<u>**SCIENTIFIC COMMITTEE ON PLANTS**</u>   **SCP/KOC/002 - Final**

OPINION OF THE SCIENTIFIC COMMITTEE ON PLANTS ON METHODS FOR THE DETERMINATION OF THE ORGANIC CARBON ADSORPTION COEFFICIENT (K_{oc}) FOR A PLANT PROTECTION PRODUCT ACTIVE SUBSTANCE IN THE CONTEXT OF COUNCIL DIRECTIVE 91/414/EEC

(Opinion adopted by the Scientific Committee on Plants, 18 July 2002)

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B. TERMS OF REFERENCE

The Scientific Committee on Plants (SCP) is requested to respond to the following questions in the context of the Commission's work on the implementation of Council Directive 91/414/EEC[1] concerning the placing of plant protection products on the market.

Does the Committee agree that valid alternative method to the batch adsorption method exist for determining the organic carbon adsorption coefficient (K_{OC}) for active substances degrading rapidly in water? In addition the SCP is requested to provide specific guidance on the conditions that should trigger the use of alternative methods and on which alternatives are preferable.

C. OPINION OF THE COMMITTEE

The Committee recommends to assess firstly the environmental fate based on worst-case sorption properties of the test substance and to decide thereafter whether studies with alternative methods are necessary.

Soil column leaching studies can provide reliable and useful lower limits of the K_{OC} if the expected K_{OC} value is less than about 25 L/kg. Soil TLC studies are less reliable and are not recommended. HPLC[2] methods are based on the correlation between chromatographic parameters measured on one or more HPLC stationary phases and K_{OC}. To ensure a reliable result, K_{OC} values for a range of structurally related test substances have to be available. As this is not guaranteed, the Committee does not recommend HPLC[3] methods.

The Committee suggests that alternative methods should be triggered if more than 10% per day of the test substance is hydrolysed under the conditions of the batch adsorption study. This implies a hydrolysis half-life of shorter than 7 days.

For weakly sorbing substances (i.e. K_{OC} less than about 25 L/kg) the Committee prefers soil column studies and for the other substances the Committee prefers a

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[1] OJ No L 230 of 19.8.1991, p.1.
[2] High Performance Liquid Chromatography

batch adsorption study with an equilibration time that is short enough to prevent too much transformation.

A. TITLE

OPINION OF THE SCIENTIFIC COMMITTEE ON PLANTS ON METHODS FOR THE DETERMINATION OF THE ORGANIC CARBON ADSORPTION COEFFICIENT (K_{OC}) FOR A PLANT PROTECTION PRODUCT ACTIVE SUBSTANCE IN THE CONTEXT OF COUNCIL DIRECTIVE 91/414/EEC

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C. BACKGROUND

In certain circumstances the batch equilibrium adsorption method is unsuitable for determining the K_{oc} due to instability of the test substance in water under the study conditions.

Where the accuracy of the adsorption method is low, due to instability of the test substance, for example as shown by significant deviation[4] of the Freundlich coefficient (1/n) from 1.0, alternative methods should be used to determine K_{OC}.

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[4] A large range of 1/n is not necessarily evidence for low accuracy of the study. The variability of study conditions, including soil properties, should be taken into account.

Alternative methods have already been accepted by ECCO[5] 117 Experts in certain cases, for example for ETU[6] (major metabolite of EBDC[7] compounds), Phenmedipham and Desmedipham.

Alternative methods envisaged for determining the K_{OC} include:

- the derivation of K_{OC} from soil column studies

- the derivation of K_{OC} from soil TLC studies

- the provision of data using an HPLC method

Source documents made available to the Committee: none.

D. SCIENTIFIC BACKGROUND ON WHICH THE OPINION IS BASED

Question

Does the Committee agree that valid alternative method to the batch adsorption method exist for determining the organic carbon adsorption coefficient (K_{OC}) for active substances degrading rapidly in water? In addition the SCP is requested to provide specific guidance on the conditions that should trigger the use of alternative methods and on which alternatives are preferable.

Opinion:

The Committee recommends to assess firstly the environmental fate based on worst-case sorption properties of the test substance and to decide thereafter whether studies with alternative methods are necessary.

