EUROPEAN CHEMICALS AGENCY

Topical Scientific Workshop on Risk Assessment for the Sediment Compartment
7-8 May 2013, Helsinki, Finland

CASE STUDY – SUMMARY FORM

8

(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.

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8

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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

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

Authors: Francesca Pellizzato (provided a summary of EFSA assessment)
Title: Bixafen
Keywords: pesticide, sediment-dwelling organisms, accumulation, monitoring
Summary: The tiered approach used for the risk assessment of the pesticide active substance Bixafen on sediment organisms is described. The risk is estimated as Toxicity Exposure Ratios (TERs). Toxicity to dwelling organisms has been derived from two toxicity studies to *Chironomus riparius* (water and sediment spiking). Exposure has been predicted from generic scenarios for pesticides (FOCUS). In this approach a theoretical worst case estimate of accumulation in sediment was considered. An assessment of long term risk to sediment dwelling organisms is provided. The post-inclusion environmental monitoring of soil and sediment levels and possible effects on relevant fauna is also discussed.

Poster exhibition

The case study will be presented also as a poster

	Yes	x	No

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8

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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 Bixafen and its representative formulations has been evaluated on the basis of the representative uses as a fungicide on cereals as proposed by the applicant. Bixafen is a broad spectrum fungicide for foliar application in winter and spring wheat, winter and spring barley, winter rye, triticale and oats. The product is applied by broadcasting spraying over the target area.

Identity and Physico-chemical properties:

Molecular formula:	
Molecular mass:	414.21 g/mol
Melting point:	146.6 °C
Vapour pressure:	4.6×10^{-8} Pa at 20 °C
Henry's law constant:	3.89×10^{-5} Pa m^3 mol^{-1}
Water Solubility	0.00049 g/l at 20 °C (5-9 pH)
Partition coefficient:	logKow=3.3 at 40 °C
Dissociation constant:	no dissociation found in the pH range 1 to 12

Fate and behaviour in the environment:
Bixafen is hydrolytically stable, and aqueous photolysis is not a significant route of degradation. The substance has a high adsorption coefficient (Koc=3869 l/Kg) and it is slowly degrading both under aerobic and anaerobic conditions. Very low amounts of unextracted residues were formed. No major metabolites were identified. For the purpose of FOCUS surface water modelling, default DT50 values of 1000 days have been assumed for degradation in both water and sediment phases of natural surface water systems.

Aquatic toxicity information of the active substance:
Bixafen is very toxic to aquatic organisms (NOEC fish=0.0046 mg a.s./L; NOEC Daphnia=0.05 mg a.s./L; ErC50= 0.0965 mg a.s./L). The chronic risk to fish drives the aquatic risk assessment. High risk was identified for fish for all FOCUS step 3 scenarios. For FOCUS step 4 scenario a low risk for aquatic organisms was demonstrated for the representative uses.

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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 fungicide on cereals 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. The long-term risk from repeated annual applications has been also considered.

The risk assessment has been performed in a tiered approach comprising the following subsequent steps:

- Predicted environmental concentrations (PEC) in surface water (PEC_{sw}) and sediment (PEC_{sed}) were calculated for **Steps 1, 2 and 3**, as outlined in the FOCUS (2001) surface water scenarios report. Simulations were run for use of the active substance on winter wheat in northern and southern Europe, applied in the spring.
- In order to address the risk assessment for aquatic organisms for those FOCUS SW scenarios which resulted in the highest global maximum PEC_{sw} values, additional **Step 4** PEC_{sw} calculations were provided based on 2 applications to winter cereals with 5 m, no spray buffer zones and 10-12 m of vegetative strips to mitigate run-off.
- Whilst the overall aquatic risk assessment was driven by the chronic risk to fish, a **theoretical worst case estimate of accumulation in sediment** was also provided, as it was not possible to exclude potential for accumulation in sediment. Exposure concentrations in the water were estimated using the maximum PEC_{sed} concentrations from FOCUS SW Steps 3 and 4 simulations that were then compared to the regulatory ecotoxicology concentration identified for sediment dwelling organisms from a water-spiked study.
- It was felt that the risk of sediment-bound active substance had not been adequately addressed, based on the water-spiked *Chironomus riparius* endpoint. Therefore a second *Chironomus riparius* study, spiked in the sediment phase was performed. **Accumulated exposure concentrations** estimated for the sediment were compared with the ecotoxicology endpoint from this study.

