GROUNDWATER EXPOSURE ASSESSMENT FOR WOOD PRESERVATIVES

(SOIL STUDIES APPLICABILITY FOR MOBILE OR PERSISTENT SUBSTANCES AND DT_{50}/K_{OC} INPUT VALUES FOR PELMO/PEARL MODELS)

This document was agreed upon at the Technical Meeting on Biocides for the implementation of Directive 98/8/EC concerning the placing of biocidal products on the market 13-17 October 2008.

A/ In the Review Programme the assessment for wood preservatives includes the groundwater exposure assessment which is described in the OECD ESD on wood preservatives [**1**]. In this document (Appendix 4, p. 178) it is stated that, based on German experience with PELMO, substances (parent and metabolites) with a K_{oc} < 500 l kg^{-1} **and** a DT_{50} > 21 d in soil may leach to groundwater and the assessment of groundwater exposure must be performed. Substances with higher K_{oc} **and** lower DT_{50} values are not likely to leach to ground water and no assessment is therefore necessary.
However, it is not specified in this document if an assessment should be perform in the cases of K_{oc} < 500 l kg^{-1} **or** DT_{50} > 21 d.

- During the review program several RMS considered that is was not necessary to perform the groundwater assessment in intermediate cases, low K_{oc}s **or** high DT_{50}s in soil, basing their argumentation on the low mobility of the compounds shown in laboratory and/or field soil studies.

B/ In order to perform the groundwater assessment the OECD ESD on wood preservatives suggests using the PEARL/PELMO models from the PPP area with recommendations for their applicability to estimate the ground water concentration resulting from treated wood scenarios (industrial storage and wood in-service).
Further guidance had been developed by UK in a Groundwater Exposure Assessment proposal for PT08 [**2**] to perform this assessment. First, it states that only the house scenario is necessary to perform, as this can be considered worst-case for soil exposure. Second, it proposed a list of inputs factors to run the PEARL/PELMO models.

- The question was raised at the TMIV07, why the worst case DT50 in soil normalised at 12 ºC was used as input value of the PEARL/PELMO models instead of the average at 20 ºC with a temperature correction as it is usually done in the PPP area.

The present document aims at proposing future guidance on the situations described above however it should be noticed that it is not the intention of this paper to modify the general scheme of groundwater assessment and that Tier 1 assessment according to the TGD should be maintained.

A/ FATE AND BEHAVIOUR OF A COMPOUND IN SOIL:

Fate and behaviour can be estimated by laboratory tests on adsorption/desorption, soil column leaching, volatilisation, chemical degradation and microbial transformation. In certain cases (e.g. for mobile **and/or** persistent chemicals), it may be necessary to conduct experiments under outdoor conditions, for example in lysimeters or field plots.

A.1/ Soil studies to estimate the potential of a substance to contaminate the groundwater

Different soil studies assessing the Absorption/Desorption and mobility properties of a compound could be available in the CAR.

A.1.1/ Soil Adsorption/ Desorption test:

The test of reference OECD 106_Adsorption-Desorption Using a Batch Equilibrium Method. [**3**] stated that:
- The information can be used in the *prediction or estimation of run-off from land surfaces into natural waters*
- 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.
- The percentage desorption and adsorption 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.
- The test includes three tiers:

Tier 1: *Preliminary study*
Tier 2: *Screening test*: the adsorption is studied in five different soil types by means of adsorption kinetics at a single concentration and determination of distribution coefficient: Kd and Koc.
Tier 3: *Freundlich adsorption isotherms:* to determine the influence of concentration on the extent of adsorption and desorption on soils: K_F and K_d

TNGs_Data requirements for active substances in Biocidal Products [**4**]
Adsorption/desorption screening test is required in the core data set according to, for example, the new EC method C.18 or the corresponding *OECD guideline 106 Tier 2 (Adsorption/desorption).*
A full scale adsorption test (isotherms, mass balance, desorption) is required if a substance is used directly on, released to or disposed in/on soil in relevant amounts, unless it can be shown that it is readily biodegradable. Screening tests on the adsorption/desorption of metabolites and other degradation products are required for compounds which at any sampling time during the soil degradation studies account for more than 10% of the active substance added.

