

German Environment Agency

Umwelt   
Bundesamt

10<sup>th</sup> European Modelling Workshop, 29<sup>th</sup> to 31<sup>st</sup> of August 2022, York

# Developing a guidance to consider pH-dependent degradation and adsorption in soil for environmental exposure assessment

Janina Wöltjen, Wolfram König, Wolfgang Janzen, Anne Osterwald<sup>1</sup>

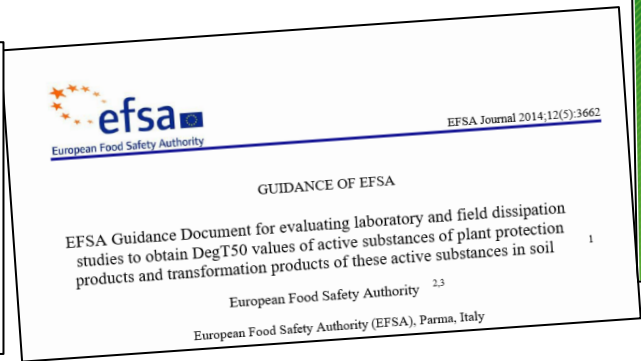
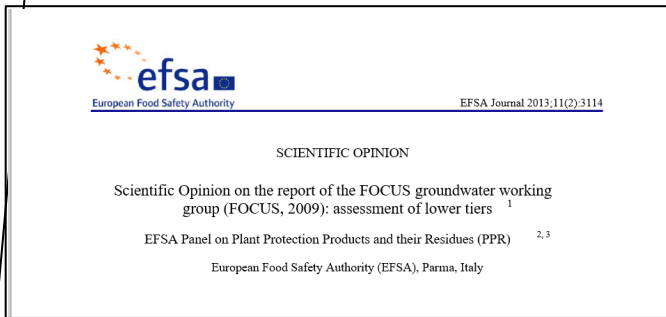
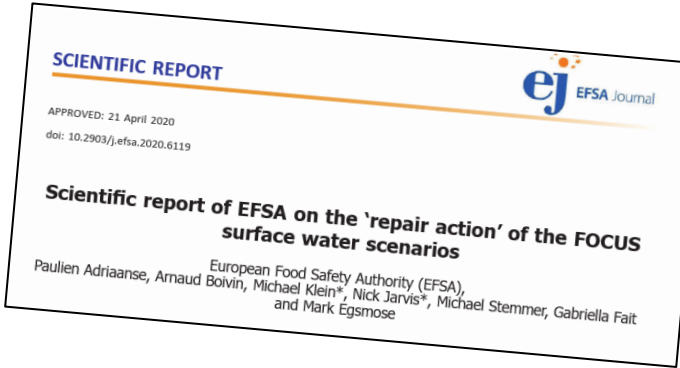
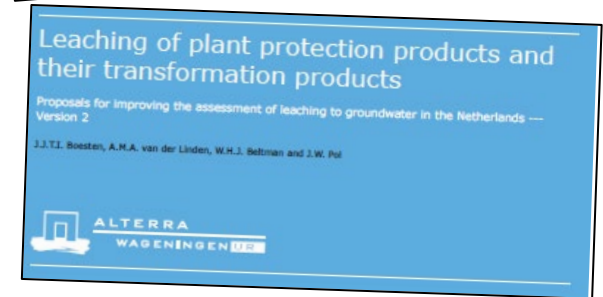
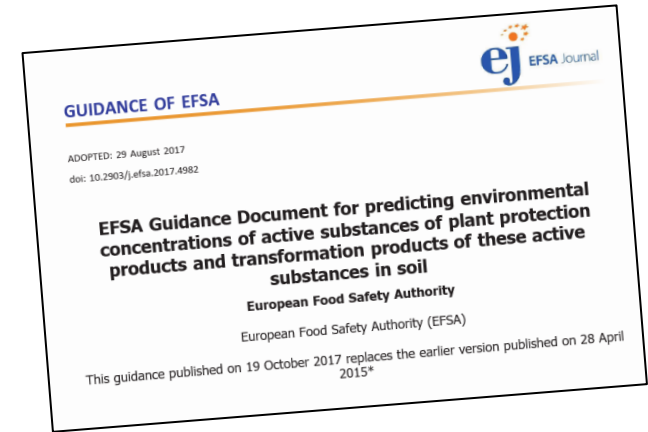
<sup>1</sup> Section IV 1.3-2 Environmental Exposure and Groundwater Risk Assessment of Plant Protection Products

# Outline

- **Background**
- **New draft pH Guidance**
- **Work in progress**
- **Outlook**

# Background

- Active substances and metabolites can exhibit **pH-dependent degradation and/or adsorption** in soil, which can have a strong impact on their environmental concentrations, e.g. in groundwater
- Several **documents of EFSA** (EFSA 2013, 2014, 2017 und 2020) and some **national guidance** (Boesten et al. 2015 und Holdt et al. 2011) discuss the topic in different regulatory contexts and for different environmental compartments
- **Individual solutions** were often developed during EU approval processes to address pH-dependencies in soil thereby establishing a **recurring methodology**



## New Draft pH Guidance

- We developed a **standardized step-wise procedure** to be used for EU approval and zonal registration on active substances and metabolites
  - To decide on possible pH-dependencies of degradation and/or adsorption in soil
  - To choose suitable endpoints for groundwater leaching assessment
- We programmed an easy-to-use **software tool** based on R to facilitate the evaluation of possible pH-dependencies and the choice of suitable endpoints

## Approach

- We compiled and evaluated information from existing guidance together with the individual solutions for active substances and metabolites
- We tested the newly developed step-wise procedure on real data of active substances and metabolites with known pH-dependency

### The pHADe\* tool:

Name of active substance or metabolite:

How many soils do you want to analyse:

1 Update/Clear Table

Inputdata

	Soil	pH <sub>H<sub>2</sub>O</sub>	pH <sub>KCl</sub>	pH <sub>CaCl<sub>2</sub></sub>	DT <sub>50</sub> (d)
1					
2					
3					

Note: clear existing entries in pH<sub>H<sub>2</sub>O</sub> column if they should be recalculated again.

