SCIENTIFIC OPINION

Statement on the FERA guidance proposal: 'Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments' (FERA, 2012)[1]

EFSA Panel on Plant Protection Products and their Residues[2,3]

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ABSTRACT

The European Food Safety Authority (EFSA) asked the Panel on Plant Protection Products and their Residues to prepare a scientific opinion on the Food and Environment Research Agency guidance proposal 'Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments'. The Panel concluded that the experimental and modelling approaches described in the proposed guidance are reasonable compromises between the required effort and what is desirable from a theoretical point of view. However, the Panel has concerns about the interpretation of the experiments and how the results of the experiments should be used in the leaching assessment. The Panel investigated options for improvement, but could not complete its evaluation on these two topics because underlying data to test these options were not made available to the Panel. For this reason, the Panel prepared a statement instead of a scientific opinion. Therefore, the Panel cannot recommend the use of the guidance for the time being.

KEY WORDS

plant protection products, aged sorption, guidance, Freundlich exponent, PEARLNEQ, leaching

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SUMMARY

The European Food Safety Authority (EFSA) asked the Panel on Plant Protection Products and their Residues (PPR), following a recommendation from the EFSA Pesticide Steering Network, to prepare a scientific opinion on the Food and Environment Research Agency (FERA) guidance proposal 'Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments' (FERA, 2012). In particular, the PPR Panel was asked to address whether or not:

- the recommendations are consistent with the state-of-the-art science in the field of aged sorption for derivation of aged sorption parameters for use in regulatory risk assessment;

- the proposed procedures for study conduct are scientifically robust for the intended use of derivation of aged sorption parameters;

- the proposed procedures for derivation of aged sorption parameters from the experimental data are suitably robust for the intended use;

- the use of derived parameters are scientifically robust within the tiered framework of the models proposed for use with revised FOCUS Groundwater guidance (FOCUS, 2009). In particular, whether the parameter selection is considered suitable in relation to the existing scenario selection in the FOCUS groundwater leaching models.

It was noted in the background information to the mandate that experience of groundwater assessment using the Forum for the Coordination of Pesticide Fate Models and their Use (FOCUS) (2009) approach has shown that achieving an acceptable regulatory risk assessment using first-tier approaches with standard substance datasets can be problematic in the case of some substances. This has led to a number of higher-tier approaches being developed by applicants and notifiers of active substances, one of the principal approaches being to investigate the potential for the strength of soil sorption of a substance to increase over time ('aged sorption'). The procedures used to derive parameters to allow the inclusion of aged sorption as a higher-tier refinement for regulatory submissions are very uncertain, as demonstrated by the variety of different approaches employed for different substances.

The review of the draft guidance by the PPR Panel revealed that the experimental and modelling approaches in the proposed guidance are reasonable compromises between the required effort and what is desirable from a theoretical point of view. However, the Panel has concerns about the interpretation of the experiments and how the results of the experiments should be used in the leaching assessment. The Panel investigated options for improvement, but could not complete its evaluation on these two topics because underlying data were not made available. For this reason, the Panel prepared a statement instead of a scientific opinion. Therefore, the Panel cannot recommend the use of the guidance for the time being.

The Panel recommends an update of the current FERA draft guidance document, taking into account the conclusions and recommendations provided in this statement. This updated guidance document could be resubmitted to the Panel, together with supporting data, so that the Panel can finalise its review.

The Panel noted that the draft guidance document did not systematically review uncertainties arising from the use of aged sorption data in regulatory leaching assessments. Uncertainties may result from, for example, the experimental procedure (extraction procedures), the conceptual model and the quality of the fitted parameters. It is recommended that a systematic review of uncertainties is carried out when updating the draft guidance document.

More detailed conclusions and recommendations are listed hereafter.

- Sorption of pesticides onto soil is a complex phenomenon influenced by both substance properties and the nature of soil organic matter and mineral components. Sorption is usually progressive in nature, starting with a fast initial phase followed by a slower phase that may go on for weeks or months. As a result, the apparent sorption often increases with time (i.e. aged or time-dependent sorption). Analytical approaches that attempt to quantify aged sorption and its dynamics should take into account the release of pesticides from various domains. In this respect, the two-step extraction procedure proposed in the draft guidance consisting of a 24-hour extraction with a 0.01 M calcium chloride ($CaCl_2$) solution and a sufficiently harsh solvent extraction to characterise the total extractable mass (OECD, 2002) on the same soil is a reasonable compromise between the experimental effort and what is desirable from a theoretical point of view.

- If the solvent extraction is not harsh enough, leaching may be underestimated. The Panel therefore recommends that a justification of the extraction method, which meets the requirements of an appropriate mass recovery, should always be given by the applicant.

- The Panel concludes that the two-site modelling approach proposed in the draft guidance is in line with the proposed analytical approach. This modelling approach reflects a reasonable compromise between (i) the ability of the model to describe aged sorption under a range of situations, and (ii) the possibility to determine model parameters from experiments with reasonable effort.

- The draft guidance document proposes to fit five model parameters against measured data. The Panel is not convinced that fitting the Freundlich sorption coefficient ($K_{OM,EQ}$) is necessary. The Panel recommends always checking first if the fitted model is capable of adequately describing the measured data without excluding any time points and fixing $K_{OM,EQ}$ to that measured at day 0 of the time-dependent sorption experiment. However, the Panel could not test this recommendation, because the experimental data underlying the draft guidance document were not provided to the Panel.

- The fitting procedure of the aged sorption parameters is insensitive to the value of the Freundlich exponent. The Panel therefore agrees that the Freundlich exponent should be derived from batch experiments using the same soil. In this respect, the Panel recommends using the guidance included in Boesten et al. (2015), taking into account the modifications in this statement. The Panel also recommends using the Boesten et al. (2015) guidance for lower-tier leaching assessments and for calculating the pore water concentration in soil.

- The Panel observes that the default value of 0.9 for the Freundlich exponent may not be conservative enough in a tiered approach. A Freundlich exponent of 1 would be more appropriate in a tiered approach. The Panel recommends reconsidering the default value in view of the tiered approach introduced by FOCUS (2009).

- The Panel recommends assuming that aged sorption does not occur unless reliable values for the desorption rate coefficient (k_{des}) and the factor describing the ratio between the non-equilibrium and the equilibrium Freundlich coefficients (f_{NE}) have been derived. This implies that the default values of k_{des} and f_{NE} should be set to zero.

- The draft guidance states that, when at least two out of four experiments show aged sorption, aged sorption can be taken into account. The Panel is of the opinion that this is a small number for such an important process. A criterion that states that the majority of experiments (with a minimum of four) should show aged sorption behaviour would be more in line with a conservative approach.

- If, in a degradation scheme, the parent substance shows time-dependent sorption but the daughter or daughters does or do not, then it will, in general, still be necessary to re-interpret the kinetic behaviour of the daughter substances as the aged sorption process will affect the formation of the daughter and, consequently, the degradation rate. The leaching assessment should be done with a consistent dataset.

- The draft guidance document mentions two options for including aged sorption parameters in the leaching assessment, i.e. average-first and calculate-first options. Given that the calculate-first approach is extremely resource demanding, the Panel is of the opinion that the average-first approach is the preferred option. Further exploration based on the underlying experimental data is, however, necessary.

- The draft guidance states that a decision on the leaching potential may be based on the results of four aged sorption experiments. Implicitly, this means that available lower-tier information is no longer used. The Panel concludes that such an approach is not correct. The Panel gives some options for including lower-tier data. However, these options could not be further elaborated because the underlying experimental data were not available to the Panel.

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1.1. Background and Terms of Reference as provided by requestor

1.1.1. Background

FOCUS Groundwater guidance has been available for use since FOCUS (2000) to assist in the assessment of potential groundwater contamination of pesticides and their metabolites within the framework of authorisation under Directive 91/414/EEC[4] and Regulation (EC) 1107/2009[5]. Experience of use of the scenarios, models and guidance developed by the FOCUS Groundwater group led to a number of revisions which were considered by the PPR Panel in two scientific Opinions (EFSA PPR Panel 2013a, b).

Experience of groundwater assessment using the FOCUS approach has shown that achieving an acceptable regulatory risk assessment can be problematic for some substances using 'first tier' approaches with standard substance data sets. This has led to a number of higher tier approaches being developed by applicants and notifiers of active substances, one of the principle approaches being to investigate the potential for the strength of soil sorption of a substance to increase over time ('aged sorption'). Whilst being a generally accepted scientific phenomenon, the procedures to derive parameters to allow the inclusion of aged sorption as a higher tier refinement for regulatory submissions are very uncertain, demonstrated by the variety of different approaches employed for different substances.

The interest in aged sorption led to the inclusion of recommendations relating to the use of aged sorption parameters in the revised FOCUS Groundwater report (FOCUS, 2009). Although the extent of investigation into this subject was relatively limited, a general recommendation was made that default parameters for aged sorption could be adopted at the higher tier for any substance.

Separate experiences of the difficulties in considering aged sorption data in the EU pesticide peer review process led the Chemicals Regulation Directorate (CRD), the UK competent authority for authorisation of pesticides, to commission independent research into aged sorption processes and development of guidance on study conduct and generation of aged sorption parameters suitable for use in computer models simulating leaching. Initial work, conducted by the Food and Environment Research Agency (FERA) in the UK and Wageningen University and Research centre (WUR) in the Netherlands, culminated in production of a draft guidance which was presented to a workshop of academics, regulators and industry held in York in April 2010 (Beulke et al, 2010). The workshop recommended additional work, particularly testing of the draft guidance against real aged sorption datasets. The European Crop Protection Association (ECPA) subsequently commissioned an independent evaluation of a large number of datasets from experiments conducted to support the authorisation of plant protection products (PPP). Following verification of this evaluation by FERA, amendments which have been discussed between CRD, FERA, WUR and ECPA have been made to the guidance.

Given the pertinence of this guidance to an important recommendation in the revised FOCUS Groundwater guidance document (FOCUS, 2009), the preparation of a scientific Opinion on the FERA Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments (FERA, 2012) by the PPR Panel is sought, preferably in a time frame close to the finalisation of the PPR Opinions (EFSA PPR Panel 2013a, b). This is supported by the Pesticide Steering Network of EFSA.

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[4] Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market. Official Journal L 230 , 19/08/1991 P. 0001 - 0032
[5] EC (European Commission), 2009. Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. OJ L 309/1, 24.11.2009, p. 1-50.

1.1.2. Terms of Reference

The Scientific Panel on Plant Protection Products and their Residues (PPR Panel) was asked by EFSA to prepare a Scientific Opinion on the FERA guidance proposal 'Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments' (FERA, 2012). In particular the PPR Panel was to address whether:

 i. the recommendations are consistent with the state of the art of the science in the field of aged sorption for derivation of aged sorption parameters for use in regulatory risk assessment;

 ii. the proposed procedures for study conduct are scientifically robust for the intended use of derivation of aged sorption parameters;

 iii. the proposed procedures for derivation of aged sorption parameters from the experimental data are scientifically robust for the intended use;

 iv. the use of derived parameters are scientifically robust within the tiered framework of the models proposed for use with revised FOCUS Groundwater guidance (FOCUS, 2009). In particular, whether the parameter selection is considered suitable in relation to the existing scenario selection in the FOCUS Groundwater leaching models.

However, the Panel could not completely address all Terms of Reference, because the experimental data underlying the draft guidance document were not made available to the Panel. This particularly holds for the third and fourth item of the Terms of Reference. Underlying experimental data (see Glossary) are needed to draw conclusions in a transparent and reproducible way (see the EFSA Scientific Committee guidance on transparency in risk assessment (EFSA Scientific Committee, 2009). Because the Panel could not draw final conclusions for the third and fourth items of the Terms of Reference, the Panel provided recommendations instead of final conclusions. These recommendations could be used to update the draft guidance document. This updated guidance document might be resubmitted to the Panel together with the supporting data so that the Panel can finalise its review. Because not all Terms of Reference were fully addressed, the Panel prepared a Statement instead of a Scientific Opinion.

1.2. Additional information

The following supporting information was provided by CRD for the review of the draft guidance.

 i. Beulke S and van Beinum W, 2012. Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments. The Food and Environment Research Agency, Sand Hutton, York, UK.

 ii. van Beinum W and Beulke S, 2012. Consideration of additional experimental datasets to support the development of the revised guidance on aged sorption studies. The Food and Environment Research Agency, Sand Hutton, York, UK.

 iii. ECPA (European Crop Protection Association), 2012. Opinion of the ECPA non-equilibrium sorption working group on the: 'Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments'.

 iv. Hardy I, 2011. Evaluation of aged-sorption studies: Testing of the draft guidance. Battelle report number PS/10/001A.

 v. van Beinum W, Beulke S, Boesten JJTI and Ter Horst MMS, 2010. Development of draft guidance on the implementation of aged soil sorption studies into regulatory exposure assessments. The Food and Environment Research Agency, Sand Hutton, York, UK.

The Panel did not have access to the underlying supporting data (for more information refer to the amended Terms of Reference (section 1.1.2) and to sections 4 and 5).

1.3. Existing guidance on aged sorption

Guidance on deriving aged sorption parameters was given in the Forum for the Coordination of Pesticide Fate Models and their Use (FOCUS) degradation kinetics report (FOCUS, 2006) and in the revised FOCUS groundwater report (FOCUS, 2009).

The FOCUS degradation kinetics report (FOCUS, 2006) describes in detail how to estimate aged sorption parameters from laboratory degradation experiments showing bi-phasic degradation kinetics (see Appendix A, section A1 for more details). The Panel is of the opinion that, because of the restrictions mentioned in the FOCUS 2006 report and observations by van Beinum et al. (2010), the double first order in parallel (DFOP) model should not be used to derive aged sorption parameters. The Panel also observes that the aged sorption guidance in the FOCUS (2006) report is no longer necessary, as a dedicated approach and supporting software for deriving aged sorption parameters are now available.

The revised FOCUS groundwater report (FOCUS, 2009) deals with aged sorption in more detail. The Standing Committee on Plants, Animals, Food and Feed (SCoPAFF) noted this guidance (EC, 2014) in combination with adaptations described by the EFSA PPR Panel (2013a, b). Note that the EFSA PPR Panel (2013a, b) did not review the sections on aged sorption.

The FOCUS (2009) report recommends measuring aged sorption as part of a standard degradation rate study (OECD, 2002) and deriving aged sorption parameters via a dedicated fitting procedure taking into account both the concentration of pesticides in total soil and the concentration in the soil pore water (see Appendix A, section A2, for more details).

The FOCUS (2009) guidance on aged sorption has been the basis for developing the FERA draft guidance document on aged sorption (Beulke and van Beinum, 2012). In this regard, the FOCUS (2009) report clearly does not cover all aspects of, for example, data selection or fitting quality criteria, which turned out to be rather important based on further evaluation. The Panel therefore recommends that aged sorption parameters are not derived on the basis of the FOCUS (2009) report alone. The same applies to the European Commission report (EC, 2014), because the section on aged sorption was copied without changes into the noted guidance document.

1.4. Readers guidance

This statement generally follows the structure of the draft guidance document (Beulke and van Beinum, 2012). Section 2 provides an overview of sorption processes in soil. Section 3 reviews the experiments used to derive aged sorption parameters. Section 4 reviews the procedures to fit the aged sorption parameters. Section 5 reviews the use of aged sorption in regulatory risk assessments. Special considerations for the Freundlich exponent are described in section 6 and for metabolites in section 7. All aspects concerning so-called legacy studies are reviewed in section 8. The appendices give background information on previous guidance (Appendix A) and the model used (Appendix B). Appendices C and D describe some exploratory calculations to support sections 4 and 5.

