# Topical Scientific Workshop on Risk Assessment for the Sediment Compartment

7-8 May 2013, Helsinki, Finland

## CASE STUDY – SUMMARY FORM

**7**

(Number to be filled by the organisers)

The case studies covering concrete examples of sediment risk assessments for particular chemicals and/or conditions are intended to support the breakout group discussions. All submitted case studies will be distributed to the participants as supporting background material for the workshop and will be included in the workshop proceedings. The Scientific Committee will select some case studies or selected areas of the case studies and will invite the authors to present these cases during the workshop, either at the plenary session or during the break-out groups.

*NOTE: By submitting this form, the authors confirm that they have the ownership of the information presented in the case study and that they authorise ECHA to distribute the submitted information to the workshop participants and to publish it in paper and/or electronic format as part of the workshop proceedings.*

### Contact details for the submitter


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EUROPEAN CHEMICALS AGENCY

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**Case study details**

Case study is particularly relevant for the subthemes:
*Note: the case study should cover all three areas, but please indicate if it is particularly relevant/informative for one or more subthemes*

- [X] Problem definition and conceptual model for sediment risk assessment
- [X] Exposure assessment
- [X] Effect assessment

| |
|---|
| Authors: Francesca Pellizzato (provided a summary of EFSA risk assessment) |
| Title: Bifenthrin |
| Keywords: insecticide, sediment-dwelling organisms, bioaccumulation, modelling, assessment factor |
| Summary:<br><br>The tiered approach used for the risk assessment of the insecticide Bifenthrin and its major degradation products on sediment organisms is described. The risk is estimated as Toxicity Exposure Ratios (TERs). Toxicity to dwelling organisms has been derived from three toxicity studies to *Chironomus riparius* (water and sediment spiking) to the parent compound and the major metabolite. Results from two higher tier tests studies, a pond and a mesocosm studies, were also used. Exposure has been predicted from generic scenarios for pesticides (FOCUS). To further address the risk assessment from bioaccumulation through the food chain, a food web bioaccumulation model was used. The main shortcomings of the model are presented. The most appropriate assessment factor for sediment risk assessment when using higher tier studies are also discussed. |

**Poster exhibition**
The case study will be presented also as a poster

- [ ] Yes
- [X] No

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## 1. BACKGROUND AND PROBLEM DEFINITION

The assessment has been prepared in the framework of Commission Regulation 1107/2009 concerning the placing of plant protection products on the market. The assessment has been performed by the Rapporteur Member State on the basis of the information provided by the applicant for submission to the European Commission to enable a decision to be made on the approval of the active substance.

The risk assessment on the active substance and the representative formulation has been evaluated on the basis of the representative uses of Bifenthrin as an insecticide on cereals, ornamentals and head cabbage, as proposed by the applicant.

**Identity and Physico-chemical properties of the active substance:**

| | |
|---|---|
| Molecular formula: | $C_{23}H_{22}ClF_3O_2$ |
| Molecular mass: | 422.88 g/mol |
| Melting point: | 79.6 °C |
| Vapour pressure: | $1.78 \times 10^{-5}$ Pa at 20 °C |
| Henry's law constant: | $7.739 \times 10^{-5}$ Pa $m^3$ $mol^{-1}$ |
| Water Solubility | <0.001 mg/l at 20 °C (pH 5 and 7)<br>0.00376 mg/l at 20 °C (pH 9) |
| Partition coefficient: | logKow=6.6 |
| Dissociation constant: | no dissociation |

**Fate and behaviour of the active substance:**

Bifenthrin is stable under sterile aqueous hydrolysis conditions at 25 °C at pH 5, 7 and 9. It has a high adsorption potential and it is not readily biodegradable. In water-sediment studies (2 systems studied at 20°C in the laboratory, sediment pH 7.1-7.9, water pH 7.7-7.8) Bifenthrin dissipated rapidly from the water partitioning to sediment (87.8 to 95.3% between 7 and 14 days). Degradation in sediment subsequently occurred with single first order whole system DT50 being calculated as 278 (4.8% OC sediment system, geom. mean of experiments with two radiolabels) and 93 days (0.7% OC sediment system, geom. mean of experiments with two radiolabels) (overall geomean value 161 days). In sediment, the only major (>10%AR) metabolite except carbon dioxide present at any sampling time was 4'-OH Bifenthrin which accounted for up to 11.1% AR at study end (99 days). The minor breakdown products identified were: BP alcohol and TFP acid.

