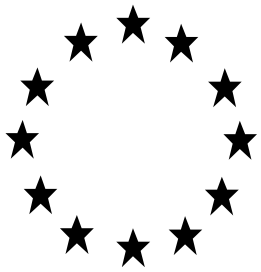
Regulation (EU) No 528/2012 concerning the making available on the market and use of biocidal products

Evaluation of active substances

COMPETENT AUTHORITY REPORT

(submitted by the evaluating Competent Authority)

Addendum



Permethrin

Product types 8 & 18

(Wood Preservatives & Insecticide)

Evaluating Competent Authority: Ireland

March 2017

Substance Name: Permethrin

EC Name: None available. However, IUPAC name: 3-phenoxybenzyl (1RS,3RS;1RS,3SR)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate ()

EC Number: 258-067-9

CAS Number: 52645-53-1

Applicant(s):

Tagros Chemicals India Ltd, Bayer Environmental Science, and LANXESS Deutschland GmbH

1 GENERAL SUBSTANCE INFORMATION

1.6 ANALYTICAL METHODS FOR DETECTION AND IDENTIFICATION

Analytical methods								
Analyte (type of analyte e.g. active substance, metabolite etc.)	**Compartment**	**Linearity**	**Specificity**	**Recovery rate (%)**			**Limit of quantification (LOQ), Maximum Residue Limits or other limits**	**Reference**
				Fortification range / Number of measurements	Mean	RSD		
All four permethrin stereoisomers	Technical active substance	CIPAC Validated	Chiral HPLC-DAD	CIPAC Validated	CIPAC Validated	CIPAC Validated	CIPAC Validated	CIPAC/4946*

* Bayer developed a suitable method of analysis which has been peer-validated by CIPAC. The method is available under the pre-publication scheme (CIPAC/4946).

3 SUMMARY OF THE ENVIRONMENTAL RISK ASSESSMENT

Fate and behaviour in the environment

Effects assessment

Summary table on calculated PNEC values	
Compartment	**PNEC**
Soil	PNECsoil: 0.198 mg/kg dry weight (0.175 mg/kg wwt).

4 ENVIRONMENTAL EFFECTS ASSESSMENT

4.1 FATE AND DISTRIBUTION IN THE ENVIRONMENT

4.1.1 Degradation

4.1.1.3 Rate and route of degradation including identification of metabolites and degradation products

4.1.1.3.2 Biodegradation in freshwater

Water/sediment degradation test

Summary table – fresh water/sediment degradation									
Method, Guideline, GLP status, Reliability	**Test type[1]**	**Exposure**	**Test system**		**Test substance concentra-tion**	**Incubation period**	**Degradation (DT_{50})**	**Remarks**	**Reference**
			Water	Sediment					
Aerobic and Anaerobic Transformation in Aquatic Sediment Systems, OECD guideline 308, GLP, The study was considered acceptable with a Reliability score of 1.	Biodegradation of DCVA (metabolite of AS permethrin) in freshwater		*Leverkusen, North Rhine Westphalia, Germany*		50µg/mL (trans/cis ratio = 3/1)	98 days	26 days @ T = 20°C = 49.3 days @ T = 12°C	See below	Hellpointner, E., Kasel, D., 2015, Permethrin-DCVA: Aerobic Aquatic Metabolism, Bayer CropScience AG, BCS-D-EnSa-Testing, 40789 Monheim, Germany, laboratory report number M1512320-4, (final-unpublished)
			Nespen, Reichshof, North Rhine Westphalia, Germany		50µg/mL (trans/cis ratio = 3/1)	113 days	49.8 days @ T = 20°C = 94.4 days @ T = 12°C		
[1] Test according to OECD criteria									

The route and rate of degradation of [cyclopropane-1-14C]DCVA (permethrin-DCVA, a mixture with a trans/cis ratio of 3/1 (w/w), as it is to be expected from degradation of the parent compound permethrin) were studied in two water/sediment systems under aerobic laboratory conditions in the dark at 20 ± 2 °C for 113 days at maximum. A study application rate of 20 µg permethrin-DCVA/test system (corresponding to 38 µg permethrin-DCVA/L) was applied, based on a maximum predicted environmental concentration of DCVA in surface waters (PECSW) and considering an over-dose factor of 3.8 due to technical needs.