Convert pH<sub>KCl</sub>/pH<sub>CaCl<sub>2</sub></sub> to pH<sub>H<sub>2</sub>O</sub> Save table as .csv

\* **pH**-dependent **A**dsorption and **D**egradation

# New draft pH Guidance

Dessau-Roßlau, 10 March 2021

## Recommendations for considering pH-dependent degradation and adsorption in groundwater modelling

Draft version 0.1, March 2021

### Abstract

During EU approval and for zonal and national registration processes of active substances and metabolites of plant protection products (PPP), their leaching potential to groundwater needs to be assessed. Several active substances of PPP and/or their metabolites exhibit degradation and/or adsorption behaviour, that depend(s) on the pH value of the soils, which can have a strong impact on their leaching behaviour and thus needs to be considered in groundwater

The screenshot shows the pHADe tool interface. At the top, there are tabs for 'pHADe', 'pH dependent Degradation?', and 'pH dependent Adsorption?'. Below the tabs, there is a text input field for 'Name of active substance or metabolite:'. Underneath that is a numeric input field for 'How many soils do you want to analyse:' with a value of '1' and an 'Update/Clear Table' button. Below this is a table titled 'Inputdata' with columns for 'Soil', 'pH<sub>H<sub>2</sub>O</sub>', 'pH<sub>KCl</sub>', 'pH<sub>CaCl<sub>2</sub></sub>', and 'DT<sub>50</sub> (d)'. The table has three rows numbered 1, 2, and 3. Below the table, there is a note: 'Note: clear existing entries in pH<sub>H<sub>2</sub>O</sub> column if they should be recalculated again.' At the bottom, there are two buttons: 'Convert pH<sub>KCl</sub>/pH<sub>CaCl<sub>2</sub></sub> to pH<sub>H<sub>2</sub>O</sub>' and 'Save table as .csv'.



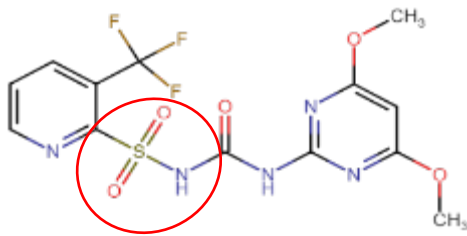
- **First commenting round** on new draft guidance and the pHADe tool from **May to Sept 2021**
- Currently revision and extension of the draft guidance

## New Draft pH Guidance

<b>Chapter 1</b>	Introduction
<b>Chapter 2</b>	Theoretical background on pH-dependent degradation and adsorption in soil
<b>Chapter 3</b>	Determination of pH-dependent degradation and/or adsorption in soil
<b>Chapter 4</b>	Choosing appropriate endpoints for groundwater modelling
<b>Appendices</b>	Reference, additional information, performed tests plus an example exercise

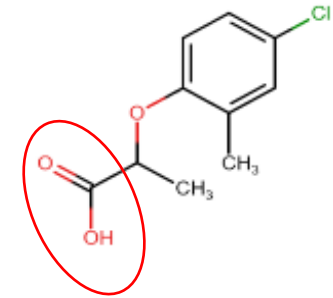
## Chapter 3 : Determination of pH-dependent degradation and/or adsorption in soil

### Check indications for pH-dependent behaviour in soil:



sulfonamide-group in Flazasulfuron

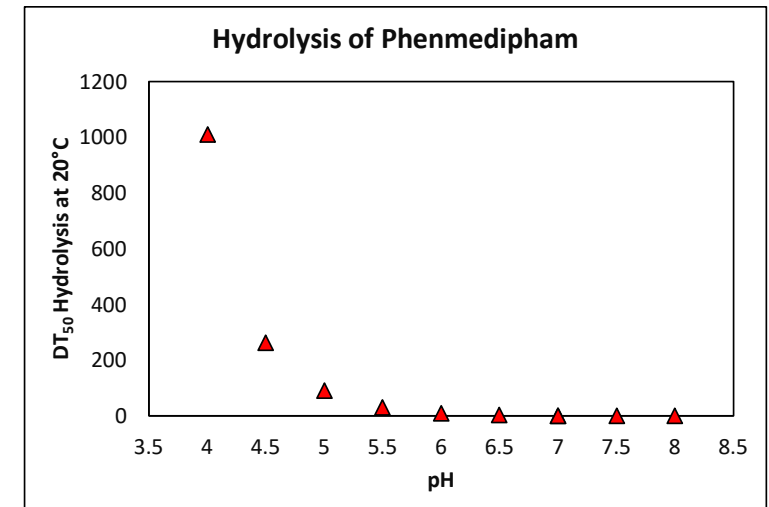
→ Check the chemical structure of the molecule for functional groups indicating pH-dependency



carboxyl-group in Mecoprop-P

→ Is the substance dissociating in the environmental pH range?  
Is a dissociation constant ( $pK_a$ ) available or can one be estimated and lies in the pH range between 2 and 9?

→ Check whether the other physiochemical properties such as  $\log K_{ow}$ , water solubility and hydrolysis are pH dependent