Soil column leaching studies can provide reliable and useful lower limits of the K_{OC} if the expected K_{OC} value is less than about 25 L/kg. Soil TLC studies are less reliable and are not recommended. HPLC methods are based on the correlation between chromatographic parameters measured on one or more HPLC stationary phases and K_{OC}. To ensure a reliable result, K_{OC} values for a range of structurally related test substances have to be available. As this is not guaranteed, the Committee does not recommend HPLC methods.

The Committee suggests that alternative methods should be triggered if more than 10% per day of the test substance is hydrolysed under the conditions of the batch adsorption study. This implies a hydrolysis half-life of shorter than 7 days.

For weakly sorbing substances (i.e. K_{OC} less than about 25 L/kg) the Committee prefers soil column studies and for the other substances the Committee prefers a batch adsorption study with an equilibration time that is short enough to prevent too much transformation.

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[5] European Commission Co-ordination
[6] Ethylenethiourea
[7] Ethylenebisdithiocarbamate

<u>Scientific background on which the opinion is based:</u>

Terms of reference

For test substances which degrade rapidly in water, the batch equilibrium adsorption method (Guideline OECD 106; see OECD, 2000a) which is proposed in Annex II point 7.2.1 of Directive 91/414/EEC appears to be unsuitable due to instability of the test substance under the study conditions. Where the accuracy of the adsorption method is low, due to instability of the test substance, for example as shown by significant deviation of the Freundlich coefficient, alternative methods may be better suited to determine the K_{OC} constant. Possible alternative methods identified by the experts at the peer review were:

- the derivation of K_{OC} from soil column studies

- the derivation of K_{OC} from soil TLC studies

- the provision of data using an HPLC method.

Can the Committee comment on the validity of these alternative methods for the derivation of the K_{OC} constant?
Can the Committee further provide its opinion concerning possible criteria that should trigger the use of alternative methods (e.g. a DT_{50} in water below a certain value) and on which alternative method is preferable?

1. Introduction

In batch equilibrium adsorption studies a substance is added to a soil-water suspension which is shaken sufficiently long (usually 24-48 h) to ensure sorption equilibrium. The sorption coefficient is calculated assuming that the decrease in the concentration in the liquid phase can be completely attributed to sorption to the solid phase. Other loss processes (such as degradation in the liquid phase) lead to a systematic overestimation of the measured sorption coefficient. If the degradation is very rapid, this systematic error becomes unacceptably large.

Before commenting on the validity of alternative methods, the Committee discusses the need for applying such alternative methods.

For assessment of leaching to groundwater and surface water within the peer review of active substances, a low sorption coefficient is worse than a high sorption coefficient. So if no reliable sorption studies are available, a first assessment may be based on a sorption coefficient of zero which is a realistic worst-case assumption (for anions "negative adsorption" is possible resulting from anion exclusion but this will only very rarely be of any environmental significance). Usually such a first assessment will show that safe uses exist for a rapidly degrading substance and no further information on adsorption is required (it will often be more appropriate to concentrate on the metabolites that are formed).

For assessment of exposure in surface water resulting from run-off, a high sorption coefficient leads to more sediment-associated run-off than a low sorption coefficient

whereas a low sorption coefficient leads to more run-off via the water phase. So for run-off, a first assessment without requiring an adequate sorption study is more complicated but in principle is possible using assessments for both low and high sorption coefficients. The Committee expects that also in this case such a first assessment based on worst-case sorption coefficients will often demonstrate safe uses.

2. Validity of alternative methods

2.1 The derivation of K_{OC} from soil column studies

A draft OECD guideline on leaching from soil column studies is available (OECD, 2000b). The guideline prescribes the use of sieved soil (mesh 2 mm) and recommends to apply a substance to the surface of soil columns with a length of 30 cm which have been wetted previously. Subsequently 200 mm of water is leached through the soil columns within a period of 48 h. At the end of the study the column is sliced into layers and the concentration of the pesticide in the soil layers and in the leachate is determined via appropriate extraction and analytical methods.