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8

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4. EFFECT ASSESSMENT

Chironomus riparius 28-day chronic toxicity test in water-sediment system using spiked water (OECD 219): 28d NOEC (based on emergence ratio) = 0.0156 mg nom/L overlying water

Chironomus riparius 28-day chronic toxicity test in water-sediment system using spiked sediment (OECD 218) (dosed at peak residue for accumulated PEC_{sed}): 28d NOEC = 20 mg a.s/Kg sediment nom
The study showed that the substance mostly remained in the sediment phase with little partitioning to overlying or pore water during the study.

5. EXPOSURE ASSESSMENT & RISK CHARACTERISATION

PEC_{sed} have been calculated using the FOCUS Surface Water models.

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

PEC_{sed} concentrations from the single application pattern gave much lower concentration than from the multiple application pattern. Therefore, Two applications at 125 g a.s./ha were assumed to be made annually to winter and spring cereals, with a 14 days interval. Only the parent substance was modelled as no major metabolites were identified.

A summary of the maximum PEC_{sw} and PEC_{sed} calculated for steps 1, 2, and 3 scenarios as defined in the FOCUS Surface Water Scenarios Report is reported below. Simulations were run for use of the active substance on winter wheat in northern and southern Europe, applied in spring. (Member states are invited to consider at the national level whether the substance may be applied in the autumn and any implications for the surface water and sediment assessment.)

	PECsw µg/l	**PECsed µg/kg**	**Remarks**
Step 1	15.83	537.59	Occurring at day 0 and 1, 2 applications
Step 2 for Southern Europe	3.07	113.46	Occurring at day 18 and 19 2 applications

Step 2 for Northern Europe	1.76	63.06	2 applications
Step 3	0.8 at D2 ditch scenario 1 application 0.77 at D1 scenario 2 applications	21.4 at R4 stream scenario	
Step 4	0.573 at R1 scenario	20.90 at R4 stream scenario	2 applications

Parameters used in FOCUSsw:
KOC/KOM (L/kg): 3869 l/kg (mean)
DT50 soil (d): 203.2 days* (geometric mean, normalised field. In accordance with FOCUS SFO)
DT50 water/sediment system (d): 1000 days (default); DT50 water (d): 1000 days (default); DT50 sediment (d): 1000 days (default); Crop interception (%): 50% (BBCH 25-69); * Based on the original geometric mean field DT50 value normalised with a Q10 of 2.2, in place of the subsequently revised geomean field DT50 of 200.2 days based on a Q10 of 2.58
1/n: 0.88 (Freundlich exponent general or for soil, susp. solids or sediment respectively)
Half-life on crop canopy 10 d; Wash-off factor from crop 0.05; Uptake factor 0.5; Incorporation depth 4 cm

Pseudo PEC_{sw} concentration (using FOCUS Step 1 and 2 output)

As the initial study performed to investigate toxicity to sediment dwelling organisms wad dosed by spiking in the water phase and the NOEC expressed as water concentration, pseudo PEC_{sw} were also calculated.
Generating total load (or pseudo) PEC_{sw} at Step 1-2 was done to take into account total load entering the aquatic system via drift, run-off and drainage. This sums all input events before partitioning and provides exposure as a water phase concentration, for direct comparison with the SW NOEC values from the Chironomid toxicity study spiked in the water phase.
Assuming 2x 125 g a.s./ha applications, with 14d interval.

At Step 1:
loading to water body via drift = 0.6897 mg/m2
loading to water body via run-off/drainage = 25.000 mg/m2 (N. & S. EU)
(0.6897 + 25.000) x 3.32 = 85.29 µg/l

At Step 2:
loading to water body via drift = 0.6095 mg/m2 loading to water body via run-off/drainage = 2.4085 mg/m2 (N.EU)
loading to water body via run-off/drainage = 4.8171 g/m2 (S.EU)
(0.6095 + 2.4085) x 3.32 = 10.02 µg/l (N.EU)
(0.6095 + 4.8171) x 3.32 = 18.02 µg/l (S.EU)

The total load PEC_{sw} at step 1 and 2 compared to the ecotoxicology endpoint (water-spiked study) to calculate a Toxicity exposure Ratio (TER). PEC_{sw} exceeded the regulatory concentration of 1.56 µg/l for sediment dwelling organisms (NOEC divided by Annex VI uncertainty factor of 10). Therefore, further refined risk assessments were performed.

The NOEC based on spiking in water was then compared against the FOCUS step 3 global maximum PEC_{sw} values. The resulting TER values were above the Annex VI trigger of 10 of the FOCUS surface water scenarios.

