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Scientific Opinion about the Guidance of the Chemical Regulation Directorate (UK) on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments

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Abstract

The EFSA Panel on Plant Protection Products and their Residues reviewed the guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessment. The inclusion of aged sorption is a higher tier in the groundwater leaching assessment. The Panel based its review on a test with three substances taken from a data set provided by the European Crop Protection Association. Particular points of attention were the quality of the data provided, the proposed fitting procedure of aged sorption experiments and the proposed method for combining results obtained from aged sorption studies and lower-tier studies on degradation and adsorption. Aged sorption was a relevant process in all cases studied. The test revealed that the guidance could generally be well applied and resulted in robust and plausible results. The Panel considers the guidance suitable for use in the groundwater leaching assessment after the recommendations in this Scientific Opinion have been implemented, with the exception of the use of field data to derive aged sorption parameters. The Panel noted that the draft guidance could only be used by experienced users because there is no software tool that fully supports the work flow in the guidance document. It is therefore recommended that a user-friendly software tool be developed. Aged sorption lowered the predicted concentration in groundwater. However, because aged sorption experiments may be conducted in different soils than lower-tier degradation and adsorption experiments, it cannot be guaranteed that the higher tier predicts lower concentrations than the lower tier, while lower tiers should be more conservative than higher tiers. To mitigate this problem, the Panel recommends using all available higher- and lower-tier data in the leaching assessment. The Panel further recommends that aged sorption parameters for metabolites be derived only from metabolite-dosed studies. The formation fraction can be derived from parent-dosed degradation studies, provided that the parent and metabolite are fitted with the best-fit model, which is the double first-order in parallel model in the case of aged sorption.

Keywords: plant protection products, aged sorption, guidance, modelling, leaching, review

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Summary

In April 2014, the EFSA Panel on Plant Protection Products and their Residues (PPR Panel) was mandated by the Pesticide Steering Committee (now the Pesticide Steering Network, PSN) to provide a Scientific Opinion on the guidance proposal on aged sorption. However, the PPR Panel prepared a Statement (EFSA PPR Panel, 2015) instead of a Scientific Opinion as they could not completely address all the terms of reference. In particular, the experimental data required for testing the guidance was not available. The PPR Panel therefore recommended an update of the guidance proposal, taking into account the conclusions and recommendations provided in the Statement (EFSA PPR Panel, 2015). As a follow-up of the publication of the Statement, the Chemicals Regulation Directorate (CRD) (UK) consulted the authors of the draft guidance and the guidance was updated based on the recommendations in the PPR Statement (EFSA PPR Panel, 2015). Together with this updated guidance document, the European Crop Protection Association (ECPA) provided the underlying data sets so that the Panel could test the guidance using real data and finalise its review according to the provided terms of reference.

The Panel based its review on a test with three substances from the provided data set covering a wide range of properties. Particular points of attention were the quality of the data provided, the proposed fitting procedure of aged sorption experiments and the proposed method for combining results obtained from aged sorption experiments and lower-tier studies on degradation and adsorption.

Aged sorption was a relevant process in all cases studied. The test revealed that the guidance could generally be well applied and resulted in robust and plausible results. The Panel considers the guidance suitable for use in the regulatory process once the recommendations in this Scientific Opinion have been implemented. The Panel notes, however, that this guidance should only be used for the simulation of pesticide losses to groundwater because the applicability for other cases (e.g. FOCUS surface water scenarios) has not been evaluated.

The draft guidance could only be used by experienced users because there is no software tool that fully supports the work flow in the guidance document. In particular, the combination of lower-tier results with results from aged sorption experiments obtained at Tier 2a required a number of manual steps. It is recommended that a user-friendly software tool be developed that supports the full workflow in the guidance document and that all graphs, statistics and tables needed in the regulatory process are produced. It is further recommended that this tool be developed after consultation with applicants and regulators.

The EFSA PPR Panel (2015) mentions that the extraction procedure should be sufficiently harsh to characterise the total extractable mass. However, based on a numerical analysis by Boesten (2016), the Panel acknowledges that the extraction efficiency is of minor importance for the leaching assessment in the case of time-dependent sorption experiments with an additional focus on pesticide mass in the liquid phase ($CaCl_2$ extract). It is nevertheless desirable that for future submissions addressing aged sorption, consistent extraction procedures should be used within one regulatory assessment. Furthermore, a justification of the extraction method, which meets the requirements of an appropriate mass recovery, should always be given by the applicant.

The Panel does not recommend refinement options in the fitting procedure, because this may lead to additional discussions and expert judgement in the absence of clear recommendations on when to consider a refinement fit superior to the fit obtained without refinement. The Panel tested a simplified procedure and because this procedure works well, the Panel recommends using this procedure without refinement options.

Aged sorption experiments may be available for different soils than first-tier adsorption and degradation experiments. The consequence is that the predicted concentration may be higher when using only adsorption and degradation data from the aged sorption experiments obtained at Tier 2a. This is because of the high variation of degradation and adsorption data, which may by change result in a sample that generates more leaching compared to the first tier. To get the best estimate of the average of the underlying statistical population of all agricultural fields, the Panel recommends that all available data on degradation and adsorption be considered in higher-tier groundwater risk assessments. Note that even when all available adsorption and degradation data are used in the groundwater leaching assessment, the higher tier (Tier 2a) may generate more leaching than Tier 1. This may happen in those cases where aged sorption is not the dominant process; for example when the sorption constant is very low. In the three cases studied by the Panel, however, the combination of lower-tier and higher-tier data always generated less leaching.

Degradation half-lives from first-tier experiments are conceptually different from the degradation half-lives in the time-dependent sorption concept so the first-tier degradation data need to be converted before an average degradation half-life can be calculated. The draft guidance document describes a number of options for making this conversion. From these, the Panel considers a refit of residue data to the original residue data as the preferred option.

Lower-tier sorption parameters, such as the K_{om} and 1/n, may have a higher effect on the total leaching concentration than aged sorption parameters. For this reason, the Panel recommends that the quality checks outlined in EFSA (2017a) are always applied. Given the importance of the curvature of the Freundlich isotherm, it is further recommended to only accept Freundlich exponents from studies of which sorption coefficients are accepted to be included in the further analysis. This is based on the argument that if the sorption coefficient is not considered sufficiently reliable then the curvature would also be unreliable.

The Panel recommends that aged sorption parameters for metabolites be derived only from metabolite-dosed studies. When metabolite-dosed studies are used to derive aged sorption parameters, the guidance also applies to the metabolite. The formation fraction can be derived from parent-dosed aerobic degradation studies, provided that the parent and metabolite are fitted with the best-fit model, which is the double first-order in parallel (DFOP) model in the case of aged sorption. When such studies are not available, the formation fraction should be set to the conservative value of 1.

The procedure for deriving aged sorption parameters from field studies in the draft guidance document does not appear to be well worked out and tested. Because this may lead to confusion in the regulatory process, the Panel recommends that the guidance be further developed and tested with real world data. Until this has been done, field studies should not be used to derive aged sorption parameters. However, if agreed matrix DegT50 values from field studies have been derived in accordance with EFSA (2014), the Panel recommends that these values not be ignored but they should be accounted for in the leaching assessment in line with EFSA (2014). This includes checking whether laboratory and field degradation data are from different populations. If the field degradation data indeed represent a different population, the Panel recommends using the matrix DegT50 values without converting them into DegT50_{EQ} values.

The draft guidance estimates that most sources make a minor contribution to the overall uncertainty in the leaching assessment. The Panel notes that the wording 'minor' is optimistic in view of the potentially large effect of including aged sorption in the leaching assessment and therefore recommends reconsidering this wording. The Panel also notes that variability of degradation and sorption data may affect the leaching assessment considerably. The procedure described in the EFSA guidance document to derive predicted environmental concentrations (PECs) in soil (EFSA, 2017b) could be a starting point.

The Panel confirms the finding by the EFSA PPR Panel (2013b) that the groundwater assessment scheme described by the European Commission (2014) does not strictly follow the general principles of a tiered approach. The combination of data from different soils may, for example, lead to higher concentrations in Tier 2a (aged sorption studies) than in Tier 1. The Panel also notes that this is not unique to Tier 2a. Inconsistencies may also occur when developing crop-specific scenarios at Tier 2b or applying advanced spatial modelling at Tier 3b. It is possible to avoid such inconsistencies by calibrating Tier 1 against Tier 2b (see EFSA PPR Panel, 2012).

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1. Introduction

1.1. Background and history

In April 2014, the EFSA Panel on Plant Protection Products and their Residues (PPR Panel) was mandated by the Pesticide Steering Committee (now the Pesticide Steering Network, PSN) to provide a Scientific Opinion on the guidance proposal on aged sorption. However, the PPR Panel prepared a Statement (EFSA PPR Panel, 2015) instead of a Scientific Opinion as the Panel could not completely address all the terms of reference. In particular, the experimental data required for testing the guidance was not available. The PPR Panel therefore recommended an update of the guidance proposal, taking into account the conclusions and recommendations provided in the Statement (EFSA PPR Panel, 2015). The PPR Panel further recommended that the updated guidance document be resubmitted, together with supporting data, so that it could finalise its review. This approach is in line with the EFSA Scientific Committee guidance (EFSA Scientific Committee, 2015) where appropriate circumstances are outlined that indicate when EFSA should revise its outputs. As a follow-up of the publication of the statement, the Chemicals Regulation Directorate (CRD) (UK) consulted the authors of the draft guidance and the guidance was updated based on the recommendations in the PPR Statement (EFSA PPR Panel, 2015).

The need to keep the guidance on aged sorption studies on the PSN priority list for guidance and the need for a PPR Panel Opinion on an updated version of the same guidance was discussed at the PSN meeting in October 2015. The PSN concluded that the guidance should be revised. Furthermore, it was agreed that EFSA should contact the European Crop Protection Association (ECPA) to provide the underlying data sets so the Panel could test the guidance using real data. The ECPA data were received in January 2017. Furthermore, the PSN concluded at the October 2015 meeting that a PPR Panel Opinion on the revised guidance was needed.

Given the pertinence of this guidance to an important recommendation in the revised FOCUS (Forum for co-ordination of pesticide fate models and their use) groundwater guidance document (European Commission, 2014) and the PPR Statement (EFSA PPR Panel, 2015), the preparation of an Opinion on the updated CRD ‘Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments’ (CRD, 2016) by the PPR Panel is sought, preferably in a time frame under the PPR mandate (2015 to 2018). As background, reports from the Defra project PS2254 (Defra, 2015a,b) should also be considered.

1.2. Terms of Reference as provided by the requestor

The Scientific Panel on Plant Protection Products and their Residues (PPR Panel) is asked by EFSA to prepare a Scientific Opinion on the CRD guidance proposal ‘Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments’ (CRD, 2016).

In particular, the PPR Panel is to address whether:

- the information relating to the description of the aged sorption process as defined in the guidance is adequately and unbiasedly accounted for by the mathematical description prescribed, also considering the simplifying assumptions that have been made.
- the model used to take into account time-dependent sorption in higher-tier modelling is unbiased and can properly produce a more realistic description of adsorption time-dependent processes both for situations that can result in a decrease of leaching and those where the time-dependent processes may cause an increase of leaching.
- the experiments proposed provide direct information on the parameters assumed in the model proposed to consider time-dependent sorption in the higher-tier model; or, if parameters are indirectly derived, the correlation and mathematical connection between the experimental parameters and the modelled ones is robust and transparently explained.
- the recommendations for an appropriate extraction procedure to extract the total mass can be improved based on the experimental data provided.
- the proposed procedures for the derivation of aged soil adsorption parameters from the experimental data (for active substances based on laboratory studies) are sufficiently scientifically robust for the intended use (including statistical robustness in relation to the amount of experimental data used).
- the use of derived parameters (with their associated uncertainty) are scientifically robust within the tiered framework of the models proposed for use with revised FOCUS groundwater

guidance (European Commission, 2014). In particular, whether the parameter derivation and subsequent selection regarding combining and averaging substance parameters from different soils being recommended is considered suitable in relation to the existing scenario selection in the FOCUS groundwater leaching models.
- the guidance has been validated with a sufficient and unbiased number of data sets.
- the recommendations given in draft guidance in Appendix 5 (use of field data) and Appendix 6 (use of metabolite data) for the consideration of field-derived data and for the consideration of time-dependent sorption in the leaching assessment of the metabolites are useful for a future extension of the guidance to consider these aspects and which further investigations could be needed in order to obtain time-dependent sorption information from field studies and to model time-dependent sorption of metabolites.

1.3. Aged sorption in the groundwater assessment scheme

Aged sorption is a higher-tier approach in the revised FOCUS groundwater guidance (European Commission, 2014).

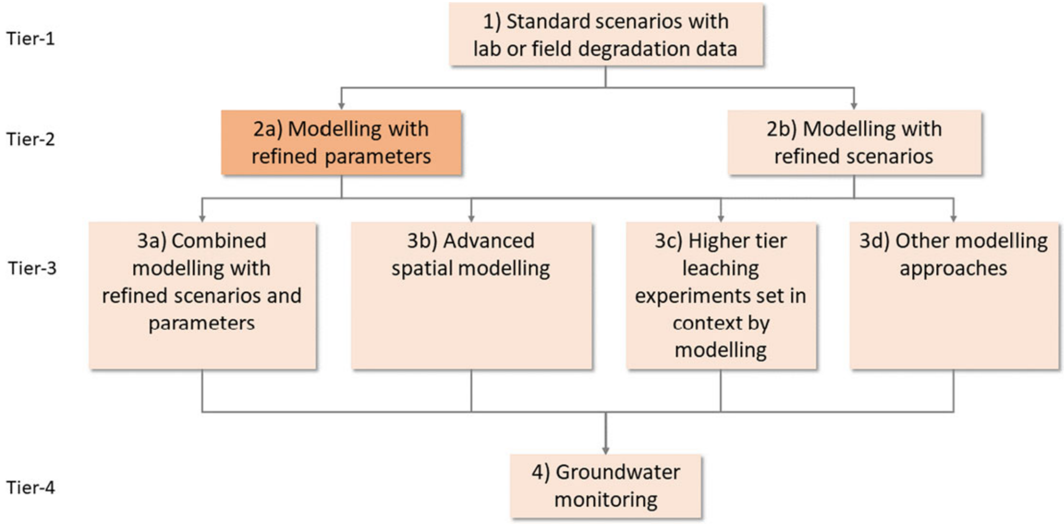


Figure 1: The groundwater assessment scheme in the FOCUS groundwater guidance (European Commission, 2014). Aged sorption is one of the options in Tier 2a, i.e. modelling with refined parameters

Tier 1 consists of the nine FOCUS standard scenarios. Degradation rates may be from either laboratory or normalised degradation rates from field dissipation studies. Tier 2 consists of more refined modelling approaches. Tier 2a consists of modelling with refined parameters. This includes providing data on specific processes including aged sorption. Tier 2b consists of modelling with refined scenarios. This approach is appropriate when the standard Tier 1 scenarios are not representative of a specific crop or use area. Tier 3 consists of more sophisticated modelling approaches and modelling combined with experiments. Finally, Tier 4 consists of monitoring concentrations in the groundwater.

An evaluation of the tiered approach has been given by the EFSA PPR Panel (2013b). An important conclusion was that the assessment scheme generally followed the principles of the tiered approach. However, no tests as to whether the basic principles of a tiered approach are met were presented by the European Commission (2014). The Panel concluded that it can therefore not be guaranteed that lower leaching values are predicted at higher tiers.

1.4. Documentation provided to EFSA

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

CRD (Chemicals Regulation Directorate), 2016. Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments. Prepared by The Food and Environmental Research Agency. Funded by Defra, UK.

Defra (Department for Environment, Food and Rural Affairs), 2015a. Use of field data to generate aged sorption parameters for regulatory leaching assessments. Report to Defra for project PS2254. The Food and Environment Research Agency. 91 pp. (Not published).

Defra (Department for Environment, Food and Rural Affairs), 2015b. Use of metabolite data to generate aged sorption parameters for regulatory leaching assessments. Report to Defra for project PS2254. The Food and Environment Research Agency. 33 pp. (Not published).

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'.

ECPA (European Crop Protection Association), 2016. ECPA time dependent sorption data provided to EFSA for testing the draft guidance proposal.

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

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, York.

Van Beinum W and Beulke S, 2012. Consideration of additional experimental data sets to support the development of the revised guidance on aged sorption studies. The Food and Environment Research Agency, York.

1.5. Structure of Opinion

This Opinion starts with an overview of issues already covered in the previous Statement (Section 2). We will then test the guidance document based on three case studies (Section 3). This test includes the proposed fitting procedure of time-dependent sorption (TDS) experiments, and the proposed combinations of results obtained from such higher-tier experiments with lower-tier results on degradation and adsorption. These case studies are based on real data sets provided by the ECPA. In Section 3, we will further describe issues resulting from the testing and provide recommendations for further improvement of the guidance document.

New issues that were not yet covered in the previous version of the guidance document are described in Sections 4 and 5. These include the derivation of aged sorption parameters from field studies and the calculation of aged sorption parameters for soil metabolites. Section 6 describes some remaining issues that arose from the testing. Section 7 reviews the most important uncertainties. Finally, Section 8 gives conclusions and recommendations for improvement and finalisation of the guidance document.

2. Issues already covered in the Statement

As described in Section 1.1, the Panel reviewed an earlier version of the guidance document (EFSA PPR Panel, 2015). The main conclusions with respect to the experimental and modelling approaches are listed in this section and not further elaborated on in this Opinion.

In the earlier statement, the Panel reviewed existing literature and the draft guidance document with respect to the sorption process. The Panel concluded that 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 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 TDS).

Experimental 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 two-step extraction procedure proposed in the draft guidance consisting of a 24-h 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 was considered a reasonable compromise between the experimental effort and what is desirable from a theoretical point of view (EFSA PPR Panel, 2015). Note that for practical reasons more extraction steps are often carried out (sequential organic extraction). This is not a problem as long as the amount desorbed by $CaCl_2$ and the remaining residue (adsorbed to soil) is adequately quantified for by the subsequent extraction. For legacy studies, the Panel highlighted some issues that should be considered before legacy studies are used for leaching assessments. These concerns are further elaborated on later in this Opinion.

In line with the two-step extraction method, the draft guidance document proposes use of the two-site modelling approach implemented in the PEARLNEQ model (Boesten and Ter Horst, 2012) for simulating TDS. The Panel confirms that this two-site modelling approach is in line with the proposed experimental approach. The $CaCl_2$ extract represents the readily available fraction of pesticides in soil and is experimentally unequivocally 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 model (see Appendix E and Boesten and Ter Horst, 2012). The extraction with a mild organic substance also extracts a residual fraction, with a slow, but reversible exchange of pesticides with the liquid phase. So, this extraction lumps the equilibrium and non-equilibrium sorption domains together in the PEARLNEQ model.

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 conducted in a regulatory framework with reasonable effort. The Panel had, however, concerns about the interpretation of the experiments and how results of the experiments should be used in the leaching assessment. The Panel investigated options for improvement that triggered an update of the guidance document. This updated guidance document together with the supporting data is reviewed in the following sections.

3. Case studies

3.1. Description of the cases

To evaluate the work flow as proposed in the draft guidance document, the Panel selected three case studies from the data set provided by the ECPA (2016). The ECPA data set consists of data on roughly 50 substances and was the basis for Fera Science Ltd to develop the draft guidance document. These case studies were used by the Panel to thoroughly test:

- the proposed fitting procedure of aged sorption experiments;
- the proposed combinations of results obtained from such higher-tier experiments with lower-tier results on degradation and adsorption.

It was considered essential that sufficient and high-quality data on both TDS and lower-tier degradation and sorption were available. For this reason, the ECPA provided additional lower-tier degradation and sorption data for seven substances in their database. These substances are referred to as ECPA-01, ECPA-03, ECPA-04, ECPA-06, ECPA-07, ECPA-11 and ECPA-50.

Closer inspection revealed that for two of these substances (ECPA-06 and ECPA-07) complete dossiers and published EFSA conclusions are available (EFSA, 2016 for substance ECPA-06; EFSA, 2015 for substance ECPA-07). In addition, independent public data on TDS of ECPA-06 are also available (Gulkowska et al., 2016). For this reason, these two substances were considered good candidates for evaluating the work flow. With respect to lower-tier degradation and sorption of these two substances, reference is made to agreed and already published endpoints in the EFSA conclusions as far as possible. Both substances are relatively persistent, with laboratory DegT50 values ranging from 115 to 318 days for substance ECPA-06 (EFSA, 2016) and 50 to 173 days for substance ECPA-07 (EFSA, 2015). The K_{om} value of ECPA-06 ranges from 122 to 238 mL/g (EFSA, 2016) and that of ECPA-07 from 43 to 77 mL/g (EFSA, 2015).

In order to cover a wider range in degradation and sorption properties, the Panel also included substance ECPA-01 in the case studies as this compound has a relatively low K_{om} value of circa 10 mL/g. The identity of ECPA-01 is unknown to the Panel, so only data provided by the ECPA were used.

Table 1 gives an overview of the most important substance parameters. Note that data on TDS in Table 1 are based on preliminary evaluation work done by the ECPA.

Table 1: Overview of data sets provided by the ECPA used for testing the guidance document

Substance name	ECPA-01	ECPA-06	ECPA-07
Lower-tier data			
Full study reports	No	Yes	Yes
DegT50 lab (days)	Data not evaluated	115–318	50–173
DegT50 field (days)	No data	68–224	No data
K_{om} (mL/g)	2–28	122–238	43–77
1/n (–)	0.86–0.95	0.87–0.97	0.84–0.90

Substance name	ECPA-01	ECPA-06	ECPA-07
Data on time-dependent sorption			
Full study reports	No	Yes	Yes
Number of studies	4	4	4
f_{NE} (–)	0.43–0.49	0.63–0.79	0.35–0.76
k_{des} (days^{-1})	0.042–0.058	0.027–0.047	0.028–0.039
DegT50$_{EQ}$ (days)	62–144	78–177	45–80

The Panel first evaluated all available lower-tier degradation and adsorption data. As indicated above, data provided by the ECPA were supplemented, where possible, by data available in EFSA conclusions. In a second step, the aged sorption experiments provided by the ECPA were evaluated using the work flow in the draft UK guidance document. This included the following two elements: (i) a check of the quality of the supplied data, and (ii) a check of the quality of the fits including all refinement options suggested in the draft UK guidance document. In a third step, the procedure for combining lower-tier and higher-tier data was checked. Finally, the effect of including aged sorption in the leaching assessment was simulated. This was done using realistic application rates. However, the time of application was set to 1 day before crop emergence for all substances to avoid the effect of canopy processes.

The cases are described in detail in Appendices A–C. In the following sections, results are summarised (Section 3.2) and recommendations for the improvement of the guidance document are given (Section 3.3).

3.2. Main findings

3.2.1. Main recommendations

The test revealed that the guidance could generally be well applied and resulted in robust and plausible results. The application of the guidance was complicated and time consuming because no software tool is available that fully supports the work flow in the guidance document. In particular, the combination of lower-tier results with higher-tier results required a number of manual steps that could only be performed by experienced users. It is recommended that a user-friendly software tool be developed that supports the full workflow in the guidance document and that all graphs, statistics and tables needed in the regulatory process are produced. It is further recommended that this tool be developed after consultation with applicants and regulators. The Panel further notes that a flow chart summarising the procedure for combining different data sets would be helpful (see Section 3.3.6 for recommendations).

The Panel is concerned about the refinement options for the inverse optimisation as described in the guidance document, because this may lead to additional discussions and expert judgement decisions in the absence of clear recommendations on when to consider a refinement superior to a fit without refinement. The Panel tested a simplified procedure and because this procedure works well, the Panel recommends use of this procedure without refinement options.

Degradation half-lives from first-tier experiments are conceptually different from the degradation half-lives in the TDS concept so the first-tier data need to be converted before they can be used in the averaging procedure. The draft guidance document describes a number of options to make this conversion. From these, the Panel considers a refit of residue data to the original residue data as the preferred option.

Lower-tier sorption parameters such as the K_{om} and 1/n may have a higher effect on the total leaching concentration than aged sorption parameters. For this reason, the Panel recommends that the quality checks outlined in EFSA (2017a) are always applied. Given the importance of the curvature of the Freundlich isotherm, it is further recommended to only accept Freundlich exponents from studies of which sorption coefficients are accepted to be included in the further analysis. This is based on the argument that if the sorption coefficient is not considered sufficiently reliable then the curvature would also be unreliable.

3.2.2. Results of the three cases

Results were obtained using the workflow in the draft guidance document with the modifications recommended by the Panel (see Section 3.2.1 for the most important recommendations).

Results of the fitting

Aged sorption was a relevant process in all cases studied. This can clearly be seen when comparing the fitted apparent sorption constant for the equilibrium model and the non-equilibrium model (Figure 2). Furthermore, all aged sorption experiments met the quality criteria provided in the draft guidance document (i.e. relative standard deviation for each of the fitted parameters is less than 0.4 and the χ^2-error (mass and concentration) is less than 15%; refer to Appendices A–C for details). The optimised parameters can therefore be used in the groundwater leaching assessment.

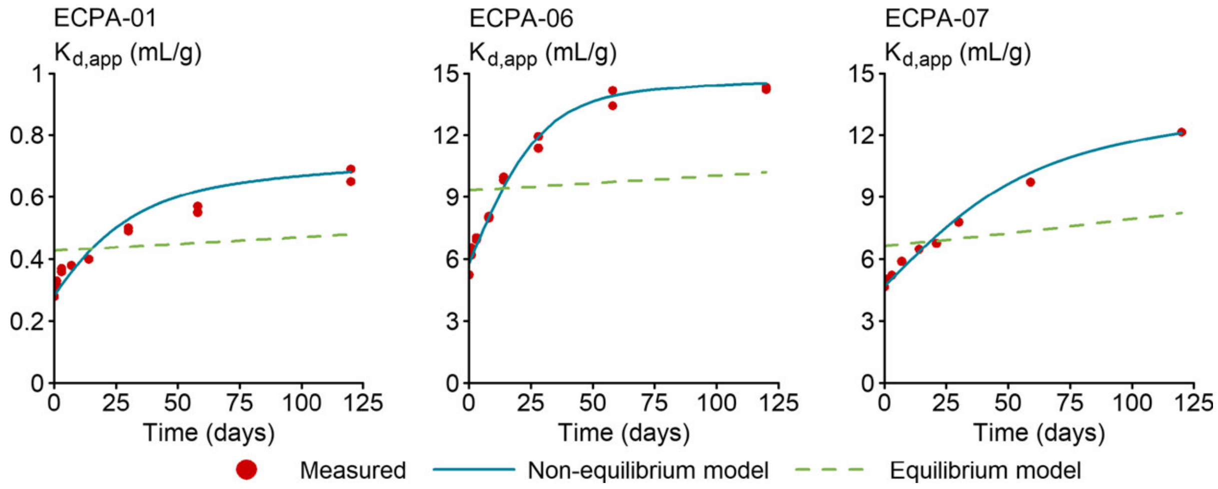


Figure 2: Fit of the apparent sorption constant for the equilibrium model and the non-equilibrium model for substance ECPA-01 (left), ECPA-06 (middle) and ECPA-07 (right). Only one example per substance is given

Combining Tier 1 studies and aged sorption studies

Table 2 shows the substance properties derived using the following assessment approaches:

- Tier 1: Laboratory degradation studies conducted in line with OECD Guideline 307 (OECD, 2002). TDS is not considered, so f_{NE} and k_{des} are zero.
- Aged sorption only: Degradation studies with an addition $CaCl_2$ extraction step in line with the draft guidance document.
- Tier 2a: Results of Tier 1 and aged sorption studies are combined. Half-lives at Tier 1 are recalculated to $DegT50_{EQ}$ values according to the recommendations in this Opinion.

Table 2: Substance properties of pesticides ECPA-01, ECPA-06 and ECPA-07 in different assessment approaches. Tier 2a refers to the combination of Tier 1 and aged sorption data

Substance	Tier	$DegT50_{EQ}$ (days)	$K_{om,eq}$ (mL/g)	$K_{om,tot}$[(c)] (mL/g)	1/n (–)	f_{NE} (–)	k_{des} ($days^{-1}$)
ECPA-01	Tier 1[(a)]	118	9.3	9.3	0.91	0	0
	Aged sorption only	91.1	5.6	8.4	0.91	0.50	0.0530
	Tier 2a	63.3	9.3	13.95	0.91	0.50	0.0530
ECPA-06[(b)]	Tier 1[(a)]	238	138	138	0.882	0	0
	ECPA soils 6A–D						
	Aged sorption only	108	191	312.3	0.915	0.635	0.0335
	Tier 2a	147	138	225.6	0.882	0.635	0.0335
	Soil G1–4						
	Aged sorption only	174	95.3	183.3	0.835	0.923	0.0229
	Tier 2a	147	138	265	0.882	0.923	0.0229

Substance	Tier	$DegT50_{EQ}$ (days)	$K_{om,eq}$ (mL/g)	$K_{om,tot}$ [(c)] (mL/g)	1/n (–)	f_{NE} (–)	k_{des} ($days^{-1}$)
ECPA-07	Tier 1[(a)]	94.8	56.2	56.2	0.86	0	0
	Aged sorption only	56.6	46.9	71.8	0.86	0.53	0.0330
	Tier 2a	50.9	56.2	86	0.86	0.53	0.0330

(a): At Tier 1, the DegT50 is given.

(b): This data set contains data derived using two different extraction procedures and therefore two sets of higher-tier data are given.

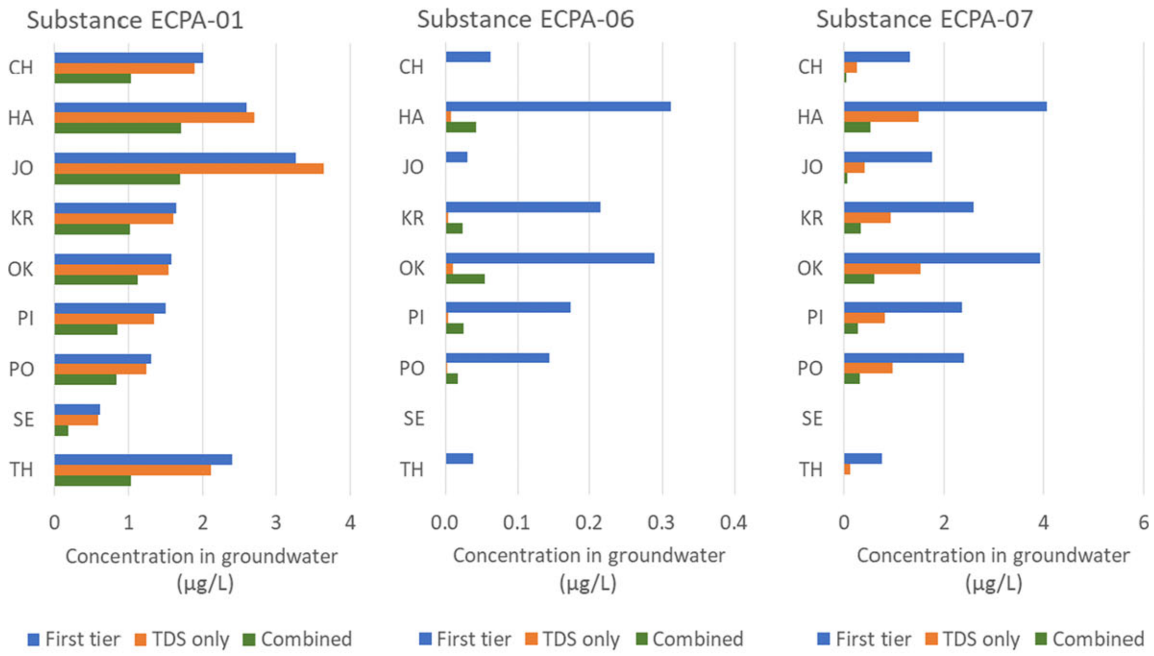
(c): The potential sorption resulting from both equilibrium and non-equilibrium sorption calculated according to the equation (1 + f_{NE}) $K_{om,eq}$.

Table 2 shows that substance properties are dependent on the assessment approach. Degradation half-lives generally decrease when including aged sorption, which is caused by the conceptual difference between the two models (at Tier 1, the degradation half-life refers to the entire system whereas in aged sorption studies the degradation half-life refers only to the equilibrium domain). The potential sorption capacity (i.e. the total number of equilibrium and non-equilibrium sorption sites) also generally increases when including aged sorption (refer to parameter $K_{om,tot}$ for a proxy of the potential sorption capacity). Note, however, that there are exceptions to these general rules. For example, for substance ECPA-01, the total number of sorption sites is lower in the aged sorption studies than at Tier 1. This is caused by the fact that aged sorption studies are sometimes derived in different soils. This can result in higher PEC_{gw} values at higher tiers (see next paragraph for further explanation).

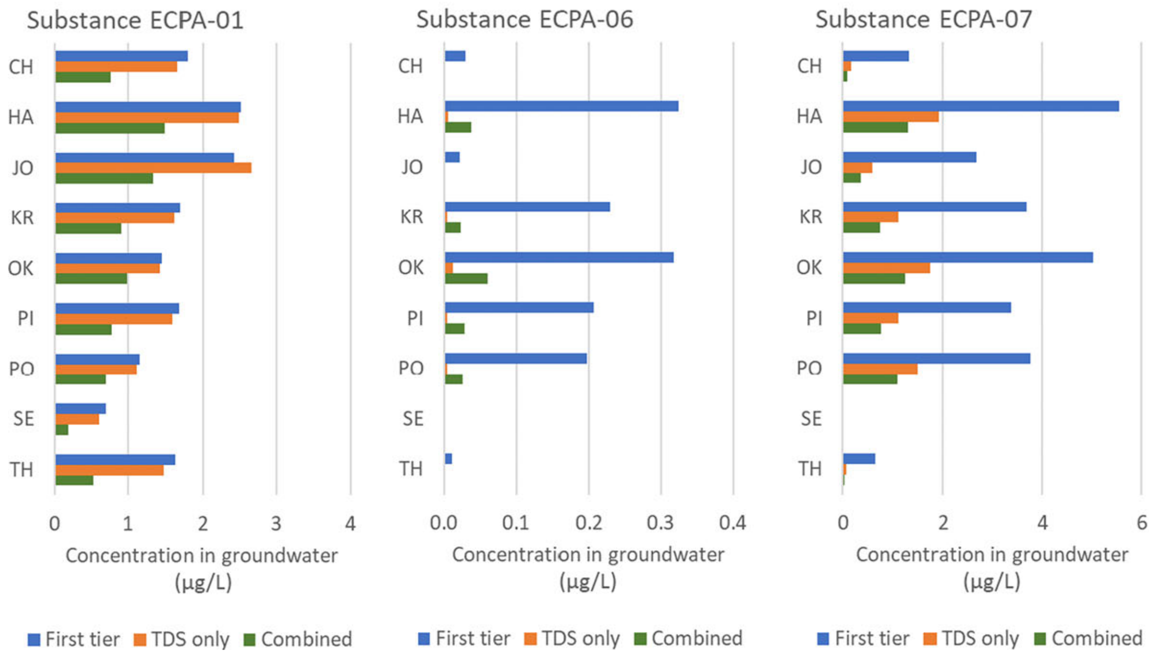
Effect of including aged sorption in the leaching assessment

The effect of including aged sorption differs between the three cases studied (Figure 3A for PEARL and Figure 3C for PELMO). Substance ECPA-01 is a strongly leaching substance and the impact of aged sorption as a higher-tier assessment is quite limited due to the low $K_{om,eq}$ of this substance. Obviously, the increase in sorption over time hardly compensates for the overall slow degradation rate of pesticide ECPA-01 in soil. For the other two substances, the effect of including aged sorption is more pronounced.

