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SQC (EQS_{sed}) – Proposal by the Ecotox Centre for: *Hexachlorobutadiene*

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Summary

SQC (EQS_{sed}): 2.4 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 hexachlorobutadiene (HCBD) of 131 µg/kg d.w. is proposed for standard sediments with 1 % OC.

Zusammenfassung

SQK (EQS_{sed}): 2.4 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 Hexachlorbutadien (HCBD) und unter Verwendung der Methode, die in der Technischen Richtlinie der EU zur Ableitung von Umweltqualitätsnormen beschriebenen wird, schlägt das Oekotoxzentrum einen vorläufiger SQK für HCBD von 2.4 µg/kg TS für Standardsedimente mit 1 % OC vor.

Résumé

CQS (EQS_{sed}): 2.4 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 l'hexachlorobutadiène (HCBD) de 2,4 µg/kg p.s. est proposé pour les sédiments standards avec 1 % CO.

Sommario

CQS: 2,4 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 preliminare per l’esaclorobutadieno (HCBD) di 2,4 µg/kg p.s. è proposto per sedimenti standard con 1 % CO.

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1 General Information

Selected information on hexachorobutadiene relevant for sediment is presented in this chapter. Registration information and risk assessments referred to are:

- Common Implementation Strategy for the Water Framework Directive. Environmental Quality Standards (EQS) Substance Data Sheet Priority Substance No. 17 Hexachlorobutadiene CAS-No. 87-68-3. Final version Brussels 31 July 2005.
- UNEP (2012). Risk profile on hexachlorobutadiene. Persistent Organic Pollutants Review Committee. UNEP/POPS/POPRC.8/16/Add.2 (01 November 2012).
- Euro Chlor Risk Assessment for the Marine Environment OSPARCOM Region - North Sea. Hexachlorobutadiene. March, 2002.
- C.T.A. Moermond E.M.J. Verbruggen. Environmental risk limits for hexachlorobenzene and hexachlorobutadiene in water using bioaccumulation data to convert biota standards into water risk limits. RIVM letter report 601714015/2011.
- Canadian Environmental Protection Act, 1999. Hexachlorobutadiene. Priority substances list assessment report. ISBN 0-662-29297-9 Cat. N° En40-215/58E

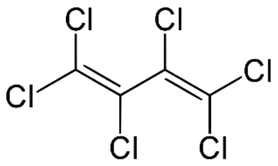
1.1 Identity and physico-chemical properties

Hexachlorobutadiene (HCBD) is a halogenated aliphatic hydrocarbon.

Reliable log K_{OC} reported for HCBD are in the range of 5.1-6.1, estimated log K_{OC} is 3.97 (Table 1; Appendix 1). Reported experimental log K_{OW} is 4.78 (Table 1). Both parameters trigger an effect assessment for sediments according to the EC TGD EQS (EC 2018).

Table 1 summarizes identity and physico-chemical parameters for HCBD required for EQS derivation according to the TGD (EC 2018). 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.

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

Characteristics	Values	References
Common name	Hexachlorobutadiene Perchlorobutadiene HCBD	PubChem (2020)
IUPAC name	1,1,2,3,4,4-hexachlorobuta-1,3-diene	PubChem (2020)
Chemical group	Halogenated aliphatic hydrocarbon	
Structural formula		PubChem (2020)
Molecular formula	$CCl_2{=}CClCCl{=}CCl_2$	PubChem (2020)
CAS	87-68-3	PubChem (2020)
EC Number	201-765-5	PubChem (2020)
SMILES code	C(=C(Cl)Cl)(C(=C(Cl)Cl)Cl)Cl	PubChem (2020)
Molecular weight [g/mol]	260.8	PubChem (2020)

