HARMONISATION OF LEACHING RATE DETERMINATION FOR ANTIFOULING PRODUCTS UNDER THE BIOCIDAL PRODUCTS DIRECTIVE

Workshop Report
Ispra, Italy, 12 December 2006

A workshop for technical experts evaluating active substances used in antifouling products for the Competent Authorities implementing the Biocidal Products Directive, assessing the leaching from ship hulls to the environment.

This workshop report was endorsed at the 26th meeting of representatives of Members States Competent Authorities for the implementation of Directive 98/8/EC concerning the placing of biocidal products on the market (11-14 September 2007).

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Introduction

Directive 98/8/EC of the European Parliament and of the Council on the placing on the market of biocidal products was adopted in 1998. Two basic principles of the Directive are:

- Active substances have to be assessed and the decision on their inclusion into Annex I of the Directive shall be taken at Community level;
- Member States (MS) shall authorise the biocidal products in accordance with the rules and procedures set in Annex VI of the Directive. They can only authorise products which contain active substances included in Annex I.

The time limit for transposition of the Directive in MS was 14 May 2000. Active substances introduced on the market after this date are already subject to the provisions of the Directive. At this same date a 10-year review program of active substances already on the market (so-called existing active substances) was started. The aim of the program is to assess all active substances that were already on the market before 14 May 2000. Guidance on the assessment of active substances and biocidal products is laid down in the so-called Technical Notes for Guidance (TNsG).

Applicants for existing active substances used in antifouling products (product type (PT) 21) for which the notification was accepted, had to submit the complete dossier to the competent authorities of the Rapporteur Member State (RMS) before 30 April 2006. After this date the evaluation process of the RMS started, leading eventually to a decision on Annex I inclusion in the Competent Authorities meeting.

The assessment of environmental risks consists of an exposure and effects assessment, subsequently compared in the risk characterization. For active substances used in antifouling products the emission from the treated surface (for example ships hulls or fish nets used in aquaculture) is critical in the exposure assessment. Within the review program the guidance produced by the OECD entitled “Emission Scenario Document on Antifouling Products” is used (OECD, 2005). A critical input parameter for estimating the emission is the leaching rate, which is part of the additional data set for this product type. The OECD-ESD contains a chapter on the determination of the leaching rate. However, no guidance is given on how to derive the leaching rate to be used in the exposure assessment from the different testing and calculation methods available.

The progress of the review program is discussed in the Biocides Technical Meeting (TM). At several TMs the determination of the leaching rate was several times discussed. All the MS identified problems around this issue. Therefore, it was decided at the TM II 06 to send out a questionnaire to all RMS to collect the information available on leaching rate determination in the dossiers submitted by the applicants followed by a decision to discuss these findings in a separate workshop. Based on the information received via the questionnaires the UK drafted a document which was the basis for the discussions at the workshop.

The Leaching Rate Workshop took place 12 December 2006. The documents distributed for the workshop are listed in Annex I and the participants in Annex II. Representatives from all seven RMS for this PT participated as well as representatives

from industry. The meeting was chaired by K. Rasmussen from the European Chemicals Bureau (ECB). Rapporteur was E. van de Plassche from the ECB.

Setting the scene

The participants were welcomed by the chair K. Rasmussen.

The main objective of the workshop was: "to agree on an approach to derive the leaching rate to be used in the review program by the RMS for PT 21".

An introduction was given by E. van de Plassche (see Annex IV) on the backgrounds for organising the workshop, introducing the agenda and the documents distributed before the workshop. He thanked the UK for providing the discussion document "Harmonisation of leaching rate determination for antifouling products under BPD" based on the information received via the questionnaires. This document is included in this report as Annex III. Written comments were sent in by The European Council of the Paint, Printing Ink and Artists Colours Industry (CEPE) before the workshop.

The discussions at the workshop followed the items listed in the document provided by the UK, where "Initial proposals for a way forward" are indicated. The workshop report is structured according to these proposals.

Discussion on initial proposals

The following issues were discussed from the UK paper:

Issue 1

Based upon responses from MS, it is clear that the dossiers submitted for active substances used in PT21 rely heavily upon the CEPE calculation method to determine leaching rate for their supporting products. Therefore, in order to adopt a harmonised approach, MS should all accept the CEPE model as a means to mathematically derive leaching rates, provided that robust efficacy data are submitted to support the service life of the product used in the model.

