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SQC (EQS_{sed}) – Proposal from the Ecotox Centre for: *Chlorpyrifos-ethyl*

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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_{sed}): 0.028 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 chlorpyrifos of 0.028 µg/kg d.w. is proposed for standard sediments with 1 % OC.

Zusammenfassung

SQK (EQS_{sed}): 0.028 µg/kg TS

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 Tebuconazol 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 Chlorpyrifos von 0.028 µg/kg TS für Standardsedimente mit 1 % OC vor.

Résumé

CQS (EQS_{sed}): 0,028 µg/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 préliminaire pour le chlorpyrifos de 0,028 µg/kg p.s. est proposé pour les sédiments standards avec 1 % CO.

Sommario

CQS (EQS_{sed}): 0,028 µg/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 provvisorio per il clorpirifos di 0,028 µg/kg p.s. è proposto per sedimenti standard con 1 % CO.

Table of content

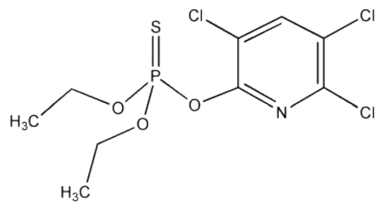
1 General Information

General information for this organophosphate pesticide can be found in the Ecotox Centre Dossier for chlorpyrifos in water[1] (Ecotox Centre 2017). Only complementary information relevant for sediment has been added to this chapter.

1.1 Identity and physico-chemical properties

Table 1 summarizes the identity and physico-chemical parameters for chlorpyrifos. Where available, experimentally collected data is identified as (exp) and estimated data as (est). When not identified, it means that no indication is available in the cited literature.

Table 1 Information required for EQS derivation according to the TGD (EC 2011). Chlorpyrifos and chlorpyrifos-ethyl are used as synonyms.

Characteristics	**Values**	**References** (*cited in Ecotox Centre, 2017)
IUPAC name	O,O-diethyl-O-3,5,6-trichloro-2-pyridyl Phosphorothioate	ESIS*
Chemical group	Organophosphate	Tomlin 2009*
Structural formula		Kegley et al. 2016
Molecular formula	$C_9H_{11}Cl_3NO_3PS$	EC 2005a
CAS No	2921-88-2	EC 2005a*
EINECS	2208644	EC 2005a*
Code SMILES	CCOP(=S)(OCC)Oc1nc(Cl)c(Cl)cc1Cl	EPI 2011*
Molecular weight (g/mol)	350.6	EC 2005a*
Melting point (°C)	41-42 (exp; purity 97-99%)	EC 2005a*
Boiling point (°C)	No boiling point at normal pressure; decomposes at 160°C (exp)	Kim et al. 2016
Vapour pressure (Pa)	(1) $3.35 \cdot 10^{-3}$ (exp; at 25ºC purity 99.8%) (1) $1.43 \cdot 10^{-3}$ (exp; at 20ºC purity 99.8%) (2) $1.0 \cdot 10^{-3}$ (exp; at 25ºC)	(1) EC 2005a* (2) EC 2005b *
Henry's law constant ($Pa \cdot m^3/mol$)	(1) 0.478 (2) 0.91 (it is concluded that chlorpyrifos is non-volatile from water surfaces) (3) moderatly volatile	(1) EC 2005a* (2) EC 2005b * (3) Racke 1993
Water solubility (mg/l)	(1) 1.05 (exp; at 20°C in an unbuffered solution - pH dependency not reported) (2) 0.39 (exp; at 19.5°C and pH 6.28) (2) 0.7623 (exp; at 20°C and pH 7.0-7.6) (2) 1.04 (exp; at 25°C and pH 4) (2) 1.07 (exp at 25°C and pH 7)	(1) EC 2005a* (2) EC 2005b*

[1] The dossier can be requested to info@oekotoxzentrum.ch

Dissociation constant (pK_a)	Not assignable - Chlorpyrifos contains no ionizable protons	Karickhoff et al. 1979
Octanol-water partition coefficient (log K_{ow})	(1) 4.7 (exp; at 20°C and neutral pH) (2) 4.69 - 5.3 (no indication whether exp or est) (3) 5.21±0.02 (EEC Method A.8/OECD 107) (4) Mean : 5.09	(1) EC 2005a* (2) EC 2005b* (3) EFSA 2017 (4) EC 2003*
Sediment-water partition coefficient log K_{OC} or Kp	Log K_{oc} (1) 3.44 - 4.49 (2) 3.65 - 4.19 (no indication if exp or est, only range provided) (3) 2.81-4.49 (exp) (3) 3.66 (est; from mean K_{ow}=5.09 using equation phosphates $\log K_{OC}=0.49*\log K_{OW}+1.17$ (EC, 2011)) Geometric mean (n=85): 3.79	(1) EC 2005a* (2) EC 2005b* (3) Appendix I and chapter 2.2
Kd	(1) 13-1863 Geometric mean exp. (n=102): 116	(1) Appendix I and chapter 2.2
Aqueous hydrolysis DT_{50} (d)	(1) pH ≤ 7: 72 d (exp; 25°C) (1) pH 9: 16 d (exp; 25°C) (2) pH 5: 63-73 d (exp; 25°C) (2) pH 7: 16-35 d (exp; 25°C) (2) pH 8: 23 d (exp; 25°C)	(1) EC 2005a* (2) EC 2005b*
Aqueous photolysis DT_{50} (d)	(1) 39.9 days (exp; natural river water under natural sunlight) (1) 29.6 d (at pH 7 under natural sunlight) (2) 15 d (midsummer 20°N) (2) 30 d (midsummer 40°N) (2) 29200 d (deep winter 60°N)	(1) EC 2005a* (2) EC 2005b*
Biodegradation in aqueous environment DT_{50} (d)	(1) Not readily biodegradable; (1 & 2) Water sediment study: Water: 3-6 d Whole system: 22-51 d (2) Not readily biodegradable (exp; 22% after 28 days OECD 301 (no further information on this subject) (3)11.9-30.6 d in natural sediment/water system. (4) 6-58 d in aerobic system and 58-223 d in anaerobic system.	(1) EC 2005a* (2) EC 2005b* (3) Racke 1993 (4) Mackay et al. 2014

1.2 Regulation and environmental limits

Table 2 summarizes existing regulation and environmental limits in Switzerland, Europe and elsewhere for chlorpyrifos.

Table 2 Existing regulation and environmental limits for chlorpyrifos in Switzerland and elsewhere.

Europe	
Directive 2013/39/EU	Identified as a priority substance in the field of water policy
EQS – EC (15.01.05)	AA-EQS: 0.03 µg/l MAC-EQS: 0.1 µg/l
Switzerland	
EQS- Ecotox Centre (23.06.17)	AA-EQS: 0.00046 µg/l MAC-EQS: 0.0044 µg/l
Ordinance on phytosanitary products (OPPh) (01.07.17)	Annex 1 Active substances approved as a phytosanitary product
Water protection ordinance (WPO) (02.02.16) Annex 2 Requirements on Water Quality for plant protection products Annex 22 Additional requirements for groundwater which is used for drinking water or is intended as such	Maximum concentration authorized: Surface water : 0.1 µg/l for individual substance Groundwater : 0.1 µg/l for individual substance
FDHA Ordinance on the maximal limits for pesticide residues on vegetal and animal products (OPOVA) (01.05.17)	Annex 2 Maximum limit authorized for pesticide residues
Register relating to Pollutant Release Ordinance (PRTRO) (01.03.07)	Annex 2 Threshold value for reporting obligation for water and land

1.3 Use and emissions

Chlorpyrifos is an insecticide in the form of spray, emulsion, suspension or granulate used mainly in arboriculture (43%) and viticulture (14%), and sugar beet (4%). It is used for pest control in apple blossom weevil, codling moth, European apple sawfly, summer fruit tortrix, citrus flatid planthopper, thrips, and diamondback moth among others. The active substance is among the top 5 most sold insecticides in Switzerland (OFAG 2017; Wittmer et al. 2014). In Lake Geneva watershed, it is estimated that 5395 kg/year of chlorpyrifos are applied for pome and stone fruits (CIPEL 2016).