Characteristics	**Values**	**References**
Melting point [°C]	-21 °C	Lide (2000) cited in PubChem (2020)
Boiling point [°C]	215	UNEP/POPS/POPRC.8/3 (2012)
Vapour pressure [Pa]	[1] 20 (20°C), 2926 (100°C) [2] 36 (20°C)	[1] UNEP/POPS/POPRC.8/3 (2012) [2] Hillenbrand et al. (2006)
Henry's law constant [$Pa \cdot m^3/mol$]	1044 (exp.) 2604 (est.) High volatility	UNEP/POPS/POPRC.8/3 (2012)
Water solubility [mg/L]	[1] 3.2 (25°C) (exp.)	[1] Banerjee *et al.* (1980) cited in UNEP/POPS/POPRC.8/3 (2012)
Dissociation constant (pK_a)	--	--
Octanol-water partition coefficient ($\log K_{OW}$)	[1] 4.78 (exp., shake flask-HPLC method)[1] [2] 4.9 (exp. shake flask-GC method)[1]	[1] Banerjee et al. (1980) cited in UNEP/POPS/POPRC.8/3 (2012) and EC (2005) [2] Chiou (1985) cited in UNEP/POPS/POPRC.8/3 (2012) and EC (2005)
Sediment/soil-water partition coefficient ($\log K_{OC}$) [a]	[1] 5.44 (exp. desorption lab experiment, historically contaminated lake sediment, 4.1 % OC) [2] 5.1 (exp. sorption/desorption lab experiment, lake sediments, 1.5 and 4.1 % OC) [3] 6.1 (exp. freshwater river sediment, mean, n=9) [4] 4.02 (est.)	[1] Chen et al. (1999) [2] Chen et al. (2000) [3] Lau et al. (1989) [4] Estimated from $\log K_{OW}$ $\log K_{OC}=0.81*\log K_{OW}+0.1$
Sediment adsorption coefficient (K_d [L/kg])	11 292 (Sediments, 4.1 % OC)	Recalculated from Chen et al. (1999)[2]
Aqueous hydrolysis DT_{50} [d]	Hydrolytically non-degradable	Hillenbrand et al. (2006)
Aqueous photolysis DT_{50} [d]	Direct photolysis of hexachloro-1,3-butadiene is expected to occur due to absorption of light in the environmental UV spectrum (>290 nm)	UNEP/POPS/POPRC.8/3 (2012)
Biodegradation in aqueous environment DT_{50} [d]	[1] 4-52 weeks [2] 3-30 (rivers), 30-300 (lakes)	[1] EuroChlor (2002) cited in EC (2005) [2] Zoeteman et at. 1980 cited in US EPA (2019)
Biodegradation in sediment DT_{50} [d]	> 3 years (aerobic conditions) > 4 months (anaerobic)	Bosma et al. (1994)
Biodegradation in soil DT_{50} [d]	4–26 weeks	Howard et al. 1991 cited in UNEP/POPS/POPRC.8/3 (2012)

[1] For substances with expected $\log K_{OW}$ values >4, the slow stirring method (OECD 2006) is recommended, because – due to the formation of octanol micro-droplets – the shake flask method (OECD 1995) may lead to an underestimation of the $\log K_{OW}$. [2] Recalculated from $\log K_{OC}$ and f_{OC}.

1.2 Regulatory context and environmental limits

Table 2 summarizes existing regulation in Switzerland, Europe and international conventions.

HCBD is subject to a number of national and international regulations and treaties. HCBD is regulated by the Stockholm Convention on POPs, being listed in Annex A (elimination) without specific exemptions (decision SC-7/12) and in Annex C (unintentional production) (decision SC-8/12). Parties must take measures to eliminate the production and use of HCBD and to reduce the unintentional releases of HCBD.

In Switzerland, HCBD is regulated by the Ordinance on the Register relating to Pollutant Release and the Transfer of Waste and of Pollutants in Waste Water (PRTRO) of 15 December 2006 (status as on 23 January 2007). HCBD is a pollutant with reporting obligations for installations in accordance with Annex 1 if released in larger quantities than 1 kg/year according to Annex 2, transferred in more than 2 tonnes of hazardous waste or more than 2000 tonnes of other waste, or transferred in a larger quantity than 1 kg/year in wastewater.

According to the previous EU Chemical regulation, HCBD fulfilled PBT, vPvB and POP criteria(PBT List N° 60; Rapporteur: Denmark) and was included in the Annex III Inventory (criteria for 1-10 tonnes registered substances) as suspected bioaccumulative, suspected carcinogen, suspected hazardous to the aquatic environment, suspected mutagen, suspected persistent in the environment, suspected skin sensitiser and suspected toxic for reproduction. It is also regulated by Directive 2010/75/EU on Industrial Emissions (Integrated Pollution Prevention and Control - IPPC) with emission limit values for all qualifying facilities and Directive 2008/68/EC, last amended by Regulation 2019/1243/EU of 25 July 2019. The European Agreements on the international transport of dangerous goods by road (ADR) and inland waterways (ADN) apply to HCBD, and the Regulations concerning the international carriage of dangerous goods by rail (RID).

At EU level, HCBD is a priority hazardous substance listed in Annex X of Directive 2000/60/EC listing priority substances for water policy. According to Article 16 of Directive 2000/60/EC, Directive 2013/39/EU of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy sets a Maximum Permissible Concentration (MAC-EQS) of 0.6 µg/L for inland waters and other waters, and a Biota EQS of 55 µg/kg wet weight applies to fish or another taxon or matrix as long as the EQS applied provides an equivalent level of protection.

Table 2 Existing regulation and environmental limits for HCBD.

POPs Stockholm Convention	Listed in Annex A (elimination) without specific exemptions (decision SC-7/12) and in Annex C (Unintentional production) by the Stockholm Convention on POPs (decision SC-8/12)
Europe	
Directive 2000/60/EC, Annex X, Priority Substances, Water Policy	Priority Hazardous Substance, N°13
Directive 2008/105/EC, Water Environmental Quality Standards	Annex I, Part A: - MAC-EQS (Inland waters): 0.6 µg/L - MAC-EQS (Other waters): 0.6 µg/L - Biota EQS: 55 µg/kg wet weight
REACH	Annex III Inventory (criteria for 1-10 tonnes registered substances)