The existing laboratory methods were discussed. There was overall agreement that the standardised ASTM and ISO (rotating cylinder) methods overestimate the leaching rate compared to the situation under field conditions (steady state conditions).

Next it was discussed if the CEPE mass-balance method can be used as a harmonised approach for deriving leaching rates. This method is discussed in Chapter 2.2 of the OECD-ESD (including a paper from CEPE describing the method in detail in Annex II). It was explained that the method is based on leaching rate determinations for copper and organotin containing antifouling paints using the ASTM and ISO methods. This data set included a range of oganotin copolymer and first-generation TBT-free antifouling paints. The method was originally derived from a data set of measurements of about 40 paints in total.

Several remarks were made with respect to the CEPE mass-balance method:

- The question was raised if the method can also be used for the type of antifouling paints which are used nowadays as the method is based on a data set containing among others data for organotin containing paints. CEPE stated that the data on which the method is based, are indeed also from paints which continue to be on the market. Once more data for paints currently on the market become available the CEPE mass-balance method can be re-evaluated.
- In contrast to the traditional paints with a high initial release rate, there are antifouling paints on the market with a low initial biocide release rate that increases during a number of days to reach a steady state level. This is in contrast to the pattern assumed in the mass balance method. The core issue is how long the initial phase is and what is the ratio between the initial and steady state leaching rate.

It was concluded that the CEPE mass-balance method can be accepted as the method to be used for deriving leaching rates for Annex I listing without any additional data requirements. The steady state leaching rate will be used as an input parameter in the scenarios described in the OECD ESD. Under product authorization further data can be requested to take into account specific environmental conditions.

Issue 2

In order for MS to confirm the leaching rate value determined by the CEPE model, it is imperative that the dossier includes information on all of the parameters required in the calculation, so that it is clear how the theoretical value was calculated. Where values such as the concentration of active substance in the biocidal product may be expressed as a range, then MS should assess leaching rate based upon the highest specified values.

This was agreed by the workshop.

Issue 3

Although most antifouling products may be applied as a single coat, some products may need to be applied 2 or 3 times to achieve a smooth finish with the necessary dry film thickness. It is essential that MS always determine the number of coats required for each antifouling product plus the predicted dry film thickness of each coat in order to ensure that the total dry film thickness is used in the CEPE calculation method (for example, if a product must be applied as 3 coats of 150 μm per coat, then the total dry film thickness used in the CEPE model must be 450 μm).

It was stated that these data should be available in the dossier submitted by the applicant.

Issue 4

The model requires an estimation of the active substance assumed to be released over the lifetime of the paint (L_a) and whilst regulating antifouling products under national legislation, the UK is aware that CEPE have suggested a typical loss of only 70%. However, considering that most coating types work by erosion/polishing of the existing paint layer to expose new layers containing active substance, the UK believes that such a value could be a considerable underestimate as products would still be effective until the very last layer was exposed. As such, the potential release of biocide over lifetime of the paint would be much nearer 100%. It is evident from published literature that erosion on some parts of the hull occurs more slowly than other areas, so not all of the active substance would be released at the end of the service life of the paint. Therefore, whilst the UK cannot support a loss of 70% of active substance, we also consider that 100% loss is unrealistic. Therefore, we suggest that the determination of leaching rate be based upon anticipated loss of 90 % of active substance into the environment (L_a of 0.90).

It was agreed to set the anticipated loss to 90% as a default value until data could be provided to support the use of an alternative value.

Issue 5

Representatives for the antifouling industry gave a brief presentation on the CEPE calculation method at the Technical Meeting on 27 – 31 March 2006 (TM-I-06) indicating that the trade association had evidence to support their conclusion that the CEPE model overestimated actual leaching rate over the service life of a product by a factor of 4.0 – 11.6 (and the ASTM/ISO by a factor of 10.0 – 25.0). As a consequence, CEPE proposed correction factors of 2.9 for leaching rates derived from their model and 5.4 if derived using the ASTM/ISO method.

The proposed correction factors are based on measurements of the leaching rate using the US Navy Dome Method. CEPE proposed that a correction factor of 2.9 is used for leaching rates calculated with the CEPE mass-balance method.

