

Schweizerisches Zehtrum für angewandte Okotoxikologie Centre Suisse d'écotoxicologie appliquée

# SQC (EQS<sub>sed</sub>) – Proposal from the Ecotox

# Centre for: Cypermethrin

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Please note that the suggested EQS and contents of this dossier do not necessarily reflect the opinion of the external reviewer.

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#### Summary

#### SQC (EQS<sub>sed</sub>): 0.018 μg/kg d.w.

In the framework of the Module Sediment, which is intended to help cantons in sediment quality assessment, the Ecotox Centre develops proposals for Environmental Quality Criteria for sediment (SQC). SQC are derived applying the methodology described in the EU-Technical Guidance (TGD) for Deriving Environmental Quality Standards (EQS). In order to ensure that the dossiers are internationally comparable, the English terminology of the TGD will be used in the remainder of the dossier. These criteria provide a first screening tool to evaluate sediment chemical quality and the potential risk for the aquatic ecosystem. Based on the scientific literature available at present a preliminary SQC for cypermethrin of  $0.018 \,\mu$ g/kg d.w. is proposed for standard sediments with 1% OC.

#### Zusammenfassung

#### SQK (EQS<sub>sed</sub>): 0.018 $\mu$ g/kg d.w.

Im Rahmen des Sedimentmoduls, das den Kantonen bei der Bewertung der Sedimentqualität helfen soll, entwickelt das Oekotoxzentrum Vorschläge für Umweltqualitätskriterien für Sedimente (SQK). Diese Kriterien dienen als Methode für ein erstes Screening zur Bewertung der chemischen Sedimentqualität und des potenziellen Risikos für aquatische Ökosysteme. Auf der Basis von Literaturdaten für die Wirkung von Cypermethrin und unter Verwendung der Methode, die in der Technischen Richtlinie der EU zur Ableitung von Umweltqualitätsnormen beschriebenen wird, schlägt das Oekotoxzentrum einen vorläufigen SQK für Cypermethrin von 0.018  $\mu$ g/kg d.w. für Standardsedimente mit 1 % OC vor.

#### Résumé

#### CQS (EQS<sub>sed</sub>): 0.018 $\mu$ g/kg p.s.

Dans le cadre du module Sédiments qui devrait aider les cantons à évaluer la qualité des sédiments, le Centre Ecotox élabore des propositions de critères de qualité environnementale pour les sédiments (CQS). Les CQS sont dérivés en appliquant la méthodologie décrite dans le Guide Technique de l'UE (TGD) pour la Dérivation des Normes de Qualité Environnementale (EQS). Afin que les dossiers soient comparables au niveau international, la terminologie anglaise du TGD est utilisée ci-dessous. Ces critères fournissent un premier outil de dépistage pour évaluer la qualité chimique des sédiments et le risque potentiel pour l'écosystème aquatique. Sur la base des données sur les effets existants dans la littérature un CQS preliminaire pour la cyperméthrine de 0.018 µg/kg p.s. est proposé pour les sédiments standards avec 1 % CO.



#### Sommario

#### CQS (EQS<sub>sed</sub>): $0.018 \mu g/kg p.s.$

Nell'ambito del modulo Sedimenti, che è finalizzato ad aiutare i Cantoni nella valutazione della qualità dei sedimenti, il Centro Ecotox sviluppa proposte per i criteri di qualità ambientale per i sedimenti (CQS). I CQS sono derivati applicando la metodologia descritta nella Guida Tecnica dell'UE (TGD) per la Derivazione degli Standard di Qualità Ambientale (EQS). Per garantire che i dossier siano comparabili a livello internazionale, viene utilizzata la terminologia inglese del TGD. Questi criteri forniscono un primo strumento di screening per valutare la qualità chimica dei sedimenti e il potenziale rischio per l'ecosistema acquatico. Sulla base della letteratura scientifica disponibile allo stato attuale un CQS provisorio per la cipermetrina di 0.018  $\mu$ g/kg p.s. è proposto per sedimenti standard con 1 % CO.



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# 1 General Information

Extended general information on the pyrethroid insecticide cypermethrin is provided in the Ecotox Centre EQS Dossier for cypermethrin in water (Ecotox Centre 2016)<sup>1</sup>. Selected information from the EQS water Dossier and additional information relevant for sediment is presented in this chapter. Registration and EQS dossiers referred to are:

- EC cypermethrin EQS dossier (2011)
- EC DRAR alpha-cypermethrin (2018)
- EC DAR zeta-cypermethrin (2006)
- EC DAR beta-cypermethrin (2013a)
- EC DRAR cypermethrin (2017)
- EC AR cypermethrin cis:trans/40:60 (2013b)

#### 1.1 Identity and physico-chemical properties

Cypermethrin contains three asymmetric carbon atoms resulting in four diastereomeric pairs of enantiomers. The non-defined mixture of these stereoisomers has the CAS number 52315-07-8. Some subsets of cypermethrin isomer pairs have distinct ISO common names and CAS numbers (Table 1). Based on the conclusion that no significant differences in toxic effects have been reported for the individual stereoisomers/mixtures, the EU EQS Dossier for cypermethrin considers all isomeric mixtures (EC 2011).

The EU Assessment report for the biocide cypermethrin cis:trans/40:60 Product-type 8 (Wood Preservative) (EC 2013b) states that cis-isomers in R-configuration exert stronger effects on non-target arthropods than other isomers. As alpha-cypermethrin consists of two cis-isomers while the other mixtures contain only trans-isomers or cis- and trans-isomers, alpha-cypermethrin potentially exerts stronger effects on arthropods than the other mixtures. Further, S-configuration of the  $\alpha$ -cyano group results in higher toxicity to mammals than R-configuration, which is mostly non-toxic to mammals. Published data do not provide unambiguous proof of higher toxicity of alpha-cypermethrin to arthropods compared to other cypermethrin isomer mixtures.

As all isomers may occur in water bodies due to the registered cypermethrin containing products, available data on all isomeric mixtures are considered in this Dossier, as in the EU and Ecotox Centre EQS Dossiers for water (EC 2011, Ecotox Centre 2016).

The log  $K_{oc}$  and  $K_{ow}$  reported for cypermethrin are above the trigger for sediment effects assessment according to the TGD (EC 2018a).

Table 1 summarizes identity and physico-chemical parameters for cypermethrin required for EQS derivation according to the TGD (EC 2018a). Where available, experimentally collected data is identified as (exp.) and estimated data as (est.). When not identified, no indication is available in the cited literature.

<sup>&</sup>lt;sup>1</sup> The dossier can be requested to <u>info@oekotoxzentrum.ch</u>



Table 1 Information required for EQS derivation according to the TGD (EC 2018a).

Characteristics	Values	References
Common name	Cypermethrin <sup>2</sup>	EC (2011)
IUPAC name	Cyano(3-phenoxyphenyl)methyl 3-(2,2- dichloroethenyl)-2,2- dimethylcyclopropanecarboxylate	EC (2011)
Chemical group	Pyrethroid insecticide	EC (2011)
Structural formula	$CI \qquad O \qquad CN \\ CI \qquad CH_3 CH_3 CH_3 O \qquad O $	EC (2011)
Molecular formula	$C_{22}H_{19}Cl_2NO_3$	EC (2011)
CAS	52315-07-8: cypermethrin 67375-30-8: alpha-cypermethrin 65731-84-2: beta-cypermethrin 71697-59-1: theta-cypermethrin 1315501-18-8 (formerly 52315-07-8): zeta-cypermethrin	EC (2011)
EINECS	257-842-9	EC (2011)
Code SMILES	CC1(C(C1C(=O)OC(C#N)C2=CC(=CC=C2)O C3=CC=CC=C3)C=C(Cl)Cl)C	PubChem (2019)
Molecular weight [g/mol]	416.3	EC (2011)
Melting point [°C]	<ul> <li>[1] Onset 41.2 °C, peak 47.3 °C (exp., cypermethrin, 98.3 %)</li> <li>[2] 81.5 °C (alpha-cypermethrin, 97.3 %)</li> <li>[3] -3 °C (zeta-cypermethrin, 85.3 %)</li> </ul>	<ul> <li>[1] Bates, M. (2002),</li> <li>in EC (2017) B2 p. 4</li> <li>[2] van Helvoirt, 1992a</li> <li>(Cyanamid Agro) cited</li> <li>in EC (2018b) B2 p. 4</li> <li>[3] de Ryckel, 2001a</li> <li>cited in EC (2006) p.</li> <li>2-2</li> </ul>
Boiling point [°C]	<ul> <li>[1] No boiling observed, but decomposition &gt;200 °C (exp., cypermethrin, 98.3 %)</li> <li>[2] &gt;360 °C (zeta-cypermethrin, 86.8 % purity)</li> </ul>	<ul> <li>[1] Bates, M. (2002),</li> <li>cited in EC (2017) B2</li> <li>p. 4</li> <li>[2] Alvarez, 1994 cited</li> <li>in EC (2006) p. 2-2</li> </ul>
Vapour pressure [Pa]	[1] $1.9 \cdot 10^{-7}$ at 20 °C (extrapolated mean for 98.4 % and 94.2 % cypermethrin) [2] $1.1 \cdot 10^{-7}$ at 25 °C (99 % cypermethrin)	[1] Terence-Grayson et al. (1982) cited in EC (2017) B2 p.7

 $<sup>^2</sup>$  It is stated in the EC dossier (EC 2011) that cypermethrin refers to « Isomer mixture of cypermethrin, alphacypermethrin (CAS 67375-30-8), beta-cypermethrin (CAS 65731-84-2), theta-cypermethrin (CAS 71691-59-1) and zeta-cypermethrin (52315-07-8). No significant differences in toxicity between isomers were found in the literature studied. »