- Mean **material balances** were 98.1% AR for system Anglersee (range from 92.7 to 101.5% AR) and 99.6% AR for system Wiehltalsperre (range from 97.5 to 101.1% AR).

- The maximum amount of **carbon dioxide** was 54.2 and 28.6% AR at study end (DAT-98 and DAT-113) in system Anglersee and Wiehltalsperre, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of ≤ 0.1% AR at all sampling intervals for both water/sediment systems. Residues in water decreased from 91.2% AR at DAT-0 to 9.0% AR at DAT-98 in system Anglersee and from 86.0% AR at DAT-0 to 3.6% AR at DAT-113 in system Wiehltalsperre.

- **Extractable residues** in sediment of system Anglersee increased from 8.3 AR at DAT-0 to 13.4% AR at DAT-4 and then decreased to 2.3% AR at DAT-98. In system Wiehltalsperre extractable residues in sediment increased from 11.4% AR at DAT-0 to 23.4% AR at DAT-98 and then decreased to 13.2% AR at DAT-113. Extractable residues in the total system (water and sediment extracts) decreased from 99.5% AR at DAT-0 to 11.3% AR at DAT-98 in system Anglersee and from 97.5% AR at DAT-0 to 16.8% AR at DAT-113 in system Wiehltalsperre. **Non-extractable residues (NER)** in system Anglersee increased from 0.9% AR at DAT-0 to 29.6% AR at DAT-70 and then slightly decreased to 28.7% AR at DAT-98. In system Wiehltalsperre NER increased from 3.2% AR at DAT-0 to 52.1% AR at DAT-113.

- Permethrin-DCVA dissipated from the **water** due to degradation and translocation into the sediment. In system Anglersee the amount of permethrin-DCVA (sum of trans-DCVA and cis-DCVA) in the water decreased from 90.7% AR at DAT-0 to 2.0% AR at DAT-98. The amounts of trans-DCVA and cis-DCVA decreased from DAT-0 to DAT-98 from 67.5 to 2.0% AR and from 23.1% AR to non-detectable amounts, respectively. In system Wiehltalsperre the amount of permethrin-DCVA (sum of trans-DCVA and cis-DCVA) in the water decreased from 86.0% AR at DAT-0 to 1.0% AR at DAT-113. The amounts of trans-DCVA and cis-DCVA decreased from DAT-0 to DAT-113 from 65.8 to 1.0% AR and from 20.3% AR to non-detectable amounts, respectively.

- In system Anglersee the amount of permethrin-DCVA (sum of trans-DCVA and cis-DCVA) in **sediment** extracts increased from 8.3% AR at DAT-0 to 13.4% AR at DAT-4 and then decreased to 1.2% AR at DAT-98. The amount of trans-DCVA in sediment extracts of system Anglersee increased from 6.4% AR at DAT-0 to 10.0% AR at DAT-4 and then decreased to 1.2% AR at DAT-98. The amount of cis-DCVA in sediment extracts of system Anglersee increased from 1.9% AR at DAT-0 to 3.4% AR at DAT-4 and then decreased to non-detectable amounts at DAT-98. In system Wiehltalsperre the amount of permethrin-DCVA (sum of trans-DCVA and cis-DCVA) in sediment extracts increased from 11.4% AR at DAT-0 to 22.0% AR at DAT-98 and then decreased to 6.7% AR at DAT-113. The amount of trans-DCVA in sediment extracts of system Wiehltalsperre increased from 8.5% AR at DAT-0 to 17.2% AR at DAT-98 and then decreased to 5.3% AR at DAT-113. The amount of cis-DCVA in sediment extracts of system Wiehltalsperre increased from 2.9% AR at DAT-0 to 5.9% AR at DAT-35 and then decreased to 1.3% AR at DAT-113.