Measurements using the US Navy Dome Method are available for six different antifouling paints and for copper only. It was argued that this data set is too limited to accept the use of a correction factor. In addition it shall be considered that the measurements with the US Navy Dome Method are measurements in a static situation when the ships are moored in a harbor. CEPE mentioned it has to be considered that the correction factors proposed are based on 95% confidence intervals of the data available. Nevertheless, it is considered important that the size of the correction factor is further investigated and validated. Until information is available from such validation, the factor 2.9 may be used.

A proposal was made and agreed to carry out the first tier of the risk assessment without a correction factor. If the PEC/PNEC ratio at tier 1 is higher than one a correction factor of 2.9 is applied at a second tier. However, this correction factor of 2.9 was only accepted for the marina scenario and not for the other scenarios. The factor of 2.9 was derived by comparing results from the CEPE calculation method to the field results using the US Navy Dome method. Since the dome can only be attached to a boat that is not moving, this comparison was accepted only for boats moored in a marina. CEPE believed that this correction factor is also applicable to harbour scenarios as the US Navy Dome data was taken directly from ship measurements in a harbour. If the PEC/PNEC ratio at tier 2 is lower than one, additional data are needed to support this conclusion in a weight of evidence approach. In case the PEC/PNEC ratio still is above one when applying a correction factor of 2.9 at tier 2, non-inclusion into Annex I should be suggested for this scenario and the final decision should be taken at CA-level.

Issue 6

In Nordic countries where boats may be stored on land when waters freeze over, constant long-term release of biocide derived by the CEPE model may underestimate the initial release of biocide when a large number of vessels return to the water when the ice breaks thus opening up waterways. The CEPE calculation discounts the initial surge of biocide release over the first 14 days of contact between paint film and water to concentrate on the steady release required to ensure product effectiveness over its service life.

It was discussed if there is a need for a specific scenario for the Nordic countries. In April the boats, which were stored on land during the winter, are repainted and then returned in the water. This usually occurs over a two week period. In national schemes this situation is taken into account. For example, in Finland this situation is specifically assessed using a leaching rate averaged over the first 14 days. The following remarks were made:

- It was questioned how specific this situation is as also in other countries boats are repainted and returned to the water. Percentages of 50% of the boats moored, and 50% boats taken out of the water to be repainted were mentioned. Some participants stated that the assessment should be limited to using the steady state leaching rate.
- If the CEPE mass-balance method is applied there is a 'fixed' ratio between the 14 days averaged leaching rate and the steady-state leaching rate of circa two. As this ratio is based on data for copper and organotin containing antifouling paints, the question was raised if there are other data available to support this ratio (for example for co-biocides).
- It was stated that, as the temperature is lower in the Nordic countries compared to the temperature used in the ASTM and ISO method on which results the CEPE mass-balance method is based, the higher leaching rate caused by returning freshly painted boats in the water may be compensated by this phenomenon. The effect of temperature on the leaching rate was shortly discussed. In one of the reports (Thomas and Waldock (2000)) provided by the UK for the workshop this effect was studied: no effects were observed for short-term (4 days) in contrast to long-term. CEPE indicated that for the effect the Arrhenius equation applies, however the system needs to re-equilibrate causing a time-lag before the effect is observed.
- The derivation of the PNEC for such an acute situation was shortly discussed. It was stated the current TGD does not provide guidance here, with the exception of intermittent release which is however not fully comparable to this situation for antifouling products.
- It was stated that the situation is also specific with respect to the fact that in the beginning of April the sensitive life stages of aquatic organisms may be present in marinas as it is the spawning season.

No conclusion could be reached for this issue at the workshop. In a follow-up discussion at the TM Biocides in February 2007 it was decided that a specific scenario will not be used in the Review Program. Such a scenario may be used in product authorization.

Conclusions

1. The CEPE mass-balance method will be used in the Review Program as the method to determine the steady state leaching rate. At product authorization stage the MS has the possibility to ask for additional data if considered necessary.

2. The anticipated loss of the active substance to the environment, La in the CEPE mass-balance method, is set at 90%.

3. The environmental exposure assessment will be carried out using the leaching rate calculated with the CEPE mass-balance method. If at this tier the PEC/PNEC for the marina scenario is higher than one, a correction factor of 2.9 can be applied for the marina scenario in a second tier. If the PEC/PNEC ratio is higher than 1 without a correction factor, but below 1 when using the correction factor of 2.9 a weight of evidence approach using additional information can be considered for the risk characterization. In case the PEC/PNEC ratio still is above one when applying a correction factor of 2.9 at tier 2, non-inclusion into Annex I should be suggested for this scenario and the final decision should be taken at the Competent Authority level.