## Chapter 3 : Determination of pH-dependent degradation and/or adsorption in soil

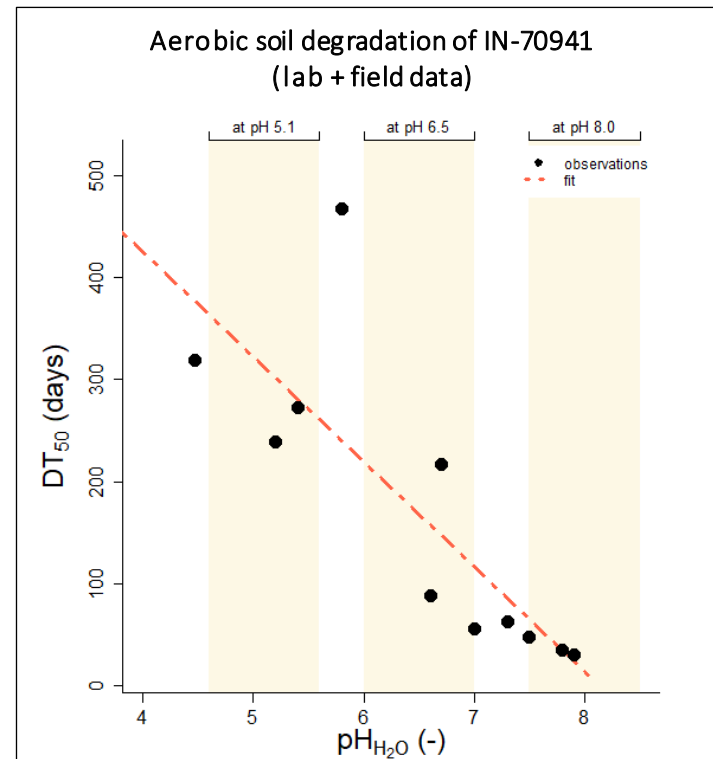
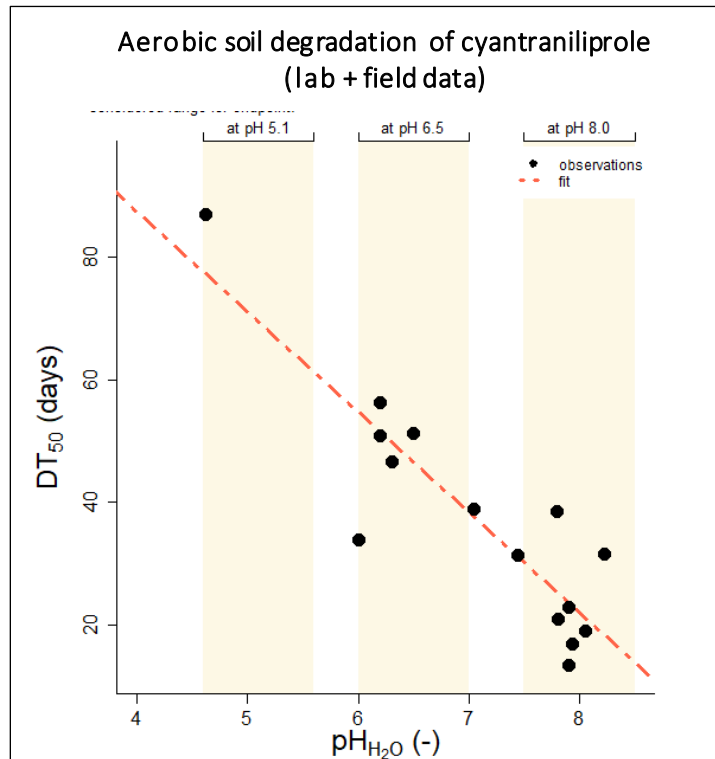
### Data preparations:

- Use pH values measured using the same method, preferentially in  $H_2O$
- For  $\geq 4$  data pairs (pH –  $K_{foc}$ , pH -  $DT_{50}$ ) perform **two-sided Kendall test** to test for correlation of the two parameters
- Prepare **visual fit** of the data pairs:
  - linear fit for  $DT_{50}$
  - sigmoid curve for  $K_{foc}$  of weak acids with one dissociating group (having a single  $pK_a$  value)
  - test different mathematical approaches for other dissociating substances (bases, amphoteric substances) and other parameters (formation fractions,  $1/n$ )
- Check whether pH values of investigated soils cover typical agriculture soil conditions in the EU or the respective registration zone in the EU or whether there are **data gaps**

# Chapter 3 : Determination of pH-dependent degradation and/or adsorption in soil

## Visual fit of $DT_{50}$ values versus pH in soils

- Use modelling endpoints (temp. and moisture normalized)
- Test laboratory and field data separately and together
- Test f.f. vs. pH in cases when  $DT_{50}$  values show pH-dependency



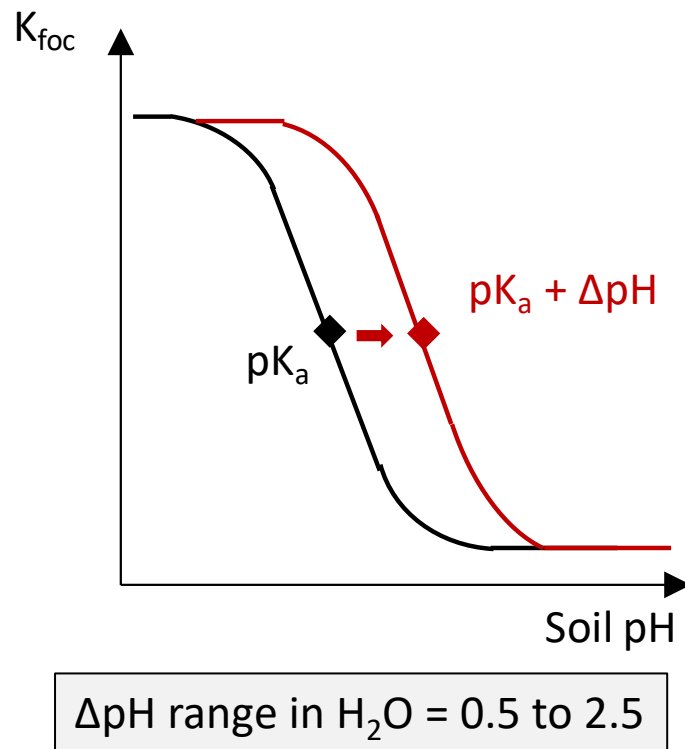
### Comments:

- How to deal with biphasic kinetics?
- Criterion for acceptability of linear relationship?
- ...

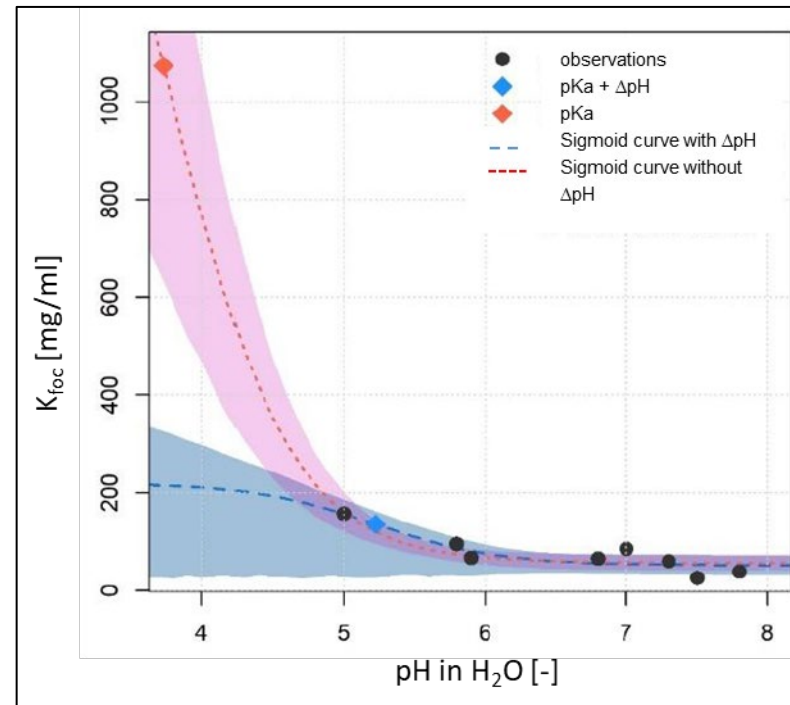
## Chapter 3 : Determination of pH-dependent degradation and/or adsorption in soil