Characteristics	Values	References
	[3] 2.53 · 10 <sup>-7</sup> at 25 °C (zeta- cypermethrin)	<ul> <li>[2] Waghmare, 2000c</li> <li>cited in EC (2017) B2 p.</li> <li>7</li> <li>[3] Alvarez, 1991 cited</li> <li>in EC (2006) p. 2-3</li> </ul>
Henry's law constant [Pa·m³/mol]	<ul> <li>[1] 0.024 at 20 °C (calculated,</li> <li>cypermethrin)</li> <li>[2] 0.069 at 20 °C (alpha-cypermethrin)</li> </ul>	<ol> <li>Bates, M. (2002), cited in EC (2017) B2</li> <li>8</li> <li>Craig 1999 cited in EC (2018b) B2 p. 6</li> </ol>
Water solubility [mg/l]	<ul> <li>[1] cypermethrin</li> <li>9 at 20°C, pH 6 (98.3 %)</li> <li>9 at 20°C, pH 4 (98.3 %)</li> <li>[2] alpha-cypermethrin</li> <li>0.014 at 20°C, pH 5.02 (97.9 %)</li> <li>0.013 at 20°C, pH 7.05 (97.9 %)</li> <li>0.016 at 20°C pH 9.02 (97.9 %)</li> <li>[3] alpha-cypermethrin at 20°C (98 %):</li> <li>0.67 · 10<sup>-3</sup> (pH 4)</li> <li>3.97 · 10<sup>-3</sup> (pH 7)</li> <li>4.54 · 10<sup>-3</sup> (pH 9)</li> <li>1.25 · 10<sup>-3</sup> (bidest. water)</li> <li>[4] beta-cypermethrin</li> <li>&lt;0.9 at 20°C, pH 7 (98.7 %)</li> <li>&lt;0.9 at 20°C, pH 9 (98.7 %)</li> <li>&lt;1.9 at 20°C, pH 9 (98.7 %)</li> <li>[5] zeta-cypermethrin 0.0387 at 20 °C</li> <li>pH 7 in distilled water</li> <li>[6] 0.004 at 20 °C, pH 7, isomer not specified</li> </ul>	<ul> <li>[1] Bates, M. (2002), cited in EC (2017) B2</li> <li>p. 14</li> <li>[2] WHO (2015)</li> <li>[3] Baldwin 1990 cited in EC (2018b) B2 p. 9</li> <li>[4] Thompson 1997, cited in EC (2013b) B2</li> <li>p. 9</li> <li>[5] de Ryckel 2001a</li> <li>cited in EC (2006) B2</li> <li>p. 2-8</li> <li>[6] Anonymous 2002</li> <li>cited in EC (2011) B2</li> <li>p. 4</li> </ul>
Dissociation constant (pK <sub>a</sub> )	no dissociation in water (cypermethrin)	EC (2017)
Octanol-water partition coefficient (log K <sub>ow</sub> ) <sup>a</sup>	<ul> <li>[1] 6.6 (cypermethrin, method not listed)</li> <li>[2] 5.3–5.6 (exp., 98.3 %, OECD 117, EEC A8, HPLC method) range of discrete cypermethrin isomer pairs, mean of 5.45 used for risk assessment/ecotoxicology)</li> <li>[3] 5.5 (exp., alpha-cypermethrin; 95.4 % at 20 °C; OECD 117, RP-HPLC-method)</li> <li>[4] 6.83 (exp., alpha-cypermethrin; 97.86 %, OECD 117, HPLC-method)</li> </ul>	<ul> <li>[1] Iomlin (2009)</li> <li>[2] Bates, M. (2002)</li> <li>cited in EC (2017) B2</li> <li>p. 16, EC (2013a);</li> <li>[3] Langner &amp; Fisk,</li> <li>1993</li> <li>(Cyanamid Agro),</li> <li>cited in EC (2018b) B2</li> <li>p. 10</li> <li>[4] Study Number</li> <li>10206 (2010) cited in</li> <li>WHO (2015) p. 27</li> </ul>



Characteristics	Values	References		
	<ul> <li>[5] 5.7 (peak 1) and 5.8 (peak 2) (exp.; beta-cypermethrin 98.7 %; OECD 117, HPLC-method (GLP))</li> <li>[6] 5-6 (exp., zeta-cypermethrin; 85.3 %, OECD 117, RP-HPLC method )</li> <li>[6] 6.48 (exp., zeta-cypermethrin; 86.8 %, "slow stirring" equilibration method and GC-ECD analysis)</li> </ul>	<ul> <li>[5] Thompson 1997,</li> <li>cited in EC (2013b) B2,</li> <li>p. 10</li> <li>[6] EC (2006), B2, p.</li> <li>11</li> </ul>		
	[1] adsorption (exp., >99 % cypermethrin): $5.38 (K_{oc} 238,000; SD = 38,000, 1 % OC)$ $5.7 (K_{oc} 502,000; SD = 7,000, 3 % OC)$ $5.25 (K_{oc} 177,000; SD = 40,000; 13 % OC)$	[1] Maund <i>et al.</i> (2002)		
Sediment-water partition coefficient (log K <sub>oc</sub> or K <sub>p</sub> )	[2] desorption (exp., >99 % cypermethrin): 5.45 (K <sub>oc</sub> 281,000; SD = 28,000, 1 % OC) 5.76 (K <sub>oc</sub> 582,000; SD = 75,000, 3 % OC) 5.26 (K <sub>oc</sub> 182,000; SD = 73,000; 13 % OC) [3] 3.72 (est. from log K <sub>ow</sub> 5.45)	<ul> <li>[2] Maund <i>et al.</i></li> <li>(2002)</li> <li>[3] Based on the equation for esters in TGD EC (2018a) where logK<sub>oc</sub> = 0.49*logK<sub>ow</sub>+1.05</li> </ul>		
Sediment adsorption coefficient (K <sub>d</sub> [I/kg])	8976	Brice and Cooke (2006c) cited in EC (2017)		
Log K <sub>susp</sub>	4.54 calculated, isomer not specified	EC (2011)		
Aqueous hydrolysis DT₅o	[1] cypermethrin (99:1 H <sub>2</sub> O:Ethanol, 25 °C) pH 4.5: 99 weeks pH 7: 63 weeks pH 8: 50 weeks [2] alpha-cypermethrin pH 9: 8.94 - 17.34 d (50°C and 20°C, respectively) [3] alpha-cypermethrin pH 4: no degradation pH 7: 69.8 d (mean, 25 °C) pH 9: 3.7 d (mean, 25 °C) [4] cypermethrin cis:trans/40:60 (50 °C) pH 4: 1 yr pH 7: 4.73 d pH 9: 1.9 h [5] zeta-cypermethrin (85.3 % pure, cis/trans 51/49 ; 25 °C and 50 °C): pH 4: < 10 % degradation in 5 days (50 °C), hydrolytically stable at both temperatures pH 7: DT <sub>50</sub> = 4.6 d (50 °C), moderate hydrolysis at both temperatures	<ol> <li>Chapman <i>et al.</i></li> <li>(1982)</li> <li>WHO (2015)</li> <li>Hassink 2005 cited</li> <li>in EC (2018a) B8 p.</li> <li>280</li> <li>EC (2013a)</li> <li>Class 2003c cited</li> <li>in EC (2006) p. 2-11</li> </ol>		



Characteristics	Values	References			
	pH 9: DT <sub>50</sub> = 1.5 h (50 °C), hydrolytically labile at both temperatures				
Aqueous photolysis DT₅₀ [d]	[1] 1.2 (Cp-label) - 2.2 (Bz-label) (alpha- cypermethrin 99.4 and 99.7 % pure, pH 5, 22 °C; SETAC-procedures: Suntest CPS+apparatus: Xenon lamp with UV- filter blocking $\lambda < 290$ nm) [2] 0.8 (beta-cypermethrin, exp.; 25 °C and pH 7; SETAC guideline 1995) [3] 3.05 (zeta-cypermethrin; sun light, 20-25 °C, pH 7, clear water; degradation also in dark samples/hydrolysis) [4] 0.6-1 (cypermethrin, river water and salt water), 2.6-3.6 (distilled water) <sup>3</sup> [5] 12.4-14.8 (cypermethrin, summer sunlight days, pH 4, 20 °C)	<ul> <li>[1] Concha 2001 cited</li> <li>in EC (1999) p. 2-2</li> <li>[2] Mamouni 2005</li> <li>cited in EC (2013b) B2</li> <li>p. 11</li> <li>[3] Brodsky 2003 cited</li> <li>in EC (2006) p. 2-14</li> <li>[4] Crane <i>et al.</i> (2007)</li> <li>[5] EC (2005) p. 2</li> </ul>			
Biodegradation in aqueous environment DT <sub>50</sub> [d]	<ul> <li>[1] Not ready biodegradable (alpha- cypermethrin)</li> <li>[2] Not ready biodegradable (zeta- cypermethrin)</li> <li>[3] not readily biodegradable (cypermethrin cis:trans/40:60)</li> </ul>	<ul> <li>[1] Stone 1983 cited in EC (2018b) B8 p. 248</li> <li>[2] RMS assumption in EC (2006) p. 8-56</li> <li>[3] EC (2013a) p. 28</li> </ul>			
Biodegradation in water- sediment systems DT <sub>50</sub> [d]	<ul> <li>[1] 1.5 – 2.5 (zeta-cypermethrin, aerobic degradation)</li> <li>[2] 13.8 – 15.6 (zeta-cypermethrin, anaerobic degradation)</li> <li>[3] 8.85- 10.09 (zeta-cypermethrin, aerobic degradation)</li> <li>[4] 8 - 14.8 (alpha-cypermethrin, aerobic degradation)</li> </ul>	<ol> <li>Lucas, T. 1998</li> <li>Lucas, T. 1998</li> <li>cited in EC (2006) p. 8-60</li> <li>Ramsey, A.A. 1998</li> <li>cited in EC (2006) p. 8-67</li> <li>Elmarakby, S.A.</li> <li>1998 cited in EC</li> <li>(2006) p. 8-64</li> <li>trigger endpoints</li> <li>recalculated by RMS,</li> <li>EC (2018b) p. 364</li> </ol>			
Biodegradation in soil DT <sub>50</sub> [d]	<ul> <li>[1] 2 – 20 (cypermethrin, different soils)</li> <li>[2] 19.6 (cypermethrin, geometric mean)</li> </ul>	<ol> <li>Yeomans, P. Kelly,</li> <li>D. 2015, cited in EC</li> <li>(2017) B8 p. 180</li> <li>Drechsler et al</li> <li>2015 cited in EC</li> <li>(2017) B8 p. 228</li> </ol>			

<sup>a</sup> Data obtained from HPLC-based or unknown methods not used for EQS derivation.