4. In some countries pleasure crafts are taken out of the water in the winter season and returned to the water more or less simultaneously in spring. A large percentage of these boats will be repainted just before they return to the water. Such a scenario is not considered in the Review Program but may be used in product authorization.

Annex I: List of participants

MEMBER STATES

FI	Jaana Pasanen
FR	Sandrine Andres
IE	Brendan Dolan
NL	Roel Fleuren
NO	Susanne Hardt
SE	Markus Johansson
UK	Jennifer Hagan
UK	Chris Walton

INDUSTRY

Marianne Pereira
Alistair Finnie
Jack Poppleton

COMMISSION

Kirsten Rasmussen
Erik van de Plassche

Annex II: References

Alistair A. Finnie (2006). Improved estimates of environmental copper release rates from antifouling products. Biofouling **22**, 279-291.

CEPE (2006). Comment Document on the Leaching Rate Harmonisation Paper (Leaching rate document comECB.doc).

Comber, S. et al. (2001). Environmental modelling of antifoulants. Prepared by the Water Research Centre plc for the Health and Safety Executive. Contract Research Report 342/2001. ISBN 0 7176 2018 2.

OECD Environment, Health and Safety Publications Series on Emission Scenario Documents No. 13: Emission Scenario Document on Antifouling Products. Environment Directorate Organisation for Economic Co-operation and Development (OECD) and Inter-organisation Programme for the Sound Management of Chemicals (IOMC), Paris 2005, ENV/JM/MONO(2005)8 (including Annex).

Harmonisation of leaching rate determination for antifouling products under BPD. Discussion paper prepared by the UK, 6 November 2006

Thomas, K.V. and M.J. Waldock (2000). Effects of environmental factors on the leaching rates of biocides from antifoulants coatings. Prepared by CEFAS Burnham Laboratories for the Health and Safety Executive. Contract Research Report 292/2000. ISBN 0 7176 1848 X.

Annex III: UK Paper

HARMONISATION OF LEACHING RATE DETERMINATION FOR ANTIFOULING PRODUCTS UNDER BPD

Background

At the most recent Technical Meeting on 16 – 19 October 2006, the UK agreed to initiate discussions on harmonisation of leaching rate determination between those MS acting as rapporteur for active substances supported by dossiers in PT21 (namely Finland, France, Ireland, Netherlands, Norway, Sweden and UK).

This paper will focus on leaching rate determination only. Modelling of scenarios for risk assessment purposes will not be discussed. However, it is very important that a suitable leaching rate is available for use in these risk assessments. For an accurate assessment of the environmental impact of antifouling products, it is vital that the leaching rate of supporting products accurately reflects that of the paint under normal conditions of use.

Data submitted by participants to address leaching rate

In line with the Technical Notes for Guidance on dossier preparation and study evaluation, leaching rate determination is required under Doc III-B, Section 7.1 to address foreseeable routes of entry of active substances from biocidal products into the environment.

Leaching rate can be determined in three ways:

1) Laboratory studies
   Laboratory tests for the determination of active substance release rates based on standardised ASTM and ISO (rotating cylinder) methods were not designed to reflect “real life” situations in environmental risk assessments and are of more use in comparing the leaching rates of different paints. They are very simple, inexpensive tests that can be carried out to recognised standards but are known to considerably overestimate product leaching rate (typically by as much as 5 – 20 times) and results may not be reproducible.
   As testing need only last for 45 days, it may only determine the initial surge of biocide release when the paint film first comes into contact with water and may be too brief to detect the lower steady state release rate from products likely to be in service for $\geq$ 3 years.

2) Calculation methods (such as the CEPE (Conseil Europeen de l’Industrie des Peintures, des Encres d’Imprimerie et des Couleurs d’Art) mass-balance model)

The concept of a calculated leaching rate has been developed in order to compensate for the gross overestimation of rates derived by laboratory methods and the excessive cost of undertaking field tests. However, it is recognised that they also overestimate actual leaching rates, but are considered to be more representative than laboratory studies as they aim to consider typical leaching over the service life of a product.