A PEARL results



B PELMO results

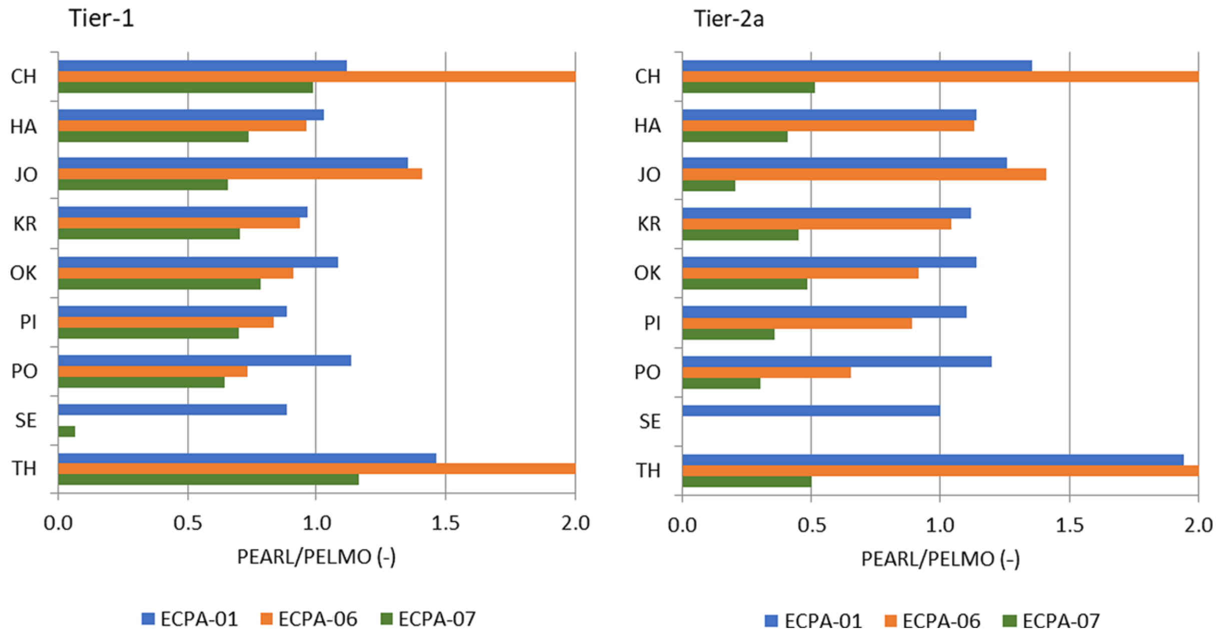


CH = Châteaudun, HA = Hamburg, JO = Jokioinen, KR = Kremsmünster, OK = Okehampton, PI = Piacenza, PO = Porto, SE = Sevilla, TH = Thiva.

Figure 3: Effect of including aged sorption in the leaching assessment calculated with PEARL 4.4.4 (upper graphs) and PELMO 5.5.3 (lower graphs). Calculations were done for winter wheat. Pesticide application was to the soil surface, 1 day before crop emergence. The application rate was 10 g/ha for substance ECPA-01, 20 g/ha for substance ECPA-06 and 200 g/ha for substance ECPA-07. The blue bars indicate results obtained at Tier 1, the orange bars show the predicted concentration using only the data from aged sorption experiments and the green bars show the concentration obtained at Tier 2a (i.e. using the combined data set according to the procedure in the draft guidance document)

Aged sorption experiments may be available for different soils other than first-tier adsorption and degradation experiments (see previous paragraph). The consequence is that the predicted concentration may be higher when using only adsorption and degradation data from the aged sorption experiments (see case ECPA-01). This is because of the high variation in degradation and adsorption data, which may by change result in a sample that generates more leaching compared to the first tier (see Section 3.3.5). Nevertheless, the Panel recommends that all available lower-tier data on degradation and adsorption be considered in higher-tier groundwater risk assessments. Averaging all available data gives the best possible estimate of the underlying statistical population of agricultural fields. Note that even when degradation data from both tiers are used in the groundwater leaching assessment, the higher tier may still generate more leaching. This may happen in those cases where aged sorption is not the dominant process; for example, when the sorption constant is very low. In the three cases studied by the Panel, however, the combination of lower-tier data and data from aged sorption experiments always generated less leaching.

Figure 4 shows that the differences between PEARL and PELMO are generally within a factor of two except for a few scenarios where very low leaching concentrations were predicted. Adding aged sorption appears to increase the difference between the models slightly. However, given all uncertainties in the assessment, the Panel judges these differences to be small. Nevertheless, the Panel sees no reason to change the recommendation in EFSA PPR Panel (2013a) that PEC_{gw} calculations should not be based on one model. The reason is that in some cases a different decision on approval would be reached (see EFSA PPR Panel, 2013a). This finding, however, already applied to the first tier of the assessment.



CH = Châteaudun, HA = Hamburg, JO = Jokioinen, KR = Kremsmünster, OK = Okehampton, PI = Piacenza, PO = Porto, SE = Sevilla, TH = Thiva.

Figure 4: Ratio of results from PEARL 4.4.4 and PELMO 5.5.3 for the nine FOCUS scenarios. Left: Tier 1 results. Right: results of the combined first-tier and aged sorption results (i.e. Tier 2a). In the event of a division by zero in Tier 2a (which is the case for scenarios CH, JO and TH for substance ECPA-06), results of the Tier 1 assessment are plotted

3.3. Recommendations

Based on the three case studies, detailed recommendations for improvement of the guidance document are given below.

3.3.1. Outliers

In the draft guidance, outliers are defined as measurements that strongly differ from others without any obvious experimental reason. In line with the FOCUS guidance (2006) on degradation kinetics, the

Panel requires that all measurements should initially be included in the optimisation. Removal of any data points as outliers must be clearly documented and justified, but the draft guidance provides no criteria for a justification. Given the fact that statistical tests for identifying observations as outliers may not be appropriate for the limited amount of data available, the Panel recommends that the removal of data points as outliers must be justified by a (significant) improvement of the goodness of fit criteria (lower χ^2-error for both total mass and concentration in the liquid phase as well as for the apparent k_D) and of the acceptability criterion of the fitted parameters (lower relative standard error) for the optimisation without the outlier(s). Notice that this recommendation implies that the results for the fits with and without outliers are reported, as was already a requirement in the draft guidance.

If a measurement is identified as an outlier in one of the dependent variables (total mass or concentration in the $CaCl_2$ suspension) only, both the measurements of total mass and of concentration in the $CaCl_2$ suspension have to be eliminated for that sampling time point. If after this elimination only one measurement (single replicate) of mass and concentration is available at a specific sampling time point, the Panel recommends also eliminating these measurements for the following two reasons:

- The additional elimination of a single replicate measurement after elimination of outliers reduces the degrees of freedom, so that the fit without the outlier must improve significantly to meet the criterion that the χ^2-error is smaller than for the fit with the outlier.
- The χ^2-error is, strictly speaking, calculated after averaging the replicate measurements.

3.3.2. $K_{om,eq}$ as a variable

In the Statement (EFSA PPR Panel 2015), the Panel expressed its concern on whether or not measurements of total mass and concentration in the $CaCl_2$ suspension could be treated independently. This question directly relates to the degrees of freedom for estimating variability (χ^2-test), which is either (2n−p) when measurements of mass and concentration are independent, or (n−p) when measurements of mass and concentration are dependent, where n is the number of sampling time points and p the number of fitting parameters.

However, actual deviations between model prediction and observation (‘errors’) and not the actual observations are used in the χ^2-test. Therefore, the number of degrees of freedom does not rely on the independence of the response variables (measurements of total mass and concentration), but on the independence of the ‘errors’ (deviation of the actual observation from the model prediction). This can easily be shown by generating two correlated data series with a simple linear model to which normally distributed errors have been added from different distributions.

Analysis of sorption studies on three soils by Van Beinum et al. (2010) confirmed that the measurement errors of total mass and liquid concentration can be considered independent. This implies that the number of degrees of freedom is (2n−p). Because the deviations between the model prediction and observation are independent, the number of degrees of freedom are sufficient to perform the χ^2-test. The Panel therefore no longer sees any justification to restrict $K_{om,eq}$ to the arithmetic mean of the measured values at time $t = 0$ (fixed parameter). The Panel therefore recommends using $K_{om,eq}$ as a fitting parameter without refinement options (see also next section).

3.3.3. Stepwise refinement of data

The Panel does not recommend refinement options for the inverse optimisation, since this may lead to additional discussions and expert judgement decisions in the absence of clear recommendations on when to consider a refinement fit superior to the fit obtained without refinement. As described above, the Panel now recommends using $K_{om,eq}$ as a fitting parameter (first refinement option in the draft guidance). This choice puts less weight on the early stage of the sorption than using a $K_{om,eq}$ that is fixed to its measured value at time $t = 0$. A variable $K_{om,eq}$ therefore has the tendency to better describe the long-term dynamics (weeks, months), which represents the timescales that are relevant in ground water risk assessments.

The Panel is generally reluctant to eliminate data points from a data set and therefore recommends that early time point(s) (< 2 days) are not eliminated from the model fitting, other than when these points can be considered as outliers (see Section 3.3.1 on the procedure for handling outliers).

3.3.4. Visual assessment of weighted residuals

The draft guidance is not clear on how to proceed when the visual assessment of the weighted residuals reveals systematic deviations between predictions and observations. Ideally, the residuals are randomly distributed without any trend in under- or overpredictions. A trend in the residuals hints at relevant processes that are not included in the aged sorption model, such as biphasic degradation other than aged sorption, a lag-phase or multiple (more than two) sorption sites.

The Panel acknowledges that the two-site aged sorption model is a simplification of the complex reality of sorption in soils with the ability to describe aged sorption under a range of situations and the possibility to determine model parameters with a reasonable effort (EFSA PPR Panel, 2015; see also Section 2). However, the Panel also noted a trend in the residuals in some of the case studies provided by the ECPA, especially for total mass. Total mass mainly reflects the potential of a compound for degradation. In contrast to first-tier degradation studies, where alternative models such as double first-order in parallel (DFOP), first-order multi-compartment (FOMC) or first-order sequential biphasic (hockey stick) models can be used if the single first-order (SFO) model fails to describe the observed behaviour (trend in the residues), these options are not available for aged sorption.

Due to a lack of alternative model descriptions for degradation (biphasic models) and sorption complexity (multiple sorption sites), the Panel recommends that only a trend in the weighted residuals of both total mass and concentration in the $CaCl_2$ suspension invalidates the aged sorption model used. The soil should then be classified as having 'zero aged sorption' according to the terminology in the decision tree in the draft guidance document.

3.3.5. Combining Tier 1 studies and aged sorption studies

In the EFSA statement on the Fera guidance proposal (EFSA PPR Panel 2015), the Panel concludes that available lower-tier data on degradation and adsorption should always be considered in higher-tier groundwater risk assessments. Averaging all available data on degradation or adsorption gives the best possible estimate of the underlying statistical population of agricultural fields.

DegT50

The DegT50 values from the first tier are conceptually different from the $\mathrm{DegT50_{EQ}}$ values from the aged sorption model. Whereas the DegT50 concept implicitly assumes equal degradation in the bulk soil (the same degradation rate coefficient in the solid and liquid phase), the aged sorption concept assumes no degradation in the non-equilibrium domain.

Combining Tier 1 data and aged sorption data require conversion of the DegT50 values. The guidance document proposes three options, which are listed below in the order of decreasing ability to describe a soil-specific conversion (and on a decreasing demand for information):

1) *PEARLNEQ refit on residue data (total mass only).*
   Section 5.3.3 of the draft guidance document describes how to perform a refit of residue data using only total mass. The following points need to be added to the procedure: (i) set the volume of liquid added to zero; and (ii) set the volume of liquid in soil, mass of soil and organic matter content as usual. The Panel generally agrees to the procedure with the exception of the following points:

   a) The draft guidance document requires inverse weighting for total mass (as in normal fitting for aged sorption). The Panel is of the opinion that observations in an inverse optimisation with one dependent variable (here total mass) should not be weighted. This is in line with current guidance for first-tier degradation studies (FOCUS, 2006).
   b) The Panel further does not recommend adding the non-extractable residue fraction and possible metabolites to the compound at sampling time t = 0, as is required for kinetic analysis of first-tier degradation studies (FOCUS, 2006).

2) *Scaling factor 1*

$$\mathrm{DegT50_{EQ}} = 1.1\mathrm{DegT50}\frac{w + K_{om}f_{om}}{w + (1 + f_{NE})K_{om}f_{om}} \qquad (1)$$

where w is the incubation soil moisture content (mL/g) and f_{om} is the fraction of organic matter content (note that the unit of w is not mentioned in the draft guidance).

3) Scaling factor 2

$$\mathrm{DegT50_{EQ}} = 1.2\mathrm{DegT50}\frac{1}{1 + f_{NE}}. \tag{2}$$

The restriction in both scaling factor approaches is that the estimated $\mathrm{DegT50_{EQ}}$ cannot be higher than the DegT50. The factors 1.1 and 1.2 for the scaling factor methods are introduced in the draft guidance based on a comparison between fitted and calculated $\mathrm{DegT50_{EQ}}$ values by Van Beinum and Beulke (2016a,b). The Panel accepts these factors because they ensure that higher $\mathrm{DegT50_{EQ}}$ values are predicted that are not overly conservative.

The Panel recommends that a refit of the aged sorption model to the original data (total mass only) is always the preferred option for the conversion of lower-tier degradation endpoints. If raw data and sufficient information from the Tier 1 study are not accessible for the performance of an inverse optimisation, scaling factor method 1 is recommended, and finally, if not all information for this method is accessible, scaling factor method 2 is to be used.

The geometric mean of the converted DegT50 values from the first-tier degradation studies and the fitted $\mathrm{DegT50_{EQ}}$ values from the aged sorption studies should all be used in the groundwater risk assessment.

In regulatory practice, aged sorption experiments may be available from different studies, e.g. in the reassessment procedure of active substances. If different extraction procedures have been used for total mass, the Panel recommends that these studies are treated as different data sets. In that case, the Panel recommends that the fitted $\mathrm{DegT50_{EQ}}$ from aged sorption experiments is always used, if available for this parameter, since this is the best estimate for $\mathrm{DegT50_{EQ}}$. For first-tier soils without an additional $\mathrm{CaCl_2}$ extraction, the geometric mean f_{NE} and k_{des} parameters should be derived from all available higher-tier studies.

PEARLNEQ v5 offers an option to perform temperature normalisation. However, the Panel argues that this procedure is prone to error and therefore recommends that the normalisation of $\mathrm{DegT50_{EQ}}$ to the reference temperature is performed outside PEARLNEQ. In PEARLNEQ v5, this is achieved by setting the reference temperature to the incubation temperature.

In older degradation studies, which may be used in refitting the residue data with the aged sorption model, the experimental condition may deviate considerably from the reference conditions. In this case, the Panel still considers the need for a proper normalisation of k_{des} as minor with respect to all other simplifications that have been made in the refitting option.

K_{om}

$K_{om,eq}$ derived from aged sorption experiments is theoretically equivalent to the sorption constant from batch equilibrium sorption experiments according to OECD Guideline 106 (OECD, 2000), except that the latter was derived from data covering a range of concentrations. For that reason, the Panel argues that K_{om} values derived from batch sorption studies are more reliable. K_{om} values obtained from the aged sorption study should not be used in the averaging because this would result in double-counting of the same soil. Note that this is not a problem because soil-specific adsorption parameters are always required for aged sorption studies. The Panel recommends averaging all available lower-tier adsorption data in the combined lower-tier and aged sorption assessment (geometric mean for K_{om} and arithmetic mean for 1/n).

$\mathrm{PEC_{gw}}$

The general principles of tiered approaches are according to EFSA PPR Panel (2010): (i) lower tiers are more conservative than higher tiers, (ii) higher tiers aim at being more realistic than lower tiers, (iii) lower tiers usually require less effort than higher tiers, (iv) all tiers aim to assess the same protection goal, and (v) in each tier all available relevant scientific information is used.

Aged sorption experiments are performed at Tier 2a (Figure 1). The criteria (i) to (iv) apply to aged sorption if the lower- and higher-tier assessment is performed for groundwater risk assessment with the same soils. However, to fulfil criterion (v), degradation and adsorption endpoints for the lower and higher tier needs to be combined.

In general, a representative sampling is not possible with the small number of soils required in the authorisation procedure for pesticides compared to the huge variation in degradation and sorption between agricultural soils. Based on Walker and Thompson (1977) and Allen and Walker (1987), the

EFSA PPR Panel (2012) assumed that the coefficient of variation of both DegT50 and K_{om} was 0.25. So, it is possible that Tier 1 yields by chance a subsample of the entire population with properties that generate less leaching, as is illustrated in Figure 5 for the DegT50. As aged sorption is not always a dominant process, the combination of first-tier and aged sorption data sets might result in higher PEC_{gw} values for the combined data set compared to the first tier (see example of the application of ECPA-01 to spring cereals) which contradicts the first principle of tiered approaches.

To conclude, averaging all available data on degradation gives the best possible estimate of the underlying statistical population of agricultural fields and the Panel recommends this approach. Note that the combination of data from different soils may lead to an inconsistency in the tiered approach (Section 3.2.2).

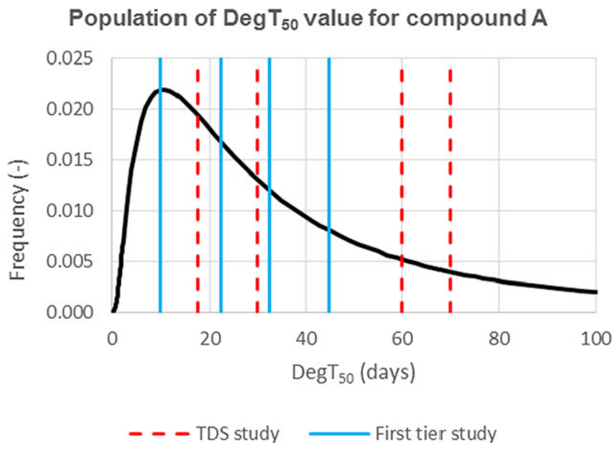


Figure 5: Hypothetical frequency distribution for compound A for a population of agricultural fields in Europe. Compound A degrades with a DegT50 value of 30 days and its variation is described by a moderate coefficient of variation of 25%. Soils sampled for first-tier degradation studies are in blue (geomean DegT50 = 24 days) and aged sorption experiments are in red (geomean DegT50 = 39 days). The geomean of all DegT50 values is 30 days

3.3.6. Recommended flow charts for combining Tier 1 and aged sorption studies

The Panel recommends combining all available lower-tier degradation and adsorption parameters with the parameters from the aged sorption studies obtained at Tier 2a for use in the groundwater leaching assessment. Furthermore, the Panel recommends merging aged sorption studies into the same set of soils only if the same extraction procedure was employed. Figure 6 illustrates the flow chart that must be applied to combine the parameters of Tier 1 and the aged sorption studies (Tier 2a) in the case that all soils in the higher-tier experiments were extracted with the same procedure for the determination of total mass (one set of parameters). The boxes on the left side represent the first- and higher-tier studies, each of them directing to their resulting parameter(s). The first-tier DegT50 values need to be converted to $DegT50_{EQ}$ values in an appropriate way before averaging. The calculated PEC_{gw} values can be directly used in groundwater leaching assessments. Note that agreed matrix DegT50 values can be used (see Section 5 for additional recommendations).

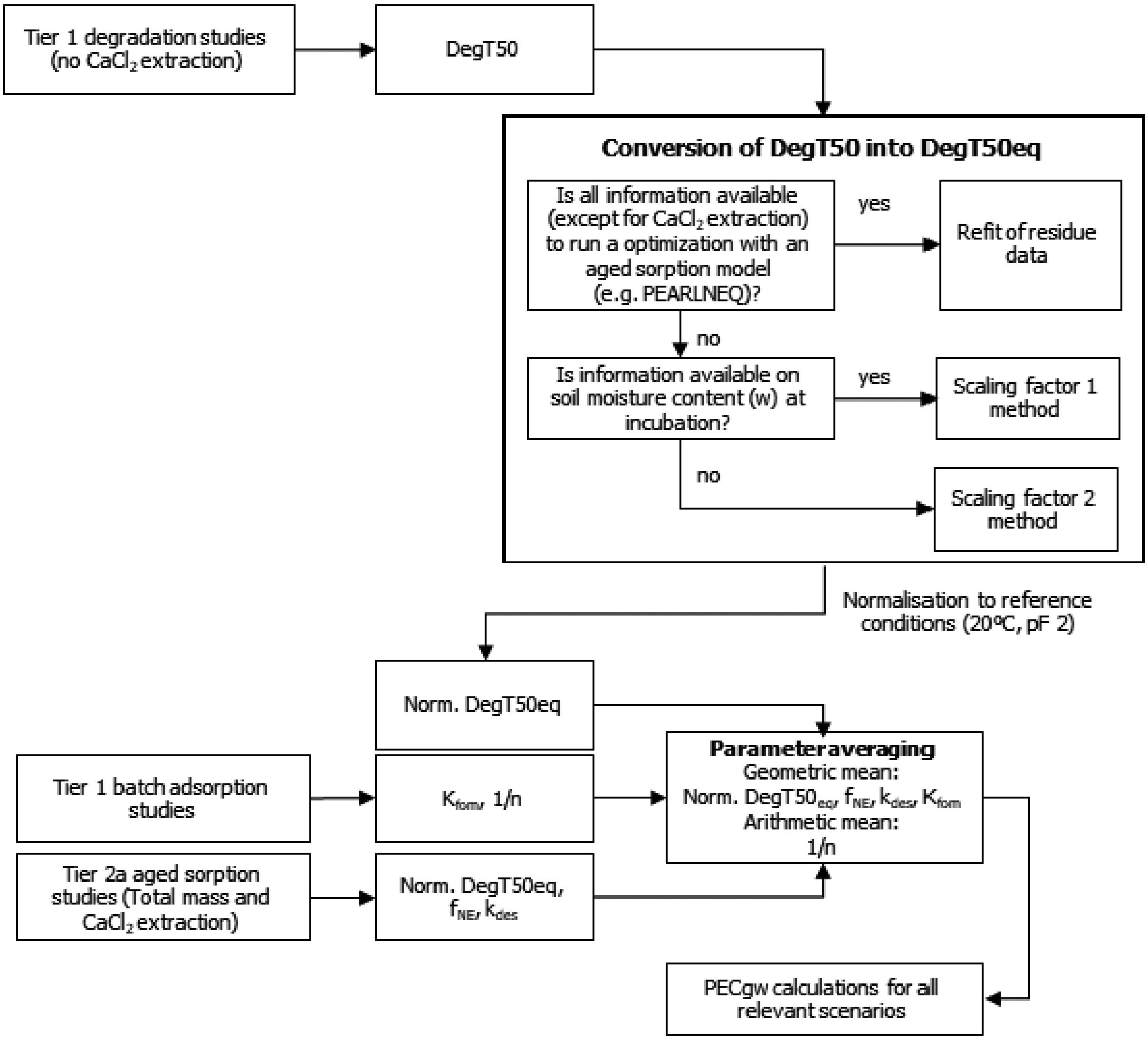


Figure 6: Flow chart for combining Tier 1 and Tier 2a (aged sorption) parameters for groundwater risk assessment in the case that all soils in the aged sorption study were extracted with the same procedure for the determination of total mass

Figure 7 illustrates the flow chart that must be applied to combine the parameters of the first-tier and the aged sorption studies (Tier 2a) in the case that the soils in the higher-tier studies were extracted with two different procedures for the determination of total mass (two sets of parameters). For the aged sorption parameters (f_{NE} and k_{des}), a check for the extraction procedure assigns the parameters to either set 1 (extraction procedure 1) or to set 2 (extraction procedure 2). These sets are combined with the available $DegT50_{EQ}$, K_{om} and 1/n value parameters, which are derived independently of the extraction procedure. PEC_{gw} calculations were performed for each data set and the worst-case value for each scenario is used in groundwater leaching assessment. The flow chart can be easily extended to account for aged sorption studies with three or even more different extraction procedures for the determination of total mass.

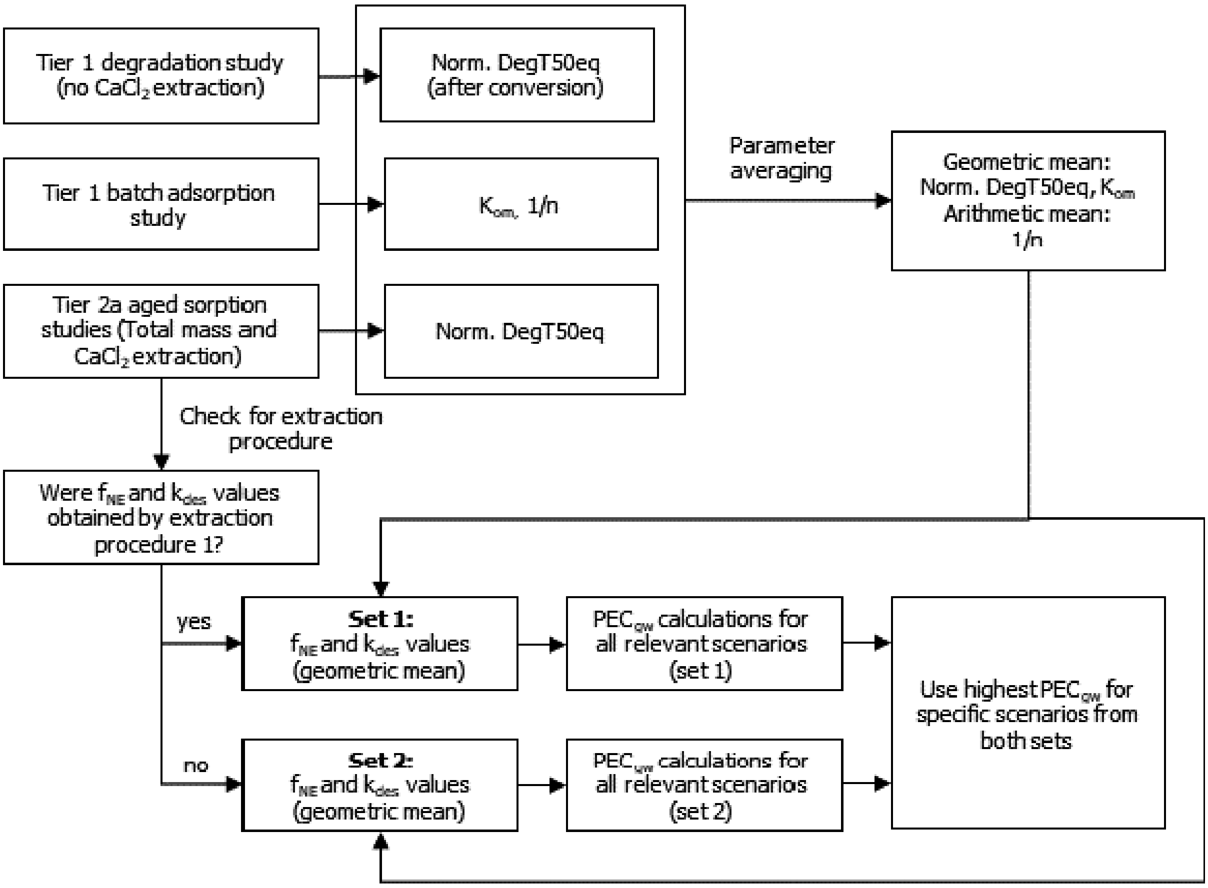


Figure 7: Flow chart for combining first-Tier and Tier 2a (aged sorption) parameters for groundwater leaching assessment in the case that the soils in the aged sorption studies were extracted with two different procedures for the determination of total mass

4. Handling of metabolites

Aged sorption parameters for metabolites can be derived from parent-dosed or metabolite-dosed incubation studies. In principle, both types of study should give the same set of aged sorption parameters for a metabolite where the metabolite shows the same adsorption behaviour whether it is gradually formed over time (parent-dosed study) or whether it is directly applied (metabolite-dosed study), provided that the concentration of the metabolite in the water phase is below its water solubility. Based on the numerical evaluation of Van Beinum and Beulke (2015),[1] the updated guidance document recommends that aged sorption parameters for metabolites should be derived from metabolite-dosed experiments, where the metabolite is directly applied to the soil. In that case the guidance for the parent can be used.

One main assumption in the conceptual aged sorption model is that degradation only takes place in the equilibrium phase – i.e. the liquid phase and the equilibrium sorption domain. If degradation in the non-equilibrium sorption is a relevant dissipation process, metabolite-dosed (application in the equilibrium domain) and parent-dosed studies (formation in the non-equilibrium domain) will not provide the same parameterisation for the aged sorption process. In that case, however, the current conceptual model is not suitable for a parent compound either. The Panel agrees that there is no strong evidence that invalidates the current conceptual model for most substances. Therefore, metabolite-dosed studies are adequate to derive aged sorption parameters, unless evidence states otherwise.

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[1] Van Beinum and Beulke (2015) performed a benchmark study to retrieve parameter values for aged sorption from a large number of artificial data sets calculated with known parameter combinations (total mass and concentration in $CaCl_2$ supplemented with an error). In their numerical study, they assumed no aged sorption for the parent with a degradation following first-order kinetics (SFO-DegT50 was 10 or 50 days) combined with the formation of a metabolite with aged sorption ($DegT50_{EQ}$ was 10 or 100 days).

The lack of a formation fraction is inherent to metabolite-dosed aged sorption studies. The guidance document recommends that the formation fraction is derived from other parent-dosed studies (such as aerobic degradation studies according to OECD Guideline 307 (OECD, 2002). When such studies are not available, the formation fraction should be set to the conservative value of 1. Based on theoretical considerations of conservation of mass, the formation fraction of a metabolite is unique, irrespective of the sorption process (equilibrium sorption or TDS). This implies that formation fractions obtained from total mass fits with and without TDS should be the same as long as the fits are adequately describing the total mass. Nevertheless, the Panel tested the procedure in the draft guidance document by generating artificial degradation experiments with a model that can deal with aged sorption (PELMO) for the following cases:

i) the parent shows aged sorption and the primary metabolite does not (also performed in Van Beinum and Beulke, 2016a,b);
ii) the metabolite shows aged sorption and the parent does not;
iii) both the parent and the metabolite show aged sorption.

The results of this analysis show that correct formation fractions are estimated from a degradation study according to OECD Guideline 307 (OECD, 2002), provided that the parent and metabolite are fitted with the best-fit model, which is the DFOP model in the case of aged sorption (see Appendix D). At least for linear sorption ($1/n = 1$), it can be shown that the effective description of the temporal decrease in total mass caused by degradation and TDS is equivalent to the biphasic degradation kinetics given by the DFOP model (FOCUS, 2006, Appendix 4). Therefore, the Panel agrees that it is possible to correctly derive the formation fraction for the metabolite without explicitly modelling the aged sorption behaviour of either the parent, the metabolite or both, as long as the substances which exhibit aged sorption are described by the DFOP model.

The Panel also noted that the DFOP kinetic degradation model is not recommended for metabolites according to current guidance (FOCUS, 2006). The use of the SFO model for a metabolite is currently the recommended practice for evaluating regulatory degradation studies. If a metabolite shows aged sorption, the formation fraction will be underestimated when the SFO model is used in a first-tier analysis. The degree of underestimation depends on substance-specific properties (both parent and metabolite). However, a more thorough analysis falls outside the remit of this Opinion.

Conclusions and recommendations

The Panel recommends deriving aged sorption parameters for metabolites only from metabolite-dosed studies. In this case the guidance for the parent compound also applies to the metabolite. The formation fraction can be derived from parent-dosed aerobic degradation studies, provided that the parent and metabolite are fitted with the best-fit model, which is the DFOP model in the case of aged sorption. When such studies are not available, the formation fraction should be set to the conservative value of 1.

5. Deriving aged sorption parameters in field studies

In this section, the draft guidance on how aged sorption studies should be performed is compared with EFSA's DegT50 guidance (EFSA, 2014) focusing on the aspect design and quality of field experiments.

There are some differences between the two documents because the EFSA guidance only gives recommendations for field degradation experiments, whereas the draft UK guidance document deals with both DegT50 and kinetic sorption parameters. Consequently, EFSA (2014) only allows a study design that minimises the impact of surface processes (e.g. photolysis and volatilisation) on the $\mathrm{DegT50}_{\mathrm{matrix}}$ value. The draft UK guidance on aged sorption gives more freedom with regard to the methodology by mentioning several possible options for determining the additional kinetic sorption parameters[2]:

- Aged sorption is measured in laboratory studies. Field data are used to determine a field $\mathrm{DegT50}_{\mathrm{EQ}}$ to be used in conjunction with laboratory-derived aged sorption parameters.
- Field studies where aged sorption is measured by sampling the topsoil at different time intervals after application. Soil samples are extracted with $CaCl_2$ solution to determine the readily available pesticide and extracted with solvents to determine the total extractable residue.

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[2] Note that in the UK guidance document the first two options were listed in a different order. We recommend listing from a simple option to more complex options (i.e. the order in this Opinion).

- Profiles of the pesticide concentrations with depth are determined at different time intervals following pesticide application in the field and interpreted using aged sorption.
- Pesticide concentrations are measured in percolate water at a certain depth and interpreted using aged sorption.

However, the draft UK guidance on aged sorption only considered the first two options to be suitable for regulatory purposes. The Panel considers the third option scientifically the best option because this relaxes the restriction of no leaching from the top layer. However, the Panel acknowledges that this option is practically less suitable for regulatory use, because of the high demand for additional information and expert knowledge to run and judge the optimisation (see Kasteel et al. (2009) for a way to proceed for equilibrium sorption). The third and fourth options are therefore not discussed further here.

Option 1 – combine DegT50 from the field with aged sorption in the laboratory

The first option is not aimed at measuring aged sorption in the field, but rather to derive a field DegT50$_{EQ}$ that can be used in combination with aged sorption parameters from the laboratory. With regard to the study design and quality criteria, the UK guidance explicitly refers to EFSA (2014). This includes procedures to avoid surface processes such as photolysis and volatilisation, and the design of field studies. There is no difference between the two guidance documents when aged sorption is measured in the laboratory and only the half-life is measured in the field: Measurements are taken from several soil layers up to 1 m depth. The measured pesticide mass (e.g. in μg/kg) is converted to areic mass (e.g. kg/ha) and then added up over all layers for each individual time point. Samples taken before 10 mm rainfall must be excluded.