The most straightforward procedure to derive K_{OC} values from such studies is to apply simple chromatographic theory. This theory (see for instance Bolt, 1976) implies that the average penetration depth Z of a substance in soil can be described with

$$Z = W / (\theta + \rho \, C \, K_{OC})$$

in which W is the thickness of the applied water layer (m), θ is the volume fraction of water in the soil during the leaching, ρ is the dry bulk density of the soil (kg/L), C is the mass fraction of organic carbon of the soil and K_{OC} is the organic carbon adsorption coefficient (L/kg). This leads to the following equation for K_{OC}

$$K_{OC} = (W - \theta \, Z) / \rho \, C \, Z$$

Both systematic and random errors in K_{OC} may occur. We consider first the random errors. The quantities W, θ, ρ and C can be measured accurately[8]. So the measurement of the average penetration depth Z is mainly responsible for the random error in K_{OC}. K_{OC} is a strong function of Z as is illustrated by the following example. We assume that W = 200 mm, $\theta = 0.5$, $\rho = 1.5$ kg/L and C = 0.02 which are all realistic values. This results in the following relationship between Z and K_{OC}:

Z (cm)	K_{OC} (L/kg)
0	infinity
1	650

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[8] The Committee recommends that the final version of this OECD guideline includes reporting of the total mass of dry soil in the column because this is needed to calculate the dry bulk density (the draft version requires measurement of this mass to check the reproducibility of the packing procedure but not its reporting).

5	117
10	50
15	28
20	17
25	10
30	6

The guideline recommends slicing the soil columns into at least 5 segments of equal length (so 6 cm each). A typical value of the error in the average penetration depth will therefore be say 5 cm. The listed Z - K_{OC} combinations show that such a random error in Z may result in a random error in K_{OC} of about 100% for K_{OC} values below 100 L/kg and even considerably larger errors at higher K_{OC} values. However, a lower limit of K_{OC} can be obtained via estimating an upper limit of Z from the experimental data. E.g. if the 0-6 cm layer contains 40% of the total amount in the soil column and the 6-12 cm layer contains 40%, then the average penetration depth is only slightly deeper than 6 cm depth but the corresponding upper limit of Z is 12 cm.

We now consider systematic errors in K_{OC}. Rapid degradation of the substance during the leaching study should be no problem as long as the measured concentrations remain above the quantification limit. According to chromatographic theory, the shape of the relationship between the pesticide concentration and depth in the soil (which determines the average penetration depth Z) is not influenced by degradation if the degradation rate coefficient is uniform with depth. This is a plausible assumption because the soil has been sieved and because packing of the column is as uniform as possible (OECD, 2000b).

Another possible cause of a systematic error in K_{OC} is the limited time for sorption equilibration during the leaching study. It can be expected that contact between pesticide molecules and the solid phase in soil column experiments is more limited by diffusion in the liquid phase than in batch experiments with soil-water suspensions. As a result K_{OC} values obtained in 48-h soil column experiments will be lower than those obtained in soil-water suspensions. So this systematic error leads to an underestimation of K_{OC}.

It is concluded that soil column leaching studies as described by the OECD guideline can produce valid lower limits of K_{OC}. The underestimation of K_{OC} becomes considerable if K_{OC} exceeds 100 L/kg.

Recently, Xu et al. (1999) described an interesting new soil column technique for measuring sorption. They used small, densely packed soil columns that were integrated into an HPLC-system with aqueous solutions of the test substance as the mobile phase and soil as the stationary phase. Once the concentration in the effluent has become equal to the concentration in the influent, the soil column is rinsed with an appropriate extractant and the total mass present in the soil column is determined. From these measurements the content sorbed in the soil and the corresponding sorption coefficient can be calculated. Although a soil column is used, the principle of this measurement differs from that in the soil column studies based on OECD (2000b): Xu et al. (1999) measure sorption after a certain equilibration time whereas in the OECD soil column study movement is measured. As a result the effect of random errors in measured

quantities on the random error in the sorption coefficient is different for these two methods (e.g. the OECD method is suitable for weakly sorbing substances whereas the HPLC-system method is not). The Committee does not recommend this HPLC-system method because it has not yet been tested by various laboratories for a range of soils.