### Visual fit of $K_{foc}$ values versus pH in soils (weak acids with a single $pK_a$ value)

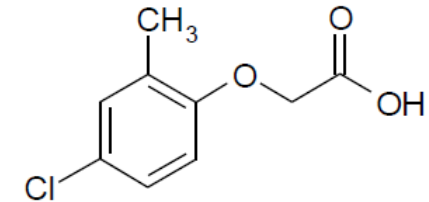
→ Sigmoid curve of  $K_{foc}$  values versus soil pH including  $\Delta pH$  to account for surface activity of soil particles (proposed by Boesten et al, 2015)<sup>1</sup>



→ Impact on fit using real data:



Example MCPA

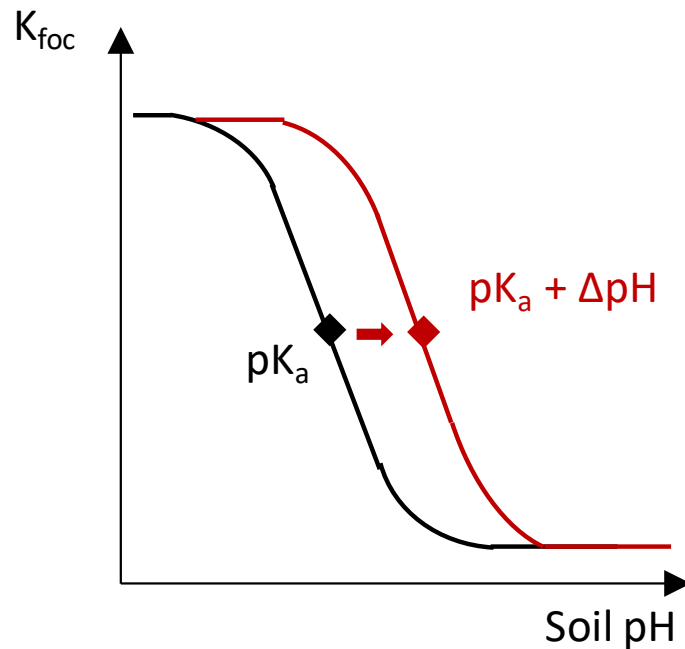


<sup>1</sup> Boesten et al, 2015. Leaching of plant protection products and their transformation products. Proposals for improving the assessment of leaching to groundwater in the Netherlands - Version 2, Wageningen: Alterra Wageningen UR (University & Research centre)

# Chapter 3 : Determination of pH-dependent degradation and/or adsorption in soil

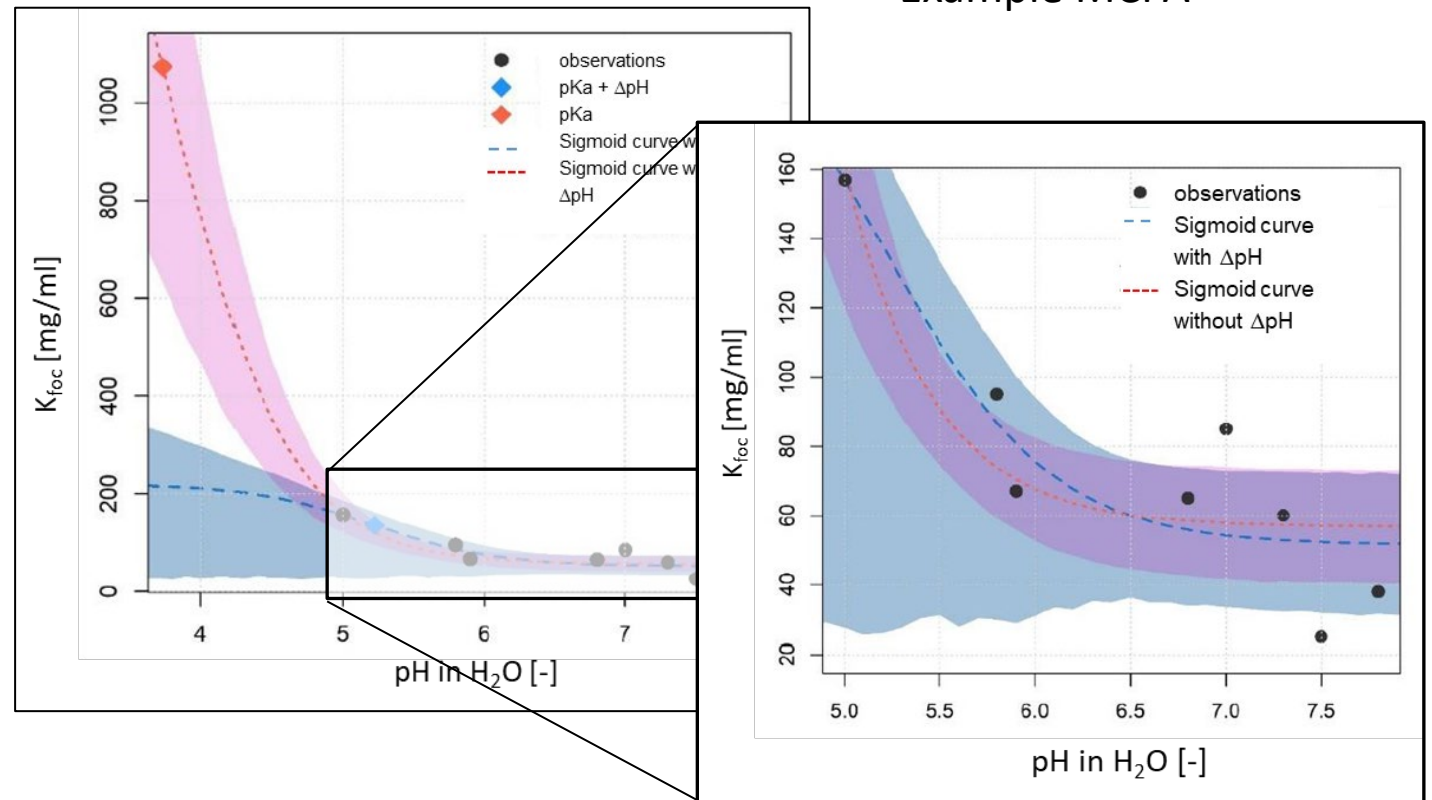
## Visual fit of $K_{foc}$ values versus pH in soils (weak acids with a single $pK_a$ value)