The DegT50 from field studies cannot be used directly in the groundwater assessment in combination with aged sorption. In these cases, a field DegT50$_{EQ}$ needs to be derived. This is achieved by fitting the DegT50$_{EQ}$ to the field data applying a numerical leaching model coupled with an optimisation tool, e.g. PEST, while accounting for aged sorption. During the model fitting, the aged sorption parameters are set to those derived in laboratory experiments. Preferably those laboratory experiments should be performed in the same soil as the field experiments.

Option 2 – assessing aged sorption from field experiments

The second method aims at directly measuring aged sorption in field experiments. Again, the UK guidance requires that the study is performed in line with field degradation according to EFSA (2014) with regard to design and quality: for deriving field DegT50 values, it is required that the soil should be sampled up to 1 m depth and divided into depth segments for analysis. Furthermore, in both guidance documents, field sites with excessive leaching should be avoided so that losses below 1 m are minimised.

In the UK guidance, there are additional recommendations for deriving the field aged sorption parameters. It is suggested that only the top 15 cm is extracted with $CaCl_2$ solution, and only the measurements from this top layer are used to determine aged sorption parameters. The UK guidance states that the majority of the substance should remain in the top 15 cm throughout the study period. This is, however, inconvenient for pesticides that are tested for aged sorption, as these are likely to be relatively mobile substances. To overcome this problem, the UK guidance recommends soil sampling up to 1 m depth and checking for residues up to this depth in accordance with EFSA (2014). This is considered acceptable, because a leaching model will be used to interpret the data. The model should in principle simulate the amount of leaching from the sampling layer, and therefore distinguish degradation from losses due to leaching. Note that the application of this approach requires inverse modelling with one of the numerical leaching models (see below), which is a relatively complex procedure for which additional guidance would be needed. After the optimisation, the total residue up to 1 m depth predicted by the model should be compared against the measured sum of residues. If necessary, the obtained DegT50$_{EQ}$ can be adjusted in a separate fit to the residue data of the top layer.

Conclusion from the comparison

The comparison between the two guidance documents showed no significant differences with regard to the design of field studies for deriving DegT50 values as the UK guidance explicitly refers to EFSA (2014). The Panel considers the quality of the experimental design to be sufficient for deriving aged sorption parameters. However, the additional modelling, which is necessary to calculate the final kinetic sorption parameters, could lead to extra uncertainty in both methodologies suggested by the UK guidance:

- Option 1 involves the use of laboratory aged sorption data to derive a field $\text{DegT50}_{\text{EQ}}$. That directly results in some extra uncertainty as parameters from different studies or soils are mixed for the optimisation.
- Option 2 involves the use of laboratory data on, for example, the Freundlich exponent. Furthermore, the modelling procedure is more complicated since a leaching model is used to account for environmental factors that influence sorption and degradation. This could lead to higher uncertainty even if the field measurements were obtained with high quality.

The Panel considers it unacceptable to mix different studies or soils in the inverse modelling procedure and therefore only considers option 2 to be acceptable. If this option is used, field studies have to meet the quality criteria as given in FOCUS (2006) and EFSA (2014). For model fitting, a numerical leaching model must be used that considers aged sorption according to the UK guidance document. The model must be combined with an optimisation tool such as PEST. The use of a numerical leaching model is necessary to correct the degradation rate in the field for actual soil temperature and moisture content.

Modelling

For both option 1 and option 2, a numerical leaching model must be used that considers the aged sorption according to the guidance document, e.g. one of the FOCUS groundwater models. The chosen model has to be combined with an optimisation tool such as PEST. The use of a numerical leaching model is necessary to correct the degradation rate in the field for actual soil temperature and moisture content. That means that, in contrast to EFSA (2014) which recommends time-step normalisation, this inverse modelling technique would be based on a rate-constant normalisation. Please note that the numerical models do not consider any temperature or moisture dependency of the aged sorption rate constant k_{des}.

The Panel further notes that there is a lack of guidance on how to parameterise the numerical models. Furthermore, the procedure in the draft guidance document does not appear to be well worked out and tested. Because this may lead to confusion in the regulatory process, the Panel recommends that the guidance be further developed and tested with real world data. Until this has been done, field studies should not be used to derive aged sorption parameters.

Dealing with agreed DegT50 values from field studies

If agreed matrix DegT50 values from field studies have been derived according to EFSA (2014), the Panel recommends that these values should not be ignored but accounted for in the leaching assessment in line with EFSA (2014). This includes checking whether laboratory and field degradation data are from different populations. To keep consistency with EFSA (2014), this check should carried out on the basis of matrix DegT50 values instead of $\text{DegT50}_{\text{EQ}}$ values. There are two options (Figure 8):

- If, according to EFSA (2014), the laboratory and field DegT50 are shown to be from the same population, the Panel recommends that field DegT50 values be converted into appropriate $\text{DegT50}_{\text{EQ}}$ values using the second scaling factor unless a soil-specific water holding capacity (measured at pF 2) is available. Note that refitting field residue data is not a feasible option.
- If field DegT50 values represent a different population, the Panel considers that rescaling the field DegT50 data on the basis of laboratory TDS data is not justifiable because there is no experimental evidence that the extent of aged sorption in the laboratory and in the field is the same. So in this particular case, the Panel recommends using the field DegT50 values together with the laboratory aged sorption data in the leaching assessment without scaling the field DegT50 values as a conservative approach (see Figure 8).

Note that the Panel considers this to be an interim solution. The ideal solution would be to obtain both the aged sorption parameters and the field degradation half-lives simultaneously using inverse modelling (see option 2 above). That option should replace this interim solution as soon as appropriate guidance has been developed and tested.

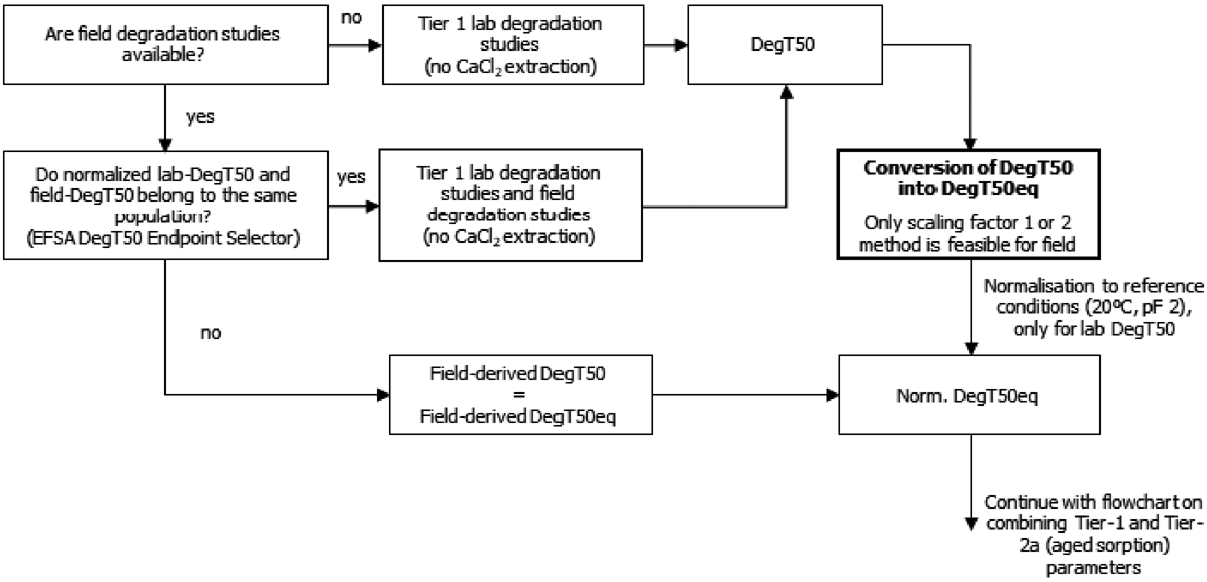

Figure 8: Flow chart for combining field degradation data and laboratory degradation data

6. Other issues

In this section, the Panel first reviews the requirements for the tools to derive aged sorption parameters, then gives some recommendations on data quality (in particular with regard to soil selection) and legacy studies. In the remainder of the section, some specific aspects of the fitting procedure are reviewed.

6.1. Deriving aged sorption parameters using the DFOP model

It has previously been suggested that aged sorption parameters can be obtained from Tier 1 degradation experiments using the DFOP model (FOCUS, 2006). The two-site aged sorption model is mathematically equivalent to a DFOP model where both f_{NE} and k_{des} are functions of the parameters of the DFOP model, namely g (representing the distribution between the two compartments), and k_1 and k_2 (the rate of dissipation from the 'fast' and 'slow' compartments, respectively). The Panel considers that this option is not feasible because it only applies to linear sorption. Furthermore, the Panel is of the opinion that first-tier degradation studies do not contain enough information for an unequivocal determination of the aged sorption parameters because there is no extraction with a $CaCl_2$ solution (e.g. exhaustion of soil microbial biomass in the incubation experiment may also lead to a biphasic decline pattern of total mass). Note further that a perfect SFO-fit in Tier 1 degradation studies does not exclude aged sorption, particularly for slowly degrading substances (see Appendix D).

6.2. Requirements for tools used to derive aged sorption parameters

The draft guidance document mentions three software tools that have been used to derive aged sorption parameters from experimental data sets: PEARLNEQ, MODELMAKER and MATLAB. Of these, PEARLNEQ was specially developed for this purpose, while MODELMAKER and MATLAB are more versatile tools in which the aged sorption model is implemented. The three software packages deliver nearly identical results for aged sorption parameters for example data sets.

It cannot be excluded that other software tools might be used for the same purpose in the future. As with models and other software tools, the Panel is of the opinion that any software tool is acceptable provided that it fulfils a minimum set of requirements as described in the Opinion on Good Modelling Practice (EFSA PPR Panel, 2014). The minimum requirements are listed below:

- Capabilities
    - It should be able to calculate all parameters of the aged sorption model.
    - It should be able to deliver all statistics that are used to assess the goodness of fit.
    - It should provide graphical information of the fits and the residuals.

- Documentation
  - A description of the implementation of the aged sorption concept in the software must be available.
  - A user manual, i.e. a detailed description on how the tool is operated, must be available. This should include a description of model inputs and model outputs.
  - A description of all statistics or a reference to documentation in which the statistical methods are fully described must be available.
  - A description that the tool works correctly (e.g. by testing against a benchmark data set) should be provided.
- Compatibility
  - The tools should be available for major operating systems (like Windows 7–10).
- Availability
  - Easily obtainable, for example downloadable from a website.
  - Support from the developer or distributor of the software.
  - Earlier versions, if applicable, should be available upon request.
  - Preferably the tool is available free of charge.
- User interface
  - To facilitate use of the tool by regulators, the software tool should be accessible via a graphical user interface. The general setup of the user interface should be discussed with regulators and developers of the tool.
  - Functionality to run the tool in batch mode would be a helpful addition.

6.3. Soil selection

In the draft guidance, it is stated that batch adsorption experiments (OECD, 2000) should be performed on the same soils as used for the aged sorption experiments, and that sorption parameters measured on soils from the same location should be averaged prior to calculating the overall average. The Panel notes that the same should apply to the degradation studies.

An important question is when soil samples can be regarded as being from the same soil. The properties of a soil are a function of the five soil-forming factors: parent material, climate, topography, organisms (including human activity) and time. So, for soil samples to represent the same soil, the samples must have been taken from soil where the five factors are the same. Hence, it is not enough that the samples are taken from locations with the same name in the same region. If the locations are close to each other, then the climate and the parent material may be the same but topography, human activity and perhaps also the time may differ. Even if samples are taken from the same field they may not be regarded as being from the same soil if they have been sampled in different years or if the field is very heterogeneous. Even short time intervals between two samplings are problematic if there has been activity on the field which affects soil properties. An example of this is liming of the soil.

The way soil sampling is done can also affect whether samples can be regarded as being from the same soil. If sampling is done by going to the field and digging up a bucket of soil and then a month later another bucket is sampled from another part of the field, then the samples may represent different soils as there can be variations in, for example, topography and parent material even within a single field. If the sampling is performed by taking many small subsamples from a field which are pooled and mixed to one soil sample, then the pooled sample will represent an average of the field and a new sampling performed in the same way is likely to represent the same soil. It is important to sample to the same depth every time sampling is done.

In the light of these considerations, care must be taken when assuming that two samples are from the same soil. It is not enough that the samples are from soils with the same name. The five soil-forming factors should be considered and if these are the same, then the samples may be considered to be from the same soil. In reality, this may be difficult to assess. In the assessment, this can be done by examining the information about the sampling procedure and the soil properties of the samples. If the pH, texture and organic matter content are the same in two samples taken from the same field, then this is an indication that the samples are from the same soil. If other soil properties like the cation-exchange capacity are given, these should also be included in the assessment. As soil is a heterogeneous media, variation in soil properties can be expected even for soil samples taken spatially and temporally close to each other, so two soil samples can be from the same soil even if there is some deviation in one or more of the properties. It is difficult to give criteria for how much variation can be expected as even the degree of heterogeneity will differ from soil to soil. The time span between two sampling times should be considered and information about the agricultural practice should be included in the assessment. Samples taken within the same growth season can be considered as being from the same soil, whereas if several years have passed between two samplings from the same field then the samples are not from the same soil.

It is preferred that soil for the batch adsorption experiment and the aged sorption experiment is sampled at the same time, so that there is no doubt that the two experiments have been done on the same soil.

Conclusions and recommendations

Based on the above, the Panel recommends that:

- soil is sampled for the batch adsorption experiment (OECD, 2000) and the aged sorption experiment at the same time;
- sampling is performed by taking a number of small subsamples and pooling them to get an average of the soil in a given field or plot;
- care take is taken when assuming that samples from the same location are from the same soil if more than one growth season has passed between samplings.

6.4. Use of legacy studies in the assessment of aged sorption

Legacy studies are defined as studies that were performed before the experimental setup laid down in this guidance was published. However, when such a study is consistent with the setup in this guidance and meets the requirements, it is not considered a legacy study. In the case of legacy studies, the draft guidance recommends accepting less stringent requirements on three specific issues. In all other respects, the studies should follow the draft guidance.

The three deviations from the guidance, which are proposed to be acceptable in the draft guidance document, are related to the number of sampling points, the extraction time for the $CaCl_2$ extraction and the use of equilibrium sorption data from other soils.

In the draft guidance, it is proposed that five sampling points (after elimination of outliers and data below the limit of quantification (LOQ)) are sufficient for legacy studies. For standard aged sorption studies, a minimum number of six sampling points are required. The reason for this is that the number of sampling points should be appreciably larger than the number of model parameters and the pattern of decline of mass and concentration should be well established. The Panel notes that the χ^2-test cannot be applied to the graph of apparent K_D values if only five sampling points are available because the number of data points in time would be equal to the number of parameters. Based on this, the Panel does not agree with a minimum of five sampling points for legacy studies and proposes a minimum of six sampling points be also used for legacy studies.

In the case of legacy studies, extraction times of between 8 and 48 h are proposed to be allowed. The 24-h 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 h, or even mixed extraction times. A comparison of a 1-h and a 24-h extraction with a $CaCl_2$ solution during a 48-day incubation experiment showed similar measured concentrations in the suspension, except for significantly lower concentrations for the 24-h 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 h.

It is proposed that if batch sorption data were not measured on the same soil, then equilibrium sorption data from other soils can be used. 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 data set, 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.

If both legacy studies and new studies are available, the studies can only be considered as one data set if they have been performed using the same extraction procedure. If different extraction procedures have been used then the studies have to be considered as different data sets and a PEC_{gw} should be calculated for each of the data sets where the same extraction procedure has been used. The worst-case PEC_{gw} calculated should then be used in the risk assessment.

Conclusions and recommendations

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

- A minimum of six sampling points (after elimination of outliers and data below the LOQ) is also required for legacy studies.
- Extraction times of between 8 and 48 h can be accepted for legacy studies.
- 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.
- If both legacy studies and new studies are available, the studies can only be considered as one data set if they have been performed using the same extraction procedure.
- No other deviations are accepted for legacy studies.

6.5. Consistency of extraction procedures

The Panel (EFSA PPR Panel, 2015) points out the importance of selecting an appropriate solvent extraction method. The solvent extraction should be harsh enough to extract the fraction that is potentially available for leaching. However, the definition of the poorly available fraction that is potentially available for leaching is ambiguous and depends on the experimental method. Therefore, it was requested that a justification of the extraction method, which meets the requirements of an appropriate mass recovery, should be given by the applicant.

The Statement (EFSA PPR Panel, 2015) emphasised the uncertainty caused by the solvent extraction method: The extraction method needs to be strong enough to avoid overestimation of the non-extractable fraction. If the extraction method is too weak and becomes less efficient over time due to stronger sorption, degradation would be overestimated and the increase in sorption over time would be underestimated. This was confirmed in a numerical analysis performed by Boesten (2016). He showed that mild extraction methods are expected to give smaller f_{NE} values (less extracted residue means less aged sorption) and shorter DegT50 values (faster degradation). The effect on the fitted $DegT50_{EQ}$ was shown to be small as this parameter is partly compensated for by the reduced f_{NE}. Parameter values derived by harsh extraction resulted in higher PEC values than those from mild extraction. At concentrations between 0.01 and 0.1 mg/L, the maximum difference in PEC values was a factor of 2 (estimate based on the ‘best-guess’ scenario, which assumed 50% extraction efficiency for mild extraction). The Panel acknowledges that the extraction efficiency is of minor importance in the case of TDS experiments with an additional focus on pesticide mass in the liquid phase ($CaCl_2$ extract). In the case of assessing total mass only (e.g. DegT50 without aged sorption), extraction efficiency is of course a dominant factor.

The Statement (EFSA PPR Panel, 2015) also described that for aged sorption experiments, it is of the 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), steadily creating new sorption sites until the soil constituents are fully rewetted. Rewetting thus mimics an artificial TDS (experimental artefact). Therefore, the soil should not become dryer than necessary to sieve. A limit of $pF = 4.2$ (permanent wilting point for plants) could be proposed, 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.

Conclusions and recommendations

According to the numerical analysis by Boesten (2016), it is not anticipated that the overall impact of the extraction procedure (soft vs harsh) would strongly influence the risk assessment if TDS is taken into account. Still, it is desirable that for future submission addressing aged sorption process, adequate and consistent extraction procedures should be used. The following recommendations are made:

- The same extraction procedure should be used in all laboratory experiments investigating aged sorption in a dossier (the same extraction procedure applied to the different soils). Once an extraction procedure has been selected for a particular compound, the same procedure should be used for all soils to derive specific aged sorption parameters.
- The selected method to perform the extraction procedure should be proven to provide adequate and consistent results by producing yield of extraction in line with current standards. For the initial time point, the extraction should be close to complete (yield of extraction of 100% +/− 10%). Mass balance should also be available for later time points.
- If different extraction procedures are used, results on aged sorption parameters should be treated independently for the same compound (results from the same soil using different extraction procedures should not be mixed) (see case ECPA-06).
- Values from one extraction procedure should not be converted for use in a data set with another extraction procedure.
- Very dry conditions during all phases of the experiment should be avoided. Preferably, freshly collected soil should be used. Freezer storage of the soil samples should also be avoided and storage in a cold place (4°C) should be preferred.

6.6. Dealing with zeroes and minimum number of studies showing aged sorption

The Panel agrees that the geometric mean values of f_{NE} and k_{des} should be used for input in groundwater risk assessments. Note that the Panel recommends that the majority of experiments (with a minimum of four experiments) should show aged sorption behaviour (i.e. f_{NE} and k_{des} values are reliable) as a conservative approach (EFSA PPR Panel, 2015). If the data set includes soils with 'zero aged sorption' (i.e. f_{NE} and k_{des} values are equal to zero), the Panel proposes that the weighted average geomean g should be used, which is calculated as follows (Habib, 2012):

$$g = \frac{n_2}{n} g^{+} \tag{3}$$

where n_2 is the number of non-zero, positive values, n is the total number of values and g^+ is the geometric mean of the positive values. In words, the values in the data set are divided into two groups: one with zeroes and one with the positive values. The geomean of the positive values is calculated and then multiplied by the fraction of positive values in the data set. When there are no zero values in the data set (i.e. $n = n_2$), the weighted average geomean equals the commonly used geomean in groundwater risk assessments.

6.7. Calculation of the χ^2-error of the apparent distribution coefficient

The draft guidance requires that the χ^2-error percentage for the apparent distribution coefficient, $K_{D,app}$, for the aged sorption model must be smaller than that for the equilibrium model to show the relevance of aged sorption. Since the apparent K_D is not used as a dependent variable in the fitting procedure, the calculation of its χ^2-error is not *a priori* clear and no instruction is given in the draft guidance.

In principle, two options are available: the weighted and the unweighted χ^2-error. The weighted χ^2-error is used in aged sorption studies, where the two dependent variables (total mass and concentration in $CaCl_2$ suspension) are weighted in the inverse optimisation to account for differences in absolute values. The χ^2-error for weighted observations is defined as follows:

$$\chi^2\text{-error}(\%) = 100 \times \sqrt{\frac{1}{\chi^2_{\text{tabulated}}} \sum_{i=1}^{t} \frac{(P_i - O_i)^2}{O_i^2}} \tag{4}$$

where t is the sum of the number of time points with measurements of mass and concentration, P_i and O_i are the predicted and observed value for measurement I, respectively (note that replicates should be averaged first for each time point i), and $\chi^2_{\text{tabulated}}$ is the standard tabulated value at the 5% significance level and the degree of freedom being twice the number of time points minus the number of fitting parameters.

The unweighted χ^2-error is used for cases with one dependent variable, e.g. for degradation studies (total mass) where FOCUS (2006) recommends that the observations are not weighted. The χ^2-error for unweighted observations is defined as follows:

$$\chi^2\text{-error}(\%) = 100 \times \sqrt{\frac{1}{\chi^2_{\text{tabulated}}} \sum_{i=1}^{t} \frac{(P_i - O_i)^2}{\bar{O}^2}} \quad (5)$$

where $\bar{O}$ is the mean of all observed values.

There is no obvious right or wrong method, since the χ^2-error of the apparent K_D is not related to the fitting procedure itself. As the observations of the apparent K_D are rather close to each other, i.e. not orders of magnitude apart, the impact of weighting is also expected to be small. For comparison of the performance of the non-equilibrium and the equilibrium models, it should also not matter whether the weighted or unweighted χ^2-error calculation method is used for the apparent K_D.

Recommendations

Nevertheless, to harmonise the calculations of the χ^2-error of the apparent K_D, the Panel recommends using the unweighted method using the same numbers of fitting parameters as for the accompanying fit on mass and concentration. This recommendation is not based on any statistical justifications, but on the fact that the observations only consist of one dependent variable (apparent K_D). This is in line with the existing guidance on kinetic degradation (FOCUS, 2006). The Panel also recommends implementing the calculation of the χ^2-error for weighted and unweighted observation in the software tool.

7. Uncertainty review

The EFSA Scientific Committee (2018) *Guidance on uncertainty in EFSA scientific assessments* provides guidance on the treatment of uncertainty when standardised assessment procedures are being developed. Appendix 3 of the draft guidance document describes the main sources of uncertainty in the aged sorption procedures that affect the leaching assessment. We here evaluate the uncertainty of a particular source regarding its influence on the endpoint in the risk assessment, i.e. the calculated concentration in groundwater.

The uncertainty review in the draft guidance document considers three main sources of uncertainty, i.e. the conceptual model, the experimental procedures (referred to as 'methods') and the interpretation of the experiments ('PEC calculations'). The draft guidance document reviews the contribution relative to the overall uncertainty in the leaching assessment. Sources are judged qualitatively and classified as 'minor', 'medium' or 'high'. What this means is not further specified.

The draft guidance estimates that most sources of uncertainty make a minor contribution to the overall uncertainty in the leaching assessment. The Panel notes that the wording 'minor' is optimistic in view of the potentially large effect of including aged sorption in the leaching assessment and recommends that this wording be reconsidered. For example, Boesten (2017) found that adding aged sorption decreased the leaching concentration in four FOCUS scenarios by a factor of 30 and occasionally by a factor of 100. Boesten (2017) also pointed to the possible interaction of aged sorption parameters and parameters obtained at lower tiers. Lowering the Freundlich exponent (1/n) from 0.9 to 0.7 would increase this factor 30 to a factor of typically 1,000. Note, however, that the calculations by Boesten (2017) were performed using a dosage of 1 kg/ha. Calculations with pesticide ECPA-06 demonstrated that the relative effect of adding aged sorption increases at lower dosages (refer to Appendix B). A quantitative uncertainty analysis that also includes parameters obtained in lower-tier studies would be needed to explore such interactions in more detail but this is outside the scope of this Opinion. Despite this, the Panel agrees that lower-tier sorption parameters such as the K_{om} and 1/n may have a higher effect on the total leaching concentration. For this reason, the Panel recommends that the quality checks outlined in EFSA (2017a) are always applied. Given the importance of the curvature of the Freundlich isotherm, it is further recommended to only accept Freundlich exponents from studies of which sorption coefficients are accepted to be included in the further analysis. This is based on the argument that if the sorption coefficient is considered not sufficiently reliable then the curvature would also be unreliable (refer to Section 6.2 in EFSA PPR Panel, 2015).

The Panel does not share the opinion that aged sorption is expected to be fully reversible. Actually, there is ample evidence in peer-reviewed literature that aged sorption is not a fully reversible process (e.g. Bialk et al., 2005; Sittig et al., 2012; Gulkowska et al., 2014). The Panel wants to emphasise that the proposed aged sorption model does implicitly account for the formation of non-extractable residues in a sink term, which represents, apart from non-extractable residues, CO_2, minor unidentified residues, as well as any metabolite, identified or not. Thus non-extractable residues in the aged sorption model are treated as conforming to existing guidance on degradation kinetics (FOCUS, 2006). Therefore, the Panel does not consider the non-attainment of full reversibility of aged sorption to be a source of uncertainty. However, the formation of non-extractable residues does not necessarily meet the requirement of a first-order degradation process which is restricted to the equilibrium domain (Sittig et al., 2012). The Panel considers that to be an additional source of uncertainty.

The Panel notes that OECD Guideline 106 (OECD, 2000) is not entirely conclusive with respect to non-extractable residues. In principle, they should be handled in a consistent way in soil degradation experiments and aged sorption as well as OECD 106 batch experiments. This implies that non-extractable residues, if found in significant amounts in OECD batch studies applying similar extraction methods as used in the soil degradation experiments, should be explicitly excluded from the calculation of the equilibrium distribution coefficients. Note that this applies to the indirect as well as to the direct method. By experience, study authors commonly ignore this and consider non-extractable residues to contribute equally to the sorption equilibrium even if using the direct method. The Panel recommends that EFSA (2017a) be amended accordingly.

The Panel is of the opinion that the assumption of identical sorption non-linearity in the equilibrium and non-equilibrium domain, i.e. the same Freundlich exponent derived from standard batch adsorption experiments, is a source of uncertainty. In view of the sensitivity of the 1/n value on the estimation of PEC_{gw} values, any judgement of a possible impact on groundwater risk assessment caused by the violation of this assumption is premature without experimental or numerical (sensitivity analysis with appropriate model) evidence.

The Panel agrees that sorption measurements are more prone to experimental errors for mobile substances (very little sorption). The Panel considers that the uncertainty in the aged sorption experiments is of a similar magnitude to that in standard adsorption studies according to OECD Guideline 106 (OECD, 2000) only when the direct method is applied, i.e. both the concentration in the equilibrium $CaCl_2$ solution and the adsorbed amount after extraction are measured. Note that for mobile substances the soil-to-water ratio before the extraction is more favourable in the aged sorption experiments. By applying the direct method, non-extractable residues are treated in the same way as in an aged sorption study.

Compared to the indirect method, however, where the adsorbed amount of substance to the soil is calculated based on mass considerations, the Panel assigns less uncertainty to aged sorption studies for mobile substances. The indirect method is by experience still the most commonly used method in batch adsorption studies even for mobile substances. The main source of error for mobile substances using the indirect method is that the concentration in the input and in the equilibrium solution is almost equally large. The calculation of the adsorbed amount of substance to the soil introduces a large uncertainty, because it is based on the subtraction of two almost equally large concentration values. Calculating the adsorbed mass by subtraction is not part of the procedure in aged sorption studies and therefore it is not a source of uncertainty. Another difference with aged sorption studies is that possible non-extractable residues are considered as being adsorbed in the indirect method.

In combining lower- and higher-tier parameters, the Panel changed the procedure for adsorption and now recommends that all available values from OECD 106 batch adsorption studies are used for groundwater risk assessments. Thus, no additional uncertainty is introduced by combining adsorption parameters from different types of studies to describe the overall sorption. The conversion of first-tier DegT50 values into $DegT50_{EQ}$ values introduces additional uncertainty, but the Panel considers that the best possible estimate of $DegT50_{EQ}$ is obtained with the recommendation to use the refit to the residue data as the preferred option.

The Panel does not support the statement in the draft guidance document that uncertainty of variability in aged sorption parameters is expected to have less impact on the risk assessment than variability in K_{om} at the lower tier. Based on Walker and Thompson (1977) and Allen and Walker (1987), the coefficient of variation of both DegT50 and K_{om} was assumed to be 0.25. To the Panel's knowledge, very little is known about the variability between soils for the aged sorption parameters f_{NE} and k_{des}, and possible correlations with soil properties. As long as there is no comparable information on variation for the aged sorption parameters as there is for the first-tier parameters DegT50 and K_{om}, a reliable assessment of its impact on ground water risk assessment is not possible. Furthermore, the Panel emphasises the sensitivity of the 1/n value on PEC_{gw} values in the groundwater risk assessment, which is a parameter in the simulations with and without aged sorption.

Additional uncertainty is introduced by the dependence of sorption and degradation parameters on soil properties. It is well known that 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. The same might apply for the factor describing the ratio between the non-equilibrium and equilibrium Freundlich coefficients (f_{NE}) and the desorption rate coefficient (k_{des}). The Panel recommends that TDS is not applied to cases where there is strong evidence for, for example, pH-dependent sorption, unless more evidence becomes available on how to handle it.

8. Conclusions and recommendations

The guidance document was updated according to the recommendations provided by the EFSA PPR Panel (2015). Together with this updated guidance document, the ECPA provided the underlying data sets (ECPA, 2016) so that the Panel could test the guidance using real data and finalise its review according to the terms of reference. From this data set, the Panel selected three substances covering a wide range of properties. Particular points of attention were the quality of the provided data, the proposed fitting procedure of TDS experiments and the proposed method for combining results obtained from aged sorption experiments and lower-tier studies on degradation and adsorption.

Aged sorption was a relevant process in all cases studied. The test revealed that the guidance could generally be well applied and resulted in robust and plausible results. The Panel considers the guidance suitable for use in the regulatory process after the recommendations in this Scientific Opinion have been implemented. The Panel agrees with the guidance document, however, that the guidance should only be used for the simulation of pesticide losses to groundwater and not for the simulation of losses to surface water. The reason is that the use of the 24-h batch value as an operational definition of equilibrium sorption is less appropriate for the description of pesticide losses to surface water than to groundwater. Entry into surface waters via drain flow or runoff is often determined by short-term response to rainfall soon after application of pesticides and less affected by long-term sorption. This is particularly true where preferential flow is an important process. In this case, movement to drains can occur within the first hours or days of application and a correct description of sorption at this time is important.

The application of the guidance was complicated because no software tool was available that fully supports the work flow in the guidance document. In particular, the combination of lower-tier results with higher-tier results required a number of manual steps that could only be performed by experienced users. It is recommended that a user-friendly software tool be developed that supports the full workflow in the guidance document and that all graphs, statistics and tables needed in the regulatory process are produced. It is further recommended that this tool be developed after consultation with applicants and regulators. The Panel further notes that a flow chart summarising the procedure for combining different data sets would be helpful.

The Panel is concerned about the refinement options for the inverse optimisation as described in the draft guidance document, because this may lead to additional discussions and expert judgement decisions in the absence of clear recommendations on when to consider a refinement superior to a fit without refinement. The Panel tested a simplified procedure that worked well.

Higher-tier aged sorption experiments may be available for different soils than first-tier adsorption and degradation experiments. The consequence is that the predicted concentration may be higher when using only adsorption and degradation data from the higher-tier aged sorption experiments. This is because of the high variation of degradation and adsorption data, which may by change result in a sample that generates more leaching compared to the first tier. For this reason, the Panel recommends that all available lower-tier data on degradation and adsorption be considered in higher-tier groundwater risk assessments. Averaging all available data gives the best possible estimate of the underlying statistical population of agricultural fields. Note that even when all available adsorption and degradation data from Tier 1 and Tier 2a are used in the groundwater leaching assessment, the higher tier may generate more leaching. This may happen in those cases where aged sorption is not the dominant process, for example when the sorption constant is very low. In the three cases studied by the Panel, however, the higher tier always generated less leaching.

The Panel confirms the statement by the EFSA PPR Panel (2013b) that the groundwater assessment scheme in European Commission (2014) does not strictly follow the general principles of a tiered approach. The combination of data from different soils may, for example, lead to higher concentrations in Tier 2a than in Tier 1. The Panel also notes that this is not unique for Tier 2a. Inconsistencies may also occur when developing more specific scenarios at Tier 2b or applying advanced spatial modelling at Tier 3b. It is possible to avoid such inconsistencies by calibrating Tier 1 against the higher tiers (see EFSA PPR Panel, 2012).

The most important recommendations are listed hereafter; detailed recommendations can be found in Appendix F.