1.4 Mode of action and sensitivity of taxonomic groups

Like other organophosphate insecticides, chlorpyrifos inhibits the activity of the enzymes acetylcholinesterase and butyrylcholinesterase involved in the termination of synaptic transmission. Acetylcholinesterase is inhibited by the active metabolite, chlorpyrifos oxon (Giddings et al. 2014). As a result, the nervous system is continuously stimulated, which leads to tetany, paralysis and death. Chlorpyrifos biological activity targets insects (Orthoptera, Diptera, Homoptera, Coleoptera, Lepidoptera, Hymenoptera and Hemiptera), arachnids (spiders, mites, ticks) and other arthropods including aquatic insects and crustaceans. Its mechanism of action makes it toxic for most animals because the amino-acid chain that composes acetylcholinesterase has been conserved through evolution. However, susceptibility to chlorpyrifos differs greatly among taxa (Timchalk 2010) with insects, arachnids and crustaceans being the most sensitive (Solomon et al. 2014).

Chlorpyrifos exerts toxicity through contact or ingestion and stomach toxicity, affecting ecological relevant parameters like reproduction, fitness and survival (OSPAR 2013; Racke 1993; Sidney et al. 2016).

2 Environmental fate

2.1 Stability and degradation products

Chlorpyrifos is subject to biotic and abiotic degradation (photolysis, abiotic hydrolysis) which depend strongly on environmental conditions such as pH, alkalinity, aerobic and anaerobic conditions as well as microbial activity. In the natural environment, chlorpyrifos is considered to have a short to moderate persistence, with reported half-life in natural water-sediment systems of 11.9 to 30.6 days although half-life can reach up to 58 to 223 days in anaerobic conditions (Racke 1993; Mackay et al. 2014). The major metabolite of chlorpyrifos degradation is TCP (3,5,6-trichloropyridinol), which in turn is reversibly transformed in TMP (3,5,6-trichloro-2-methoxypyridinol). Both degradation products are formed by biotic and abiotic degradation (Racke 1993; Solomon et al. 2014).

Organic carbon (OC) in sediment is often colonized by microorganisms that accelerate the degradation of chlorpyrifos in one of its degradation products (TCP) (Racke 1993). Ankley et al. (1994) observed an 80 to 95 % decrease in chlorpyrifos concentrations after 40 days aging in natural sediments under laboratory conditions, in agreement with sediment half-life of 10 to 16 days.

2.2 Sorption/desorption processes

Chlorpyrifos can volatilize shortly after field application, but once it reaches the soil chlorpyrifos binds strongly to the particulate phase according to its relatively high hydrophobicity. Chlorpyrifos can enter the aquatic environment directly by dispersion through the air during application but mostly through erosion processes. Leaching is also of minor importance. Once in the aquatic system, chlorpyrifos is found mainly bound to the sediment (Racke 1993; Solomon et al. 2014).

According to experimental data for K_{oc} and Kd (Hooftman et al. 1993; Racke 1993; Gebremariam 2011; Solomon et al. 2014; Williams et al. 2014; DOW 2015) summarized in Appendix 1:

- Kd values for soil range from 8 to 1862 l/kg (n=91, mean: 237 l/kg, geometric mean: 112 l/kg)
- Kd values for sediment range from 35 to 767 l/kg (n=11, mean: 264 l/kg, geometric mean: 152 l/kg)
- K_{OC} values for soil range from 652 to 31000 l/kg (n=71, mean: 7816 l/kg, geometric mean: 5804 l/kg)
- K_{OC} values for sediments range from 3000 to 25565 l/kg (n=13, mean: 11378 l/kg, geometric mean: 8993 l/kg)

Given the small number of data for sediments, Kd and K_{OC} values for sediments and soil have been used to plot the probability distribution for these two parameters (Fig. 1):

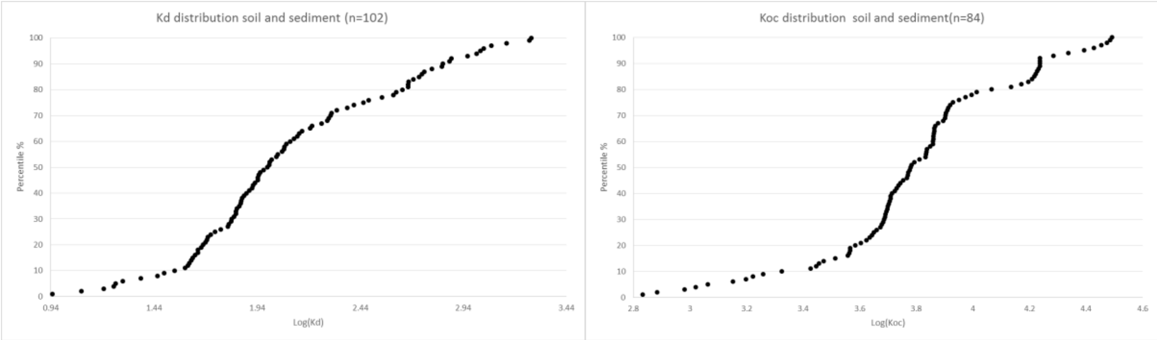


Figure 1 Plot of K_{OC} and Kd reported in the literature.

- The geometric mean of available experimental Kd is 116 L/kg (log Kd= 2.06).
- The geometric mean of available experimental K_{oc} is 6211 L/kg (log K_{oc}= 3.79).

Kd is strongly correlated to OC content in soil and sediment but not correlated to clay content, cation exchange capacity and pH.

The sorption coefficient Kd/K_{oc} of its main metabolite TCP (pK_a =4.55) depends on pH, with a K_{OC} of 3344 l/kg for its neutral form and 54 l/kg for the anionic form (Gebremariam 2011; Racke 1993).

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 chemicals like chlorpyrifos. Organic carbon has a certain influence on the bioavailability of chlorpyrifos, with adsorption capacity highly varying depending on the OC composition (fulvic and humic acids, quantity and types of organic functional groups, etc.; Essington, 2004). A research conducted by Ankley et al. (1994) on two sediments with different OC content demonstrated that OC plays a key role on chlorpyrifos bioavailability to the midge *Chironomus tentans*. Normalization of effect data to OC content did not decrease variability compared to effect data normalized by dry weight. However, the apparent lack of improved prediction of chlorpyrifos bioavailability upon OC normalization was attributed by the authors to the two test sediments that were used in the experiments, which differed in OC content by only about a factor of three, and the chlorpyrifos concentration intervals in the test sediments spanning almost three orders of magnitude. Based on the comparison of effect concentrations in water-only exposures to effects in the sediment tests corresponding to predicted or measured pore-water concentrations, Ankley et al. (1994) showed that the equilibrium partitioning model provided "reasonable" consistent results to evaluate the toxicity of chlorpyrifos to this macroinvertebrate in the range of 3.0-8.5 % OC (Ankley et al. 1994).

Organic carbon content has been shown to reduce the bioaccumulation of chlorpyrifos in the oligochaete *Lumbriculus variegatus*, although when exposed to sediments with low OC content bioaccumulation was higher than expected (Jantunen et al. 2008). This oligochaete, which is exposed to chlorpyrifos through both the body wall and ingested sediment, may be feeding selectively on sediment particles with high OC content and pesticide concentration when exposed to sediments with low OC content.

Additionally colonization of OC by microorganisms accelerate chlorpyrifos degradation (Racke 1993), which may also have an impact in reducing chlorpyrifos bioavailability from the sediment compartment.

2.4 Bioaccumulation and biomagnification

Due to its high hydrophobicity, chlorpyrifos tends to bioaccumulate moderately to highly in fish, with a Biaccumulation Factor (BCF) of 1374 l/kg (unspecified fish species) according to EC (2005). This BCF is above the trigger for derivation of QS for the protection from secondary poisoning for top predators (BCF≥ 100; EU-TGD (EC, 2011)). To account for protection of top predators, a QS_{water} based on EQS_{biota} has been derived by the Ecotox Centre with a value of 0.048 µg/l (Ecotox Centre 2017).

