solution at adsorption equilibrium (μg);

m_{soil} =   quantity of the soil phase, expressed in dry mass of soil (g);

V_0 =   initial volume of the aqueous phase in contact with the soil (cm^3).

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

$$(5)$$

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

where:

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

86.   The <u>organic carbon normalized adsorption coefficient</u> K_{oc} relates the distribution coefficient K_d to the content of organic carbon of the soil sample:

$$(6)$$

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

where:

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

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

Adsorption isotherms

87.   The <u>Freundlich adsorption isotherms</u> 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:

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

The Freundlich adsorption equation is shown in (8):

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

or in the linear form:

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

where:

K_F^{ads} = Freudlich 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 nonlinear.

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.
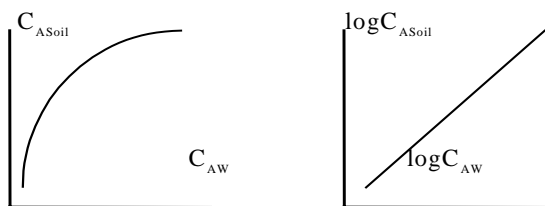
Fig. 2 Freundlich Adsorption Plot, normal and linearized

Mass balance

88.   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.

89.   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.

90.   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:

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

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 (µg cm^{-3});

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

Desorption

91.   The <u>desorption</u> is defined as the percentage of the test substance which is desorbed, related to the quantity of substance previously adsorbed, under the test conditions:

$$D_{t_i} = \frac{m_{aq}^{des}(t_i)}{m_s^{ads}(eq)} \cdot 100 \quad (\%)$$ (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 6.

92.   The <u>apparent desorption coefficient</u> (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 <u>desorbed</u> substance in the aqueous solution, when desorption equilibrium is reached:

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

where:

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

$m_{aq}^{des}(eq)$ = 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 6 under the heading "Desorption".

Remark

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

Desorption isotherms

93.   The <u>Freundlich desorption isotherms</u> 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).

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

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

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

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

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);

$m_{aq}^{ads}(eq)$ = mass of the substance in the solution at adsorption equilibrium (μg);

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

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 attainement 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):

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

or in the linear form:

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

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

TEST REPORT

95.   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 solubilizing 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 7) and graphical presentations;
- all information and observations helpful for the interpretation of the test results.