Directive 2010/75/EU on Industrial Emissions (Integrated Pollution Prevention and Control - IPPC)	Applies for emissions to water
Directive 2008/68/EC, last amended by Regulation 2019/1243/EU, 25 July 2019 (Inland Transport of Dangerous Goods Directive)	EU Dangerous Goods List (ADN, Chap. 3.2, Table A): Directive establishes rules for the safe transport of dangerous goods between EU countries by road, rail, and waterway.
PBT	fulfilling PBT & vPvB criteria & POP (PBT List N° 60; Rapporteur: Denmark)
Switzerland	
Ordinance on the Register relating to Pollutant Release and the Transfer of Waste and of Pollutants in Waste Water (PRTRO) of 15 December 2006 (Status as at 23 January 2007)	Pollutant with reporting obligations for installations in accordance with Annex 1 if: - released a larger quantity of a pollutant into the air, water or land than the quantity stipulated in the form of a threshold value in Annex 2: a) Threshold value to water: 1kg/year b) Threshold value to land: 1 kg/year - transferred more than two tonnes of hazardous waste; - transferred more than 2000 tonnes of other waste; or - transferred a larger quantity of a pollutant in waste water than the quantity stipulated in the form of a threshold value for water in Annex 2; or - transferred a larger quantity of a pollutant in waste water than the quantity stipulated in the form of a threshold value for water in Annex 2.

Table 3 presents available regulatory limit values and sediment quality guidelines for HCBD.

In addition to the regulatory EU MAC-EQS and Biota EQS, proposals for threshold values were derived using the TGD (EC 2003 cited in EC 2005). An AA-EQS for general toxicity set at 0.44 µg/L and a $QS_{sec.pois.,freshwater}$ for protecting top predators from secondary poisoning at 0.003 µg/L are available. More recently Moermond and Verbruggen (2011) also derived a $QS_{sec.pois.,freshwater}$ using the TGD (EC 2011) of 0.0025 µg/L. Additional quality values are available from Environment Canada and Health Canada (2001) and EuroChlor (2002), this last intended for marine waters, but both set at 0.13 µg/L.

Specific quality values for sediments are available from different agencies ranging from 24.4 to 493 µg/kg d.w. They are all derived from PNEC or QS for surface waters using the Equilibrium Partitioning but use different PNEC/quality standards for surface waters and different partitioning coefficients, leading to one order of magnitude difference.

Table 3 PNEC/quality standards available from authorities and reported in the literature.

Description	**Value**	**Development method**	**References**
Sediment general toxicity [µg/kg d.w.]			
QS_{sed} (tentative)	493	EU TGD (EC 2003): derived using the EqP, based on $QS_{freshwater}$ of 0.44 µg/L and default values for suspended matter.	EC (2005)
PNEC / QS_{sed}	107	EU TGD (EC 2011): derived using the EqP.	INERIS (2018)
EQS_{marine}	49		Miljødirectoratet (2016) (M608)
$PNEC_{sed}$	24.4	TGD (EC 1996): derived using the EqP, based on $PNEC_{water}$ of 0.13 µg/L and K_{OC} of 9371 L/kg (log K_{OC} = 3.97).	EuroChlor (2002)
ENEV	210	Derived from a critical toxicity value of 20.8 µg/g d.w. estimated using the EqP and a 28-d LOEC for fathead minnow (13 µg/L) and K_{OC} of 80 000 L/kg (log K_{OC} = 4.90) and AF of 100.	Environment Canada and Health Canada (2001)
Water [µg/L]			
General toxicity			
MAC-EQS	0.6	EU TGD (EC 2003): Based on LC50 for *Mysidopsis bahia* (59 µg/L) and AF of 100.	EC (2005)
AA-QS	0.44	EU TGD (EC 2003): Based on NOEC for *Daphnia magna* (4.4 µg/L) and AF of 10; for total concentration.	EC (2005)
EQS	0.1	Based on the existing EQS in Council Directive 86/280/EEC	EC (2005)
ENEV (Estimated No Effect Value)	0.13	Based on LOEC for *P. promelas* (13 µg/L) and AF of 100.	Environment Canada and Health Canada (2001)
PNEC	0.13	Based on NOEC for *P. promelas*, NOEC (6.5 µg/L) and AF of 50.	EuroChlor (2002)
Secondary poisoning for top predators			
$QS_{secpois.freshwater}$	0.003	EU TGD (EC 2003): derived from a QS_{biota} of 55.3 µg/kg w.w.; for total concentration.	EC (2005)
$MPC_{secpois.freshwater}$ (Maximum Permissible Concentration)	0.0025	EU TGD (2011): derived from a QS_{biota} of 55 µg/kg w.w.; for dissolved concentration.	Moermond and Verbruggen (2011)

1.3 Use and emissions

Historically HCBD was used as a solvent for rubber and other polymers, heat transfer fluids, transformer liquid, hydraulic fluid and washing liquor for removing hydrocarbons. It was also used in some countries in agriculture as an insecticide in vineyards, as a seed dressing, and fungicide for a variety of crops (EuroChlor 2002).