A.1.2/ Mobility tests

Laboratory studies

The test of reference OECD 312-Leaching in Soil Columns [**5**] stated that:

- The test allows determining the *leaching or mobility potential in soil* of the test substance (in the parent leaching study) and/or its transformation products (in the aged residue leaching study).
- The test *doesn't quantitatively measure* the percentage of applied chemical that might reach ground water but *may assist in deciding whether additional semi-field or field testing* has to be carried out for substances showing a high mobility potential in laboratory tests.
- for leaching studies of the parent substance, 3 to 4 soils with varying pH, organic carbon content and texture should be used. For the metabolites mobility one soil aged for 5 days is used.
- The substance is applied one time on the top of the column and continuous artificial rain is applied over a period of 48 hours simulating an extremely high rainfall.

Field studies

The test of reference OECD 22 guideline- Performance of Outdoor Monolith Lysimeter Studies [**6**] stated that:

- The tests are used to study the fate and behaviour of chemicals in an undisturbed soil profile under outdoor conditions.
- The tests are *higher Tier studies, c*ompared to laboratory tests, which *take into account more biological and physical factors along with their complex interactions*
- The tests allow for the monitoring of the volume of leaching/drainage water as well as the concentrations of a chemical and its transformation products therein.
- The type of soil selected depends on the purpose of the study and should represent *worst case conditions with regard to leaching*.
- For general chemicals, the application of the test substance should simulate their *most relevant route of entry into soil* (e.g. sewage sludge, wet/dry deposition).

Most of those studies have been performed for the Testing of Plant Protection Products (PPP). Those tests were made on agricultural soil and the application according to the use pattern of pesticides: one to three times a year at higher concentrations compared to the expected wood leachate. The sampling is made generally every month and up to 3 years.

TNGs_Data requirements for active substances in Biocidal Products [**4**]

In most cases the mobility of a substance in soil can be estimated by means of *running mathematical model calculations*, processing adsorption coefficient and degradation rates of the substance (and its transformation products) but also pedological and climatic parameters.
Where it is indicated from data on adsorption and degradation in soil that relevant amounts of a substance may reach groundwater it may become necessary to *carry out an outdoor confirmatory study*. For guidance on how to perform a long-term study on mobility of a substance in undisturbed soil under outdoor conditions it is referred to *OECD guideline (Performance of Outdoor Monolith Lysimeter Studies).*

A.2/ Applicability of soil tests to assess the groundwater contamination potential from treated wood emissions:

A case-by-case approach is suggested to decide if a groundwater assessment should be performed or not according to the combination of DT_{50} and K_{oc} values and other information available in the CAR of the active substance. The following information could be used in a weight of evidence approach:

- DT_{50}< 21d but Koc< 500l.kg^{-1}:
The substance is not persistent in the soil but quite mobile. The potential risk is related to the repeated exposure of the soil occurring for wood preservatives that could lead to an increase of the concentration in the soil and a secondary accumulation in groundwater.

- Koc> 500l.kg^{-1} but DT_{50}>21d:
The substance is persistent in the soil but slightly mobile or immobile. The potential risk is related to the capacity of the substance absorbed and accumulated into the soil to desorbs and reach the groundwater compartment.

- Soil Adsorption/Desorption tests:
Are useful when a Tier 3 estimation of the *influence of concentration on adsorption on soils* and the *reversibility of the adsorption process* is included. An adsorption increasing with the concentration and the absence of reversibility of the adsorption process will decrease the potential risk and then performing an assessment is not necessary. If the adsorption is not modified or reduced by increasing the concentration and/or is reversible, then there will be a potential risk for accumulation and an assessment should be performed.