<sup>&</sup>lt;sup>3</sup> Experimental light conditions not mentioned



#### **1.2** Regulation and environmental limits

Table 2 summarizes existing regulation and environmental limits in Switzerland and Europe for cypermethrin.

Table 2 Existing	regulation an	d environmental	limits for	cypermethrin in	Switzerland and	l elsewhere.
· • • • • • • • • • • • • • • • • • • •				-,,		

Europe					
Directive 2013/39/EU	Identified as a priority substance in the field of water policy.				
EQS – Water Framework Directive (inland water)	AA-EQS: 0.00008 μg/l MAC-EQS: 0.0006 μg/l OSfreshwater sed: 0.033 μg/kg d.w.				
Switzerland					
EQS- Ecotox Centre (07.03.17)	AA-EQS: 0.00003 μg/l MAC-EQS: 0.00044 μg/l				
Ordinance on phytosanitary products (916.161) (01.01.2019)	Annex 1 Active substances approved as a phytosanitary product: alpha-cypermethrin (67375-30-8), cypermethrin and cypermethrin high-cis (52315-07-8), zeta-cypermethrin (52315-07-8).				
Ordinance on Biocidal Products (OBP)	Annex 2 List of approved active substances according to Art. 9 of the regulation (EU) No. 528/20122 (Union list of approved active substances).				
Water protection ordinance (WPO) (01.06.18)	Annex 2 Requirements on Water Quality for plant protection products: 0.1 μg/l per individual substance. Annex 22 Additional requirements for groundwater which is used for drinking water or is intended as such: 0.1 μg/l per individual substance.				
FDHA Ordinance on the maximal limits for pesticide residues on vegetal and animal products (OPOVA) (01.05.18)	Annex 2 Maximum limit authorized for pesticide residues.				

#### 1.3 Use and emissions

Cypermethrin is an active substance used in Switzerland as a biocide (OBP) and phytosanitary product (OPPh) against insect pest (i.e. cabbage shoot weevil, rose-grain aphid, lymexylon, bark beetle) like in rapeseed culture (70 %), silviculture (30 %), wood treatment and pest control in urban areas (Wittmer *et al.* 2014). Cypermethrin is used in a number of phytosanitary products in Switzerland, either as single active ingredient, or in combination with other active ingredients, e.g. chlorpyrifos. Moreover, formulated products may also contain piperonyl butoxide as a synergist and/or other co-formulants such as sodium dodecylbenzenesulfonate (Office fédéral de l'agriculture 2019).

Emission of cypermethrin in agricultural areas occurs mainly by spray drift during its application. The main route of transport to surface waters is by soil erosion, since cypermethrin adsorbs strongly to soil particles. The sources from urban areas can be the wash-out from treated building materials, effluent from wastewater treatment plants (WWTP) and stormwater runoff (Trask *et al.* 2014, U.S. EPA 2006, Weston *et al.* 2010). In Switzerland, cypermethrin was not selected as a relevant substance for WWTP monitoring (Micropoll project, Federal Office for the Environment) but in a project developing strategies to manage micropollutants from diffuse sources, especially in agriculture, also funded by the Federal Office for the Environment (Wittmer *et al.* 2014).



#### 1.4 Mode of action and sensitivity of taxonomic groups

Pyrethroids are synthetic insecticides derived from pyrethrins, naturally active substances found in flowers of the genus *chrysanthemum*. The natural pyrethrins and synthetic pyrethroids can affect sodium channels in neurons by prolonging their opening. They are divided in subgroups I and II according to the symptoms they cause and their toxicity (Chalmers *et al.* 1986, Li *et al.* 2017). Type I molecules cause hyperactivity and incoordination due to repetitive firing in multiple nerves. Type II molecules (containing an  $\alpha$ -cyano group, including cypermethrin) cause single depolarization of axon and nerve terminals. Cypermethrin can also target the central nervous system by inhibition of  $\gamma$ -aminobutyric acid (GABA) type synapse receptor and ATPase activity necessary for active transport and homeostasis (Antwi *et al.* 2015, Chalmers *et al.* 1986). Cypermethrin also affects non-target organisms like aquatic insects, which showed a greater sensitivity than terrestrial insects when exposed to topically applied cypermethrin without water contact (aquatic insects that can survive in the absence of water for 48 h were chosen) (Siegfried 1993). A comparative toxicity study on brain sensitivity to cypermethrin showed that frog and fish were much more sensitive compared to birds and mammals based on measured concentrations of cypermethrin in the brain (Edwards *et al.* 1986).

#### 2 Environmental fate

#### 2.1 Stability and degradation products

The suggested primary route of degradation of cypermethrin in soil/sediment is the conversion to cypermethrin carboxamide and then breakdown of cypermethrin carboxamide or of cypermethrin directly into DCVA (3-(2,2-dichlorovinyl)- 2,2-dimethylcyclopropane carboxylic acid) and 3-PBA (3-phenoxybenzoic acid) (EC 2017).

DCVA, 3-PBA and cypermethrin carboxamide are common metabolites of cypermethrin, zetacypermethrin and beta-cypermethrin, for which published EFSA conclusions are available (EFSA 2009, 2014).

In a soil laboratory study (aerobic conditions, in the dark), cypermethrin showed low to moderate persistence, with the major (> 10 %) metabolites being DCVA (cis- and trans-isomer; max. 47.4 %) and 3-PBA (max. 10.2 %), with low to moderate and very low to low persistence, respectively (Wimbush *et al.* (2006) cited in EC (2017)). Degradation of cypermethrin was similar under anaerobic conditions. Cypermethrin carboxamide is a transient intermediate and only found at marked levels (18.9 %) under irradiated conditions (artificial irradiation, 300-800 nm) on the soil surface (Swales *et al.* (2003a) cited in EC (2017)).

In a study using standard English soils, cypermethrin was metabolised to one main identified metabolite in soil, DCVA, along with "major unknown metabolites" (> 5 %, according to the RMS assessment). Further metabolism lead to bound residues and mineralisation to  $CO_2$ .  $DT_{50}$  values were within 2 to 20 days (Yeomans and Kelly (2015) cited in EC (2017)).

Similarly, in field dissipation studies at two sites in Germany, one site in France and one site in Spain, cypermethrin showed low to moderate persistence. Sample analyses were only carried out for the parent cypermethrin (Gezahegne *et al.* (2015) cited in EC (2017)). Based on the presented results, the best-fit  $DT_{50}$  values calculated as non-normalised persistence endpoints of cypermethrin ranged from 9.3 to 31.2 days, resulting in a geometric mean  $DT_{50}$  value of 19.6 days (Drechsler and Lobe (2015) cited in EC (2017)).

In a water-sediment laboratory study (aerobic conditions, in the dark, natural sediment water systems), cypermethrin exhibited low persistence, with the major metabolites DCVA (max. 66.1 % in both water and sediment, high persistence), 3-PBA (max. 25.4 % in both water and sediment, low to moderate persistence), and an unknown metabolite (Unk1, max. 12.2 % in both water and sediment,



moderate to very high persistence). The unextractable (bound) residues extracted by acetonitrile/water accounted for 10.1–18.8 % of applied radioactivity after 100 d, mineralisation accounted for 25.1–68.8 % of applied radioactivity (Drechsler and Lobe 2015 cited in EC (2017)).

Unk1 was also detected in another water-sediment study, as it is structurally similar to DCVA, was postulated to result from further oxidation of DCVA (Lewis (2015) cited in EC (2017)).

Overall, cypermethrin and its major metabolites showed low to moderate persistence in both, soil and sediment analyses.

Similarly, aqueous photolysis of cypermethrin yielded two major metabolites, PBAcid and DCVA (cisand trans-isomers; Swales *et al.* (2003b) and Cashmore and Lewis (2014) cited in EC (2017)). Cypermethrin degraded with a half-life of 7.5 and 8.4 days, respectively. The DT<sub>50</sub> values for the eight individual isomers ranged from 4.6 to 13.7 days (Swales *et al.* (2003a) cited in EC (2017)).

#### 2.2 Sorption/desorption processes

In general, pyrethroids have a high affinity to soil or sediment particles (Laskowski 2002). Due to the physiochemical properties of cypermethrin (especially the low water solubility and the high log  $K_{ow}$ ), a decrease of the exposure concentration in the water phase by sorption to particles, sediment or vessel walls is expected. A rapid decrease in cypermethrin concentration is observed in aquatic biotests, with the concentrations in the water phase typically decreasing to less than 80 % of the initial concentration after 24 h (Barata *et al.* 2012, Mugni *et al.* 2011, Shen *et al.* 2012, Yang *et al.* 2016).

According to Agnihotri *et al.* (1986), cypermethrin aqueous concentration was reduced by 95 % within 24 h after application to water and sediment in open trenches. The decrease in concentration was primarily due to rapid sorption to sediment and suspended particles and not degradation.

Influence of sediment particle size on the desorption, bioavailability, and bioaccumulation potential of cypermethrin was investigated in field collected sediment (Zhang *et al.* 2018). The sediment was wet sieved to obtain five particle-size fractions (<20, 20–63, 63–180, 180–500, and >500  $\mu$ m) and spiked with cypermethrin. Consecutive Tenax extraction unexpectedly yielded a significant decrease of rapid desorption fractions and rate constants with increasing particle size. Adsorption of fine particles by Tenax beads was considered a possible explanation, thus results should be considered against this background.