→ Sigmoid curve of  $K_{foc}$  values versus soil pH including  $\Delta pH$  to account for surface activity of soil particles (proposed by Boesten et al, 2015)



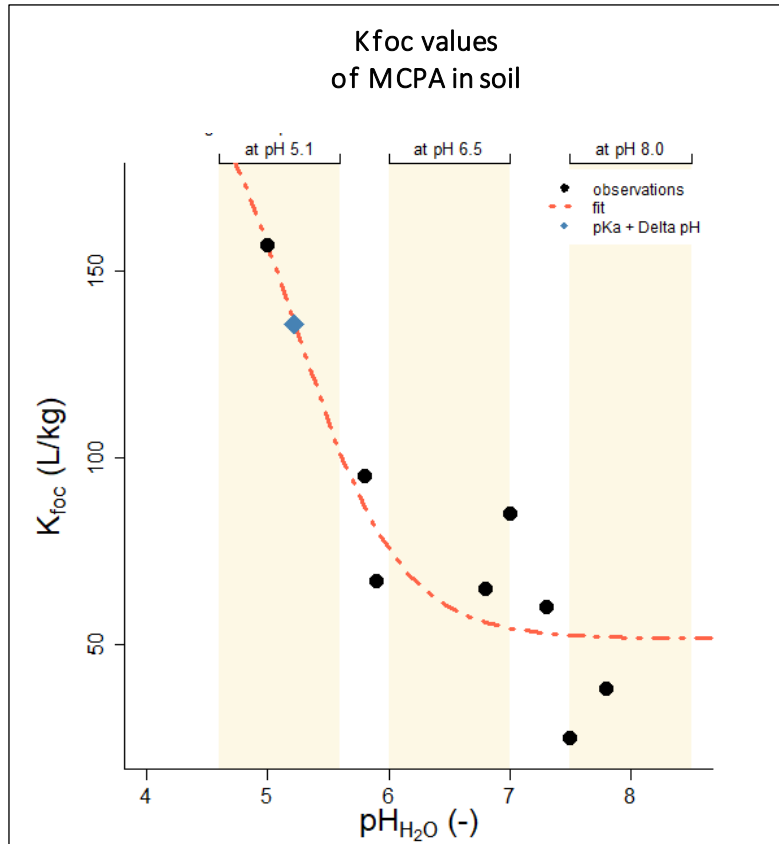
$\Delta pH$  range in  $H_2O$  = 0.5 to 2.5

→ Impact on fit using real data:



# Chapter 3 : Determination of pH-dependent degradation and/or adsorption in soil

## Visual fit of $K_{foc}$ values versus pH in soils (weak acids with a single $pK_a$ value)



- Also test  $K_f$  values
- test 1/n value in cases when  $K_{foc}$  values show pH- dependency




### Comments:









- Weak points of OECD 106 studies affecting soil pH
- Criterion for acceptability of fit?
- Suitability of two-sided Kendall test/ Kendall test at all
- ...

# Chapter 3 : Determination of pH-dependent degradation and/or adsorption in soil

## Decision:

- Use all information available
- Weight the information in relation to the data availability

minor weight	
normal or equal weight	
higher weight	

Number of available data pairs (pH-DT <sub>50</sub> &/or pH-K <sub>foc</sub> )	case 1	case 2	case 3
	≥ 6 & pH-range well covered	4 – 5 &/or pH-range not well covered	≥ 1 to 3
Chemical structure/ physicochemical properties			
Visual fit			
Statistical test			-

# Chapter 4 : Choosing appropriate endpoints for groundwater modelling

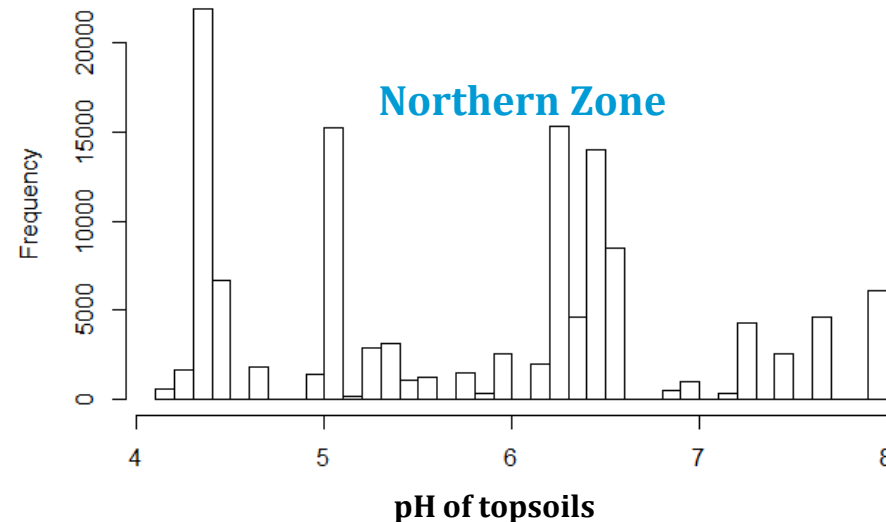
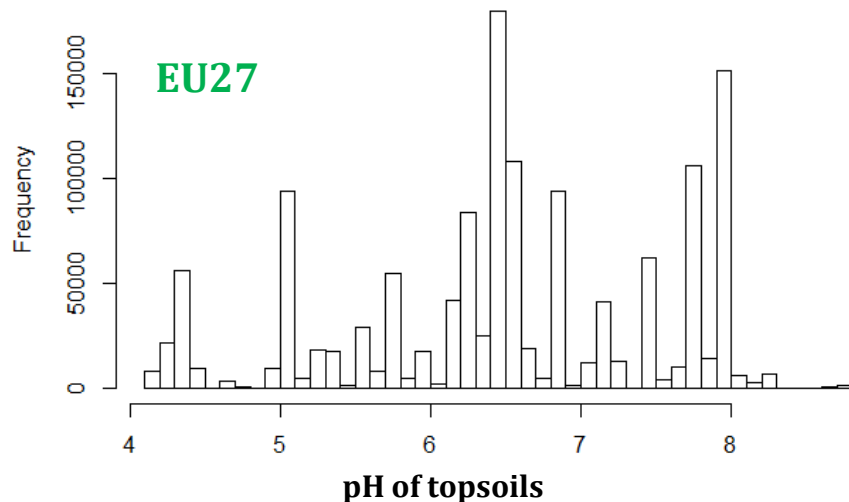
## pH range of European agricultural soils:

- For EU in agreement with EFSA (2020)<sup>2</sup>
- Central zone: comparable with EU27
- Southern zone: within the pH range of EU27
- Northern zone: more acidic soils, not covered by 10<sup>th</sup> perc. of EU27

### EFSA spatial data (version 1.1)

Report EUR 25546 EN, European Commission, Joint Research Centre (JRC), doi:10.2788/54453

Spatial unit	10 <sup>th</sup> p.	median	90 <sup>th</sup> p.
EU	5.1	6.5	8.0
Northern zone	4.4	6.2	7.5
Central zone	5.1	6.5	7.8
Southern zone	5.4	6.9	8.0



<sup>2</sup> EFSA, 2020. Scientific report of EFSA on the 'repair action' of the FOCUS surface water scenarios. *EFSA Journal* 2020;18(6):6119, chapter 3.3.