It should be noted that the methods of analysis used in the majority of the fate and behaviour studies were not stereoselective. All residues reported as Bifenthrin or the two metabolites in this conclusion are for the sum of the 2 enantiomers. Limited information on the behaviour of each individual Bifenthrin enantiomer in the environment was available in the regulatory dossier, but no data were provided for the enantiomers of the metabolites

TFP acid and 4'-OH Bifenthrin. However, there were indications that in water systems, significant enantioselective degradation would not be expected.

**Aquatic toxicity information of the active substance:**
Based on the available acute toxicity data, Bifenthrin was proposed to be classified as very toxic to aquatic organisms. LC50 for fish and EC50 for Daphnids were 0.10 and 0.11 µg a.s./L, respectively. With regard to chronic toxicity, aquatic invertebrates are more sensitive than fish. The NOEC for reproductive effects is 0.95 ng a.s./L for Daphnia magna.

## 2. MAIN CASE STUDY DESCRIPTORS

- Generic pre-marketing (including revision) authorisation for active ingredients in PPP
- Continental risk assessment
- Freshwater only
- Targeted to uses as a insecticides as proposed by the applicant.

## 3. CONCEPTUAL MODEL

The risk is estimated as Toxicity Exposure Ratios (TERs) and the legal triggers for these TERs. Toxicity values are taken directly from the experimental studies (e.g. NOECs from long-term studies), and the exposure is predicted from generic scenarios for pesticides (FOCUS) covering release to water via spray drift or run-off/drainage and subsequent partition into sediment.

## 4. EFFECT ASSESSMENT

Bifenthrin bioaccumulation and depuration study with Midges *Chironomus tentans. Non-guideline.* Sediment and water only exposure. No apparent adverse effects or mortality observed in both exposure phases. BSAF=0.47 (BCF=223 in pore water, BCF=775 in overlaying water). Depuration DT50=0.45 days

*Chironomus riparius* 28-day chronic toxicity test in water-sediment system using spiked sediment with Bifenthrin (OECD 218): 28d NOEC (based on emergence ratio) = 40 µg a.s/Kg sediment nom. EC50=345.5 µg a.s/Kg sed d.w.
28d NOEC (based on development rate) = 398 µg a.s/Kg sediment nom., EC50 could not be determined.

*Chironomus riparius* 28-day chronic toxicity test in water-sediment system using spiked water with Bifenthrin (OECD 219): 28d NOEC (based on emergence ratio) = 1.06 µg/L nom overlying water, 28d NOEC (based on development rate) = 1.06 µg/L, 28d NOEC (mortality)=0.32 µg/L nom overlying water, EC50 =3.96 µg/L nom overlying water.

*Chironomus riparius* 28-day chronic toxicity test in water-sediment system using spiked sediment with 4'-hydroxy Bifenthrin (OECD 218): 28d NOEC (based on emergence ratio) = 1581 µg a.s/Kg sediment nom. EC50=3593.5 µg a.s/Kg sed d.w.

Pond study performed in a cotton field in Alabama (USA). This study investigated the effects of aerial applications (10 applications) at a distance of 5 meters from a pond on the indigenous populations (including fish). Bifenthrin concentrations were checked both in the water column and the sediment. The study showed strong effects (elimination) on calanoid copepods without recovery throughout the study (more than one year), strong effect on *Caenis* without recovery throughout the study (more than one year) and strong effect on *Chaoboridae* with recovery after one year. Since no recovery was observed in some taxa, no NOEC could be determined from this study. It could simply be stated that the NOEC could be lower than the measured concentrations in this study, being: 6-18 ng a.s./L in the water column and 52-60 µg a.s./kg in the sediment.