- Column leaching studies:
Are useful to *determine the leaching potential* of substances. No or limited degradation will occur over the 48h test for substances with 2d<DT_{50}<21d. However it should be kept in mind that the test result is not quantitative and represents neither a repeated exposure nor a long term leaching potential.

- The Field Lysimeter studies:
-Are useful as *higher tier study to estimate the leaching potential in outdoor conditions.* However the *persistence of the substance* should be taken into account to use the results of PPP studies. Indeed if the substance is persistent, the high concentrations of pesticide applied on soil and washed during rain events could simulate repeated wood leachate emissions. In this case, the DT_{50} of the substance will be taken into account to establish the range of measured concentrations to consider for the evaluation (e.g. if DT_{50}=180days the results will be taken into account up to the 6th month). On the other hand, the PPP field studies cannot be used for rapid degradable substances because the application and sampling schemes doesn't allow simulating semi-continuous exposure.

B/ DEGRADATION AND SORPTION INPUT FACTORS OF THE PELMO/PEARL MODELS FOR GROUNDWATER ASSESSMENT OF BIOCIDES

In the UK Guidance for Groundwater Assessment it is not specify which DT_{50} and K_{oc} values should be used in the house scenario. It is indicated indeed that specific guidance available for both PEARL and PELMO FOCUS models were not addressed and recommended to make adjustments to the data in accordance with the FOCUS (2006) Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration [**7**]

B.1/ The use of mean values versus worse case values in the PPP area

In the pesticide regulatory procedure [**8**], the FOCUS groundwater scenarios were selected to describe an overall vulnerability approximating the 90^{th} percentile of all possible situations (this percentile is often referred to as a realistic worst case) and vulnerability is split evenly between soil properties and weather.
The vulnerability is covered by the choice of soils and climates, therefore choice of extreme values of substance-specific parameters would result in model predictions beyond the 90th percentile. Indeed, more favourable situations in one sub-scenario (e.g. weather or soil hydrology) should be theoretically balanced by less favourable situations elsewhere (e.g. dissipation or degradation).
The variability of substance degradation (DT_{50}) and sorption (Koc) in various soils has been estimated to have a high coefficient of variation. The use of appropriate mean values (arithmetic or geometric means/medians) for those relatively variable input values can reduce the uncertainty of model predictions, compared to the use of a single value from one experimental year or soil.
Repeated use of the same substance over 20 years is already a worst case assumption. To also assume worst-case substance properties for each of these 20 applications would be truly extreme.

The Generic guidance for FOCUS groundwater scenarios [**9**] defined the appropriate soil degradation (DT_{50}) and sorption (Kfoc, Koc or Kfom, Kom) inputs value for simulation models depending on the available dataset (p.28):

- **mean value** is used when the minimum dataset requirement, *four soils for parent compound or three soils for relevant metabolites* is available. It is only appropriate to use geometric means for degradation rates and half-lives. For sorption values, it is recommended to use an arithmetic mean. Either laboratory or field degradation approach may be defensible depending on the circumstances but in all cases the modeller should take into account the effect of this decision on the parameterisation of the model. PEARL and PELMO have the ability to operate using *first order laboratory degradation rates normalised at 20°C and 10kPa* for temperature and moisture content and *sorption constant normalised for organic carbon (Kfoc, Koc, Kom or Kfom)* unless the sorption is known to be pH-dependent.

- **median value** may be justified when *a large number of additional data points* are available. In some cases the range of the results may be too large for this to be acceptable. This should be judged on a case by case basis and in this situation a value from a single study should be used, with appropriate justification of the study chosen.

- **the worst case value** is generally appropriate in situations where *less than the recommended number of soils* have been studied..

In addition there will be certain compounds for which sorption and degradation are pH dependent and the values are linked (e.g. lower sorption at high pH but faster degradation). Under these conditions it is appropriate to use linked values of Koc and half life rather than average values of either. Inputs should be selected with the aim of obtaining a realistic rather than an extreme situation and the values used should be justified in the report.