- DCVA) in the **total system** decreased from 99.0% AR at DAT-0 to 3.2% AR at DAT-98. The amounts of trans-DCVA and cis-DCVA decreased from DAT-0 to DAT-98 from 73.9 to 3.2% AR and from 25.1% AR to non-detectable amounts, respectively. In system Wiehltalsperre the amount of permethrin-DCVA (sum of trans-DCVA and cis-DCVA) in the total system decreased from 97.5% AR at DAT-0 to 7.7% AR at DAT-113. The amounts of trans-DCVA and cis-DCVA decreased from DAT-0 to DAT-113 from 74.3 to 6.3% AR and from 23.2% AR to 1.3% AR, respectively.

- Besides carbon dioxide, no **degradation products** of permethrin-DCVA > 5% AR in each compartment or > 10% AR in the total system were found. The total unidentified residues in the total system amounted to a maximum of 7.9% AR and no single component exceeded 6.4% AR at any sampling interval in both water/sediment systems.

Kinetic analysis: The experimental data could be best described by the single first order (SFO) kinetic model. The DT50 values for the dissipation of permethrin-DCVA from the water were 22.6 and 29.8 days (sum of DCVA isomers), 24.7 and 32.1 days (trans-DCVA) as well as 16.8 and 22.4 days (cis-DCVA in the water of the tested water/sediment systems under aerobic conditions in system Anglersee and Wiehltalsperre, respectively. Dissipation of sum of isomers and of both individual isomers from water was faster in Anglersee as in Wiehltalsperre system. Further it is indicated that cis-DCVA is dissipating faster from water than trans-DCVA.

The DT50 values for the degradation of permethrin-DCVA in the total water/sediment system were 26.0 and 49.8 days (sum of DCVA isomers), 28.4 and 52.5 days (trans-DCVA) and 19.8 and 42.0 days (cis-DCVA). Degradation of sum of isomers and of both individual isomers in total test system was faster in Anglersee than in Wiehltalsperre system. Further it is indicated that cis-DCVA is degrading faster in both total systems than trans-DCVA.

These kinetic parameters are summarised in the table below along with the equivalent values back-calculated to 12°C*. Overall DCVA will be well degraded in water/sediment systems under aerobic conditions. Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle and the potential for a complete mineralization of DCVA. Any potential for DCVA to persist in the aquatic environment is discussed in section 5.1.3 below.

Anglersee

			20°C		12°C	
		Kinetic Model	**DT_{50}**	**DT_{90}**	**DT_{50}**	**DT_{90}**
Sum of trans- and cis- DCVA	Water	SFO	22.6	75.1	42.9	142.4
	Total system	SFO	26.0	86.5	49.3	164.0
trans-DCVA	Water	SFO	24.7	82.0	46.8	155.5
	Total system	SFO	28.4	94.2	53.9	178.6
cis-DCVA	Water	SFO	16.8	56.0	31.9	106.2
	Total system	SFO	19.8	65.9	37.6	125.0

Wiehltalsperre

			20°C		12°C	
		Kinetic Model	**DT_{50}**	**DT_{90}**	**DT_{50}**	**DT_{90}**
Sum of trans- and cis- DCVA	Water	SFO	29.8	98.9	56.5	187.6
	Total system	SFO	49.8	165	94.4	312.9
trans-DCVA	Water	SFO	32.1	107	60.9	202.9
	Total system	SFO	52.5	174	99.6	330.0
cis-DCVA	Water	SFO	22.4	74.3	42.5	140.9
	Total system	SFO	42.0	139	79.7	263.6

* $DT_{50}(12\ °C) = DT_{50}(20\ °C) \bullet e^{(0.08\ (20\ -12))}$; Guidance on the Biocidal Products Regulation, Volume IV: Environment, Part A: Information Requirements, IV Testing Strategies, Section 4.2.3

