Evidence for aged sorption to be used in combination with field degradation studies in regulatory assessments

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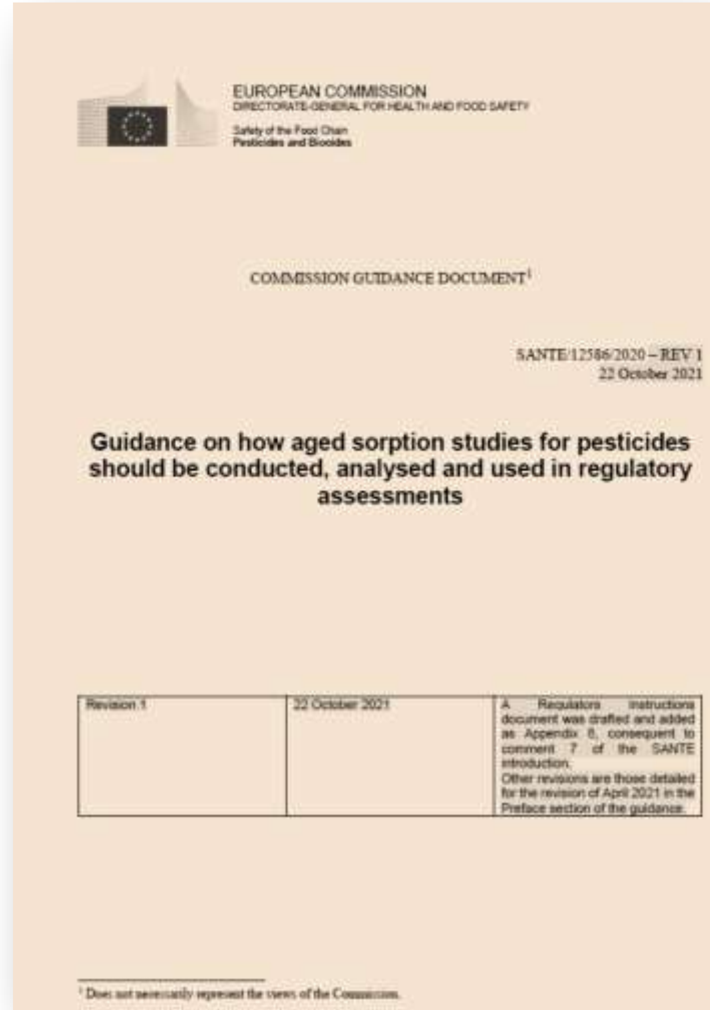
Situation: EU aged sorption guidance

- Finally approved in EU (not yet in GB) after approximately 14 years of development
- Great achievement in considering an important efate process in regulatory exposure (leaching) assessments
- Filling a gap in the FOCUS tiered approach
- However, applicability limited due to restrictions regarding field DegT50 in combination with aged sorption
- Use of aged sorption as higher tier process often at cost of using field DegT50 values



EUROPEAN COMMISSION
DIRECTORATE-GENERAL FOR HEALTH AND FOOD SAFETY
Safety of the Food Chain
Pesticides and Biocides

COMMISSION GUIDANCE DOCUMENT[1]

SANTE/12586/2020 – REV 1
22 October 2021

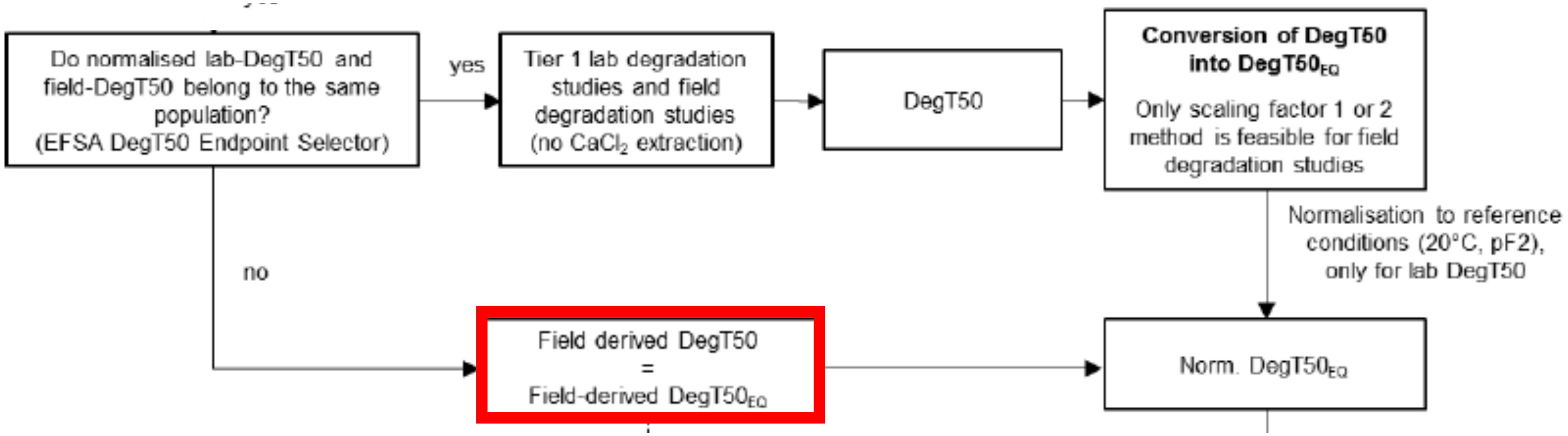
Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments

Revision 1	22 October 2021	A Regulatory instructions document was drafted and added as Appendix 8, consequent to comment 7 of the SANTE introduction. Other revisions are those detailed for the revision of April 2021 in the Preface section of the guidance.

[1] Does not necessarily represent the views of the Commission.

Use of field data in the aged sorption guidance

- If lab **and** field DegT50 values are the same statistical population, then:
  - $DegT50_{EQ}$ is calculated from the Field DegT50 with Scaling Factors
  - The overall geomean $DegT50_{EQ}$ is then calculated [lab+field]
- If the field $DegT_{50}$ values are a different statistical population, representing the majority of cases, then:
  - Leaching assessment is based on geomean of field DegT50
  - $DegT_{50EQ}$ is set equal to un-corrected field DegT50 (also for lab DegT50 >240 days)
  - This option underestimates degradation in (leaching) modelling (will be demonstrated later in this talk)