Mesocosm study performed in Austria (Bay of Fussach, lake Constance). The study reproduced two applications at 14 days interval and tested concentrations ranging from 0.001 to 0.935 µg a.s./L. The study lead to a No Observed Ecological Adverse Effect Concentration (NOEAEC) of 0.015 µg a.s./L which covers the most sensitive invertebrate species (Gammarids, copepods and chaoboridae). The Rapporteur Member state concluded that this value should be used in the risk assessment.

## 5. EXPOSURE ASSESSMENT & RISK CHARACTERISATION

For the representative uses in cereals and head cabbage, the necessary surface water (PECsw) and sediment exposure assessments (PECsed) were carried out for Bifenthrin as well as for the metabolites 4'-OH bifenthrin and TFP acid using the **FOCUS** (FOCUS, 2001) **step 1 and step 2** approaches.

*Sediment and suspended solid characteristics of all FOCUS water bodies (there is no differentiation at different scenarios)*

| **Characteristic** | **Value** |
|---|---|
| Sediment layer depth (cm) | 5 |
| Organic carbon content (%) | 5 (approx. 9% organic matter) |
| Dry bulk density ($kg.m^{-3}$) | 800 |
| Porosity (%) (only defined for Step 3) | 60 |
| Concentration of suspended solids in water column (mg.L-1) (only defined for Step 3) | 15 |

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This first tier risk assessment indicated a high acute and long-term risk to fish, aquatic invertebrates and sediment-dwelling organisms for both cereal and cabbage uses.

Therefore, **FOCUS step 3 and step 4** calculations were also carried out for Bifenthrin. The TER calculations based on PECsw step 3 did not meet the Annex VI criteria for fish and aquatic invertebrates (cereals and cabbage use) and sediment-dwelling organisms (only cabbage use).

To further address the risk, TER calculations were provided based on the **FOCUS PECsw step 4**. The mitigation measures implemented at FOCUS step 4 level included no-spray buffer zones of 20 m or 25 m combined with a maximum of 90% runoff mitigation for the run-off scenarios. Additionally, for the representative uses in cereals, taking into consideration that Bifenthrin is persistent in water sediment systems, PECsed values considering the accumulation potential of Bifenthrin were calculated at step 4 level (20 m no spray buffer zone + runoff mitigation). These values were lower than the standard step 3 results that were sufficient to demonstrate low risk to sediment-dwellers.

As drift-reducing nozzle technology is commonplace throughout the EU, additional calculations were also made using a 25m no-spray buffer combined with 75% nozzle reduction. To highlight that additional mitigation options can be available at the Member state level.

Bifenthrin's rapidly transfers to sediments where it degrades at a slower rate than in surface water. To evaluate **potential longer term build up in the sediments**, calculations were made with repeated applications over 5 years according to FOCUS SW guidance. To calculate the accumulated PECsed values the sediment concentration remaining at the end of each evaluation was entered as the starting concentration for the next. TOXSWA simulation was then rerun and the process repeated for a total of 5 years. For 4'hydroxy Bifenthrin a 5 year accumulated sediment calculation was made at step 3 only for the worst case scenario resulting in a PECsed=0.1965 ug/Kg

The representative use for ornamentals comprised both indoor and outdoor applications. For indoor use the PECsw calculations were based on a simple assumption that 0.1% of the active substance reaches a receiving static water body of 30 cm depth. For outdoor use the peer review concluded that no reliable estimations for the exposure were available. Consequently, a data gap was identified for PECsw/sed calculations for outdoor use in ornamentals.

Two **higher tier studies**, one **pond study** from a cotton field in Alabama and one **mesocosm study** performed in Austria, were available to refine the assessment for invertebrates. On the basis of the available information, it was concluded that the NOEAEC of 0.015 µg a.s./L should be used with an assessment factor of 3, as proposed by the Rapporteur Member State. The assessment factor

of 3 should cover variation in potential for recovery depending on the nature of the ecosystem. The higher tier risk assessment resulted in a $TER_{lt}$>3 based on the NOEAEC from the mesocosm and initial FOCUS PECsw Step 4 with 20 m no-spray buffer zone and run-off reduction in cereals and cabbage, in all scenarios.
For the use in cabbage, the higher tier risk assessment for sediment-dwelling organisms resulted in a $TER_a$>10 based on initial FOCUS PECsw Step 4 with 20 m no-spray buffer zone and run-off reduction, in all scenarios.
Although the potential accumulation in sediment was not taken into account in this risk assessment, the TER calculations were well above the trigger to cover this issue. One major metabolite, 4'-OH Bifenthrin, was detected in sediment. The toxic effects of this metabolite are considered to be covered by the mesocosm study. However, the risk assessment for aquatic organisms was provided and a low risk was indicated with FOCUS step 1 & 2. Since no TERs have been provided for the outdoor use in ornamentals it was not possible to finalise the risk and a data gap was identified.