However, a study performed with a two-level food chain consisting of fish (*Aphanius iberus*) fed with pre-contaminated crustaceans (*Artemia franciscana* and *Artemia parthenogenetica*) showed no biomagnification, probably due to the physico-chemical properties of chlorpyrifos and the biotransformation ability of fish for this type of pollutant (Varó et al. 2002).

Its main metabolite (TCP) does not tend to accumulate neither in fish (BCF= 3.06) nor in smaller organisms like daphnids (BCF= 21.77) or snails (BCF= 13.67) (CCME 2008; Racke 1993).

Concerning the risk of benthic invertebrates to transfer toxic and bioaccumulative substances to higher trophic levels, the EFSA scientific opinion for sediment risk assessment proposed to perform spiked sediment bioaccumulation tests with benthic invertebrates for substances that show significant bioaccumulation in fish (BCF> 2000 l/kg) when the substance is 1) persistent in sediment (DT_{50}> 120 d in water-sediment fate studies) and log K_{ow}> 3; or 2) non-persistent in sediment, log K_{ow}> 3 and > 10% of the substance found in the sediment in a water-sediment fate study (EFSA 2015). The BCF for chlorpyrifos is below the EFSA threshold.

3 Analysis

3.1 Methods for analysis and quantification limit

The limit of detection of chlorpyrifos according to available literature ranges from 0.145 to 0.41 µg/kg whereas the limit of quantification ranges from 0.484 to 0.6 µg/kg (Table 3). A reference method for pesticides analysis in France is available from AQUAREF according to the norm NF T90-210 (Aquaref 2014). Schäfer et al. (2011) reported a limit of quantification of 5 µg/kg using gas chromatography-pulse flame photometric detector (GC-PFPD).

Table 3 Methods for chlorpyrifos 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
0.41	n.a.	GC/MS	Davidson et al. 2012
0.2	0.6	GC-EI-MS/MS LC-ESI-MS/MS	Aquaref, 2014
0.145	0.484	GC-MS/MS	Pintado-Herrera et al. 2016

3.2 Environmental concentrations

Measured environmental concentrations (MEC_{sed}) in sediments for Switzerland are only available for 5 sites selected to represent small streams affected mainly by agricultural pressures (Table 4). The MEC_{sed} range from <0.145 to 156 µg/kg d.w. in sediments and from <0.145 to 363 µg/kg d.w. in suspended particulate matter. MEC_{sed} for chlorpyrifos in sediments from other European countries are in the range <LOD-36.17 µg/kg d.w.

While MEC_{sed} of chlorpyrifos are rather scarce in Switzerland, surface waters have been screened for the presence of chlorpyrifos, ranging from 0.01 to 7.4 µg/L (Table 4). Using the equilibrium partitioning model (Di Toro et al., 1991), default values of the TGD (EC, 2011) and K_{OC} values from section 2.2, the estimated predicted environmental concentrations in sediments ($PEC_{sed,EqP}$) range from 3.1 to 2310 µg/kg d.w. based on maximum MEC_{water} and the geometric mean for K_{OC}.

Table 4 Measured environmental concentrations (MEC_{sed}) of chlorpyrifos in sediments for several European countries and Switzerland. Predicted environmental concentrations in sediments ($PEC_{sed,EqP}$) *estimated using the equilibrium partitioning model (Di Toro et al., 1999) and measured concentrations* in surface waters *(MEC_{water})* in Switzerland are included for comparison purposes. All concentrations expressed as µg/kg d.w. and µg/l*. Sed= sediment; spm= suspended particulate matter*.

Country	MEC_{sed} (min-max)	--	Nr sites	Comments	Reference
Switzerland	<0.145-156 (sed) <0.145-363 (spm)	--	5	Small streams with agricultural use in catchment; monthly sampling from March to October	Ecotox Centre, unpublished data
France	0.01-0.02 (sed)	--	16	Arc river, Aix-en-Provence	Kanzari et al. 2011
Denmark	11 (max; spm)*	--	4	Not detected in sediment	McKnight et al. 2015
Spain	0.18-36.17 (sed)	--	24	Ebro river, two campaigns in consecutive years: 45% and 82% detection frequency respectively	Ccanccapa et al. 2016
Projects (Switzerland)	**$PEC_{sed,EqP}$[a]**	**MEC_{water}[b]**	**Nr sites**	**Comments**	**Reference**
Micropoll	2310 (1122-9471)	7.4	565	Situation analysis 2005-2012; all types of water bodies and sampling strategies; >LOQ at 12% of 230 sites	Munz et al. 2013
NAWA SPEZ 2012	3.1 (1.5-12.8)	0.01	5	Small streams with agricultural use in catchment; 100% detection frequency; from March to July	Moschet et al. 2015

NAWA SPEZ 2015	12.2 (5.9-49.9)	0.039	5	Small streams with agricultural use in catchment; 100% detection frequency; from March to July	Langer et al. 2017

[a] Only maximum values are available in the cited references

[b] $PEC_{sed,EqP}$ derived for 5% OC and using the geometric mean (6211), and maximum and minimum K_{oc} values for sediment (3000-25565) according to section 2.2.

4 Effect data (spiked sediment toxicity tests)

Several substance dossiers are available from different national and international agencies for chlorpyrifos, which contained 59 different effect data from spiked sediment toxicity tests. A bibliographic search was performed in the US Ecotox Data Base with an output of 8504 entries for aquatic data (years 1965-2015, both included), from which only 5 data addressed the sediment compartment. A key word search was performed on Scopus for the years 2015-2017 to complete the available data base.

Relevance ("R" score in the table below) and reliability ("C" score in the table below) of studies are evaluated according to the CRED-criteria (Moermond et al. 2016) adapted for sediments (Casado-Martinez et al. 2017).

Data for freshwater species:

Chronic data is available for two different test species, all of them from the report "Development of ecotoxicological test systems to assess contaminated sediments. Joint report no 1: Acute and (sub) chronic tests with the model compound chlorpyrifos", which includes results from studies performed at three different laboratories following the same testing protocols with little variations. Studies for the model organism *Daphnia magna* were considered not relevant (C3) to evaluate sediment toxicity according to the list of EFSA relevant species for the sediment compartment[2]. The results for tests using *Chironomus riparius* were considered relevant (C1) but not reliable (R3) according to levels of dissolved oxygen not meeting the acceptability criteria for this species according to standard operational procedures (OECD 2018).

Acute toxicity data from spiked sediment toxicity tests are available for five species: *D. magna,* three insects *C. riparius, C. tentans, C. dilutus,* and the amphipod *Hyalella azteca* species.

Acute 96 h NOECs are available for *D. magna* and *C. riparius* from Hooftman et al. (1993), which are classified as not relevant (C3) and not reliable (R3) respectively for the same reasons as for the chronic effect data.

Three different acute 10 d LC50s are available for *H.azteca* which are classified as reliable with restrictions (R2; see section 3.3 for details). One acute 10 d LC50 is available for *C. dilutus* that is considered reliable with restrictions, while two 10 d LC50s are available for *C. tentans*, which are considered not assignable (R4).

[2] Benthic test species cited in EFSA, 2015 for pesticide risk assessment in sediment: *Anabaena flosaquae, Chironomus acutus, Chironomus riparius, Chironomus tentans, Chironomus yoshimatsui, Chironomus dilutus, Craticula accomoda, Diporeia spp, Elodea sp., Fragilaria rumpens, Glyceria maxima, Gomphonema parvulum, Hexagenia spp, Hyalella azteca, Lumbriculus variegatus, Mayamaea fossalis, Myriophyllum aquaticum, Myriophyllum spicatum, Pseudokirchneriella subcapitata, Pseudomonas putida, Sellaphora minima, Tubifex tubifex.*

Data for marine species:

Acute toxicity data from spiked sediment toxicity tests are available for four species: the amphipods *Ampelisca abdita* and *Eohaustorius estuarius*, the clam *Ruditapes decussatus*, and the copepod *Amphiascus tenuiremis*. These studies are classified as relevant with restrictions (C2), pending comparison of sensitivities of marine and freshwater species to consider them relevant without restrictions (C1) or not relevant (C3) for EQS_{sed} derivation.

