Consideration of pH dependent adsorption and degradation in FOCUS Tier2a leaching assessments

Gerald Reinken, Heidemarie Borchers

Bayer AG, Monheim, Germany

Abstract

The European FOCUS groundwater models and scenarios are intended to assess the potential for movement of pesticide active substances and their metabolites to groundwater. Consideration of pH dependent behaviour needs special attention as this is not directly covered by the default FOCUS assessment.

Historically, the dependence of adsorption and degradation on pH is considered by most EU Member State authorities in different ways but generally as part of higher-tier assessments. Here we present an approach that could serve as a harmonized EU Tier2a assessment for such cases.

Materials and Methods

➢ **Test substance: Metabolite M12**
➢ **Basic check of potential pH dependency** ✓
   • ionisable functional group, pKa, log Kow, water solubility
➢ **Adsorption:** Koc based on sigmodal S shaped curve
   • in this case no pH dependency of Freundlich exponent
➢ **Degradation:** DT50 based on linear dependency
   • pH effect confirmed by different statistical methods
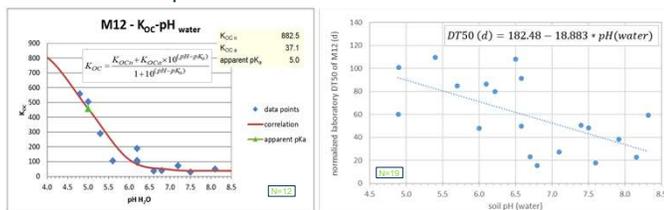   e.g.; Kendall tau test, Gaussian process surrogate model, EFSA Endpoint Selector

Fig. 1: pH dependency in Efate data

➢ **Tier2a: pH dependent modelling input**
   • employing fitted curves to derive endpoints
   • selected on paired-data basis
   • preventing potential issue of a *"demarcation point"*

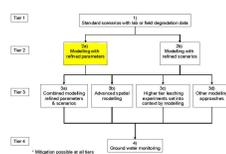| pH (H$_2$O)	DegT$_{50}$ [days]	K$_{oc}$ [L/kg]	K$_{om}$ [L/kg]
4.7	95.3	600.3	348.2
4.9	91.6	508.3	294.8
5.1	87.9	411.3	238.6
5.3	84.1	319.3	185.2
5.5	80.4	240.2	139.3
5.7	76.7	177.7	103.1
5.9	73.0	131.6	76.4
6.1	69.3	99.3	57.6
6.3	65.6	77.4	44.9
6.5	61.9	63.0	36.6
6.7	58.2	53.6	31.1
6.9	54.5	47.6	27.6
7.1	50.8	43.8	25.4
7.3	47.0	41.3	24.0
7.5	43.3	39.8	23.1
7.7	39.6	38.8	22.5
7.9	35.9	38.2	22.1
8.1	32.2	37.8	21.9
8.3	28.5	37.5	21.8

Fig. 2: pH dependent modelling input

Conceptual Tier2a Approach

• <u>Fundamental FOCUS concept</u>: mean values are selected for input parameter (e.g., DT50, Koc) as the worst case lies within selection of scenarios and 80th%ile PECgw
• The effect of pH may be assessed by allocating a steadily changing pH to each FOCUS scenario.
• As an example, the Hamburg scenario may be employed to evaluate potential leaching at different pH values relevant for a Member State e.g., ranging from 5.5 to 7.7 and not only the original scenario pH of 6.4.
• The relevant modelling input parameters (e.g., DT50 and Koc) then need to be selected on paired-data basis regarding the evaluated soil pH (Fig. 2).
• A safe use may be concluded in case the predicted leaching concentrations are below the relevant threshold for all relevant soil pH values.

Resulting PECgw at Tier2a

➢ pH dependent PECgw based on pH dependent input
➢ Regulatory decision may be based on
   • Overall maximum PECgw (conservative)
   • 80th%ile PECgw of individual scenarios (MS specific)
   • Area weighted PECgw based on pH distribution of the relevant arable land (complex)
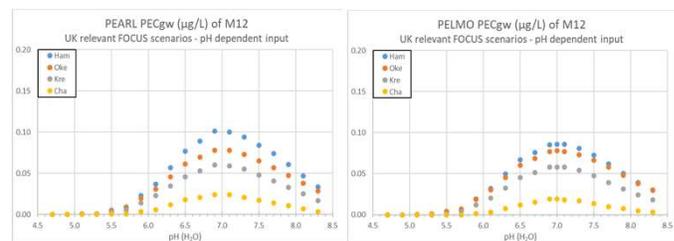

Fig. 3: pH dependent PECgw

Conclusions

The standard FOCUS groundwater scenarios can be used to evaluate the impact of pH dependent behaviour.

Based on the presented approach, a safe product use can be concluded in case the predicted leaching concentrations are below the relevant threshold for all relevant soil pH values of all relevant FOCUSgw scenarios.

A parameter selection tool may be useful to further standardise the data evaluation. (see UBA poster P-03)