Reduced bioavailability of cypermethrin to *Chironomus dilutus* (formerly *Chironomus tentans*) from sediments and water phase above silt and clay sediments (compared to sand sediments) has been explained by the higher sorption capacity of the tested sediments and the presence of dissolved organic carbon (DOC) in the overlying water released by tested natural sediment (Muir *et al.* 1985). The sediments tested were sand, a silty-clay river sediment (2.3 % OC) and a pond bottom clay (3.7% OC). Sorption/desorption dynamics were not analysed. Bioavailability of cypermethrin is further discussed in section 2.3.

Based on the assessment of adsorption characteristics of radiolabelled cypermethrin in four soils and one sediment using the batch equilibrium method, cypermethrin was shown to be immobile (McCall classification system), since minimum adsorption  $K_{doc}$  values, derived from adsorption coefficients, were in the range from 80653 to 574360 l/kg (Brice and Cooke (2006c) cited in EC (2017)). In experiments with three European soils using the batch equilibrium method, PBAcid showed low mobility (McCall classification system), (adsorption coefficients from 59 to 2078 l/kg), while cis- and trans-DCVA showed medium mobility (McCall classification system, adsorption coefficients for cis-DCVA from 13 to 640 l/kg, for trans-DCVA from 7 to 625 l/kg) (Wimbush and Cooke (2006) cited in EC



(2017)). It was concluded that the adsorption of cypermethrin and its metabolites was not pH dependent (EFSA 2018).

Due to the low photostability of cypermethrin and the known losses due to sorption and biodegradation in sediment, analytical verification of the exposure concentration in biotests is mandatory for the validity of a test result. This procedure corresponds to that in the EU dossier (EC 2011).

#### 2.3 Bioavailability

Bioavailability is a complex process which depends on many factors including the sorption capacity of the sediment considered (e.g. OC content), the hydrophobicity of the compound, and the physiology, feeding behaviour and burrowing activity of the benthic organism considered (Warren *et al.* 2003).

The scientific opinion of the EFSA on the effect assessment for pesticides on sediment organisms recognizes that "the most appropriate metric for bioavailability in soils and sediments appears to be the 'freely dissolved pore water concentration' rather than the total sediment concentration, particularly for compounds with a log  $K_{OW} < 5$ " (EFSA 2015).

The mechanistic Equilibrium Partitioning model by Di Toro *et al.* (1991) considers the OC content in sediment as being the main driver of bioavailability for non-ionic organic chemical like cypermethrin. This assumption is based among others on a study by Muir *et al.* (1985) in which *C. dilutus* (formerly *C. tentans*) was exposed to water above sediment (48 h, larvae kept on nylon screen above the sediment) and direct exposure (24 h) to sand (0.1 % OC), silty–clay river sediment (2.3 % OC) and pond bottom clay sediment (3.7 % OC). Sediments were spiked at nominal concentrations of 64 and 640  $\mu$ g/kg of trans-cypermethrin and 12, 17 and 174  $\mu$ g/kg of cis-cypermethrin. After 24 h of equilibration, 20 larvae were added to each duplicate. The bioaccumulation rate is reported as BCF (bioconcentration factor) based on cypermethrin concentration in larvae divided by the concentration in water and pore water. BCF was higher for sand compared to silt and clay (for larvae exposed directly to sediment as well as to water only). The reduced bioavailability in silt- and clay-systems was explained by the higher sorption capacity of the sediment and the presence of dissolved organic carbon (DOC) in the overlying water released by natural sediment (Muir *et al.* 1985). It was assumed that ingestion is a slower process than direct uptake from water but should be evaluated through a long-term study.

Maund *et al.* (2002) presented a bioaccumulation study on *Daphnia magna* and *C. dilutus* (formerly *C. tentans*) using sediments with different OC content (1 %, 3 % and 13 % OC). After 96 h, the biotasediment accumulation factor (BSAF; concentration in the insect divided by the concentration in sediment) decreased with an increase of OC content. However, the relation between OC content and accumulation was not linear in all cases. The ratio of bioavailability was 1:3 between OC content 1 % and 3 % but only of 1:2 between 3 % and 13 % OC. It was suggested that the lower surface area (higher sand content) in the sediment with the highest OC content might explain this difference.

Zhang *et al.* (2018) studied the influence of sediment particle size on the desorption, bioavailability, and bioaccumulation potential of cypermethrin by using two biomimetic techniques (Tenax extraction and solid-phase microextraction (SPME)) and bioaccumulation testing with *Lumbriculus variegatus*. Natural sediment (1.83 % TOC, 2 mm-sieved) and 5 fractions (>20, 20–63, 63–180, 180–500, and >500  $\mu$ m) were spiked with nominal concentrations of cypermethrin between 31.1 and 34.8  $\mu$ g/kg d.w. (no chronic effect reported for these concentrations). After allowing the system to reach equilibrium for 30 days, 20 worms were added to each fraction and tests were performed in triplicate. Tests had a total duration of 350 h (~14.6 d) and concentrations in worms were measured after 24 h, 48 h, 96 h, 7 d and 14 d and pore water concentration was calculated based on SPME measurement (solid-phase



microextraction). Maximum concentrations in oligochaetes were reached after 96 h (except 63–180  $\mu$ m, maximum after 48 h) and then decreased due to biotransformation. Pore water concentration of cypermethrin in the fine sediment (<20  $\mu$ m) was significantly lower than in the other fractions. While this would suggest a lower bioavailability, the measured BSAF were not significantly different from those determined in the other sediment fractions. The authors concluded that other exposure routes, such as ingestion, might contribute to the bioaccumulation in the fine sediment (selective feeding on fine particles), while freely dissolved cypermethrin does not influence accumulation (Zhang *et al.* 2018).

Bioavailability of a mixture of pyrethroids (including cypermethrin) from 17 contaminated natural sediments was assessed through the comparison of 10 d - toxicity to *Hyalella azteca* and derived Toxic Units ( $TU_{bioavailable}$ : Tenax-extracted concentration of pyrethroids divided by LC<sub>50</sub>, both all normalized by OC content), assuming additive effects of all pyrethroids (You *et al.* 2008). The derived TU showed good associated predictive toxicity of the sediments, except sediments with considerably greater amounts of sand (particle size, >63 µm), which resulted in lower  $TU_{bioavailable}$  and lower *H. azteca* mortality. It was concluded that OC was confirmed as important variable in determining bioavailability in sediments, but that adsorption to sand might play a controlling role in pyrethroid bioavailability, which is not taken into consideration solely by normalizing for OC.

In conclusion, benthic organisms can be exposed to cypermethrin through both, aqueous phase (overlying water and pore water) and ingestion. Bioavailability in the aqueous phase seems to be influenced by OC content but it should be kept in mind that other binding surfaces might reduce bioavailability as well, in particular at increasing grain sizes.

#### 2.4 Bioaccumulation and biomagnification

Reported bioconcentration factors (BCF, fish) in fish vary within one order of magnitude between the different cypermethrin isomeric mixtures. Whole body BCF of cypermethrin (cis:trans/40:60; fish species unknown) is 373 (±45.35) (EC 2013b), of alpha-cypermethrin 1204 (at 0.2  $\mu$ g a.s./l; *Oncorhynchus mykiss*) (EC 2018b), 846 of beta-cypermethrin (at 13  $\mu$ g a.s./l; *Lepomis macrochirus*) (EC 2013b), and of zeta-cypermethrin 356 or 443 (benzyl-labelled or cyclopropyl-labelled; *Lepomis macrochirus*) (EC 2006).

This BCF is above the trigger for derivation of QS for the protection from secondary poisoning for top predators (BCF  $\geq$ 100, EC (2018a)). To account for protection of top predators, a QS<sub>water</sub> based on EQS<sub>biota</sub> has been derived by the Ecotox Centre with a value of 0.0028 mg/l (Ecotox Centre 2016).

Concerning the risk of benthic invertebrates to transfer toxic and bioaccumulative substances to higher trophic levels, the EFSA scientific opinion for sediment risk assessment proposes to perform spiked sediment bioaccumulation tests with benthic invertebrates for substances that show significant bioaccumulation in fish (BCF >2000 l/kg) when the substance (1) is persistent in sediment (DT50 >120 d in water-sediment fate studies) and has a log K<sub>ow</sub> >3; or (2) is non-persistent in sediment, log K<sub>ow</sub> >3 and >10 % of the substance found in the sediment in a water-sediment fate study (EFSA 2015). The BCF for cypermethrin is below the EFSA threshold thus it is concluded that benthic invertebrates should not contribute significantly to the risk to higher organisms through trophic transfer.



# 3 Analysis

#### 3.1 Methods for analysis and quantification limit

Different approved methods to analyse cypermethrin in sediment exist, each with different detection limits. The method "5-C2" from the U.S. Geological Survey (Hladik *et al.* 2009) for pyrethroids reports a method detection limit of 1-2.6  $\mu$ g/kg d.w. for GC/MS and 0.2-0.5 for GC-MS/MS. The method detection limit decreases considerably when using high resolution methods such as in the U.S. Environmental Protection Agency EPA 1699 method, with a quantification limit of 0.0024  $\mu$ g/kg d.w. using HRGC/MRMS (high resolution gas chromatography/magnetic resonance mass spectroscopy, (U.S. EPA 2007)). However, these techniques are most often not available and LOQ reported in water monitoring networks (e.g. France) may only reach LOQ of approx. 10  $\mu$ g/kg d.w. (Lionard *et al.* 2012). Analytical methods implemented at research laboratories may reach intermediate LOQ, for example 0.26  $\mu$ g/kg d.w. (Pintado-Herrera et al. 2016).

Table 3 Methods for cypermethrin analysis in sediments and corresponding limits of detection (	LOD) and limits of
quantification (LOQ) (μg/kg d.w.). n. a. means not reported.	