2.   Review of relevant sorption processes

2.1.   Introduction

The fate of pesticides reaching the soil is determined by interactions of substance-specific properties (polarity, type and distribution of functional groups), environmental conditions, and biological and physicochemical soil properties (Kah et al., 2007). Pesticides and their metabolites are exposed to a multiplicity of processes such as dissipation (biotic or abiotic mineralisation and metabolisation, as well as forming non-extractable (bound) residues (NERs)), adsorption and desorption, transport, and plant or animal uptake (Helling et al., 1971; Cheng, 1990); see the conceptual scheme in Figure 1. For pesticide fate, sorption processes play a key role, because they affect the concentration of pesticides in the soil solution (Wauchope et al., 2002); thereby, sorption determines mobility (Walker et al., 2005) and bioavailability (Alexander, 2000) of the substances. Sorption can influence the rate and extent of biodegradation (mineralisation and metabolisation), because bioavailability may decrease when the substance is removed from the aqueous solution. However, this decrease in bioavailability depends on substance properties, species and soils (Alexander, 2000).
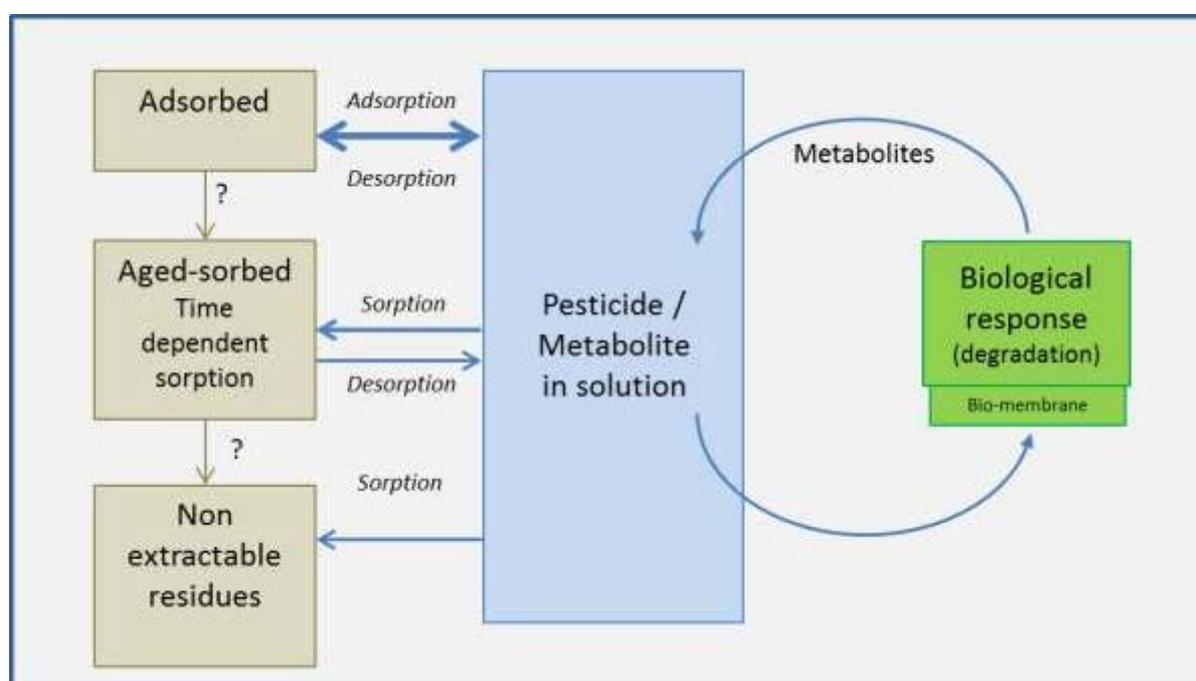
Figure 1:   Simplified conceptual model of adsorption/sorption of pesticides and their metabolites to soils. Figure prepared by the PPR WG.

Wauchope et al. (2002) distinguished at least three phases during pesticide sorption–desorption in soils. The first phase is a rapid, reversible mass flow or diffusion of the dissolved substance towards accessible sorption sites followed by adhesion. In a second phase, a slower but still reversible exchange of the substances between soil and water takes place, progressing for only hours or days until a first, although transient, equilibrium is reached. The third phase, also referred to as ageing, is a slow reaction proceeding for weeks to years. It is characterised by a removal of the solute from the soil solution and a progressive decrease in extractability.

2.2.   Sorption processes

Sorption is one of the most important reactions between soils and pesticides; it controls the concentration of pesticides in the soil water phase. Sorption processes range from completely reversible to totally irreversible reactions. The magnitude of sorption depends on the properties of the soil and the substances, including size, shape, configuration, molecular structure, chemical functions,

solubility, polarity and charge distribution of interacting species, and the acid–base nature of the molecule.

Adsorption can be purely physical, as with van der Waals forces, or chemical, depending on the pesticide structure. Sorption and aged sorption between unaltered pesticides or their degradation products with soil components may be due mostly to physical interactions or hydrogen and electrostatic bonds, which may be reversible as a result of changes in the chemical and or physical status of the soil. Less probable are the stronger chemical interactions that permanently bind pesticides by covalent bonds and lead to an irreversible persistence of residues in soil, and the loss of their chemical identity.

2.2.1. Interaction mechanisms between the substance and soil

The nature and mechanisms of binding forces onto soil organic materials and humic–clay microaggregates determine the adsorption of the different pesticides. The binding forces may be weak, such as van der Waals forces, ligand exchange and hydrophobic interactions, or stronger, such as ionic, hydrogen and electron donor–acceptor interactions, and, possibly, covalent bonds. A major question regards the reversibility or irreversibility of the adsorption process, that is whether the residues can be considered definitely inactivated through the formation of strong bonds with humic molecules or whether they are only momentarily inactivated in reversibly bound forms in humic supramolecular structures, thus representing a possible source of contamination after a time delay.

Pesticides and their degradation products are adsorbed by ionic bonding or cation exchange when they either exist in the cationic form in solution or are protonated and so become cationic (Gavao et al, 2000). These positively charged pesticides form ionic bonds with the acidic (carboxyl, phenol and hydroxyl) functional groups of humic substances (HSs) which bear negative charges when the soil pH is above 4. Ideally, cationic pesticides, such as diquat and paraquat, bind to soil HSs by ion exchange, and form highly stable and unreactive bonds with HSs. Similarly, some triazines can be protonated at low soil pH and can form ionic bonds with dissociated humic functional groups.

Because of the numerous oxygen and hydroxyl functional groups of HSs, hydrogen bonds can be formed with complementary groups on pesticide molecules. Hydrogen bonding plays a vital role in the adsorption of several non-ionic polar pesticides, such as substituted ureas and phenylcarbamates (Gavao et al, 2000). Furthermore, acidic and anionic pesticides, such as dicamba and the phenoxyacetic acids 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (MCPA), can interact with soil organic matter by hydrogen bonding depending on the pH of the soil and the pK_a of the substance.

Van der Waals forces consist of weak, short-range dipolar or induced dipolar forces that exist in all sorbent–sorbate interactions (Gevao et al, 2000). Such weak interactions between non-ionic, apolar and medium-polar pesticides with humic and fulvic molecules are relevant for sorption. As these forces may be additive, their contribution increases with the size of the molecule and with its capacity to adapt to the surface. However, as van der Waals forces decrease rapidly with distance, the adsorption would be highest for substances that are in closest contact with the surface. The sorption of pesticides by weak dispersive forces is regarded within the partitioning theory, by which soil organic matter is viewed as a water immiscible liquid phase forming hydrophobic interaction between pesticides and soils. This implies that HSs, in both the solid and dissolved phase, should be treated as non-aqueous solvents into which the pesticide can partition from water. However, this theory fails to take into account the novel understanding of humic matter as a supramolecular association of heterogeneous molecules in amphiphilic domains.

Sorption by ligand exchange involves the replacement by anionic pesticides of relatively weak ligands, for example water molecules forming complexes with polyvalent cations, which are, in turn, associated with oxygen-containing functional groups of humus in soil.

The formation of covalent bonds between pesticides or their metabolites and soil humic substances may occur when mediated by chemical, photochemical or enzymatic oxidative catalysts, thereby leading to a possibly irreversible incorporation into the soil (Gavao et al, 2000). Pesticides that structurally resemble phenolic substances may covalently bind to HSs under catalytic oxidative conditions (Gavao et al, 2000). However, since these intermolecular couplings are bimolecular reactions that need to proceed in solution with the assistance of a biotic or abiotic catalyst, their real occurrence in soil may not be frequent.

Conversely, non-polar and hydrophobic substances may undergo sequestration during a longer residence in soil. Sequestration is closely related to sorption phenomena. Pignatello and Xing (1996) and Gavao et al (2000), in these review of sorption mechanisms, referred to sequestration as slow sorption. Further, sequestered chemicals can be extracted from soil with organic solvents, although the extraction procedures require protracted extraction times compared with other adsorption mechanisms. Another difference between the two processes is their kinetics. Adsorption is known to occur within a few minutes after the addition of the chemical to soil, whereas sequestration may take much longer to become important (Gavao et al, 2000).

Even if organic matter represents only a few per cent of the total dried material in soil, it is a major sorbent of pesticides in soil. HSs are the dominant constituents (> 80 %) of soil organic matter and they are recognised to control more than 99 % of pesticide sorption. The interactions between diuron and several humic fractions have been shown to be significant. Diuron adsorbed significantly, but reversibly, to humic acid, while sorption to fulvic acid was less pronounced. The sorption abilities of the humic fractions correlate with their total aromatic content. In the case of triazines, sorption and desorption on humic matter of different molecular composition is a function more of alkyl than of aromatic components and of humic conformational structures (Piccolo et al., 1998; Celano et al., 2008). In natural soils, soil organic matter was the main adsorbent of diuron; however, the organic matter partition coefficient was larger in sandy than in clayey soils. The main metabolite produced during diuron degradation, 3,4-dichloroaniline, was bound irreversibly to HSs within days of formation. Sorption studies with seven purified soil humic fractions showed that these could sorb glyphosate and that the aromatic content, possibly phenolic groups, seems to aid the sorption (Albers et al. 2008, 2009). After an 80-day fate experiment, approximately 40 % of the added glyphosate was associated with the humic and fulvic acid fractions in sandy soils, while this was only 10 % in the clayey soils. However, glyphosate sorbed to HSs in natural soils still seemed to be easier to desorb than glyphosate sorbed to amorphous iron/aluminium oxides (Piccolo et al., 1994).

Significant sorption of the selected pesticides onto sediments with low organic matter content (total organic carbon (TOC) < 1 g/kg has been observed. Generally, the level of sorption decreases in the order metamitron, atrazine, isoproturon, mecoprop, 2,4-D, metsulfuron-methyl and bentazone. The sorption coefficient (K_d) values for the specific pesticides vary from 3 to 30 for the sediments, reflecting the different sediment characteristics. Analyses demonstrate that soil surface area, pH and TOC are the most important parameters to describe the sorption at low TOC (Madsen et al., 2000). For the specific pesticides, it was observed that metamitron sorption is controlled mainly by iron silicates (glauconite and clay size iron-bearing smectites), i.e. the sorption increases with increasing total iron content in the sediments. By contrast, the easily extractable iron oxides have no influence on the sorption.

2.1.1 Aged sorption

Ageing is a process in the soil that occurs upon increased contact time between a chemical and soil, and which may allow a substance to become more strongly associated with soil components over time, leading to a decrease in bioavailability and a reduction in the fraction that can be extracted by mild extraction procedures (Gevao et al, 2000). Ageing may consist in the progressive formation of strong interactions between a substance and soil organic matter, thereby resulting in a physical entrapment/occlusion of the substance in the humic-clay microaggregates. This process is directly related to the nature of soil organic matter and is viewed as a supramolecular association of

heterogeneous molecules held together as an apparently large molecular complex by weak dispersive forces, such as hydrophobic interactions (Piccolo 2001, 2002). Passive processes, including a number of intra-soil processes, e.g. sorption onto soil humic-clay microaggregates (Ball and Roberts, 1991a; Fu et al., 1994; Burgos et al., 1996; Gevao et al, 2000), occur during the diffusion of pesticides through spatially remote areas, such as soil macro- and micropores (Ball and Roberts, 1991b; Beck and Jones, 1995; Burgos et al., 1996; Pignatello and Xing, 1996), and in the entrapment within soil organic matter (Brusseau et al., 1991a, b; Fu et al., 1994; Gevao et al, 2000) based on the chemical affinity between the substance structure and the amphiphilic domains of soil organic matter (Mazzei and Piccolo, 2012). Aged sorption is directly correlated with the amount of organic matter; however, the mineral composition may be the governing component for ageing in soils or sub-soils low in organic matter. There are some studies addressing the environmental behaviour of pesticides at elevated concentration levels (Racke and Lichtenstein, 1987; Gan et al., 1995). Persistence of pesticides in soils has been found to increase with increasing concentration (Gevao et al, 2000), whereas mineralisation and formation of metabolites and NERs may decrease at higher concentrations.

2.1.2 Dynamics of aged sorbed pesticides in soil organic matter

The aged sorption of pesticides to soils is directly related to the structure of humic associations as stabilised in soil aggregates (Dalkmann et al., 2012; Chaplain et al., 2008). Moreover, the spreading of organic matter molecules over soil microstructure and their stability and dynamics control the adsorption or the release of pesticides in the soil environment (Woignier et al., 2013; Romina et al., 2012). The humic supramolecular conformations may be perturbed by interactions with organic acids (Piccolo et al., 1999, 2003; Cozzolino et al., 2001) originating from root exudates and/or microbial metabolism. In fact, the organic acids exuded from plants are capable of dispersing the apparently large original superstructures into smaller aggregate sizes (Piccolo, 2002). This phenomenon is attributed to the gain in energy content of the hydrogen bonds formed between the organic acids and the complementary humic molecules, as compared with the metastable humic conformations stabilised mainly by weak dispersive forces (Piccolo, 2002). The disruption of large humic molecules into smaller aggregate sizes is likely to affect the sorption of pesticides, which could then be released into the soil solution and become bioaccessible to microbial degradation or available to leaching and environmental transport (Piccolo et al., 2003; Mazzei and Piccolo, 2015).

2.2.2. Non-extractable residues

The original definition of NERs given by Roberts (1984)was 'chemical species originating from pesticides, used according to good agricultural practice, that are non-extractable by methods which do not significantly change the chemical nature of these residues.' A later modification Fuhr (1996) took into account not only pesticides but also metabolites: 'substances in soils, plants or animals which persist in the matrix after extraction in the form of the parent substance or its metabolite(s) that are indistinguishable from naturally occurring substances. The extraction must not substantially change the substances themselves nor the structure of the matrix.'

However as described by Gevao et al (2000), the distinction between extractable and non-extractable (bound) fractions is not clear, because, although both fractions are present in soil, even the free or extractable residues are not entirely free from any form of binding. On the contrary, at any time after the chemical enters the soil, the extractable fraction may be sorbed on and incorporated into the soil solid phases (humic-clay microaggregates) and, therefore, show reduced bioavailability and degradation. Ageing may result from the formation of stronger bonds with increased residence times in soil or physical entrapment/occlusion of the substance in the soil organic matter or mineral lattice. The formation of covalent bonds of parent substances or their degradation products may be possible, but only in limited kinetic circumstances (Gevao et al, 2000).

The processes responsible for the formation of NERs are time dependent, but at the same time are ill-defined, leading to the formation of a larger proportion of substances being retained 'permanently' in soil. With longer residence times in the soil, bound pesticide residues tend to lose their biological activity and become even more resistant to degradation and extraction (Gevao et al, 2000).

Chemisorption/sequestration possibly involves a further strengthening of sorption bonds, after an initial rapid sorption followed by a slower but sustained rate of sorption (Gevao et al , 2000; Pignatello, 1990; Pignatello and Xing, 1996; Xing and Pignatello, 1997). The concern about the possible release of bound pesticide residues from soil seems relevant, as released residues could be of toxicological and/or ecological significance (Gevao et al, 2000). It is believed that the new release of NERs is linked to the changes in the supramolecular organisation of organic matter, due to chemical factors such as the flushes of organic acids and other biomolecules exuded by soil microorganisms and/or plant roots (Canellas et al., 2010). Other factors, resulting from changes in soil management, may lead to the release of NERs in soil, e.g. (i) deep ploughing causing the biotic and abiotic oxidation of organic matter newly exposed on the aggregates' surfaces and (ii) application of agrochemicals that may alter soil structure and/or the supramolecular arrangement of organic matter. These phenomena may re-introduce the substances into the soil solution and eventually lead to their uptake by plants or leaching to groundwater. The available data indicate that the microbial and chemical release of NERs occurs extremely slowly. It is believed that released NERs can be re-incorporated into humus or taken up by plants and the soil biotic community, or leached into groundwater.

Relatively few publications have investigated the relationships between the formation of NERs and their molecular properties. Some general publications have pointed out that dinitroanilines have lower capacity to form NERs than triazines or chloroacetamides (Laabs et al., 2007). In general, pesticides or metabolites supporting free reactive chemical groups, such as aniline or phenol, have a tendency to give a larger proportion of NERs (Helling, 1975; Katan and Liechtenstein, 1977; Bollag et al., 1980; Talebi and Walker, 1993). The degradation of pesticides presenting metabolites with hydroxyl or amine groups leads to an increase in the formation of NERs because of an increased affinity to the amphiphilic humic molecules (Bollag et al., 1980; Mazzei and Piccolo, 2015).

Approaches aimed at linking pesticide environmental and molecular properties for sorption (Reddy and Locke, 1994) are typically based on (i) the generation of a large number of molecular properties using quantitative structure–activity relationships (QSARs) and (ii) statistical analyses aimed at relating environmental and structural traits. In the case of NERs, it has been suggested that the distribution of the electron densities could promote nucleophile or electrophile attacks and that differences between energy levels of the frontier molecular orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), could be used as an indicator of the chemical reactivity (Barriuso et al., 2004). However, calculations of these kinds of molecular indicators are valid if not only the substance (pesticide or metabolite) reacting with soil is known, but the molecular properties of soil organic matter as well.