- Aged sorption: 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 TDS). Experimental 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-h 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.
- The model: The Panel concludes that the two-site modelling approach proposed in the draft guidance is in line with the proposed experimental approach. This modelling approach reflects a reasonable compromise between (i) the ability of the model to describe aged sorption in a range of situations and (ii) the possibility to determine model parameters from experiments with reasonable effort.
- Experimental procedures: The Panel acknowledges that the extraction efficiency is of minor importance in the case of TDS experiments with an additional focus on pesticide mass in the liquid phase ($CaCl_2$ extract). When assessing total mass only (e.g. DegT50 without aged sorption) extraction efficiency is of course a dominant factor. Nevertheless, the extraction method used should always be justified. If different extraction methods are used for different data sets, then these cannot be pooled into one data set but should be treated as separate data sets. PEC_{gw} should then be calculated for the different data sets and the worst case should be chosen for the risk assessment.
- Soil selection: In the draft guidance, it is stated that batch adsorption experiments (OECD, 2000) should be performed on the same soils as used for the aged sorption experiments, and that sorption parameters measured on soils from the same location should be averaged prior to calculating the overall average. The Panel recommends that soil is sampled for the batch adsorption experiment (OECD, 2000) and the aged sorption experiment at the same time and to take care when assuming that samples from the same location are from the same soil if more than one growth season has passed between sampling.
- Fitting procedure: Analysis of sorption studies on three soils by Van Beinum et al. (2010) showed that the deviations between model predictions and observations of total mass and liquid concentration can be considered independent. After reconsideration, the Panel no longer sees any justification to restrict $K_{om,eq}$ to the arithmetic mean of the measured values at time $t = 0$ (fixed parameter) and this requirement can be relaxed. The Panel therefore recommends that $K_{om,eq}$ is only used as a fitting parameter.
- Removal of outliers: The Panel recommends that the removal of data points as outliers is not desirable and must be justified by a (significant) improvement of the goodness of fit criteria (lower χ^2-error for both total mass and concentration in the liquid phase as well as for the apparent k_D) and of the acceptability criterion of the fitted parameters (lower relative standard error) for the optimisation without the outlier(s). If a measurement is identified as an outlier in one of the dependent variables only (total mass or concentration in the $CaCl_2$ suspension), then both measurements on total mass as well as on concentration in the $CaCl_2$ suspension, have to be eliminated for that sampling time point. If after this elimination only one measurement (single replicate) of mass and concentration is available at a specific sampling time point, the Panel recommends that this single replicate is also eliminated.
- Refinement options in the inverse modelling procedure: The Panel does not recommend refinement options in the inverse modelling procedure because this may lead to additional discussions and expert judgement in the absence of clear recommendations on when to consider a refinement fit superior to the fit obtained without refinement. Furthermore, in line with FOCUS (2006), the Panel is reluctant to eliminate data points from a data set and therefore does not recommend elimination of early time point(s) from the model fitting unless these points can be considered to be outliers.

- χ^2-error of the apparent distribution coefficient: To harmonise the calculations of the χ^2-error of the apparent K_D, the Panel recommends using the unweighted method using the same numbers of fitting parameters as for the accompanying fit on mass and concentration. This recommendation is not based on any statistical justifications, but on the fact that the observations only consist of one dependent variable (apparent K_D). This is in line with existing guidance on kinetic degradation (FOCUS, 2006). The Panel also recommends that the calculation of the χ^2-error for weighted and unweighted observation is implemented in the software tool.
- Visual assessment of weighted residuals: Due to a lack of alternative model descriptions for degradation (biphasic models) and sorption complexity (multiple sorption sites), the Panel recommends that only a trend in the weighted residuals of both total mass and concentration in the $CaCl_2$ suspension invalidates the aged sorption model used. The soil should then be classified as having 'zero aged sorption' according to the terminology in the draft guidance document.
- Dealing with zeroes: The Panel agrees that the geometric mean values of f_{NE} and k_{des} should be used for input in groundwater risk assessments. If the data set includes soils with 'zero aged sorption' (i.e. f_{NE} and/or k_{des} values are equal to zero), the Panel proposes that the weighted average geomean g be used, calculated according to Habib (2012).
- Combining first-tier and higher-tier sorption and degradation data: Lower-tier data should always be considered because this gives the best possible estimate of the underlying statistical population of agricultural fields and the Panel recommends the approach described in the guidance document. A refit of the aged sorption model to the original data (total mass only) is always the preferred option for the conversion of lower-tier degradation endpoints. If raw data and sufficient information from the tier 1 study is not accessible to perform an inverse optimisation, scaling factor method 1 is recommended, and finally, if not all information for this method is accessible, scaling factor method 2 is to be used.
- Software tool: It is recommended that a user-friendly software tool be developed that supports the full workflow in the guidance document and that all graphs, statistics and tables needed in the regulatory process are produced. It is further recommended that this tool be developed after consultation with applicants and regulators.
- Legacy studies: Legacy studies are experiments that were performed before the experimental setup laid down in this guidance was published. However, when such a study is consistent with the setup in this guidance and meets the requirements, it is not considered to be a legacy study. The following requirements should apply to legacy studies:

  - A minimum of six sampling points (after elimination of outliers and data below the LOQ) is also required for legacy studies.
  - Extraction times of between 8 and 48 h can be accepted for legacy studies.
  - 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.
  - If both legacy studies and new studies are available, the studies can only be considered as one data set if they have been performed using the same extraction procedure.
  - No other deviations are accepted for legacy studies.

- Lower-tier adsorption parameters: Lower-tier sorption parameters, such as the K_{om} and 1/n, may have a higher effect on the total leaching concentration than aged sorption parameters. For this reason, the Panel recommends that the quality checks outlined in EFSA (2017a) are always applied. Given the importance of the curvature of the Freundlich isotherm, it is further recommended to only accept Freundlich exponents from studies of which sorption coefficients are accepted to be included in the 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.
- Metabolites: The Panel recommends that aged sorption parameters for metabolites be derived only from metabolite-dosed studies. In this case the guidance for the parent compound applies to the metabolite too. The formation fraction can be derived from parent-dosed aerobic degradation studies, provided that the parent and metabolite are fitted with the best-fit model, which is the DFOP model in the case of aged sorption. When such studies are not available, the formation fraction should be set to the conservative value of 1.

- Field studies: The Panel notes that there is a lack of guidance on how to parameterise the numerical models that are needed in the inverse modelling procedure. Furthermore, the procedure in the draft guidance document does not appear to be well worked out and tested. Because this may lead to confusion in the regulatory process, the Panel recommends that the guidance be further developed and tested with real world data. Until this has been done, field studies should not be used to derive aged sorption parameters. However, if agreed matrix DegT50 values from field studies have been derived according to EFSA (2014), the Panel recommends that these values are not ignored but accounted for in the leaching assessment in line with EFSA (2014). This includes checking whether laboratory and field degradation data are from different populations. If the field degradation data indeed represent a different population, the Panel recommends using the matrix DegT50 values without converting them into $\text{DegT50}_{\text{EQ}}$ values.
- Uncertainty review: The draft guidance estimates that most sources make a minor contribution to the overall uncertainty in the leaching assessment. The Panel notes that use of the word 'minor' is optimistic in view of the potentially large effect of including aged sorption in the leaching assessment and therefore recommends that this wording is reconsidered. The panel also noted that variability of degradation and sorption data may affect the leaching assessment considerably. The Panel therefore recommends that a procedure is developed to handle this uncertainty. The procedure described in the PECs in soil guidance document (EFSA, 2017b) could be a starting point.
- Using two leaching models: The differences between PEARL and PELMO are generally within a factor of 2 except for a few scenarios where very low leaching concentrations were predicted. Adding aged sorption appears to increase the difference between the models slightly; however, given all the uncertainties in the assessment, the Panel judges these differences to be small. Nevertheless, the Panel sees no reason to change the recommendation in EFSA PPR Panel (2013a) that PEC groundwater calculations should not be based on one model.

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Abbreviations

χ^2-error	the maximum error in the data that would allow the model fit to pass the χ^2 test with a probability of 95% ($p = 0.05$)
1/n	Freundlich exponent (–) used in the Freundlich sorption equation
apparent K_d	apparent sorption coefficient (mL/g); ratio between total adsorbed concentration (μg/g) and the concentration in soil solution (μg/mL)
batch $K_{om,eq}$	coefficient of equilibrium sorption on organic matter (mL/g) obtained in a batch sorption experiment
CAKE	computer-assisted kinetic evaluation
CRD	Chemicals Regulation Directorate
c_L	concentration in the liquid phase (μg/mL)
$c_{L,R}$	reference concentration in the liquid phase (μg/mL)
CofRatDes	acronym used in PEARLNEQ for desorption rate constant (days^{-1})
Defra	Department for Environment, Food and Rural Affairs
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)
DFOP	double first-order in parallel
ECPA	European Crop Protection Association
ExpFre	acronym used in PEARLNEQ for Freundlich exponent (–)
FacSorNeqEql	acronym used in PEARLNEQ for the factor describing the ratio between the equilibrium and non-equilibrium Freundlich coefficients (–)
f_{Moist}	soil moisture correction factor
f_{NE}	a factor for describing the ratio between the non-equilibrium and equilibrium Freundlich coefficients (–)
$f_{NE\ MACRO}$	fraction of the non-equilibrium sorption sites in MACRO (–)
$f_{NE\ PEARL}$	ratio between the non-equilibrium and equilibrium Freundlich coefficients (–) in PEARL (–)
FOCUS	Forum for co-ordination of pesticide fate models and their use
FOMC	first-order multi-compartment
f_{Temp}	temperature correction factor
initial mass	initial mass of pesticide in each jar (μg)
K_D	sorption coefficient (mL/g); ratio between total adsorbed concentration (μg/g) and the concentration in soil solution (μg/mL)
$K_{D,app}$	apparent sorption coefficient (mL/g); ratio between total adsorbed concentration (μg/g) and the concentration in soil solution (μg/mL)
k_{des}	desorption rate constant (days^{-1})
$k_{des\ PEARL}$	desorption rate constant in PEARL (days^{-1})
$K_{F,EQ}$	equilibrium Freundlich sorption coefficient (mL/g)
$K_{F,NE}$	non-equilibrium Freundlich sorption coefficient (mL/g)
K_{OC}	sorption coefficient for sorption on soil organic carbon (mL/g org. carbon)
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)
KomEql	acronym used in PEARLNEQ for coefficient of equilibrium sorption on organic matter (mL/g)

$K_{om,tot}$	The potential sorption coefficient resulting from sorption on both equilibrium and non-equilibrium sites
k_t	degradation rate constant (per day) in the equilibrium domain
LOQ	limit of quantification; smallest concentration at which the substance concentration can be quantified in a certain medium
Mas	acronym used in PEARLNEQ for total mass of pesticide in each jar (μg)
MasSol	acronym used in PEARLNEQ for the mass of soil (dry weight) incubated in each jar (g)
m_{OM}	mass fraction of organic matter in the soil (g/g)
M_p	total mass of pesticide in each jar (μg)
M_s	the mass of soil (dry weight) incubated in each jar (g)
OM	organic matter
PEC	predicted environmental concentration
PEC_{gw}	predicted environmental concentration in groundwater
PPR Panel	EFSA Panel on Plant Protection Products and their Residues
PSN	Pesticide Steering Network
RSE	relative standard error for the estimated parameter value
SFO	single first-order
TDS	time-dependent sorption
USDA	US Department of Agriculture
V	the volume of water in the soil incubated in each jar (mL)
VolLiq	acronym used in PEARLNEQ for the volume of water in the soil incubated in each jar (mL)
W	incubation moisture content (mL/g)
X_{EQ}	pesticide mass sorbed at equilibrium sites (μg/g)
X_{NE}	pesticide mass sorbed at non-equilibrium sites (μg/g)
Aged sorption	Increased sorption after extended contact between pesticide and soil
Aged sorption study	An incubation study whereby sorption is measured at different time intervals after application of the test substance
Batch sorption study	A sorption study in which soils are shaken with pesticide solution for a certain period of time
Equilibrium domain	The liquid phase and the equilibrium sorption sites together
Equilibrium sorption sites	Locations in the soil where sorption occurs rapidly. In the two-site model this part of sorption is assumed to reach equilibrium instantaneously, while non-equilibrium sorption is the additional sorption that takes place with prolonged contact time. The cut-off between equilibrium and non-equilibrium sorption is arbitrary. Here equilibrium sorption is defined as the sorption that would occur after the soil is shaken with pesticide solution for 24 h
Legacy study	An experiment that was performed before the experimental setup laid down in this guidance was published. However, when such a study is consistent with the setup in this guidance and meets the requirements, it is not considered a legacy study
Non-equilibrium sorption sites	Locations in the soil where sorption occurs with time, when the pesticide is exposed to the soil for a longer period. See also the description of 'Equilibrium sorption sites'. In this guidance non-equilibrium sorption is defined as the sorption that occurs beyond equilibrium sorption
Recovery	The percentage of test compound that can be recovered from the soil by extraction
Two-site model	A model that describes sorption at two types of sorption sites: equilibrium sites and non-equilibrium sites. Sorption at the equilibrium sites is assumed to reach equilibrium instantaneously, while adsorption and desorption at the non-equilibrium sites take time to reach equilibrium

Appendix A – Detailed description of case ECPA-01

Pesticide ECPA-01 is one of the data sets provided by the ECPA that includes both lower-tier soil degradation and adsorption experiments, and aged sorption experiments. Pesticide ECPA-01 represents a rather stable compound with low sorption.

The data set on ECPA-01 was used by the PPR Panel to investigate and to demonstrate the entire work flow as suggested in the draft guidance document. The proposed workflow basically starts with fixing $K_{om,eq}$ as a first step and, if necessary, to consider refinement options (free fitting of $K_{om,eq}$ and omitting early sampling points) in subsequent steps. On the basis of all three working examples and taking into account further considerations, the PPR Panel came to the conclusion that the $K_{om,eq}$ should not be fixed in the fitting procedure. Finally, this recommendation was also followed in this worked example.

A.1. Lower-tier assessment (without aged sorption)

A.1.1. Degradation (total mass)

Data set ECPA-01 contains seven laboratory degradation studies conducted in line with OECD Guideline 307 (OECD, 2002). In four studies, an additional $CaCl_2$ extraction step was carried out, so these experiments are also considered to represent aged sorption studies in line with the draft guidance document on aged sorption. As no EFSA conclusion is available on pesticide ECPA-01, degradation rates were recalculated by the Panel on the basis of the total mass extracted in line with the pertinent guidance (FOCUS, 2006). Table A.1 gives the main characteristics of soils used for the degradation and aged sorption experiments. Table A.2 gives the data needed to normalise the degradation rates obtained.

Table A.1: Main characteristics of soils used for degradation and aged sorption experiments (soils used for aged sorption experiments are shaded in grey)

Soil	TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)
A	No	Sandy loam	10	74	1.9	6.9
B	No	Loam	15	50	2.4	5.5
C	No	Silt loam	18	8	3.8	6.5
D	Yes	Sandy loam	7	72	4.3	6.0
E	Yes	Loam	13	40	6.9	5.1
F	Yes	Loam	15	50	4.7	6.1
G	Yes	Loam	11	40	6.7	5.4

OM: organic matter; TDS: time-dependent sorption; USDA: US Department of Agriculture.

Table A.2: Study and reference moisture and temperature of soils used for degradation and aged sorption experiments (soils used for aged sorption experiments are shaded in grey)

Soil	TDS study	Study soil moisture (g/100 g)	Reference soil moisture (pF2)(a) (g/100 g)	f_{Moist}(b) (–)	Study soil temperature (°C)	Reference temperature (°C)	f_{Temp}(c) (–)
A	No	25.7	19	1.0	20.0	20.0	1.0
B	No	31.4	25	1.0	20.0	20.0	1.0
C	No	35.2	26	1.0	20.0	20.0	1.0
D	Yes	27.7	19	1.0	20.0	20.0	1.0
E	Yes	28.2	25	1.0	20.0	20.0	1.0
F	Yes	30.3	25	1.0	20.0	20.0	1.0
G	Yes	42.0	25	1.0	20.0	20.0	1.0

TDS: time-dependent sorption.
(a): FOCUS default values based on soil texture (no measured data available).
(b): f_{Moist} is the soil moisture correction factor $(\theta_{act}/\theta_{ref})$^0.7).
(c): f_{Temp} is the temperature correction factor $(Q_{10}$^$((T_{act} - T_{ref})/10))$ with $Q_{10} = 2.58$.

Table A.3 gives the degradation results obtained from fitting the total extractable mass to best fit kinetics in line with the FOCUS degradation kinetics guidance (FOCUS, 2006) applying the software tool CAKE 3.3. With the exception of soil C, the best fit was obtained with the DFOP model, which indicates that processes like aged sorption are likely to take place. Following recommendation of FOCUS (2006), the slow DFOP degradation rate (k_2) was selected as a conservative DegT50 modelling endpoint for these soils.

Table A.3: Degradation kinetics of pesticide ECPA-01 in degradation and aged sorption experiments based on total extractable mass applying CAKE 3.3 (data from aged sorption experiments are shaded in grey)

Soil	TDS study	Kinetics	DegT50 (days)	DegT90 (days)	DFOP-k_1 DegT50 (days)	DFOP-k_2 DegT50 (days)	g (–)	χ^2-error (%)	DegT50 at reference conditions (pF2, 20°C) (days)
A	No	DFOP	31.0	199	12.0	80.4	0.44	1.5	80.4[(a)]
B	No	DFOP	189	803	9.3	265	0.18	1.9	265[(a)]
C	No	SFO	14.9	49.5	n.a.	n.a.	n.a.	3.9	14.9
D	Yes	DFOP	90.3	438	15.6	150	0.25	0.7	150[(a)]
E	Yes	DFOP	134	693	15.4	241	0.27	1.0	241[(a)]
F	Yes	DFOP	63.9	281	21.7	97.7	0.27	0.8	97.7[(a)]
G	Yes	DFOP	211	864	12.8	281	0.16	0.8	281[(a)]
Geometric mean									**118**

DFOP: double first-order in parallel; SFO: single first-order TDS: time-dependent sorption.
(a): DFOP slow phase (k_2).

Ignoring aged sorption, the modelling DegT50 endpoint of pesticide ECPA-01 based on the seven laboratory degradation studies is 118 days. Note that this DegT50 value of 118 days is indeed conservative for pesticide ECPA-01 but not necessarily conservative for its metabolites. However, this issue is not further considered here.

A.1.2. Adsorption (batch studies)

Nine batch adsorption experiments in line with OECD guidance 106 (OECD, 2000) were available for pesticide ECPA-01. The main soil characteristics and measured Freundlich adsorption parameters ($K_{om,eq}$ and 1/n) are given in Table A.4. Two of these soils (soil D and soil E) are considered identical with two of the four soils used for the aged sorption experiments. Thus, soil-specific 1/n values were also considered in the aged sorption fitting procedure. It may be noted that in the case of soil D, the organic matter content in the soil used for the OECD 106 batch experiment was significantly lower than that in the soil used for the aged sorption experiment. It is therefore questionable whether these two soil batches can indeed be considered the same (Section 6.3). In the context of this case study, this issue is ignored.

The geometric mean $K_{om,eq}$ of the entire set of these nine soils is 9.3 mL/g with an arithmetic mean 1/n of 0.91 (Table A.4).

Table A.4: Main characteristics of soils used for Freundlich adsorption experiments and obtained Freundlich adsorption parameter (soils used for aged sorption fitting are shaded in grey)

Soil	Applicable for TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)	$K_{f,eq}$ (mL/g)	$K_{om,eq}$ (mL/g)	1/n
D	Yes	Sandy loam	10	73	2.8	6.1	0.17	5.9	0.91
E	Yes	Silt loam	14	33	4.5	4.9	0.50	11.1	0.90
H	No	Silt loam	18	12	3.6	6.5	0.26	7.3	0.94
I	No	Sandy loam	12	68	1.7	5.3	0.48	27.7	0.86
J	No	Clay loam	28	36	3.6	5.7	0.78	21.5	0.86
K	No	Loam	16	47	3.6	5.6	0.30	8.4	0.93

Soil	Applicable for TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)	$K_{f,eq}$ (mL/g)	$K_{om,eq}$ (mL/g)	1/n
L	No	Loam	26	37	7.9	7.3	0.33	4.2	0.95
M	No	Clay loam	29	43	0.9	7.1	0.19	22.2	0.91
N	No	Loam	27	29	4.3	7.6	0.10	2.4	0.95
Geometric mean								**9.3**	–
Arithmetic mean								–	**0.91**

OM: organic matter; TDS: time-dependent sorption; USDA: US Department of Agriculture.

A.2. Time-dependent sorption studies

As mentioned above, four of the seven soil laboratory degradation studies available are considered to represent aged sorption studies in line with the draft guidance on aged sorption (additional $CaCl_2$ extraction step). Additional information on the experimental setup necessary to derive aged sorption parameters for these four soils is given in Table A.5.

Table A.5: Experimental setup of the four aged sorption experiments

Parameter[(a)]	Description	Soil D	Soil E	Soil F	Soil G
TimStart (days)	Start time	0	0	0	0
TimEnd (days)	End time	120	120	120	120
MasIni (μg)	Initial total mass of test substance	8.042	8.042	8.042	8.042
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Volume of liquid in moist soil	27.7	38.2	30.3	42.0
VolLiqAdd (mL)	Volume of liquid added	72.3	61.8	69.8	58.1

(a): Parameter naming according to PEARLNEQ 5.1.

A.2.1. Checking of quality criteria

Soil selection

As can be seen in Table A.1, the four soils used for the aged sorption experiments (soils D–G) are quite similar with respect to soil texture, organic matter and soil pH. It is obvious that the soils cover a relatively narrow pH range; neutral and alkaline soils are not covered. This limits the applicability of the data set because sorption to soil may be pH dependent. This issue is, however, ignored in this case study.

Data requirements

As aged sorption experiments with pesticide ECPA-01 were conducted before the draft guidance document was available, these experiments have to be referred to as legacy studies. According to the draft guidance document, the quality criteria are less stringent in the case of legacy data, e.g. average Freundlich 1/n values may be used for the fitting procedure. The data set on ECPA-01 consists of eight sampling time points and soil-specific 1/n values are available for two of the soils. On the basis of the data available, the data set on pesticide ECPA-01 can be considered to fulfil the requirements for legacy studies in the draft guidance document.

Handling of outliers

As can be inferred from the fitting results (refer to the figures in the following sections), one of the replicates of the total mass in soil E at day 58 is likely to be an outlier. The outlier is only in the total mass observations. The Panel recommends that in such a case both the data point for the total mass and the data point for the liquid phase are removed. Note that the draft guidance document is not entirely clear about this. In any case, the draft guidance requires that results for the fits with and without outliers are reported (refer to the next section) and that removal of any data points must be clearly documented and justified.

A.2.2. Data fitting (aged sorption model vs equilibrium sorption model)

The procedure as outlined in the draft guidance document starts with fitting the total mass and the concentration in the liquid phase ($CaCl_2$ extraction) of each soil to either the aged sorption or the equilibrium sorption model. At the first step the $K_{om,eq}$ should be fixed to the $K_{om,eq}$ measured at t_0 (arithmetic mean of all replicates). In the case of soils D and E, the 1/n was set to soil-specific values obtained from OECD Guideline 106 (OECD, 2000) batch experiments. In the case of no available soil-specific 1/n values (soils F and G), the arithmetic mean 1/n of the entire data set available (1/n = 0.91) was applied in line with the draft guidance document. Usually, the draft guidance document recommends four different sets of starting values for f_{NE} and k_{des} in the fitting procedure (i.e. 0.2/0.004 days^{-1}, 0.2/0.05 days^{-1}, 1.5/0.004 days^{-1} and 1.5/0.05 days^{-1} for f_{NE} and k_{des}, respectively). In the case of pesticide ECPA-01, all four starting options for f_{NE} and k_{des} resulted in almost the same aged sorption parameters, indicating that this data set is not prone to non-global minimum results in the fitting procedure (data not shown). Finally, initial f_{NE} (0.2) and k_{des} (0.05 days^{-1}) values were set closest to results obtained for these two parameters. The initial guess of $DegT50_{EQ}$ was set to the slow-phase DegT50 obtained from fitting the total mass (Table A.3). Table A.6 gives an overview of the initial guess of aged sorption parameter set for pesticide ECPA-01 at the first step.

Table A.6: Initial guess on aged sorption parameters for the fitting procedure at the first step (without refinement) and with refinement

Parameter[(a)]	Description	Parameter fixed?		Soil D	Soil E	Soil F	Soil G
		No refinement	Refinement				
ExpFre (–)	Freundlich exponent (1/n)	Yes	Yes	0.91	0.90	0.91[(b)]	0.91[(b)]
KomEql (mL/g)	Sorption coefficient ($K_{om,eq}$)	Yes	No	5.9[(c)]	8.1[(c)]	5.0[(c)]	5.8[(c)]
$DegT50_{EQ}$ (days)	Initial guess of $DegT50_{EQ}$	No	No	90[(d)]	134[(d)]	64[(d)]	212[(d)]
FacSorNeqEql (–)	Initial guess of f_{NE}	No	No	0.2	0.2	0.2	0.2
CofRatDes (days^{-1})	Initial guess of k_{des}	No	No	0.05	0.05	0.05	0.05

(a): Parameter naming according to PEARLNEQ 5.1.
(b): Arithmetic mean 1/n value of OECD 106 batch sorption studies (entire data set).
(c): Arithmetic mean $K_{om,eq}$ measured at t_0 (arithmetic mean of two replicates).
(d): DFOP slow phase DegT50.

As indicated above, soil E is considered to comprise one outlier. Results on aged sorption fits for soil E with and without this outlier are given in Table A.10 and in Figure A.2. The decrease in χ^2-error for total mass and concentration in the liquid phase as well as for the $K_{d,app}$ without this outlier justifies the elimination of the outlier.

Following the draft guidance document, a fit is considered reliable if the relative standard deviation for the each fitted parameter is ≤ 0.4, the χ^2-error (mass and concentration) is $< 15\%$ (indicative trigger) and there is clear evidence for time-dependent sorption on the basis of the non-equilibrium and equilibrium fits (on the basis of the χ^2-error for $K_{d,app}$). The guidance document is not clear how to calculate the χ^2-error for $K_{d,app}$ (weighted vs unweighted values, calculation of the number of degrees of freedom). In line with the recommendations in Section 6.6, the χ^2 for $K_{d,app}$ was calculated using unweighted values with the number of degrees of freedom based on the number of parameters fitted (i.e. four in the case of time-dependent sorption and two in the case of equilibrium sorption).

The results for the aged sorption fits of the four soils are given in Tables A.9–A.12; the fits obtained are given in Figures A.1–A.4. On the basis of the fitting criteria stated above, it can be concluded that all fits at this first step are already considered reliable. Inadequate fits (χ^2-error $> 15\%$) in the case of equilibrium sorption give strong evidence for time-dependent sorption in all four soils. Following the decision tree in the draft guidance document, there is no need to further refine the aged sorption fits and the results can be used for the exposure assessment.

In the case of insufficient fits at the first step, the draft guidance document sets out a stepwise procedure for refinement of the fitting procedure, i.e. also fitting the $K_{om,eq}$ and/or omitting the first or second sampling point, which usually gives more weight to the long-term sorption behaviour. Although these refinements are not considered necessary in this case study, the Panel also tested the impact of different refinement options given in the draft guidance document. Results on refinement fits either following free fitting of $K_{om,eq}$ and/or omitting the first and second sampling point are given in Tables A.9–A.12 and in Figures A.1–A.4 Similar to the first step (fixing $K_{om,eq}$ and using all data), relative standard errors for fitted parameters following refinement were ≤ 0.4 in all cases as well. Slightly lower χ^2-errors (mass and concentration) in most cases also indicate that the refinement fits (despite lower degrees of freedom) are slightly better than the fits obtained at the first step. In contrast, the χ^2-errors on $K_{d,app}$ of the refinement fits were always significantly higher. Note that in the case of free fitting of $K_{om,eq}$ and omitting the first and second sampling point, the degree of freedom has decreased to 1 in this data set (six sampling time points remaining and five parameters fitted). The visual inspection of the fitting results (Figures A.1–A.4) indicates that in some cases the refinement fits may be considered better than the fits obtained in the first step (e.g. for soil F).

The refinement options lead to a high work load for both notifiers and regulators. Furthermore, because it is not entirely clear when a refinement option is considered better, this may lead to lengthy discussions in expert meetings, which is not desirable. The Panel therefore recommends simplifying the work flow by following the procedure in Section 3.3. The suggested simplified procedure is tested for substance ECPA-06.

As outlined in Section 3.3, the Panel recommends not to fix $K_{om,eq}$ but to allow for free fitting of $K_{om,eq}$ in any case (without any further refinement). Note that fitting of $K_{om,eq}$ is actually the first refinement step according to the workflow in the draft guidance document. Final aged sorption parameters for the four soils with free fitting of $K_{om,eq}$ are given in Table A.7, the statistics are given in Table A.8.

Table A.7: Aged sorption parameters obtained for the four soils applying PEARLNEQ 5.1 (free fitting of $K_{om,eq}$) (soils used for aged sorption studies are shaded in grey)

Soil	$DT50_{EQ}$ (days)	k_{des} (days^{-1})	f_{NE} (–)	$K_{om,eq}$ (mL/g)	1/n (–)	$DegT50_{EQ}$ at reference conditions (pF2, 20°C) (days)
D	79.5	0.050	0.58	5.2	0.91(a)	79.5
E(c)	99.7	0.078	0.49	7.5	0.90(a)	99.7
F	60.7	0.043	0.44	4.8	0.91(b)	60.7
G	143	0.048	0.52	5.4	0.91(b)	143
Geometric mean	–	0.053	0.50	5.6	–	91.1
Arithmetic mean	–	–	–	–	0.91	–

(a): Fixed to value from soil-specific batch experiment.
(b): Fixed to arithmetic mean 1/n of the entire data set available.
(c): Outlier omitted.

Table A.8: Parameter acceptability (relative standard error), goodness of fit (χ^2-error) and evidence for aged sorption for the aged sorption fits obtained for the four soils applying PEARLNEQ 5.1 (free fitting of $K_{om,eq}$) (soils used for aged sorption studies are shaded in grey)

Soil	Relative standard errors (–)				χ^2-error (%)			Criteria
	$DT50_{EQ}$ (days)	k_{des} (days^{-1})	f_{NE} (–)	$K_{om,eq}$ (mL/g)	Mass/conc NEQ	$K_{D,app}$ NEQ	$K_{D,app}$ EQ	
D	0.03	0.23	0.14	0.08	2.2	12.5	24.0	Pass
E(a)	0.04	0.29	0.14	0.05	2.5	14.5	21.2	Pass
F	0.02	0.20	0.11	0.06	1.5	8.7	22.6	Pass
G	0.04	0.23	0.12	0.05	1.9	10.6	21.7	Pass

Conc: concentration; NEQ: non-equilibrium; eq: equilibrium.
(a): Outlier omitted.

Considering only these four dedicated aged sorption studies, the modelling endpoints of pesticide ECPA-01 to be used in the exposure assessment are: $DegT50_{EQ}$ = 91.1 days, $K_{om,eq}$ = 5.6 mL/g, 1/n = 0.91, k_{des} = 0.053 $days^{-1}$ and f_{NE} = 0.50.

Table A.9: Aged sorption fitting results for soil D (without and with refinement options)

Soil D		**All data ($K_{om,eq}$ fixed to $K_{om,eq}$ at t_0)**	**Refinement options**		
			All data ($K_{om,eq}$ fitted)	**First data point omitted ($K_{om,eq}$ fitted)**	**First and second data point omitted ($K_{om,eq}$ fitted)**
Aged sorption model					
Parameter					
f_{NE} (–)	Value	0.49	0.58	0.59	0.58
	RSE	0.10	0.14	0.17	0.19
K_{des} ($days^{-1}$)	Value	0.045	0.050	0.047	0.042
	RSE	0.26	0.23	0.26	0.27
$DegT50_{EQ}$ (days)	Value	80.5	79.5	80.6	83.5
	RSE	0.03	0.03	0.04	0.04
M_{ini} (μg)	Value	7.4	7.3	7.3	7.2
	RSE	0.01	0.01	0.01	0.01
$K_{om,eq}$ (mL/g)	Value	5.9	5.2	5.2	5.2
	RSE	n.a.	0.08	0.11	0.13
1/n (–)	Value	0.91	0.91	0.91	0.91
χ^2-error (mass and concentration)					
Number of observations		16	16	14	12
Parameter fitted		4	5	5	5
Degree of freedom		12	11	9	7
χ^2-error (%)		2.2	2.2	2.5	1.9
χ^2-error ($K_{d,app}$)					
Number of observations		8	8	7	6
Parameter fitted		4	5	5	5
Degree of freedom		4	3	2	1
χ^2-error (%)		9.2	12.5	14.7	16.6
Equilibrium sorption model					
χ^2-error (mass and concentration)					
Number of observations		16	16	nc	nc
Parameter fitted		2	3	nc	nc
Degree of freedom		14	13	nc	nc
χ^2-error (%)		6.7	5.1	nc	nc
χ^2-error ($K_{d,app}$)					
Number of observations		8	8	nc	nc
Parameter fitted		2	3	nc	nc
Degree of freedom		6	5	nc	nc
χ^2-error (%)		55.2	24.0	nc	nc

RSE: relative standard error.

Table A.10: Aged sorption fitting results for soil E (without and with refinement options)

Soil E		All data ($K_{om,eq}$ fixed to $K_{om,eq}$ at t_0)	Outlier omitted ($K_{om,eq}$ fixed to $K_{om,eq}$ at t_0)	Refinement options		
				Outlier omitted ($K_{om,eq}$ fitted)	First data point and outlier omitted ($K_{om,eq}$ fitted)	First and second data point and outlier omitted ($K_{om,eq}$ fitted)
Aged sorption model						
Parameter						
f_{NE} (–)	Value	0.37	0.44	0.49	0.47	0.42
	RSE	0.19	0.12	0.14	0.17	0.19
K_{des} ($days^{-1}$)	Value	0.062	0.066	0.078	0.059	0.041
	RSE	0.53	0.30	0.29	0.32	0.31
$DegT50_{EQ}$ (days)	Value	96.0	101	99.7	104	112
	RSE	0.07	0.04	0.04	0.05	0.05
M_{ini} (μg)	Value	7.0	7.1	7.0	7.0	6.8
	RSE	0.02	0.01	0.01	0.01	0.01
$K_{om,eq}$ (mL/g)	Value	8.1	8.1	7.5	7.8	8.3
	RSE	n.a.	n.a.	0.05	0.07	0.07
1/n (–)	Value	0.90	0.90	0.90	0.90	0.90
χ^2-error (mass and concentration)						
Number of observations		16	14	14	12	10
Parameter fitted		4	4	5	5	5
Degree of freedom		12	10	9	7	5
χ^2-error (%)		3.2	2.5	2.5	2.2	1.9
χ^2-error ($K_{d,app}$)						
Number of observations		8	7	7	6	5
Parameter fitted		4	4	5	5	5
Degree of freedom		4	3	2	1	0
χ^2-error (%)		12.5	11.2	14.5	17.8	n.a.
Equilibrium sorption model						
χ^2-error (mass and concentration)						
Number of observations		nc	14	14	nc	nc
Parameter fitted		nc	2	3	nc	nc
Degree of freedom		nc	12	11	nc	nc
χ^2-error (%)		nc	7.1	5.5	nc	nc
χ^2-error ($K_{d,app}$)						
Number of observations		nc	7	7	nc	nc
Parameter fitted		nc	2	3	nc	nc
Degree of freedom		nc	5	4	nc	nc
χ^2-error (%)		nc	40.5	21.2	nc	nc

RSE: relative standard error; n.a.: not applicable.