LOD	LOQ	Analytical method	Reference
2.6	n. a.	GC/MS	Hadik at $a/(2000)$
0.4	n.a.	GC/MS/MS	Hiadik <i>et di.</i> (2009)
0.0024	0.02	HRGC/HRMS	U.S. EPA (2007)
0.08	0.26	GC/MS/MS	Pintado-Herrera et al. (2016)

#### **3.2 Environmental concentrations**

Measured environmental concentrations (MEC<sub>sed</sub>) in sediments for Switzerland are only available for five sites selected to represent small streams affected mainly by agricultural pressures (Table 4). The MEC<sub>sed</sub> range from <0.26 (limit of quantification of the method; Pintado-Herrera *et al.* (2016) to 10.40  $\mu$ g/kg d.w. MEC<sub>sed</sub> for cypermethrin in sediments from other European countries are in the range <LOD-50  $\mu$ g/kg d.w.

Measured environmental concentrations in surface waters (MEC<sub>water</sub>) in Switzerland range from <LOD to 0.45  $\mu$ g/l, with a low detection frequency (7/5829 measurements, Micropoll database).

Table 4 Measured environmental concentrations (MEC) of cypermethrin in Switzerland and Europe. All concentrations expressed as  $\mu$ g/kg d.w. for sediment or  $\mu$ g/l for water.

Measured Environmental Concentrations in sediment (MEC <sub>sed</sub> )								
Country	MEC (min-max) [μg/kg]	No. of sites	Comments	Reference				
Switzerland	< LOD-10.40	5	Normalized to 1 % TOC; small streams with agricultural use in catchment; monthly sampling from March to October	Ecotox Centre, unpublished data				
France	7.37 (max)	134	Alpha-cypermethrin; Non-normalized concentrations per dry weight;	Botta <i>et al.</i> (2014)				



			2% quantification			
			frequency;			
			LOQ 0.5 µg/kg			
			Non-normalized			
Spain	2.6-62.4	1	concentrations <sup>a</sup> ;	Feo <i>et al.</i> (2010)		
			Ebro river			
	21.79 (mass)		Concentration per dry			
EU		n. a.	weight; most often	EC (2011)		
50 (90 <sup>44</sup> PC)		MEC < LOQ				
N	leasured Environment	tal Concer	ntrations (MEC) in surface	water		
Project	MEC <sub>water</sub>	No. of	Commente	Deference		
(Switzerland)	[µg/I]	sites	comments	Reference		
NAWA SPEZ	0.4E(max)	-	16 complex	Ecotox Centre		
2012-2015	0.45 (Max)	5	46 samples	(2017)		
Micropoll	0.05 (median)	565	Detected 7/5829	Vermeirssen <i>et al.</i>		
database	0.16 (PC 90 <sup>th</sup> )	505	measurements	(2017)		

<sup>a</sup> Reference weight (dry or wet weight) not reported

# 4 Effect data (spiked sediment toxicity tests)

A bibliographic search was performed in the US Ecotox Data Base (U.S. EPA 2019) with an output of 3875 entries for aquatic data (years 1978-2017, both included), from which only four data addressed the sediment compartment. A key word search was performed on Scopus (66 results) and Web of sciences (83 results) (cypermethrin + sediment + toxicity) for the years 1982-2018 to complete the available database. Finally, potentially unpublished data was searched for in registration and EQS dossiers from European Commission and United States for the different enantiomers (EC 1999, 2005, 2006, 2011, 2013a, 2013b, 2017, 2018b, U.S. EPA 2006).

Relevance ("C" score in the table below) and reliability ("R" score in the table below) of studies are evaluated according to the CRED-criteria (Moermond *et al.* 2016). From the list of 32 effect data to be evaluated for relevance and reliability, six are reported in Maund *et al.* (2002) "Partitioning, bioavailability, and toxicity of the pyrethroid insecticide cypermethrin in sediments." Based on the acceptance of the study in the EC EQS dossier (EC 2011), it has been accepted although reliability was not assignable due to lack of information according to CRED criteria ("accepted as face value", Notes in Table 5).

According to the EU TGD (EC 2018a) "What is considered chronic or acute is very much dependent on 1) the species considered and 2) the studied endpoint and reported criterion". According to EFSA, true chronic tests should cover a range of 28-65 d when half-life of a pesticide in sediment is >10 d (EFSA, 2015). Therefore, effect data from 10 d tests with *H. azteca* and *C. dilutus* (formerly *C. tentans*) were considered as acute effect data. The only true long-term study is that from Putt ((2005b) cited in Sappington *et al.* (2011)) for *C. dilutus* (formerly *C. tentans)*, which reported larval survival and growth after 20 d, and emergence and development rate after 60 d. These endpoints are considered as relevant and reliable without restrictions after assessment against CRED-relevant information (in the US EPA data evaluation report by Sappington *et al.* (2011); see Table 5 and section 3.3 for further details on data quality assessment).

The 21 acute effect data considered reliable and relevant cannot be used directly to derive  $EQS_{sed}$  but they are retained as they can be used as supporting information for example when choosing the assessment factor (AF).



Table 5 Sediment effect data collection for cypermethrin in µg/kg. Data were evaluated for relevance and reliability according to the CRED criteria for sediments (Casado-Martinez et al. 2017). Data assessed as not-relevant and not-reliable is in grey font. Data used for QS development is underlined. Abbreviations: n. a. = not available. In case water instead of sediment was spiked, respective information is provided (column "Notes").

Group	Species <sup>a</sup>	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentra tion	Value (µg /kg d.w.)	Sediment type	Normal ized value (μg /kg d.w., 1 % OC)	Normali zed value (μg /kg d.w., 5 % OC)	Chem. analytics	Notes	Validity	References
						Acute	toxicity data	in freshwater		. ·			•		
Crustacea (Amphipoda)	Echinogammarus finmarchicus	Formulation with cypermethrin	Static	Overnight	Mortality	10 d	LC50	80	Natural sediment (87% sand, 13% silt/clay), 3% OC	26.67	133.35	Measured	Spiked water; sediment was not spiked	R3, C3	Van Geest <i>et al.</i> (2014)
Crustacea (Amphipoda)	Hyalella azteca	cypermethrin	Static	48 h	Mortality	10 d	LC50	3.6	Natural sediment (24 % clay, 6 % sand, 70 % silt), 1% OC	3.6	18	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Crustacea (Amphipoda)	Hyalella azteca	cypermethrin	Static	48 h	Mortality	10 d	LC50	18	Natural sediment (25 % clay, 10 % sand, 65 % silt), 3% OC	6	30	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Crustacea (Amphipoda)	Hyalella azteca	cypermethrin	Static	48 h	Mortality	10 d	LC50	23	Natural sediment (25 % clay, 30 % sand, 45 % silt), 13% OC	1.77	8.85	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Crustacea (Amphipoda)					Mortality, geometric mean			11.4		3.37	16.84				
Crustacea (Amphipoda)	Hyalella azteca	cypermethrin	Static	48 h	Growth	10 d	NOEC	<1.8	Natural sediment (24 % clay, 6 % sand, 70 % silt), 1% OC	<1.8	<9	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Crustacea (Amphipoda)	Hyalella azteca	cypermethrin	Static	48 h	Growth	10 d	NOEC	2.3	Natural sediment (25 % clay, 10 % sand, 65 % silt), 3% OC	0.767	3.835	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Crustacea (Amphipoda)	Hyalella azteca	cypermethrin	Static	48 h	Growth	10 d	NOEC	1.8	Natural sediment (25 % clay, 30 % sand, 45 % silt), 13% OC	0.138	0.69	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Crustacea (Amphipoda)					Growth, geometric mean			2.03		0.33	1.63				
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Continuous renewal	31 d	Mortality	10 d	NOEC	<22	Natural sediment (83% sand, 12% silt, and 5.5% clay), 5.5 % TOC	<4	<20	Measured		R2, C2	Putt 2005a cited in Solliday <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Static	48 h	Mortality	10 d	LC50	13	Natural sediment (24 % clay, 6 % sand, 70 % silt), 1% OC	13	65	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Static	48 h	Mortality	10 d	LC50	67.0	Natural sediment (25 % clay, 10 % sand, 65 % silt), 3% OC	22.33	111.65	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Static	48 h	Mortality	10 d	LC50	62.0	Natural sediment (25 % clay, 30 % sand, 45 % silt), 13% OC	4.43	22.15	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Insecta	Chironomus dilutus <sup>a</sup>				Mortality, geometric mean			37.8		10.88	54.37				