For the copepod *A. tenuiremis* one chronic study is available that addressed nauplii production (reproduction). This datum is considered not reliable (R3) because only 10 gravid females were tested, each considered a single replicate that was observed during 7 weeks exposures.

Table 5 Sediment effect data collection for chlorpyrifos. Data were evaluated for relevance and reliability according to the CRED criteria for sediments (Casado-Martinez et al. 2017)[3]. Used data for QS development is underlined, nor relevant or not reliable data in grey color. Abbreviations: n.a. = not available.

Group	Species	Test compound	Administration of tested substance	Equilibration time	Endpoint	Test duration	Effect concentration	Value (mg /kg d.w.)	Normalized value (mg /kg OC d.w.)	Normalized value (mg /kg 5% OC d.w.)	Nominal/ measured exposure concentrations	Comments	Sediment type	Validity	Reference
Acute toxicity data for freshwater species															
Cladoceran	*Daphnia magna*	Chlorpyrifos-ethyl	Spiked sediment; static	20 h	Mobility	96 h	EC50	0.88	8.8	0.44	Measured		Natural sediment 10% OC	C3	RIZA cited in Hooftman et al. 1993
Cladoceran	*Daphnia magna*	Chlorpyrifos-ethyl	Spiked sediment; static	20 h	Mobility	96 h	EC50	0.42	4.2	0.21	Measured		Natural sediment 10% OC	C3	TNO cited in Hooftman et al. 1993
					Mobility, geometric mean			0.61	6.08	0.30					
Amphipod	*Hyalella azteca*	Chlorpyrifos-ethyl	Spiked sediment; water renewal daily	24-48 h	Mortality	10 d	LC50	n.a.	1.77	0.0885	Measured ?	Chemical analyses performed on 1 concentration; not reported if nominal or measured	Natural sediment, 1.7-2.1% TOC	R2, C1	Amweg and Weston 2007
Amphipod	*Hyalella azteca*	Chlorpyrifos-ethyl	Spiked sediment; water renewal daily	7-14 d	Mortality	10 d	LC50	n.a.	2.96	0.148	Measured ?	Chemical analyses performed on 1 concentration; not reported if nominal or measured	Natural sediment, 2% TOC	R2, C1	Weston and Amweg 2007
Amphipod	*Hyalella azteca*	Chlorpyrifos-ethyl	Spiked sediment; continuous water renewal	16-22 d	Mortality	10 d	LC50	na	4.1	0.21	Nominal	LC50 determined at 18°C. Slightly higher LC50 determined at 23°C	Natural river sediment 1.87% OC	R2, C1	Weston et al. 2009
					Mortality, geometric mean				<u>2.78</u>	0.14					
Insecta	*Chironomus dilutus*	Chlorpyrifos-ethyl	Spiked sediment; semi-static	14 d	Mortality	10 d	LC50	na	<u>6.68</u>	0.33	Measured	LC50 determined at 23°C. Slightly higher LC50 determined at 13°C	Soil 0.97% OC; 23°C	R2, C1	Harwood et al. 2009
Insecta	*Chironomus tentans*	Chlorpyrifos-ethyl	Spiked sediment; continuous water renewal	42 h	Mortality	10 d	LC50	0.468	5.51	0.275	Measured		Lake sediment 8.5% OC	R4, C1	Ankley et al. 1994
Insecta	*Chironomus tentans*	Chlorpyrifos-ethyl	Spiked sediment; continuous water renewal	42 d	Mortality	10 d	LC50	0.299	9.96	0.50	Measured		Lake sediment 3% OC	R4, C1	Ankley et al. 1994
					Mortality, geometric mean			0.374	7.40	0.37					

[3] Validity categories for Reliability (R) and Relevance (C) are those from CRED (Moermond et al. 2016): R1 / C1 = Reliable / Relevant without restriction; R2 / C2 = Reliable / Relevant with restriction; R3 / C3 = not reliable / relevant; R4 / C4 = not assessable. An assessment of reliability was not performed when a study was rated as not relevant.

Cladoceran	*Daphnia magna*	Chlorpyrifos-ethyl	Spiked sediment; static	20 h	Mobility	96 h	NOEC	0.32	3.2	0.16	Measured	Same NOEC for three laboratories	Natural sediment 10% OC	C3	Hooftman et al. 1993
Insecta	*Chironomus riparius*	Chlorpyrifos-ethyl	Spiked sediment; static	20 h	Mortality	96 h	NOEC	0.1	1	0.05	Measured ?	Exposure concentrations measured but not reported	Natural sediment 10% OC	R3, C1	TNO cited in Hooftman et al. 1993
Insecta	*Chironomus riparius*	Chlorpyrifos-ethyl	Spiked sediment; static	20 h	Mortality	96 h	NOEC	0.1	1	0.05	Measured ?	Exposure concentrations measured but not reported	Natural sediment 10% OC	R3, C1	RIZA cited in Hooftman et al. 1993
Insecta	*Chironomus riparius*	Chlorpyrifos-ethyl	Spiked sediment; static	20 h	Mortality	96 h	NOEC	0.056	0.56	0.028	Measured ?	Exposure concentrations measured but not reported	Natural sediment 10% OC	R3, C1	RIVM cited in Hooftman et al. 1993
Insecta	*Chironomus riparius*				Mortality, geometric mean			0.08	0.8	0.04					
Acute toxicity data for marine and estuarine species															
Amphipod	*Ampelisca abdita*	Chlorpyrifos-ethyl	Spiked sediment; static	28 d	Mortality	10 d	LC50	0.124	15.9	0.795	Nominal	Measured concentrations 33-90% nominal	Formulated sediment 0.78% OC ; 20°C and salinity of 28‰	R2, C2	Anderson et al. 2008
Amphipod	*Eohaustorius estuarius*	Chlorpyrifos-ethyl	Spiked sediment; static	28 d	Mortality	10 d	LC50	0.103	13.2	0.661	Nominal	Measured concentrations 25-157% nominal	Formulated sediment 0.78% OC ; 15°C and salinity of 20‰	R2, C2	Anderson et al. 2008
Mollusca	*Ruditapes decussatus*	Chlorpyrifos-ethyl	Spiked sediment; static	24 h	Development	24 h	EC50	0.96	Na		Nominal	Measured concentrations > 80% of nominal	Coastal sediment (15.5% silt, 13.9% clay); salinity 34‰. TOC not reported	R4, C2	Fathallah et al. 2014
Mollusca	*Ruditapes decussatus*	Chlorpyrifos-ethyl	Spiked sediment; static	96 h	Mortality	96 h	LC50	2.53	Na		Nominal	Measured concentrations > 80% of nominal	Coastal sediment (15.5% silt, 13.9% clay); salinity 34‰. TOC not reported	R4, C2	Fathallah et al. 2014
Copepod	*Amphiascus tenuiremis*	Chlorpyrifos-ethyl	Spiked sediment; static	3h	Mortality	96 h	LC50	0.04	1.053	0.052	Measured	For the most sensitive life stage: nauplius	Natural sediment <40 µm, 3.8% OC; salinity 30‰	R2, C2	Green et al. 1996

4.1 Graphic representation of effect data

Effect data available from spiked sediment toxicity tests in Table 5 are presented in Fig. 2. Only one single datum is presented per species.

Chronic data are only available for a crustacean (*D.magna*) and an insect (*C.riparius*), with the insect being more sensitive to chlorpyrifos than the cladoceran. A chronic NOEC is also available for the marine copepod *A. tenuiremis*, which appears as the most sensitive among the tested species according to an unbounded NOEC (LOEC). There is large uncertainty in this conclusion because NOECs for *D. magna* and *A. tenuiremis* are unbounded and not reliable (R3).

Based on R2 reliable with restriction 10 d LC50s, freshwater amphipods are more sensitive than insects but marine amphipods are not.