2.2 The derivation of K_{OC} from soil TLC studies

The Committee assumes that the procedure is followed as described by Helling (1971). A thin film of soil (about one millimetre thick, about 5 cm wide and 15 cm long) is coated on a glass plate. The soil film is dried. At one of the ends of the glass plate, radioactively labelled pesticide is applied in a spot with a diameter of 1-2 cm. Subsequently this end of the glass plate is wetted until the water front has moved over a distance of about 10 cm leading to pesticide movement via ascending chromatography. This takes usually a time period of 2 to 10 hours. Via autoradiography the movement of the pesticide with the water is determined and compared to the movement of the water front. The result of such studies are reported in terms of the retardation factor, R, which is defined as:

$$R_F = PF / WF$$

in which is PF the distance over which the pesticide front has moved during the chromatography process and WF is the distance over which the water front has moved during this process (so R_F is always between 0 and 1).

Results of soil TLC studies can be interpreted in principle via chromatographic theory following the same procedure as for the soil column leaching experiments. This leads to the following expression for K_{OC}:

$$K_{OC} = \theta (1 - R_F) / \rho C R_F$$

We assume that $\theta = 0.5$, $\rho = 1.5$ kg/L and $C = 0.02$ which are all realistic values. This results in the following relationship between R_F and K_{OC}:

R_F (-)	K_{OC} (L/kg)
0	infinity
0.1	117
0.25	50
0.5	17
0.75	6
1	0

First we consider the random error. Because the application spot has a diameter of 1-2 cm, errors in R_F of about 0.05 are very common. The listed R_F - K_{OC} combinations show

that such a random error in R_F may result in a very large error in K_{OC} if K_{OC} exceeds about 100 L/kg. However, if an upper limit of the depth of the pesticide front (PF) is derived from the experimental data, a lower limit of K_{OC} is generated.

Secondly we consider the systematic errors. Firstly there is only a limited contact time between solid and liquid phase which leads to an underestimation of the K_{OC}. Because the contact time between pesticide and solid phase is much shorter than with soil column studies, the systematic underestimation of K_{OC} in soil TLC studies will usually be larger than in soil column studies. Secondly, the equations from chromatographic theory are valid for the average transport distance whereas in soil TLC studies the distance of the front movement is measured. This leads to an overestimation of PF and R_F which results also in an underestimation of K_{OC}.

It is concluded that soil TLC studies as described by Helling (1971) can produce valid lower limits of K_{OC}. In general the underestimation will be larger than for soil column studies because there is more limited contact time between solid and liquid phases in soil TLC studies and because of the assessment of the distance of the front movement in soil TLC studies. The Committee expects that lower limits generated by soil TLC studies produce K_{OC} values that are close to zero for many substances.

Results of soil TLC studies can also be used to correlate R_F values with K_{OC} values. The procedure is then to perform soil TLC studies with the test substance and a few substances whose K_{OC} values are available. Thus the systematic underestimation of K_{OC} is avoided. However, the relationship between R_F and K_{OC} implies that such an approach can only work for K_{OC} values below 100 L/kg. Moreover it can be expected that the accuracy of such a method is low because the correlation between substances introduces additional errors.

2.3 The provision of data using an HPLC method

OECD (1998) provides a guidline on estimation of K_{OC} using an HPLC method. The principle of the method is that a linear relationship exists between chromatographic parameters (retention times or capacity factors) of solutes and the K_{OC} determined by batch equilibrium adsorption studies with soils. The chromatographic parameters are determined on an analytical column packed with cyanopropyl-modified silica gel stationary phase, which is a moderately polar phase containing both polar and lipophilic moieties, eluted under isocratic conditions with methanol:water mixtures for neutral substances or methanol:citrate-buffer (pH 6.0) mixtures for ionizable substances. This is done for the test substance and six reference substances whose K_{OC} values should be available. The guideline states that the reference substances should be preferably structurally related to the test substance. The K_{OC} of the test substance is then estimated via correlation between retention times and K_{OC} values of the test compounds. However, it will usually be difficult to find reference substances that are structurally related and have well known K_{OC} values. In any case there will be considerable uncertainty because K_{OC} is estimated via correlation based on a property in an artificial system and not on studies with soils.