Restriction to use $DegT50_{EQ}$ from field studies

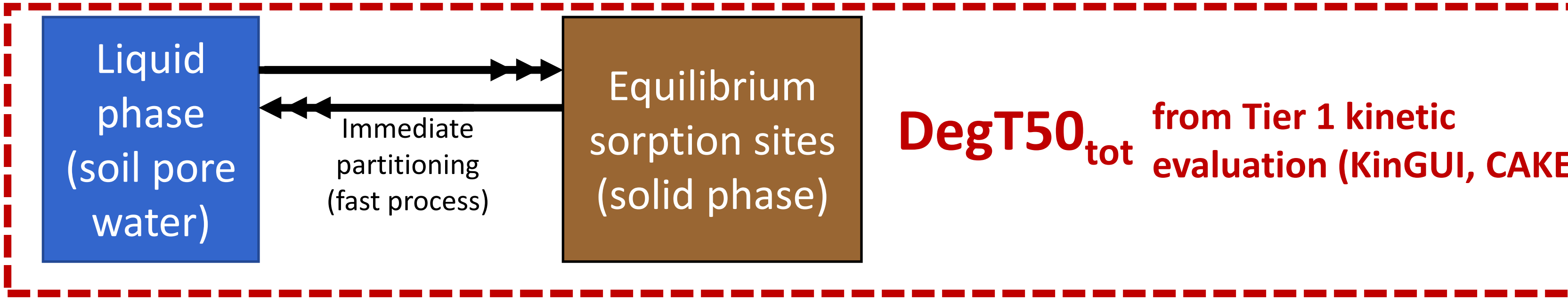
If field *DegT50* values represent a different population, and the field *DegT50* values are statistically shorter than the laboratory *DegT50* values, the EFSA PPR panel (2018) considers that rescaling the field *DegT50* data on the basis of laboratory aged sorption data is not justifiable because there is no experimental evidence that the extent of aged sorption in the laboratory and in the field is the same.

=> guidance includes an opening clause

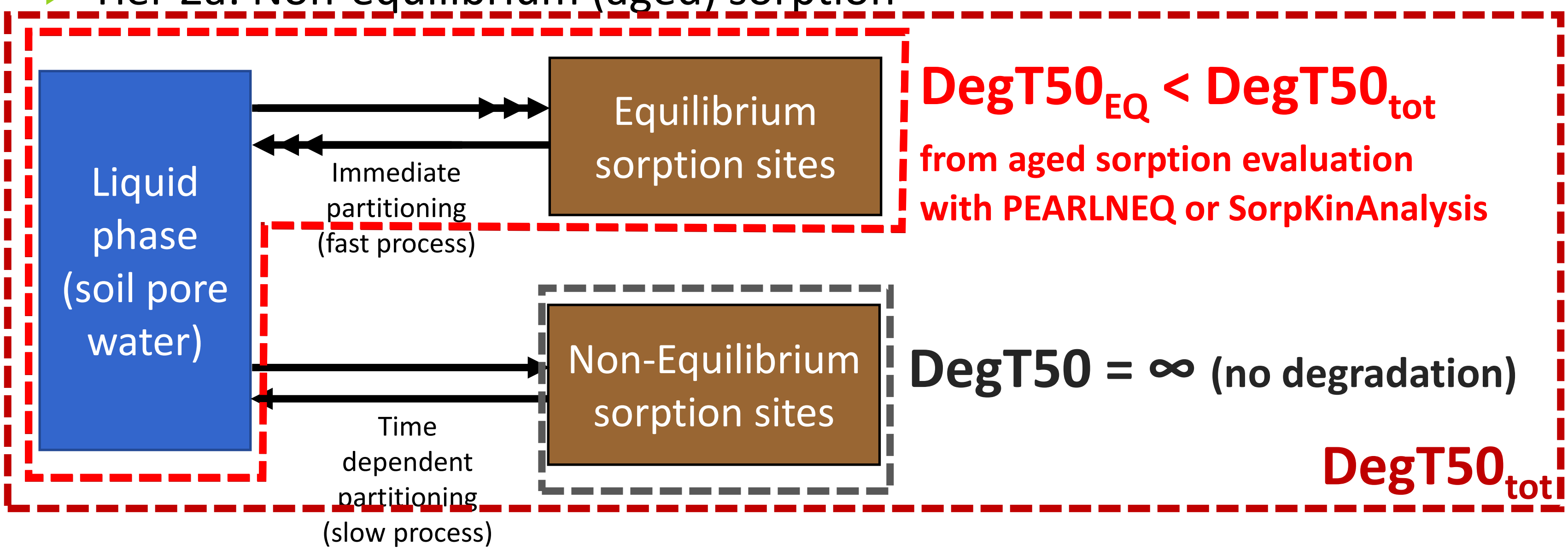
The PPR Panel (2018) considers that ideally the aged sorption parameters and the field degradation half-lives would be obtained simultaneously using inverse modelling. Industry are preparing evidence for aged sorption in field studies and this option should replace the current recommendations as soon as appropriate guidance has been developed and tested.

Why is scaling of DegT50 to $DegT50_{EQ}$ needed ?

- Tier 1: Equilibrium sorption

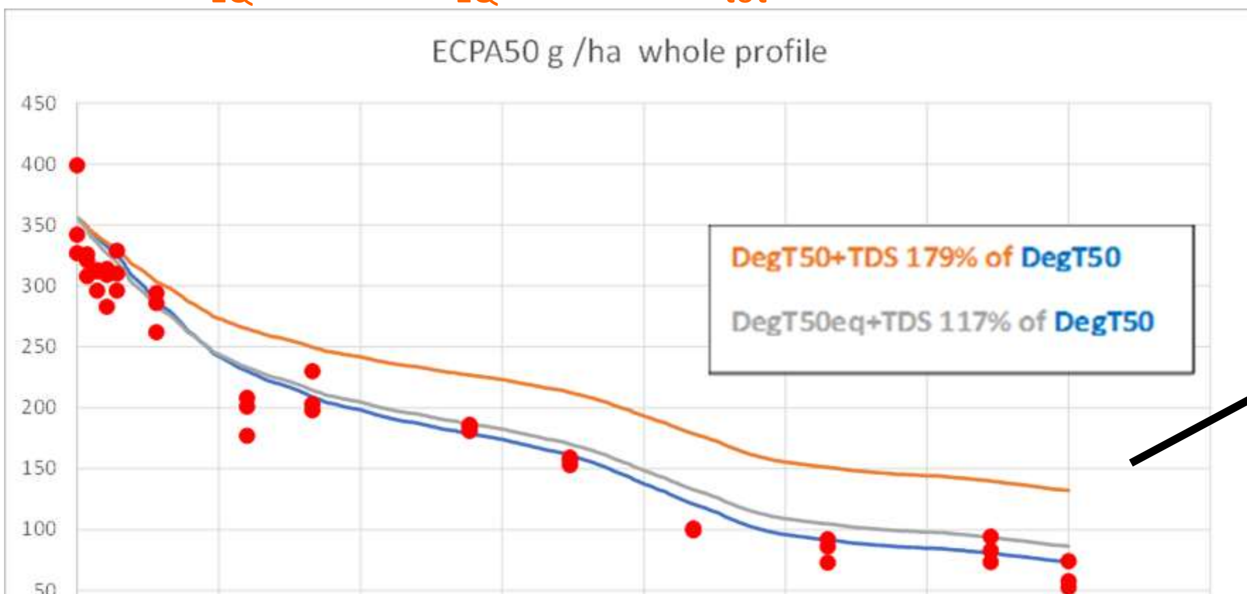


- Tier 2a: Non-equilibrium (aged) sorption



Effect of non-scaling of $DegT50_{EQ}$ with aged sorption

- Blue line: Optimized Tier 1 $DegT50_{tot}$ (time-step according to $FOCUS_{kinetics}$)
- Grey line: Simulated with aged sorption model (TDS) with scaling of $DegT50_{EQ}$ (Scaling Factor 1) => 117% of residues at last sampling
- Orange line: Simulated with aged sorption (TDS) model without scaling of $DegT50_{EQ}$ ($DegT50_{EQ}$ = $DegT50_{tot}$) => 179% at last sampling