The formation of NERs of most pesticides is usually correlated to soil biological activity and to the amount of soil organic matter in soil (Kaufman and Blake, 1973). The total microbial activity has a direct effect on the formation of NERs, as shown in pesticide incubation experiments, in which soil samples are taken from different depths in a profile and which reveal that NER formation is lower in deeper soil samples, which usually have a low microbial activity (Baluch et al., 1993; Stolpe and Shea, 1995; Kruger et al., 1997). In general terms, most environmental factors affecting biological activity, such as temperature or soil moisture content, are likely to have an influence on NER formation. Nevertheless, much of the uncertainty regarding the elucidation of NER formation arises from our poor understanding of the structure of soil organic matter. The nature of the organic matter influences the formation of NERs for most pesticides.

The understanding of the nature of humic matter has been revised in recent years, and the traditional view of the difference between humified and non-humified fractions no longer holds true (Piccolo et al., 1996a). In fact, humification as a process that entails a progressive enhancement of molecular weight due to molecular coupling among humic molecules can no longer be accepted in the light of modern experimental results. The updated general consensus regards humified matter in soil as a supramolecular association of relatively small heterogeneous molecules surviving degradation by vegetal and animal cells and self-assembling into structures with apparently large molecular size mainly because of hydrophobic interactions or hydrogen bonds (Piccolo, 2001, 2002). Humification is

hence regarded as a progressive accumulation of mostly hydrophobic molecules in soils, which are thermodynamically separated from water (the hydrophobic effect) and thus become recalcitrant to microbial degradation. This thermodynamic drive to separate non-polar and slightly polar substances from the water solution, and their accumulation on surfaces of soil minerals and particles, also implies that some more polar substances, not yet microbially degraded (some carbohydrates or peptides), are confined away from water into the humic hydrophobic domains. Pesticides may follow the same fate and become progressively incorporated into the humic inner domains.

Such a view influences the interpretation of the results stemming from experiments of interactions of pesticides with soil organic matter. For instance, a medium polar pesticide such as atrazine was found to interact strongly with the most hydrophobic fraction of soil organic matter and less with the more hydrophilic humic fractions (Piccolo et al., 1998). Moreover, adsorption of *s*-triazines was shown to be mainly related to the carbon content, hydrophobicity and aromaticity of humic extracts, thereby implying a predominant binding role for weak dispersive forces and indicating that humic matter rich in hydrophobic and aromatic constituents is more likely to adsorb *s*-triazines and reduce their environmental mobility (Celano et al., 2008). Even glyphosate, a polar, easily water-soluble, herbicide, was found to interact with humic matter more strongly than with clay minerals (Piccolo et al., 1996b; Mazzei and Piccolo, 2012). Glyphosate adsorption was explained by the multiple hydrogen bonds which can form among the various acidic and oxygen-containing groups of both molecules (Piccolo and Celano, 1994). However, the order of adsorption did not simply follow the order of acidity but, rather, followed that of increasing aliphaticity and molecular size of HSs. Thus, the extent of glyphosate adsorption on humic matter varies considerably with its supramolecular structure and dimension and is favoured by a high degree of stereochemical flexibility combined with an apparently large molecular size (Piccolo et al., 1996b; Mazzei and Piccolo, 2012). The increasingly recognised importance of organic matter in regulating sorption and environmental behaviour of pesticides, and the need to take its chemical properties into account when predicting environmental behaviour, has been recently recalled in an EFSA PPR Panel opinion (EFSA PPR Panel, 2013b), in which the conclusions of the FOCUS (2009) document were examined and discussed.

2.3. Conclusions

Based on literature research and the information provided by CRD, the Panel drew the following conclusions:

- Sorption of substances onto soils is a complex phenomenon, influenced by both substance properties and the nature of soil organic matter and mineral components. Sorption can be described according to a variety of interactions, ranging from van der Waals forces to electrostatic forces and sequestration into soil HSs. Because of the organic matter distribution in soil structural aggregates and the complexity of sorption processes, the apparent sorption may change with time. A fast (minutes to hours) initial sorption may be followed by a slower phase, which may continue over weeks to months. Especially at low organic matter content, clay and silt minerals are the dominant sorbers whereas at higher organic matter contents (> 0.5 %) the organic composition is the predominating sorber. However, the highest affinity of some pesticides and their metabolites may be to clay minerals or sesquioxides. The sorption process can be visualised as a progressively stronger encapsulation of the pesticide into the inner hydrophobic domains of the humic matter present in the humic-clay soil microaggregates.

- A pesticide may eventually interact so strongly with the soil humified organic matter that the substance is not extractable readily, or even at all, from the soil and can no longer be distinguished from the soil organic matter. This fraction may be referred to as the NERs. However, if the soil is affected by a change in the soil solution, due to the exudation of organic acids from plant roots or other amphiphilic metabolites exuded from microorganisms, the humic structure may be perturbed and even the strongly sorbed pesticides may be released again into the soil solution.

3. Experiments to derive aged sorption parameters

Section 3 of the draft guidance document (FERA, 2012) describes the recommended experiments for deriving aged sorption parameters. This draft guidance document states that aged sorption studies in the laboratory are preferred to field studies, because laboratory studies are well defined and well controlled. The Panel agrees with this because laboratory experiments provide consistent and repeatable results that are relatively easy to interpret. The guidance proposes the use of a standard incubation experiment to measure degradation kinetics (OECD, 2002), supplemented with a 24-hour extraction period with a 0.01 M CaCl$_2$ solution, as the most suitable laboratory method for characterising aged sorption. The Panel endorses the modification of an existing method, which is performed at realistic water content, to avoid duplication of effort, since applicants routinely perform degradation studies.

Batch adsorption experiments are, in principle, also suited to investigating aged sorption over the required time scale (Sittig et al., 2012). However, the Panel does not recommend the use of batch experiments because they are performed at unrealistically low soil to solution ratios and the disturbance of soil aggregates by shaking enhances the contact between the substance and the soil constituents. Furthermore, batch adsorption experiments are routinely run for, at most, 24 to 48 hours in the regulatory context, whereas the relevant time scale for pesticide leaching at the field scale is in the order of weeks to months or even longer.

In contrast to incubation experiments, laboratory column experiments also take leaching into account. They are therefore considered to better reflect the conditions of pesticide use in practice and may be proposed as an alternative method to derive aged sorption parameters (e.g. Spurlock et al., 1995; Jene, 2009). Column experiments run at constant irrigation rate and constant water content (unit pressure gradient under unsaturated conditions) are also well-defined systems. The use of re-packed soil columns minimises the effect of possible physical non-equilibrium flow, including preferential flow, and provides consistent and repeatable results. Nevertheless, the greater complexity of such studies would require a complex evaluation of the model parameters and even more expert knowledge (Freijer et al., 1995; Unold et al., 2009). Furthermore, the time scale of column experiments is restricted to at most a few weeks, but is generally much shorter. A flexible adaptation of the time scale is restricted, because it depends on the experimental set-up (water flux density and column length), the soil (water content) and the chemical or substance parameters (mobility and degradation). Thus, the method may be limited to less persistent substances only.

3.1. Soil selection and preparation

The draft guidance (FERA, 2012) recommends performing aged sorption studies with at least four contrasting soils. This is also currently the minimally required number of sorption and degradation experiments for active substances for regulatory purposes. For aged sorption studies, this number is a compromise between the substantial experimental effort and the large parameter variability, coupled with a strong sensitivity of leaching models for the aged sorption parameters. To our knowledge, no studies exist that have experimentally investigated the number of soils needed to get leaching concentrations with a predefined uncertainty. Unless such a study becomes available, the use of at least four contrasting soils is a workable compromise.

Both the Freundlich distribution coefficient, K_F (batch adsorption experiments), and the degradation half-life, $DegT50$ (aerobic degradation experiments), may depend on soil properties such as organic matter, pH and/or clay content. It is therefore highly likely that both parameters also vary considerably between soils with different physical and chemical properties in aged sorption experiments. The same might even apply for the factor describing the ratio between the non-equilibrium and equilibrium Freundlich coefficients (f_{NE}) and the desorption rate coefficient (k_{des}). It is therefore important to stress that the soils have contrasting properties.

Incubation experiments are carried out at only one input concentration, with a range of concentrations measured in the CaCl$_2$ suspension of generally less than a factor of 5. The information content of such

an experiment is not sufficient to give a reliable estimate of the concentration-dependent sorption behaviour, reflected by the Freundlich exponent, $1/n$. Therefore, an independent batch adsorption test (OECD, 2000) should be performed to derive the Freundlich exponent. The draft guidance (FERA, 2012) recommends using the same soils selected for the standard OECD 106 batch adsorption tests (OECD, 2000) in the degradation/aged sorption experiments. The Panel agrees that the same soils should be used for the aged sorption and the batch experiments, because of the low sensitivity of the Freundlich exponent ($1/n$) as a fitting parameter combined with its large impact on the leaching concentrations (see also section 6).

According to OECD (2002), soil should be gently dried, to give a moisture content suitable for sieving, and stored in a dark and cool place for, at most, three months. For aged sorption experiments, it is of utmost importance to carry out the experiments in field-moist soil. The use of air- or oven-dried soil in an incubation experiment requires rewetting of the soil constituents during the pre-incubation period. Rewetting of soil organic matter is a time-dependent process which may last for weeks (Altfelder et al., 1999), creating steadily new sorption sites until the soil constituents are fully rewetted. Rewetting thus mimics an artificial time-dependent sorption (experimental artefact). Therefore, the soil should not become drier than necessary to sieve. A pF value limit of 4.2 (permanent wilting point for plants) could be proposed, but probably with the exception of clayey soils, which can be dried to a degree that facilitates sieving for pragmatic reasons. It is expected that the problem of rewetting of the organic matter will not be so severe if this limit is not exceeded.

3.2. Sample preparation and incubation

Sample preparation and incubation should be conducted as described by OECD Guideline 307 (OECD, 2002) for aerobic transformation rate studies. Approved guidance also applies to the aged sorption studies.

If the incubation conditions (temperature and moisture content) deviate from reference conditions (20 °C and pF 2), the Panel agrees to normalise degradation in the two-site model (*DegT50*) using the same approach as for bulk soil (Q_{10} for describing the influence of temperature on the degradation process and Walker`s equation for moisture). Furthermore, van Beinum et al. (2010) considered the rate coefficient for desorption (k_{des}) and the distribution coefficients for sorption domains to be independent of the incubation conditions. Strictly speaking, they are not. However, the scientific understanding is very limited as regards how much and in which direction both parameters are affected by the incubation conditions. The Panel noticed that it is current practice in regulatory modelling not to correct the batch distribution coefficient for temperature. Overall, the Panel judges the need for a proper normalisation as minor, because the prescribed incubation conditions in the draft guidance document (FERA, 2012), i.e. a constant temperature of 20 °C (± 2 °C) and a constant moisture content of between pF 2 and pF 2.5 are at, or close to, the reference conditions (OECD, 2002).

3.3. Extraction and analysis

The complex interaction of pesticides with the organic fractions of soils implies that an analytical approach that attempts to quantify the aged sorption in soil and its dynamics should take into account the release of pesticides from various sorption domains caused by organic substances. The $CaCl_2$ extraction reflects the readily available fraction of the test substance in soil. To release the fraction of sorbed pesticides that is encapsulated deeply into the hydrophobic domains of soil organic matter, additional extractions are needed, capable of progressively releasing substances, which are potentially available for leaching.

To access this fraction, the draft guidance (FERA, 2012) proposes the use of a solvent extraction, in accordance with OECD (2002), to quantify the total extractable mass of the test substance (see Figure 2a). However, OECD (2002) is conclusive on neither the choice of the solvents nor the method. It just states that '… the soil samples (should be) extracted with appropriate solvents of different polarity …'. A recovery of between 90 and 110% for labelled chemicals (between 70 and 110% for

non-labelled chemicals) immediately after the addition of the test substance is given as a quality criterion to judge on the appropriateness of the extraction procedure. The differences in total mass extracted and mass in the $CaCl_2$ extract can be assigned to the poorly available fraction.
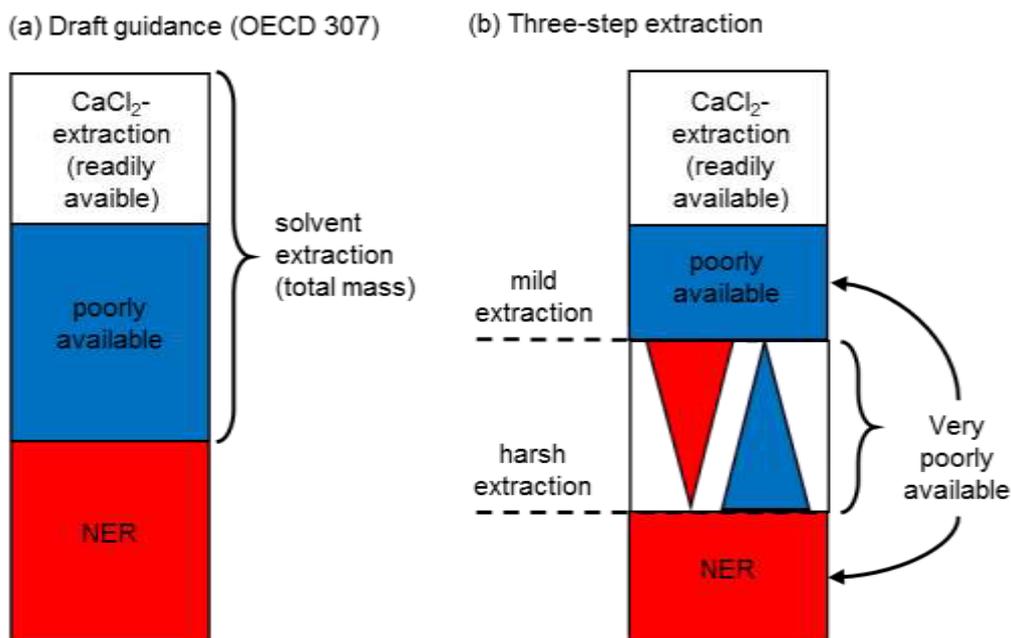
Figure 2: Distribution of the test substance in different fractions of the soil after (a) a sequential extraction, in accordance with the draft guidance (FERA, 2012), with an experimenter-specific, adequate choice of the extraction method used to determine total mass, in accordance with OECD (2002), or (b) a sequential extraction consisting of three steps. Figure prepared by the PPR WG.

The experimental method used to characterise the readily available fraction is explicitly given in the draft guidance (extraction with a 0.01 M $CaCl_2$ solution for 24 hours at 20 °C at the same soil to solution ratio as used in the adsorption experiments; FERA, 2012); the experimental protocol used to extract the total mass depends upon the choice of the experimenter, with the only restriction being an appropriate mass recovery. Therefore, the definition of the poorly available fraction, and consequently the NER fraction, is ambiguous and heavily relies on the experimental protocol (the choice of solvent, number of extractions, method (mild or harsh)). Figure 2b illustrates this for a mild and a harsh extraction, with an increase in the poorly available fraction and a concomitant decrease in the NER fraction.

Because of the progressive nature of the sorption there will never be a unique sequential extraction procedure that can characterise sorption in soil. A general extraction scheme involves extractions with (i) an aqueous solution, (ii) a mild organic solvent and (iii) a strong organic solvent. The use of an organic solvent speeds up the release of reversibly bound pesticides. An example of such a sequential extraction scheme (see Figure 2b), based on existing general literature (Gamble et al., 2000; Menasseri et al., 2004; Dalkmann et al., 2012), is given below:

   i.   Aqueous extraction with 0.01 M $CaCl_2$ for 24 hours.

   ii.   Mild extraction with an aqueous solution of a dipolar solvent and an organic acid (e.g. acetonitrile–water–acetic acid extraction (ACN–H_2O–AcOH) at pH 2). The addition of acetic acid is a consequence of our current knowledge on the capacity of organic acids exuded by plant roots to open organic matter super-associations and release entrapped pesticides (see section 2). After the $CaCl_2$ extraction, a three-step extraction with a mixture of ACN–H_2O–AcOH, maintained at pH 2 by the addition of glacial AcOH, should be performed at ambient temperature to extract the aged sorbed pesticides. The first step is performed with a

ratio of 50:50 (v/v), the second step with a ratio of 80:20 (v/v), and the last one with pure ACN to allow for the diverse polarities of substances. At each step, samples are shaken for 30 minutes on a reciprocal shaker. After centrifugation and decantation, all extracts are combined and considered as total extraction at ambient temperature (ACN–H_2O–AcOH extract).

    iii.   Harsh extraction with water–acetone (ACT–H_2O). An ultrasonic extraction to extract quantitatively the sorbed pesticide with a ACT–H_2O (1:1, v/v) mixture. A power of 55 W is applied for 12 minutes to the soil suspensions to obtain a total energy of 39.6 kJ. After sonication, the suspension is filtered through Whatman® 40 filter paper, in order to separate the residues from the extract.