# Chapter 4 : Choosing appropriate endpoints for groundwater modelling

## pH range of European agricultural soils:

- For EU in agreement with EFSA (2020)<sup>2</sup>
- Central zone: comparable with EU27
- Southern zone: within the pH range of EU27
- Northern zone: more acidic soils, not covered by 10<sup>th</sup> perc. of EU27

### EFSA spatial data (version 1.1)

Report EUR 25546 EN, European Commission, Joint Research Centre (JRC), doi:10.2788/54453

Spatial unit	10 <sup>th</sup> p.	median	90 <sup>th</sup> p.
EU	5.1	6.5	8.0
Northern zone	4.4	6.2	7.5
Central zone	5.1	6.5	7.8
Southern zone	5.4	6.9	8.0

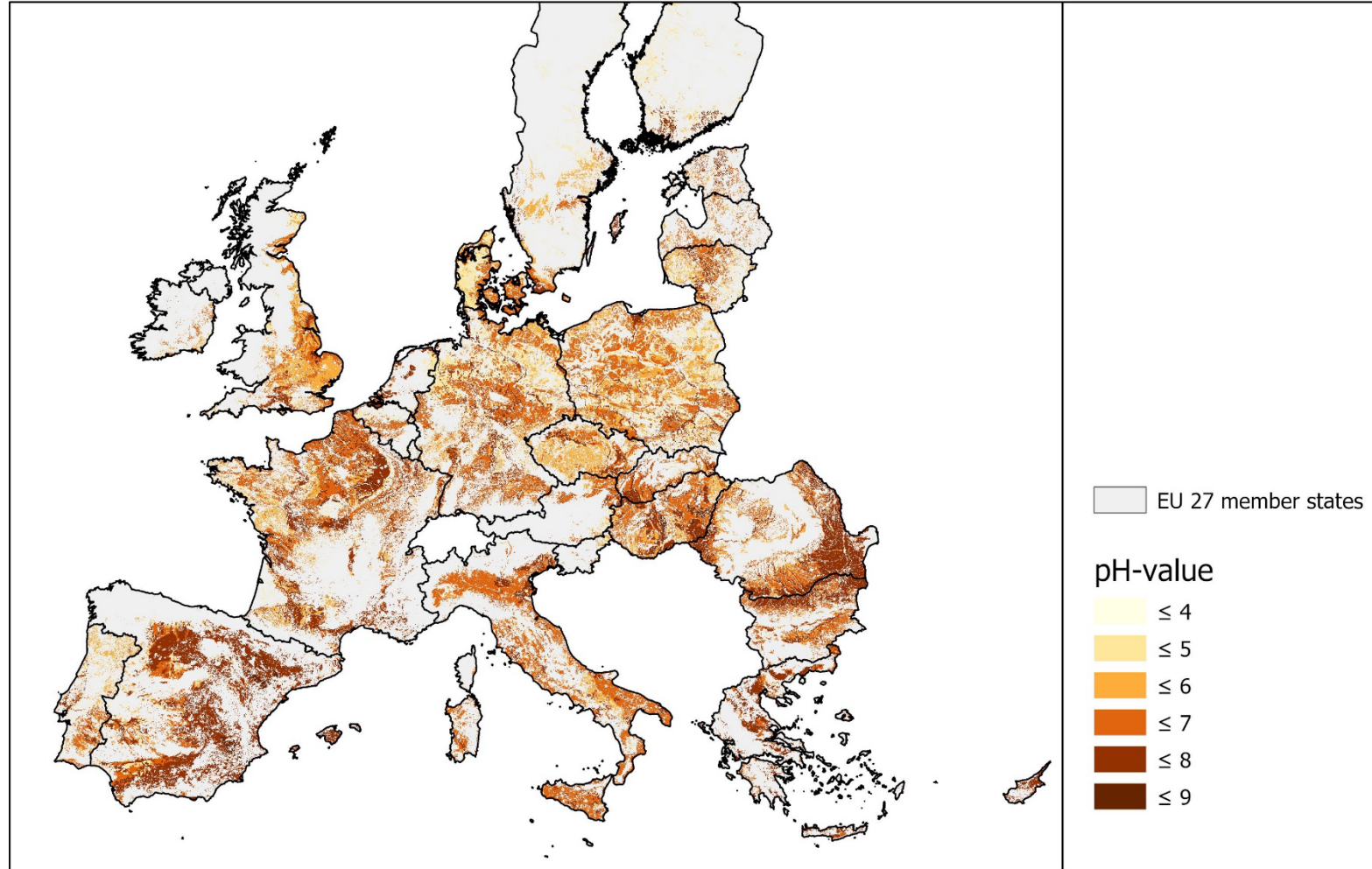
### Comments:

- MS of Northern zone: dependent on underlying data base, national assessment showed 10<sup>th</sup> percentile within the EU range → discussion in Northern zone required
- Include opinion of agronomists on pH values probable for agricultural soils

<sup>2</sup> EFSA, 2020. Scientific report of EFSA on the 'repair action' of the FOCUS surface water scenarios. *EFSA Journal* 2020;18(6):6119, chapter 3.3.