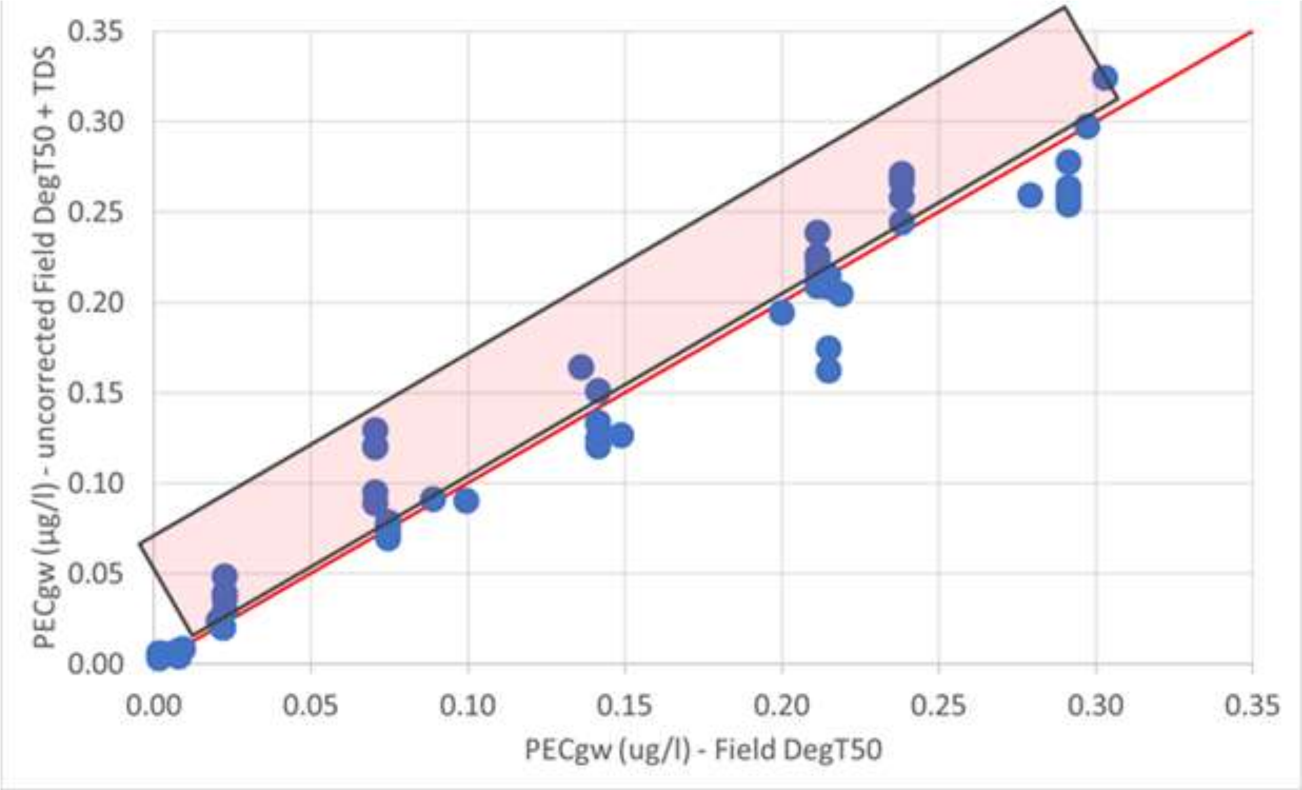


	$DegT50_{EQ}$ $=DegT50_{tot}$
ECPA 50 #1	147
ECPA 50 #2	231
ECPA 50 #3	137
ECPA 50 #4	155
ECPA 50 #5	179
ECPA 50 #6	192
ECPA 06 #1	162
ECPA 06 #2	198
ECPA 06 #3	161

Conclusion:
- Non-scaling of $DegT50_{EQ}$ results in an overly conservative prediction of residues
- Scaling of $DegT50_{EQ}$ results in a conservative but realistic estimate of residues

Impact of non-scaling of $DegT50_{EQ}$ on PECgw

- PEARL maize, all 8 FOCUS scenarios, 14 test substances with range of efate properties
- PECgw is similar: Aged-sorption 'compensates' for increase in DT50
- A significant number of PECgw values are even higher which does not make sense
- Counterintuitive: Significantly lower PECgw expected if sorption clearly increases with time



Conclusions so far and possible solutions

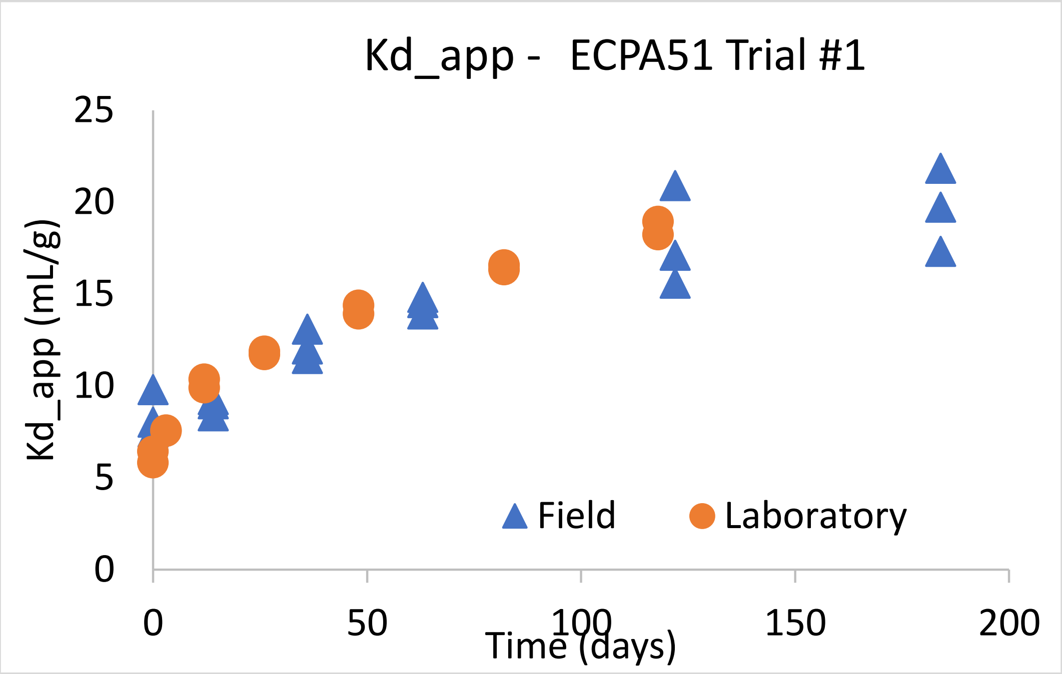
- Non-scaling of the $DegT50_{EQ}$ combined with lab aged sorption parameters is overly conservative => use of appropriate $DegT50_{EQ}$ is required
- Two options:
  - Option 1: $DegT50_{EQ}$ to be derived from field aged sorption studies, however:
    - Legacy field studies cannot be used
    - Tests have shown that scattering of field data do not allow for deriving aged sorption parameters (including $DegT50_{EQ}$) that fulfil the statistical quality requirements of the aged sorption guidance
  - Option 2: Use of laboratory aged sorption parameters and scaling of field $DegT50_{EQ}$ values using scaling factors (or inverse modelling)
    - A method is required for checking for the relevance of aged sorption in field comparable to lab to justify scaling of $DegT50_{EQ}$

Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing apparent K_d-values (K_{d_app}):

- Available from $CaCl_2$ extraction in lab aged sorption studies)
- Additional $CaCl_2$ extraction data from soil samples of field study necessary (some examples might be sufficient)

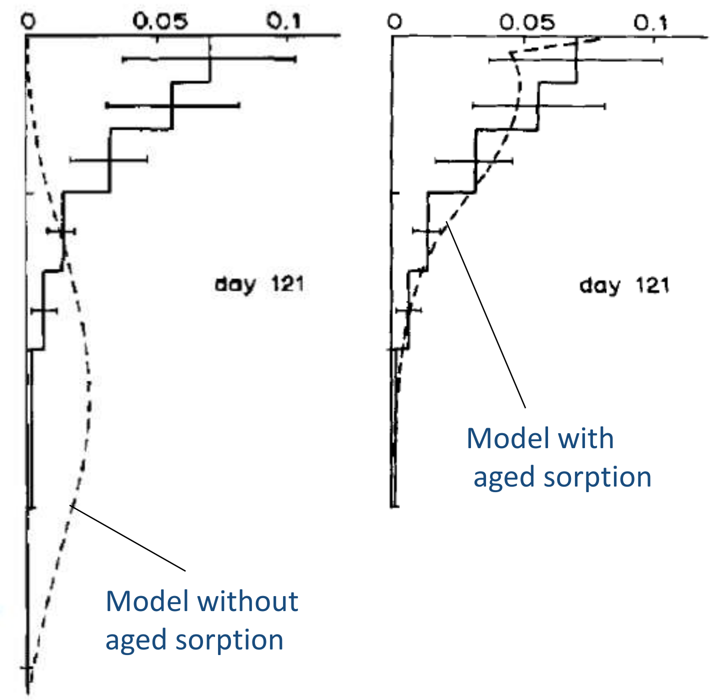
- Available data show that increase in K_{d_app} with time is comparable in lab and field soils
- Data indicate comparable aged sorption behaviour



Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles

- Predict field study leaching profiles with and without aged sorption
- Test hypothesis:
  If observed leaching in field study is less or equal than simulated with aged sorption using lab aged sorption parameters, the field soils show a comparable or even stronger effect of aged sorption as in the lab
- Evidence from literature:
  e.g. Boesten et al. (1989)



Simulated measured cyanazine depth profiles with and without aged sorption model (Boesten 1989)

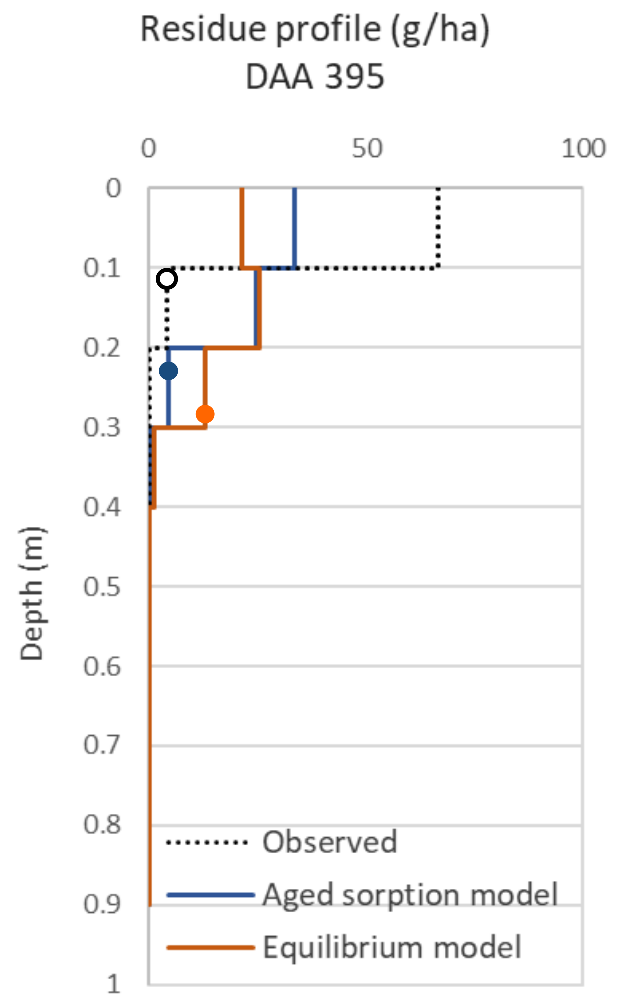
Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles

- Metric for leaching depth, to allow quantitative comparison between graphs
- Assuming that substance is evenly distributed in measured (and simulated) sample layer =>no better info available

P5 [cm] = 5% of residue below this depth (95% above)

- ○ Field observations: P5 is 11.3 cm
- ● Aged sorption model: P5 is 23.0 cm
- ● Equilibrium model: P5 is 28.6 cm