The calculation method developed by CEPE is a simplified, generic model that assumes an initial 14-day burst of biocide release followed by a constant rate of leaching over the lifetime of the antifouling paint. Its basic principles are that the amount of active substance released into the environment cannot exceed the amount that is added to the paint and that the lifetime of the product can be supported by robust efficacy data. CEPE also believe that, in future, it may be possible to apply validated correction factors to their model to determine "real-life" rates of environmental emission from antifouling products.

3) Field tests (such as US Navy Dome Method)

These tests are conducted using the product that is likely to be placed on the market (where a small area of a ship's hull is painted with antifouling product and leaching rates measured over time by taking paint scrapings or water samples from the "dome") so can be expected to give reliable and realistic leaching rate measurements. However, these data are very expensive to generate and of limited statistical value due to the small number of data points and low reproducibility.

In an attempt to determine the level of information and type of data provided to each MS in support of the leaching rate determination of associated biocidal products, the UK has already contacted all MS who have received dossiers for active substances used in PT21. We would like to express our thanks to all MS for taking the time to complete the proforma.

Appendix I contains a summary of the information supplied by MS on each active substance and their supporting product(s). Some additional data will also be required to ensure that all of the parameters used in the CEPE calculation are included in order to ensure transparency and to permit duplicate calculations to be performed to confirm theoretical leaching rates.

Initial proposals for a way forward

a) Based upon responses from MS, it is clear that the dossiers submitted for active substances used in PT21 rely heavily upon the CEPE calculation method to determine leaching rate for their supporting products. Therefore, in order to adopt a harmonised approach, MS should all accept the CEPE model as a means to mathematically derive leaching rates, <u>provided</u> that robust efficacy data are submitted to support the service life of the product used in the model.

b) In order for MS to confirm the leaching rate value determined by the CEPE model, it is imperative that the dossier includes information on all of the parameters required in the calculation, so that it is clear how the theoretical value was calculated. Where values such as the concentration of active substance in the biocidal product may be expressed as a range, then MS should assess leaching rate based upon the highest specified values.

c) Although most antifouling products may be applied as a single coat, some products may need to be applied 2 or 3 times to achieve a smooth finish with the necessary dry film thickness. It is essential that MS always determine the number of coats required for each antifouling product plus the predicted dry film thickness of each coat in order to ensure that the total dry film thickness is used in the CEPE calculation method (for example, if a product must be applied as 3 coats of 150 μm per coat, then the total dry film thickness used in the CEPE model must be 450 μm).

d) The model requires an estimation of the active substance assumed to be released over the lifetime of the paint (L_a) and whilst regulating antifouling products under national legislation, the UK is aware that CEPE have suggested a typical loss of only 70%. However, considering that most coating types work by erosion/polishing of the existing paint layer to expose new layers containing active substance, the UK believes that such a value could be a considerable underestimate as products would still be effective until the very last layer was exposed. As such, the potential release of biocide over lifetime of the paint would be much nearer 100%. It is evident from published literature that erosion on some parts of the hull occurs more slowly than other areas, so not all of the active substance would be released at the end of the service life of the paint. Therefore, whilst the UK cannot support a loss of 70% of active substance, we also consider that 100% loss is unrealistic. Therefore, we suggest that the determination of leaching rate be based upon anticipated loss of 90 % of active substance into the environment (L_a of 0.90).

e) Representatives for the antifouling industry gave a brief presentation on the CEPE calculation method at the Technical Meeting on 27 – 31 March 2006 (TM-I-06) indicating that the trade association had evidence to support their conclusion that the CEPE model overestimated actual leaching rate over the service life of a product by a factor of 4.0 – 11.6 (and the ASTM/ISO by a factor of 10.0 – 25.0). As a consequence, CEPE proposed correction factors of 2.9 for leaching rates derived from their model and 5.4 if derived using the ASTM/ISO method.