Group	Speciesª	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentra tion	Value (µg /kg d.w.)	Sediment type	Normal ized value (μg /kg d.w., 1 % OC)	Normali zed value (μg /kg d.w., 5 % OC)	Chem. analytics	Notes	Validity	References
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Continuous renewal	31 d	Growth	10 d	NOEC	81	Natural sediment (83% sand, 12% silt, and 5.5% clay), 5.5 % TOC	14.7	73.5	Measured		R1, C1	Putt 2005a cited in Solliday <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Static	48 h	Growth	10 d	NOEC	3.8	Natural sediment (24 % clay, 6 % sand, 70 % silt), 1% OC	3.8	19	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Insecta	Chironomus dilutusª	cypermethrin	Static	48 h	Growth	10 d	NOEC	25.0	Natural sediment (25 % clay, 10 % sand, 65 % silt), 3% OC	8.33	41.65	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Static	48 h	Growth	10 d	NOEC	14.0	Natural sediment (25 % clay, 30 % sand, 45 % silt), 13% OC	1	5	Measured	Accepted as face value	R4, C1	Maund <i>et al.</i> (2002)
Insecta	Chironomus dilutus <sup>a</sup>				Growth, geometric mean			18.1		3.16	15.82				
Crustacea (Ostracoda)	Heterocypris incongruens	cypermethrin	Static	24h	Mortality	6 d	LC50	2480	Artificial sediment			Nominal		R3, C1	Bebon (2013)
Crustacea (Ostracoda)	Heterocypris incongruens	cypermethrin	Static	24h	Growth	6 d	EC50 EC10	2330 1000	Artificial sediment			Nominal		R3, C1	Bebon (2013)
						Acute to	oxicity data for	or marine wate	er						
Crustacea (Amphipoda)	Ampelisca abdita	cypermethrin	Static	10 d	Mortality	10 d	LC50	469	Artificial sediment (medium sand 13.57 %; fine sand 48.17 %; silt and clay 38.27%), 0.78% OC	601.28	3006.4	Measured		R2, C1	Anderson <i>et al.</i> (2008)
Crustacea (Amphipoda)	Eohaustorius estuarius	cypermethrin	Static	10 d	Mortality	10 d	LC50	11	Artificial sediment (medium sand 13.57 %; fine sand 48.17 %; silt and clay 38.27%), 0.78% OC	14.1	70.5	Measured		R2, C1	Anderson <i>et al.</i> (2008)
Crustacea (Amphipoda)	Monocorophium insidiosum	cypermethrin	Static	not reported	Mortality	10 d	LC50	56	Natural sediment (Coarse sand, < 1 mm), 5.5 % OM <sup>c</sup>	(17.5- 24.4) <sup>c</sup>	(87.5- 121.7) °	Nominal		R3, C2	Tucca <i>et al.</i> (2014)
Crustacea (Decapoda)	Palaemonetes pugio	cypermethrin	Static	overnight	Mortality	96h	LC50	175	Reconstituted sediment, 0.5-1% OM			Measured	Mix of natural sand and sediment, dried and autoclaved before mixture	R4, C2	Clark <i>et al.</i> (1987)
Crustacea (Decapoda)	Palaemonetes pugio	cypermethrin	Continuous renewal	overnight	Mortality	96h	LC50	270 <sup>b</sup>	Reconstituted sediment, 0.5-1% OM			Measured	u	R4, C2	Clark <i>et al.</i> (1987)
Crustacea (Decapoda)	Palaemonetes pugio	cypermethrin	Static	10 d	Mortality	10d	NOEC	10 <sup>b</sup>	Reconstituted sediment, 0.5-1% OM			Measured	u	R4, C2	Clark <i>et al</i> . (1987)
Crustacea (Decapoda)	Palaemonetes pugio	cypermethrin	Continuous renewal	10 d	Mortality	10d	NOEC	100 <sup>b</sup>	Reconstituted sediment, 0.5-1% OM			Measured	u	R4, C2	Clark et al. (1987)



Group	Speciesª	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentra tion	Value (µg /kg d.w.)	Sediment type	Normal ized value (μg /kg d.w., 1 % OC)	Normali zed value (μg /kg d.w., 5 % OC)	Chem. analytics	Notes	Validity	References
						Chronie	c toxicity dat	a in freshwate							
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	Continuous renewal	24 h	Population Growth Rate	67 d	NOEC	< 49	According to OECD 1984 (70% sand, 20% kaolin clay and 10% peat)			Measured	Unbounded, effect observed already at lowest conc. 49 μg /kg	R3, C3	Hooper <i>et al.</i> (2003)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	static renewal	27 d	Survival	60 d	NOEC (20 d)	≥82	Natural sediment (87% sand, 10% silt, 3% clay), 5.6 % OC	≥14.6	≥73	Measured	Unbounded	R2, C1	Putt 2005b cited in Sappington <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	static renewal	27 d	Growth	60 d	NOEC (20 d)	39	Natural sediment (87% sand, 10% silt, 3% clay), 5.6 % OC	6.96	34.8	Measured		R1, C1	Putt 2005b cited in Sappington <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	static renewal	27 d	Emergence	60 d	NOEC	39 <sup>d</sup>	Natural sediment (87% sand, 10% silt, 3% clay), 5.6 % OC	6.96	34.8	Measured		R1, C1	Putt 2005b cited in Sappington <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	static renewal	27 d	Development rate	60 d	NOEC	<u>10</u>	Natural sediment (87% sand, 10% silt, 3% clay), 5.6 % OC	<u>1.79</u>	<u>8.95</u>	Measured		R1, C1	Putt 2005b cited in Sappington <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	static renewal	27 d	Time to death	60 d	NOEC	≥82	Natural sediment (87% sand, 10% silt, 3% clay), 5.6 % OC	≥14.6	≥73	Measured	Unbounded, not relevant endpoint	R2, C3	Putt 2005b cited in Sappington <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	static renewal	27 d	Reproduction (as number of eggs)	60 d	NOEC	39	Natural sediment (87% sand, 10% silt, 3% clay), 5.6 % OC	6.96	34.8	Measured	No replicates reported, no dose- response curve	R4, C1	Putt 2005b cited in Sappington <i>et al.</i> (2011)
Insecta	Chironomus dilutus <sup>a</sup>	cypermethrin	static renewal	27 d	Percent hatched	60 d	NOEC	≥82	Natural sediment (87% sand, 10% silt, 3% clay), 5.6 % OC	≥14.6	≥73	Measured	No replicates reported	R4, C1	Putt 2005b cited in Sappington <i>et al.</i> (2011)

<sup>a</sup> Formerly Chironomus tentans.

<sup>b</sup> Reference sediment weight (dry or wet weight) not reported.

<sup>c</sup> OC content not reported. Conversion of OM to OC using a standard factor between 1.7 – 2.2 yields 3.2 – 2.3 % OC.

<sup>d</sup> Based on reviewer's evaluation in Sappington *et al.* (2011).



#### 4.1 Graphic representation of effect data

All available data for chronic and acute data have been plotted independently of their relevance and reliability before and after normalization to OC content of the sediment (Figures 1a and 1b).

Without OC-normalization, the LC<sub>50</sub> of amphipods (geom. mean: 12  $\mu$ g/kg) is the lowest followed by insects (represented by *C. dilutus* (formerly *C. tentans*) only, geom. mean: 35  $\mu$ g/kg) and crustaceans (geom. mean: 83  $\mu$ g/kg). Ostracods are only represented by one study and thus not included in the comparison.

Where OC content was reported, normalization of data was performed (Figure 2b). The OC content normalized  $LC_{50}$  of amphipods (geom. mean: 491 µg/kg-OC) is the lowest followed by insects (geom. mean: 765 µg/kg-OC). Due to lack of information on OC content in sediments used for ostracod exposure, the respective data could not be normalized.



The ratio of relevant acute to chronic data for insects (C. dilutus (formerly C. tentans)) is 2.

Figure 1a Graphical representation of acute and chronic single effect data from spiked sediment toxicity tests with cypermethrin. Data are not normalized for OC. Geometric means are not displayed.  $\Delta$  marine species,  $\circ$  freshwater species. Grey symbols: Non-relevant/non-reliable data.



Figure 1b Graphical representation of acute and chronic single effect data from spiked sediment toxicity tests with cypermethrin, normalized to OC content of the sediment used. Geometric means are not displayed.  $\Delta$  marine species,  $\circ$  freshwater species. Grey symbols: Non-relevant/non-reliable data.



#### 4.2 Comparison between marine and freshwater species

Regarding effect concentrations for pelagic organisms, the EC EQS dossier (EC 2011) reports that no statistically significant difference was found between marine and freshwater data. The Ecotox Centre aquatic EQS dossier (Ecotox Centre 2016) states that no further indication of different sensitivities of marine vs. freshwater species are available, thus, data was pooled.

For sediment dwelling organisms, only acute tests on both, marine and freshwater benthic amphipods are available, with effect data ranges for marine and freshwaters overlapping. Normalization to sediment OC content is only possible for 2 out of 7 effect concentrations. No chronic effect data is available for marine benthic species. Overall, the number of marine data is too small to assess whether the sensitivity of marine vs. freshwater species is significantly different.

Consequently, EQS<sub>sed</sub> derivation is based on freshwater chronic data only.

#### 4.3 Overview of the most sensitive relevant and reliable long-term study

According to the EC EQS TGD (EC (2018a) p. 25): "All available data for any taxonomic group or species should be considered, provided the data meet quality requirements for relevance and reliability". The chronic effect data for *C. dilutus* (formerly *C. tentans*) from Putt (2005b, cited in Sappington *et al.* (2011)) have been evaluated as R1/C1 (Q1, the results can be used for the calculation of QSs without restriction<sup>4</sup>) and R2/C1 (Q2, the results of the study can be used for the calculation of QSs with restriction: they will be used as supportive information<sup>5</sup>) for the endpoints mortality and growth at 20 d and percent emergence and development rate at 60 d.

<u>Putt et al. (2005b)</u>: Cypermethrin – Life-Cycle Toxicity Test with Midge (*C. dilutus* (formerly *C. tentans*)) During a 60-Day Sediment Exposure.

- Species: Chironomus dilutus (formerly C. tentans).
- Origin: Aquatic BioSystems, Fort Collins, CO
- Experimental sediment: Natural sediments from Glen Charlie Pond, Wareham, Massachusetts, with an average OC content of 5.6 % composed with 87 % sand, 10 % silt, and 3 % clay. pH was 5.3 and total ammonia concentration in the pore water was 4.5 mg/l as nitrogen.
- Spiking and equilibration time: First, 5 g of sand were spiked with 9 ml of stock solution of [<sup>14</sup>C]cypermethrin (prepared in acetone), the solvent was evaporated for half an hour. The spiked sand was then added to 2 kg of wet sediment, mixed 4 h at room temperature, then stored overnight. Equilibration time was 27 days.
- Overlying water: culture water (laboratory well water); total hardness and total alkalinity ranged (as calcium carbonate) from 34 to 54 and from 28 to 34 mg/l, respectively, conductivity ranged from 130 to 180 Omhos/cm and pH range from 7.1 to 7.9. Dissolved oxygen levels dropped to levels below the threshold for initiating extra aeration of 2.5 mg/l on three replicates on two days during the course of the study but did not fall below the threshold at which long-term effects in midge larvae is expected (1.5 mg/l). Because the concentrations at which the DO levels dropped (25 and 50 µg a.i./kg nominal) did not show statistically significant effects and a dose-response curve is observed over time, it is considered that DO levels did not

<sup>&</sup>lt;sup>4</sup> Casado-Martinez, M.C., Mendez-Fernandez, L., Wildi, M., Kase, R., Ferrari, B.J.D. and Werner, I. (2017) Incorporation of sediment specific aspects in the CRED evaluation system: recommendations for ecotoxicity data reporting. , Brussels.