According to the 2012 draft risk profile from the Stockholm Convention (UNEP/POPS/POPRC.8/3, 2012), HCBD was no longer intentionally produced in the UN-ECE region nor in the USA by 2012. Its intentional production in Europe ended in the late 1970s and it was never generated at commercial quantities in the US or Canada. Data about intentional production outside the UN-ECE region was not available at the time the draft risk profile was completed but monitoring data suggested that (by)production continued in countries such as China and Taiwan (UNEP/POPS/POPRC.8/3, 2012). Worldwide production of HCBD was estimated at 10 000 tonnes in 1982 although HCBD generated as waste by-product was estimated at 14 000 tonnes (1982) in the USA alone (IPCS 1994 cited in Lecloux 2004).

HCBD is unintentionally generated during the production of chlorinated hydrocarbons (perchloroethylene, trichloroethylene and carbon tetrachloride), and to a lesser extent vinyl chloride, allyl chloride and epichlorohydrin. In the UN-ECE region, the combined production of perchloroethylene and tetrachloromethane was estimated to be the only remaining significant by-production of HCBD, which is generally destroyed or recycled in the plant (Lecloux 2004). Total cessation of industrial emissions is not considered due to economic and social impact of plant closures (Euro Chlor annual report 2006–2007 cited in UNEP/POPS/POPRC.8/3, 2012). HCBD is also produced during incineration of acetylene, chlorine residues caused by poor abatement control.

According to the European Pollutant Release and Transfer Register (E-PRTR 2020), 1.3 tonnes of HCBD were released in 2017 (last year entry), 322 kg in 2016 and 197 kg in 2015. There is a relatively constant release of HCBD from industrial scale production of basic organic chemicals of 170 kg in 2015 and 2016 and 115 kg in 2017. Urban wastewater treatment plants are the second highest contributor over the last years, with 43 kg in 2015 and 103 kg in 2016, followed by thermal power stations and other combustion installations. The disposal or recovery of hazardous waste only accounts for several kg per year to the total release. The countries reporting HCBD in the last years are France, Italy, Serbia, Belgium and Spain. Switzerland has not reported HCBD release to the European PRTR for the years 2007-2017.

1.4 Mode of action and sensitivity of taxonomic groups

HCBD is a chlorinated organic substance suspected bioaccumulative, suspected carcinogen, suspected mutagen, suspected persistent in the environment, suspected skin sensitiser and suspected toxic for reproduction according to estimates from its chemical structure (Annex X Inventory ECHA 2020). It has been shown to be harmful if swallowed (H302 CLP classification), harmful in contact with skin (H312), causes skin irritation (H315) and may cause an allergic skin reaction (H317), and have shown to cause nervous system depression and kidney damage when inhaled (H332).

According to the risk profile prepared for the Persistent Organic Pollutants Review Committee of the Stockholm Convention (UNEP/POPS/POPRC.8/3 2012), HCBD is toxic after repeated and chronic exposure at low exposure levels (i.e. 0.2 mg/kg), with females at very young age being the most susceptible according to studies with rodents. The target organ of toxicity is the kidney; biotransformation to reactive compounds leads to organ toxicity, genotoxicity and carcinogenicity after lifelong dietary exposure conditions. Based on the available literature it was concluded that reproductive effects appear at concentrations that are toxic to maternal animals, and therefore the risk of reproductive effects below levels revealing maternal toxicity are considered to be relatively low. No studies on effects on the immune system are available. Exposure to HCBD and chemicals with similar mode of action has been shown to lead to additivity of toxic effects.

HCBD is also very toxic to aquatic life and very toxic to aquatic life with long lasting effects (H400 CLP classification), with EC50 and NOEC values in the µg/L range. The EQS data sheet for HCBD (EC 2005) provided long-term toxicity data for fish, daphnia and algae and short-term acute data for fish, crustaceans and one mollusk species. Based on the available information the crustacean species

Daphnia magna appeared to be the most sensitive species in long-term tests (NOEC 4.4 µg/L). Chronic effect concentrations determined in fish tests are very close to those determined in *Daphnia magna*.

2 Environmental fate

2.1 Stability and degradation products

HCBD is hydrolytically non-degradable (EC 2005). Direct photolysis is expected to occur due to absorption of light in the environmental UV spectrum (>290 nm) (UNEP/POPS/POPRC.8/3 2012).

EuroChlor (2002) reports several biodegradation studies. Under aerobic conditions, HCBD was completely degraded by wastewater microbiota within seven days (Tabak et al. 1981 cited in EuroChlor 2002 and UNEP/POPS/POPRC.8/3 2012), however only limited information on this study is provided. A further study in a pilot wastewater treatment plant showed approx. 72 % of the HCBD sorbed to sewage sludge, while only 8 % was degraded during a test duration of 8 d (Schröder 1987 cited in UNEP 2012). Degradation of HCBD is reported as very slow under anaerobic conditions (Johnson and Young 1983, Govind et al. 1991 and Howard 1991 cited in UNEP/POPS/POPRC.8/3 2012).

In one study on column experiments packed with river Rhine sediments, Bosma et al. (1994) also found no biodegradation under aerobic conditions within a period of 3 years. Removal of HCBD in the same study was observed under anaerobic conditions after an acclimation time of four months (Bosma et al. 1994). This was explained by the authors as HCBD being strongly adsorbed to sediments in aerobic conditions and thus less bioavailable than in anaerobic conditions. The main product was 1,2,3,4-tetrachloro-1,3-butadiene (>90 %), which may be further degraded aerobically. Similarly, sequential reductive dechlorination of HCBD was achieved by a culture enriched from contaminated estuarine sediment under anaerobic conditions (Booker and Pavlostathis 2000). The predominant HCBD dechlorination products were isomers of tri- and dichloro-1,3-butadiene.