The $CaCl_2$ extract represents the readily available fraction of pesticides in soil and is unequivocally experimentally defined. The exchange of pesticides between the solid and the liquid phase is very fast and reversible (instantaneous or equilibrium sorption). This fraction is equivalent to the equilibrium domain in the two-site PEARLNEQ (software package to fit aged sorption parameters) model (see Appendix B and Boesten and Ter Horst, 2012). The extraction with a mild organic solvent also extracts a residual fraction, with a slow, but reversible, exchange of pesticides with the liquid phase. Therefore, this extraction lumps the equilibrium and non-equilibrium sorption domains in the PEARLNEQ model. A harsh extraction with a strong organic solvent will probably also partly release a fraction of the residues that is irreversibly bound under ambient environmental conditions. This fraction can either be treated as an additional non-equilibrium domain with an even slower exchange with the liquid phase (a three-site model) or it can be lumped into the non-equilibrium domain or NERs (both being equivalent to the two-site PEARLNEQ model).

The draft guidance document (FERA, 2012) is compatible with Figure 2b when the extraction of the poorly available fraction is performed with a mild organic solvent and the rest is assigned to the NER fraction. If, however, the extraction with the organic solvent in the second step is too mild, part of the substance will not be extracted and will, improperly, be called the NER. The current models do not make a distinction between formation of NERs and degradation of the substance (section 4). This implies that using an extraction method that is not harsh enough would lead to an overestimation of the total degradation rate and hence an underestimation of pesticide leaching. On the other hand, the non-equilibrium domain is less distinct (lower f_{NE}), with most likely a faster exchange of pesticides between the equilibrium and non-equilibrium domain (larger k_{des}), resulting in less pesticide leaching.

A rigorous check of the implication of extraction procedures on pesticide leaching was not carried out in the draft guidance (FERA, 2012) or its supporting information. Furthermore, the procedure could not be checked by the Panel because of the lack of supporting information. It is therefore the responsibility of the notifiers to justify the extraction procedure used.

In the current time-dependent sorption model, the formation of both the metabolites and bound residues occurs in the equilibrium domain (the liquid phase and the equilibrium sorption domain), being characterised by an overall first-order transformation rate coefficient combining both processes. Although the Panel agrees that the formation of metabolites occurs in this so-called equilibrium domain, it is not convinced that this also applies to the formation of NERs. The Panel considers the formation of the NERs from the non-equilibrium domain to be more likely. The current model does not allow verifying this assumption. This, however, is not expected to influence the leaching results to a large extent, because NERs are not available for transport.

Nevertheless, the Panel accepts a two-site model as a workable compromise. In the near future, a three-site model will be too data demanding. Furthermore, a three-site model is outside the current modelling approaches used in the regulatory assessment of the leaching potential of pesticides.

3.4.   Conclusions

Based on literature research and information provided by CRD, the Panel drew the following conclusions:

- The draft guidance recommends performing aged sorption studies with at least four soils. Given that the parameters describing the aged sorption process depend strongly on soil properties, the Panel stresses that it is important that the experiments used to characterise aged sorption are performed using soils with contrasting properties. Furthermore, soils should not become drier than necessary for sieving to avoid artefacts related to difficulties with rewetting of the soil organic matter.

- The two-step extraction procedure consisting of a 24-hour extraction period with a 0.01 M $CaCl_2$ solution and a sufficiently harsh solvent extraction to characterise the total extractable mass (OECD, 2002) on the same soil is a reasonable compromise between the experimental effort and what is desirable from a theoretical point of view.

- No unique sequential extraction method exists to measure the total extractable mass, because sorption in soil depends on both the substance characteristics and soil characteristics. The definition of the poorly available fraction which is potentially available for leaching is ambiguous and depends on the experimental method. A justification of the extraction method, which meets the requirements of an appropriate mass recovery, should be given by the applicant.

4. Fitting of kinetic models to data from aged sorption studies

4.1. Modelling approaches

As indicated in van Beinum et al. (2010), several reviews of non-equilibrium model approaches exist in the literature (Ma and Selim, 1997; Scow and Johnson, 1997; Pignatello, 2000; Maraqa, 2001). The most commonly used model approaches are the mobile–immobile two-region models (e.g. Ma and Selim, 1997) and the two-site or multi-site kinetic sorption models (e.g. Streck et al., 1995; Leistra et al., 2001). The draft guidance document recommends using the PEARLNEQ model (Leistra et al., 2001), which is a two-site kinetic sorption model consisting of two sorption sites in parallel, both interacting with the pesticide concentration in the liquid phase.

The Panel adopts the same conclusion as van Beinum et al. (2010), i.e. that using a two-site modelling approach for regulatory purposes reflects a reasonable compromise between (i) the ability of the model to describe aged sorption under a range of situations and (ii) the possibility to determine model parameters from experiments with reasonable effort. An important argument is that the two-site model already has six parameters that need to be estimated from experiments. Any additional sorption site would increase the number of parameters. This would make the estimation of accurate model parameters from the available experiments even more difficult. Both of the two-site models implemented in PEARLNEQ (Leistra et al., 2001; Tiktak et al., 2000) and Streck et al. (1995) can be used since they are mathematically equivalent when parameters are converted appropriately.

During the last few years, it has become common practice to distinguish between dissipation, indicated by *DT50*, and degradation, indicated by *DegT50*. The draft guidance, however, uses *DT50* for degradation in the total system and *DegT50* for degradation in the equilibrium domain. This may become confusing in the peer review of substances. The Panel therefore recommends using the following definitions (see also the Glossary):

- *DT50*   dissipation half-life for the total system (days)

- *DegT50*   degradation half-life for the total system (days)

- *DegT50$_{EQ}$*   degradation half-life in the equilibrium domain (days)

4.2. Tools

Several parameter optimisation algorithms exist in the literature (see Janssen and Heuberger (1995) for a review). The most important distinction is between local and global optimisation procedures. The Levenberg–Marquardt algorithm (Levenberg, 1944) is clearly the most commonly used local search method and is used in the parameter estimation (PEST) software tool (Doherty, 2005). The advantage of the Levenberg–Marquardt method is that it is relatively easy to use and it gives reproducible results when the optimisation settings are fixed. However, the method finds only a local minimum, which is not necessarily the global minimum. This could be overcome by using global search methods, such as the Markov chain Monte Carlo method as used in Görlitz et al. (2011). The drawback of global search methods is that they are computationally more expensive.

In the 2009 FOCUS report (FOCUS, 2009) several algorithms and tools were tested and it was concluded that optimisation results were almost identical. The Panel therefore does not recommend a specific software tool. The only requirements are that the tool and optimisation settings provide a robust fit. This means, for example, that the user should demonstrate that the software is not trapped in a local minimum by using different initial parameter settings. Furthermore, the software tool should provide the output to assess the goodness of fit in accordance with the draft guidance document.

The draft guidance document is based on a combination of PEST and PEARLNEQ (Boesten and Ter Horst, 2012) approaches. The Panel observes that the PEST–PEARLNEQ combination does not come

with a graphical user interface. The development of such a shell would ease its applicability for regulatory purposes.

4.3. Optimisation procedure

This section describes some concerns related to the fitting procedure in the draft guidance document.

4.3.1. Sampling time points to be included in the fitting procedure

The draft guidance recommends that at least six valid time points are used for the derivation of aged sorption parameters (after omitting early time points). The issue of the minimum number of valid data points relates to the question of whether or not measurements of total mass and concentration in the $CaCl_2$ suspension can be treated independently. If this is not the case, the number of degrees of freedom left for the χ^2-test would only be 1 (five parameters to be fitted according to the draft guidance), limiting the applicability of the fitted model parameters. Whether or not the measurements of total mass and concentration in the $CaCl_2$ suspension can be treated independently depends on the correlation between the two parameters. The Panel could not come to a conclusion here because the original data were not provided.

The draft guidance recommends omitting early time sampling points *by default*. This approach gives more weight (and therefore better fit) to the later stage of the aged sorption experiment as the fit is not forced through the early sampling time points. In the draft guidance, the exclusion of earlier data points from the fitting procedure is justified for the following two reasons:

i.   Processes other than long-term sorption, such as short-term adsorption, precipitation and dissolution, are likely to influence the measurements of both mass and concentration during the first two days after pesticide application.

ii. The two-site model is not able to describe the rapid reactions that occur within the first hours and days after application, as well as the slower processes operating at a time scale of weeks or months, because it contains only one kinetic sorption site.

The Panel does not necessarily agree that sampling points (with the exception of clear outliers) should be excluded *by default* in order to obtain a better fit. In general, the appropriateness of the model should be challenged if it is not capable of fitting the measured data in an adequate way. Therefore, the Panel recommends always first checking whether or not the PEARLNEQ model is capable of adequately describing the entire period of the experiment. If this is not the case, a stepwise approach may be taken into account, excluding certain sample points in a second step. The Panel recommends thorough evaluation of the pros and cons of excluding certain data points on the basis of real aged sorption experiments.

4.3.2. Parameter values to be optimised

The draft guidance recommends fitting five parameters of the PEARLNEQ model ($M_{p,ini}$, $K_{OM,EQ}$, k_t, k_{des} and f_{NE}) against measured data, which implies that only the Freundlich exponent ($1/n$) is not fitted. Therefore, the guidance recommends also fitting $K_{OM,EQ}$ with the argument that the $K_{OM,EQ}$ obtained from the corresponding batch study might be different to that obtained in the aged sorption experiment. This recommendation is in contrast to that made by FOCUS (2009), which recommended fixing $K_{OM,EQ}$ to the value measured in the batch experiment (see Appendix A, section A2). In order to keep the fitted $K_{OM,EQ}$ in an 'acceptable range', the draft guidance recommends that the fitted $K_{OM,EQ}$ should be within 20 % of the $K_{OM,EQ}$ measured for the day 0 sample.

The Panel notes that the $K_{OM,EQ}$ obtained from the aged sorption experiment should, in principle, be identical to that obtained from the batch experiment. In the aged sorption experiment, the aqueous extraction is performed using $CaCl_2$ with a soil to solution ratio equal to the ratio for the batch sorption experiment. The extraction is for 24 hours, which is approximately the same duration as the contact time in most batch sorption experiments. With the same contact time and the same (gentle) shaking,

one would expect a distribution constant that is not different from the distribution constant that can be derived from the Freundlich equation for the same concentration. Small deviations may occur because of the slightly different procedures that may be used for adding the substance to the soil. As the aged sorption study is performed for a single concentration only, this concentration should be taken into account when calculating the Freundlich equilibrium ($K_{OM,EQ}$) that is used for the fitting of the other parameters.

Adding an extra fitting parameter may result in a better model fit (in terms of the sum of squares of residuals), but at the expense of losing one degree of freedom. Because this will increase the likelihood of parameter unidentifiability, a model with more model parameters is not, by definition, the better model. This is particularly a problem if the number of fitting parameters is almost equal to the number of time points.

Based on these considerations, the Panel recommends fixing the $K_{OM,EQ}$ value to the value obtained in the aged sorption experiment and not to fit the $K_{OM,EQ}$ value. The Panel proposes using the value obtained at time zero in the aged sorption study, because this avoids the problem of variability between soil samples. Moreover, a corresponding batch $K_{OM,EQ}$ value may not be available in the case of legacy studies (refer to section 8). In any case, the Panel recommends thoroughly evaluating the pros and cons of relaxing this requirement (e.g. by allowing for free fitting of the $K_{OM,EQ}$) and possible consequences for the risk assessment on the basis of the underlying experimental data. The final procedure should not lead to inconsistencies with lower-tier data (with $K_{OM,EQ}$ values typically derived from batch experiments).

4.3.3. Optimisation settings

As described in section 4.2, the Levenberg–Marquardt algorithm is used for parameter fitting. Since this is a local search method, the optimised parameters may depend on the initial parameter setting (starting values) for f_{NE} and k_{des}, in particular because the number of parameters to be fitted is rather high and parameters may be correlated with each other. The Panel therefore adopts the recommendation of repeating the fitting with at least four different initial values of f_{NE} and k_{des}.

The draft guidance recommends constraining f_{NE} during the parameter fitting procedure to between 0.001 and 10 and k_{des} to between 0.0001 and 0.5 d^{-1}. Note that an additional acceptance criterion for f_{NE} and k_{des} is provided to limit their upper values (10 and 0.5 d^{-1}, respectively); however, curiously, the guidance does not limit their lower values.

The Panel recognises that it is necessary to discriminate between parameter constraints in the fitting procedure and parameter constraints in relation to an acceptability criterion. Non-linear parameter optimisation routines require wisely chosen upper and lower bounds for each parameter to find the global minimum. One reason is that parameters can lie only within certain well-defined physical limits determined by the theory. Another reason is that PEST may try to force a fit between model and measurements by adjusting some parameters to extremely large or extremely small values, which may result in floating point errors or numerical convergence difficulties (Doherty, 2005).

The draft guidance recommends constraining f_{NE} to between 0.001 and 10 in the optimisation procedure, with $f_{NE} < 10$ being an additional acceptance criterion. There is no scientific reason to limit f_{NE} to 10. According to equations 7–21 in FOCUS (2009), the proposed boundaries are equivalent to a fraction of the equilibrium sorption site of 0.999 and 0.09 in the two-stage, one-rate Streck model. For batch sorption experiments with the same soils but with different experimental conditions, Kasteel et al. (2010) and Sittig et al. (2012) found that even fractions of the equilibrium sorption site as low as 0.022−0.069 and 0.018–0.052, respectively, were necessary to correctly describe the partitioning of the veterinary antibiotic sulphadiazine between the liquid and the solid phase(s). In this context, an f_{NE} value of 50 (fraction of the equilibrium sorption site ≈ 0.02) or an even higher value (e.g. $f_{NE} = 100$, equivalent to the fraction of equilibrium sorption site of ≈ 0.01) can be proposed as the upper parameter bound in the optimisation.

Two approaches can be followed to address the maximum value for the additional acceptance criterion of f_{NE}:

i. limit f_{NE} to a value of 50 (or 100), which is still an arbitrary, but realistic, value;

ii. adopt a procedure similar to equilibrium sorption as an objective method to judge the acceptability of f_{NE} and k_{des}.

The lower bound of $f_{NE} = 0.001$ (fraction of the equilibrium sorption site of 0.999) in the optimisation procedure reflects a situation close to equilibrium. The equilibrium sorption model (a one-site model with only the equilibrium domain) is already part of the decision tree. If the answer to the question 'Does the aged sorption model describe the data better than the equilibrium fit?' (i.e. is the χ^2-error of the apparent sorption coefficient ($K_{D,app}$) calculated for the non-equilibrium model lower than the χ^2-error of $K_{D,app}$ calculated for the equilibrium model?) is 'no', then the relevance of aged sorption is not proven and an exposure assessment with aged sorption is not appropriate. In other words, f_{NE} is not accepted. This procedure avoids the occurrence of f_{NE} values that are too low (or k_{des} values that are too high).

If the fraction of the equilibrium sorption site tends to zero, i.e. $f_{NE} \rightarrow \infty$, then the two-site, one-rate sorption model reduces to the rate-limited sorption model (a one-site model with only the non-equilibrium domain). In line with the equilibrium scenario, a f_{NE} value is accepted only when the χ^2-error of $K_{D,app}$ calculated for the two-site, one-rate model is lower than the χ^2-error of $K_{D,app}$ calculated for the rate-limited sorption model.

This concept also applies to k_{des}, with large values reflecting a situation close to equilibrium and vice versa. In this respect, a k_{des} value of 0.5 d^{-1} may contradict the assumption that mass exchange between the equilibrium and non-equilibrium domains should be negligible during the 24-hour aqueous extraction with CaCl$_2$. This is highly unlikely for k_{des} values of 0.5 d^{-1} or higher.

The Panel proposes using a large range between the upper and lower bound of each parameter in the non-linear parameter optimisation routine in order to find the global minimum (f_{NE} of 0.001−50 (or 100) and k_{des} of 0.0001−0.5 (or even larger)). It is not recommended that an upper (or lower) limit of f_{NE} and k_{des} be provided as an additional acceptance criterion to some arbitrary values without much scientific justification. Instead, the χ^2-error of $K_{D,app}$ calculated for the two-site, one-rate model should be compared with the χ^2-errors of $K_{D,app}$ calculated for the one-site models for equilibrium and rate-limited sorption. The Panel recommends accepting all parameter values in case the χ^2-error of the two-site, one-rate model is lower than the corresponding value for either of the one-site models. As long as the rate-limited sorption model is not operational for fitting, f_{NE} may be limited to < 50 (or 100) as an additional acceptance criterion.