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ANNEX 1

TESTING SCHEME
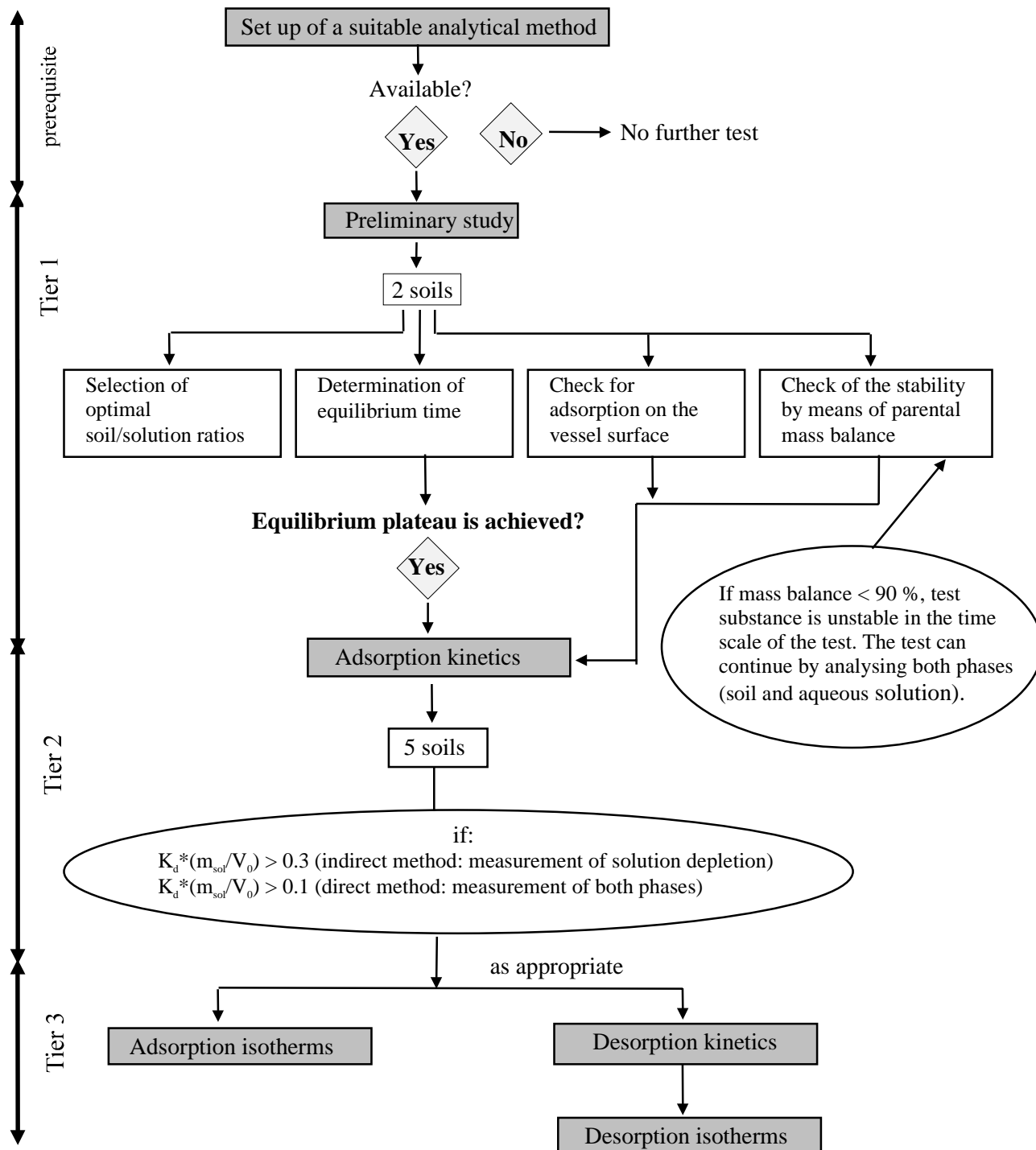
ANNEX 2

DEFINITIONS AND UNITS

Symbol	Definition	Units
A_{t_i}	adsorption percentage at the time point t_i	%
A_{eq}	adsorption percentage at adsorption equilibrium	%
$m_s^{ads}(t_i)$	mass of the test substance adsorbed on the soil at the time t_i	µg
$m_s^{ads}(\Delta t_i)$	mass of the test substance adsorbed on the soil during the time interval Δt_i	µg
$m_s^{ads}(eq)$	mass of the substance adsorbed on the soil at adsorption equilibrium	µg
m_0	mass of the test substance in the test tube, at the beginning of the adsorption test	µg
$m_m^{ads}(t_i)$	mass of the substance measured in an aliquot (v_a^A) at the time point t_i	µg
$m_{aq}^{ads}(eq)$	mass of the substance in the solution at adsorption equilibrium	µg
m_{soil}	quantity of the soil phase, expressed in dry mass of soil	g
C_{st}	mass concentration of the stock solution of the substance	µg cm^{-3}
C_0	initial mass concentration of the test solution in contact with the soil	µg 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	µg cm^{-3}
$C_s^{ads}(eq)$	content of the test substance adsorbed on soil at adsorption equilibrium an equilibrium	µg g^{-1}
$C_{aq}^{ads}(eq)$	mass concentration of the substance in the aqueous phase at adsorption equilibrium	µg 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	cm^3 g^{-1}
K_{oc}	organic carbon normalized adsorption coefficient	cm^3 g^{-1}
K_{om}	organic matter normalized distribution coefficient	cm^3 g^{-1}
K_F^{ads}	Freundlich adsorption coefficient	µg$^{1-1/n}$ (cm^3)$^{1/n}$ 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	cm^3 g^{-1}