B.2/ Applicability of FOCUS input values for the PPP evaluation to the Biocides area:

In order to define if the rules established for the Pesticides can be implemented for the Wood Preservatives the similarities and differences between those areas are listed below:

Similarities

The same worst case scenarios and parameterisation within the models (climate and soil hydrology descriptions) are used in both areas. The argument that a more favourable situation in one sub scenario can be balanced by less favourable situations elsewhere is valid for wood preservatives.

Differences

- Repeated exposure of the soil to the same substance over 20 years is a realistic assumption for the wood preservatives because the active substances will be leached from the treated wood at each rain event. The application rate input in the house scenario is estimated from the leaching rate over 5 years (corresponding to the service life of dipped wood or brushed wooden houses) converted to 10 equal applications per annum (kg ha^{-1}).
- According to the TGD (PartII, 2003) the test standard temperature should be recalculated at 12°C to reflect an average EU outdoor temperature for the Biocides.

Summary

According to the above observations, the following proposal is made to determine the degradation rates and sorption input values of the FOCUS models for calculation of groundwater concentration resulting from treated wood emissions:

- Four soils for parent compound or three soils for relevant metabolites: the **geometric mean** for degradation rates and the **arithmetic mean** for sorption values.

- A larger number of additional data points: the **median value** for degradation rates and sorption values.

However, in order to improve the harmonisation of approaches, it was suggested to apply a more detailed guidance for the case-by-case decision of the use of the median. Therefore it is proposed to follow the national authorisation procedure of PPP in Germany where the median of the rate constants is used for the following datasets: ≥ 6 values for active substances and ≥ 5 values for the metabolites as indicated in Michalski et al. (2004) [**10**]

- Less than the recommended number of soils: **the worst case value** for degradation rates and sorption values is generally appropriate in situations where less than the recommended number of soils has been studied.

In addition there will be certain compounds for which sorption and degradation are pH dependent and the values are linked (e.g. lower sorption at high pH but faster degradation). Under these conditions it is appropriate to use linked values of Koc and half life rather than average values of either. Inputs should be selected with the aim of obtaining a realistic rather than an extreme situation and the values used should be justified in the report.

- the DT_{50} input value should be adjusted to a reference temperature of 20°C.

REFERENCES

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[**2**] Groundwater exposure assessment for wood preservatives-Factors to consider (November 2006). Drafted by the UK CA on behalf of the ECB. Endorsed at the 24th 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. http://ecb.jrc.it/documents/Biocides/EMISSION_SCENARIO_DOCUMENTS/ESD_PER_PRODUCT_TYPE/PT_08/PT_8_ground_water_assessment.pdf

[**3**] OECD 106. GUIDELINE FOR THE TESTING OF CHEMICALS. Adsorption - Desorption Using a Batch Equilibrium Method. Organisation for Economic Co-operation and Development (OECD): Paris 2000, p. 45.

[**4**] TECHNICAL GUIDANCE DOCUMENT IN SUPPORT OF THE DIRECTIVE 98/8/EC CONCERNING THE PLACING OF BIOCIDAL PRODUCTS ON THE MARKET. GUIDANCE ON DATA REQUIREMENTS FOR ACTIVE SUBSTANCES AND BIOCIDAL PRODUCTS. October 2000, 149p. http://ecb.jrc.it/documents/Biocides/TECHNICAL_NOTES_FOR_GUIDANCE/TNsG_DATA_REQUIREMENTS/TNsG-Data-Requirements.pdf

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[**10**] Michalski, B., H. Resseler, K. Aden, F. Dechet, M. Dust, R. Fischer, B. Gottesbüren, G. Holdt, A. Huber, B. Jene, W. Koch, G. Reinken and B. Stein. Recommendations for simulation calculations of predicted environmental concentrations in ground water (PECgw)

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