Table A.11: Aged sorption fitting results for soil F (without and with refinement options)

Soil F		**All data ($K_{om,eq}$ fixed to $K_{om,eq}$ at t_0)**	**Refinement options**		
			All data ($K_{om,eq}$ fitted)	**First data point omitted ($K_{om,eq}$ fitted)**	**First and second data point omitted ($K_{om,eq}$ fitted)**
Aged sorption model					
Parameter					
f_{NE} (–)	Value	0.41	0.44	0.43	0.40
	RSE	0.07	0.11	0.13	0.14
K_{des} (days^{-1})	Value	0.041	0.043	0.040	0.035
	RSE	0.20	0.20	0.22	0.22
$DegT50_{EQ}$ (days)	Value	61.0	60.7	61.4	62.9
	RSE	0.01	0.02	0.02	0.02
M_{ini} (μg)	Value	7.5	7.5	7.5	7.4
	RSE	0.01	0.01	0.01	0.01
$K_{om,eq}$ (mL/g)	Value	5.0	4.8	4.8	5.0
	RSE	n.a.	0.06	0.07	0.07
1/n (–)	Value	0.91	0.91	0.91	0.91
χ^2-error (mass and concentration)					
Number of observations		16	16	14	12
Parameter fitted		4	5	5	5
Degree of freedom		12	11	9	7
χ^2-error (%)		1.5	1.5	1.5	1.3
χ^2-error ($K_{d,app}$)					
Number of observations		8	8	7	6
Parameter fitted		4	5	5	5
Degree of freedom		4	3	2	1
χ^2-error (%)		7.1	8.7	9.9	11.0
Equilibrium sorption model					
χ^2-error (mass and concentration)					
Number of observations		16	16	nc	nc
Parameter fitted		2	3	nc	nc
Degree of freedom		14	13	nc	nc
χ^2-error (%)		5.4	3.9	nc	nc
χ^2-error ($K_{d,app}$)					
Number of observations		8	8	nc	nc
Parameter fitted		2	3	nc	nc
Degree of freedom		6	5	nc	nc
χ^2-error (%)		50.3	22.6	nc	nc

RSE: relative standard error; n.a.: not applicable.

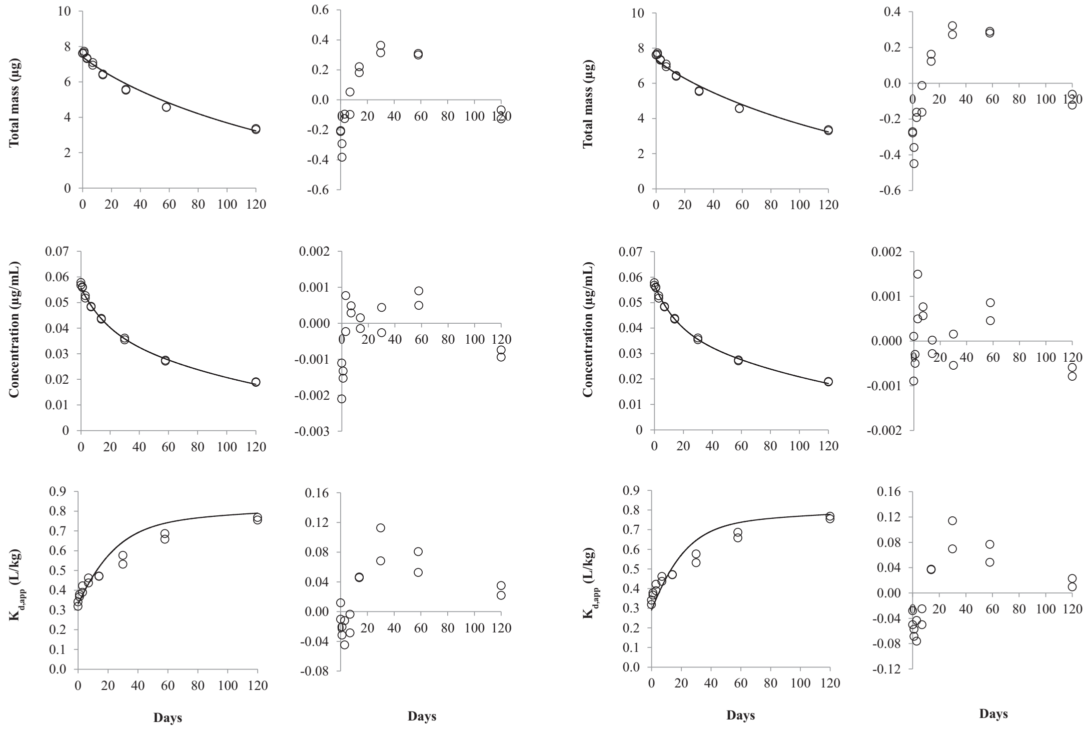
Table A.12: Aged sorption fitting results for soil G (without and with refinement options)

Soil G		All data ($K_{om,eq}$ fixed to $K_{om,eq}$ at t_0)	Refinement options: All data ($K_{om,eq}$ fitted)	Refinement options: First data point omitted ($K_{om,eq}$ fitted)	Refinement options: First and second data point omitted ($K_{om,eq}$ fitted)
Aged sorption model					
Parameter					
f_{NE} (–)	Value	0.45	0.52	0.52	0.48
	RSE	0.10	0.12	0.13	0.16
K_{des} (days^{-1})	Value	0.042	0.048	0.041	0.031
	RSE	0.25	0.23	0.24	0.28
$DegT50_{EQ}$ (days)	Value	143.5	142.6	147.8	156.0
	RSE	0.04	0.04	0.04	0.05
M_{ini} (μg)	Value	7.2	7.2	7.1	7.1
	RSE	0.01	0.01	0.01	0.01
$K_{om,eq}$ (mL/g)	Value	5.8	5.4	5.4	5.7
	RSE	n.a.	0.05	0.06	0.07
1/n (–)	Value	0.91	0.91	0.91	0.91
χ^2-error (mass and concentration)					
Number of observations		16	16	14	12
Parameter fitted		4	5	5	5
Degree of freedom		12	11	9	7
χ^2-error (%)		2.0	1.9	1.7	1.8
χ^2-error ($K_{d,app}$)					
Number of observations		8	8	7	6
Parameter fitted		4	5	5	5
Degree of freedom		4	3	2	1
χ^2-error (%)		8.3	10.6	11.9	13.0
Equilibrium sorption model					
χ^2-error (mass and concentration)					
Number of observations		16	16	nc	nc
Parameter fitted		2	3	nc	nc
Degree of freedom		14	13	nc	nc
χ^2-error (%)		6.1	4.7	nc	nc
χ^2-error ($K_{d,app}$)					
Number of observations		8	8	nc	nc
Parameter fitted		2	3	nc	nc
Degree of freedom		6	5	nc	nc
χ^2-error (%)		38.9	21.7	nc	nc

RSE: relative standard error; n.a.: not applicable.

A First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0

B Refinement – free fitting of $K_{om,eq}$



C Refinement – omitting first sampling point and free fitting of $K_{om,eq}$

D Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

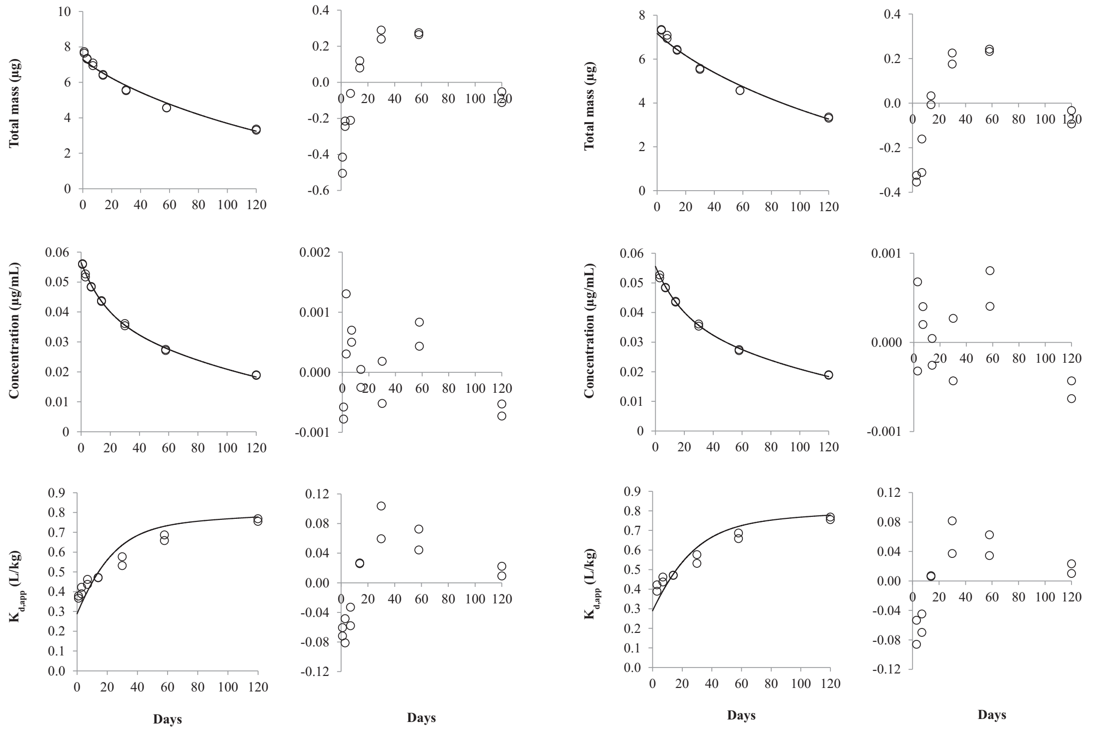
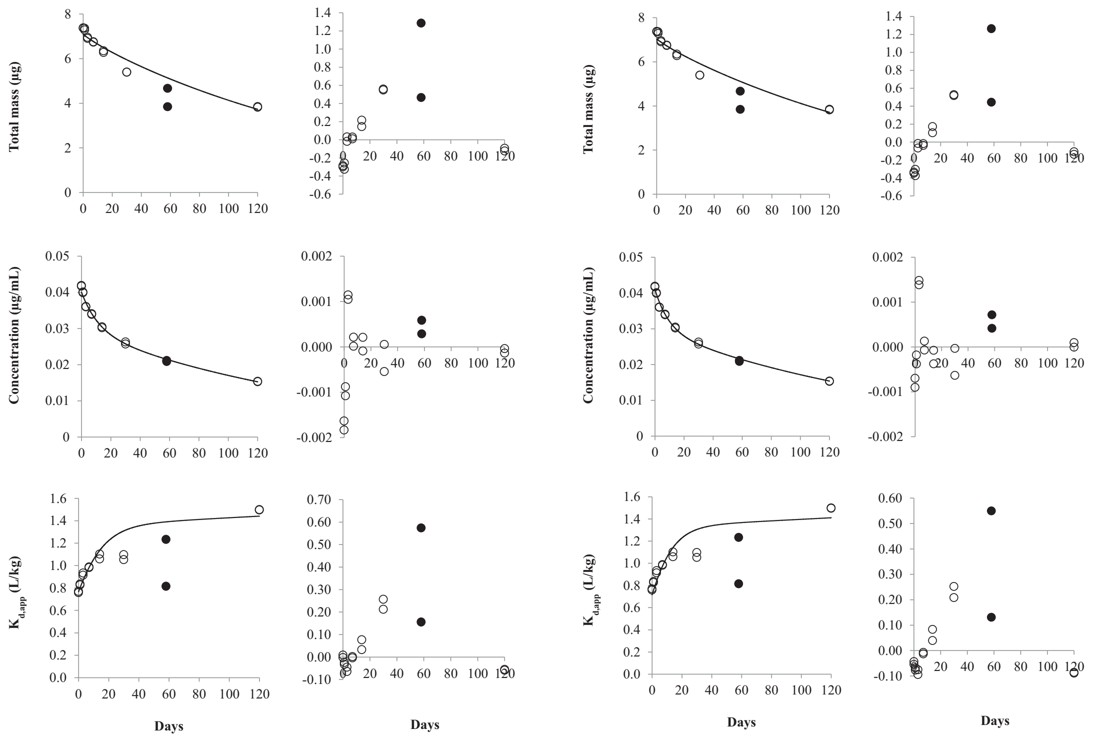


Figure A.1: Aged sorption fitting results for soil D (without and with refinement options). (A) First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0. (B) Refinement – free fitting of $K_{om,eq}$. (C) Refinement – omitting first sampling point and free fitting of $K_{om,eq}$. (D) Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

A First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0

B Refinement – free fitting of $K_{om,eq}$



C Refinement – omitting first sampling point and free fitting of $K_{om,eq}$

D Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

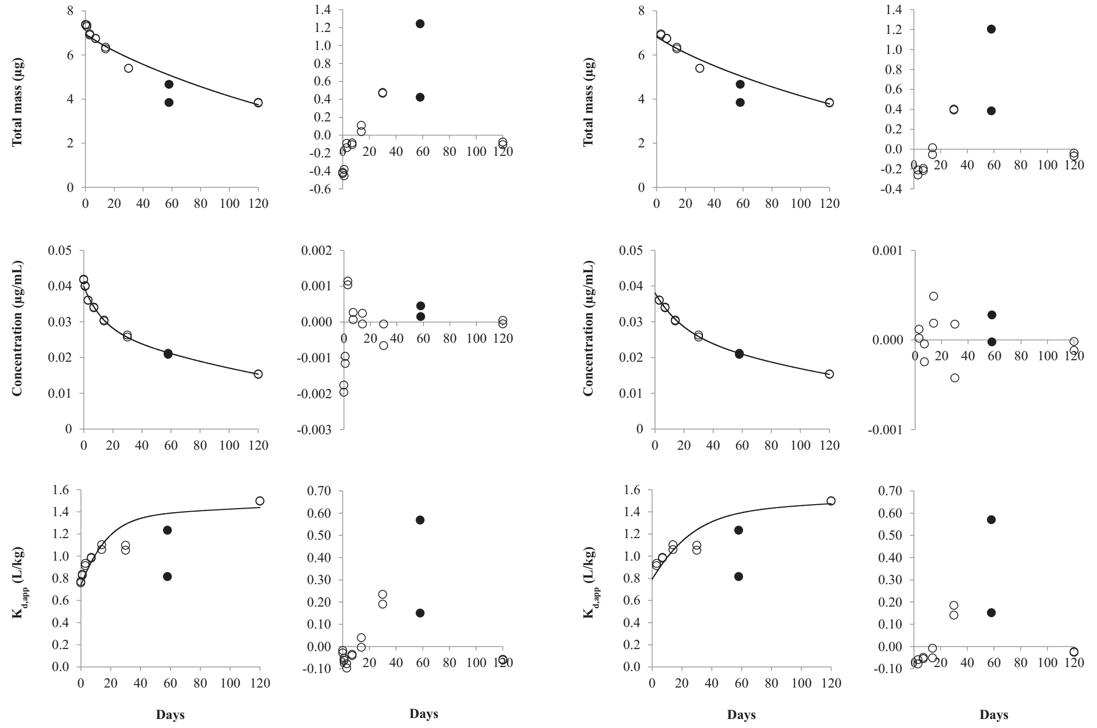
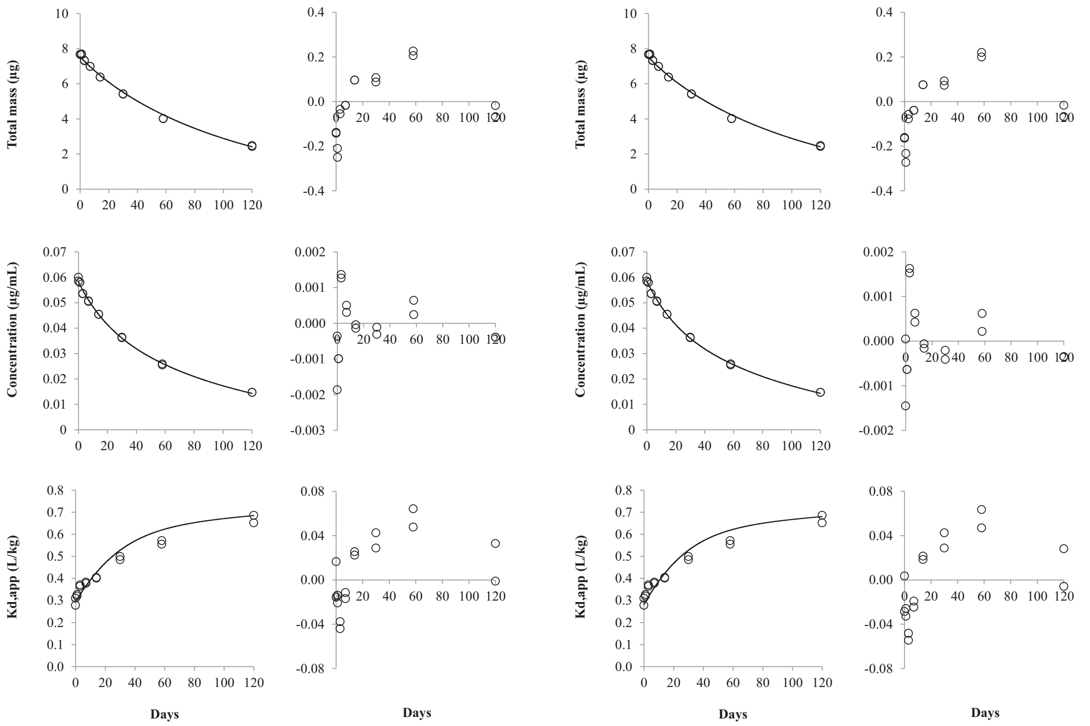


Figure A.2: Aged sorption fitting results for soil E (without and with refinement options), black circle indicates outlier. (A) First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0. (B) Refinement – free fitting of $K_{om,eq}$. (C) Refinement – omitting first sampling point and free fitting of $K_{om,eq}$. (D) Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

A First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0

B Refinement – free fitting of $K_{om,eq}$



C Refinement – omitting first sampling point and free fitting of $K_{om,eq}$

D Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

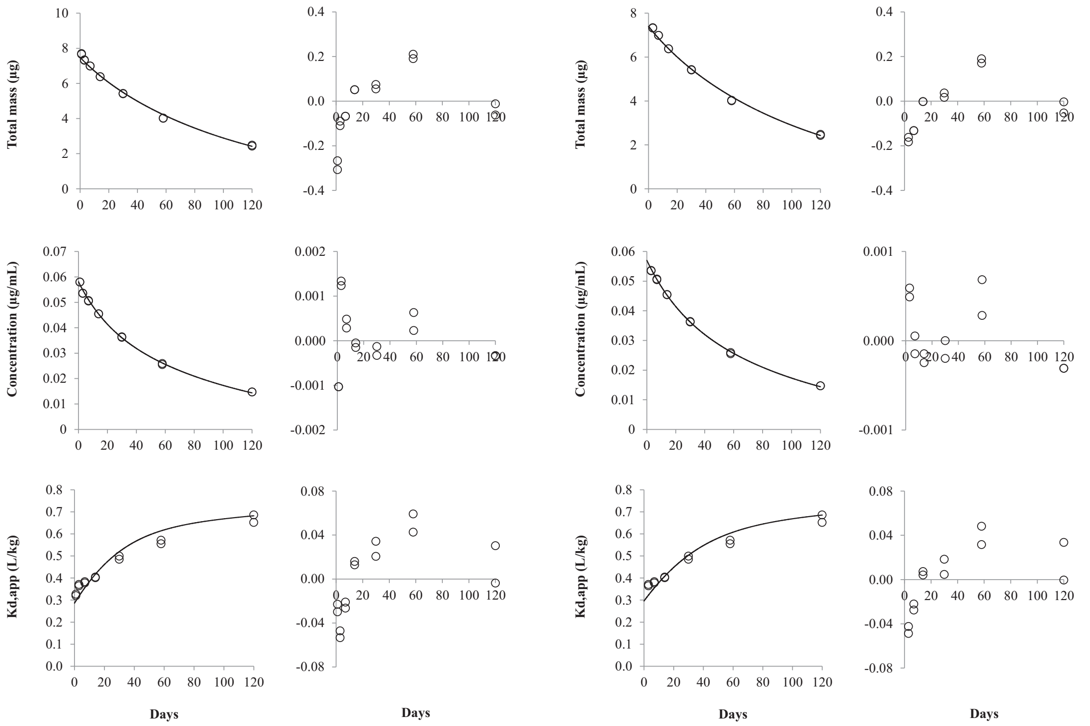
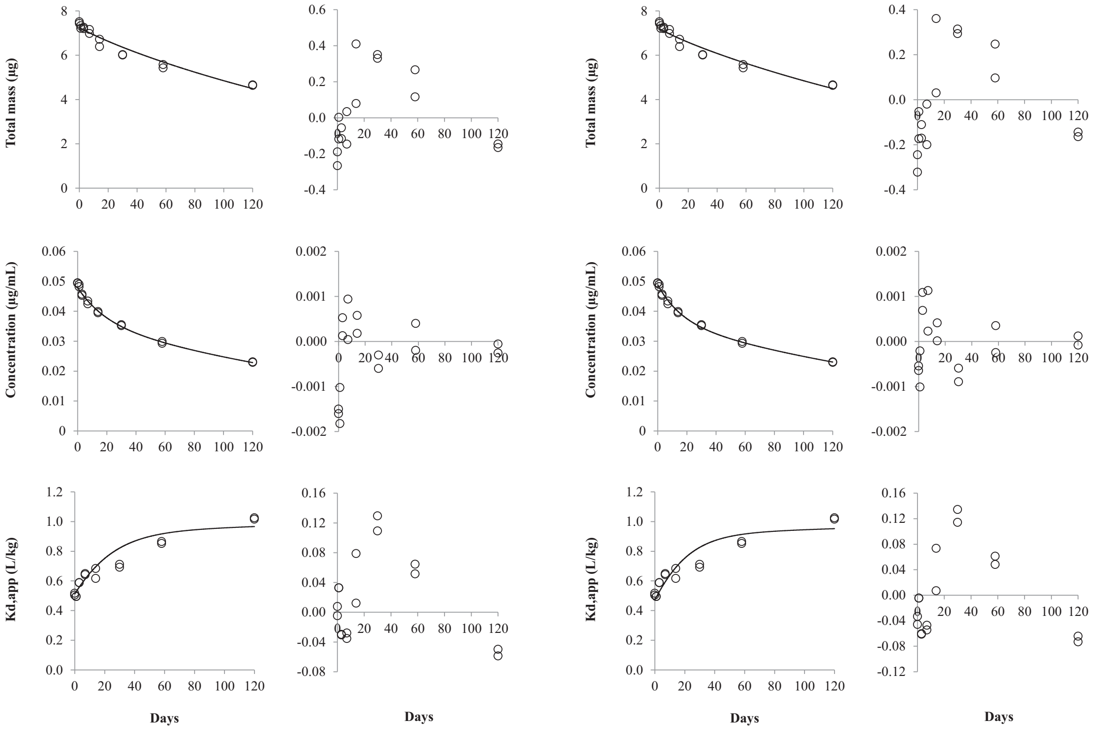


Figure A.3: Aged sorption fitting results for soil F (without and with refinement options). (A) First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0. (B) Refinement – free fitting of $K_{om,eq}$. (C) Refinement – omitting first sampling point and free fitting of $K_{om,eq}$. (D) Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

A First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0

B Refinement – free fitting of $K_{om,eq}$



C Refinement – omitting first sampling point and free fitting of $K_{om,eq}$

D Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

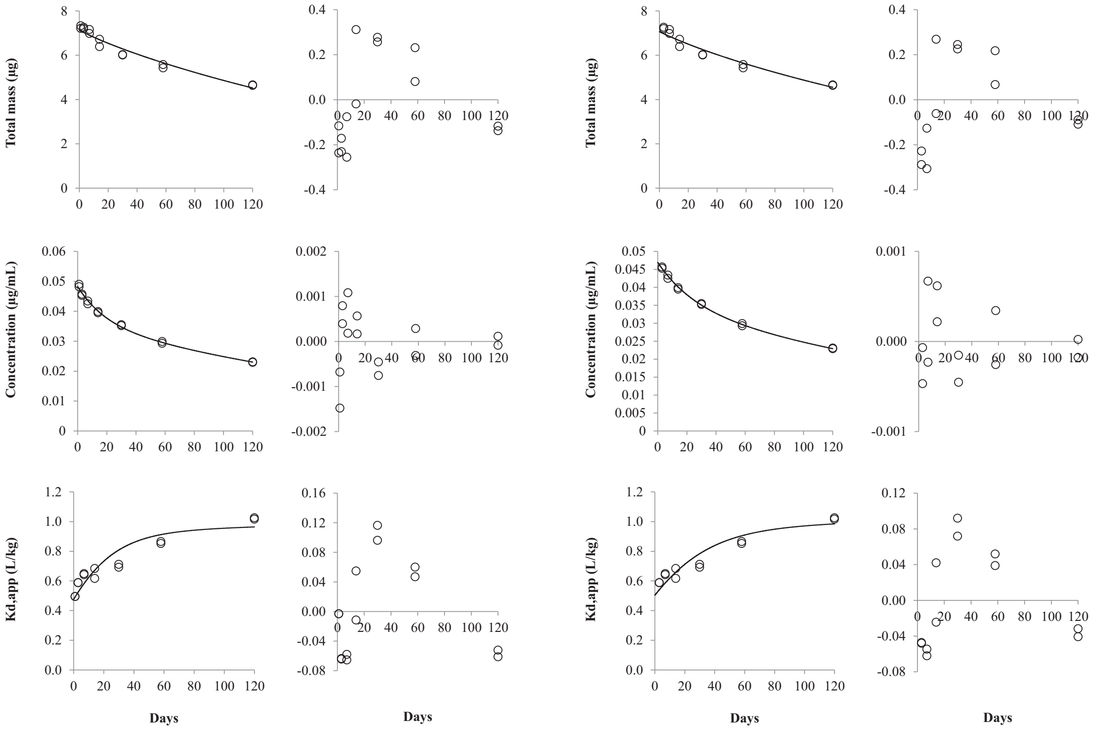


Figure A.4: Aged sorption fitting results for soil G (without and with refinement options). (A) First step – $K_{om,eq}$ fixed to $K_{om,eq}$ at t_0. (B) Refinement – free fitting of $K_{om,eq}$. (C) Refinement – omitting first sampling point and free fitting of $K_{om,eq}$. (D) Refinement – omitting first and second sampling point and free fitting of $K_{om,eq}$

It may be noted that in the case of pesticide ECPA-01, aged sorption fits obtained (with and without refinement) are always characterised by a systematic overestimation of the $K_{d,app}$ at earlier sampling time points (approximately up to 70–80 days), followed by an underestimation of the $K_{d,app}$ at the very latest sampling time point (120 days). Indeed, measured $K_{d,app}$ values indicate that sorption is likely to further increase beyond the study duration. It is also noted that the aged sorption fits do not always mirror the total mass in soil in an accurate way. Particularly, in soil E, the total mass of pesticide ECPA-01 is significantly underestimated at later sampling time points. This indicates that the aged sorption model is not fully capable of describing the experimental results. The fitting results obtained may be considered conservative with respect to leaching as aged sorption is likely to be underestimated on the basis of the aged sorption results obtained.

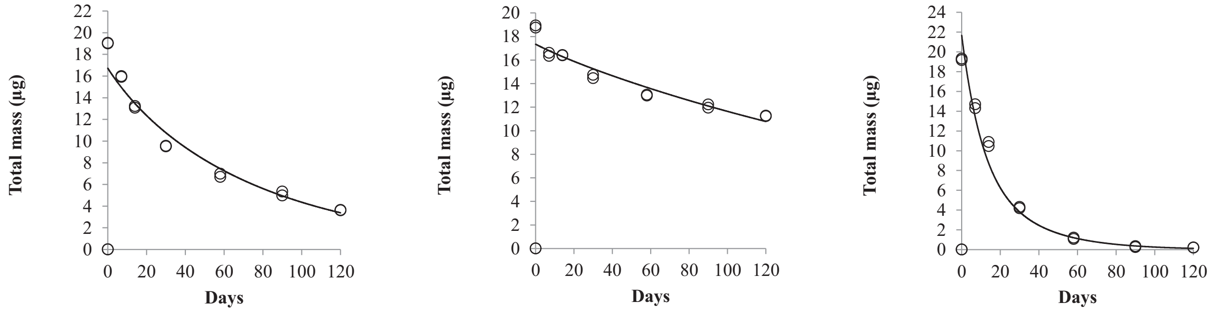
A.3. Combination of degradation and adsorption data from Tier 1 and aged sorption studies

The final step combines the results on lower-tier degradation and sorption with those of aged sorption studies. This step involves the transformation of lower-tier DegT50 (based on total mass), available for soils A, B and C, into DegT50_{EQ}. The draft guidance document gives three options for performing this transformation. Table A.13 summarises the calculation of DegT50_{EQ} values from lower-tier DegT50 values for soils without $CaCl_2$ extraction using the three methods. Figure A.5 shows the corresponding fits (refit approach only).

Table A.13: Estimation of DegT50_{EQ} values from lower-tier DegT50 values

Soil	Study moisture content (mL/g)	f_{OM} (–)	$K_{om,eq}$ (mL/g)	1/n (–)	f_{NE} (–)	k_{des} (days^{-1})	DegT50 (days)	Calculated DegT50_{EQ} (days)		
								Scaling factor 1	Scaling factor 2	Refit of residue data
A	0.257	0.019	9.3[(a)]	0.91[(a)]	0.50[(b)]	0.053[(b)]	80.4	73.5	64.3	42.1
B	0.314	0.024					265	241	212	146
C	0.352	0.038					14.9	13.1	11.9	9.6

(a): No soil-specific data available, geometric $K_{om,eq}$ and arithmetic mean 1/n from entire data set used.
(b): Geometric mean from aged sorption studies.



Soil A **Soil B** **Soil C**

Figure A.5: Refit of the residue data (total mass) of lower-tier degradation studies (soil A, B and C) without $CaCl_2$ extraction applying PEARLNEQ (f_{NE} = 0.5, k_{des} = 0.053 days^{-1})

The Panel recommends that a refit of the aged sorption model to the original residue data (total mass only) is always the preferred option for the conversion of lower-tier degradation endpoints. Since all necessary information for a refit on residue data is available in the case of ECPA-01, refitted DegT50_{EQ} values of 42.1, 146 and 9.6 days are used for soils A, B and C, respectively.

In the next step, the results on lower-tier degradation and adsorption and those of aged sorption studies are combined (Table A.14).

Table A.14: Summary on degradation and adsorption results obtained in lower-tier and aged sorption studies for pesticide ECPA-01 (soils used for aged sorption studies are shaded in grey)

Soil	DegT50 at pF2, 20°C (days) Lower tier (no TDS)	$DegT50_{EQ}$ at pF2, 20°C (days) Higher tier (TDS)	$K_{om,eq}$ (mL/g) Lower tier (batch study)	1/n (–) Lower tier (batch study)	k_{des} ($days^{-1}$) Higher tier (TDS)	f_{NE} (–) Higher tier (TDS)
A	80.4	$42.1^{(a)}$	–	–	–	–
B	265	$146^{(a)}$	–	–	–	–
C	14.9	$9.6^{(a)}$	–	–	–	–
D	150	79.5	5.9	0.91	0.050	0.58
E	241	99.7	11.1	0.90	0.078	0.49
F	97.7	60.7	–	–	0.043	0.44
G	281	143	–	–	0.048	0.52
H	–	–	7.3	0.94	–	–
I	–	–	27.7	0.86	–	–
J	–	–	21.5	0.86	–	–
K	–	–	8.4	0.93	–	–
L	–	–	4.2	0.95	–	–
M	–	–	22.2	0.91	–	–
N	–	–	2.4	0.95	–	–
Geometric mean	118	63.3	9.3	–	0.053	0.50
Arithmetic mean	–	–	–	0.91	–	–

TDS: time-dependent sorption.
(a): Calculated from DegT50 in line with the draft guidance document using the PEARLNEQ refit approach (option 3 in the draft guidance document).

Combining data from lower-tier degradation and adsorption experiments, as well as from aged sorption experiments, the following aged sorption modelling endpoints were obtained: $DegT50_{EQ}$ = 63.3 days, $K_{om,eq}$ = 9.3 mL/g, 1/n = 0.91, k_{des} = 0.053 $days^{-1}$ and f_{NE} = 0.50.

A.4. Effect of including aged sorption in the leaching assessment

This section gives an impression on the impact of implementing data from higher-tier aged sorption experiments in the case of pesticide ECPA-01. Table A.15 gives substance properties regarding degradation and soil sorption (without and with aged sorption) for pesticide ECPA-01 assuming: (i) all experiments as lower-tier data, (ii) only results from higher-tier aged sorption experiments and (iii) combining both lower-tier degradation and sorption data with higher-tier data from TDS experiments. No volatilisation and no plant uptake were assumed in these example calculations.

Table A.15: Substance properties of pesticide ECPA-01 in different assessment approaches

Assessment approach	$DegT50_{EQ}$ (days)	$K_{om,eq}$ (mL/g)	1/n (–)	f_{NE} (–)	k_{des} ($days^{-1}$)
Tier 1	118	9.3	0.91	0.00	0.000
Aged sorption	91.1	5.6	0.91	0.50	0.053
Tier 1 and aged sorption	63.3	9.3	0.91	0.50	0.053

Example calculations on PEC groundwater were provided for the FOCUS groundwater scenarios applying FOCUS PEARL 4.4.4 and FOCUS PELMO 5.5.3, assuming winter and spring cereals and one single application one day before emergence. As sorption of pesticide ECPA-01 is rather low and degradation is quite slow, the application rate was limited to 10 g/ha (note that the actual intended use rate for ECPA-01 is unknown to the Panel).

Table A.16: Predicted concentration (μg/L) of pesticide ECPA-01 in the FOCUS groundwater scenario Hamburg based on different assessment approaches applying FOCUS PEARL 4.4.4 and FOCUS PELMO 5.5.3 (application rate of 10 g/ha one day before emergence)

FOCUS crop	Scenario	PEARL 4.4.4			PELMO 5.5.3		
		Lower tier	TDS only	Lower tier and TDS	Lower tier	TDS only	Lower tier and TDS
Winter cereals	Châteaudun	2.01	1.90	0.83	1.80	1.67	0.76
	Hamburg	2.60	2.71	1.48	2.52	2.49	1.50
	Jokioinen	3.27	3.66	1.39	2.42	2.66	1.34
	Kremsmünster	1.64	1.61	0.87	1.70	1.63	0.91
	Okehampton	1.58	1.54	1.00	1.46	1.43	0.98
	Piacenza	1.50	1.35	0.70	1.69	1.60	0.78
	Porto	1.30	1.24	0.78	1.15	1.12	0.70
	Sevilla	0.62	0.61	0.11	0.70	0.60	0.19
	Thiva	2.40	2.13	0.77	1.64	1.48	0.53
Spring cereals	Châteaudun	1.36	1.29	0.49	1.05	0.99	0.40
	Hamburg	2.78	2.84	1.31	1.80	1.82	0.93
	Jokioinen	2.05	2.28	0.93	1.52	1.58	0.77
	Kremsmünster	1.55	1.52	0.81	1.51	1.44	0.76
	Okehampton	1.32	1.32	0.75	1.15	1.16	0.69
	Porto	0.83	0.78	0.39	0.64	0.63	0.36

TDS: time-dependent sorption.