The draft guidance document recommends weighting the input data by their inverse values. This is considered essential if data to be fitted (concentration in total soil and soil pore water in the case of aged sorption) differ by orders of magnitude. Hardy (2011) proposed relaxing this requirement when the data on concentrations in total soil and soil pore water are of the same order of magnitude. The Panel does not endorse this recommendation by Hardy (2011) because this could lead to less standardisation of the fitting procedure and hence less transparency.

The Panel recommends reporting the parameter correlation coefficient matrix (as given by PEST) as well. Correlation coefficients between, for example, f_{NE} and k_{des} close or equal to 1 or −1 indicate a strong interaction between these two parameters. In this case, f_{NE} and k_{des} cannot be adequately determined because several combinations of f_{NE} and k_{des} would lead to an acceptable fit (parameter unidentifiability).

4.4. Goodness of fit criteria

The draft guidance document proposes to base the decision on whether or not a model fit is acceptable on a combination of visual and statistical methods. The Panel endorses such a combination of methods because statistics give objective and reproducible results, and visual methods capture the sometimes complex patterns in experiments (see also Janssen and Heuberger, 1995).

The visual assessment of the model fit should be based on (residual) plots of the total mass concentration (M_{tot}) and that of the liquid-phase concentration (C_L). Furthermore, the draft guidance document requires that the apparent K_d values be plotted against time. The Panel endorses this addition to the original guidance by Boesten et al. (2007), because this provides important evidence regarding whether or not aged sorption is occurring.

The guidance document recommends using a modified version of the χ^2-test to evaluate the goodness of fit as proposed by FOCUS (2006). The revision of the χ^2-test was considered necessary, as fitting to weighted data is proposed in the draft guidance document (in FOCUS, 2006, non-weighted data are considered). The Panel agrees with this modification. Note that a factor of 100 is missing in equation 18 of the draft guidance document.

4.5. Evidence for aged sorption

The Panel agrees that it is important to demonstrate that aged sorption is relevant. The first judgement should be made based on a visual comparison of the plots of the apparent K_d against time. Additionally, evidence should be provided based on a χ^2-test: the χ^2 error for the apparent K_d for the aged sorption model must be smaller than that of the equilibrium model. The Panel considers this test sufficiently strict, because the number of degrees of freedom is less for the non-equilibrium model than for the equilibrium model.

4.6. Criteria for the acceptability of the fitted parameters

The most restrictive criteria for the acceptability of the fitted aged sorption parameters $K_{OM,EQ}$, f_{NE} and k_{des} are their confidence intervals and their relative standard errors (RSEs). The RSE is defined as the 95 % confidence interval (upper limit minus lower limit) of an estimated parameter divided by four times the estimated value. Wide confidence intervals imply that the parameters are very uncertain. The choice of what is considered acceptable is of course arbitrary. The draft guidance document proposes that the RSE for any of the fitted parameters should not be greater than 0.4. This implies that the width of the 95 % confidence interval may not be greater than 160 % (i.e. ±80 % of the parameter estimate). The argument against using this value is that, with this value, approximately the same number of model fits were 'wrongly rejected' and 'wrongly accepted'. The value of 0.4 is slightly lower than the value of 0.5 proposed by FOCUS (2009) and considerably higher than the value of 0.25 proposed in an previous version of the guidance document (van Beinum et al., 2010). The Panel considers the value of 0.4 a reasonable compromise, but proposes to re-evaluate this value two years after the guidance has become operational.

4.7. Conclusions and recommendations for improvement of the guidance

Based on scientific literature and the information provided by CRD, the Panel concluded that the model and the tools for parameter optimisation are fit for purpose. The Panel has, however, concerns about the optimisation procedure. The Panel investigated options for improving the guidance in this respect, but could not provide final conclusions because the underlying experimental data were not made available. More specific conclusions and recommendations are listed hereafter:

- The Panel adopts the conclusion of van Beinum et al. (2010), that is that using a two-site modelling approach for regulatory purposes reflects a reasonable compromise between (i) the ability of the model to describe aged sorption under a range of situations and (ii) the possibility to determine model parameters from experiments with reasonable effort.

- The number of independent sample points determines the degrees of freedom in the fitting procedure depending on the number of parameters to be fitted and has strong impacts on the acceptability of the fit. Whether or not the measurements of total mass and concentration in the $CaCl_2$ suspension can be treated independently depends on the correlation between the two state variables. The Panel could not come to a conclusion here because the original data were not provided.

- The Panel recommends always first checking whether or not the fitted model is capable of adequately describing the measured data without excluding any time points and fixing $K_{OM,EQ}$ to that measured at day 0 of the time-dependent sorption experiment. The Panel could, however, not test this recommendation, because the experimental data to test this recommendation were not provided.

- The Panel adopts the recommendation of repeating the fitting with at least four different initial values of f_{NE} and k_{des}. The Panel recommends not providing an upper (or lower) limit of f_{NE} or k_{des} as an additional acceptance criterion to some arbitrary values without scientific justification. In this regard, f_{NE} values of up to 50 or 100 may be considered acceptable.

- The Panel endorses the combination of the statistical and visual methods, as suggested in the draft guidance, in order to judge the acceptability of the fits. The Panel agrees that it is important to demonstrate that aged sorption is relevant.

- The Panel considers the value of 0.4 for the root mean square error (relative standard error for the estimated parameter value) (RSE) of the fitted aged sorption parameters a reasonable compromise, but proposes to re-evaluate this value two years after the guidance has become operational.

5. Use of aged sorption parameters in regulatory exposure assessments

This section addresses the use of aged sorption parameters in regulatory exposure assessments.

The draft guidance is limited, without stating this explicitly, to substances for which organic matter is assumed to provide the sorption capacity. If mineral soil components (clay minerals or sesquioxides) determine or influence the sorption capacity, derivation of aged sorption parameters becomes very complex. In addition, the minimally required number of four aged sorption studies is, in these cases, far too low to derive parameters appropriately. For the time being, the Panel recommends not using aged sorption for such substances.

The Panel noted that the draft guidance document did not systematically review uncertainties arising from the use of aged sorption data in regulatory leaching assessments. Uncertainties may result from, for example, the experimental procedure (extraction procedures), the conceptual model and the quality of the fitted parameters (Dubus et al., 2003; Vanclooster et al., 2004). It is recommended that a systematic review of uncertainties is carried out when updating the draft guidance document.

5.1. Source of input data for regulatory exposure assessments

The Panel agrees that f_{NE} and k_{des} should not be estimated from soil or pesticide properties as there is currently insufficient basis for such estimations. Furthermore, to our knowledge, comprehensive databases containing relevant soil characteristics and aged sorption parameters are not available. Therefore, time-dependent sorption parameters should be derived from dedicated experiments, as outlined in section 3.

5.1.1. Using default values

The draft guidance document recommends using default values of 0.3 for f_{NE} and 0.01 for k_{des}. The Panel recognises that the stated values rank rather low in the distribution of available values. However, section 5.1.3 of the draft guidance mentions that it may be difficult to obtain a robust estimate of non-equilibrium parameters in cases with small f_{NE} and k_{des} values and therefore these values may be not reliable. Furthermore, the flow chart in section 5.2 of the draft guidance might result in using default values that are not conservative enough for such cases. Furthermore, the Panel observes that using default values is not in line with higher-tier approaches where parameter refinement should be based on dedicated experiments. The Panel therefore recommends assuming that aged sorption does not occur unless reliable values for f_{NE} and k_{des} have been derived (i.e. the default values for k_{des} and f_{NE} should be zero).

5.2. Aged sorption in tiered pesticide leaching assessment

Section 5.2 of the draft guidance describes how aged sorption parameters should be used in the regulatory risk assessment. In the following sections, the Panel addresses a number of concerns.

5.2.1. Minimum number of studies showing aged sorption

Time-dependent sorption may have a large influence on the results of the leaching assessment. Therefore, a well-informed decision on the required number of experiments to be performed and showing aged sorption should be taken. The draft guidance states that, when at least two out of four experiments show aged sorption, aged sorption can be taken into account. The Panel notes that, in situations in which potential leaching was concluded to occur in a lower tier, 50 % is a rather low value. A criterion that states that the majority of experiments (with a minimum of four experiments) should show aged sorption behaviour would be more in line with a conservative approach.

5.2.2. Averaging aged sorption parameters

The draft guidance document considers two options for using aged sorption parameters in the leaching assessment. The first option is to perform calculations for each parameter combination and to average the predicted environmental concentration (PEC) thereafter ('calculate first, average later'). The

second approach is to average the parameters before using the leaching model ('average first, calculate later'). Furthermore, the draft guidance states that both approaches should be followed, and that the most conservative value from both approaches should be taken.

Leterme et al. (2007) used the spatially distributed version of the Pesticide Emission Assessment at Regional and Local Scale (PEARL) model (GeoPEARL) to study the effect of calculating first or averaging first on the simulation of pesticide leaching. They included both soil properties and pesticide properties (K_{OM} and *DegT50*) in their assessment. They concluded that the calculate-first approach generally resulted in higher PECs than the average-first approach. To check the consequences of first averaging the aged sorption parameters, the Panel performed some exploratory simulations with the PEARL model (see Appendix C). These simulations revealed that the two approaches generally gave similar results. In those studies in which differences were observed, these were also observed when calculations were performed without considering aged sorption. The consequence is that application of the average-first approach to aged sorption parameters does not introduce additional uncertainty in the environmental risk assessment. Given that the calculate-first approach is extremely resource demanding, the Panel is of the opinion that the average-first approach is the preferred option. An additional advantage of the average-first approach is that it is more straightforward to include lower tier sorption and degradation data (see section 5.2.3).

5.2.3. Including lower tier sorption and degradation data

The draft guidance states that a decision on the leaching potential may be based on the results of four aged sorption experiments. Implicitly, this means that available lower tier information is not used any more. The Panel is of the opinion that such an approach is not correct and that information from lower tiers should always be considered. This is particularly important for lower-tier sorption and degradation data.

With respect to sorption data, the Panel notes that the $K_{OM,EQ}$ derived from aged sorption experiments is theoretically equivalent to the sorption constant from batch equilibrium sorption experiments (when normalised to the same conditions). The geometric mean of all available data, i.e. values from lower tier and aged sorption experiments, would therefore be the best estimate. (Note that the draft guidance mentions calculating the arithmetic mean, which was probably based on existing guidance at that time.)

DegT50 is different from *DegT50$_{EQ}$*, so incorporation of lower-tier data is less straightforward. The Panel identifies at least two options for including lower tier *DegT50* value data, i.e.:

   i.   combining *DegT50$_{EQ}$* from aged sorption studies with *DegT50* from lower-tier studies <u>without</u> correction of *DegT50*;

   ii.   combining *DegT50$_{EQ}$* from aged sorption studies with *DegT50* from lower-tier studies <u>with</u> correction of *DegT50*; this correction could, for example, be done with the correction procedure described in FOCUS (2009), using average values for the aged sorption parameters.

Option (i) is a conservative approach, whereas option (ii) gives a more realistic description of *DegT50$_{EQ}$*. The Panel recommends evaluating the above options using real-world sorption studies.

5.3. Conclusions and recommendations for improvement of the guidance

The Panel concluded that the draft guidance document does not strictly follow the principles of the tiered approach described by FOCUS (2009). For this reason, the Panel gives options for improving the guidance. The Panel could, however, not test these options because the experimental data underlying the draft guidance document were not made available. Specific conclusions and recommendations follow below:

- The draft guidance acknowledges that the default values for f_{NE} and k_{des} may not be conservative enough in view of the tiered approach described by FOCUS (2009). The Panel therefore recommends assuming that aged sorption does not occur unless reliable values for f_{NE} and k_{des} have been derived. This implies that the default values for k_{des} and f_{NE} should be set to zero.

- The draft guidance states that, when at least two out of four experiments show aged sorption, aged sorption can be taken into account. The Panel is of the opinion that this is a small number for such an important process. A criterion that states that the majority of experiments (with a minimum of four experiments) should show aged sorption behaviour would be more in line with a conservative approach.

- The draft guidance document mentions two options for including aged sorption parameters in the leaching assessment, i.e. the average-first and calculate-first approaches. Given that the calculate-first approach is extremely resource demanding, the Panel is of the opinion that the average-first approach is the preferred option. An additional advantage of the average-first approach is that it is more straightforward to include lower-tier sorption and degradation data. Further exploration based on real aged sorption experiments is, however, necessary before a final conclusion can be drawn.

- The draft guidance states that a decision on the leaching potential may be based on the results of four aged sorption experiments. Implicitly, this means that available lower tier information is not used any more. The Panel concludes that such an approach is not correct and that information from lower tiers should always be considered.

- The Panel gives some options for including lower-tier data. These options could, however, not be further elaborated because the experimental data underlying the draft guidance were not available to the Panel.

6. Special considerations for deriving the Freundlich exponent

The Panel is aware that the fitting procedure is rather flexible with respect to parameter settings, as inappropriate parameter settings (e.g. the Freundlich exponent, which has to be fixed during the fitting procedure) may be compensated by other ones. Hardy (2011) has already indicated that the aged sorption fitting procedure is rather insensitive to the setting of the Freundlich exponent. The Panel made some additional calculations, based on example 1 given in the appendix of the draft guidance document, by setting the Freundlich exponent to 0.7, 0.9 or 1.0 (in addition to the measured value of 0.83). The results in Appendix D show that using different Freundlich exponents hardly affected the quality of the fit; all quality criteria given in the draft guidance document were met. Because the leaching models are highly sensitive to the Freundlich exponent (Boesten and van der Linden, 1991; Tiktak et al., 1994), using an appropriate Freundlich exponent for the groundwater exposure assessment is extremely important. The Panel therefore recommends using the guidance included in Boesten et al. (2015) with some modifications. Note that this applies not only to the situation of aged sorption, but also to the first-tier assessments in the 2009 FOCUS report (FOCUS, 2009). The slightly modified text is included hereafter.

6.1. General considerations

The Freundlich exponent ($1/n$) describes the curvature of the Freundlich sorption isotherm. Most measured $1/n$ values (with regard to pesticides) are between 0.7 and 1.1, although lower and higher values have been reported (e.g. Allen and Walker, 1987; Boesten and van der Pas, 1988; Brouwer et al., 1990; Scorza Júnior et al., 2004). It has been known since the early 1990s that the Freundlich exponent may have a large effect on the leaching concentration. If all other parameters are kept constant, the leaching concentration may decrease by a factor of more than 100 when the Freundlich exponent decreases from 1.0 to 0.8 (Figure 2 of Boesten, 1991). Therefore, it is important that the Freundlich exponent is measured accurately.

Let us consider the guidance that is currently available at EU level for the Freundlich exponent. FOCUS (2000) (p. 93) stated: 'For models which require the Freundlich adsorption coefficient (see above) the exponent of the isotherm ($1/n$) is also required and this is determined in each experiment. However where the results of a number of adsorption coefficient determinations are averaged then the average value of $1/n$ should also be used. When there is no data, a default value of 0.9 should be used.'

FOCUS (2001) (p. 201) stated: 'Information on the mechanism of sorption should generally be available from the dossier used to establish the monograph of the substance. If the kinetics of sorption follows the Freundlich adsorption kinetics model one of the regression coefficients available will be the $1/n$-value. For models, which require the Freundlich adsorption coefficient, the exponent of the isotherm ($1/n$) is also required and values of this parameter are typically determined in each sorption experiment. If a number of $1/n$ have been determined (e.g. for a number of soils), the average value of $1/n$ should also be used. A default value of 0.9 is assumed if no information on the $1/n$ value is present. If a linear relation for sorption has been determined the value may be set to 1.'

Therefore, the guidance provided by the different FOCUS documents (2000, 2001) is almost exactly the same. However, these guidance documents provide no justification for their recommendations. Thus, there is a gap between the uncertainty resulting from the estimation of the Freundlich exponent, on the one hand, and the lack of scientific underpinning of the recommendations by FOCUS (2000, 2001), on the other hand. It is likely that the guidance provided by FOCUS was inspired by Boesten and van der Linden (1991), who recommended using 0.9 as a default for Dutch scenario calculations on the basis of the argument that it was the average of the values found in a literature review by Calvet et al. (1980). No guidance is available on how to check the accuracy of Freundlich coefficients. In the literature, no error analyses of Freundlich exponents are available. Such analyses could be based on hypothetically generated sorption isotherms using Monte Carlo techniques.