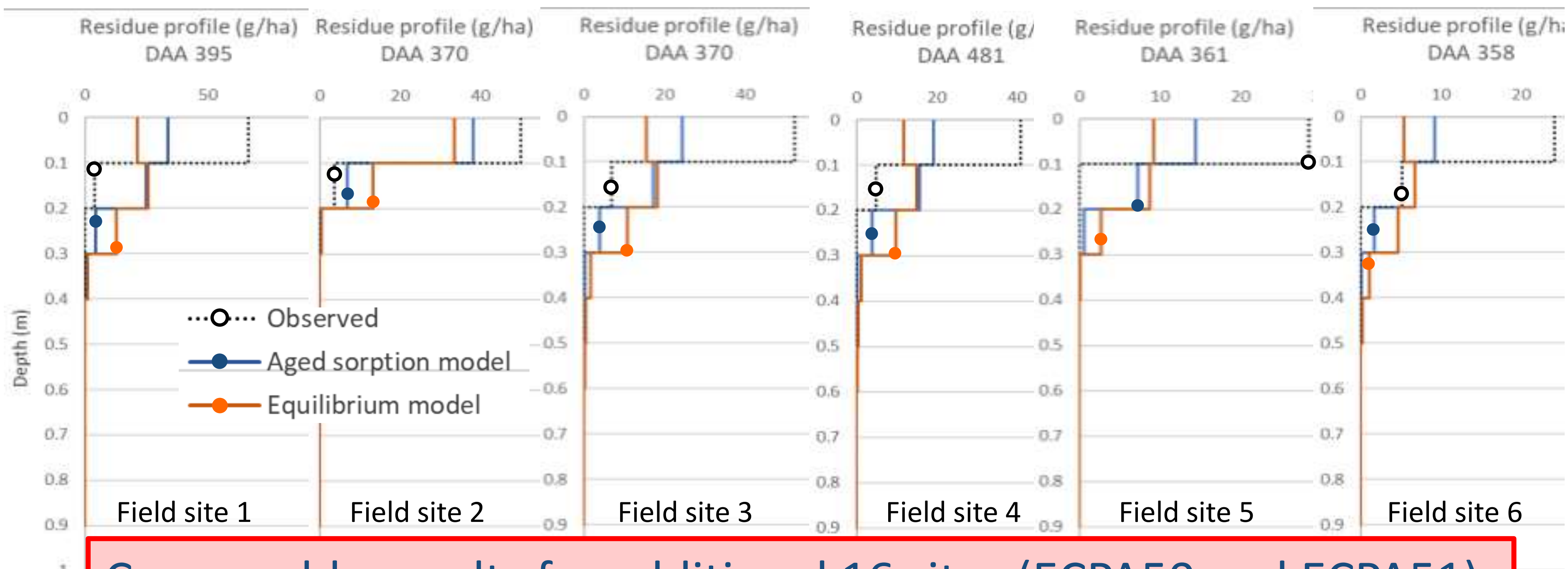


Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles

- P5 calculated for latest sampling times
- Consistent picture - depth of: Equilibrium model > aged sorption model > measured
- Evidence that considering aged sorption in modelling is more realistic but still conservative

Data set ECPA06



Comparable results for additional 16 sites (ECPA50 and ECPA51)

Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles

Uncertainty analysis

- Standard FOCUS default values have been used for the modelling, but some of those factors can influence the results
- Checks were made on the uncertainty effects of ***dispersion length*** and ***evapotranspiration*** on the observed mobility:
  - Dispersion length reduction to 1.25 cm (default 5 cm)
  - Evapotranspiration increased by 20%
  - Both of these reduce apparent mobility, but how do they impact on the significance of aged sorption effects?
- ECPA06: No site-specific K_{OM} available - effect of min/max vs geomean tested

Factors did have an influence on the simulated depth profiles but the simulations were still more conservative than the measurements ($P5_{sim\text{-}Tier\text{-}1}$ > $P5_{sim\text{-}aged\text{-}sorption}$ > $P5_{measured}$)

Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Conclusions on comparing concentration depth profiles

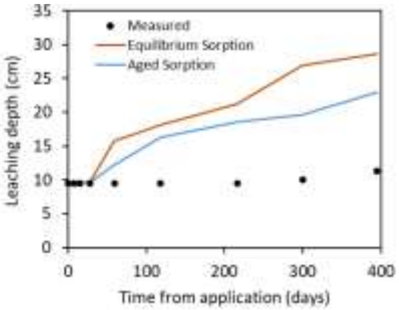
- All **22 field data sets** evaluated showed the same qualitative picture
  - $P5_{sim\text{-}Tier\text{-}1} > P5_{sim\text{-}aged\text{-}sorption} > P5_{measured}$
  - Simulation closer to reality when aged sorption included
- Equilibrium sorption (Tier-1) significantly over-predicts mobility
  => aged sorption was a relevant process in the field
- Inclusion of lab aged sorption parameters reduces, but still over-predicts observed mobility
  => indication that lab aged sorption parameters are conservative
- P5 can easily be calculated also for legacy field studies
  => testing evidence of lab aged sorption for field conditions can be performed on individual basis

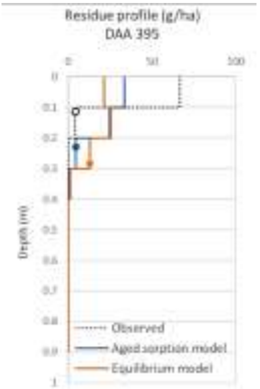
Overall conclusions

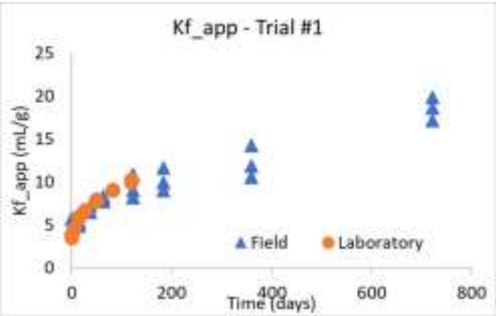
- In depth analysis as weight-of-evidence using high quality data sets have shown that aged sorption in field is relevant
  - Comparable increase of apparent K_d - values in lab and field soils
  - Predicted vs observed concentration profiles show conservative estimation of leaching when using lab aged sorption parameters
- The P5-value (5% of residue below this depth) is considered to be an appropriate measure for characterizing the leaching
- P5-value can be used to demonstrate relevance and conservativeness of lab aged sorption parameters versus field aged sorption
- If $P5_{sim\text{-}aged\text{-}sorption} > P5_{measured}$ it should be allowed to combine lab aged sorption parameters with field degradation value
  => scaling of $DegT50_{field}$ to $DegT50_{EQ,field}$

Next Steps

- Write up the proposals….. For revision of the Guidance Document
- **Weight-of-evidence approach to show that aged-sorption is relevant under field conditions:**
  - The P5 metric (P5: depth of 5% mass) can be calculated for all studies – legacy and new
  - Residue decline profiles can be calculated for all studies – legacy and new
  - K_{f_app} data may be available for a few studies but mostly not for legacy studies: It is not seen necessary to include it as standard requirement







Thank you for your attention – Questions?