Symbol	Definition	Units
K_F^{des}	Freundlich desorption coefficient	$\mu g^{\,1-1/n}\,(cm^3)^{1/n}\,g^{-1}$
$m_{aq}^{des}(t_i)$	mass of the test substance desorbed from soil at the time t_i	μg
$m_{aq}^{des}(\Delta t_i)$	mass of the test substance desorbed from soil during the time Δt_i	μg
$m_m^{des}(eq)$	mass of substance determined analytically in the aqueous phase at desorption equilibrium	μg
$m_{aq}^{des}(eq$	total mass of test substance desorbed at desorption equilibrium	μg
$m_s^{des}(\Delta t_i)$	mass of the substance remaining adsorbed on the soil after the time interval Δt_i	μg
m_{aq}^A	mass of the test substance left over from the adsorption equilibrium due to incomplete volume replacement	μg
$C_s^{des}(eq)$	content of the test substance remaining adsorbed on the soil at desorption equilibrium	$\mu g\,g^{-1}$
$C_{aq}^{des}(eq)$	mass concentration of the substance in the aqueous phase at desorption equilibrium	$\mu g\,cm^{-3}$
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 attainement 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 tume (i), during the desorption kinetics experiment performed with the serial method	cm^3
V_r^i	volume of the solution taken from the tube (i) for the measurement of the test substance, in desorption kinetics experiment (parallel method)	cm^3
V_r^F	volume of the solution taken from the tube for the measurement of the test substance, at desorption equilibrium	cm^3
MB	mass balance	%
m_E	total mass of test substance extracted from the soil and walls of the test vessel in two steps	μg
V_{rec}	volume of the supernatant recovered after the adsorption equilibrium	cm^3
P_{ow}	octanol/water partition coefficient	
pKa	dissociation constant	
S_w	water solubility	$g\,l^{-1}$

ANNEX 3

Influence of Accuracy of Analytical Method and Concentration Change
on Accuracy of Adsorption Results

From the following table (part of ref. 84) it becomes obvious that when the difference between the initial mass ($m_0 = 110$ μg) and equilibrium concentration ($m_{aq}^{ads}(eq) = 100$ μg) 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 ($m_s^{ads}(eq)$) and of 52.4% in the calculation of the K_d.

Amount of soil m_{soil} =   10 g
Volume of solution V_0 =   100 cm³

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

(Leftmost vertical label: $m_o = 110$ μg or $C_o = 1.100$ μg / cm³)

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

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

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

$C_s^{ads}(eq)$ =   content of the test substance in the soil phase at equilibrium, μg g⁻¹;

$C_{aq}^{ads}(eq)$ =   mass concentration of the test substance in the aqueous phase at equilibrium, μg cm⁻³.

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

R‡   =   calculated error due to the analytical error R.

ANNEX 4

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:

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

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 see refs. 12 and 68.

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

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

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

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[*]   Draft OECD Test Guideline *"Estimation of Adsorption Coefficient (Koc) on Soil and on Sewage Sludge using High Performance Liquid Chromatography (HPLC)"* , July 1997.

ANNEX 5

Calculations for Defining the Centrifugation Conditions

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

$$t = \frac{9}{2} \left[\frac{\eta}{\omega^2 \, r_p^2 (\rho_s - \rho_{aq})} \right] \ln \left(\frac{R_b}{R_t} \right) \tag{1}$$

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

where:

ω =   rotational speed ($= 2\pi\, rpm/60$), rad s^{-1};

rpm   =   revolutions per minute;

η =   viscosity of solution, g s^{-1} 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, $\eta = 8.95 \times 10^{-3}$ g s^{-1}cm^{-1} and $\rho_{aq} = 1.0$ g cm^{-3}.

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

$$t = \frac{3.7}{(rpm)^2 \cdot r_p^2 (\rho_s - 1)} \ln \frac{R_b}{R_t} \tag{2}$$

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.