As can be deduced from Table A.16, ECPA-01 is a strongly leaching pesticide and the impact of aged sorption as a higher-tier assessment is quite limited due to the low $K_{om,eq}$ of this pesticide. Obviously, the increase in sorption over time hardly compensates for the overall slow degradation rate of pesticide ECPA-01 in soil.

Appendix B – Detailed description of case ECPA-06

Pesticide ECPA-06 is a rather stable compound with moderate sorption. An independent data set with four soils was available from peer-reviewed literature, including a forest soil (non-agricultural use). Strictly speaking, the independent data set does not fulfil the requirement of at least four agricultural soils showing aged sorption behaviour. Nevertheless, this data set was included in the analysis to test the procedure when two data sets are available with different extraction procedures.

B.1. Tier 1 assessment (without aged sorption)

B.1.1. Degradation (total mass)

Data set ECPA-06 contains six laboratory degradation studies (soil 6A–6F) conducted in line with OECD Guideline 307 (OECD, 2002). An additional $CaCl_2$ extraction step was performed on four soils. Thus, these four experiments are considered to also represent aged sorption studies in line with the draft guidance on aged sorption.

The independent data set contains four laboratory degradation studies (soils G1–G4) conducted in line with OECD 307, all of them with an additional $CaCl_2$ extraction step. Table B.1 gives a short overview of the main soil characteristics and Table B.2 gives study and reference moisture and study temperature necessary to allow normalisation of degradation rates obtained.

Table B.1: Main characteristics of soils used for degradation and aged sorption experiments (soils used for aged sorption experiments are shaded in grey)

Soil	TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)
6A	Yes	Sandy loam	10	71.4	2.19	6.4
6B	Yes	Loam	16	46.8	1.93	6.6
6C	Yes	Loam	16.1	47.8	2.65	5.4
6D	Yes	Silty loam	17	8.8	3.1	6.7
6E	No	Silty loam	26.9	11.5	3.0	6.5
6F	No	Sandy loam	1.9	51.5	1.0	7.7
G1	Yes	Clay loam	30	40	4.3	6.9
G2	Yes	Sandy loam	19	70	6.4	5.3
G3	Yes	Clay loam	36	40	12.9	7.2
G4	Yes	Sandy loam	17	62	18.4	3.6

OM: organic matter; TDS: time-dependent sorption; USDA: US Department of Agriculture.

Table B.2: Study and reference moisture and temperature of soils used for degradation and aged sorption experiments (soils used for aged sorption experiments are shaded in grey)

Soil	TDS study	Study soil moisture (g/100 g)	Reference soil moisture (pF2)[(a)] (g/100 g)	Soil moisture correction (–)	Study soil temperature (°C)	Reference temperature (°C)	Temperature correction (–)
6A	Yes	25.1	19[(a)]	1.0	20	20	1.0
6B	Yes	28.6	25[(a)]	1.0	20	20	1.0
6C	Yes	31.6	25[(a)]	1.0	20	20	1.0
6D	Yes	36.9	26[(a)]	1.0	20	20	1.0
6E	No	18.6	31.6	0.69	25	20	1.61
6F	No	11.3	34.6	0.46	25	20	1.61
G1	Yes	31.6	28[(a)]	1.0	20	20	1.0
G2	Yes	40.5	19[(a)]	1.0	20	20	1.0
G3	Yes	39.2	28[(a)]	1.0	20	20	1.0
G4	Yes	62.2	19[(a)]	1.0	20	20	1.0

TDS: time-dependent sorption.
(a): FOCUS default values based on soil texture.

Table B.3 gives the degradation results obtained from fitting the total extractable mass to best fit kinetics in line with FOCUS (2006) guidance. Degradation rates of the ECPA-06 soils rely on an EFSA conclusion. For the independent data set G1–G4, degradation rates were recalculated on the basis of total mass extracted in line with pertinent guidance (FOCUS, 2006) using the software tool CAKE 3.3.

Table B.3: Degradation kinetics of pesticide ECPA-06 in degradation and aged sorption experiments based on total extractable mass applying CAKE 3.3 (data from aged sorption experiments are shaded in grey)

Soil	TDS study	Kinetics	DegT50 (days)	DegT90 (days)	DFOP-k_1 DegT50 (days)	DFOP-k_2 DegT50 (days)	g (–)	χ^2-error (%)	DegT50 at reference conditions (pF2, 20°C) (days)
6A	Yes	SFO	162	538	–	–	–	1.8	162
6B	Yes	SFO	128	425	–	–	–	1.6	128
6C	Yes	SFO	239	794	–	–	–	2.4	239
6D	Yes	SFO	115	382	–	–	–	1.9	115
6E	No	SFO	252(a)	837	–	–	–	5.5/3.2(b)	279(a)
6F	No	SFO	433(a)	1,437	–	–	–	1.6/1.7(b)	318(a)
G1	Yes	DFOP	90.9	369	3.79	120	0.15	2.5	120(c)
G2	Yes	SFO	384	1,276	–	–	–	2.9	384
G3	Yes	SFO	445	1,478	–	–	–	2.6	445
G4	Yes	SFO	556	1,847	–	–	–	2.9	556
Geometric mean									**238**

DFOP: double first-order in parallel; SFO: single first-order; TDS: time-dependent sorption.
(a): Geometric mean of the DegT50 obtained from degradation studies with phenyl- and pyrazol-labelled active compound.
(b): χ^2-error for the individual fits to the phenyl- and pyrazol-labelled active compound.
(c): DFOP slow phase (k_2).

With the exception of soil G1, best-fit degradation was obtained by SFO kinetics. Following the recommendations of FOCUS (2006), the slow DFOP degradation rate (k_2) was selected as a conservative DegT50 modelling endpoint for soil G1. Without considering aged sorption, the modelling DegT50 endpoint of pesticide ECPA-06 based on the 10 laboratory degradation studies (handling the aged sorption studies as lower-tier studies as well) is 238 days.

B.1.2. Adsorption (batch studies)

Nine batch adsorption experiments in line with OECD Guideline 106 (OECD, 2000) are available for pesticide ECPA-06. The main soil characteristics as well as measured Freundlich adsorption parameters ($K_{om,eq}$ and 1/n) are given in Table B.4. Three of these soils (soils 6A, 6C and 6D) are considered to be identical to three of the four ECPA soils used for the aged sorption experiments.

The geometric mean $K_{om,eq}$ of the entire set of these nine soils is 138.5 L/kg with an arithmetic mean 1/n of 0.882.

Table B.4: Main characteristics of soils used for Freundlich adsorption experiments and obtained Freundlich adsorption parameters (soils used for aged sorption fitting are shaded in grey)

Soil	Applicable to TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)	$K_{f,eq}$ (L/kg)	$K_{om,eq}$ (mL/g)	1/n
6A	Yes	Sandy loam	10	69	2.9	6.1	4.93	168	0.895
6C	Yes	Loam	18	47	2.1	5.3	2.71	131	0.974
6D	Yes	Silt loam	18	19	4.0	6.3	4.82	122	0.908
6G	No	Loamy sand	5	76	2.2	5.2	5.32	238	0.948
6H	No	Clay loam	31	37	4.0	5.9	6.10	154	0.875
G1	Yes	Clay loam	30	40	4.3	6.9	3.07	71	0.799
G2	Yes	Sandy loam	19	70	6.4	5.3	7.66	120	0.838

Soil	Applicable to TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)	$K_{f,eq}$ (L/kg)	$K_{om,eq}$ (mL/g)	1/n
G3	Yes	Clay loam	36	40	12.9	7.2	15.7	122	0.858
G4	Yes	Sandy loam	17	62	18.4	3.6	33.6	183	0.845
Geometric mean								**138**	–
Arithmetic mean								–	**0.882**

OM: organic matter; TDS: time-dependent sorption; USDA: US Department of Agriculture.

B.2. Time-dependent sorption studies

As mentioned above, eight of the 10 soil laboratory degradation studies available are considered to represent aged sorption studies in line with the draft guidance on aged sorption (additional $CaCl_2$ extraction step). Additional information on the experimental setup necessary to derive aged sorption parameters according to the draft guidance is given for the four ECPA soils in Table B.5 and for the four soils of the independent data set in Table B.6.

Table B.5: Experimental setup of the four aged sorption experiments with ECPA soils

Parameter[(a)]	Description	Soil 6A	Soil 6B	Soil 6C	Soil 6D
TimStart (days)	Start time	0	0	0	0
TimEnd (days)	End time	120	120	120	120
MasIni (μg)	Initial guess of total mass	68.4	64.7	69.8	67.0
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Volume of liquid in moist soil	25.1	28.6	31.6	36.9
VolLiqAdd (mL)	Volume of liquid added	400	400	400	400

(a): Parameter naming according to PEARLNEQ.

Table B.6: Experimental setup of the four aged sorption experiments with soils from an independent data set

Parameter[(a)]	Description	Soil G1	Soil G2	Soil G3	Soil G4
TimStart (days)	Start time	0	0	0	0
TimEnd (days)	End time	170	170	170	170
MasIni (μg)	Initial guess of total mass	1.2	1.2	1.2	1.2
MasSol (g)	Dry mass of soil	4.56	4.27	4.31	3.70
VolLiqSol (mL)	Volume of liquid in moist soil	1.44	1.73	1.69	2.30
VolLiqAdd (mL)	Volume of liquid added	30	30	30	30

(a): Parameter naming according to PEARLNEQ.

B.2.1. Checking of quality criteria

Soil selection

As can be seen in Table B.1, the four ECPA soils used for the aged sorption experiments (soils 6A to 6D) are quite similar regarding clay content and cover only a small pH range (5.4–6.7). To assess the possibility for pH-dependent sorption it would be essential to cover a wider pH range.

The soils in the independent data set cover a much larger range in organic matter content and pH. Note that this data set includes a forest soil (non-agricultural use).

Data requirements

All aged sorption experiments with pesticide ECPA-06 were conducted before the draft guidance document was available and can be considered as legacy studies with less stringent requirements, such as the use of averaged Freundlich 1/n values when no soil-specific adsorption data are available. The data set for ECPA-06 with the ECPA soils consists of eight sampling time points, and soil-specific 1/n values are available for three of the soils. The independent data set fully complies with the draft guidance, including soil-specific adsorption data and 12 sampling time points. Both data sets fulfil the quality criteria mentioned in the draft guidance document.

Extraction procedure

The ECPA soils (6A–6D) were extracted three times with acetonitrile/water (80/20 v/v) at ambient temperature followed by one extraction with acetonitrile/water (80/20 v/v) at elevated temperature (~75°C). An additional $CaCl_2$ extraction step was performed on four soils. The soils in the independent data set (G1 to G1) were extracted twice with methanol at elevated temperature (80°C) and pressure (100 bar).

The Panel recommends that aged sorption experiments are merged into the same set of soils, if the same extraction procedure has been employed. Since different extraction procedures were used for the substance, the studies with the ECPA soils and the soils of the independent data set have to be considered as different data sets and therefore require separate analysis.

Handling of outliers

As can be deduced from the fitting results (see Figure B.1), total mass in all ECPA soils is likely to comprise an outlier at the 14-day sampling time interval (both replicate measurements). The concentration in the liquid phase was not affected. In the analysis below, the outlier was not removed. Note that the removal of outliers (data on both total mass and concentration in the liquid phase needs to be eliminated) is only justified by a (significant) improvement of the goodness of fit criteria and of the acceptability criterion of the fitted parameters. In that case the draft guidance requires that results for the fits with and without outliers are reported.

B.2.2. Data fitting (aged sorption model vs equilibrium sorption model)

The fitting procedure starts with fitting the total mass and the concentration in the liquid phase ($CaCl_2$ extract) of each soil to either the aged sorption or the equilibrium sorption model. Soil-specific 1/n values from OECD Guideline 106 batch experiments (OECD, 2000) were assigned as fixed parameters to each soil, with the exception of ECPA soil 6B (no soil-specific adsorption data available). In the case of soil 6B, the 1/n was set to the arithmetic mean 1/n of all soils (1/n = 0.882).

Different starting values for f_{NE} and k_{des} in the fitting procedure did not affect the values of the optimised parameters, indicating that the global minimum was most likely found. The initial guess of $DegT50_{EQ}$ was set to the DegT50 obtained from fitting the total mass (Table B.3). Tables B.7 and B.8 give an overview of the initial guess of aged sorption parameters set.

Table B.7: Initial guess on aged sorption parameters for the fitting procedure of the ECPA data set

Parameter[(a)]	Description	Soil 6A	Soil 6B	Soil 6C	Soil 6D
ExpFre (–)	Freundlich exponent (1/n)	0.895	0.882[(b)]	0.974	0.908
KomEql (mL/g)[(c)]	Sorption coefficient ($K_{om,eq}$)	181.3	153.5	216.1	173.6
$DT50_{EQ}$ (days)	Initial guess of $DegT50_{EQ}$	162	128	239	115
FacSorNeqEql (–)	Initial guess of f_{NE}	0.2	0.2	0.2	0.2
CofRatDes ($days^{-1}$)	Initial guess of k_{des}	0.004	0.004	0.004	0.004

(a): Parameter naming according to PEARLNEQ 5.1.
(b): Arithmetic mean 1/n value of OECD 106 batch sorption studies for all soils.
(c): Arithmetic average of the replicate measurements of $K_{om,eq}$ at time t = 0.

Table B.8: Initial guess on aged sorption parameters for the fitting procedure of the independent data set

Parameter[(a)]	Description	Soil G1	Soil G2	Soil G3	Soil G4
ExpFre (–)	Freundlich exponent (1/n)	0.799	0.838	0.858	0.845
KomEql (mL/g)[(c)]	Sorption coefficient ($K_{om,eq}$)	57.3	131.1	108.5	137.7
$DT50_{EQ}$ (days)	Initial guess of $DegT50_{EQ}$	120[(b)]	384	445	556
FacSorNeqEql (–)	Initial guess of f_{NE}	1.5	1.5	1.5	1.5
CofRatDes ($days^{-1}$)	Initial guess of k_{des}	0.004	0.004	0.004	0.004

(a): Parameter naming according to PEARLNEQ 5.1.
(b): DFOP slow phase DegT50.
(c): Arithmetic average of the replicate measurements of $K_{om,eq}$ at time t = 0.

Table B.9 summarises the best estimates of the aged sorption parameters for the ECPA soils and Table B.10 shows the statistics of the optimisation; the fits obtained are given in Figure B.1.

Table B.9: Aged sorption parameters obtained for the four ECPA soils applying PEARLNEQ 5 (soils used for aged sorption studies are shaded in grey)

Soil	$DT50_{EQ}$ (days)	k_{des} ($days^{-1}$)	f_{NE} (–)	$K_{om,eq}$ (mL/g)	$1/n^{(a)}$ (–)	$DegT50_{EQ}$ (days) at reference conditions (pF2, 20°C)
6A	108	0.0394	0.706	199	0.895	108
6B	91.4	0.0253	0.576	161	0.882	91.4
6C	176	0.0456	0.598	224	0.974	176
6D	78.7	0.0278	0.668	185	0.908	78.7
Geometric mean		0.0335	0.635	191		108
Arithmetic mean					0.915	

(a): Not fitted, fixed to value from batch adsorption experiment.

Table B.10: Parameter acceptability (relative standard error), goodness of fit (χ^2-error) and evidence for aged sorption for the aged sorption fits obtained for the four ECPA soils applying PEARLNEQ 5 (soils used for aged sorption studies are shaded in grey)

Soil	Relative standard errors (–)				χ^2-error (%)			Criteria
	$DT50_{EQ}$ (days)	k_{des} ($days^{-1}$)	f_{NE} (–)	$K_{om,eq}$ (mL/g)	Mass/conc NEQ	$K_{D,app}$ NEQ	$K_{D,app}$ NEQ	
6A	0.035	0.092	0.052	0.024	1.79	3.43	26.5	Pass
6B	0.044	0.180	0.105	0.042	2.91	4.19	27.6	Pass
6C	0.083	0.169	0.090	0.037	2.88	4.00	21.3	Pass
6D	0.037	0.140	0.080	0.031	2.89	3.08	26.3	Pass

Conc: concentration; NEQ: non-equilibrium.

Considering only the four dedicated aged sorption studies, the modelling endpoints of pesticide ECPA-06 to be used in the exposure assessment are: $DegT50_{EQ} = 108$ days, $K_{om,eq} = 191$ mL/g, $1/n = 0.915$, $k_{des} = 0.0335$ $days^{-1}$ and $f_{NE} = 0.635$.

Table B.11 summarises the best estimates of the aged sorption parameters for the soils of the independent data set and Table B.12 shows the statistics of the optimisation; the fits obtained are given in Figure B.1.

Table B.11: Aged sorption parameters obtained for the four soils of the independent data set applying PEARLNEQ (soils used for aged sorption studies are shaded in grey)

Soil	$DT50_{EQ}$ (days)	k_{des} ($days^{-1}$)	f_{NE} (–)	$K_{om,eq}$ (mL/g)	$1/n^{(a)}$ (–)	$DegT50_{EQ}$ (days) at reference conditions (pF2, 20°C)
G1	67.1	0.0114	0.762	50.9	0.799	67.1
G2	207	0.0327	0.654	122.2	0.838	207
G3	236	0.0339	1.085	96.9	0.858	236
G4	281	0.0216	1.342	137.0	0.845	281
Geometric mean		0.0229	0.923	95.3		174
Arithmetic mean					0.835	

(a): Not fitted, fixed to value from batch adsorption experiment.

Table B.12: Parameter acceptability (relative standard error), goodness of fit (χ^2-error) and evidence for aged sorption for the aged sorption fits obtained for the four ECPA soils applying PEARLNEQ 5 (soils used for aged sorption studies are shaded in grey)

Soil	Relative standard errors(–)				χ^2-error (%)			Criteria
	$DT50_{EQ}$ (days)	k_{des} (days^{-1})	f_{NE} (–)	$K_{om,eq}$ (mL/g)	Mass/conc NEQ	$K_{D,app}$ NEQ	$K_{D,app}$ NEQ	
G1	0.034	0.157	0.108	0.065	4.27	11.2	38.2	Pass
G2	0.089	0.158	0.095	0.042	4.02	6.28	22.3	Pass
G3	0.098	0.081	0.055	0.030	3.07	4.16	24.3	Pass
G4	0.126	0.071	0.052	0.024	2.61	3.84	28.4	Pass

Conc: concentration; NEQ: non-equilibrium.

Considering only the four dedicated independent aged sorption studies, the modelling endpoints of pesticide to be used in the exposure assessment are: $DegT50_{EQ} = 174.3$ days, $K_{om,eq} = 95.3$ mL/g, $1/n = 0.835$, $k_{des} = 0.0229$ days^{-1} and $f_{NE} = 0.923$.

Following the draft guidance document, the fits of all soils meet the reliability criteria (relative standard deviation for each of the fitted parameters is ≤ 0.4 and the χ^2-error (mass and concentration) is $< 15\%$) and there is clear evidence for time-dependent sorption on the basis of the non-equilibrium and equilibrium fits (on the basis of the χ^2-error for $k_{d,app}$). The optimised aged sorption parameters can be used for the exposure assessment.

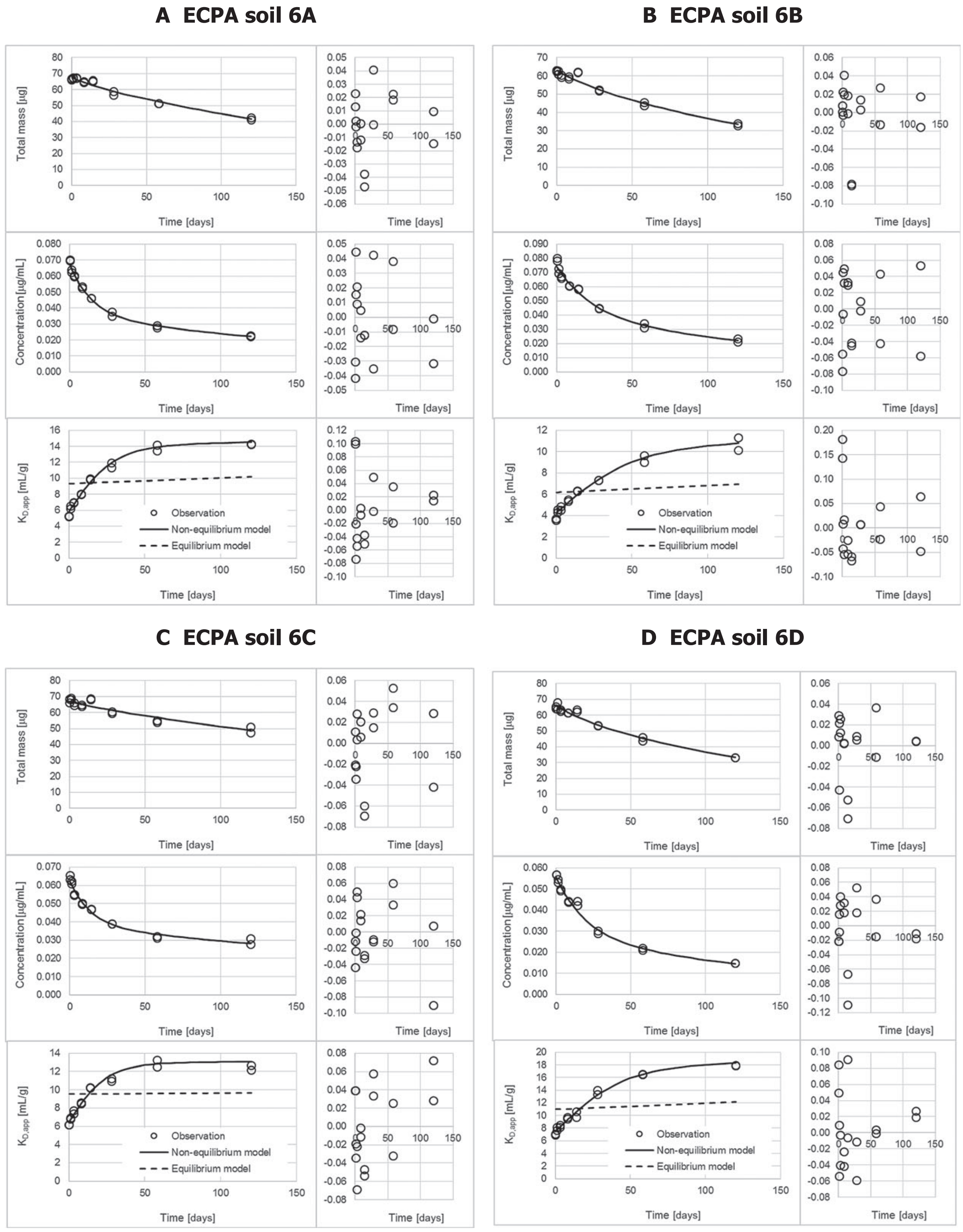


Figure B.1: Aged sorption fitting results for the ECPA soils (free fitting of $K_{om,eq}$). (A) ECPA soil 6A. (B) ECPA soil 6B. (C) ECPA soil 6C. D) ECPA soil 6D

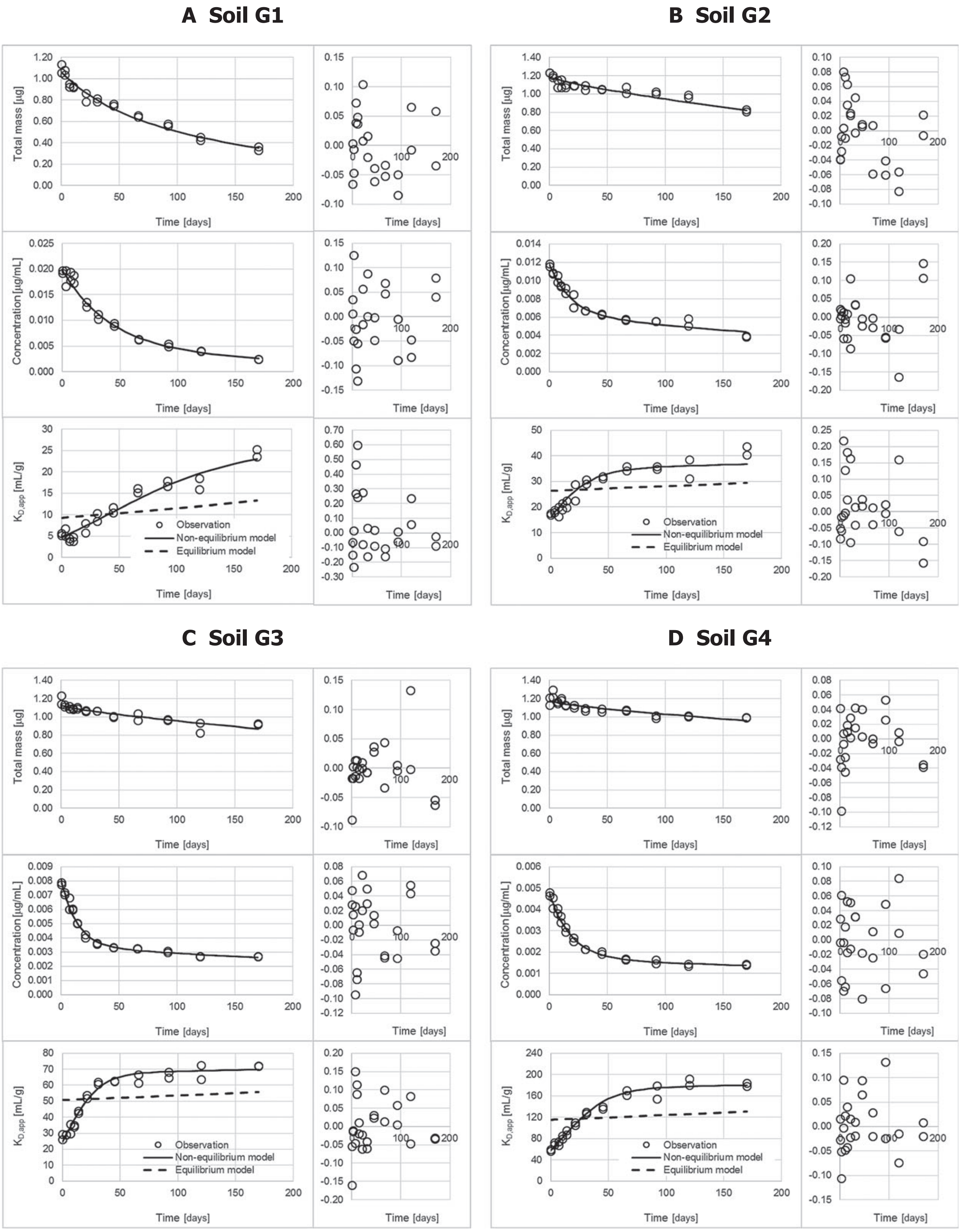


Figure B.2: Aged sorption fitting results for the soils from the independent data set (free fitting of $K_{om,eq}$). (A) Soil G1. (B) Soil G2. (C) Soil G3. (D) Soil G4

B.2.3. Data fitting: Refinement

In the case of insufficient fits for long-time behaviour at the first step, the draft guidance permits a stepwise refinement, i.e. also fitting the $K_{om,eq}$ and/or omitting early sampling points < 2 days. The Panel is not in favour of any refinement options for the inverse optimisation, since this may lead to additional discussions and expert judgement decisions in the absence of clear recommendations. In the Opinion, the Panel now recommends the use of $K_{om,eq}$ as the fitting parameter. The Panel also recommends that sampling points < 2 days are only omitted when these data points fulfil the requirements of outliers. This does not apply to this example evaluation.

B.3. Combination of degradation and sorption data from Tier 1 (without aged sorption) and aged sorption studies

The combination of degradation and sorption data from lower-tier (without aged sorption) and higher-tier (aged sorption) studies requires the transformation of lower-tier DegT50 into $DegT50_{EQ}$ values. The draft guidance document gives three options for performing this transformation (see Section 3.3.5). Table B.13 summarises the calculation of $DegT50_{EQ}$ values from lower-tier DegT50 values for soils without $CaCl_2$ extraction using the three methods. Figure A.3 shows the corresponding fit.

Table B.13: Estimation of $DegT50_{EQ}$ values from lower-tier DegT50 values

Soil	Study moisture content (mL/g)	f_{OM} (–)	Batch $K_{F,OM}$ (L/kg)	1/n (–)	f_{NE} (–)	k_{des} ($days^{-1}$)	DegT50 (days)	Calculated $DegT50_{EQ}$ (days)		
								Refit of residue data	Scaling factor 1	Scaling factor 2
6E	0.193	0.030	138 [(a)]	0.882[(a)]	0.727[(b)]	0.0277[(b)]	278.8	147	163	174
6F	0.116	0.010					317.5	259	188	198

(a): No soil-specific isotherms were measured. Geomean for $K_{F,OM}$ and arithmetic mean for 1/n of all soils were used.
(b): Geometric mean from all eight aged sorption studies.

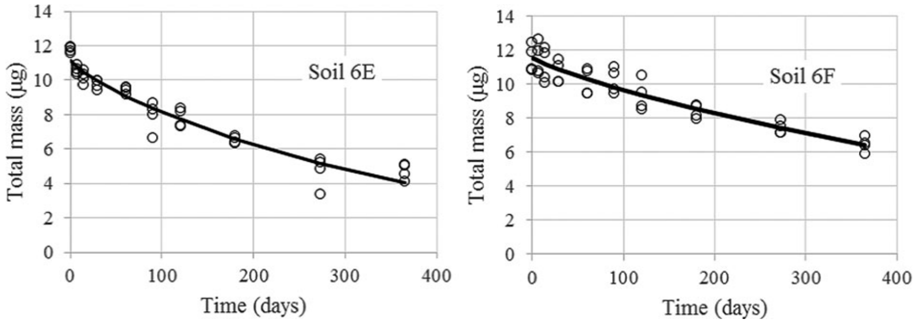


Figure B.3: Refit of the residue data for the degradation studies without $CaCl_2$ extraction

The normalised $DegT50_{EQ}$ values were 163 and 235 days for soils 6E and 6F, respectively, for the refit of the residue data.

The Panel recommends that a refit of the aged sorption model to the original residue data (total mass only) is always the preferred option for the conversion of lower-tier degradation endpoints. Since all necessary information for a refit on residue data is available, $DT50_{EQ}$ values of 146.7 and 259.3 days are used as lower-tier values for soils 6E and 6F, respectively.

In the next step, results on lower-tier degradation and adsorption as well as on aged sorption studies are combined with results of the ECPA soils in Table B.14 and with the results of the independent data set in Table B.15 (independent data set due to different extraction procedure of the aged sorption experiments).

The combination of data obtained from lower-tier degradation and adsorption experiments resulted in the following Tier 1 modelling endpoints and is identical for both aged sorption data sets: DegT50 = 238 days, K_{om} = 138 mL/g and 1/n = 0.882.

The combination of data obtained from lower-tier degradation and adsorption experiments as well as from aged sorption experiments with the ECPA soils resulted in the following aged sorption modelling endpoints: $DegT50_{EQ}$ = 147 days, $K_{om,eq}$ = 138 mL/g, 1/n = 0.882, k_{des} = 0.0335 $days^{-1}$ and f_{NE} = 0.635.

The combination of data obtained from lower-tier degradation and adsorption experiments as well as from aged sorption experiments with the independent data set resulted in the following aged sorption modelling endpoints: $DegT50_{EQ}$ = 147 days, $K_{om,eq}$ = 138 mL/g, 1/n = 0.882, k_{des} = 0.0229 $days^{-1}$ and f_{NE} = 0.923.

Table B.14: Summary on degradation and adsorption results obtained in lower-tier and aged sorption studies of the ECPA soils (soils used for aged sorption studies are shaded)

Soil	DegT50 at pF2, 20°C (days)	$DegT50_{EQ}$ at pF2, 20°C (days)	$K_{om,eq}$ (mL/g)	1/n (–)	k_{des} (days^{-1})	f_{NE} (–)
	Lower tier (no TDS)	**Higher tier (TDS)**	**Lower tier (batch study)**	**Lower and higher tier**	**Higher tier (TDS)**	**Higher tier (TDS)**
6A	162	108	168	0.895	0.0394	0.706
6B	128	91.4	–	–	0.0253	0.576
6C	239	176	131	0.974	0.0456	0.598
6D	115	78.7	122	0.908	0.0278	0.668
6E	279	163(a)	–	–	–	–
6F	318	235(a)	–	–	–	–
6G	–	–	238	0.948	–	–
6H	–	–	154	0.875	–	–
G1	120	67.1(b)	71	0.799	–	–
G2	384	207(b)	120	0.838	–	–
G3	445	236(b)	122	0.858	–	–
G4	556	281(b)	183	0.845	–	–
Geometric mean	238	147	138		0.0335	0.635
Arithmetic mean				0.882		

TDS: time-dependent sorption.
(a): Calculated from DegT50 in line with the draft guidance document using the refit on residue data only.
(b): Values from aged sorption fit.

Table B.15: Summary on degradation and adsorption results obtained in lower-tier and aged sorption studies of the independent data set (soils used for aged sorption studies are shaded in grey)

Soil	DegT50 at pF2, 20°C (days)	$DegT50_{EQ}$ at pF2, 20°C (days)	$K_{om,eq}$ (mL/g)	1/n (–)	k_{des} (days^{-1})	f_{NE} (–)
	Lower tier (no TDS)	**Higher tier (TDS)**	**Lower tier (batch study)**	**Lower and higher tier**	**Higher tier (TDS)**	**Higher tier (TDS)**
6A	162	108(a)	168	0.895	–	–
6B	128	91.4(a)	–	–	–	–
6C	239	176(a)	131	0.974	–	–
6D	115	78.7(a)	122	0.908	–	–
6E	279	163(b)	–	–	–	–
6F	318	235(b)	–	–	–	–
6G	–	–	238	0.948	–	–
6H	–	–	154	0.875	–	–
G1	120	67.1	71	0.799	0.0114	0.762
G2	384	207	120	0.838	0.0327	0.654
G3	445	236	122	0.858	0.0339	1.09
G4	556	281	183	0.845	0.0216	1.34
Geometric mean	238	147	138		0.0229	0.923
Arithmetic mean				0.882		

TDS: time-dependent sorption.
(a): Values from aged sorption fit.
(b): Calculated from DegT50 in line with the draft guidance document using the refit on residue data only.

B.4. Effect of including aged sorption into the leaching assessment

PEC_{gw} were calculated using FOCUS PEARL 4.4.4 and FOCUS PELMO 5.5.3 for all available FOCUS scenarios with a single yearly application at a rate of 20 g/ha in autumn to winter cereals one day before emergence. Eightieth percentile concentrations in leachate at 1 m depth were taken from the model output. No volatilisation and no plant uptake were assumed.

Table B.16 summarises the substance properties regarding degradation and soil sorption (without and with aged sorption) for pesticide ECPA-06 assuming: (i) all experiments as lower-tier data, (ii) only results from higher-tier aged sorption experiments and (iii) combining both lower-tier degradation and sorption data with higher-tier data from aged sorption experiments. The results of calculations on PEC groundwater are provided in Table B.17 for FOCUS PEARL and in Table B.18 for FOCUS PELMO.