How to perform the scaling of $DegT50_{EQ}$

- The guidance document provides two Scaling Factors that can be used to derive conservative estimates of $DegT50_{EQ}$ from $DegT50_{tot}$ values:

1. Scaling factor 1 (Boesten and van der Linden, 2001, modified by safety factor):

$$DegT50_{EQ} = DegT50 * \frac{1.1 * (w + K_{OM} * f_{OM})}{w + (1 + f_{NE}) * K_{OM} * f_{OM}}$$

2. Scaling factor 2 (Boesten-van der Linden, 2001, simplified and modified):

$$DegT50_{EQ} = DegT50 * \frac{1.2}{(1 + f_{NE})}$$

where:

ω = volumetric soil water content

$\mathbf{f_{NE}}$ = ratio of non-equilibrium and equilibrium sorption (aged sorption fitting parameter)

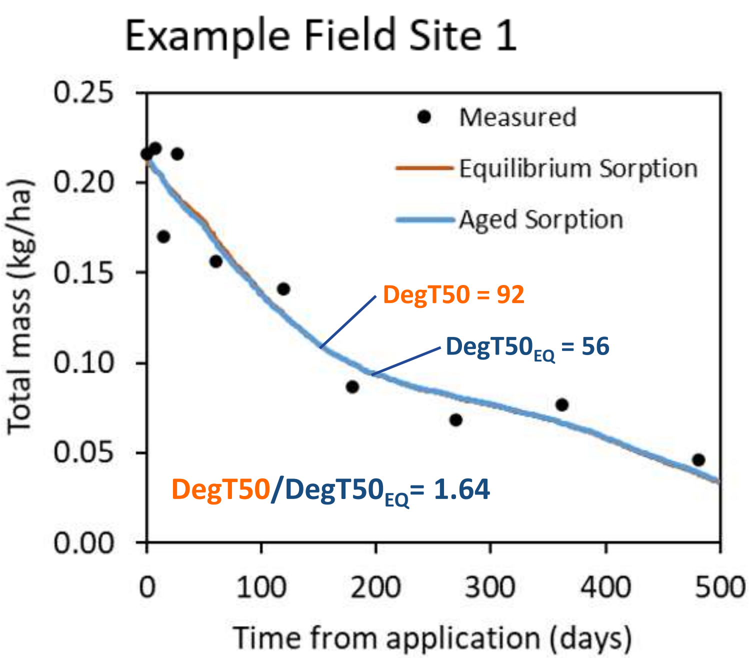
$\mathbf{f_{OM}}$ = organic matter fraction

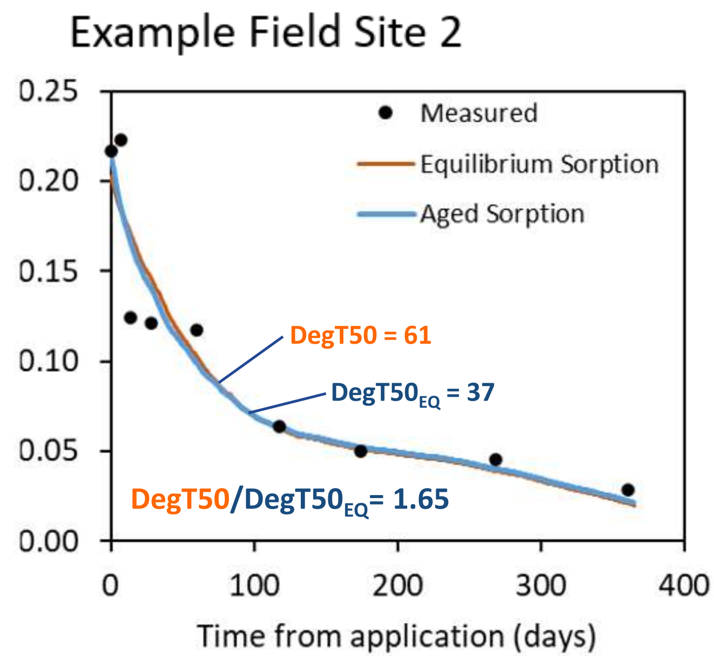
K_{OM} = organic matter normalised sorption coefficient => $\mathbf{f_{OM} * K_{OM} = K_f}$

3. Inverse modelling of field study under consideration of aged sorption => currently not considered in guidance

Deriving $DegT50_{EQ}$ with inverse modelling (Option 3)

- Aged sorption parameters from lab study (geomean)
- Optimise DegT50 / $DegT50_{EQ}$ using parameter fitting tool PEST in combination with PEARL
- Significant differences between $DegT50_{tot}$ and $DegT50_{EQ}$ found