# Chapter 4 : Choosing appropriate endpoints for groundwater modelling

**pH range  
(in water) of  
agricultural  
topsoils  
in Europe:**



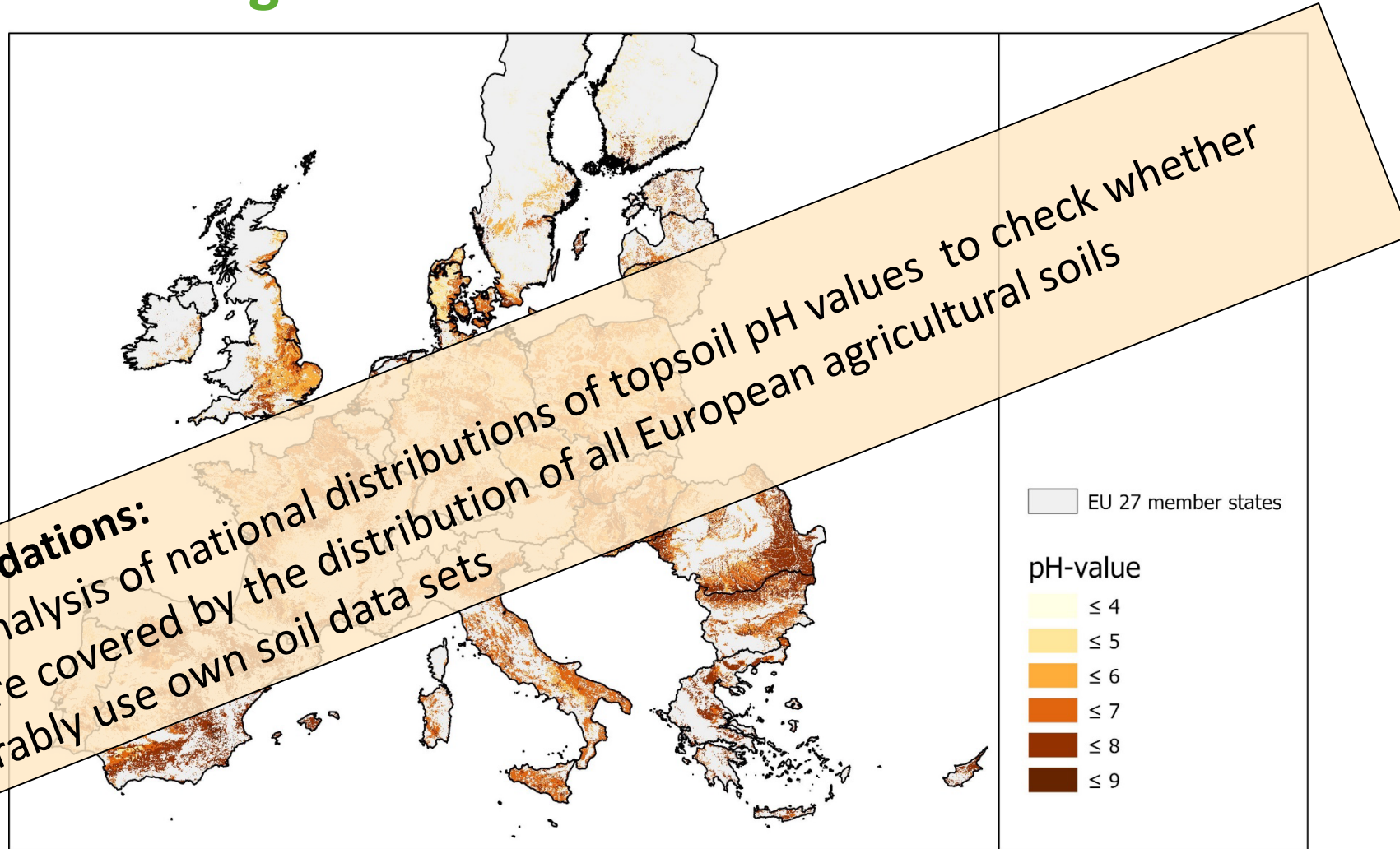
Source: EFSA Spatial Data Version 1.1, (Hiederer et al, 2012)

# Chapter 4 : Choosing appropriate endpoints for groundwater modelling

pH range  
(in water) of  
agricultural  
topsoils  
in Europe:

**Recommendations:**

- Make analysis of national distributions of topsoil pH values to check whether they are covered by the distribution of all European agricultural soils
- Preferably use own soil data sets

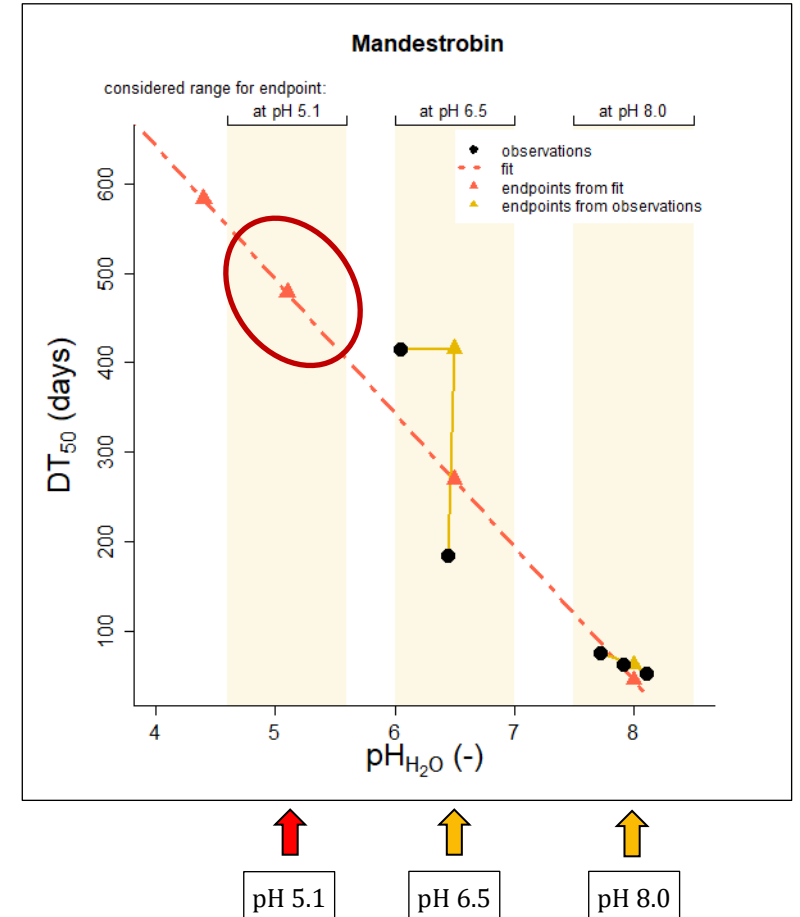
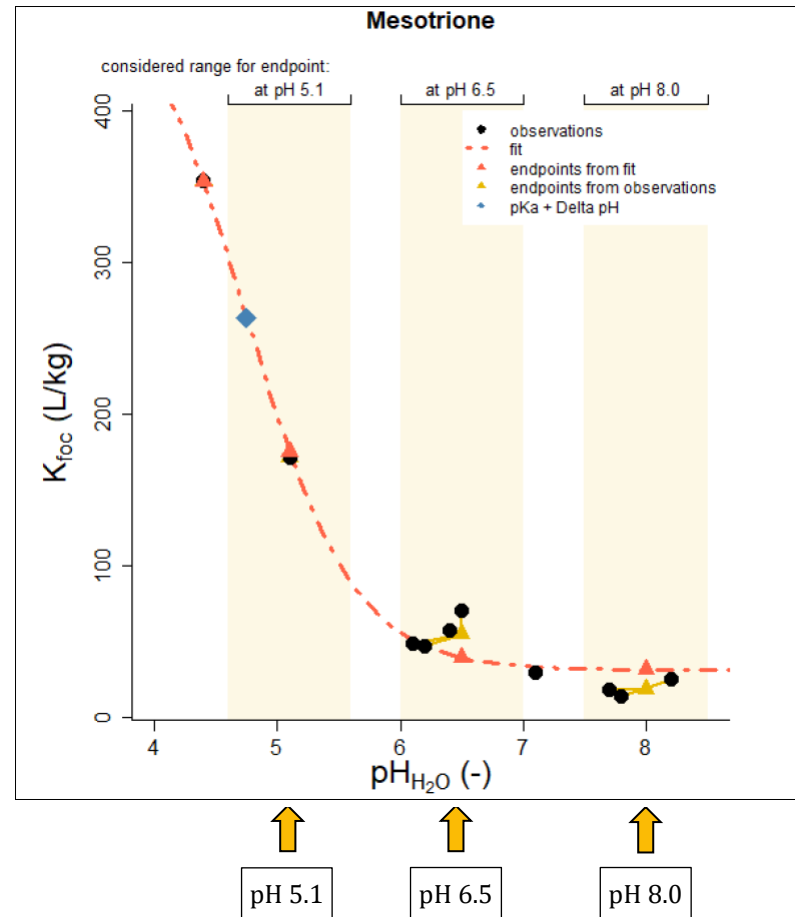