4.2 EFFECTS ON ENVIRONMENTAL ORGANISMS

4.2.4 Toxicity to terrestrial organisms, chronic tests

Summary table – long term terrestrial toxicity							
Method, Guideline, GLP status, Reliability	**Species**	**End point/ Type of test**	**Exposure**		**Results**	**Remarks**	**Reference**
			Design	**Duration**	**LOEC/NOEC/EC_{10}**		
Earthworm/soil-dwelling non-target invertebrates reproduction							
Permethrin a.s.: Effects on the reproduction of the collembolan *Folsomia candida* OECD guideline 232 2009, GLP, The study was considered acceptable with a Reliability score of 1	*Folsomia candida*	Reproduction	0, 18, 32, 56, 100, 178, 316, 562, 1000 mg a.s./kg soil dry weight nominal concentration	28 days	NOEC (Reproduction) 562 mg/kg soil d.w. LOEC (Reproduction) 1000 mg/kg soil d.w. EC10: (Reproduction) 579 mg/kg soil d.w.(Probit analysis)	None	Section A7.5.6-01

Value used in Risk Assessment	
Value/conclusion	NOEC = 562*(0.034/0.050) = 382.16 mg/kg soil, dwt LOEC = 1000*(0.034/0.050) = 680 mg/kg soil, dwt. Values have been amended in accordance with the Guidance for BPR, vol. IV, part B, p. 132.
Justification for the value/conclusion	Not applicable

4.4 DERIVATION OF PNECS

Compartment	PNEC	Remarks/Justification
Soil	*PNECsoil: 0.198 mg/kg dry weight (0.175 mg/kg wwt).*	Organism: *Soil micro-organism* Endpoint: EC_{50} *> 9.9 mg/kg dry weight (8.76 mg/kg wwt)* Assessment factor: *50* Extrapolation method: *Assessment factor* Justification: *As there are results from two long-term studies for two species of two trophic levels are available, an assessment factor of 50 is applied.*

5.1.3 PBT Assessment (following Annex XIII to Regulation (EC) No 1907/2006)

Assessment of persistence

Screening

The Permethrin CAR prepared by IE in 2013 did not contain any water sediment simulation studies where DCVA was applied as parent. Rather DCVA was detected as a breakdown product when Permethrin was applied in two aerobic water sediment system (pond and creek). The relevant extract from the CAR reads:

"There appeared to be slow degradation of DCVA in both test systems. DCVA reached high maximum whole-system levels of 84.1% AR for the pond system and 84.3% AR for the creek system, by day 62 in both cases. It had only declined slightly by the end of the incubations (120 days) to levels of 75.3% AR for the pond system and 70.6% AR for the creek system. Due to these small declines a reliable DT50 value could not be determined."

The evaluator concludes:

"There might (also) be potential for DCVA to exhibit persistence in aquatic systems, on the basis of slow degradation in the presented test systems."

The results of the study presented in this addendum may now be used to further the PBT discussion with respect to DCVA by comparing the **whole system DT50 values** against the triggers for water and sediment given in the ECHA PBT guidance:

- In system Anglersee none of the DT50 values exceed the P trigger for fresh or estuarine water (40 days) at 20°C. However when converted to 12°C the value for the trans isomer (53.9 days) and for the sum of isomers (49.3 days) do exceed the trigger. None of the calculated DT50 values exceed the corresponding vP criterion.

- In system Anglersee none of the DT50 values exceed the P trigger for fresh or estuarine sediment (120 days) at either temperature.

- In system Wiehltalsperre the DT50 values for cis, trans and sum of isomers all exceed the 40 day P trigger for fresh or estuarine water (42, 52.5, 49.8 days) at 20°C. When converted to 12°C they also exceed the 60 day vP criterion (79.7, 99.6, 94.4 days).

- In system Wiehltalsperre none of the DT50 values exceed the P trigger for fresh or estuarine sediment (120 days) at either temperature.