Based on monitoring data, half-life of HCBD in aqueous environment is 3-30 d in rivers and 30-300 d in lakes, being proportional to the amount of organic matter in the aqueous media (Howard et al. 1991 cited in UNEP/POPS/POPRC.8/3 2012). In sediments with high organic content, HCBD is not expected to persist although half-life values for sediment are not available (UNEP/POPS/POPRC.8/3 2012). HCBD will eventually biodegrade in aerobic sediments (UNEP/POPS/POPRC.8/3 2012).

In soil, HCBD half-life depends upon the physico-chemical and biological properties of the soil and the climatic conditions, ranging from 4–26 weeks based on anaerobic biodegradation rates to no biodegradation in anaerobic zones of soil (Howard et al. 1991 cited in UNEP/POPS/POPRC.8/3 2012).

2.2 Sorption/desorption processes

Based on the log K_{OW} of 4.78 and 4.90 (Table 1), HCBD is expected to adsorb strongly to organic matter. The organic carbon-water partition coefficient (log K_{OC}) can be estimated to be 4.02 on the basis of a log K_{OW} of 4.84 using the semi-empirical equation for predominantly hydrophobic substances (EC 2018). Log K_{OC} values derived from laboratory studies with freshwater sediments and field studies are slightly higher than estimated one, ranging from 5.1 to 6.1 (Table 1, Appendix 1).

Adsorption to sediments and suspended particulates is therefore an important factor in the fate of HCBD in aqueous systems.

Field studies reporting sediment and soil partitioning of HCBD are cited in Lecloux (2004) but were not available for review (Leeuwangh et al. 1975, Laseter et al. 1976 and Oliver & Charlton 1984 cited in

Lecloux 2004). According to Lecloux (2004), these studies report soil-water partition coefficients ranging over 2 to 4 orders of magnitude assuming equilibrium with a degree of adsorption to soil highly dependent on the organic matter content and being less pronounced in sandy soils. However, specific information on the K_{OC} values is not provided.

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).

Studies specifically addressing the bioavailability of HCBD from sediments to benthic invertebrates could not be located. One study on the extractability (five different extraction methods, including Soxhlet extraction, sonication and solvent extraction, saponification and solvent extraction, and supercritical fluid extraction) of HCBD from contaminated surface sediments has shown slow desorption and estimated partitioning coefficients from interstitial, liquid and solid-phase concentrations higher than those previously reported (see Prytula and Pavlostathis 1996 and references cited therein). This suggested that bioavailability of HCBD from historically contaminated sediments is reduced and that the use of the equilibrium partitioning for risk assessment at these sites should be applied with caution. In fact, the partitioning coefficients reported in Table 1 and Appendix 1 are derived from historically contaminated sediments.

2.4 Bioaccumulation and biomagnification

Bioconcentration Factors (BCF) for HCBD from bioaccumulation studies with fish are highly variable ranging from 1.4 to 19 000 L/kg (EC 2005), with a BCF value for whole fish used for risk assessment and EQS derivation of 17 000 L/kg (EC 2005; EuroChlor 2002). According to the reliability assessment performed by Moermond and Verbruggen (2011) none of these studies were reliable for the derivation of EQS protective for secondary poisoning following the EU TGD (EC 2011). The only valid data were from a study from the Japanese NITE database reporting BCFs of 6 608 and 7 555 L/kg wet weight for carp (*Cyrinus carpio*) at exposure concentrations of 0.831 and 0.087 µg/L, respectively. Normalised to 5 % lipids these BCFs are 6 480 and 7 410 L/kg (NITE 2012 cited in Moermond and Verbruggen 2011).

EC (2005) also used BCF of 700 L/kg for the EQS derivation for human consumption from fishery products, most probably resulting from the bioaccumulation study reporting BCF for plaice (*Pleuronectes platessa*) and dab (*Limanda limanda*) of about 500 to 700 for muscle (Pearson and McConnell 1975 cited in UNEP/POPS/POPRC.8/3 2012). The maximum BCF of 2 000 L/kg reported for mussel (*Mytilus edulis*) was also used (EC 2005).

Bioaccumulation factors (BAF) in plankton, crustaceans, molluscs, insects and fish in surface waters are comparable to BCF derived in the laboratory, ranging from 33 to 11 700 L/kg on a wet weight basis (UNEP/POPS/POPRC.8/3 2012). The only value deemed valid by Moermond and Verbruggen (2011) after reliability assessment were the BAF values for the Crustacea *Mysis relicta* and *Pontoporeia affinis* of 9 260 and 250 000 L/kg (normalized for 5 % lipids), respectively and 17 360 L/kg (normalized for 5 % lipids) for the fish *Cottus cognatus* (Oliver and Niimi 1988 cited in Moermond and Verbruggen 2011).