Table B.16: Substance properties of pesticide ECPA-06 in different assessment approaches for the two data sets

Assessment approach	$DegT50_{EQ}$ (days)	$K_{om,eq}$ (mL/g)	1/n (–)	f_{NE} (–)	k_{des} (days^{-1})
Lower tier	238(a)	138	0.882	0	0
ECPA soils 6A–D					
Tier 1	108	191	0.915	0.635	0.0335
Tier 1 and aged sorption data	147	138	0.882	0.635	0.0335
Soil G1–4					
Aged sorption	174	95.3	0.835	0.923	0.0229
Tier 1 and aged sorption data	147	138	0.882	0.923	0.0229

(a): DegT50 for lower tier.

Table B.17: Predicted concentration (μg/L) of pesticide ECPA-06 in the FOCUS groundwater scenarios based on different assessment approaches applying FOCUS PEARL 4.4.4 (application rate of 20 g/ha one day before emergence) in winter cereals

FOCUS crop	Scenario	PEARL 4.4.4				
		Lower tier	ECPA soils (6A–6D)		Independent data set (G1–G4)	
			TDS only	Lower tier and TDS	TDS only	Lower tier and TDS
Winter cereals	Châteaudun	0.062	< 0.001	0.001	< 0.001	< 0.001
	Hamburg	0.312	0.008	0.043	0.078	0.038
	Jokioinen	0.031	< 0.001	< 0.001	< 0.001	< 0.001
	Kremsmünster	0.215	0.004	0.024	0.039	0.020
	Okehampton	0.289	0.010	0.055	0.097	0.050
	Piacenza	0.173	0.004	0.025	0.044	
	Porto	0.144	0.002	0.017	0.033	0.015
	Sevilla	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	Thiva	0.039	< 0.001	< 0.001	< 0.001	< 0.001

TDS: time-dependent sorption.

Table B.18: Predicted concentration (μg/L) of pesticide ECPA-06 in the FOCUS groundwater scenarios based on different assessment approaches applying FOCUS PELMO 5.5.3 (application rate of 20 g/ha one day before emergence) in winter cereals

FOCUS crop	Scenario	PELMO 5.5.3				
		Lower tier	ECPA soils (6A–6D)		Independent data set (G1–G4)	
			TDS only	Lower tier and TDS	TDS only	Lower tier and TDS
Winter cereals	Châteaudun	0.030	< 0.001	< 0.001	< 0.001	< 0.001
	Hamburg	0.324	0.006	0.038	0.051	0.026
	Jokioinen	0.022	< 0.001	< 0.001	< 0.001	< 0.001
	Kremsmünster	0.229	0.004	0.023	0.034	0.017
	Okehampton	0.317	0.012	0.060	0.105	0.0543
	Piacenza	0.207	0.004	0.028	0.046	0.022
	Porto	0.197	0.004	0.026	0.046	0.023
	Sevilla	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	Thiva	0.011	< 0.001	< 0.001	< 0.001	< 0.001

TDS: time-dependent sorption.

Aged sorption considerably lowered PEC$_{gw}$ values of a rather stable compound with moderate sorption. The reduction in PEC$_{gw}$ values was more pronounced for the ECPA soils 6A–6D (aged sorption only) due to a higher K$_{om,eq}$ value and a lower DegT50$_{EQ}$ value. However, the ECPA soil combined with lower tier data provided the highest PEC$_{gw}$ values for both FOCUS models. This data set is recommended for use in groundwater risk assessments as this is the worst-case scenario.

The relative effect of including aged sorption increases at lower dosages (Table B.19).

Table B.19: Predicted concentration (μg/L) of pesticide ECPA-06 in the FOCUS groundwater scenarios based on different assessment approaches applying FOCUS PEARL 4.4.4 with different application rates one day before emergence in winter cereals

FOCUS crop	Scenario	PEARL 4.4.4					
		Lower tier			Lower tier and TDS		
		20 g/ha	200 g/ha	1,000 g/ha	20 g/ha	200 g/ha	1,000 g/ha
Winter cereals	Châteaudun	0.062	2.27	22.5	0.001	0.144	2.47
	Hamburg	0.312	6.46	46.3	0.043	1.48	13.9
	Jokioinen	0.031	1.99	21.2	< 0.001(a)	0.015	1.23
	Kremsmünster	0.215	4.33	31.6	0.024	0.941	9.48
	Okehampton	0.289	5.54	40.5	0.055	1.500	13.0
	Piacenza	0.173	3.53	27.1	0.025	0.824	7.73
	Porto	0.144	3.31	24.1	0.017	0.642	6.52
	Sevilla	< 0.001(a)	0.0261	0.563	< 0.001(a)	0.001	0.021
	Thiva	0.039	2.18	23.6	< 0.001(a)	0.066	1.74
Arithmetic mean		**0.141**	**3.29**	**26.4**	**0.018**	**0.624**	**6.23**

TDS: time-dependent sorption.
(a): Treated as zero.

The arithmetic mean of the PEC$_{gw}$ with aged sorption is 23.6% (1,000 g/ha), 18.9% (200 g/ha) and 13.0% (20 g/ha) of the arithmetic mean of the PEC$_{gw}$ of the first tier. This is explained as follows: for a Freundlich isotherm (equilibrium adsorption), the retardation factor, R, is a function of the concentration. When the Freundlich exponent 1/n is < 1, retardation increases with decreasing concentration in the water phase, C$_w$, as follows:

$$R = 1 + \frac{\rho}{\theta}\frac{1}{n}K_F C_w^{\frac{1}{n}-1}$$

where ρ is bulk density, θ is volumetric water content and K_F is the Freundlich coefficient. A higher retardation factor at lower concentrations implies slower transport and, consequently, lower PEC_{gw} values. The effect is more pronounced for lower 1/n values.

For the lower tier, the reduction in PEC_{gw} (reference dose 1,000 g/ha) is by a factor of 8 and 188 for doses of 200 and 20 g/ha, respectively (dose is a factor of 5 and 50 less than the reference dose of 1,000 g/ha). For the aged sorption parametrisation, the reduction in PEC_{gw} (reference dose 1,000 g/ha) is even by a factor of 10 and 340 for doses of 200 and 20 g/ha, respectively. Thus, the reduction in PEC_{gw} is even more pronounced with aged sorption.

Appendix C – Detailed description of case ECPA-07

Substance ECPA-07 exhibits moderate to high persistency and moderate sorption. Lower-tier degradation and adsorption experiments were taken from an EFSA conclusion (EFSA, 2016). Aged sorption studies were carried out at four locations. These studies were examined following the draft guidance document; however, the recommendations in Section 3.3 were completely followed in this example. Results are therefore slightly different from those in Van Beinum and Beulke (2016a,b).

C.1. Tier 1 assessment (without aged sorption)

C.1.1. Degradation (total mass)

Standard regulatory data packages include degradation endpoints (DegT50 values) for parent compounds derived by kinetic analysis of data from OECD Guideline 307 aerobic route and rate of degradation studies (OECD, 2002). Degradation studies were performed at six different locations (A–F). An additional $CaCl_2$ extraction step was carried out in four studies (studies A2, B2, C2 and D2), so these experiments are considered to also represent aged sorption studies in line with the draft guidance document.

At each location, up to four experiments were undertaken with each soil to investigate the degradation of the substance radiolabelled in different positions (labels 1–4). Residue data from the same soil but different radiolabels were not treated as replicates in the kinetic analysis because the studies were not carried out in the same year. Furthermore, although the soil was extracted from the same location, the soil properties differed between samples because of natural variation (Table C.1).

Table C.1: Main characteristics of soils used for degradation and aged sorption experiments (soils used for aged sorption experiments are shaded in grey)

Soil	TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)
A1	No	Sandy loam	0.14	0.67	3.4	6.1
A2	Yes	Sandy loam	0.13	0.71	2.1	6.4
A3	No	Loamy sand	0.09	0.81	3.3	6.2
B1	No	Silt loam	0.2	0.21	4.3	6.5
B2	Yes	Silt loam	0.19	0.19	3.1	6.5
B3	No	Silt loam	0.17	0.23	4.1	6.5
B4	No	Silt loam	0.17	0.23	4.1	6.5
C1	No	Silt loam	0.2	0.27	5.7	4.8
C2	Yes	Loam	0.18	0.43	4.0	5.4
D1	No	Silty clay	0.42	0.17	7.1	7.1
D2	Yes	Clay loam	0.29	0.37	7.9	7.4
D3	No	Clay loam	0.31	0.43	8.8	7.1
E1	No	Sandy loam	0.072	0.678	1.0	7.0
E2	No	Sandy loam	0.072	0.678	1.0	7.0
F1	No	Silt loam	0.228	0.134	4.0	6.5
F2	No	Silt loam	0.228	0.134	4.0	6.5

OM: organic matter; TDS: time-dependent sorption; USDA: US Department of Agriculture.

Table C.2 gives the data needed for normalisation to reference conditions. Table C.3 gives the degradation results according to EFSA (2016). In the majority of the studies, degradation kinetics are best described with the SFO model. However, in six cases the DFOP model performs best. Where the DFOP model is used, the slow-phase DegT50 is used (FOCUS, 2006). In line with the EFSA conclusion on substance ECPA-07 (EFSA, 2016), geometric mean DegT50 values were calculated for soils from the same location before taking the overall geometric mean (Table C.3). The lower-tier DegT50 value for substance ECPA-07 is 94.8 days.

Table C.2: Study and reference moisture and temperature of soils used for degradation and aged sorption experiments (soils used for aged sorption experiments are shaded in grey)

Soil	TDS study	Study soil moisture (g/100 g)	Reference soil moisture (pF2)(a) (g/100 g)	f_{Moist}(b) (–)	Study soil temperature (°C)	Reference temperature (°C)	f_{Temp}(c) (–)
A1	No	28.4	19.0	1.00	20.0	20.0	1.0
A2	Yes	36.5	26.0	1.00	20.0	20.0	1.0
A3	No	41.4	26.0	1.00	20.0	20.0	1.0
B1	No	42.7	40.0	1.00	20.0	20.0	1.0
B2	Yes	27.0	37.9	0.79	20.0	20.0	1.0
B3	No	13.5	15.8	0.90	20.0	20.0	1.0
B4	No	23.2	19.0	1.00	20.0	20.0	1.0
C1	No	29.7	26.0	1.00	20.0	20.0	1.0
C2	Yes	31.4	25.0	1.00	20.0	20.0	1.0
D1	No	45.9	28.0	1.00	20.0	20.0	1.0
D2	Yes	35.6	26.0	1.00	20.0	20.0	1.0
D3	No	27.0	37.9	0.79	20.0	20.0	1.0
E1	No	13.5	15.8	0.90	20.0	20.0	1.0
E2	No	27.9	14.0	1.00	20.0	20.0	1.0
F1	No	35.6	26.0	1.00	20.0	20.0	1.0
F2	No	46.1	28.0	1.00	20.0	20.0	1.0

TDS: time-dependent sorption.
(a): FOCUS default values based on soil texture (no measured data available).
(b): f_{Moist} is the soil moisture correction factor $((\theta_{act}/\theta_{ref})$^0.7).
(c): f_{Temp} is the temperature correction factor (Q_{10}^$((T_{act} - T_{ref})/10)$) with $Q_{10} = 2.58$.

Table C.3: Degradation kinetics of substance ECPA-07 (soils used for aged sorption experiments are shaded in grey)

Soil	TDS study	Kinetics	DegT50 (b) (days)	DFOP-k_1 DegT50(b) (days)	DFOP-k_2 DegT50(a)(b) (days)	g (–)	χ^2-error (%)	Selected DegT50(b) (days)
A1	No	DFOP		10.7	141.5	0.33	1.6	141.5
A2	Yes	DFOP		15.8	169.1	0.38	1.2	169.1
A3	No	DFOP		12.7	210.3	0.4	1.6	210.3
					Geometric mean (n = 3)			**171.4**
B1	No	SFO	40.5				1.7	40.5
B2	Yes	SFO	54.4				0.6	54.4
B3	No	DFOP		12.7	90	0.45	2	90
B4	No	SFO	43				2.3	43
					Geometric mean (n = 4)			**54.0**
C1	No	DFOP		6.4	157.5	0.23	2	157.5
C2	Yes	DFOP		6.7	157.5	0.16	1.2	157.5
					Geometric mean (n = 2)			**157.5**
D1	No	SFO	55.1				2.3	55.1
D2	Yes	SFO	60.1				1.7	60.1
D3	No	SFO	38.6				1.9	38.6
					Geometric mean (n = 3)			**50.4**
E1	No	SFO	166.4				0.7	166.4
E2	No	SFO	179.7				1.3	179.7
					Geometric mean (n = 2)			**172.9**
F1	No	SFO	58.8				1.1	58.8

Soil	TDS study	Kinetics	DegT50 $^{(b)}$ (days)	DFOP-k_1 DegT50$^{(b)}$ (days)	DFOP-k_2 DegT50$^{(a)(b)}$ (days)	g (–)	χ^2-error (%)	Selected DegT50$^{(b)}$ (days)
F2	No	SFO	55.5				1.1	55.5
				Geometric mean (n = 2)				**57.1**

DFOP: double first-order in parallel; SFO: single first-order; TDS: time-dependent sorption.

(a): DFOP slow phase (k_2).

(b): DegT50 values were normalised to default values 20°C using a Q10 value of 2.58 and to a moisture content of 10 kPa (pF2) according to the methods in FOCUS (2006).

C.1.2. Adsorption (batch studies)

Sorption parameters for ECPA-07 are listed in Table C.4. Batch adsorption–desorption studies in line with OECD Guideline 106 (OECD, 2000) were performed on six locations. The geometric mean K_{OC} and K_{om} and the arithmetic mean 1/n value of the six soils were calculated, and these were used in the lower-tier PEC groundwater calculations. Four soils were also used for the aged sorption studies (A–D). Thus, soil-specific 1/n values were used in the aged sorption fitting procedure. However, the organic matter content of the soils used for the aged sorption experiments differs from the organic matter content of the batch studies. It is therefore questionable whether the soils used for the batch experiments are the same soils as those used for the aged sorption studies (Section 6.3). In the context of this case study, this issue is, however, ignored.

Table C.4: Main characteristics of soils used for Freundlich adsorption experiments and obtained Freundlich adsorption parameters (soils used for aged sorption fitting are shaded in grey)

Soil	Applicable for TDS study	Texture (USDA)	Clay (%)	Sand (%)	OM (%)	pH ($CaCl_2$)	$K_{f,eq}$ (mL/g)	$K_{om,eq}$ (mL/g)	1/n
A	Yes	Sandy loam	9.0	73.0	3.6	6.2	2.08	57.37	0.84
B	Yes	Loam	15.0	39.0	4.1	6.6	2.21	53.49	0.87
C	Yes	Loam	15.0	35.0	3.8	5.3	2.35	62.06	0.86
D	Yes	Loam	25.0	33.0	8.8	7.2	3.82	43.47	0.86
E	No	Silt loam	26.7	11.1	3.3	6.5	2.51	76.69	0.85
F	No	Sandy loam	7.6	64.3	1.2	6.8	0.60	49.47	0.90
Geometric mean								56.2	–
Arithmetic mean								–	0.86

OM: organic matter; TDS: time-dependent sorption; USDA: US Department of Agriculture.

C.2. Time-dependent sorption studies

As mentioned above, four of the seven soil laboratory degradation studies available are considered to represent aged sorption studies in line with the draft guidance on aged sorption (additional $CaCl_2$ extraction step). Additional information on the experimental setup necessary to derive aged sorption parameters for these four soils is given in Table C.5.

Table C.5: Experimental setup of the four aged sorption experiments

Parameter$^{(a)}$	Description	Soil A2	Soil B2	Soil C2	Soil D2
TimStart (days)	Start time	0	0	0	0
TimEnd (days)	End time	120	120	120	120
MasIni (μg)	Initial total mass of test substance	50.2	50.2	50.2	50.2
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Volume of liquid in moist soil	23.2	29.6	31.4	45.9
VolLiqAdd (mL)	Volume of liquid added	376.8	370.4	368.6	354.1

(a): Parameter naming according to PEARLNEQ 5.1.

C.2.1. Checking of quality criteria

Soil selection

As can be seen in Table C.4, the four soils used for the aged sorption experiments (soils A to D) cover a wide range of soil conditions, with organic matter content ranging from 3.6% to 8.8%. As described in Section C.1.2, the soils used for the aged sorption experiments are different from those used for the batch experiments. This issue is not further considered here so the use of soil-specific 1/n values is possible.

Data requirements

As aged sorption experiments with pesticide ECPA-07 were conducted before the draft guidance document was available, these experiments may be referred to as legacy studies. However, the data set fulfils all requirements of new studies; i.e. soil-specific 1/n values are available and each data set contains nine sampling time points.

Handling of outliers

As can be inferred from the fitting results (refer to Figures C.1–C.4), this data set does not contain outliers.

C.2.2. Data fitting (aged sorption model vs equilibrium sorption model)

The procedure starts with fitting the total mass and the concentration in the liquid phase ($CaCl_2$ extraction) of each soil to either the aged sorption or the equilibrium sorption model. For this substance, the final recommendations of the Panel as listed in Section 3.3 have been followed, so here we show only the fits where $K_{om,eq}$ was optimised and where the first data points have not been removed. For this reason, results are slightly different from those in Van Beinum and Beulke (2016a,b).

In line with the draft guidance document, the initial Freundlich exponent was set to soil-specific values obtained from OECD 106 batch experiments (OECD, 2000). The draft guidance document further recommends four different sets of starting values for f_{NE} and k_{des} in the fitting procedure (i.e. 0.2/0.004 $days^{-1}$, 0.2/0.05 $days^{-1}$, 1.5/0.004 $days^{-1}$ and 1.5/0.05 $days^{-1}$ for f_{NE} and k_{des}, respectively). In the case of pesticide ECPA-07, all four starting options for f_{NE} and k_{des} resulted in almost the same aged sorption parameters. The initial guess of $DegT50_{EQ}$ was set to the lower-tier endpoints (Table C.3). Table C.6 gives an overview on the initial guess of aged sorption parameters for substance ECPA-07.

Table C.6: Initial guess on aged sorption parameters for the fitting procedure

Parameter[(a)]	Description	Soil A	Soil B	Soil C	Soil D
ExpFre (–)	Freundlich exponent (1/n)	0.84	0.87	0.86	0.86
KomEql (mL/kg)	Sorption coefficient ($K_{om,eq}$)	57.3	53.5	62.0	43.5
$DegT50_{EQ}$ (days)	Initial guess of $DegT50_{EQ}$	171.4	54.0	157.5	50.4
FacSorNeqEql (–)	Initial guess of f_{NE}	0.2	0.2	0.2	0.2
CofRatDes ($days^{-1}$)	Initial guess of k_{des}	0.05	0. 05	0. 05	0. 05

(a): Parameter naming according to PEARLNEQ 5.1.

Following the draft guidance document, a fit is considered reliable if the relative standard error for each fitted parameter is ≤ 0.4, the χ^2-error (mass and concentration) is < 15% (indicative trigger) and when there is clear evidence for time-dependent sorption on the basis of the non-equilibrium and equilibrium fits (on the basis of the χ^2-error for $k_{d,app}$). In line with recommendations in Section 6.6, the χ^2-error for $k_{d,app}$ was calculated using unweighted values with the number of degrees of freedom based on the number of parameters fitted.

The results for the aged sorption fits of the four soils are given in Table C.7; the fits obtained are given in Figures C.1–C.4. On the basis of the fitting criteria stated above, it can be concluded that all fits may be considered reliable. The bad fit (χ^2-error > 15%) in the case of equilibrium sorption gives strong evidence for time-dependent sorption in all four soils. Considering only the four dedicated aged sorption studies, the modelling endpoints of pesticide ECPA-07 to be used in the exposure assessment would be: $DegT50_{EQ} = 56.6$ days, $K_{om,eq} = 46.9$ mL/g, $1/n = 0.86$, $k_{des} = 0.033$ $days^{-1}$ and $f_{NE} = 0.53$.

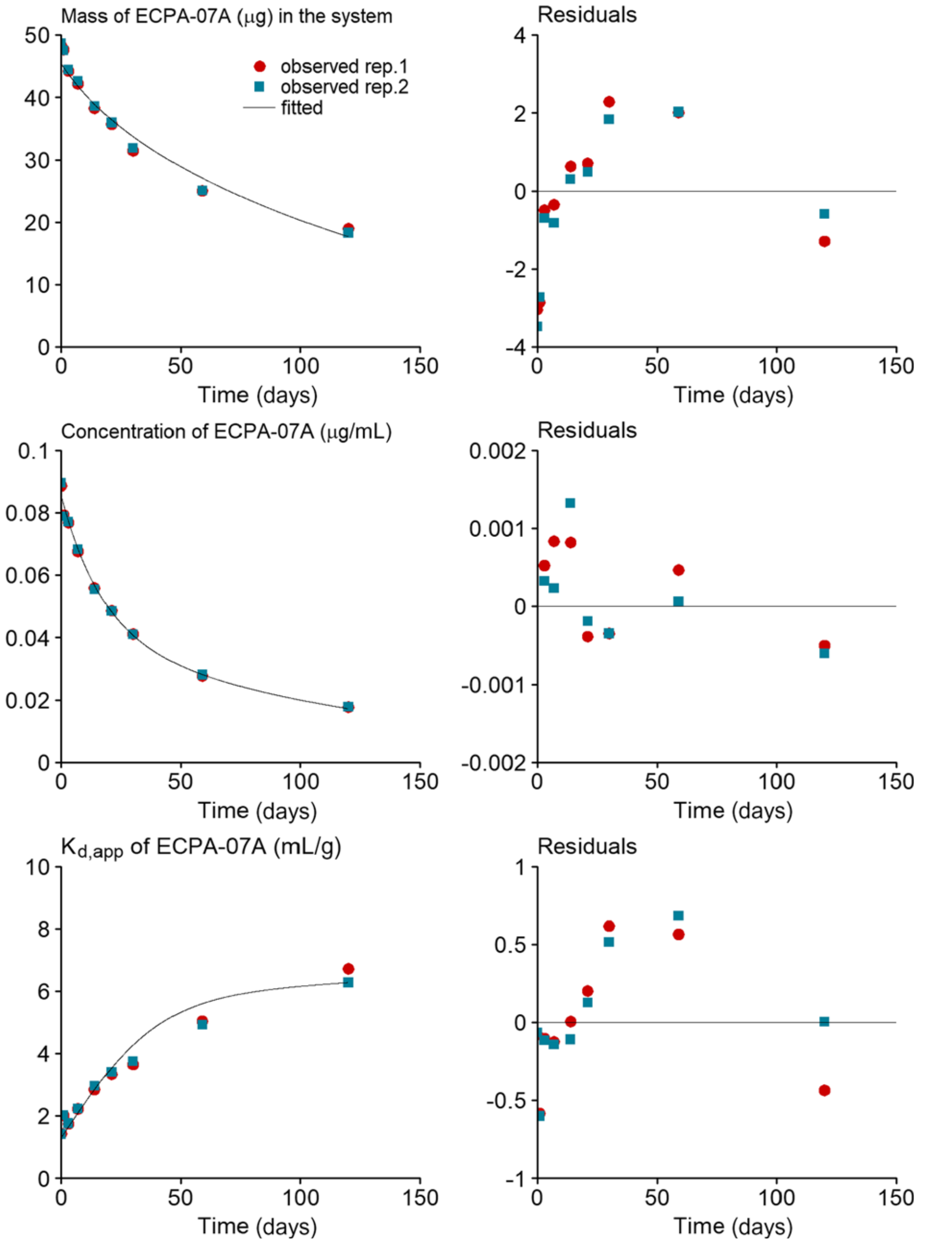


Figure C.1: Graphs of aged sorption model fits for substance ECPA-07 and soil A2. Left-hand side: Fits for the concentration in total soil, the concentration in the liquid phase and the apparent sorption constant. Right-hand side: Residuals of the respective fits on the left-hand side

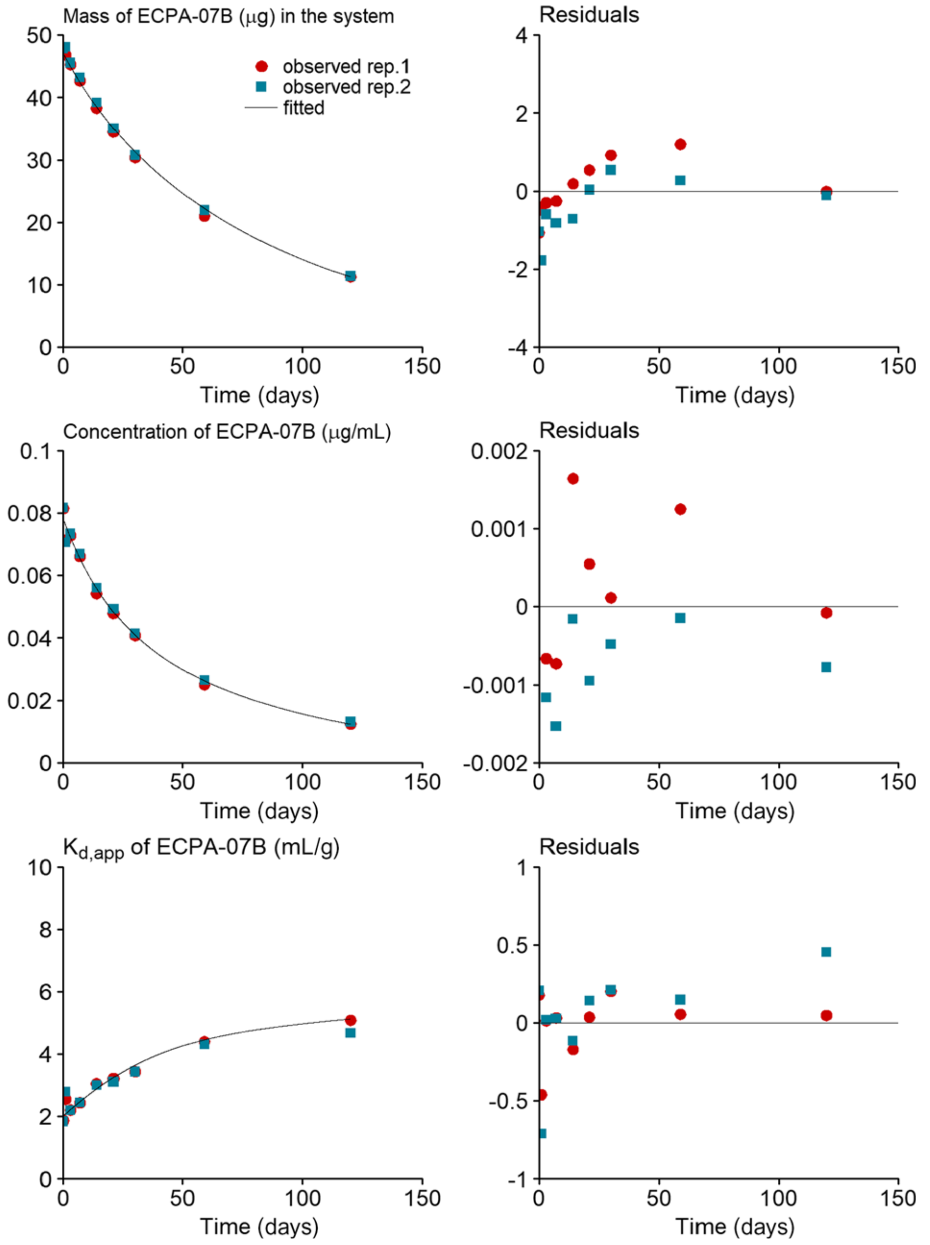


Figure C.2: Graphs of aged sorption model fits for substance ECPA-07 and soil B2. Left-hand side: Fits for the concentration in total soil, the concentration in the liquid phase and the apparent sorption constant. Right-hand side: Residuals of the respective fits on the left-hand side

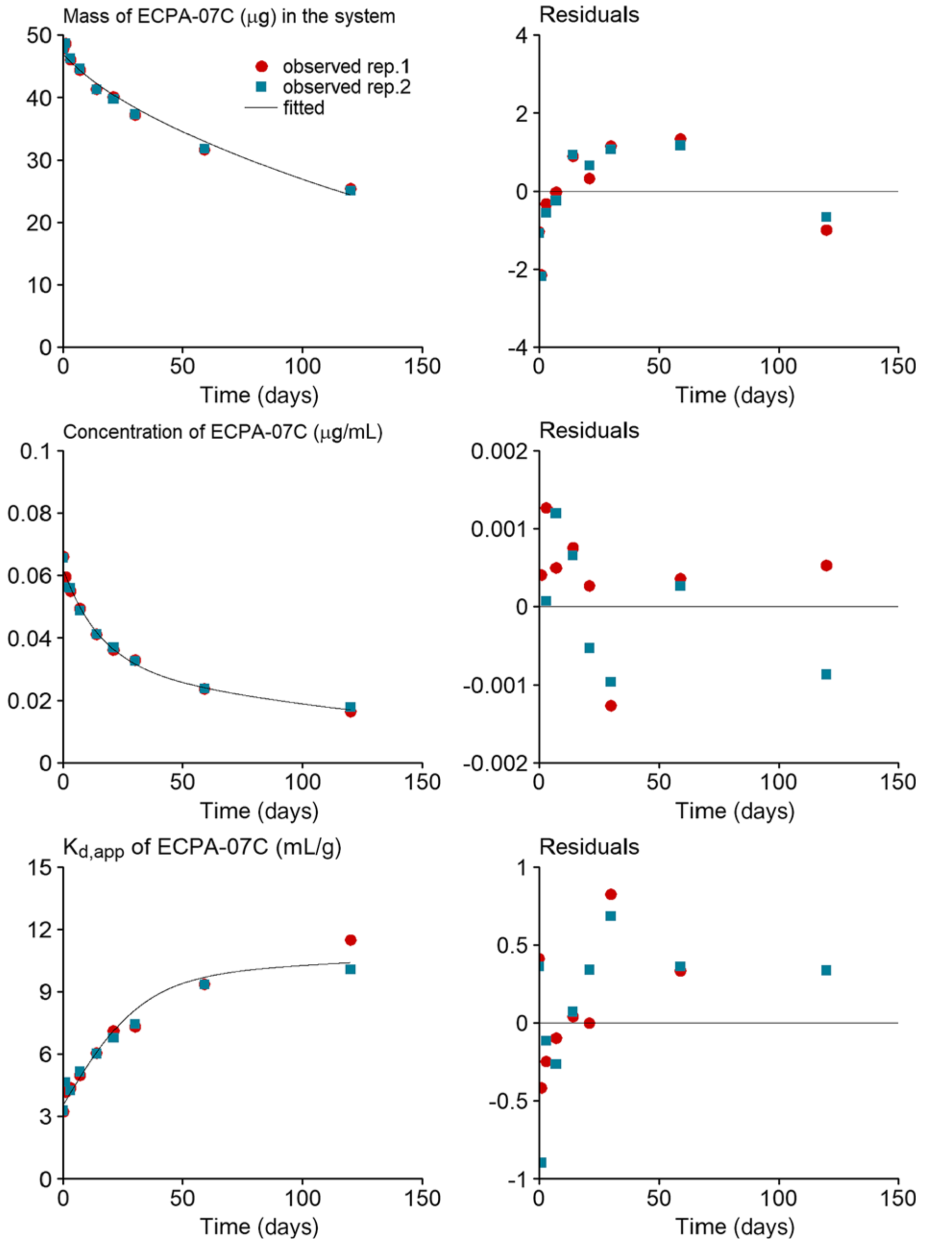


Figure C.3: Graphs of aged sorption model fits for substance ECPA-07 and soil C2. Left-hand side: Fits for the concentration in total soil, the concentration in the liquid phase and the apparent sorption constant. Right-hand side: Residuals of the respective fits on the left-hand side

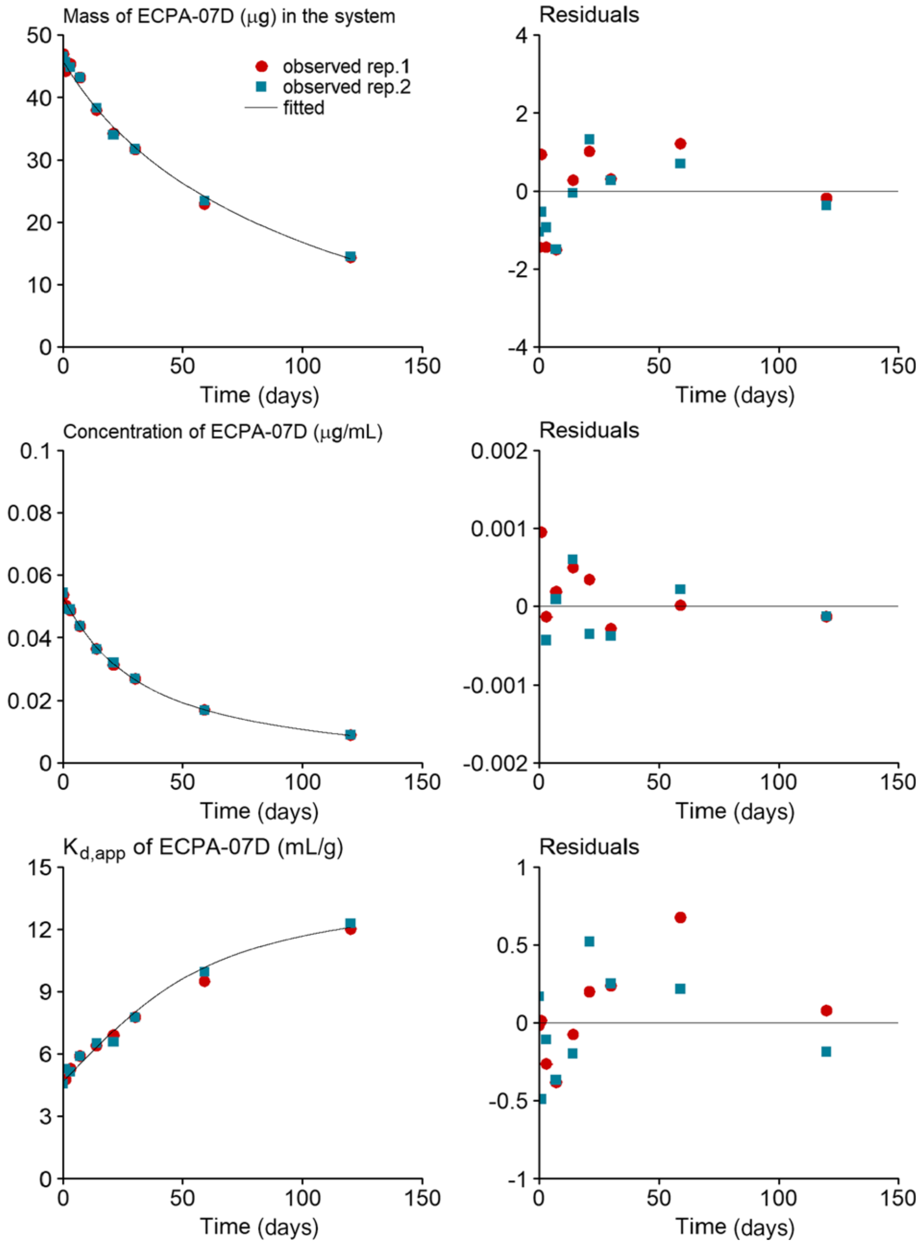


Figure C.4: Graphs of aged sorption model fits for substance ECPA-07 and soil D2. Left-hand side: Fits for the concentration in total soil, the concentration in the liquid phase and the apparent sorption constant. Right-hand side: Residuals of the respective fits on the left-hand side

Table C.7: Aged sorption fitting results for ECPA-07, soils A–D

Parameter		Soil A	Soil B	Soil C	Soil D
Aged sorption model					
f_{NE} (–)	Value	0.752	0.313	0.698	0.473
	RSE	0.088	0.088	0.064	0.053
K_{des} (days^{-1})	Value	0.032	0.037	0.037	0.027
	RSE	0.130	0.161	0.106	0.091
DegT50$_{EQ}$ (days)	Value	55.692	45.410	80.962	50.199
	RSE	0.030	0.018	0.032	0.014
M_{ini} (µg)	Value	45.375	47.037	46.902	45.759
	RSE	0.012	0.009	0.010	0.007
$K_{om,eq}$ (mL/g)	Value	42.668	46.664	61.156	39.873
	RSE	0.083	0.044	0.035	0.020
1/n (–)	Value	0.845	0.868	0.864	0.865
χ^2-error (mass and concentration) (%)		3.5	2.3	2.5	1.9
χ^2-error ($K_{d,app}$) (%)		11.0	7.5	6.1	3.7
Equilibrium sorption model					
χ^2-error (mass and concentration) (%)		11.7	6.9	11.2	9.2
χ^2-error ($K_{d,app}$)		33.7	18.7	26.0	21.0

RSE: relative standard error.