Clearly this study shows that DCVA does not meet the persistence criteria in sediment. With regard to freshwater, comparing a whole system value with the trigger value is not ideal - the whole system value has an input from both water and sediment compartments and does not give an accurate reflection of degradation in water alone. The RMS evaluator notes that there is significantly higher partitioning of DCVA out of the water compartment in system Wiehtalsperre than in Anglersee - max sediment =23.4% AR vs 13.4% AR and NER at study end = 52.1% AR vs 23.4% AR, respectively. Therefore it may be possible to conclude that a greater percentage of the degradation of DCVA occurs in the water compartment in system Anglersee

than for system Wiehtalsperre. Thus, the whole system DT50 value for Anglersee may be a closer estimate of a freshwater DegT50 than the Wietalsperre whole system value. On the other hand, it should be noted that the DT50 value in Wiehtalsperre might be even higher if the fraction of non-extractable residues was lower (NER = 52.1% AR at DAT-113). It is difficult to investigate this phenomenon more closely given the available data. Therefore, in the absence of a pure freshwater degradation constant, it must be concluded that the permethrin metabolite DCVA exceeds the vP criterion in fresh or estuarine water of 60 days.

The overall outcome of the PBT assessment in the 2013 CAR reads as follows:

"Due to this borderline status and to the difficulties pertaining to the determination of the P classification, it is recommended that permethrin should be further assessed by the ECHA PBT working group. Depending on the outcome of the ECHA PBT working group there may be a requirement for the substance to be considered as a candidate for substitution as identified in the provisions of Article 10 of Regulation (EU) No 528/2012."

It is expected that the PBT EG will consider Permethrin in 2017 so the data from the DCVA study can be discussed further.

5 GENERAL PRODUCT INFORMATION

6.5 ANALYTICAL METHODS FOR DETECTION AND IDENTIFICATION

Analytical methods for the analysis of the product as such including the active substance, impurities and residues									
Analyte (type of analyte e.g. active substance)	**Analytical method**	**Fortification range / Number of measurements**	**Linearity**	**Specificity**	**Recovery rate (%)**			**Limit of quantification (LOQ) or other limits**	**Reference**
					Range	Mean	RSD		
All four permethrin stereoisomers in an EW formulation	CIPAC for EW	CIPAC Validated	CIPAC Validated	Chiral HPLC-DAD	CIPAC Validated	CIPAC Validated	CIPAC Validated	CIPAC Validated	CIPAC/4946*
All four permethrin stereoisomers in an EC formulation	Apply CIPAC for EW to EC	1S-cis Permethrin (S,S) 0.69 %w - 4.63%w 1R-cis Permethrin (R,R) 0.69 %w -4.59 %w 1S-trans Permethrin (S,R) 1.93 %w - 12.9 %w 1R-trans Permethrin (R,S)	R^2 = 1.000 for all 1S-cis Permethrin (S,S): 0.013-0.34 mg/mL (n = 6 points) 1R-cis Permethrin (R,R): 0.013-0.33 mg/mL (n = 6 points) 1S-trans Permethrin (S,R):	Chiral HPLC-DAD No significant interference	n = 2 at each level – 3 levels 1S-cis Permethrin (S,S) 97.3 – 98.7% 1R-cis Permethrin (R,R) 98.2 – 99.5%	n = 2 at each level – 3 levels 1S-cis Permethrin (S,S) Recovery level (0.69 %w): 97.3 % Recovery level (2.31%w): 98.7 %	Six samples (single injection) from 1 batch – 1S-cis Permethrin (S,S): 0.46 %. 1R-cis Permethrin (R,R): 0.41 % 1S-trans Permethrin (S,R):	Not applicable	CIPAC/4946 & Bayer CropScience AG: VALIDATION REPORT Validation of HPLC-method AM032611FP2 - Determination of 1S and 1R-cis and 1S and 1R-trans enantiomers Permethrin in formulations - esdepallethrine + permethrin +