6.2. The Freundlich exponent—quality criteria for individual measurements

Given the high sensitivity of the leaching process on the Freundlich exponent, it is important to assess the reliability of reported values. In the absence of (i) detailed scientific analyses of the accuracy of the Freundlich exponent and (ii) tests of whether the exponent is a soil or a pesticide property, a pragmatic procedure is proposed for the evaluation of measured $1/n$ values, i.e. to apply the following quality criteria:

i.   The overall quality of the experiment should be acceptable, i.e. minimum requirements of OECD (2000) should be met.

ii. Freundlich exponents should be accepted only from studies of which sorption coefficients are accepted to be included in further analysis. This is based on the argument that if the sorption coefficient is considered not sufficiently reliable then the curvature would be unreliable as well.

iii. The correction of the measured sorption coefficient due to incomplete recovery of the substance in the experiment is less than 20 % (for further details see equation 18 in Boesten et al. (2015)).

iv. Freundlich exponents should be accepted only from studies that included at least three different initial concentrations and in which the difference between the highest and the lowest initial concentration was at least a factor of 100 (this instruction for the measuring procedure relaxes, to some extent, the recommendations in OECD (2000), section 72, which states: 'Five test substance concentrations are used, covering preferably two orders of magnitude', but stresses the required range in concentrations; see also OECD, 2002).

v.   The R^2 value of the regression between logarithms of the measured concentrations and the logarithms of measured contents sorbed should not be less than 0.975.

The third requirement applies only to sorption experiments that use the indirect method (sorption constant derived from the decrease in concentration in the liquid phase). This is more or less a minimum requirement because it is difficult to argue that a curvature would be reliable if the ratio of content sorbed to concentration in liquid phase is incorrect by more than 20 % or if the measurement of the sorption coefficient is very unreliable.

6.3. Averaging of the Freundlich exponent

The Panel recommends using the arithmetic mean of all reliable values. In view of the absence of a database of reliable $1/n$ measurements, we recommend not setting strict limits for the $1/n$ values of sorption isotherms of a specific substance–soil combination. Therefore, values in the range of 0.6–1.2 are considered acceptable. However, if the arithmetic mean $1/n$ value exceeds 1.0, a value of 1.0 should be used because an exponent higher than 1.0 is considered physically unrealistic for the soil matrix. We do not recommend using this restriction, $1/n \leq 1$, for individual sorption isotherms because this would lead to a systematic bias (refer to Boesten et al. (2015) for details).

Current data requirements state a minimum of four values for sorption coefficients (three for relevant metabolites). If the OECD (2000) guideline was followed to obtain the sorption parameters, this would also lead to four (or three in the case of metabolites) Freundlich exponents. The draft guidance on aged sorption leads to a minimum of four Freundlich exponent values, subject to the quality criteria above, if the batch equilibrium method is used, implying that current data requirements would be met.

It has been common practice in groundwater leaching assessments to use a default value of 0.9 for the Freundlich exponent, because this is the average value of a large number of sorption studies (Calvet et al., 1980). This value may, however, not be conservative enough in a tiered approach because dedicated sorption experiments (parameter refinement) may result in $1/n$ values of > 0.9. A $1/n$ value

of 1 would therefore be more appropriate in a tiered approach. The Panel recommends reconsidering the default value in view of the tiered approach introduced by FOCUS (2009).

6.4. Conclusions

Based on both the information provided by CRD and Boesten et al. (2015), the Panel concludes that:

- The fitting procedure of the aged sorption parameters is insensitive to the value of the Freundlich exponent. The Panel therefore agrees that the Freundlich exponent should be derived from batch experiments using the same soil. In this respect, the Panel recommends using the guidance included in Boesten et al. (2015) taking into account the modifications described in this section. The Panel also recommends using this guidance for lower-tier leaching assessments and for calculating the pore water concentration in soil.

- The Panel observes that the default value of 0.9 for the Freundlich exponent may not be conservative enough in a tiered approach. A Freundlich exponent of 1 would be more appropriate in a tiered approach. It is only when pesticides are applied at high rates (e.g. soil fumigants) that this value may not be conservative enough. The Panel recommends reconsidering the default value in view of the tiered approach introduced by FOCUS (2009).

7. Special considerations for metabolites

The draft guidance states that, in general, it will be impossible to derive aged sorption parameters for metabolites from experiments in which the parent substance is applied to the soil. Even in the simplest case of a parent not showing aged sorption and one metabolite showing aged sorption, the draft guidance requires seven parameters to be fitted. The number of parameters to be fitted increases to 10 if both the parent and the metabolite show aged sorption, and increases further when the degradation scheme becomes more complex. Moreover, parameters may be correlated, thereby increasing demands on the dataset. Therefore, the Panel generally agrees with the statement in the draft guidance.

However, when the metabolite is directly applied to the soil, it is possible to derive the required aged sorption parameters. The Panel is of the opinion that the same criteria should be used for metabolites when deciding whether or not aged sorption applies. In addition, however, it is important that metabolites are measured in the experiments with the parent so that data can be used to check results from the aged sorption experiments with the metabolite(s). It is necessary to check whether or not the parameters of the aged sorption experiments are consistent with the situation in which the formation of the metabolite(s) is not instantaneous. A stepwise fitting procedure followed by an all-in-one check (as shown, for example, for complex degradation schemes by FOCUS, 2006) may be acceptable.

The draft guidance states that it must be ensured that parameters are consistent when both parent and metabolites show time-dependent sorption. In addition to the observations above, the Panel notes that there is insufficient knowledge available on the conservativeness of this approach.

If a parent, but not the metabolites, show time-dependent sorption, there are consequences for the risk assessment which are not stated in the draft guidance. Most probably, the formation fraction of the metabolite, as well as the degradation rate (*DegT50*) derived from a classical degradation experiment, will not be consistent with the aged sorption behaviour of the parent. As all parameters must be consistent when performing a regulatory leaching assessment, re-interpretation of the kinetic studies using appropriate descriptions of the aged sorption behaviour of the parent will be necessary. Currently used packages (e.g. CAKE and KINGUI) do not offer routines for aged sorption. In view of this, it is desirable that these packages are extended to facilitate such re-interpretations. At the moment, it is impossible to predict whether or not the assessment is conservative when such re-interpretation is not performed.

The Panel agrees with the draft guidance on the necessity to investigate whether or not the sorption behaviour of metabolites is dependent on the reaction rate of the parent.

7.1. Conclusions and recommendations

Based on the data provided by CRD, the Panel drew the following general conclusions:

- The Panel endorses using the experimental set-up for metabolites, i.e. applying the metabolite to the soil to derive aged sorption parameters. The validity of the aged sorption parameters should then be checked against other evidence.

- When in a degradation scheme, if the parent substance shows time-dependent sorption while the daughter(s) does(do) not, it will, in general, still be necessary to re-interpret the kinetic behaviour of the daughter substances, as the aged sorption process will affect the formation of the daughter and consequently the degradation rate. The leaching assessment should be done with a consistent dataset.

The Panel is aware that CRD commissioned FERA to further develop the guidance document with respect to metabolites. The Panel recommends that this additional guidance is incorporated into the updated guidance document so that the Panel can also review the applicability of the guidance for metabolites.

8.   Special considerations for legacy studies

Legacy studies are defined as aged sorption studies that were conducted before the draft guidance was available and which were not conducted fully in line with the draft guidance document. In the case of such studies, the draft guidance recommends accepting less stringent requirements. This may include a lack of soil-specific batch experiments, in accordance with OECD (2000), or certain deviations with respect to the number of sampling data available and the sampling frequency.

In the case of a missing soil-specific Freundlich exponent for the fitting procedure, the draft guidance recommends fixing the Freundlich exponent value to the average Freundlich exponent obtained from other soils. The Panel agrees that using the average Freundlich exponent obtained from other soils is the most appropriate substitute for an unknown soil-specific Freundlich exponent. This recommendation is supported by Hardy (2011), who showed, on the basis of the industry dataset, that using the average Freundlich exponent from other soils instead of the soil-specific one has hardly any effect on the final groundwater exposure assessment. If a reliable Freundlich exponent from other soils is not available, the Panel recommends not using these legacy studies further to obtain aged sorption parameters.

In contrast to standard aged sorption studies, the draft guidance considers five valid sampling points for legacy studies to be sufficient (after omitting early time samples). The Panel notes that the χ^2-test cannot be applied to the graph of apparent K_d values because the number of data points in time would be equal to the number of parameters. For further discussion of the independence of total available mass and concentration in the liquid phase, see section 4.3. Based on this, the Panel considers fixing the $K_{OM,EQ}$ value to the value measured in the aged sorption experiment at time zero the preferred option, since this makes the χ^2-test possible with only five time points.

In the case of legacy studies, extraction times of between 8 and 48 hours are allowed. The 24-hour extraction with a $CaCl_2$ solution, in the case of standard aged sorption studies, was chosen as an operational definition to aid consistency and reproducibility. Legacy studies may have extraction times other than 24 hours, or even mixed extraction times. A comparison of a 1-hour and a 24-hour extraction with a $CaCl_2$ solution showed similar measured concentrations in the suspension during an 84-day incubation experiment, except for significantly lower concentrations for the 24-hour extraction within the first day after application, because of ongoing adsorption (van Beinum et al., 2010). The Panel concludes that the effect on the measured aqueous phase concentration is expected to be small for extraction times of between 8 and 48 hours.

8.1.   Conclusions and recommendations

Based on the data provided by CRD, the Panel drew the following general conclusions:

- The Panel agrees that using the average Freundlich exponent obtained from other soils is the most appropriate substitute for an unknown soil-specific Freundlich exponent. If a reliable Freundlich exponent from other soils is not available the Panel recommends not using legacy studies further to obtain aged sorption parameters.

- As stated previously, the Panel proposes checking whether or not the PEARLNEQ model is capable of adequately describing the entire period of the experiment and fixing the $K_{OM,EQ}$ to the $K_{OM,EQ}$ measured at day 0. In line with standard aged sorption studies, the pros and cons of relaxing these requirements (e.g. omitting early time points and/or allowing for free fitting of $K_{OM,EQ}$) have to be thoroughly evaluated on real aged sorption experiments.

9.   Conclusions and recommendations

The review of the draft guidance by the Panel revealed that the experimental and modelling approaches in the proposed guidance are reasonable compromises between the required effort and what is desirable from a theoretical point of view. However, the Panel has concerns about the interpretation of the experiments and how the results of the experiments should be used in the leaching assessment. The Panel investigated options for improvement, but could not complete its evaluation on these two topics, because underlying data were not made available. Therefore, the Panel cannot recommend the use of the guidance for the time being.

The FOCUS (2009) guidance on aged sorption has been the basis for developing the draft guidance document. In this regard, the FOCUS (2009) guidance clearly does not cover all aspects of, for example, data selection or fitting quality criteria, which turned out to be rather important based on further evaluation. The Panel therefore recommends that aged sorption parameters are not derived on the basis of FOCUS (2009) alone. The same applies to the EC report (EC, 2014), because the section on aged sorption was copied without changes into the noted guidance document.

The Panel recommends an update of the current draft guidance document, taking into account the conclusions and recommendations provided in this statement. This updated guidance document could be resubmitted to the Panel together with the supporting data so that the Panel can finalise its review.

The Panel noted that the draft guidance document did not systematically review uncertainties arising from the use of aged sorption data in regulatory leaching assessments. Uncertainties may result from, for example, the experimental procedure (extraction procedures), the conceptual model and the quality of the fitted parameters. It is recommended that a systematic review of uncertainties is carried out when updating the draft guidance document.

More detailed conclusions and recommendations are listed hereafter.

- Sorption of pesticides onto soil is a complex phenomenon influenced by both substance properties and the nature of soil organic matter and mineral components. Sorption is usually progressive in nature, starting with a fast initial phase followed by a slower phase that may go on for weeks or months. As a result, the apparent sorption often increases with time (i.e. aged or time-dependent sorption). Analytical approaches that attempt to quantify aged sorption and its dynamics should take into account the release of pesticide from various domains. In this respect, the Panel concludes that the two-step extraction procedure proposed in the draft guidance consisting of a 24-hour extraction with a 0.01 M CaCl$_2$ solution and a sufficiently harsh solvent extraction to characterise the total extractable mass (OECD, 2002) on the same soil is a reasonable compromise between the experimental effort and what is desirable from a theoretical point of view.

- If the solvent extraction is not harsh enough, leaching may be underestimated. The Panel therefore recommends that a justification of the extraction method, which meets the requirements of an appropriate mass recovery, should always be given by the applicant.

- The Panel concludes that the two-site modelling approach proposed in the draft guidance is in line with the proposed analytical approach. This modelling approach reflects a reasonable compromise between (i) the ability of the model to describe aged sorption under a range of situations and (ii) the possibility to determine model parameters from experiments with reasonable effort.

- The draft guidance document proposes to fit five model parameters against measured data. The Panel is not convinced that fitting the Freundlich sorption coefficient ($K_{OM,EQ}$) is necessary. The Panel recommends always first checking whether or not the fitted model is capable of adequately describing the measured data without excluding any time points and

fixing $K_{OM,EQ}$ to that measured at day 0 of the time-dependent sorption experiment. However, the Panel could not test this recommendation, because the experimental data underlying the draft guidance were not provided to the Panel.

- The fitting procedure of the aged sorption parameters is insensitive to the value of the Freundlich exponent. The Panel therefore agrees that the Freundlich exponent should be derived from batch experiments using the same soil. In this respect, the Panel recommends using the guidance included in Boesten et al. (2015) taking into account the modifications in this statement. The Panel also recommends using the Boesten et al. (2015) guidance for lower-tier leaching assessments and for calculating the pore water concentration in soil.

- The Panel concludes that the default value of 0.9 for the Freundlich exponent may not be conservative enough in a tiered approach. A Freundlich exponent of 1 would be more appropriate in a tiered approach. The Panel recommends reconsidering the default value in view of the tiered approach introduced by FOCUS (2009).

- The draft guidance acknowledges that the default values for f_{NE} and k_{des} may not be conservative enough in view of the tiered approach described by FOCUS (2009). The Panel therefore recommends assuming that aged sorption does not occur unless reliable values for the desorption rate coefficient (k_{des}) and the factor describing the ratio between the non-equilibrium and the equilibrium Freundlich coefficient (f_{NE}) have been derived. This implies that the default values of k_{des} and f_{NE} should be set to zero.

- The draft guidance states that when at least two out of four experiments show aged sorption, aged sorption can be taken into account. The Panel is of the opinion that this is a small number for such an important process. A criterion that states that the majority of experiments (with a minimum of four) should show aged sorption behaviour would be more in line with a conservative approach.

- When in a degradation scheme, if the parent substance shows time-dependent sorption but the daughter(s) do not then it will, in general, still be necessary to re-interpret the kinetic behaviour of the daughter substances as the aged sorption process will affect the formation of the daughter and, consequently, the degradation rate. The leaching assessment should be done with a consistent dataset.

- The draft guidance document mentions two options for including aged sorption parameters in the leaching assessment, i.e. average-first and calculate-first options. Given that the calculate-first approach is extremely resource demanding, the Panel is of the opinion that the average-first approach is the preferred option. Further exploration based on the experimental data underlying the draft guidance is, however, necessary.

- The draft guidance states that a decision on the leaching potential may be based on the results of four aged sorption experiments. Implicitly, this means that available lower tier information is not used any more. The Panel concludes that such an approach is not correct. The Panel gives some options for including lower tier data. However, these options could not be further elaborated because the underlying experimental data were not available to the Panel.

- The draft guidance document is based on a combination of PEST and PEARLNEQ (Boesten and Ter Horst, 2012). The Panel observes that the PEST–PEARLNEQ combination does not come with a graphical user interface. The development of such a user interface would ease its applicability for regulatory purposes.

- The Panel notes that taking aged sorption into account for parent substances may have consequences for the formation fraction and degradation rate of metabolites. Re-interpretation

of kinetic experiments will be necessary in order to derive consistent datasets. Currently used software packages for deriving degradation constants are not able to account for aged sorption. It is desirable that these packages are amended so that such re-interpretation is facilitated.

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APPENDICES

Appendix A.   Existing guidance on aged sorption

A1.   FOCUS degradation kinetics report

Appendix 4 (Estimating degradation and sorption parameters from laboratory degradation studies for higher-tier calculations with PEARL) of the FOCUS degradation kinetics report (FOCUS, 2006) describes in detail how to estimate time-dependent sorption (TDS) degradation and sorption parameters from laboratory degradation experiments showing bi-phasic degradation kinetics. As outlined in the report, TDS may result in an approximately bi-exponential substance decline in the total soil.

In principle, this approach assumes linear sorption ($1/n = 1$). However, in the guidance, the approach is considered to also provide reliable TDS parameters for non-linear sorption as long as f_{NE} does not exceed 1. For systems with higher f_{NE} values, the PEARLNEQ model (Boesten et al., 2007) is recommended without giving any further guidance in this case.