Regarding biomagnification, no experimental data are available for HCBD according to Moermond and Verbruggen (2011) and UNEP/POPS/POPRC.8/3 (2012). Calculated theoretical Biomagnification Factors (BMF) values based on K_{OW} for invertebrates, fish, reptiles, amphibians, birds, mammals and humans were <1 indicating no potential for biomagnification (Kelly et al 2007 cited in Moermond and Verbruggen 2011) and a similar conclusion was drawn in the EQS data sheet (EC 2005). The BMF estimated using log K_{OW} according to the EU TGD for EQS (Table 22, p.169) is 2 for the biomagnification in the prey of predators for the freshwater environment.

While no food chain studies are available, a recent review of HCBD in the Arctic showed increased concentrations of HCBD in terrestrial birds and mammals and seabirds compared to fish and marine mammals, warranting additional research on the bioaccumulation and biomagnification of HCBD in Arctic food chains (Balmer et al. 2019).

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 ≥ 2 000) 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). For HCBD, the bioaccumulation criterion (BCF ≥ 2 000) is fulfilled and a mean BCF value[1] for oligochaete worms exposed to spiked sediments from Lake Ontario of 29 000 L/kg based on dry weight of which about 8 % lipid is reported in Oliver (1987), with a half-life of 29 days. It can be argued that benthic invertebrates may contribute to the risk to higher organisms through trophic transfer.

3 Analysis

3.1 Methods for analysis and quantification limit

HCBD can be analyzed in sediment samples by gas chromatography-mass spectrometry (GC-MS) (Table 4). Standard US EPA Method 8270D for semivolatile organic compounds allows quantification. US EPA Methods 3510, 3520, 3540/41, 3550 and 3580 describe sample extraction and preparation techniques for HCBD, being 3540/41 and 3550 specific for soil and sediment samples. The method reports indicative lower limits of quantification for HCBD of approximately 660 µg/kg (wet weight) for soil/sediment samples (US EPA 2014).

Research laboratories have also proposed analytical protocols for the extraction and analysis of priority substances including HCBD. For sediments, Pinto et al. (2013) propose rapid extraction by ultrasounds irradiation, sample clean-up and pre-concentration by stir bar sorptive extraction, the compounds being quantified using GC-MS using the selective ion monitoring acquisition mode (SIM). Under optimal conditions, method detection limits and method quantification limits are 0.27 and 0.82 µg/kg d.w. Alternatively, samples can be extracted through acid digestion with hydrochloric acid achieving slightly higher detection and quantification limits.

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[1] Calculated as the quotient between concentrations in worms and concentration in pore water, which appeared as the main driver for bioaccumulation.

Table 4 Methods for HCBD analysis in sediments and corresponding limits of detection (LOD) and limits of quantification (LOQ) (µg/kg d.w. if not indicated otherwise). n. a. means not reported.

LOD	LOQ	Analytical method	Reference
n.a.	660 (wet weight)	Method 8270D: GC/MS	US EPA (2014)
0.27	0.82	GC-MS/SIM	Pinto et al. (2013)

3.2 Environmental concentrations

Measured environmental concentrations (MEC) of HCBD in sediments are summarized in Table 5.

In Switzerland, HCBD was detected in 100 % of the 78 surface sediment samples collected in Lake Geneva in 2016 (Loizeau et al. 2017) at concentrations ranging from 0.002 to 0.052 µg/kg d.w., with a median of 0.006 µg/kg d.w. Highest concentrations were measured at two sites (0.052 and 0.044 µg/kg d.w.), one of them could be related to a PVC industry nearby. In small streams, the concentrations in sediments < 2 mm ranged from 0.02 to 0.10 µg/kg d.w., with a mean and median of 0.05 and 0.06 µg/kg d.w., respectively. In the fine fraction of sediments (< 63 µm), the HCBD concentrations ranged from 0.05 to 0.17 µg/kg d.w., with a mean and median of 0.09 and 0.07 µg/kg d.w., respectively (Ecotox Centre, unpubl.).

Additional HCBD concentrations in sediments have been reported in a coastal lagoon in Portugal, which are approximately one order of magnitude higher ranging from <0.3 to 11.1 µg/kg d.w., with relatively higher levels in sediments below 12 cm due to extensive historical use of products containing HCBD (Pinto et al. 2016). Concentrations were correlated with the aluminium concentration in sediments, with aluminium content being correlated with organic matter content. This suggests that HCBD accumulation was related to sediment properties in the study area.

A study performed on archived sediment samples from the early 90s to assess the impact of an industrial complex in the Mulde River, a tributary of the Elbe, showed HCBD was not detected in the upstream area not under the influence of industrial activities while concentrations of 6 and 15 µg/kg d.w. were quantified downstream (Berger and Schwarzbauer 2016). Increased concentrations of HCBD up to several hundreds of µg/kg d.w in sediments from the St. Clair River in Canada were also measured in areas close to industrial complex (Richman and Milani 2010). Concentrations in the Arctic range from several pg/kg d.w. to 0.01 µg/kg d.w. in Lake Hazen, one of the northernmost lakes of Canada with no apparent anthropogenic pressure to 0.23 µg/kg d.w. in Great Slave Lake and Mackenzie River sediments, where several industrial activities are located (Mudroch et al. 1992 and Balmer et al. 2019).