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 descrbided 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 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 described in the following paragraphs should be also be modified accordingly, in order all three phases to be subjected to substance analysis.
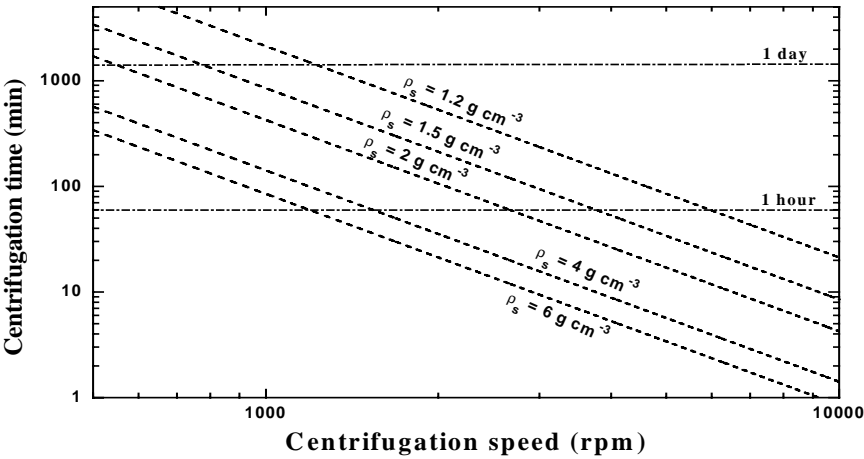
Fig. 1a   Variations of centrifugation time (t) versus centrifugation speed (rpm) for different soil densities (ρ_s). R_t = 10 cm, R_b -R_t = 10 cm, η = 8.95 x 10^{-3}g s^{-1}cm^{-1} and ρ_{aq} = 1.0 g cm^{-3} at 25°C.
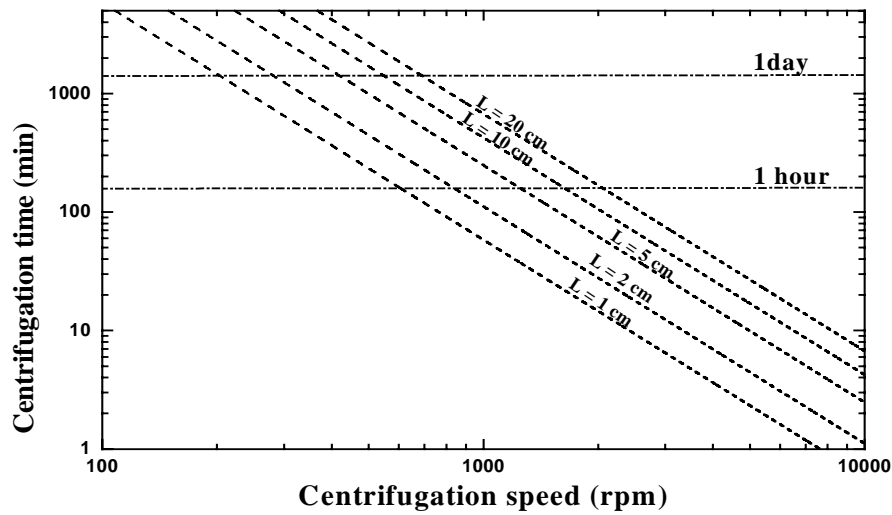
Fig. 1b Variations of centrifugation time (t) versus centrifugation speed (rpm) for different lengths of the mixture in the centrifuge tube (Rb -Rt) = L; R_t = 10 cm, η = 8.95 x 10^{-3}g $s^{-1}cm^{-1}$, ρ_{aq} = 1.0 g cm^{-3} at 25°C and ρ_s = 2.0 g cm^{-3}.

ANNEX 6

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

1.   The time scheme of the procedure is:
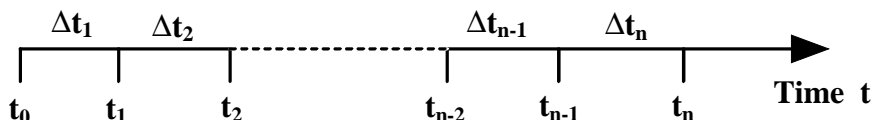
2.   For all the calculations it is assumed that the test substance is stable and does not adsorb significantly to the container walls.

ADSORPTION A(%)

a) Parallel method

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

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

The terms of this equation may be calculated as follows:

$$m_0 = C_0 \cdot V_0 \ (\mu g) \qquad\qquad (2)$$

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

where:

A_{t_i}	=	adsorption percentage (%) at the time point t_i;
$m_s^{ads}(t_i)$	=	mass of test substance on soil at the time t_i that the analysis is performed (µg);
m_0	=	mass of test substance in the test tube, at the beginning of the test (µg);
C_0	=	initial mass concentration of the test solution in contact with the soil (µg 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 (µg 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 $C_{aq}^{ads}(t_i)$ 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.