However, the UK would propose that MS proceed with evaluation on the basis of uncorrected leaching rate values determined by either the CEPE model or ASTM/ISO method until such time as agreement has

been reached that sufficient validation of proposed correction factors has been submitted by industry.

f) So far, the UK has considered that MS should adopt a harmonised approach based upon the CEPE model to determine the typical leaching rate of active substance over the lifetime of the paint. However, in Nordic countries where boats may be stored on land when waters freeze over, constant long-term release of biocide derived by the CEPE model may underestimate the initial release of biocide when a large number of vessels return to the water when the ice breaks thus opening up waterways. The CEPE calculation discounts the initial surge of biocide release over the first 14 days of contact between paint film and water to concentrate on the steady release required to ensure product effectiveness over its service life.

   Could the CEPE model be relied upon to provide an estimation of initial releases into water over 14 days (component "X" of the equation given in $\mu g/cm^2$) or would additional laboratory data on release over 45 days derived from ASTM / ISO methods be required?

g) MS may therefore wish to consider a two-tiered approach to leaching rate determination and we need to discuss how such an approach may be achieved.
   Could applicants be required to undertake a CEPE calculation to provide chronic leaching rates over the service life of the product but undertake laboratory tests to provide acute leaching rates? It must be reiterated that the UK consider that ASTM/ISO are short-term tests used in the generation of efficacy data and must not be relied upon as a sole means of generating leaching data for use in long-term environmental risk assessment.

h) Following on from this, should a decision be made on what assessment factor should be used when deriving the PNEC in circumstances in which a large number of vessels may return to the water at specific locations over a short period of time? According to the TGD on risk assessment, a factor of 1000 may be required but is it appropriate to consider such an acute risk? According to the CEPE model (that is based upon the experiences of antifouling paint formulators) this initial surge of biocide release will slow after 14 days to a much lower, constant rate so would a lower assessment factor of 100 be more appropriate?

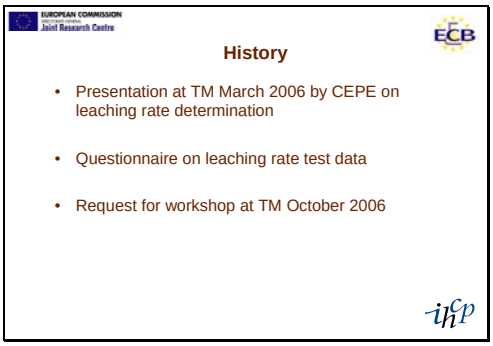
UK CA
6 November 2006

Annex IV: Introduction to the workshop

Slide 1

Slide 2

Slide 3



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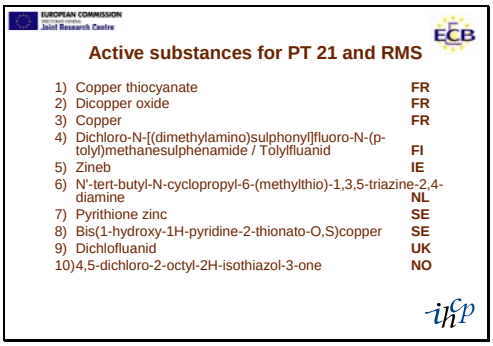

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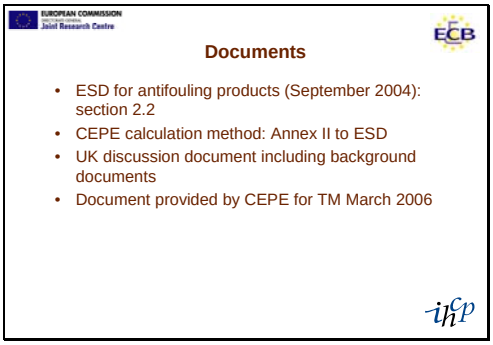

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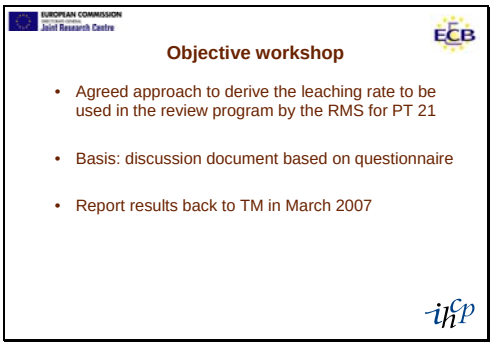
EUROPEAN COMMISSION
Joint Research Centre
ECB
Objective workshop
• Agreed approach to derive the leaching rate to be used in the review program by the RMS for PT 21
• Basis: discussion document based on questionnaire
• Report results back to TM in March 2007
ihcp