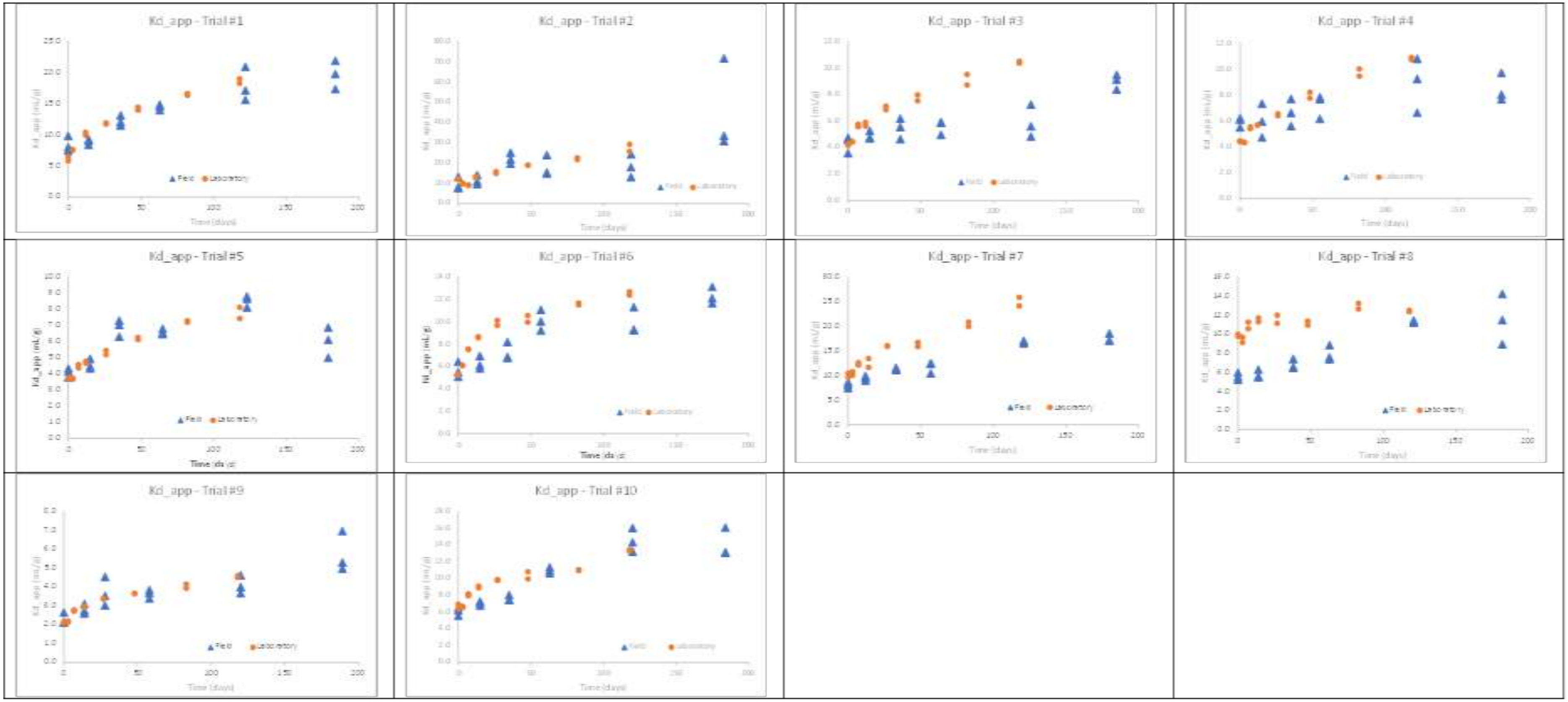




Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing apparent Kd-values - ECPA51: 10 valid datasets available

- All show evidence of comparable increased sorption under field conditions



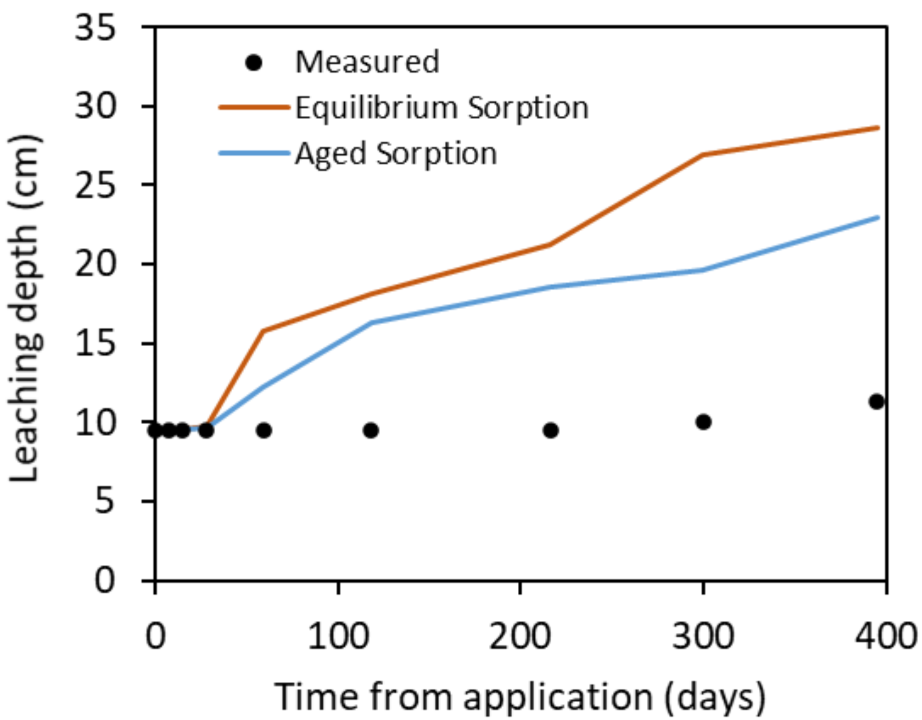
Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles

- Calculate P5 for all sampling timepoints
- The later the sampling the more visible is the effect of aged sorption

Depth (cm) reached by 5% substance

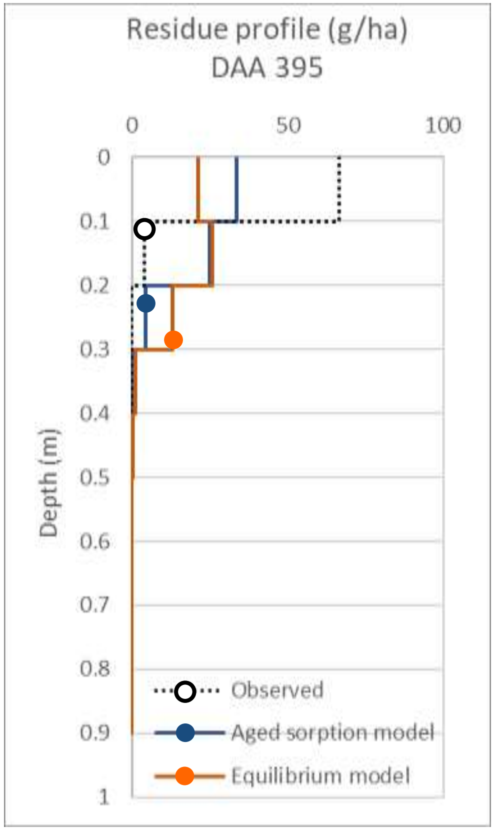
DAA	Measured	Aged sorption model	Equilibrium sorption model
0	9.5	9.5	9.5
7	9.5	9.5	9.5
15	9.5	9.5	9.5
28	9.5	9.7	9.8
59	9.5	12.2	15.8
118	9.5	16.3	18.1
216	9.5	18.6	21.3
300	10.1	19.7	26.9
395	11.3	23.0	28.6



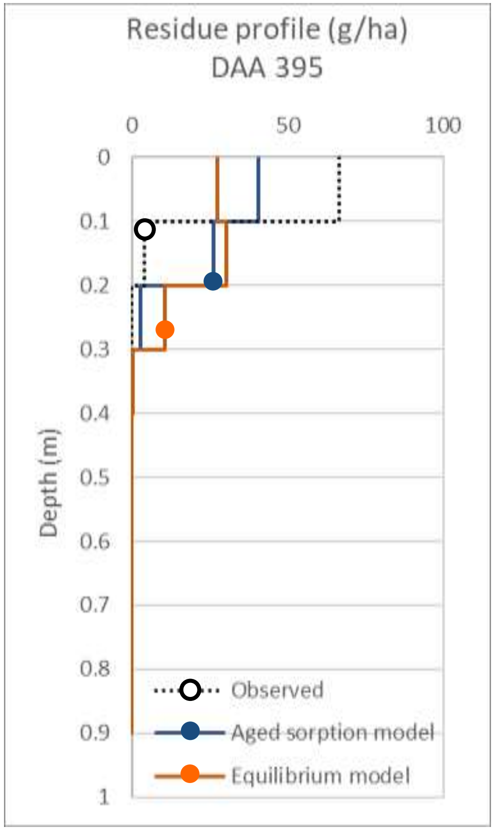
Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles - Test effect of ET_{pot}