[‡] Equations applicable to both direct and indirect methods . All the other equations are applicable only to indirect method.
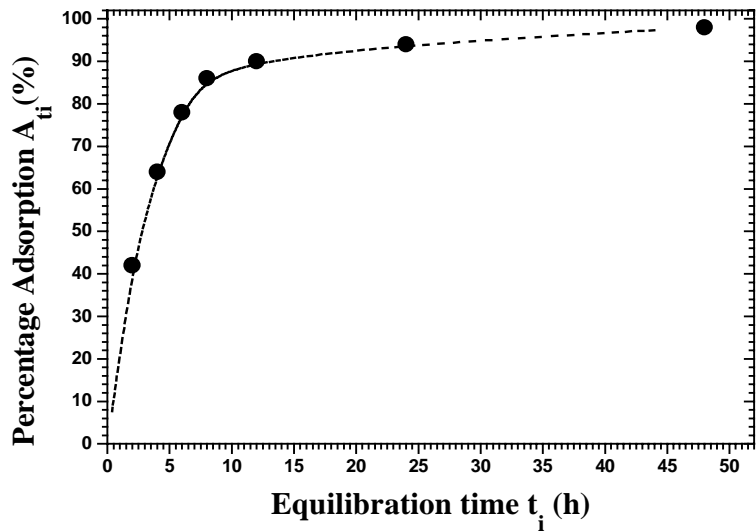
Fig. 1 Adsorption Equilibrium Plot
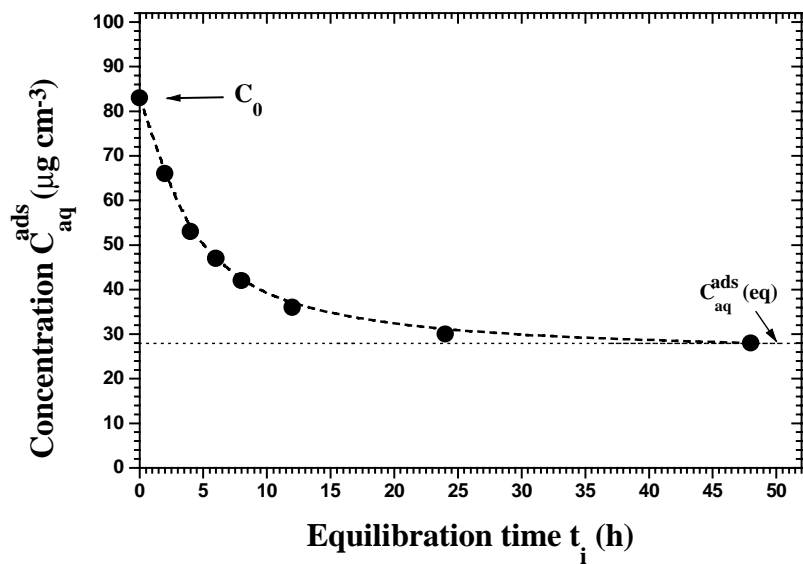
Fig. 2 Mass concentration of the test substance in the aqueous phase (C_{aq}) versus time

b) Serial method

4.   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 $\Delta t_1 = t_1 - t_0$

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

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

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

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

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

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

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

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

$$A_{\Delta t_i} = \frac{m_s^{ads}(\Delta t_i)}{m_0} \cdot 100 \quad (\%) \tag{8}[‡]$$

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

$$A_{t_i} = \frac{\sum_{j=\Delta t_1}^{\Delta t_i} m_s^{ads}(j)}{m_0} \cdot 100 \quad (\%) \tag{9}[‡]$$

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:

$$m_s^{ads}(eq) = \sum_{\Delta t_i = 1}^{n} m_s^{ads}(\Delta t_i) \tag{10}[‡]$$

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

$$m_{aq}^{ads}(eq) = m_0 - \sum_{\Delta t_i = 1}^{n} m_s^{ads}(\Delta t_i) \tag{11}[‡]$$

- and the percentage of adsorption at equilibrium is:

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

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

The parameters used above are defined as :

$m_s^{ads}(\Delta t_1), \; m_s^{ads}(\Delta t_2), \ldots, m_s^{ads}(\Delta t_n)$	=	mass of the substance adsorbed on the soil during the time intervals Δt_1, Δt_2,..., Δt_n respectively (µg);
$m_m^{ads}(t_1), \; m_m^{ads}(t_2), \ldots, m_n^{ads}(t_n)$	=	mass of the substance measured in an aliquot (v_a^A) at the time points t_1, t_2,..., 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 at a time interval Δt_i (%);
A_{eq}	=	percentage of adsorption at adsorption equilibrium (%).