In short, the guidance starts fitting the substance decline in total soil concentration to a bi-exponential (DFOP) equation which results in values of g, λ_1 and λ_2 (equation A1).

$$c^* = c_0 * \left[g \exp(-\lambda_1 t) + (1-g) \exp(-\lambda_2 t) \right]$$

(A1)

Subsequently, k_t and k_{des} can be calculated on the basis of g, λ_1 and λ_2 (equations A2 and A3)

$$k_d = \frac{\lambda_1 \lambda_2}{g\lambda_1 + (1-g)\lambda_2}$$

(A2)

$$k_t = g\lambda_1 + (1-g)\lambda_2$$

(A3)

where k_d (k_{des}) is the desorption rate coefficient (d^{-1}), k_t is the degradation rate coefficient (d^{-1}), λ_1 and λ_2 are the degradation rates (d^{-1}) of the two DFOP components, with g being the parameter determining the fraction (-) of the slowly (λ_1) degrading component.

For the calculation of f_{NE}, the soil water content and the linear equilibrium sorption coefficient ($K_{L,EQ}$) are also needed (equations A4 and A5)

$$f_{NE} = \Phi \frac{w + K_{L,EQ}}{K_{L,EQ}}$$

(A4)

$$\Phi = \frac{g(1-g)(\lambda_1 - \lambda_2)^2}{\lambda_1 \lambda_2}$$

(A5)

where f_{NE} is the factor for describing the ratio between the equilibrium and non-equilibrium Freundlich coefficients (-), w is the gravimetric water content of the incubation system, defined as volume of water divided by mass of dry soil ($L\ kg^{-1}$), and $K_{L,EQ}$ is the linear equilibrium sorption coefficient. A suitable $K_{L,EQ}$ has to be estimated from the non-linear $K_{F,EQ}$ and Freundlich exponent via iteration. The guidance recommends using the average $K_{F,EQ}$ and Freundlich exponent available from the dossier.

TDS parameters obtained by this procedure are considered reliable if f_{NE} is between 0.1 and 1.0 and k_{des} is between 0.002 and 0.1 d^{-1}. If values are outside of these ranges, dedicated TDS studies are considered necessary.

Furthermore, the guidance recommends using the average of all reliable k_{des} and f_{NE} values available in the risk assessment.

The FOCUS groundwater group (FOCUS, 2009) included this procedure as a possible option to derive aged sorption parameters in cases where the degradation rate in the fast phase (λ_2) is rapid (half-lives in the order of five days, giving a degradation rate constant of 0.139 d^{-1}).

The procedure was re-evaluated by van Beinum et al. (2010). Several concerns were raised:

- The methodology assumes that the bi-phasic nature of degradation is due to TDS. If only total mass is measured, then there is no experimental evidence to support this assumption. Bi-phasic degradation could also be a result of a decline in microbial activity.

- Tests of the procedure with artificial datasets showed that k_t, k_{des} and f_{NE} can be estimated from total residues using the procedure described above, provided sorption is linear, the measured data are of good quality, the pattern of degradation is clearly bi-phasic and the estimated DFOP parameters are robust and precise. The parameters are considered less accurate for datasets with non-linear sorption and a concentration in the liquid phase different from 1 mg/L.

- The estimated f_{NE} value strongly depends on the $K_{OM,EQ}$ value. Sorption data are rarely available for the soil used in the degradation study. The use of $K_{OM,EQ}$ values measured in other soils introduces a large uncertainty into the estimate for f_{NE}.

Van Beinum et al. (2010) concluded that evidence should be given that the bi-phasic pattern of decline in total residues is due to TDS and generally recommend that TDS parameters should be derived by fitting the aged sorption model directly to total residues and liquid-phase concentrations.

A2 Assessing potential for movement of active substances and their metabolites to groundwater in the EU

The FOCUS (2009) report deals with TDS in more detail in chapter 7.1.6 ('Non-equilibrium sorption'). FOCUS (2009) recommends measuring TDS as part of a standard degradation rate study (OECD, 2002) and deriving TDS parameters via a fitting procedure taking into account both the total content of the pesticide in soil and the concentration in the soil pore water. In contrast to the FERA (2012) draft guidance document, FOCUS (2009) recommends fitting $K_{OM,EQ}$ during the fitting procedure only if a soil-specific $K_{OM,EQ}$ obtained in batch experiments (OECD, 2000) is not available. Otherwise, $K_{OM,EQ}$ should be fixed to the batch $K_{OM,EQ}$.

In general, FOCUS (2009) gives much less stringent guidance with respect to data selection, data weighting and fitting criteria ('often expert judgement will be needed with respect to the interpretation of the data'). As a minimum quality requirement, the 95 % confidence intervals of fitted TDS parameters should be within the range 0 to 200 % of the fitted value to be acceptable. This range is equivalent to a RSE of 0.5, which is slightly larger than the RSE of 0.4 proposed in the FERA draft guidance (2012). Similar to the FERA draft guidance, graphs plotting the measured versus the fitted concentration of pesticide in soil and soil pore water as a function of time (comparing TDS with non-TDS) have to be provided for an appropriate interpretation of the quality of the fit.

FOCUS (2009) recommends using default values for f_{NE} (0.3) and k_{des} (0.01 d^{-1}) in the risk assessment. The k_{des} of 0.01 d^{-1} is considered the 'best guess' for the rate coefficient based on available measurements in TDS studies and the f_{NE} of 0.3 is a realistic worst-case estimate based on the lowest

value found in an aged sorption study. To overrule these default values, TDS studies with at least two soils are needed.

FOCUS (2009) highlights that re-calculation (re-scaling) of the *DegT50* is necessary to obtain the *DegT50_{EQ}* whenever TDS parameters (default or fitted) are applied. In order to recalculate *DegT50* values of ordinary laboratory degradation studies for the use in a TDS simulation, one of the FOCUS models which can handle TDS should be applied. The TDS parameters (f_{NE} and k_{des}) should be fixed to the values derived from the evaluation of the aged sorption studies or the default values. Additionally, FOCUS (2009) uses equation 6, below, to roughly determine the re-scaling factor $f_{deg,NE}$:

$$f_{\text{deg},NE} = \frac{w + K_{F,EQ}}{w + (1 + f_{NE,PEARL})K_{F,EQ}}$$

(6)

where *w* is the gravimetric water content of the incubation system defined as volume of water divided by mass of dry soil (L kg^{-1}), $K_{F,EQ}$ is the non-linear equilibrium sorption coefficient and f_{NE} is the factor for describing the ratio between the equilibrium and non-equilibrium Freundlich coefficients (-). This approximation assumes a linear sorption isotherm and assumes that the degradation rate coefficient is slow compared with k_{des}. Although presented in the guidance, FOCUS (2009) recommends not using this approximation in risk assessment procedures.

Appendix B. Description of the PEARLNEQ model

The draft guidance document uses the two-site model PEARLNEQ as described by Leistra et al. (2001). The same two-site model is implemented in the leaching PEARL model. The PEARLNEQ model is depicted in Figure B1.
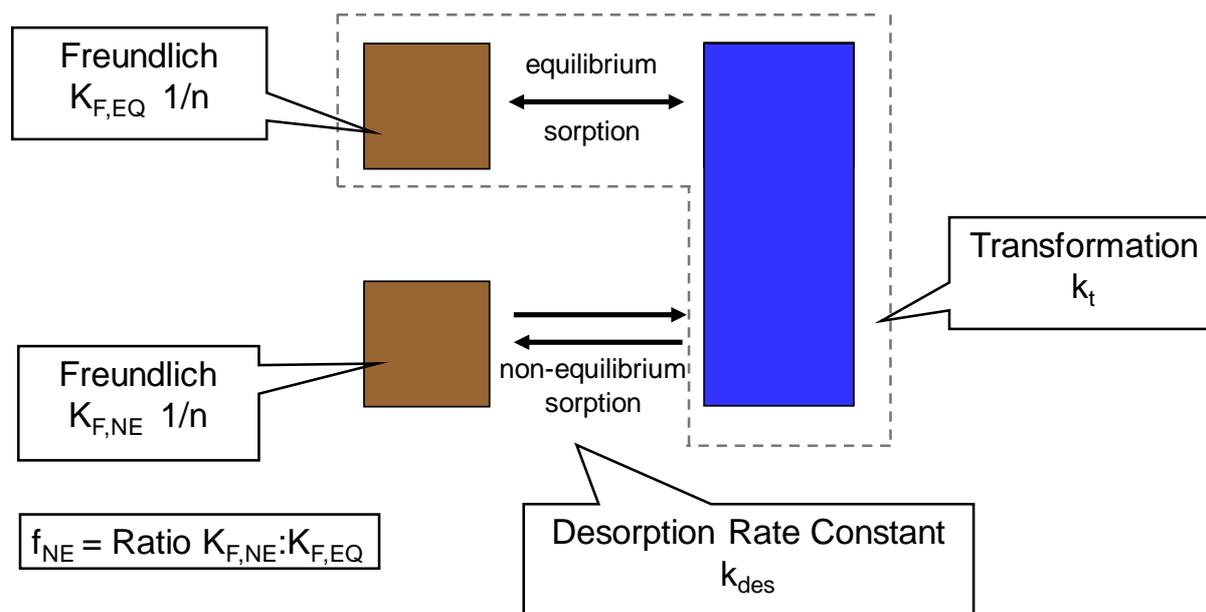
Figure B1: Schematic representation of the PEARLNEQ model showing the soil solution on the right and the equilibrium and non-equilibrium sorption sites on the left. Only pesticide in the equilibrium domain (indicated by the dashed line) is subject to degradation. Reproduced with permission from Alterra and the PEARL team.

The model assumes that sorption is instantaneous on one fraction of the sorption sites and slow on the remaining fraction (Leistra *et al.*, 2001). The model does not account for irreversible sorption. Degradation is described by first-order kinetics. Only molecules present in the equilibrium domain (the liquid phase and sorbed to the equilibrium site together) are assumed to degrade. Molecules sorbed on the slow non-equilibrium sorption site are considered not to degrade. The PEARLNEQ model can be described as follows:

$$M_p = V c_L + M_S \left(X_{EQ} + X_{NE} \right) \tag{B1}$$

$$X_{EQ} = K_{F,EQ}\, c_{L,R} \left(\frac{c_L}{c_{L,R}} \right)^{1/n} \tag{B2}$$

$$\frac{dX_{NE}}{dt} = k_{des} \left(K_{F,NE}\, c_{L,R} \left(\frac{c_L}{c_{L,R}} \right)^{1/n} - X_{NE} \right) \tag{B3}$$

$$K_{F,NE} = f_{NE} K_{F,EQ} \tag{B4}$$

$$\frac{dM_p}{dt} = -k_t \left(V c_L + M_S X_{EQ} \right) \tag{B5}$$

$$K_{F,EQ} = m_{OM} K_{OM,EQ} \tag{B6}$$

where M_p is the total mass of pesticide in each jar (µg), V is the volume of water in the soil incubated in each jar (mL), M_S is the mass of dry soil incubated in each jar (g), c_L is the concentration in the liquid phase (µg/mL), $c_{L,R}$ is the reference concentration in the liquid phase (µg/mL), X_{EQ} is the content sorbed at equilibrium sites (µg/g), X_{NE} is the content sorbed at non-equilibrium sites (µg/g), $K_{F,EQ}$ is the equilibrium Freundlich sorption coefficient (mL/g), $K_{F,NE}$ is the non-equilibrium Freundlich sorption coefficient (mL/g), $1/n$ is the Freundlich exponent (-), k_{des} is the desorption rate coefficient (d^{-1}), f_{NE} is the factor describing the ratio between non-equilibrium and equilibrium Freundlich coefficients (-), k_t is the degradation rate coefficient (d^{-1}), m_{OM} is the mass fraction of organic matter in the soil (kg/kg), and $K_{OM,EQ}$ is the coefficient of equilibrium sorption on organic matter (mL/g).

The model has six parameters: the initial concentration of the pesticide, the degradation rate constant (k_t), the equilibrium sorption coefficient ($K_{OM,EQ}$), the Freundlich exponent ($1/n$), the ratio of non-equilibrium sorption to equilibrium sorption (f_{NE}) and the desorption rate constant (k_{des}).

During the last few years, it has become common practice to distinguish between dissipation, indicated by *DT50*, and degradation, indicated by *DegT50*. The draft guidance, however, uses *DT50* for degradation in the total system and *DegT50* for degradation in the equilibrium domain. This may become confusing in the peer review of substances. The Panel therefore recommends using the following definitions (see also the glossary):

- *DT50*   dissipation half-life for the total system (days)

- *DegT50*   degradation half-life for the total system (days)

- *DegT50$_{EQ}$*   degradation half-life in the equilibrium domain (days)

Appendix C.   Assessment of the 'average first, calculate after' versus the 'calculate first, average after' approach with respect to the groundwater exposure assessment

As mentioned in section 5, the Panel could not thoroughly investigate the impact of the 'average first, calculate after' (as used at the first tier) versus the 'calculate first, average after' procedure on the leaching concentration because of the absence of real-world datasets. However, a dataset published in van Beinum and Beulke (2012) may be used to give an initial impression of the impact of the two different approaches with respect to a first-tier assessment (without aged sorption) and a higher-tier assessment (applying aged sorption parameters), respectively.

The data in Figure C1 (Table 10-2 from van Beinum and Beulke, 2012) were used without changes (aged sorption with default parameters were not accounted for at all):

	Appl. rate (g/ha)	Fitted parameters					Default parameters					Zero aged sorption parameters				
		f_{NE} (-)	k_{des} (day^{-1})	$DegT50$ (days)	$K_{OM,EQ}$ (L/kg)	$1/n$ (-)	f_{NE} (-)	k_{des} (day^{-1})	$DegT50$ (days)	$K_{OM,EQ}$ (L/kg)	$1/n$ (-)	f_{NE} (-)	k_{des} (day^{-1})	$DT50$ (days)	K_{OM} (L/kg)	$1/n$ (-)
ECPA-01A	7.5	0.5788	0.0414	83.50	5.19	0.9100	0.3	0.01	95.63	5.19	0.9100	0	0	90.0	5.86	0.9100
ECPA-01B	7.5	0.4139	0.0380	109.98	9.62	0.9400	0.3	0.01	123.45	9.42	0.9400	0	0	105.0	7.31	0.9400
ECPA-01C	7.5	0.4448	0.0353	63.00	3.22	0.9000	0.3	0.01	68.40	3.22	0.9000	0	0	67.0	3.23	0.9000
ECPA-01D	7.5	0.4763	0.0318	156.24	8.06	0.9000	0.3	0.01	174.93	8.06	0.9000	0	0	167.0	8.25	0.9000
ECPA-03A	10	0.6632	0.0159	32.34	37.00	0.9083	0.3	0.01	42.38	33.38	0.9083	0	0	42.6	31.21	0.9083
ECPA-03B	10	0.3720	0.0506	49.01	24.33	0.9264	0.3	0.01	56.94	24.33	0.9264	0	0	57.0	36.83	0.9264
ECPA-03C	10	0.8614	0.0177	15.43	70.13	0.9237	0.3	0.01	24.69	61.44	0.9237	0	0	20.8	48.55	0.9237
ECPA-03D	10	0.3347	0.0269	56.12	29.34	0.9278	0.3	0.01	61.55	29.34	0.9278	0	0	63.1	41.53	0.9278
ECPA-04A	7.5	0.3965	0.0404	153.27	21.63	0.8910	0.3	0.01	176.19	18.80	0.8910	0	0	187.0	15.20	0.8910
ECPA-04B	7.5	0.1711	0.0701	131.93	18.77	0.9000	0.3	0.01	130.30	18.77	0.9000	0	0	145.0	20.07	0.9000
ECPA-04C	7.5	0.4309	0.0452	151.87	25.86	0.9170	0.3	0.01	177.23	22.98	0.9170	0	0	188.0	22.98	0.9170
ECPA-04D	7.5	0.2895	0.0347	184.23	27.55	0.9230	0.3	0.01	195.92	26.12	0.9230	0	0	206.0	26.10	0.9230
ECPA-06A	50	0.6839	0.0387	107.88	203.97	0.8950	0.3	0.01	146.50	181.28	0.8950	0	0	165.0	168.16	0.8950
ECPA-06B	50	0.5550	0.0212	93.53	192.08	0.9200	0.3	0.01	115.36	153.51	0.9200	0	0	129.0	153.51	0.9200
ECPA-06C	50	0.5390	0.0376	194.63	240.80	0.9740	0.3	0.01	228.46	216.06	0.9740	0	0	243.0	130.74	0.9740
ECPA-06D	50	0.6420	0.0268	79.75	189.94	0.9080	0.3	0.01	104.97	173.63	0.9080	0	0	117.0	121.58	0.9080
ECPA-07A	50	0.7999	0.0298	57.74	39.55	0.8450	0.3	0.01	80.91	39.55	0.8450	0	0	73.2	57.37	0.8450
ECPA-07B	50	0.3534	0.0391	44.50	42.79	0.8680	0.3	0.01	49.34	42.79	0.8680	0	0	52.1	53.48	0.8680
ECPA-07C	50	0.6865	0.0316	86.48	62.91	0.8640	0.3	0.01	118.39	56.23	0.8640	0	0	117.0	62.06	0.8640
ECPA-07D	50	0.4845	0.0275	50.09	39.37	0.8650	0.3	0.01	60.55	39.37	0.8650	0	0	62.5	43.45	0.8650
ECPA-11A	50	0.5106	0.0178	171.05	128.15	0.8376	0.3	0.01	202.30	109.58	0.8376	0	0	221.0	151.10	0.8376
ECPA-11B	50	0.4922	0.0174	167.20	162.65	0.7645	0.3	0.01	197.05	128.80	0.7645	0	0	231.0	134.69	0.7645
ECPA-11C	50	0.4685	0.0233	236.18	156.57	0.8492	0.3	0.01	299.32	119.07	0.8492	0	0	339.0	135.56	0.8492
ECPA-11D	50	0.5662	0.0114	124.84	128.54	0.8270	0.3	0.01	144.60	87.88	0.8270	0	0	165.0	87.88	0.8270
ECPA-11E	50	0.4400	0.0226	157.60	119.88	0.8376	0.3	0.01	186.00	102.35	0.8376	0	0	210.0	151.10	0.8376
ECPA-11F	50	0.4805	0.0346	312.65	110.35	0.7645	0.3	0.01	422.71	105.83	0.7645	0	0	464.0	134.69	0.7645
ECPA-11G	50	0.4298	0.0238	190.32	143.00	0.8492	0.3	0.01	224.44	122.71	0.8492	0	0	250.0	135.56	0.8492
ECPA-11H	50	0.2786	0.0296	140.37	102.91	0.8270	0.3	0.01	150.26	93.57	0.8270	0	0	162.0	93.57	0.8270
ECPA-14A	10	0.4321	0.0422	265.75	154.34	0.9800	0.3	0.01	326.99	145.61	0.9800	0	0	348.0	145.61	0.9800
ECPA-14B	10	0.5010	0.0288	65.23	138.19	0.9800	0.3	0.01	79.89	128.93	0.9800	0	0	87.3	128.93	0.9800
ECPA-14C	10	0.3801	0.0193	101.59	155.91	0.9800	0.3	0.01	113.12	136.51	0.9800	0	0	126.0	136.51	0.9800
ECPA-14D	10	0.3159	0.0512	166.35	167.54	0.9800	0.3	0.01	197.22	147.56	0.9800	0	0	208.0	147.56	0.9800
ECPA-30B	1000	0.8487	0.0184	19.71	118.96	0.9400	0.3	0.01	34.20	91.20	0.9400	0	0	17.6	91.2	0.9400
ECPA-30C	1000	10.0000	0.0004	37.27	173.21	0.9400	0.3	0.01	44.61	91.94	0.9400	0	0	28.0	91.9	0.9400
ECPA-30D	1000	0.7590	0.0082	41.44	172.32	0.9400	0.3	0.01	51.38	108.56	0.9400	0	0	34.0	108.6	0.9400
ECPA-30F	1000	0.5174	0.0228	31.40	185.91	0.9400	0.3	0.01	40.05	128.35	0.9400	0	0	22.7	128.3	0.9400