Bioaccumulation potential in sediments
The potential accumulation in sediments was assessed because the substance is persistent and bioaccumulation cannot be excluded. How the sediment dwelling organisms were exposed in the water spiked toxicity study and how exposure would occur in practice (e.g. via the water or sediment phase or via sediment pore water) was also considered.

Maximum PEC_{sed} (FOCUS Step 3 and 4) were converted to an **equivalent water phase concentration**, using ratio of sediment to water in Chironomus (water-spiked) study, i.e. assuming 100% of residues bound to sediment are released to overlying water:

PEC_{sw} = PEC_{sed} * mass of sediment (kg) / volume of water (l)
Based on the proportions of sediment and water in the water spiked sediment dwellers study (0.14 kg wet weight sediment = 0.097 kg dry weight sediment) and 0.38 L water.

Step 3 – PEC_{sed} of 21.405 µg/kg = 5.47 µg/1
Step 4 - PEC_{sed} of 20.902 µg/kg = 5.34 µg/1
Accumulation factor of 4.47* (based on default DT50 of 1000 d in water) gives:
Step 3 – 24.45 µg/l
Step 4 - 23.87 µg/1

* accumulation factor calculated in Excel with formula: 1/(1-EXP(-k*interval)) where default DT50 of 1000d equates to k of 0.000693 and interval=365 days gives accumulation factor of 4.47

The resulting TER values were above the Annex VI trigger of 10 of the FOCUS surface water scenarios.

Assessment of long term risk to sediment dwelling organisms
Higher tier modelling of PEC_{sw} and PEC pore water were subsequently run. PEC_{sw} and sediment pore water concentrations were calculated in the FOCUS TOXSWA model, using the run-off scenarios which previously gave the max. PEC_{sed}.
Assuming 2 x 125 g a.s./ha application with 14 day interval, for the run-off scenarios R1 pond and stream and R4 stream, in TOXSWA, (using the output files from previous FOCUS PRZM modelling as input files, repeated for 20 years). The highest maximum yearly concentrations reached for surface water and sediment pore water were 0.58 µg/l (R1 stream) and 0.12 µg/l (R4 stream), respectively. The long term PEC_{sw} reached a steady state with 5-6 years.

The long-term PEC pore water reached a plateau after 18 years in the R4 stream scenario, but did not reach a plateau in the R1 scenarios over 20 years, though only very small yearly increases were observed after 15 years.
The highest yearly PEC_{sw} concentration of 0.58 ug/l was compared with the ecotox endpoint for *Chironomus riparius* (water spiked study) to calculate a TER value. The resulting TER value was above the Annex VI trigger.

Exposure via sediment
Exposure concentrations were also compared with ecotoxicology endpoints from a second Chironomid study, spiked in the sediment phase, which was subsequently submitted (NOEC≥ 20 mg/kg).
Low risk was established at FOCUS Step 1 max. PEC_{sed} concentration (0.5376 mg a.s./kg). This exposure was more worse case thatn the theoretical estimate of worse case long term sediment accumulation (FOCUS step 3, R4 scenario = PEC_{sed}. of 95.68 µg/kg (obtained from Step 3 – PEC_{sed} of 21.405 µg/kg (FOCUS R4 stream), using Accumulation factor of 4.47 (based on default DT50 of 1000 d) and accumulation factor calculated in Excel with formula: 1/(1-EXP(-k*interval)) where default DT50 of 1000d equates to k of 0.000693 and interval=365 days.

6. CONCLUSIONS

The risk assessment concluded that the risk to sediment dwellers from initial and long term accumulation of the substance in sediment following the proposed use is low.

To address the possibility that other organisms might be more susceptible consideration was given to confirmatory **post-inclusion environmental monitoring** of soil and sediment levels and possible effects on relevant fauna. It was suggested that standard studies required for the risk assessment may not sufficiently address the concerns regarding bioaccumulation and toxicity to soil and benthic organisms and environmental monitoring of potential effects of soil and sediment organisms would be preferable. This issue was discussed at the Pesticides Peer Review experts" meeting (PPR 91). It was felt that it would be difficult to ensure that effects in a monitoring programme are due to the active substance. Additionally, the experts at the meeting agreed that no monitoring data are stipulated at the EU level, but additional information may be required at national level for soil and sediment-dwelling organisms.

7. REFERENCES

EFSA Conclusion on the peer review of the pesticide risk assessment of the active substance Bixafen
http://www.efsa.europa.eu/en/efsajournal/pub/2917.htm

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CASE STUDY – SUMMARY FORM

8
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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