DESORPTION D (%)

5.   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

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

$$m_{aq}^{des}(t_i) = m_m^{des}(t_i) \cdot \left(\frac{V_0}{V_r^i}\right) - m_{aq}^A \tag{13}$$

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:

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

7.   The percentage of desorption is calculated:

• at a time point t_i from the equation:

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

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

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

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 intervals 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_r^i, which is taken for the analysis (µg);

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

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

$m_{aq}^{ads}(eq)$ = mass of the test substance in the solution at adsorption equilibrium (µg);

V_R = volume of the supernatant removed from the tube after the attainement of adsorption equilibrium and replaced by the same volume of a 0.01 M $CaCl_2$ solution (cm^3);

V_r^i = volume of the solution taken from the tube (i) for the measurement of the test substance, in desorption kinetics experiment (cm^3).

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

b) Serial method:

8.   The following equations take into account that the adsorption procedure, which was preceded, was carried out by measurements of the test substance in small aliquots (v_a^A) of the aqueous phase (serial method, paragraph 58). It is assumed that: a) the volume of the supernatant removed from the tube after the adsorption kinetics experiment was replaced by the same volume of 0.01 M $CaCl_2$ solution (V_R) and b) the total volume of the aqueous phase in contact with the soil (V_T) during the desorption kinetics experiment remains constant and is given by the equation:

$$V_T = V_o - \sum_{i=1}^{n} v_a^A(i) \tag{18}$$

9.   <u>At a time point t_i:</u>

- 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:

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

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

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

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

10. 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 $\Delta t_1 = t_1 - t_0$

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

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

$$m_{aq}^{des}(\Delta t_2) = m_m^{des}(t_2) \cdot \left(\frac{V_T}{v_a^D}\right) - m_{aq}^{des}(\Delta t_1) \cdot \left(\frac{\left(V_T - v_a^D\right)}{V_T}\right) - m_{aq}^A \cdot \left(\frac{\left(V_T - v_a^D\right)}{V_T}\right) \quad \text{and} \tag{22}$$

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

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

$$m_{aq}^{des}(\Delta t_n) = \left[m_m^{des}(t_n) \cdot \left(\frac{V_T}{v_a^D}\right) - m_{aq}^A \cdot \left(\frac{\left(V_T - (n-1) \cdot v_a^D\right)}{V_T}\right) - \sum_{i=1, n\neq 1}^{n-1} \left(\frac{\left(V_T - (n-i) \cdot v_a^D\right)}{V_T} \cdot m_{aq}^{des}(\Delta t_i)\right)\right] \tag{23}$$

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

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

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

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

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

where the above used parameters are defined as :

$m_s^{des}(\Delta t_1),\, m_s^{des}(\Delta t_2),\ldots,m_s^{des}(\Delta t_n)$	=	mass of the substance remaining adsorbed on the soil after the time intervals Δt_1, Δt_2,..., Δt_n respectively (µg);
$m_{aq}^{des}(\Delta t_1),\, m_{aq}^{des}(\Delta t_2),\ldots,m_{aq}^{des}(\Delta t_n)$	=	mass of the test substance desorbed during the time intervals Δt_1, Δt_2,..., Δt_n respectively (µg);
$m_m^{des}(t_1),\, m_m^{des}(t_2),\ldots,m_m^{des}(t_n)$	=	mass of the substance measured in an aliquot (v_a^D) at time points t_1, t_2,..., t_n, respectively (µg);

V_T = total volume of the aqueous phase in contact with the soil during the desorption kinetics experiment performed with theserial method (cm^3);

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

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

V_R = volume of the supernatant removed from the tube after the attainement 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);

$$v_a^D \le 0.02 \cdot V_T \qquad (27)$$

ANNEX 7

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 of $CaCl_2$ sol.	cm^3	
Nominal conc. final sol.	$\mu g\ cm^{-3}$	
Analytical conc. final sol.	$\mu g\ cm^{-3}$	

Principle of the analytical method used:

Calibration of the analytical method:

Substance tested:

Soil tested:

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

Temperature: ……………………………………………………………………………………………………°C

Analytical methodology followed: Indirect ☐   Parallel ☐   Serial ☐

                                         Direct ☐

Adsorption test: test samples

	Symbol	Units	Equilibration Time		Equilibration Time		Equilibration Time		Equilibration Time	
Tube No.										
Weighed soil	-	g								
Soil: dry mass	m_{soil}	g								
Water vol. in weighed soil (calculated)	V_{ws}	cm^3								
Vol. 0.01 M CaCl, to equilibrate soil		cm^3								
Vol. stock solution		cm^3								
Total volume of aq. phase in contact with soil	V_0	cm^3								
Initial concentration Test solution	C_0	µg cm^{-3}								
Mass test subst. at beginning of test	m_0	µg								
After agitation and centrifugation										
Indirect Method										
Parallel method										
Conc. test subst. aq. phase Blank correction included	$C_{aq}^{ads}(t_i)$	µg cm^{-3}								
Serial method										
Measured mass test subst. in aliquot v_a^A	$m_m^{ads}(t_i)$	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_d	cm^3 g^{-1}								
Means										
Adsorption coefficient	K_{oc}	cm^3 g^{-1}								
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 soil		g					0	0
Water amount in weighed soil (calculated)		cm³					-	-
Volume of 0.01 M CaCl₂ solution added		cm³						
Volume of the stock solution of the test substance added		cm³	0	0				
Total volume of aq. phase (calculated)		cm³					-	-
Initial concentration of the test substance in aqueous phase		µg cm⁻³						
After agitation and centrifugation								
Concentration in aqueous phase		µg cm⁻³						

Remark: Add columns if necessary

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

Mass balance

	Symbol	Units				
Tube No.						
Weighed soil	-	g				
Soil: dry mass	ms_{oil}	g				
Water volume in weighed soil (calculated)	V_{ws}	ml				
Vol. 0.01 M $CaCl_2$ sol. to equilibrate soil		ml				
Volume of stock solution		cm^3				
Total vol. of aq. phase in contact with soil	V_0	cm^3				
Initial concentration Test solution	C_0	$\mu g\,cm^{-3}$				
Equilibration time	-	h				
After agitation and centrifugation						
Conc. test subst. aq. phase at adsorption equilibrium blank correction included	C_{aq}^{ads} (eq)	$\mu g\,cm^{-3}$				
Equilibration time	t_{eq}	h				
Removed volume aq. phase	V_{rec}	cm^3				
Added volume of solvent	ΔV	cm^3				
1st extraction with solvent						
Signal analyzer in solvent	S_{E1}	var.				
Conc. test substance in solvent	C_{E1}	$\mu g\,cm^{-3}$				
Mass subst. extracted from soil & vessel walls	m_{E1}	μg				
2nd dilution with solvent						
Removed volume of solvent	ΔV_s	cm^3				
Added volume of solvent	$\Delta V'$	cm^3				
2nd extraction with solvent						
Signal analyzer solvent phase	S_{E2}	var.				
Conc. test subst. in solvent	C_{E2}	$\mu g\,cm^{-3}$				
Mass subst. extracted from soil & vessel walls	m_{E2}	μg				
Total mass test subst. extracted in two steps	m_E	μg				
Mass balance	MB	%				

Substance tested:
Soil tested:
Dry mass content of the soil (105°C, 12 h): .... %
Temperature: …………………………………………………………………………………………$^{\circ}$C

Adsorption isotherms

	Symbol	Units								
Tube No.										
Weighed soil	-	g								
Soil: dry mass	ms_{oil}	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										
Conc. test substance in aqueous phase, blank correction included	C_{aq}^{ads}(eq)	µg cm^{-3}								
Temperature		$^{\circ}$C								
Adsorbed mass per unit soil	C_s^{ads}(eq)	µg g^{-1}								

Regression analysis:

    value of K_F^{ads} :

    value of l/n:

    regression coefficient r^2:

Substance tested:

Soil tested:

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

Temperature: …………………………………………………………………………………………..$^{\circ}$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 PM	V_0	cm^3				
in contact with soil 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 solution taken from the tube (i) for PM	V_r^i	cm^3				
the measurement of the test substance 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