Table 5 Measured environmental concentrations (MEC) of HCBD in Switzerland. All concentrations expressed as µg/kg d.w. for sediment. n.d. not detected.

Country	MEC (min-max)	No. of sites	Comments	Reference
Switzerland	Sediment < 2 mm: 0.05 (mean), 0.02-0.10 (min, max), 0.06 (median) Sediments < 63 µm: 0.09 (mean), 0.05-0.17 (min, max), 0.07 (median)	18	Small streams sampled in August 2018. Different levels and sources of pollution. Detection frequency ca. 100 %	Centre Ecotox, unpubl. data
	Lake Geneva: 0.006 (median) (0.002-0.052)	5	Surficial lake sediment sampled in 2016. Detection frequency 100 %	Loizeau et al. (2017)
Portugal	Óvidos Lagoon: n.d.-11.1	14	Surficial sediment (0-2 cm), coastal lagoon. Detection frequency ca. 60%	Pinto et al. (2016)
Germany	Mulde River (Elbe tributary): n.d. (upstream of industrial complex) 15 (Max, downstream of industrial complex)	10	Superficial archive sediments from 1993	Berger and Schwarzbauer (2016)
Canada	St. Clair River: n.d. (upstream of industrial area) 300 (Max, close to and downstream of industrial area)	22	Sediments collected in 2006 and 2008	Richman and Milani (2010)
Arctic	Great Slave Lake and Mackenzie River: 0.01-0.23	3	Sediment cores from 1983, area with several anthropogenic pollution sources	Mudroch et al. (1992)
	Lake Hazen: 0.002-0.01	1	Maximum concentrations in sediment core in horizons dated to the 1970s and 1980s.	D.C.G. Muir, unpubl. data, cited in Balmer et al. (2019)

4 Effect data (spiked sediment toxicity tests)

A non-filtered bibliographic search was performed for Hexachlorobutadiene in the US EPA Ecotoxicity Data Base (U.S. EPA 2020) which did not yield data on sediment organisms. A key word search was performed on Web of Science and PubMed (Hexachlorobutadiene OR HCBD OR Hexachloro-1,3-butadiene) AND (sediment OR benthic OR benthos, no restriction regarding publication date) which resulted in 55 publications, with duplicates removed. Of the 55 publications, only two were identified as potentially relevant based on an initial screen of abstracts. An additional search was also performed on Web of Science and PubMed (Hexachlorobutadiene OR HCBD OR Hexachloro-1,3-butadiene) AND (mesocosm OR microcosm, no restriction regarding publication date) which resulted in no publications.

Relevance ("C" score in Table 6) and reliability ("R" score in Table) of studies were evaluated according to the CRED-criteria (Moermond et al. 2016; Casado-Martinez et al. 2017).

According to the EU TGD (EC 2018) "*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).

The mortality endpoint for *Hyalella azteca* was considered as relevant and reliable with restrictions after assessment against CRED-relevant information according to a number of limitations (see Table 6 and section 4.3 for further details on data quality assessment). The mortality endpoint for *Leptocheirus plumosus* was not retained for sediment EQS derivation and was retained as supportive information due to the inadequacy of the concentrations spacing for NOEC derivation in one test and the limited effects due to sediment avoidance in a follow up test, which returned a LOEC with less than 20 % effect that was used to estimate an additional NOEC for the survival endpoint of *L. plumosus*.

The growth endpoint was considered not relevant for EQS derivation because only a LOEC was provided without additional effect data to assess whether a NOEC could be derived.

Table 6 Reliable and relevant sediment effect data collection for Hexachlorobutadiene in mg/kg d.w. Data were evaluated for relevance and reliability according to the CRED criteria for sediments (Casado-Martinez et al. 2017). Data not used for QS development is in grey font. All data correspond to estuarine conditions, therefore effect data is not distinguished as freshwater and marine.

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Sediment type	Normalized value [mg/kg d.w., 1 % OC]	Normalized value [mg/kg d.w., 5 % OC]	Chem. analysis	Note	Validity	References
Amphipod	Juveniles *Hyalella azteca*	HCBD	Semi-static	6 weeks aging at 4°C and darkness, 14 d at test conditions	Survival	10 d	NOEC	Natural estuarine sediment, approx. 4.4 % TOC ; tested at salinity of 10 ‰	2.4	12	measured	ASTM test; exposure concentrations were time-averaged, normalized to 1% TOC	R2/C2	Fuchsman et al. (2000)
Amphipod	Juveniles *Hyalella azteca*	HCBD	Semi-static	"	Growth (biomass)	10 d	LOEC	Natural estuarine sediment, approx. 4.4 % TOC; tested at salinity of 10 ‰	13	65	measured	ASTM test; exposure concentrations were time-averaged, normalized to 1% TOC	R2/C3	Fuchsman et al. (2000)
Amphipod	Juveniles *Leptocheirus plumulosus*	HCBD	Semi-static	"	Survival	10 d	NOEC	Natural estuarine sediment, approx. 4.4 % TOC; tested at salinity of 10 ‰	0.3	1.5	measured	ASTM test; exposure concentrations were time-averaged, normalized to 1 % TOC	R3/C2	Fuchsman et al. (2000)
Amphipod	Juveniles *Leptocheirus plumulosus*	HCBD	Semi-static	"	Survival	10 d	NOEC [1]	Natural estuarine sediment, approx. 4.4 % TOC; tested at salinity of 10 ‰	0.7	3.5	measured	ASTM test; exposure concentrations were time-averaged, normalized to 1 % TOC	R3/C2	Fuchsman et al. (2000)
Amphipod	Juveniles *Leptocheirus plumulosus*	HCBD	Semi-static	"	Growth (biomass)	10 d	LOEC	Natural estuarine sediment, approx. 4.4% TOC; tested at salinity of 10 ‰	9.5	47.5	measured	ASTM tests; exposure concentrations were time-averaged, normalized to 1 % TOC	R2/C3	Fuchsman et al. (2000)