Based on 96 h NOECs, insects are more sensitive than crustaceans (Cladocera) but this conclusion is also highly uncertain for the same reasons as for chronic data (R3 data). The calculated acute to chronic ratio for *C. riparius* 2.5 while for *D. magna* is 19.

According to a 96 h unbounded NOEC, copepods appear more sensitive than insects and mollusks, although the data for mollusks could not be normalized to OC and is considered not reliable (R3).

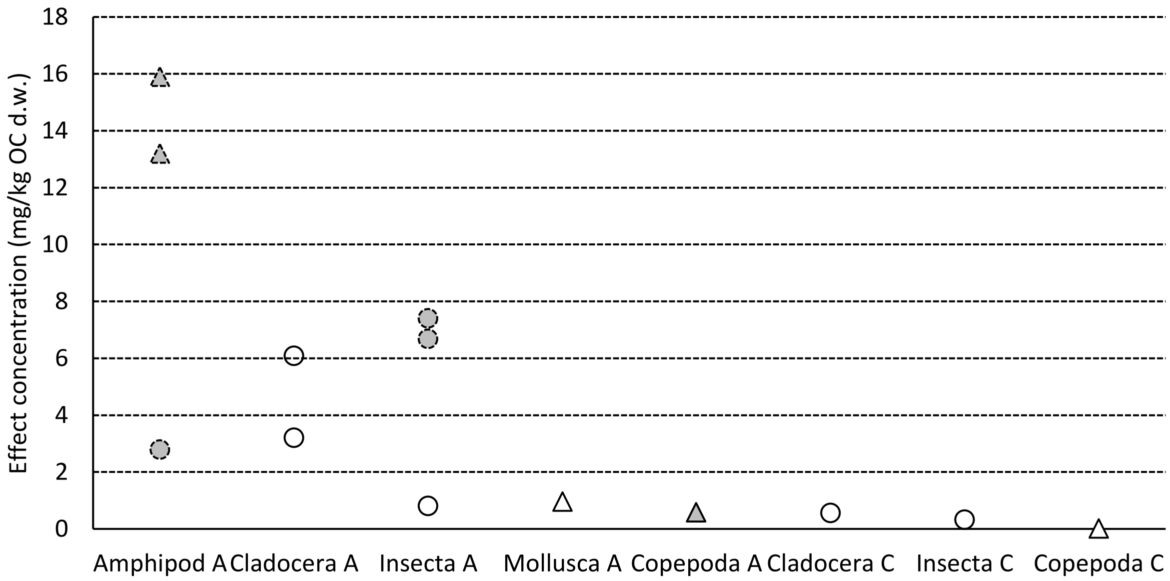


Figure 2 Graphical representation of all available acute (A) and chronic (C) effect data from spiked sediment toxicity tests with chlorpyrifos. Data are normalized for OC except effect concentrations for Mollusca, which could not be normalized in the absence of measured OC concentrations in test sediments. Triangles: marine species; circles: freshwater species. Empty symbols: not reliable (R3); Grey symbols: reliable with restrictions or not assignable. L/EC50 are dotted; N/LOEC are solid symbols. One datum is represented per species and test duration, when more than one type of effect concentration is available the lowest (e.g. NOEC) is represented.

4.2 Comparison between marine and freshwater species

Regarding effect concentrations for pelagic organisms, the Ecotox Centre dossier (2017) could only perform statistical comparisons for the acute toxicity of chlorpyrifos on fish, and no statistically significant difference was observed.

When comparing freshwater and marine data, separate comparisons are required for each type of effect concentration. For sediment-relevant species, different effect concentrations (L/EC50, NOEC and LOEC values) are available. In addition, comparisons should be based on OC normalized data, but OC normalized data is only available for two marine species. Overall, the number of data appears too small for a statistical comparison of acute and chronic effect data for sediment organisms. Marine and freshwater data were therefore not combined for EQS_{sed} development.

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

Long-term studies:

Hooftman et al. 1993: presents data for two different laboratories testing chlorpyrifos with the same test organisms, endpoints and sediments.

- Species: *Chironomus riparius.*
- Origin: Home culture under standardized conditions.
- Experimental sediment: relatively clean natural sediment from Schoonrewoerdse Wiel sieved through 500 µm sieve. Sediment is irradiated to kill remaining organisms. Stored at 4 °C and used within the following 3 months after sampling. A suspension of sediment is prepared by adding 40 g dry sediment to Dutch Standard Water to obtain a final concentration of 40 g/l (1:4 v/v). TOC of approximately 10 %.
- Spiking and equilibration time: stock solution of chlorpyrifos is added to the sediment suspension and is stirred vigorously for 20 h at 17-20°C. Then the sediment suspension is pipetted directly into the glass vials used in the test. Not mentioned if overlying water after spiking and before starting the exposure was discarded.
- Five concentrations tested: 0.018, 0.032, 0.056, 0.1, 0.18 mg/kg d.w.
- Controls: negative toxicity control and solvent control.
- Overlying water: Dutch Standard Water (DSW or DSWL) prepared from several salts and distilled or groundwater from Linschoten.
- Type of test: semi-static; replacement sediment/water system weekly.
- Exposure conditions: 20 ± 1°C; feeding twice per week a fish food suspension.
- Determination of pH, dissolved oxygen in overlying water at all institutions, nitrite/nitrate, phosphate, ammonia at some while chlorpyrifos concentrations performed at both.
- Bioassays: semi-static tests with renewal of the sediment/water system weekly. Performed in glass vessels of 50 ml.
- Number of test organisms and replicates: 25 per vessel, three replicates per test concentration.
- Test duration: 21 d.
- Test endpoints: survival.
- Statistics: Kooyman, Spearman-Karber and two-tailed Dunnett test.

→ The study is considered not reliable due to invalid dissolved oxygen levels during the tests, which are below half the 60 % saturation required by standard OECD guidelines for this species, and absence of information about behavior and acceptability of negative toxicity controls.

Short-term studies:

Weston and Amweg 2007: presents data for the freshwater amphipod *Hyalella azteca* 10 d spiked sediment toxicity test performed following standard protocol from US EPA (2000).

- Species: *Hyalella azteca.* 7-14 d old.
- Origin: not reported.
- Experimental sediment: 20:80 mixture of Lake Anza Reservoir in Berkeley (CA, USA) and San Pablo Dam Reservoir (Orinda, CA, USA) as control and spiking experiments, sieved through 1 –

mm screen and frozen before use. Concentrations of pyrethroids at non detectable concentrations (< 1 ng/g); 2 % TOC.
- Spiking and equilibration time: control and test sediments mixed with a mixing attachment in an electric drill, tests initiated 24 to 48 h later. Solvent controls with acetone carried.
- Five concentrations in a dilution series varying by a factor of 0.6. Concentrations used not reported.
- Chemical analyses: at test initiation in one concentration.
- Controls: negative toxicity control. Solvent control with acetone performed, at < 200 µl/kg wet sediment referred to an external paper as having no effects on the test species. All met acceptability criteria.
- Overlying water: reconstituted moderately hard water.
- Type of test: water changes performed every day.
- Exposure conditions: 23 °C; feeding with yeast, cerophyll, and trout chow mixture daily.
- Determination of temperature, pH, conductivity, alkalinity, hardness, and ammonia before water renewal after 24 h and end of the test; temperature and dissolved oxygen monitored regularly throughout the test. Not reported.
- Test vessels: glass 400 mL vessels, 50 to 75 ml sediment/ 250 ml overlying water.
- Number of test organisms and replicates: 10 per vessel, three replicates per concentration.
- Test duration: 10 d
- Test endpoints: survival.
- Statistics: LC50s determined by the Spearman-Karber method. Statistics were performed using ToxCalc® 5.0 (Tidepool Scientific Software, Mc-Kinleyville, CA, USA). Confidence intervals reported. Abbott's correction applied if necessary to account for control mortality.

→ The study is considered reliable with restrictions (R2) because information on water quality parameters are not reported. Chemical measurements were only performed in one concentration, results are not reported.