<sup>&</sup>lt;sup>5</sup> See footnote 4



compromise the reliability of the endpoints. No clear information is provided on the type of water exchange (semi-static or flow-through).

- Bioassays: The 60 d toxicity test was performed in line with *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates* (U.S. EPA 2000). The test was performed in glass beakers with 100 ml sediment and 175 ml of overlying water, prepared 24 h before test start. Twelve larvae were tested per vessel with 20 replicates: 12 for biological response, 4 for auxiliary male production for reproduction testing and 4 for chemical analysis. Overlying water was changed twice a day or continuously. Light/dark cycle was 16 h light, 8 h dark. Organisms were fed daily with 1.5 ml of fish food suspension (4 mg/mL). All relevant water parameters were measured. Survival and growth (dry weight) were reported after 20 d and percent emergence and development rate were reported after 60 d.
- Test endpoints: Survival and growth after 20 d, percent emergence and development rate after 60 d are considered relevant and reliable. Additional endpoints reported are mean days to death, development rate (male and females together), mean eggs/female and mean percent hatch. Time to death is not considered as a relevant endpoint, reproduction endpoints are considered not reliable because replicate data were not reported.
- Statistics: Shapiro-Wilk's Test for normality for survival and growth data from Day 20; the Chi-Square Test for normality was used for all other endpoints. Bartlett's Test was used to check on the assumption of homogeneity of variance for all endpoints. Survival and percent hatch data failed the qualifying test for normality and/or homogeneity and therefore data were analysed using Wilcoxon's Rank Sum Test. Sappington *et al.* (2011) re-evaluated the data and compared treatments to the negative control.

# 5 Derivation of QS<sub>sed</sub>

According to the EC TGD for EQS, sediment toxicity tests, aquatic toxicity tests in conjunction with equilibrium partitioning (EqP) and field/mesocosm studies are used as several lines of evidence to derive QS<sub>sed</sub> (EC 2018a). Thus, in the following, the appropriateness of the deterministic approach (AF-Method), the probabilistic approach (SSD method) and the EqP approach were examined.

#### 5.1 Derivation of QS<sub>sed, AF</sub> using the Assessment Factor (AF) method

The derivation of  $QS_{sed, AF}$  is determined using assessment factors (AFs) applied to the lowest credible datum from long-term toxicity tests.

The lowest long-term effect datum available for cypermethrin is the NOEC for the endpoint development rate in *Chironomus dilutus* of 10  $\mu$ g/kg or 178.6  $\mu$ g/kg-OC (5.6 % OC, Table 5).

Because only one long term test (NOEC or EC10) with species representing different living and feeding conditions are available, the TGD recommends the application of an assessment factor of 100 on the lowest credible datum (Table 11 in EC (2018a)):

$$QS_{sed,AF} = \frac{lowest \ EC10 \ or \ NOEC}{100}$$
$$QS_{sed,AF} = \frac{178.6 \left(\frac{\mu g}{kg - OC}\right)}{100} = 1.79 \left(\frac{\mu g}{kg - OC}\right)$$



The application of an AF of 100 to the lowest credible chronic datum results in a  $QS_{sed,AF} = 1.79 \ \mu g/kg$ -OC, which corresponds to 0.089  $\mu g/kg$  for a sediment with 5 % OC or 0.018  $\mu g/kg$  for a sediment with 1 % OC representing a worst case scenario in Switzerland.

#### 5.2 Derivation of QS<sub>sed,SSD</sub> using the species sensitivity distribution (SSD) method

The minimum data requirements recommended for the application of the SSD approach for EQS water derivation is preferably more than 15, but at least 10 NOECs/EC10s, from different species covering at least eight taxonomic groups (EC (2018a), p. 43). In this case, not enough data from spiked sediment toxicity tests are available for applying the SSD approach.

#### 6 Derivation of QS<sub>sed,EqP</sub> using the Equilibrium Partitioning approach

If no reliable sediment toxicity data are available, the Equilibrium Partitioning (EqP) can be used to estimate the EQS<sub>sed,EqP</sub>. This approach, developed for non-ionic substances, is used here for comparison purposes given the small data base of sediment toxicity studies.

#### 6.1 Selection of QS for water

An Annual Average Quality Standard (AA-QS) has been proposed by the European Commission which sets a value of  $0.000082 \mu g/l$  for the protection of pelagic species (EC 2011). In 2016, the Ecotox Centre revised the quality criteria according to the availability of new effect data collected in the scientific literature for the years 2010-2016, as well as in the homologation dossier for zeta-cypermethrin, beta-cypermethrin, trans/cis mixture and the proposed re-evaluation decision from Canada ((EC 2006, 2013a, 2013b, EFSA 2014, PMRA 2016) cited in Ecotox Centre (2016)).

Here, the AA-EQS proposed by the Ecotox Centre (0.00003  $\mu$ g/l) in 2016 is used in the application of the EqP since it takes into consideration the most recent published data.

#### 6.2 Selection of partition coefficient

One of the main factors influencing the application of the EqP model is the choice of the partition coefficient. It is stipulated in the ECHA 2017 guideline (p. 143, ECHA (2017)) that "To increase the reliability of PNEC sediment screen derived using the EqP, it is imperative that a conservative but realistic partitioning coefficient (e.g. Kd,  $K_{oc}$ ,  $K_{ow}$ ) is chosen. A clear justification must be given for the chosen coefficient and any uncertainty should be described in a transparent way."

The EC EQS TGD requires deriving a geometric mean of all available  $K_{oc}$  values including one derived from a log  $K_{ow}$  value (EC 2018a).

For cypermethrin, Maund *et al.* (2002) have provided the only available  $K_{OC}$  data found in the literature for sediment (Table 1), separated in adsorption and desorption partitioning (5.4, Table 6). The six reported values were selected for EQS<sub>sed</sub> derivation.

A dataset based on measurement of concentrations in sediment and overlying water after 24 h, 48 h, 72 h and 96 h on natural sediment with different sediment OC content (1 %, 3 % and 13 %) in presence of test organisms is presented in the same study (Maund *et al.* 2002). Equilibrium was reached within 24 h. The log K<sub>oc</sub> data range from 4.53 to 6.3 (I/kg) with 10<sup>th</sup>, 50<sup>th</sup> and 90<sup>th</sup> percentile of 4.63, 5.52 and 6.12. These values are not considered valid for EQS<sub>sed</sub> derivation.

Of the reported  $K_{ow}$  considered as valid (Table 1), the mean of 5.45 of published cypermethrin (mixture of isomers)  $K_{ow}$  values was selected for  $K_{oc}$  derivation rather than  $K_{ow}$  values published for specific



cypermethrin isomers. The same value was used as basis for risk assessment in the registration process on EU level.

All  $K_{oc}$  used for EQS<sub>sed</sub> are listed in Appendix I.

#### 6.3 Selection of OC content for a reference sediment

To account for the influence of OC content on  $QS_{sed,EqP}$  development, calculations have been performed for a standard sediment according to the EU TGD with 5 % OC (EC 2018a). As 5 % OC might not be representative for sediment in Switzerland, calculation was made as well for a worst case scenario considering measurement on total sediment with 1 % OC (approx. 10<sup>th</sup> percentile of OC content in Swiss Rivers).

#### 6.4 Derivation of QS<sub>sed,EqP</sub>

For the derivation of  $QS_{sed,EqP}$ , the partition coefficient between water and sediment has been estimated as the fraction of organic carbon multiplied by organic carbon partition coefficient (Kp=f<sub>oc</sub>\*K<sub>oc</sub>) as proposed by Di Toro *et al.* (1991) for non-ionic organic chemicals. The authors considered that, for sediment with an organic fraction higher than 0.2 %, organic carbon is the main driver for chemical sorption.

The derived  $QS_{sed,EqP}$  ranges between 0.069 µg/kg for the worst case scenario (sediment with 1 % OC) to 0.343 µg/kg for the standard sediment in the TGD (with 5 % OC; Table 6).

An additional AF of 10 should be applied to the resulting  $QS_{sed,EqP}$  for substances with log K<sub>ow</sub> >5. Reported log K<sub>ow</sub> for cypermethrin and isomeric mixtures range from 5.3-6.83 (Table 1). The resulting  $QS_{sed,EqP}$  after the application of the extra AF is 0.034 µg/kg for 5 % TOC and 0.007 µg/kg for 1 % TOC.

Table 6 Derived  $QS_{sed,EqP}$  for a mean  $K_{OC}$  reported by Maund *et al.* (2002) and the AA-EQS for water derived by the Ecotox Centre of 0.00003 µg/l (Ecotox Centre 2016). The partition coefficient solid-water sediment (Kp<sub>sed</sub>) is estimated for a sediment with 5 % OC (standard EC TGD sediment) and 1 % TOC (worst case scenario in Switzerland).

	K <sub>oc</sub> [l/kg]	Kp <sub>sed</sub> [l/kg]	K <sub>sed-water</sub> [m <sup>3</sup> /m <sup>3</sup> ]	QS <sub>sed,EqP</sub> [µg/kg w. w.]	QS <sub>sed,EqP</sub> [µg/kg d. w.]	Included AF
1 % OC	228322	2283	1142	0.026	0.007	10
5 % OC	228322	11416	5709	0.132	0.034	10

### 7 Determination of QS<sub>sed</sub> according to mesocosm/field data

No field or mesocosm studies that provide effect concentrations of the active substance cypermethrin in sediment are available, thus, no QS<sub>sed</sub> based on field data or mesocosm data has been derived.