Source: EFSA Spatial Data Version 1.1, (Hiederer et al, 2012)

# Chapter 4 : Choosing appropriate endpoints for groundwater modelling

## Recommendations for choice on endpoints:

- use available data where possible
- extrapolate from linear fit/sigmoid curve for data gaps
- Use worst case endpoints/worst case default endpoints when linear fit/sigmoid curve is not considered reliable



## Chapter 4 : Choosing appropriate endpoints for groundwater modelling

### Recommendations for groundwater modelling:

- One groundwater assessment with 'worst case' endpoints either at **pH 5.1** or **pH 8.0** is sufficient, if a safe use can be demonstrated
- Additional groundwater assessments with endpoints at two contrasting pH values (**pH 5.1** and **pH 8.0**) and in some cases also with endpoints at **pH 6.5** are required, if:
  - a safe use cannot be demonstrated with worst case endpoints
  - metabolites of a substance exhibiting pH-dependent behaviour also require groundwater assessment
  - a substance exhibits both pH-dependent degradation and adsorption behaviour with both exercising concurrent influence on its leaching behaviour

# Chapter 4 : Choosing appropriate endpoints for groundwater modelling

## Comparison with suggestions in EFSA (2020)<sup>2</sup> for FOCUS surface water:

Recommendations of EFSA (2020) <sup>1</sup>		Agreement with draft pH guidance?
Perform calculations with two contrasting soil pH values		✓
Use pH values measured in H <sub>2</sub> O		✓
Deriving endpoints by	→ applying a sigmoid curve for weak acid substances or a linear or other suitable mathematical equation and calculate endpoints at pH 5.1 and pH 8.0	(✓)
	→ splitting the data into two subsets with pH 6.5 as split point	✗
Avoid extensive extrapolation		✗

<sup>2</sup> EFSA, 2020. Scientific report of EFSA on the 'repair action' of the FOCUS surface water scenarios. *EFSA Journal* 2020;18(6):6119, chapter 3.3.

## Work in progress: Choosing endpoints for...

### PEC<sub>sw</sub> and PEC<sub>sed</sub>

#### For pH-dependent degradation in soil:

- surface water modelling with a worst case DT<sub>50</sub> at pH 5.1 or pH 8.0, if a safe use can be demonstrated

#### For pH-dependent adsorption in soil and sediment:

- surface water modelling with two contrasting endpoints at pH 5.1 and pH 8.0 according to EFSA (2020)<sup>2</sup>

### PEC<sub>soil</sub>

- Possibility to directly model pH-dependency of DT<sub>50</sub> & K<sub>foc</sub> using linear fit & sigmoid curve in PERSAM
- How to deal with substances, where a fit cannot be derived or is considered unreliable or the pH-dependency follows a different mathematical relationship?
- Implications of the not implemented pH changes in soil layers below the topsoil?



Open points also valid for spatial distributed leaching modelling of substances showing pH-dependent adsorption/degradation behaviour

<sup>2</sup> EFSA, 2020. Scientific report of EFSA on the 'repair action' of the FOCUS surface water scenarios. *EFSA Journal* 2020;18(6):6119, chapter 3.3.

## Outlook

- Currently revision and extension of the draft guidance, envisaged **in 2023**
- Another commenting round at least on the planned extensions for **PEC<sub>sw</sub>/PEC<sub>sed</sub>** and **PEC<sub>soil</sub>**
- Discussion of revised version in a PPR meeting organised by EFSA
- Publishing planned in a form of an EFSA technical report as outcome of a PPR meeting

# Acknowledgements

## Many thanks to...

- Gabriele Holdt for her engagement and work on drafting the guidance – **Happy retirement!**
- Thomas Gräff for his statistical evaluations and his advice on statistical questions
- Stephan Marahrens for his geodata analysis
- Mark Rauch and Christina Tecklenburg for programming the **pHADe** tool
- The UBA colleagues of the working groups for surface water and soil exposition for their thoughts and analysis on considering pH-dependent behaviour in  $PEC_{sw}/PEC_{sed}$  and  $PEC_{soil}$  calculations

# Many thanks for your attention!

**Janina Wöltjen, Wolfgang Janzen, Wolfram König and Anne Osterwald**

janina.woeltjen@uba.de

wolfram.koenig@uba.de