Default values



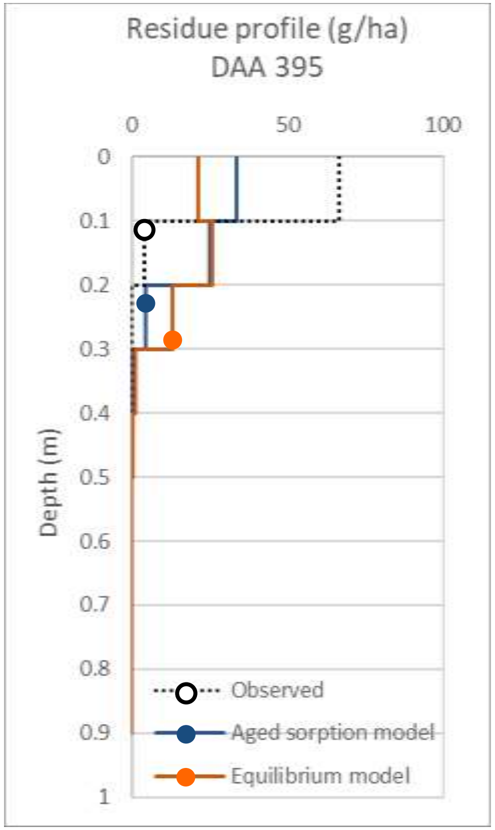
Increased ET_{pot} (+20%)



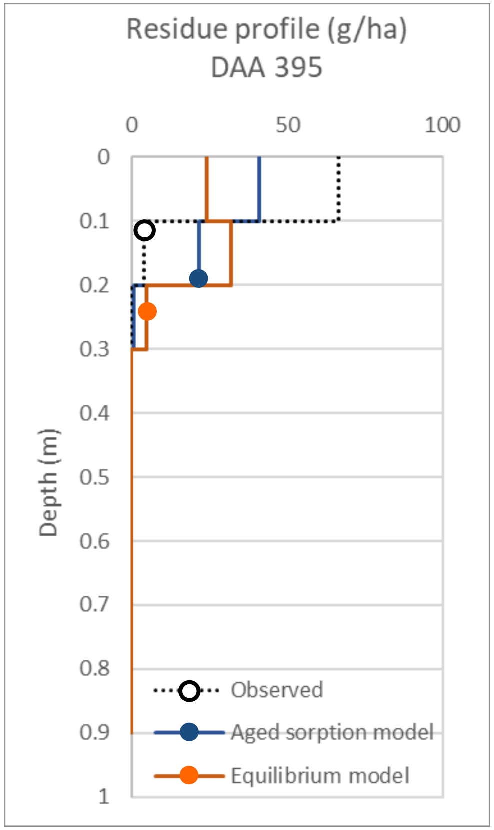
Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles - Test effect of dispersion length

Default value (5 cm)

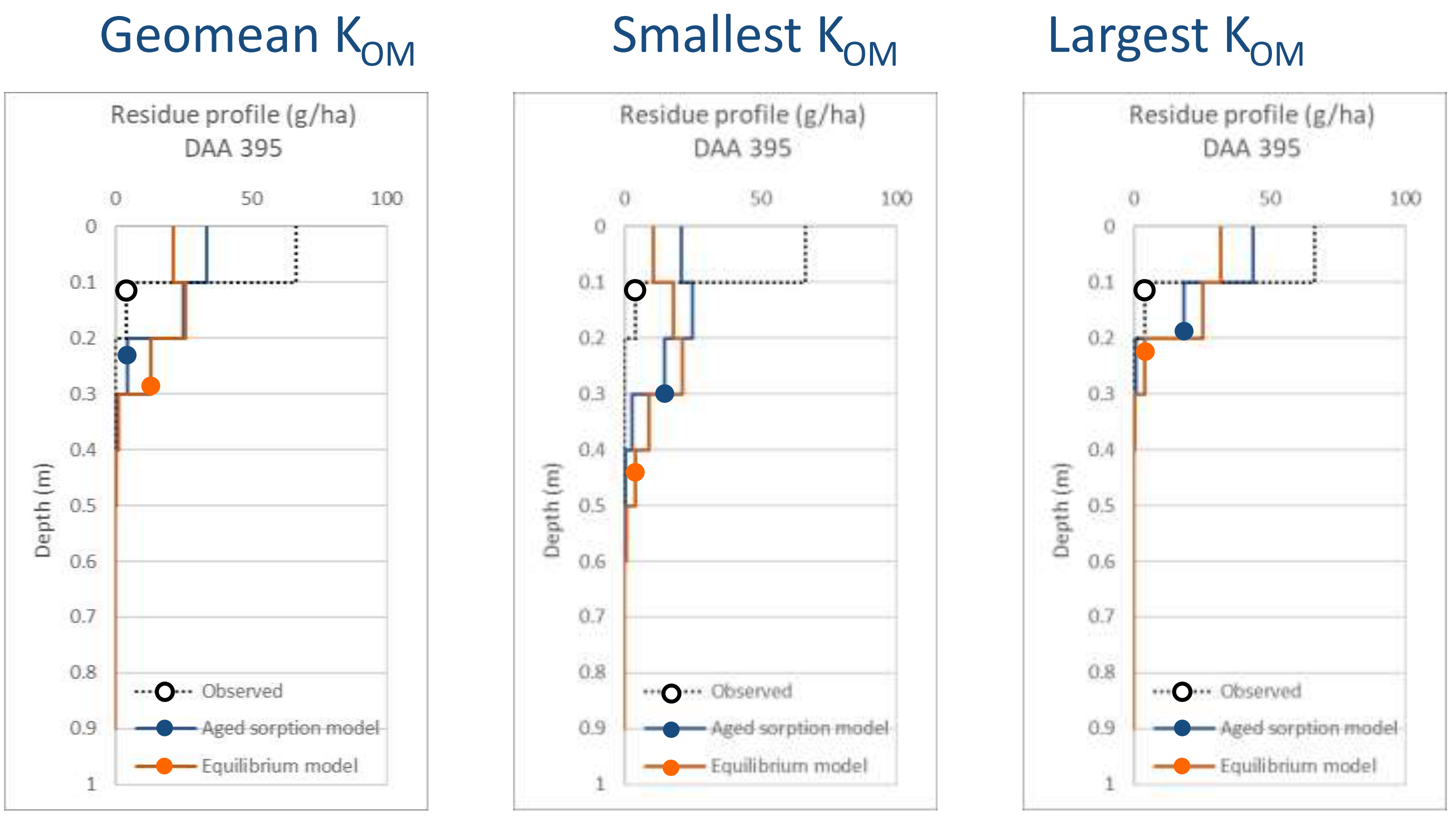


Reduced dispersion length (1.25 cm)



Option 2: Evidence of comparable extent of aged sorption under lab and field conditions

Comparing concentration depth profiles - Test effect of K_{OM}



$K_{OM,EQ}$ = 138 mL/g
1/n = 0.882

$K_{OM,EQ}$ = 71 mL/g
1/n = 0.882

$K_{OM,EQ}$ = 238 mL/g
1/n = 0.882