2.4 The measurement of K_{OC} via the batch equilibration method using a short equilibration time

The Committee suggests another alternative method, i.e. a batch method with a shorter equilibration time. The principle of this method is to limit the equilibration time to such an extent that the transformation remains less than 10%. This time may be based on a

separate test in which the decline of the test substance during the batch adsorption study is measured. The only disadvantage of this study over the conventional batch method is that the measured K_{OC} is a lower limit (because of the systematic error resulting from the shorter equilibration time). However, studies on adsorption kinetics in batch systems have shown that a large fraction of the decrease in the concentration in liquid phase takes place in the first 0.5 h (see e.g. Hance, 1967). So the systematic error of this method because of the shorter equilibration time will usually be limited. It is recommended to perform the study at the highest solid-liquid ratio that is practically feasible because adsorption kinetics proceed faster at higher solid-liquid ratios (Boesten & Van der Pas, 1991). Based on available sorption kinetic studies, the Committee expects that the underestimation of K_{OC} using a shaking time as short as 0.5 h is less to a factor two. The method is suitable for moderately and strongly sorbing compounds.

The OECD guideline 106 (OECD, 2000a, p. 12) suggests another modification in case of rapid transformation. It claims that the batch adsorption method can still be used if the test substance is unstable via determining both the concentration in the liquid phase and the content sorbed via extraction of the solid phase. However, in case of rapid degradation in the liquid phase the partitioning between solid and liquid phase will often be measured under desorption conditions which would lead to an overestimation of the sorption coefficient.

The Committee prefers its own suggestion because it is usually preferable to have a lower limit than to be uncertain whether an upper or lower limit was obtained.

3. Possible criteria for triggering the use of alternative methods

The use of alternative methods (i.e. other than the batch adsorption method of OECD Guideline 106) should be triggered if the degradation during the study would result in a too large systematic error in the sorption coefficient. The relative error in K_{OC} (denoted with the symbol r_K) is the following function of the relative error in the pesticide mass in the system, r_m:

$$r_K = (1 + 1/P) \, r_m$$

in which P is a dimensionless quantity defined by $P = M K / V$ in which M is the mass of solid phase in the system, K is the sorption coefficient (equal to the product of C and K_{OC}) and V is the volume of liquid phase (Boesten, 1990). The equation shows that an overestimation in the pesticide mass leads also to an overestimation in the K_{OC}. Additionally it shows that the relative error in K_{OC} is always larger than the relative error in the pesticide mass.

The OECD 106 guideline requires a mass balance experiment that should give at least 90% recovery of the substance. This implies that the relative error r_m is less than 10%. This is a pragmatic and defensible choice. The guideline recognises (in its item 71) that the batch adsorption method is only accurate enough if P exceeds 0.3. The above equation indicates that this results in an upper limit of the relative error in K_{OC} of 0.4 (so 40%). This is defensible because a recovery of 90% will usually not imply 10% transformation but more likely be the result of imperfect extraction and analytical methods.So 10% transformation seems a reasonable upper limit for the batch adsorption method. It is difficult to predict transformation rates in the sorption system (i.e. a soil-water suspension that is shaken continuously) from the standard transformation rate studies with topsoils. So it is better to base such a criterion on available hydrolysis rates

(as suggested in the terms of reference). This implies that the hydrolysis rate under the temperature and pH conditions of the batch adsorption study should be estimated from the available hydrolysis rates.

So the suggestion is to trigger alternative methods if more than 10% per day is hydrolysed under the conditions of the batch adsorption study. This implies a hydrolysis half-life of shorter than 7 days.

A trigger of alternative methods is only relevant for reducing experimental efforts. If transformation during the OECD 106 study would be faster than expected on the basis of hydrolysis, this will be discovered via the mass balance check prescribed within OECD 106.

4. Which alternative method is considered preferable?

For weakly sorbing substances (i.e. K_{OC} less than about 25 L/kg) the Committee prefers soil column studies and for the other substances the Committee prefers a batch study with an equilibration time that is short enough to prevent too much transformation. This implies that the expected K_{OC} has to be roughly estimated a priori from available information. For this estimation a number of methods are available (see Wauchope et al., 2002, for a recent review).

Both recommended alternative methods lead to lower limits of K_{OC}. The uncertainty resulting from this can be dealt with in the exposure assessment via sensitivity analysis of model output for K_{OC}.

E. REFERENCES

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