To further address the risk assessment **from bioaccumulation through the** food chain, a food web bioaccumulation model was also provided. In this refinement, the biotransformation process was included by taking into account the uptake efficiency for different trophic level organisms (benthic organisms included) and the biotransformation rate constants. The model was parameterized to represent food web conditions for a European pond. Time dependent bioaccumulation and exposure calculations were determined by linking the output from a five year FOCUS model pond scenario as input for the food web predictions. The model predicts a maximum concentration in the benthic invertebrates for the fifth year of application of 1.60 µg/Kg. At steady state a logBAF(L/kg ww) of 3.65 (dissolved) and 3.57 (total water) is predicted for the benthic invertebrates.
Low biomagnification in the aquatic food web is predicted by the model. Bifenthrin tightly binds to sediment and organic material, which reduces its bioavailability to sediment dwelling organisms, primary consumers and /or organisms feeding on them.

The model was considered by the experts to be an acceptable approach in principal to be considered further in the refined risk assessment.
However, the experts expressed concern regarding the BCF values used in the modelling. Secondly, it was noted that the PEC values used in the bioaccumulation risk assessment are highly refined, i.e. FOCUS step 4 including 20-25 m buffer zones. Why there were D5 scenarios considered at Step 4 was questioned and whether these cover the worst case real situation. The use of PNEC values was considered more appropriate.

The NOAEC from the full fish life cycle was 40 ng a.s./L and the NOEAEC from the mesocosm was 15 ng a.s./L, it was questioned whether these endpoints cover the effects on sediment dwellers. If a PNEC is derived using the mesocosm endpoint and using an assessment factor of 3, PNEC = 5 ng a.s./L. If the PNEC is calculated using the endpoint from the fish full life cycle and using an assessment factor of 10 the PNEC = 4 ng a.s./L. The corresponding PEC in the sediment should be considered also. The approach the Applicant has used to calculate the PEC in the sediment and appreciate the concentration the pore water seems to indicate that sediment PEC is covered when considering the PEC in the water column. It was highlighted that the PNEC of 5 is based on a mesocosm that included 2 applications and therefore does not cover more applications.

In conclusion, the experts agreed that a high risk from bioaccumulation through the food chain for aquatic organisms could not be excluded on the basis of the available data. Therefore, a data gap was identified to further address the risk from biomagnification in the aquatic food chain. The experts suggested that the model should be re-run with the PNEC values above; and the BCF values used should be clarified.
The experts agreed that the modelling approach can be used as a part of the refined risk assessment, but that it cannot be used exclusively.

## 6. CONCLUSIONS

Risk mitigation measures are necessary for uses on cereals and cabbage in order to limit water and sediment contamination. A data gap was identified for PECsw/sed calculations for outdoor use in ornamentals. Further clarifications were considered necessary regarding the bioaccumulation through the food chain.
As an efficacious insecticide, ecotoxicity data in the dossier confirm there is potential for damage to the environment. Risks to aquatic organisms and non target arthropods need to be mitigated with classification proposed as "Very toxic to aquatic organisms, may cause long-term effects in the aquatic environment" (R50/53)[Aquatic Acute Category 1 H400 and Aquatic Chronic Category 1 H410 under the CLP Regulation] .

## 7. REFERENCES

EFSA Conclusion on the peer review of the pesticide risk assessment of the active substance Bifenthrin
http://www.efsa.europa.eu/en/efsajournal/pub/2159.htm

FOCUS, 2001. "FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC". Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.2. 245 pp., as updated by the Generic Guidance for FOCUS surface water scenarios, version 1.1 dated March 2012