Figure C1: Input parameters for FOCUS PEARL for testing the effect of 'calculate-first' or 'average-first' approaches. Data were taken from Beulke and van Beinum (2012). Reproduced with permission from the authors and CRD.

Each of the nine datasets consists of four soils taking either aged sorption into account (fitted parameters) or not (zero aged sorption parameters). For the 'average first, calculate after' approach, the following averaging methods were used (for the input parameter): geometric mean for $DegT50$ (or $DegT50_{EQ}$), $K_{OM,EQ}$ and k_{des}, and arithmetic mean for f_{NE} and $1/n$. For the 'calculate first, average after' approach, the median of the four individual groundwater PEC (PEC_{gw}) values was used as this was already shown by Hardy (2011) to be most appropriate. The same scenario (winter cereals, one day before emergence) and application amount (stated in the table) as in Beulke and van Beinum (2012) were applied.

Table C1 gives the PEC_{gw} values for each of the nine datasets (fitted versus zero aged sorption) using either the 'average first, calculate after' or the 'calculate first, average after' approach.

Table C1: PEC$_{gw}$ values (µg L^{-1}) for the nine 'real-world' datasets in Table 10–2 from van Beinum and Beulke (2012) using either the 'average first, calculate after' or the 'calculate first, average after' approach for the fitted aged sorption and zero aged sorption datasets, respectively

Dataset number	Fitted aged sorption parameters		Zero aged sorption parameters	
	'Average first, calculate after'	'Calculate first, average after'	'Average first, calculate after'	'Calculate first, average after'
1	1.392	1.332	1.407	1.367
2	0.039	0.148	0.071	0.143
3	0.850	0.830	1.084	1.085
4	0.028	0.010	0.497	0.219
5	0.199	0.229	0.263	0.259
6	0.013	0.048	0.275	0.278
7	0.121	0.108	0.350	0.396
8	0.117	0.111	0.245	0.233
9	0.007	0.003	0.058	0.123

As expected, the two different approaches may of course result in deviating PEC$_{gw}$ values depending on the overall substance properties. However, based on this 'real-world' dataset, there is no trend for systematic over- or underestimating of the PEC$_{gw}$ if only one of the two approaches is used. Uncertainties observed with respect to both approaches also apply to zero aged sorption datasets (i.e. for first-tier assessments).

Appendix D. **Insensitivity of the fitting procedure with respect to setting of the Freundlich exponent**

In this exercise, example 1 from the appendix of the draft guidance (FERA, 2012) is used to demonstrate the insensitivity of the fitting procedure with respect to setting of the Freundlich exponent ($1/n$). In addition to the measured value of 0.83, $1/n$ values of 0.7, 0.9 and 1.0 were used in the fitting procedure. The fitting procedure (excluding early sampling points and allowing for free fitting of $K_{OM,EQ}$) is identical to the procedure proposed in the draft guidance.

Table D1 and Figure D1 give the results for the individual best fits.

Table D1: Fitting results (RSE in parenthesis) for example 1 from the Appendix of the draft guidance applying a Freundlich exponent of 0.7, 0.83 (measured value), 0.9 and 1.0

| $1/n$ (-)	0.7	0.83 [a]	0.9	1.0
f_{NE} (-)	0.31 (0.08)	0.43 (0.07)	0.50 (0.06)	0.61 (0.06)
k_{des} (d^{-1})	0.030 (0.15)	0.024 (0.13)	0.022 (0.13)	0.019 (0.12)
$DegT50_{EQ}$ (d)	104.0 (0.03)	98.3 (0.03)	95.6 (0.03)	91.9 (0.03)
M_{ini} (µg)	19.3 (0.01)	19.4 (0.01)	19.4 (0.01)	19.5 (0.01)
$K_{OM,EQ}$ (mL g^{-1})	208.6 (0.02)	258.4 (0.02)	289.9 (0.02)	341.5 (0.02)
$K_{OM,EQ}$, day 0 [a] (mL g^{-1})	196.3	237.3	262.9	304.2
% of $K_{OM,EQ}$, day 0	106	109	110	112

(a): Measured 1/n value.
(b): Calculated based on 1/n and day 0 measurements.

This simple example demonstrates that the fitting procedure is rather insensitive to the setting of the $1/n$ value. Indeed, applying a $1/n$ in the range 0.7 to 1.0 leads to an appropriate fit in each case (if based on draft guidance criteria, including the 20 % criterion on $K_{OM,EQ}$). It may be noted that a $1/n$ value below 1.0 already implies a steadily increasing $K_{D,app}$ with time. In this respect, aged sorption parameters (in particular f_{NE}) and $1/n$ compensate for each other (the lower the Freundlich exponent, the higher the f_{NE}).

In conclusion, the fitting procedure is insensitive to the setting of the $1/n$ and an inappropriate setting of the $1/n$ cannot be identified on the basis of the obtained fitting results.

A
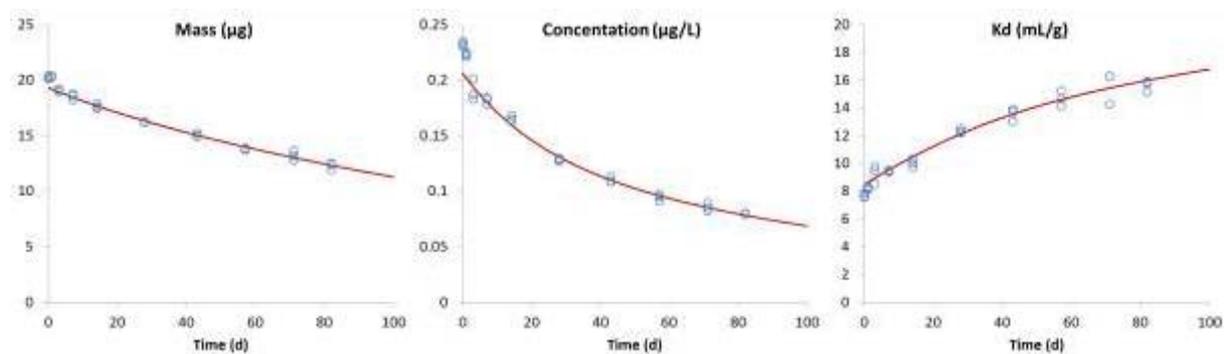
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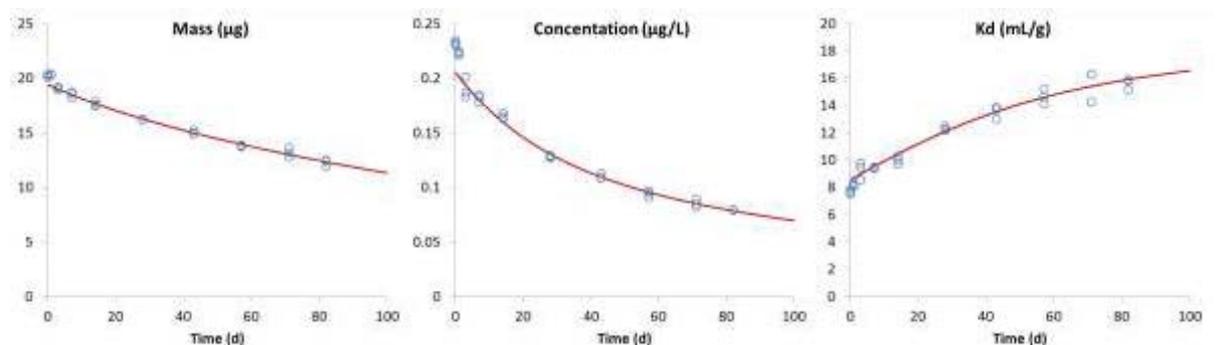
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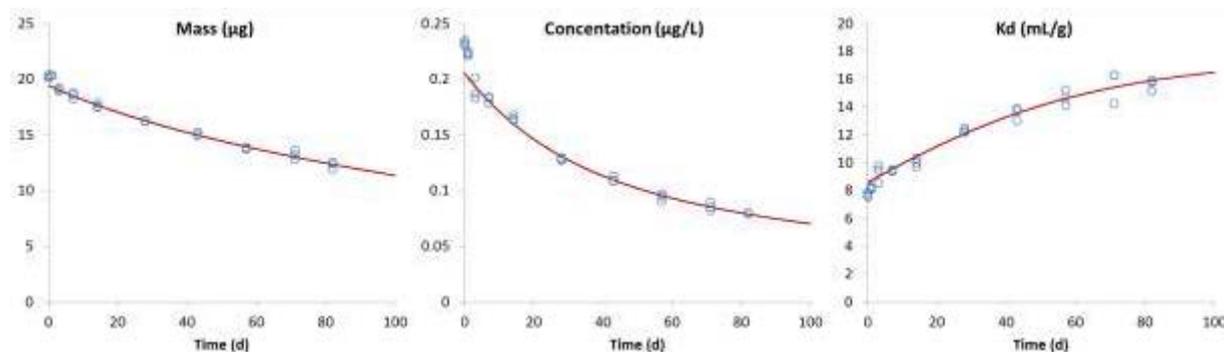
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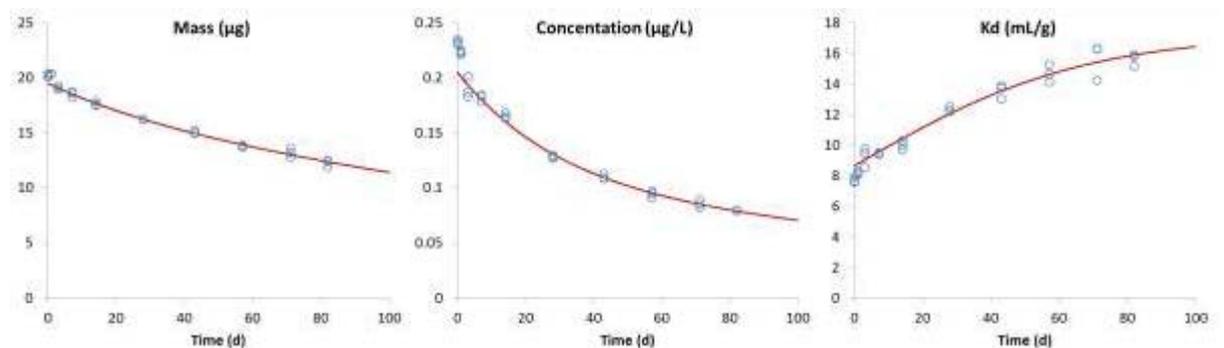
Figure D1: Fitting results for the total mass, the concentrations in the liquid phase and the $K_{D,app}$ for example 1 from the appendix of the draft guidance (FERA, 2012) applying a Freundlich exponent of 0.7 (A), 0.83 (measured value; B), 0.9 (C) or 1.0 (D). Reproduced with permission from the authors and CRD.

GLOSSARY AND ABBREVIATIONS

$1/n$	Freundlich exponent; parameter indicating the curvature of the sorption isotherm
2,4-D	2,4-dichlorophenoxyacetic acid
ACN	acetonitrile
ACT	acetone
AcOH	short-chain organic acid, i.e. acetic acid
aged sorption	Apparent increase of sorption with time
$CaCl_2$	calcium chloride
CAKE	Package for fitting degradation parameters
C_L	liquid-phase concentration
CRD	Chemicals Regulation Directorate (UK)
$DegT50$	Half-life due to degradation processes in total soil
$DegT50_{EQ}$	Half-life due to degradation processes in equilibrium domain
DFOP	double first order in parallel; an approach to bi-phasic degradation kinetics
$DT50$	half-life due to dissipation processes
ECPA	European Crop Protection Association
EU	European Union
FERA	Food and Environment Research Agency (UK)
f_{NE}	Factor for describing the ratio between the non-equilibrium and equilibrium Freundlich coefficients (please note that the draft guidance (FERA, 2012) incorrectly states that this is the ratio between the equilibrium Freundlich coefficient and the non-equilibrium Freundlich coefficient)
FOCUS	Forum for the Coordination of Pesticide Fate Models and their Use
GeoPEARL	The spatially distributed version of the PEARL model
HS	humic substance
K_d	sorption coefficient
$K_{D,app}$	apparent sorption coefficient
k_{des}	desorption rate constant (d^{-1});
K_F	Freundlich distribution coefficient
KINGUI	Package for fitting degradation parameters
K_{OM}	Sorption coefficient for sorption on soil organic matter (mL/g org. matter)
$K_{OM,EQ}$	Coefficient of equilibrium sorption on organic matter (mL/g)Degradation rate constant (d^{-1}) in the equilibrium domain
k_t	Degradation rate constant (d^{-1}) in the equilibrium domain
legacy studies	Experimental studies regarding aged residues performed before the draft guidance was published and that do not fully meet the requirements laid down in the draft guidance
M_p	Total mass of pesticide in each jar
NER	non-extractable (bound) residue
OECD	Organisation for Economic Co-operation and Development
PEARL	Pesticide Emission Assessment at Regional and Local scale
PEARLNEQ	software package to fit aged sorption parameters

PEC	predicted environmental concentration
PEC$_{gw}$	groundwater predicted environmental concentration
PEST	parameter estimation software package used for estimation/fitting of parameters
pF	negative logarithm of the soil water pressure head
pH	negative logarithm of H$^+$ ion concentration in a medium; indication of the acidity
pK$_a$	negative logarithm of the dissociation constant of a substance
PPR	Plant Protection Products and their Residues
Q$_{10}$	Parameter describing the influence of temperature on the degradation process
QSAR	quantitative structure–activity relationship
RSE	relative standard error for the estimated parameter value
SCoPAFF	Standing Committee on Plants, Animals, Food and Feed
TDS	time-dependent sorption (aged sorption)
TOC	total organic carbon
underlying experimental data	The experimental data that have been used to test and develop the draft guidance document. This includes both the aged sorption data and the corresponding lower-tier sorption and degradation data. This also includes the experimental protocols
WUR	Wageningen University and Research Centre, Netherlands