C.3. Combination of degradation and sorption data from Tier 1 and aged sorption studies

The final step combines the results on lower-tier degradation and sorption as well as of aged sorption studies (Table C.8). This step involves the transformation of lower-tier DegT50 values (based on total mass) into DegT50$_{EQ}$ values. The draft guidance gives three options for performing this transformation. As described in Section 3.3, refitting the lower-tier residue data is the preferred option. Because these data were available, this option has been used in this case study. Furthermore, the $K_{om,eq}$ is based on the lower-tier data only.

Table C.8: Summary on degradation and adsorption results obtained in lower-tier, aged sorption studies and with combining both for pesticide ECPA-07 (aged sorption studies are shaded)

Soil	DegT50$_{EQ}$ (days)	DegT50 $_{eq}$ (days)	DegT50$_{EQ}$ (days)	$K_{om,eq}$ (mL/g)		1/n (–)	k_{des} (days^{-1})	f_{NE} (–)
	Batch$^{(a)}$	TDS study	Combined	Batch	TDS	Batch	TDS	TDS
A1	56.1	–	56.1	–	–	–	–	–
A2	–	55.7	55.7	57.3	42.7	0.84	0.032	0.752
A3	59.6	–	59.6	–	–	–	–	–
Geometric mean DegT50 (n = 3)			**57.1**					
B1	32.1	–	32.1	–	–	–	–	–
B2	–	45.4	45.4	53.5	46.7	0.87	0.037	0.313
B3	34.7	–	34.7	–	–	–	–	–
B4	33.8	–	33.8	–	–	–	–	–
Geometric mean DegT50 (n = 4)			**36.2**					
C1	75.0	–	75.0	–	–	–	–	–
C2	–	80.9	80.9	62.1	61.2	0.86	0.037	0.698
Geometric mean DegT50 (n = 2)			**77.9**					
D1	41.5	–	41.5	–	–	–	–	–
D2	–	50.2	50.2	43.5	39.9	0.86	0.027	0.473

Soil	$DegT50_{EQ}$ (days)	$DegT50_{eq}$ (days)	$DegT50_{EQ}$ (days)	$K_{om,eq}$ (mL/g)		1/n (–)	k_{des} ($days^{-1}$)	f_{NE} (–)
	Batch[(a)]	TDS study	Combined	Batch	TDS	Batch	TDS	TDS
D3	28.6	–	28.6	–	–	–	–	–
Geometric mean DegT50 (n = 3)			**39.1**					
E1	131.1	–	131.1	–	–	–	–	–
E2	122.4	–	122.4	76.7	–	0.85	–	–
Geometric mean DegT50 (n = 2)			**126.7**					
F1	10.9	–	10.9	–	–	–	–	–
F2	43.3	–	43.3	49.5	–	0.90	–	–
Geometric mean DegT50 (n = 2)			**21.7**					
Geometric mean			**50.9**	**56.2**(b)		–	**0.033**	**0.53**
Arithmetic mean			–	–		**0.86**	–	–

TDS: time-dependent sorption.

(a): Calculated from lower-tier DegT50 on the basis of option 3. i.e. refitting the lower-tier residue data. Numbers taken from Van Beinum et al. (2016).

(b): Calculated using the lower-tier data only; the $K_{om,eq}$ fitted in the aged sorption experiment is not used in the leaching assessment.

Combining data from lower-tier degradation and adsorption experiments as well as from aged sorption experiments, the following aged sorption modelling endpoints were obtained: $DegT50_{EQ}$= 50.9 days, $K_{om,eq}$ = 56.2 mL/g, 1/n = 0.86, k_{des} = 0.033 $days^{-1}$ and f_{NE} = 0.53.

C.4. Effect of including aged sorption in the leaching assessment

PEC_{gw} values were calculated using FOCUS PEARL 4.4.4 for all available FOCUS scenarios using an application rate of 200 g/ha. One application was made each year one day before emergence of winter cereals and spring cereals. Eightieth percentile concentrations in leachate at 1 m depth were taken from the PEARL output. According to the EFSA conclusion (EFSA, 2015), the plant uptake factor was set to 0.5. No volatilisation was assumed. Table C.9 summarises the mean substance properties regarding degradation and soil sorption for substance ECPA-07 assuming: (i) all experiments as lower-tier data, (ii) only results from the four higher-tier aged sorption experiments, and (iii) combining both lower-tier degradation ad sorption data with higher-tier data from aged sorption experiments.

Table C.9: Substance properties of pesticide ECPA-07 in different assessment approaches

Assessment approach	$DegT50_{EQ}$ (days)	$K_{om,eq}$ (mL/g)	1/n (–)	k_{des} ($days^{-1}$)	f_{NE} (–)
Tier 1	94.8	56.2	0.86	0	0
Aged sorption studies only	56.6	46.9	0.86	0.033	0.53
Tier 1 and aged sorption	50.9	56.2	0.86	0.033	0.53

(a): DegT50 for lower tier.

The results of calculations on PEC groundwater are provided in Tables C10 and C11 (winter cereals only). The predicted concentration using the four aged sorption studies is 2–5 times lower than the concentration predicted using only the lower-tier data (i.e. without assuming aged sorption). The predicted leaching concentration is even lower when combining all degradation and sorption data. This is primarily caused by the low $DegT50_{EQ}$ value calculated for soil F1, which is not in the subset of soils available for aged sorption studies. This shows that the leaching assessment is extremely sensitive to adding new experiments. Nevertheless, combining as many studies as possible in the leaching assessment is to be preferred, because this reduces the uncertainty of the assessment.

Table C.10: Predicted concentration (µg/L) of pesticide ECPA-07 in the FOCUS groundwater scenarios based on different assessment approaches applying FOCUS PEARL 4.4.4 (application rate of 200 g/ha one day before emergence) in winter cereals and spring cereals

Assessment approach	CH	HA	JO	KR	OK	PI	PO	SE	TH
Winter cereals									
Tier 1	1.313	4.078	1.759	2.593	3.943	2.361	2.409	0.001	0.754
Aged sorption only	0.208	1.272	0.317	0.787	1.327	0.682	0.811	0.000	0.092
Tier 1 and aged sorption	0.029	0.432	0.045	0.268	0.491	0.211	0.247	0.000	0.009
Spring cereals									
Tier 1	0.685	3.142	1.358	2.225	2.631	–	1.242	–	–
Aged sorption only	0.084	0.880	0.218	0.647	0.835	–	0.306	–	–
Tier 1 and aged sorption	0.009	0.288	0.028	0.188	0.260	–	0.075	–	–

CH: Châteaudun; HA: Hamburg; JO: Jokioinen; KR: Kremsmünster; OK: Okehampton; PI: Piacenza; PO: Porto; SE: Sevilla, TH: Thiva.

Table C.11: Predicted concentration (µg/L) of pesticide ECPA-07 in the FOCUS groundwater scenarios based on different assessment approaches applying FOCUS PELMO 5.5.3 (application rate of 200 g/ha one day before emergence) in winter cereals and spring cereals

Assessment approach	CH	HA	JO	KR	OK	PI	PO	SE	TH
Winter cereals									
Tier 1	1.331	5.545	2.679	3.683	5.025	3.381	3.752	0.015	0.65
Aged sorption only	0.176	1.913	0.601	1.122	1.765	1.113	1.502	0.001	0.074
Tier 1 and aged sorption	0.088	1.322	0.358	0.751	1.257	0.763	1.094	0	0.034
Spring cereals									
Tier 1	0.604	3.672	1.483	2.666	3.19	–	2.004	–	–
Aged sorption only	0.057	1.005	0.262	0.768	0.995	–	0.539	–	–
Tier 1 and aged sorption	0.024	0.636	0.139	0.487	0.657	–	0.336	–	–

CH: Châteaudun; HA: Hamburg; JO: Jokioinen; KR: Kremsmünster; OK: Okehampton; PI: Piacenza; PO: Porto; SE: Sevilla; TH: Thiva.

Appendix D – Handling of metabolites

Artificial degradation experiments for a parent substance and its primary metabolite were run with a model that can deal with aged sorption (PELMO) for the following cases:

1) the parent shows aged sorption and the primary metabolite does not (SFO kinetics);
2) the metabolite shows aged sorption and the parent does not (SFO kinetics);
3) both the parent and the metabolite show aged sorption.

D.1. Artificial degradation experiments

The starting point was to set up an artificial degradation experiment at a constant temperature (20°C) and constant water content ($\theta_v = 0.3$ cm^3/cm^3) in a hypothetical soil with a dry bulk density of 1.5 g/cm^3 and an organic matter content of 1.724%. The initial mass was 1.33 mg/kg, corresponding to a field application rate of 1 kg/ha for a 5 cm depth interval. In this system, simulations are performed by PELMO 5.5.3 using the 'user-specific scenario' mode. Different parametrisations of aged sorption were chosen for the parent compound and its metabolite (see Table D.1) to create typical data sets for degradation experiments when applying OECD Guideline 307 (total mass of parent compound and metabolite against time) (OECD, 2002).

Table D.1: Parametrisations of parent compounds and metabolites

		f_{NE} (–)	k_{des} (days^{-1})	DT50$_{EQ}$ (days)	$K_{om,eq}$ (mL/g)	1/n (–)
Parent	Compound A	1	0.025	200	100	0.84
	Compound B	0.5	0.025	35	35	0.90
Metabolite	Metabolite A	1.2	0.01	10	58	0.90
	Metabolite B	1.2	0.01	100	58	0.90
	Metabolite C	1.2	0.01	50	58	0.90

The parametrisation of parent compound A was based on the average behaviour of penflufen from Gulkowska et al. (2016); parent compound B represents a rapidly degrading compound with aged sorption based on averaged properties of the substance ECPA-03A–D (Van Beinum and Beulke, 2012). The parametrisation of a rapidly (metabolite A) and slowly (metabolite B) degrading metabolite was chosen following Van Beinum and Beulke (2015).

In a next step, the total mass of the parent and the metabolite were sampled 0, 1, 3, 7, 14, 21, 30, 60, 90 and 120 days after application. These sample times were chosen according to OECD Guideline 307 (OECD, 2002) and were supplemented with days 180 and 240 for a slowly degrading parent. The temporal course of the total mass of the parent and the metabolite were simultaneously fitted using appropriate kinetic models for bulk soil degradation (SFO, DFOP or FOMC). Computer-assisted kinetic evaluation (CAKE) version 3.3 is used for this task using the iteratively reweighted least squares optimiser.

D.2. Case 1: parent with aged sorption, metabolite without aged sorption

The parametrisations of parent compounds A and B were used for this case in combination with a rapidly and slowly degrading metabolite (A and B) with formation fractions of 0.1, 0.5 and 0.9. Note that in the absence of aged sorption for the metabolite, its sorption parameters do not affect its formation and degradation in soil.

The data for the parent compound lumped together the effect of SFO degradation in the equilibrium domain and aged sorption which can most likely be represented by biphasic degradation models. Therefore, the parent compound is fitted using the DFOP and FOMC models. The SFO model is fitted for reasons of comparison.

The DFOP model performed best (lowest χ^2-error) of the three models for the parent compound. The fit of the metabolite was excellent given the prescribed SFO-DegT50 and formation fractions, only in the case of a correct (best fit) description of the parent compound. Table D.2 provides an example of the fitting results for the three kinetic degradation models.

Table D.2: Fitted parameters of the SFO, DFOP and FOMC kinetic degradation models for the parent compounds A and B and the formation of the rapidly degrading metabolite A (SFO-DegT50 = 10 days) with a formation fraction of 0.5

	Compound A		**Metabolite A**		
	DegT50 (days)	χ^2 **(%)**	**DegT50 (days)**	**ff (–)**	χ^2 **(%)**
SFO	357	0.70	5.05	0.999	7.1
DFOP	376	0.14	9.97	0.500	0.2
FOMC	421	0.40	6.14	0.810	3.8
	Compound B		**Metabolite A**		
	DegT50 (days)	χ^2 **(%)**	**DegT50 (days)**	**ff (–)**	χ^2 **(%)**
SFO	42.8	2.6	7.7	0.67	1.4
DFOP	41.9	0.10	10.4	0.48	0.14
FOMC	41.8	0.31	10.1	0.49	1.2

DFOP: double first-order in parallel; ff: formation fraction; FOMC: first-order multi-compartment; SFO: single first-order.

The DFOP-SFO kinetic degradation model was used in the following to fit the artificial degradation experiments for the slowly degrading parent compound A (Table D.3) and the more rapidly degrading parent compound B (Table D.4) with different formation fractions of metabolite A and B.

Table D.3: Fitted parameters of the DFOP-SFO kinetic degradation model for the parent compound A and the rapidly and slowly degrading metabolite A and B for different formation fractions

	DegT50 (days)	χ^2 **(%)**	**DegT50 (days)**	**ff (–)**	χ^2 **(%)**
	Compound A		**Metabolite A**		
ff = 0.9	375	0.14	9.87	0.907	0.05
ff = 0.5	376	0.14	9.97	0.500	0.15
ff = 0.1	376	0.14	10.3	0.097	0.13
	Compound A		**Metabolite B**		
ff = 0.9	377	0.14	101	0.893	0.13
ff = 0.5	375	0.14	98.4	0.502	0.03
ff = 0.1	377	0.14	101	0.099	0.18

DFOP: double first-order in parallel; ff: formation fraction; SFO: single first-order.

Table D.4: Fitted parameters of the DFOP-SFO kinetic degradation model for the parent compound B and the rapidly and slowly degrading metabolite A and B for different formation fractions

	Compound B		**Metabolite A**		
	DegT50 (days)	χ^2 **(%)**	**DegT50 (days)**	**ff (–)**	χ^2 **(%)**
ff = 0.9	42.0	0.10	10.4	0.866	0.21
ff = 0.5	41.9	0.10	10.4	0.481	0.14
ff = 0.1	41.9	0.10	10.4	0.0964	0.14
	Compound B		**Metabolite B**		
	DegT50 (days)	χ^2 **(%)**	**DegT50 (days)**	**ff (–)**	χ^2 **(%)**
ff = 0.9	41.9	0.10	101	0.895	0.05
ff = 0.5	42.0	0.16	100	0.498	0.04
ff = 0.1	41.9	0.10	100	0.0995	0.06

DFOP: double first-order in parallel; ff: formation fraction; SFO: single first-order.

The visual assessment for the DFOP-fits of the parent compounds were excellent for all cases. The formation fraction was slightly underestimated for the combination of a rapidly degrading parent compound and a rapidly degrading metabolite. The formation fraction was correctly predicted for the other cases. Note that the total contents in the PELMO output file had only three significant numbers, which can explain some of the observed deviations.

D.3. Case 2: parent without aged sorption, metabolite with aged sorption

Van Beinum and Beulke (2015) used DegT50, parent of 10 and 50 days with a formation fraction of 0.5 in their analysis. Note that in the absence of aged sorption for the parent compound, the choice of the sorption parameters does not affect its degradation in soil. The metabolite was parameterised either as the rapidly or as the slowly degrading metabolite A or B, respectively (see Table D.1).

Table D.5 summarises the parameters of the model fits. The DFOP model described the formation and degradation behaviour of a metabolite with aged sorption more accurately than the SFO model, especially for a rapidly degrading metabolite (see Figure D.1). The formation fraction was correctly predicted for a slowly degrading metabolite and slightly underestimated (formation fraction = 0.48) for a rapidly degrading metabolite. The working group noted that the DFOP kinetic degradation model is not recommended for metabolites according to current guidance (FOCUS, 2006).

Table D.5: Fitted parameters of the SFO-SFO and SFO-DFOP kinetic degradation model for a rapidly and a less rapidly degrading parent compound B in combination with the rapidly and slowly degrading metabolites A and B. The formation fraction was 0.5

	DegT50 (days)	χ^2 (%)	DegT50 (days)	ff (–)	χ^2 (%)
	Parent (DegT50 = 10 days)		**Metabolite A ($DegT50_{EQ}$ = 10 days)**		
SFO-SFO	10.3	0.13	18.1	0.393	11.1
SFO-DFOP	10.3	0.13	11.1	0.482	0.05
	Parent (DegT50 = 10 days)		**Metabolite B ($DegT50_{EQ}$ = 100 days)**		
SFO-SFO	10.4	0.23	179	0.473	2.6
SFO-DFOP	10.4	0.32	172	0.499	0.06
	Parent (DegT50 = 50 days)		**Metabolite A ($DegT50_{EQ}$ = 10 days)**		
SFO-SFO	50.3	0.12	20.5	0.371	7.4
SFO-DFOP	50.3	0.16	11.1	0.483	0.05
	Parent (DegT50 = 50 days)		**Metabolite B ($DegT50_{EQ}$ = 100 days)**		
SFO-SFO	50.3	0.13	187	0.465	1.8
SFO-DFOP	50.3	0.13	172	0.499	0.07

DFOP: double first-order in parallel; ff: formation fraction; SFO: single first-order.

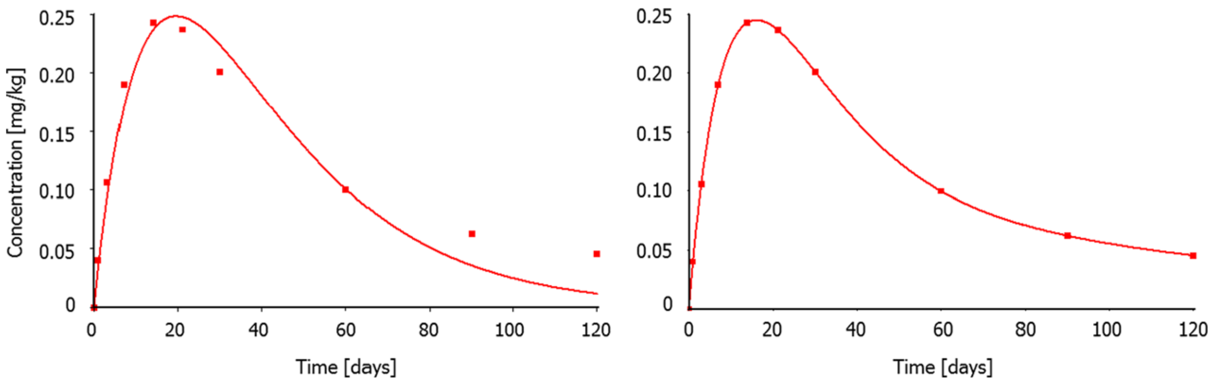


Figure D.1: The formation and degradation of the rapidly degrading metabolite A ($DegT50_{EQ}$ = 10 days) from a rapidly degrading parent compound (DegT50 = 10 days) fitted with the SFO-SFO (left) and SFO-DFOP (right) kinetic degradation model. The formation fraction was 0.5.

D.4. Case 3: parent and metabolite with aged sorption

In this case, an artificial degradation study was simulated where both the parent (compound B) and the primary metabolite (either metabolite A or C) showed aged sorption behaviour.

The fitting results are listed in Table D.6. Also in this case the DFOP-DFOP model provided the best fit for the compounds with aged sorption. The formation fraction was correctly estimated for the more slowly degrading metabolite C, and was slightly underestimated for the rapidly degrading metabolite A. The working group noted that the DFOP kinetic degradation model is not recommended for metabolites according to current guidance (FOCUS, 2006).

Table D.6: Fitted parameters of the SFO-SFO, DFOP-SFO and DFOP-DFOP kinetic degradation models for the parent compound B and the rapidly and more slowly degrading metabolites A and C. The formation fraction was 0.5

	DegT50 (days)	**χ^2 (%)**	**DegT50 (days)**	**ff (–)**	**χ^2 (%)**
	Compound B		**Metabolite A**		
SFO-SFO	47.1	2.88	15.8	0.486	14.2
DFOP-SFO	42	0.17	22.7	0.355	12.2
DFOP-DFOP	42	0.17	11.2	0.482	0.09
	Compound B		**Metabolite C**		
SFO-SFO	46.1	2.87	82.8	0.481	8.80
DFOP-SFO	42	0.16	97.8	0.441	4.00
DFOP-DFOP	42	0.17	69.9	0.500	0.04

DFOP: double first-order in parallel; ff: formation fraction; SFO: single first-order.

Appendix E – 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 models PEARL and PELMO. The PEARLNEQ model is depicted in Figure E.1.

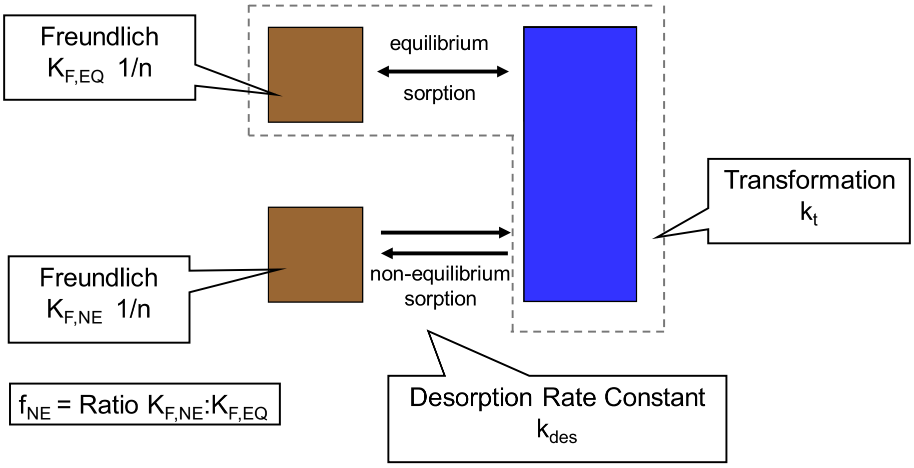


Figure E.1: Schematic representation of the PEARLNEQ model showing the soil solution on the right and the equilibrium and non-equilibrium sorption sites on the left. Only pesticide in the equilibrium domain (indicated by the dashed line) is subject to degradation

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:

$$M_p = Vc_L + M_S(X_{EQ} + X_{NE}) \tag{E1}$$

$$X_{EQ} = K_{F,EQ}c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^{1/n} \tag{E2}$$

$$\frac{dX_{NE}}{dt} = k_{des}\left(K_{F,NE}c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^{1/n} - X_{NE}\right) \tag{E3}$$

$$K_{F,NE} = f_{NE}K_{F,EQ} \tag{E4}$$

$$\frac{dM_p}{dt} = -k_t(Vc_L + M_sX_{EQ}) \tag{E5}$$

$$K_{F,EQ} = m_{OM}K_{om,EQ} \tag{E6}$$

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 (days^{-1}), f_{NE} is the factor describing the ratio between non-equilibrium and equilibrium Freundlich coefficients (−), k_t is the degradation rate coefficient (days^{-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}.

Appendix F – Overview of recommendations and editorial issues

Section in draft guidance	Issue
Section 3.1 Soil selection and preparation	Regarding soil sampling and assumptions regarding when samples are from the same soil the Panel recommends the following (see Section 6.3 of this Opinion): • sample soil for the batch adsorption experiment (OECD 106) and the aged sorption experiment at the same time; • perform sampling by taking a number of small subsamples and pool them to get an average of the soil in a given field or plot; • take care when assuming that samples from the same location are from the same soil if more than one growth season has passed between samplings.
Section 3.1 Soil selection and preparation	Regarding the minimum number of samples the Panel recommends (see Section 6.6 of this Opinion for details): • The majority of experiments (with a minimum of four experiments) should show aged sorption behaviour (i.e. f_{NE} and k_{des} values are reliable) as a conservative approach.
Section 3.3 Extraction and analysis	The Panel has the following recommendations concerning the extraction procedures (see Section 6.5 of this Opinion for details): • The same extraction procedure should be used in all laboratory experiments investigating aged sorption in a dossier (the same extraction procedure applied to the different soils). Once an extraction procedure has been selected for a particular compound, the same procedure should be used for all soils to derive specific aged sorption parameters. • The selected method to perform the extraction procedure should be proven to provide adequate and consistent results by producing yield of extraction in line with current standards. For the initial time point, the extraction should be close to complete (yield of extraction of 100% +/− 10%). Mass balance should also be available for later time points. • If different extraction procedures are used, results on aged sorption parameters should be treated independently for the same compound (results from the same soil using different extraction procedures should not be mixed). • Values from one extraction procedure should not be converted for use in a data set with another extraction procedure. • Very dry conditions during all phases of the experiment should be avoided. Preferably freshly collected soil is used. Freezer storage of the soil samples should also be avoided and storage in a cold place (4°C) should be preferred.
Sections 3.4 and 4.1.2 Legacy studies	The Panel defines legacy studies as studies that were performed before the experimental setup laid down in this guidance was published. However, when such a study is consistent with the setup in this guidance and meets the requirements, it is not considered a legacy study. The Panel has the following recommendations regarding legacy studies (see Section 6.4 for details): • A minimum of six sampling points (after elimination of outliers and data below the LOQ) is also required for legacy studies. • Extraction times of between 8 and 48 h can be accepted for legacy studies. • 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. • If both legacy studies and new studies are available, the studies can only be considered as one data set if they have been performed using the same extraction procedure. • No other deviations are accepted for legacy studies.

Section in draft guidance	Issue
4.1.4 Outliers	The following recommendations are made (see Section 3.3.1 for details): • Removal of data points as outliers must be justified by a (significant) improvement of the goodness of fit criteria (lower- χ^2-error for both total mass and concentration in the liquid phase as well as for the apparent k_D) and of the acceptability criterion of the fitted parameters (lower relative standard error) for the optimisation without the outlier (s). This implies that the results for the fits with and without outliers have to be reported. • If a measurement is identified as an outlier in one of the dependent variables (total mass or concentration in the $CaCl_2$ suspension) only, both the measurements of total mass as well as concentration in the $CaCl_2$ suspension, have to be eliminated for that sampling time point. If after this elimination only one measurement (single replicate) of mass and concentration is available at a specific sampling time point, the Panel also recommends eliminating these measurements.
Section 4.3 Tools	The Panel recommends that a user-friendly software tool be developed that supports the full workflow in the guidance document and that produces all graphs and statistics needed. This tool should meet the following minimum requirements (Section 6.2 of this Opinion): • Capabilities: – The software tool should be able to calculate all parameters of the aged sorption model. – It should be able to deliver all statistics that are used to assess the goodness of fit. – It should provide graphical information of the fits and the residuals. • Documentation: – A description of the implementation of the aged sorption concept in the software must be available: – A user manual, i.e. a detailed description of how the tool is operated, must be available. This should include a description of model inputs and outputs. – A description of all statistics or a reference to documentation in which the statistical methods are fully described must be available. – A description that the tool works correctly (e.g. by testing against a benchmark data set) should be provided. • Compatibility: – The tools should be available for major operating systems (like Windows 7–10). • Availability: – Easily obtainable, for example, downloadable from a website. – Support from the developer or distributor of the software. – Earlier versions, if applicable, should be available upon request. – Preferably the tool would be available free of charge. • User interface: – To facilitate use of the tool by regulators, the software tool should be accessible via a graphical user interface. The general setup of the user interface should be discussed with regulators and developers of the tool. – Functionality to run the tool in batch mode would be a helpful addition.
4.4.2 Fitted parameters	• The Panel does not recommend refinement options for the inverse optimisation, since this may lead to additional discussions and expert judgement decisions in the absence of clear recommendations on when to consider a refinement fit superior to the fit obtained without refinement. The only option recommended is to use $K_{om,eq}$ as a fitting parameter (see Section 3.3.2 of this Opinion for details).

Section in draft guidance	Issue
4.5.1 Visual assessment of model fit	• The Panel is generally reluctant to eliminate data points from a data set and therefore recommends that early time point(s) (< 2 days) are not eliminated from the model fitting, other than when these points can be considered as outliers (see Section 3.3.3 of this Opinion).
Section 4.5.2 Visual assessment of weighted residuals	• The Panel recommends that only a trend in the weighted residuals of both total mass and concentration in the $CaCl_2$ suspension invalidates the aged sorption model used. The soil should then be classified as having 'zero aged sorption' according to the terminology in the decision tree in the draft guidance document (see Section 3.3.4 of this Opinion).
Section 4.5.3 χ^2	• To harmonise the calculations of the χ^2-error of the apparent K_D, the Panel recommends using the unweighted method using the same number of fitting parameters as for the accompanying fit on mass and concentration. This recommendation is not based on any statistical justifications, but on the fact that the observations only consist of one dependent variable (apparent K_D). This is in line with existing guidance on kinetic degradation (FOCUS, 2006). The Panel also recommends implementing the calculation of the χ^2-error for weighted and unweighted observation in the software tool (see Section 6.7 of this Opinion).
Section 5.3.2 Calculating the average aged-sorption parameters	• If the data set includes soils with 'zero aged sorption' (i.e. f_{NE} and k_{des} values are equal to zero), the Panel proposes that the weighted average geomean is used according to Habib (2012). See Section 6.6 of this Opinion for details).
Section 5.3.3 Estimating $DegT50_{EQ}$ values from lower-tier DegT50 values	• The Panel recommends that a refit of the aged sorption model to the original data (total mass only) is always the preferred option for the conversion of lower-tier degradation endpoints. If raw data and sufficient information from the Tier 1 study is not accessible to perform an inverse optimisation, scaling factor method 1 is recommended, and finally, when not all information for this method is accessible, scaling factor method 2 is to be used (See Section 3.3.5 of this Opinion).
Section 5.3.2 Calculating the average aged sorption parameters	• In regulatory practice, aged sorption experiments may be available from different studies, e.g. in the reassessment procedure of active substances. If different extraction procedures have been used for total mass, the Panel recommends treating these studies as different data sets. In that case the Panel recommends not to use the refit or the scaling factor 1 or 2 approaches for soils with an additional $CaCl_2$ extraction, but to directly use the fitted $DegT50_{EQ}$ from the aged sorption experiments, since it is the best estimate for this parameter. For first-tier soils without an additional $CaCl_2$ extraction, the geometric mean f_{NE} and k_{des} parameters should be derived from all available higher-tier studies (Section 3.3.5 of this Opinion). • PEARLNEQ v5 offers an option to perform temperature normalisation. However, the Panel argues that this procedure is prone to error and the Panel recommends performing the normalisation of $DegT50_{EQ}$ to the reference temperature outside PEARLNEQ. In PEARLNEQ v5 this is achieved by setting the reference temperature to the incubation temperature.
Section 5.3 Combining lower-tier and higher-tier data	• All available lower-tier data on degradation and adsorption must be considered in higher-tier groundwater risk assessments because averaging all available data on degradation gives the best possible estimate of the underlying statistical population of agricultural fields (see Section 3.3.5 for details). • It is recommended that a flow chart is included describing the workflow for combining first-tier data and aged sorption studies (see Section 3.3.6 for details).

Section in draft guidance	**Issue**
Chapter 6 Special considerations for metabolites	• The Panel recommends that aged sorption parameters for metabolites are derived only from metabolite-dosed studies. In this case the guidance for the parent compound also applies to the metabolite. The formation fraction can be derived from parent-dosed aerobic degradation studies, provided that the parent and metabolite are fitted with the best-fit model, which is the DFOP model in the case of aged sorption. When such studies are not available, the formation fraction should be set to the conservative value of 1 (see Chapter 4 for details).
Chapter 3 Experiments to derive aged sorption parameters Appendix 5 Use of field data	• The procedure for deriving aged sorption parameters from field studies in the draft guidance document does not appear to be well worked out and tested. Because this may lead to confusion in the regulatory process, the Panel recommends that the guidance is further developed and tested with real world data. Until this has been done, field studies should not be used to derive aged sorption parameters. When using field studies to derive aged sorption parameters, the Panel considers that the option to measure aged sorption in the laboratory and combine this with field data to determine a field $DegT50_{EQ}$ is not acceptable because this will lead to additional uncertainty as parameters from different studies or soils are to be mixed in the optimisation (see Chapter 5). • If agreed matrix DegT50 values from field studies have been derived according to EFSA (2014), the Panel recommends that these values should not be ignored but accounted for in the leaching assessment in line with EFSA (2014). This includes checking whether laboratory and field degradation data are from different populations. If the field degradation data indeed represent a different population, the Panel recommends using the matrix DegT50 values without converting them into $DegT50_{EQ}$ values (see Chapter 5 of this Opinion).
Appendix 3 Uncertainty review	• The draft guidance estimates that most sources make a minor contribution to the overall uncertainty in the leaching assessment. The Panel notes that the wording 'minor' is optimistic in view of the potentially large effect of including aged sorption in the leaching assessment and therefore recommends that this wording be reconsidered (see Chapter 7 for details). • Given the importance of the K_{om} and 1/n values for the leaching assessment, the Panel recommends that the quality checks outlined in EFSA (2017a) are always applied. Given the importance of the curvature of the Freundlich isotherm, it is further recommended to only accept Freundlich exponents from studies of which sorption coefficients are accepted to be included in the 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 (refer to Chapter 7 of this Opinion and Section 6.2 in EFSA PPR Panel, 2015). • The Panel recommends that time-dependent sorption is not applied to cases where there is strong evidence for, for example, pH-dependent sorption unless more evidence becomes available on how to handle it (Chapter 7 of this Opinion).