Amweg and Weston 2007: presents data for the freshwater amphipod *Hyalella azteca* 10 d spiked sediment toxicity test performed following standard protocol from US EPA (2000).
- Species: *Hyalella azteca.* 7-14 d old.
- Origin: not reported
- Experimental sediment: 20:80 mixture of Lake Anza Reservoir in Berkeley (CA, USA) and San Pablo Dam Reservoir (Orinda, CA, USA) as control and spiking experiments, sieved through 1 – mm screen and frozen before use. Concentrations of pyrethroids at non detectable concentrations (< 1 ng/g); 1.7-2.1 % TOC.
- Spiking and equilibration time: control and test sediments mixed with a mixing attachment in an electric drill, tests initiated 24 to 48 h later. Solvent controls with acetone carried.
- Five concentrations in a dilution series, e.g. 100, 50, 25, 12, 6 %. Concentrations used not reported.
- Chemical analyses: at test initiation, performed at one concentration.
- Controls: negative toxicity control. Solvent control with acetone performed. All met acceptability criteria.
- Overlying water: reconstituted moderately hard water.
- Type of test: water changes performed every day.
- Exposure conditions: 23 °C; feeding not reported.

- Determination of temperature, pH, conductivity, alkalinity, hardness, and ammonia before water renewal after 24 h and end of the test; temperature and dissolved oxygen monitored regularly throughout the test. Not reported.
- Test vessels: glass 400 ml vessels, 75 ml sediment/ 300 ml overlying water.
- Number of test organisms and replicates: 10 per vessel, three to four replicates per concentration.
- Test duration: 10 d
- Test endpoints: survival.
- Statistics: LC50s determined by the Spearman-Karber method. Statistics were performed using ToxCalc® 5.0 (Tidepool Scientific Software, Mc-Kinleyville, CA, USA). Confidence intervals reported. Abbott's correction applied if necessary to account for control mortality.

→ The study is considered reliable with restrictions (R2) because information on water quality parameters are not reported. Chemical measurements were only performed in one concentration, results are not reported.

Weston et al. 2009: presents data for the freshwater amphipod *Hyalella azteca* 10 d spiked sediment toxicity test performed following standard protocol from US EPA (2000).

- Species: *Hyalella azteca.* 7-14 d old.
- Origin: not reported
- Experimental sediment: natural sediment from the American River at Folsom Lake, California, USA, 1.87 % TOC. Analyzed for 28 pesticides, all at non detectable levels (< 1ng/g).
- Spiking and equilibration time: each concentration prepared by adding the appropriate amount of toxicant dissolved in acetone, with 0.2-0.8 µg acetone/g wet sediment. Solvent controls followed the same spiking procedure. Spiked material homogenized using a paint mixing and then held at 4°C for 16 to 22 days prior to toxicity testing.
- Five to seven concentrations tested, varying by a factor of 1.7.
- Controls: negative toxicity control and solvent control.
- Overlying water: artificial water.
- Type of test: flow-through, two volume additions of water added daily by an automatic delivery system.
- Exposure conditions: 13, 18, 23 and 28 °C; feeding 1 mL yeast/cerophyll/trout chow per beaker daily; 16:8 h light/darkness.
- Determination of ammonia, hardness, alkalinity and pH at the start and end of the test; temperature and dissolved oxygen monitored throughout the test. Not reported but within acceptability criteria.
- Test vessels: glass 400 ml vessels, 50-75 ml sediment/ 250 ml overlying water.
- Number of test organisms and replicates: 10 per vessel, replicates not reported, but no deviation from US EPA (2000) assumed, it recommends eight replicates.
- Test duration: 10 d.
- Test endpoints: Survival.
- Statistics: LC50s determined by the trimmed Spearman-Karber method. Statistics were performed using ToxCalc® (Tidepool Scientific Software, Mc-Kinleyville, CA, USA).

→ The study is considered reliable with restrictions (R2) because chemical analyses were not performed to ensure exposure concentrations are not different from nominal concentrations.

Harwood et al. 2009: presents data for the freshwater midge *Chironomus dilutus* 10 d spiked sediment toxicity test performed following standard protocol from US EPA (2000).

- Species: *Chironomus dilutus.* Third instar larvae.
- Origin: cultures from Southern Illinois University and cultured according to standard protocols at 23 °C. Acclimation to temperatures performed before tests.
- Experimental sediment: natural soil from Touch of Nature reference site, IL, USA, sieved through 500 µm and hydrated with artificial water to form a sediment slurry. 0.97±0.10 % TOC.
- Spiking and equilibration time: stock added dropwise to the sediment slurry using acetone as solvent, stirred for 1 h using stainless-steel stirrer then sediment jars were covered by aluminum foil and aged for 14 d in darkness and -4 °C. Chemical analyses in sediments after storage/before exposure and at the end of the tests at each tested concentrations.
- Test vessels: 800 ml vessels, 50 g sediment in dry weight and 700 ml overlying water.
- Number of tested concentrations not reported, only range.
- Controls: negative toxicity control. Solvent control for spiked sediment toxicity tests not reported, included for spiked water toxicity tests.
- Overlying water: US EPA artificial, moderately hard water.
- Type of test: daily water renewal (75 %).
- Exposure conditions: effect concentrations reported for 13 and 23 °C; feeding 1 ml yeast/cerophyll/trout chow per beaker daily; 16:8 h light/dark.
- Determination of pH, dissolved oxygen and conductivity monitored daily throughout the test. Not reported but within acceptability criteria.
- Number of test organisms and replicates: not reported, according to US EPA (2000) 10 larvae per vessel and 8 replicates recommended.
- Test duration: 10 d
- Test endpoints: survival.
- Statistics: LC50 derived using log-probit analysis with SAS software.

→ The study is considered reliable with restrictions (R2) according to the use of soil instead of sediment and the lack of some information missing in the report.

Ankley et al. 1994: presents data for the freshwater midge *Chironomus tentans* 10 d spiked sediment toxicity test.

- Species: *Chironomus tentans.* Third instar larvae.
- Origin: not reported.
- Experimental sediment: two uncontaminated sediments: one from West Bearskin Lake, Minnesota, 3 % TOC; one from Pequaywan Lake, Minnesota, 8.5 % TOC.
- Spiking and equilibration time: spiking following Ditswort et al. using coating/rolling technique. Equilibration during 42 d at 4 °C and 4 l glass containers periodically mixed on a roller mill. No information about solvent reported.
- Chemical analyses in sediments, overlying water and pore-waters performed at the beginning and end of the test in one test vessels with no organisms but treated similarly for all tested concentrations.
- Test vessels: 300 ml vessels, 100 ml sediment and 150 ml overlying water.
- Five tested concentrations plus controls, ranging from 0.075 to 6.27 mg/kg d.w. for West Bearskin Lake and 0.242 to 23.25 mg/kg d.w. for Pequaywan Lake sediments.
- Controls: negative toxicity control. Solvent control for spiked sediment toxicity tests not reported.
- Overlying water: dechlorinated tap water.
- Type of test: water renewal four volumes per day.
- Exposure conditions: 20 °C; feeding 4 mg TetraFin per day; 16:8 h light/dark.

- Determination of overlying water quality parameters not reported. Control acceptability criteria met.
- Number of test organisms and replicates: not reported, according to US EPA (2000) 10 larvae per vessel and 8 replicates recommended.
- Test duration: 10 d.
- Test endpoints: survival.
- Statistics: LC50 calculated using trimmed Spearman-Karber. LC50 values based on the means of the day-0 and day-10 chemical analyses.

→ The study is considered not assignable (R4) according to the absence of overlying water quality data and solvent controls information.

5 Derivation of QS_{sed}

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_{sed} (EC 2011). 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 $QS_{sed, AF}$ 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.