		1.91 %w - 12.8 %w	0.035-0.93 mg/mL (n = 6 points) <u>1R-trans Permethrin (R,S):</u> 0.035-0.93 mg/mL (n = 6 points)		<u>1S-trans Permethrin (S,R)</u> 97.5 – 99.5% <u>1R-trans Permethrin (R,S)</u> 96.6 – 99.1%	Recovery level (4.63%w): 98.3 % <u>1R-cis Permethrin (R,R) (n = 2)</u> Recovery level (0.69 %w): 98.6 % Recovery level (2.30 %w): 99.5 % Recovery level (4.59 %w):98.2% <u>1S-trans Permethrin (S,R) (n = 2)</u> Recovery level (1.93 %w): 97.5 % Recovery level (6.43	0.34 % 1R-trans Permethrin (R,S): 0.62 %		piperonylbutoxide EC 337.4 (7.4+174+156 g/L), Report No. VB3-AM032611FP2, Author J. Leibold, Year 2014

						%w): 99.5 % Recovery level (12.9 %w): 98.1 % <u>1R-trans Permethrin (R,S) (n = 2)</u> Recovery level (1.91 %w): 96.6 % Recovery level (6.38 %w): 99.1 % Recovery level (12.8 %w): 98.0 %			
All four permethrin stereoisomers in an WP formulation	Apply CIPAC for EW to WP	<u>1S-cis Permethrin (S,S)</u> 0.99 %w – 6.57%w <u>1R-cis Permethrin (R,R)</u> 0.98 %w -6.52	As for EC formulation above	Chiral HPLC-DAD No significant interference	n = 2 at each level – 3 levels <u>1S-cis Permethrin (S,S)</u> 98.8 –	n = 2 at each level – 3 levels <u>1S-cis Permethrin (S,S)</u> Recovery	Six samples (single injection) from 1 batch – 1S-cis Permethrin (S,S):	Not applicable	CIPAC/4946 & Bayer CropScience AG: Validation of HPLC-method

		%w <u>1S-trans Permethrin (S,R)</u> 2.74 %w - 18.3 %w <u>1R-trans Permethrin (R,S)</u> 2.72 %w - 18.3 %w			101.2% <u>1R-cis Permethrin (R,R)</u> 98.0 – 101.4% <u>1S-trans Permethrin (S,R)</u> 99.3 – 100.9% <u>1R-trans Permethrin (R,S)</u> 99.4 – 101.0%	level (0.99% w/w): 98.8 % Recovery level (3.29%): 100.7 % Recovery level (6.57%): 101.2 % <u>1R-cis Permethrin (R,R)</u> Recovery level (0.98% w/w): 98.0 % Recovery level (3.26%): 100.8 % Recovery level (6.52%): 101.4 % <u>1S-trans Permethrin (S,R)</u> Recovery level (2.74%): 99.3 % Recovery	1.08%. 1R-cis Permethrin (R,R): 1.11 % 1S-trans Permethrin (S,R): 0.96 % 1R-trans Permethrin (R,S): 0.93 %		AM032611FP2 - Determination of 1S and 1R-cis and 1S and 1R-trans enantiomers Permethrin in formulations - (Permethrin WP 25 (250 g/kg)), Report No. VB2-AM032611FP2, Author J. Leibold, Year 2014

						level (9.13%): 100.9 % Recovery level (18.3% w/w): 100.8 % <u>1R-trans Permethrin (R,S)</u> Recovery level (2.72% w/w): 99.4 % Recovery level (9.05% w/w): 101.0 % Recovery level (18.1 % w/w): 100.9 %			
All four permethrin stereoisomers in wood preservatives with common co-formulants	Apply CIPAC for EW to some wood preservative formulations	No data provided	No data provided	Chiral HPLC-DAD No significant interference for TC or basic product formulation, however significant interference when formulations	No data provided	No data provided	No data provided	Not applicable	CIPAC/4946 & Lanxess Deutschland GmbH: Determination of 1S- and 1R- cis and 1S- and 1R-

				became more complex (higher number of actives and or higher number of common co-formulants found in wood preservatives.					tans enantiomers Permethrin in wood preservative formulations, Mr J. Leibold (2016).

* Bayer developed a suitable method of analysis which has been peer-validated by CIPAC for EW formulations. The method is available under the pre-publication scheme (CIPAC/4946). Bayer have also provided an additional validation report as part of this submission, however the validation data has not been reported above because the method is the Bayer CIPAC Method. Sample chromatograms were provided and no interference was observed at the retention times of interest.