Mesocosm studies reviewed on EU level for cypermethrin, alpha-cypermethrin (both in the alpha-cypermethrin dossiers, (EC 1999, 2018b)) and beta-cypermethrin (EC 2013b) were done with formulated products, not with the active substances. Based on the mesocosm studies on alpha-cypermethrin formulations, the EU Review Report for alpha-cypermethrin (EC 2004) lists an environmentally acceptable concentration (EAC) of 0.015  $\mu$ g/l (126 d, mesocosm, higher tier testing on aquatic invertebrates and algae). As EQS derived for Switzerland are exclusively based on active substance data, formulation data cannot be used for QS<sub>sed</sub> derivation in this context.

In the public literature, a report is available on 10 d *H. azteca* mortality tests on 17 sites in California impacted by pyrethroids where mortality was correlated with expected toxicity (You *et al.* 2008). Although a mix of pyrethroids was present in the natural sediment tested, which means that other



substances as cypermethrin might have contribute to the total toxicity, significant mortality compared to the control was observed with mortality within 11 % (4.81  $\mu$ g/kg d.w.) to 100 % (13.2  $\mu$ g/kg d.w.) for concentrations within 1.92 (14 % mortality) to 33.0 (79 % mortality)  $\mu$ g/kg. NOEC were not reported, thus, this field study cannot be used for comparison to the derived QS (sections 4.1, 5.4).

A field study by Cheng *et al.* (2017) was based on 10 pyrethroid-polluted sediments from a large urban river in China. Sediment toxicity to *C. dilutus* was assessed with 50 % of the sediments inducing mortality in *C. dilutus* in 10 d exposures. All sediments induced mortality in 20 d exposures. Pyrethroids were detected in all sediments with the concentrations ranging from 2.43 to 61.2  $\mu$ g/kg d.w., and permethrin and cypermethrin dominating pyrethroid composition. Acute toxic units for pyrethroids ranged from 0.03 to 0.56 (cypermethrin accounted for 13–81 % of the toxic units) and showed a direct relationship with sediment mortality among the midges. Again, NOEC were not reported, thus, this field study cannot be used for comparison to the derived QS (sections 4.1, 5.4).

### 8 Available sediment quality guidelines

Table 7 summarizes available sediment quality guidelines (SQGs), each of which have been derived with a different purpose and therefore a different methodology. From those presented here, the most similar to EQS<sub>sed</sub> in terms of purpose is the Target Value (TV) from The Netherlands, which is also the most stringent among the available SQGs. The TV is derived from the Maximum Permissible Concentration (MPC), which in turn was derived using the EqP.

A threshold effect benchmark (TEB) has been recently derived in the U.S. applying an acute-to-chronic ratio of 10 to the lowest 10 d effect concentration. This set of SQGs is intended for predicting toxicity in laboratory sediment toxicity tests with amphipods and insect larvae when they have not been performed in site-specific risk assessment.

Intermediate RACs have been derived by Deneer *et al.* (2013) using different types of approaches based on effect data from spiked-sediment toxicity tests. None of the approaches used by Deneer *et al.* (2013) are in agreement with the EC EQS TGD (EC, 2011).

SQG description	Value [ug/kg d w ]	Development method	References
EQS <sub>sed</sub>	0.033 (5 % TOC)	<i>EC TGD,</i> based on 10 d effect data, including an AF of 50	EC (2011)
TVª	0.0039 (10 % OC) 0.00195 (5 % OC) 0.00039 (1 % OC)	Target Value (TV) and Maximum Permissible Concentration (MPC), The Netherlands, derived by the EqP. The TV, which has the same intend as	Crommentuijn <i>et al.</i> (1997)
MPCª	0.39 (10 % OC) 0.195 (5 % OC) 0.039 (1 % OC)	EQS <sub>sed</sub> , is derived as MPC/100	
ΤΕΒ <sup>b</sup>	2.45 (5 % OC) 0.49 (1 % OC)	Threshold Effect Benchmark (TEB) and Likely Effect Benchmark (LEB): LEB defines concentrations above which there is a high probability of adverse effects on benthic invertebrates, derived from acute (10 d) effect data for <i>H. azteca</i> and <i>Chironomus</i> sp. The TEB is derived as LEB/10 to account for acute-to-chronic extrapolation.	Nowell et al. (2016)
LEB <sup>b</sup>	2.45 (5 % OC)		

Table 7 Sediment quality guidelines reported in the literature.



SQG description	Value [µg/kg d.w.]	Development method	References
	0.49 (1 % OC)		
Proposed		Scientific proposals for Regulatory	Deneer <i>et al.</i> (2013)
RAC <sup>c</sup>		Acceptable Concentration using	
		different methodologies in the context	
		of risk assessment for pesticides	
	1) RAC <sub>sed;ac</sub> = 0.035 (5 % OC)	(EFSA):	
	0.07 (1 % OC)	1) Estimated chronic value (H.azteca)	
		applying an AF of 10 to acute data	
	2) Geom-RAC <sub>sed;ac</sub> = 1.05 (5 % OC)		
	0.21 (1 % OC)	2) Geomean acute value for	
		crustaceans with an additional AF of	
	3) SSD-RAC <sub>sed;ac</sub> = 0.10 (5 % OC)	10	
	0.02 (1 % OC)		
		<ol><li>HC₅ from SSD with acute values</li></ol>	
		divided by 5 and an extra AF of 3	

<sup>a</sup> Values are expressed for a standard sediment with 10 % organic matter and 25 % clay.

 $^{\rm b}$  Originally expressed as concentration normalized by organic carbon (TEB: 0.49  $\mu g/g$ -OC; LEB: 0.049  $\mu g/g$ -OC).

<sup>c</sup> Originally expressed as concentration normalized by organic carbon (SSD-RAC<sub>sed;ac</sub>= 0.002  $\mu$ g/g-OC, Geom-RAC<sub>sed;ac</sub>= 0.021  $\mu$ g/g-OC, RAC<sub>sed;ac</sub>= 0.007  $\mu$ g/g-OC).

# 9 Toxicity of degradation products

Main degradation products of cypermethrin in soil/sediment are cypermethrin carboxamide (transient), DCVA (3-(2,2-dichlorovinyl)- 2,2-dimethylcyclopropane carboxylic acid) and 3-PBA (3-phenoxybenzoic acid) (EC 2017). Information on the effects of cypermethrin degradation products on sediment dwelling organisms in sediment exposure setups is currently not available.

Based on the submitted registration data evaluated at EU level and as the ecotoxicological risk of these metabolites was assessed as low (EFSA 2014), a risk assessment was considered not necessary for the aquatic compartment (Ecotox Centre 2016).

In particular, acute  $LC_{50}/EC_{50}$  in fish, aquatic invertebrates, and chronic  $ErC_{50}$  in algae were > 1000 µg/l for DCVA and mPBAcid/3-PBA. The metabolites PBAldehyde and cypermethrin carboxamide had an acute  $EC_{50}$  of 162 µg/l and > 22.4 µg/l, respectively in aquatic invertebrates (EC (2017), List of endpoints).

Against this background, a risk assessment for sediment is not considered necessary.

### **10** EQS<sub>sed</sub> proposed to protect benthic species

The different QS values for each derivation method included in the EC EQS TGD 2018 are summarized in Table 8. According to the TGD, the most reliable extrapolation method for each substance should be used (EC 2018a). In all cases, data from spiked sediment toxicity tests are preferred over the EqP approach.



Table 8 QS<sub>sed</sub> derived according to the three methodologies stipulated in the EU-TGD and their corresponding AF. All concentrations expressed as  $\mu g/kg d.w.$ 

	Sediment 1 % TOC	Sediment 5 % TOC	AF
QS <sub>sed,SSD</sub>			
QS <sub>sed,EqP</sub>	0.007	0.034	10
QS <sub>sed,AF</sub>	0.018	0.089	100
EC EQS <sub>sed</sub>		0.033	50
Proposed EQS <sub>sed</sub>	0.018	0.089	100

#### **10.1** Uncertainty analysis

According to the TGD, an AF of 100 is foreseen for  $QS_{sed,AF}$  when only one chronic datum is available. The following considerations apply for the selection of the AF:

- The critical datum used in QS<sub>sed,AF</sub> derivation is for the insect *C. dilutus* (formerly *C. tentans*).
- 10 d acute studies on amphipods indicate this group being more sensitive than insects (*C. dilutus* (formerly *C. tentans*)).
- No effect data for organisms exposed predominantly through sediment ingestion (e.g. oligochaetes) are available.
- After application of an extra AF of 10 for the derivation of the  $QS_{sed, EqP}$ , the latter is in the same order of magnitude as  $QS_{sed,AF}$  (AF = 100).
- No field data are available to evaluate the assessment factor.

Thus, an AF of 100 should be maintained to protect this group of species.

An EQS<sub>sed</sub> of 0.018  $\mu$ g/kg d.w. (1 % OC) for cypermethrin after the application of an AF of 100 is thus suggested.

The proposed  $EQS_{sed}$  would require the use of high resolution methods for quantification of measured environmental concentrations. These techniques are most often not available in laboratories performing monitoring activities, therefore the implementation of the derived  $EQS_{sed}$  may be challenging.

#### **11 References**

Secondary citations are not included in the reference list.

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# Appendix I. Sediment-water partition coefficients ( $K_{oc}$ ) used for EQS<sub>EqP</sub> derivation

OC content [%]	Adsorption	Desorption
1	238000	281000
3	502000	582000
13	177000	182000
Estimated from log K <sub>ow</sub> 5.45	525	54
Geometric mean all K <sub>oc</sub> + K <sub>ow</sub> -derived K <sub>oc</sub>	1648	340