Results of long-term toxicity tests with sediment organisms are preferred for deriving sediment standards. No R1 or R2 data are available. Acute 10 d data from short-term tests available for the amphipod *H. azteca* (3 data) and the insect *C. dilutus* (1 datum) can be used, in conjunction with the Equilibrium Partitioning approach for QS derivation. An AF of 1000 is applied to the lowest reliable value (Table 5):

$$QS_{sed,AF} = \frac{lowest\ EC50}{1000}$$

$$QS_{sed,AF} = \frac{2.78\left(\frac{mg}{kg-OC}\right)}{1000} = 0.00278\left(\frac{mg}{kg-OC}\right) = 2.8\left(\frac{\mu g}{kg-OC}\right)$$

The application of an AF of 1000 to the lowest credible acute datum results in a $QS_{sed,AF}$ = 2.8 µg/kg-OC, which corresponds to 0.14 µg/kg d.w. for a sediment with 5 % OC or 0.028 µg/kg d.w. for a sediment with 1 % OC. A sediment with 1 % OC is considered a worst case scenario in Switzerland.

5.2 Derivation of $QS_{sed,SSD}$ 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 (2011), p. 43). In this case, not enough data from spiked sediment toxicity tests are available for applying the SSD approach.

6 Derivation of $QS_{sed,EqP}$ using the Equilibrium Partitioning approach

If no reliable sediment toxicity data are available, the Equilibrium Partitioning (EqP) can be used to estimate the $EQS_{sed,EqP}$. 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 EC which sets a value of 0.033 µg/l for the protection of pelagic species (EC 2005b). In 2017, the Ecotox Centre has revised the quality criteria according to the availability of new effect data collected in the review of Giddings et al. (2014) and additional literature searched for the years 2014-2017. This update performed in accordance with the TGD provides an AA-QS of 0.00046 µg/l (Ecotox Centre 2017). The AA-QS proposed by the Ecotox Centre 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 2011). All K_{oc} used for EQS_{sed} 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 2011). 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. 10th percentile of OC content in Swiss Rivers).

6.4 Derivation of $QS_{sed,EqP}$

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 ($Kp=f_{OC}*K_{OC}$) 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 calculated $QS_{sed,EqP}$ using the geometric mean of all available K_{OC} values, including one value estimated from K_{OW} and the AA-EQS for water derived by the Ecotox Centre of 0.00046 µg/l (Ecotox Centre 2017) for a sediment with 5 % OC (standard EU TGD sediment) and 1 % OC (worst case scenario) are presented in Table 6. The derived $QS_{sed,EqP}$ range from 0.0292 for 1 % OC and 0.1430 µg/kg d.w. for 5 % OC.

An additional AF of 10 should be applied to the resulting $QS_{sed,EqP}$ for substances with log K_{ow} >5. In the case of chlorpyrifos, the log K_{ow} is 3.66 (see Table 1). The application of the additional AF of 10 to derive the $QS_{sed, EqP}$ is not warranted.

Table 6 $QS_{sed,EqP}$ derived using the geometric mean of all available K_{OC} values, including one value estimated from K_{OW} and the AA-EQS for water derived by the Ecotox Centre of 0.00046 µg/l (Ecotox Centre 2017) for a sediment with 5 % OC (standard EU TGD sediment) and 1 % OC (worst case scenario).

K_{OC} [l/kg]	OC [%]	Kp_{sed} [l/kg]	$K_{sed-water}$ [m³/m³]	$QS_{sed,EqP}$ [µg/kg w.w.]	$QS_{sed,EqP}$ [µg/kg d.w.]
6188	1	61.88	31.74	0.0112	**0.0292**
6188	5	309.4	155.5	0.0550	**0.1430**

7 Determination of QS_{sed} according to mesocosm/field data

No mesocosm studies are available that provide effect concentrations of chlorpyrifos for benthic organisms, only mesocosm studies related to the water phase are available (Ecotox Centre 2017).

8 Available sediment quality guidelines

According to the EU TGD p. 101, "… the standard thus derived should be compared with any evidence from field studies. Where anomalies appear, the derivation shall be reviewed to allow a more precise safety factor to be calculated…". This is to account for expected bias in laboratory data toward higher toxicity (and more stringent standards). Table 7 presents existing sediment quality guidelines, but none of them are based on results that relate chemical concentrations to the frequency of biological effects from field studies.

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_{sed} in terms of purpose is the TV from The Netherlands which is also the most stringent among the available SQGs.

Due to the scarcity of chronic toxicity data for sediments, the most common methodology for SQGs development is the Equilibrium Partitioning Model (US EPA, The Netherlands). SQGs derived using the EqP were the highest and lowest reported, varying within three orders of magnitude due to the different default values used in the application of the EqP.

A threshold effect benchmark (TEBs) has been recently derived in the US 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 when they have not been performed and is not in agreement with the EU TGD (EC 2011).

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 EU TGD (EC 2011).

Table 7 Sediment quality guidelines reported in the literature.

SQG description	Value [µg/kg d.w.]	Development method	References
TV MPC	0.011 (10 % OC) 0.0055 (5 % OC) 0.0011 (1 % OC) 1.1 (10 % OC) 0.55 (5 % OC) 0.11 (1 % OC)	*Target Value (TV) and Maximum Permissible Concentration (MPC)*, The Netherlands, derived by the EqP. The TV, which has the same intend as EQS_{sed}, is derived as MPC/100	van de Plassche 1994
FSSB	25.6 (5 % OC) 5.19 (1 % OC)	*Freshwater Sediment Screening Benchmarks* derived by the EqP.	US EPA 2006
TEB[1]	20.5 (5 % OC) 4.1 (1 % OC)	*Threshold Effect Benchmark*: concentrations below the threshold are unlikely to cause toxicity in laboratory toxicity tests with *H. azteca* and *Chironomus* sp. Based on acute (10 d) spiked sediment toxicity tests effect data divided by an AF of 10 to account for acute-to-chronic extrapolation.	Nowell et al. 2016
Proposed RAC[2]	1) $RAC_{sed;ac}$ = 2.8 (5 % OC) 0.56 (1 % OC) 2) Geom-$RAC_{sed;ac}$= 4.8 (5 % OC) 0.96 (1 % OC) 3) SSD-$RAC_{sed;ac}$ = 2 (5 % OC) 0.5 (1 % OC)	Scientific proposals for *Regulatory Acceptable Concentration* using different methodologies in the context of risk assessment for pesticides (EFSA): 1) Estimated chronic value (*H.azteca*) applying an AF of 10 to acute data 2) Geomean acute value for crustaceans with an additional AF of 10 3) HC_5 from SSD with acute values divided by 5 and an extra AF of 3	Deneer et al. 2013

[1] Originally expressed as concentration normalized by OC (0.41 µg/g-OC).
[2] Originally expressed as concentration normalized by OC (SSD-$RAC_{sed;ac}$= 0.056 µg/g-OC, Geom-$RAC_{sed;ac}$= 0.095 µg/g-OC, $RAC_{sed;ac}$= 0.040 µg/g-OC).

9 Toxicity of degradation products

The main degradation products of chlorpyrifos, chlorpyrifos-methyl and triclopyr is trichlorinated pyridinol (TCP). TCP exerts low or no toxic effects to higher organisms like trout and salmon with typical LC50 ranging from 1500 to 2500 µg/l (n=23; US EPA 2016) and NOEC of 80.8 µg/l (EC 2005b). The US EPA has judged that TCP "is not of toxicological concern" since it does not have anticholinesterase activity (US EPA 2000). However, in a sterilized medium culture, a toxicity test with *Daphnia carinata* revealed that TCP exerts a greater toxicity than chlorpyrifos. Moreover, the combination of chlorpyrifos with its degradation product showed additive if not synergistic effects on this crustacean. Nevertheless, when natural water is used with high dissolved OC (4.9 mg C/l), TCP shows no toxicity up to 2 µg/l and this is probably due to the input of microbial activity, which rapidly degrades TCP to TMP and then to CO_2 (Cáceres et al. 2007).

The affinity of TCP for sediment is, however, much lower than that for chlorpyrifos, with a log K_{OW} of 1.35 at pH 7 (ionized) and a log K_{OC} of 2.20 (Racke 1993). The half-life of TCP in sediment ranges from 2.7 to 13.3 days, which makes it not persistent at least in aerobic conditions (Petty et al. 2003). These parameters indicate that, under most circumstances, TCP is not likely to be relevant for the sediment compartment.

10 EQS_{sed} proposed to protect benthic species

The different QS values for each derivation method included in the TGD (EC, 2011) are summarized in Table 8. According to the TGD, the most reliable extrapolation method for each substance should be used (EC 2011). In all cases, data from spiked sediment toxicity tests are preferred over the EqP approach.

Table 8 QS_{sed} derived according to the three methodologies stipulated in the EU-TGD and their corresponding AF. All concentrations expressed as µg/kg d.w.

	Sediment 1 % TOC	Sediment 5 % TOC	AF
$QS_{sed,SSD}$	--	--	--
$QS_{sed,EqP}$	0.029	0.14	--
$QS_{sed,AF}$	0.028	0.14	1000
Proposed EQS_{sed}	**0.028**		

10.1 Uncertainty analysis

According to the TGD (p. 101), "In the absence of useful corroborating evidence from field or mesocosm the QS derived from chronic toxicity data is retained. If this is not possible, the lowest of the QSs derived based on the EqP approach or short term toxicity data is taken as an interim standard." An EQS_{sed} of 0.028 µg/kg d.w. is therefore proposed here as preliminary standard for sediment according to the high degree of uncertainty related to:

- The absence of reliable long-term toxicity effect data for sediment-relevant organisms from spiked-sediment toxicity tests. Only one relevant effect datum was available, which was considered not reliable due to low levels of dissolved oxygen during test exposure.
- The proposed EQS_{sed} should be challenging in view of the limits of quantification (LOQ) that are at present achieved by current analytical methodologies. Compliance monitoring for the WFD requires the achievement of a LOQ equal or below a value of 30 % of the relevant EQS. The achieved method limits of quantification (LOQs) should be therefore 0.3 × EQS = 0.0084 µg/kg dw.

In view of these elements, it is recommended to obtain reliable effect data from spiked-sediment toxicity tests using sediment-relevant organisms such as *Chironomus riparius* or *Hyalella azteca*. With these two additional long-term effect data, the AF to apply would be 50 instead of the AF of 1000 applied at present to the lowest acute effect datum.

11 References

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Appendix I. Adsorption-desorption distribution (Kd) and organic carbon-water partition (K_{oc}) coefficient

Kd [l/kg]	K_{oc} [l/kg]	Matrix	Reference
	1520	Soil	DOW 2015
	5113	Soil	DOW 2015
	4870	Soil	DOW 2015
	2825	Soil	DOW 2015
	5442	Soil	DOW 2015
	16667	Sediment	Hooftmann et al. 1993
	17250	Sediment	Hooftmann et al. 1993
	13600	Soil	WSC cited in Hooftmann et al. 1993
123	4246	Soil	Gebremariam 2011
88	3677	Soil	Gebremariam 2011
84	3952	Soil	Gebremariam 2011
64	3606	Soil	Gebremariam 2011
74	4700	Sediment	Gebremariam 2011
45	3675	Sediment	Gebremariam 2011
54	5983	Sediment	Gebremariam 2011
35	5569	Sediment	Gebremariam 2011
			Cited in Gebremariam 2011 :
118		Soil	Sharom et al. (1980)
18		Soil	Sharom et al. (1980)
50	7300	Soil	Swann et al. (1981)
66	5900	Soil	Swann et al. (1981)
100	5000	Soil	Swann et al. (1981)
83	17292	Soil	Macalady and Wolfe (1985)
116	2740	Soil	Kanazawa (1989)
13	995	Soil	Kanazawa (1989)
198	28286	Soil	Kladivko et al. (1991)
687		Soil	Valverde et al. (1992)
685		Soil	Valverde et al. (1992)
435		Soil	Valverde et al. (1992)
961		Soil	Valverde et al. (1992)
471		Soil	Valverde et al. (1992)
550		Soil	Valverde et al. (1992)
583		Soil	Valverde et al. (1992)
506		Soil	Valverde et al. (1992)
23	7931	Soil	Spieszalski et al. (1994)
190	17272	Soil	Spieszalski et al. (1994)
1036	30381	Soil	Spieszalski et al. (1994)
1813	10479	Soil	Spieszalski et al. (1994)
130	1100	Soil	Ramos et al. (2000)
110	8200	Soil	Ramos et al. (2000)
191	7247	Soil	Laabs et al. (2000)
91	696	Soil	Huang and Lee (2001)

88	652	Soil	Huang and Lee (2001)
76		Soil	Huang and Lee (2001)
73		Soil	Huang and Lee (2001)
69		Soil	Huang and Lee (2001)
57		Soil	Huang and Lee (2001)
63		Soil	Huang and Lee (2001)
48		Soil	Huang and Lee (2001)
51		Soil	Huang and Lee (2001)
42		Soil	Huang and Lee (2001)
144	6269	Soil	Baskaran et al. (2003)
96	5338	Soil	Baskaran et al. (2003)
73	6050	Soil	Baskaran et al. (2003)
43	4788	Soil	Baskaran et al. (2003)
31	5133	Soil	Baskaran et al. (2003)
210	7227	Soil	Baskaran et al. (2003)
136	6810	Soil	Baskaran et al. (2003)
101	7235	Soil	Baskaran et al. (2003)
69	6890	Soil	Baskaran et al. (2003)
40	8060	Soil	Baskaran et al. (2003)
9		Soil	Li et al. (2005)
8		Soil	Li et al. (2005)
108	8364	Soil	Romyen et al. (2007)
71	9000	Soil	Rogers and Stringfellow (2009)
17	1888	Soil	Kravvariti et al. (2010)
746	9816	Soil	Kravvariti et al. (2010)
-	-	Sediment	Sharom et al.(1980)
403	16933	Sediment	Macalady and Wolfe (1985)
307	20743	Sediment	Macalady and Wolfe (1985)
160	3000	Sediment	Ramos et al.(2000)
470	25565	Sediment	Wu and Laird(2004)
546	15500	Sediment	Lu et al.(2006)
767	7430	Sediment	Lu et al.(2006)
40	4900	Sediment	Rogers and Stringfellow (2009)
			Cited Williams et al. 2014:
295	6851	Soil	Damon and Heim (2001)
50	7300	Soil	McCall (1985)
66	5860	Soil	McCall (1985)
100	4960	Soil	McCall (1985)
1315		Soil	Wu and Laird 2004
1069		Soil	Wu and Laird 2004
1132		Soil	Wu and Laird 2004
473		Soil	Wu and Laird 2004
89		Soil	Wu and Laird 2004
45		Soil	Wu and Laird 2004
78	16250	Soil	Macalady and Wolfe (1985)
42	1662	Soil	McKenna et al. (1989)

260	5060	Soil	McCall(1987)
240	8000	Soil	McCall et al. (1984)
18	4500	Soil	Sharom et al. (1979, 1980)
47	4381	Soil	Felsot and Dahm (1979)
69	31000	Soil	McCall (1987)
1862	4261	Soil	Sharom et al. (1980)
139	8688	Soil	Sharom et al. (1980)
118	7867	Soil	Sharom et al. (1980)
28	5565	Soil	Felsot and Dahm (1979)
162	6129	Soil	Felsot and Dahm (1979)
198	28286	Soil	Kaladivko et al. (1991)
397	10452	Soil	Felsot and Dahm (1979)
82	3680	Soil	McCall (1987)
96	14400	Soil	McCall (1987)
16	973	Soil	McKenna et al. (1989)
40	3998	Soil	McKenna et al. (1989)
41	3443	Soil	McKenna et al. (1989)
			Cited et Salomon et al. 2014:
112	8600	Soil	McCall et al. (1984)
114	14000	Soil	McCall et al. (1984)
97	16000	Soil	McCall et al. (1984)
247	8900	Soil	McCall et al. (1984)
99	2785	Soil	Damon and Heim (2001)
116	7965	Soil	Damon and Heim (2001)
55	5582	Soil	Damon and Heim (2001)
68	4323	Soil	Damon and Heim (2001)
	4571		Estimated from mean K_{ow}=5.09; EC (2011)
116	6188		Geometric mean (L/kg)
	3.79		Log (geometric mean K_{oc})