[1] NOEC calculated as LOEC/2 because effect is <20 %.

4.1. Graphic representation of effect data

As there are only two reliable and relevant data entries in the sediment dataset for HCBD (one freshwater and one marine), no graphical representation of the data has been generated.

4.2. Comparison between marine and freshwater species

There are only two reliable and relevant datapoints in the sediment database for HCBD. No statistical test can be performed to check significant differences in sensitivity of marine and freshwater species.

4.3. Overview of reliable and relevant studies

According to the EC EQS TGD (EC (2018) p. 25): "*All available data for any taxonomic group or species should be considered, provided the data meet quality requirements for relevance and reliability*".

Fuchsman et al. (2000) "Three lines of evidence in a sediment toxicity evaluation for hexachlorobutadiene".

- Species: juveniles of *Hyalella azteca* and *Leptocheirus plumulosus*
- Test were performed following ASTM standard for testing marine/estuarine (E1367-92) and freshwater (E1706-95) amphipods.
- The study was not conducted according to the principles of GLP.
- Origin: Organisms were obtained from commercial suppliers, and care was taken to ensure consistent test organism size within each bioassay.
- Experimental sediment: Tests used estuarine sediment, and was tested for toxicity at 10 ‰ salinity and was determined to be suitable for spiking, based on test organism survival of 83%.
- Spiking and equilibration time: In the second test, from which the NOEC for survival of *H. azteca* was derived, involved the addition of HCBD to a small aliquot of previously homogenized reference sediment (approximately 10 % of the total sediment volume), using approximately 25 ml of methanol as a carrier solvent. The remainder of the bulk sediment was then added. Sediment containing a nominal HCBD concentration of 1 000 mg/kg d.w. was stored for 6 weeks at 4 °C in the dark and then equilibrated for 10 d, and diluted with unspiked sediment to obtain the different test concentrations. The sediments with the target HCBD concentrations were then equilibrated for 14 d with overlying water in the test beakers, and toxicity test conditions of temperature, aeration, and lighting before toxicity testing. Overlying water renewal was not conducted during the equilibration period.
- Overlying water: Overlying water consisted of natural seawater diluted with moderately hard synthetic freshwater to a salinity of 10 ‰. Test organisms were acclimated from initial conditions (freshwater for *H. azteca*; approximately 20‰ for *L. plumulosus*) to the desired salinity of 10‰ by adjusting the ambient water at a maximum rate of 3‰ per day.
- Bioassays: Five replicate 1-L test chambers per concentration, each containing 20 test organisms and approximately 200 g of sediment (2-cm approximate depth). Test chambers were aerated and held at 20°C, and continuous light. Overlying water was renewed three times during the tests, and test organisms were fed 7 mg of rabbit chow five times during the course of the test.
- Test endpoints: Survival and growth after 10 d
- Measured HCBD concentrations: HCBD concentrations in the sediment were determined after 10 d of equilibration (day -4) and end (day 10) of the experiment. Effect concentrations were derived from time-averaged measured concentrations, normalized to 1 % organic carbon.
- Statistics: Statistical evaluations of toxicity test results included independent pair-wise comparisons and analysis of variance. Parametric tests were used unless the assumptions of

normality (Kolmogorov–Smirnov test) and equality of variances (Levene's method) were not satisfied after arcsine square root transformation. Independent pairwise comparisons used *t* tests (parametric) or Mann–Whitney rank sum tests (nonparametric). Multiple comparisons used one-way analysis of variance and Dunnett's test (parametric) or Kruskal–Wallis one-way analysis of variance on ranks and Dunn's method (nonparametric). Statistical analyses were conducted using SigmaStatt. Samples were considered toxic if a given test endpoint was both statistically different from the reference or control sample (*p* , 0.05) and at least 20 % lower than the mean test organism response in the reference or control sample.

- Results: *Hyalella azteca* survival NOEC = 2.4 mg/kg d.w. (1 % OC) (measured concentration); growth LOEC = 13 mg/kg d.w. (1 % OC) (measured concentration; not relevant for EQS derivation); *Leptocheirus plumulosus* LOEC = 0.7 mg/kg d.w. (1 %OC) (measured concentration, not relevant for EQS derivation); growth LOEC = 9.5 mg/kg d.w. (1 % OC) (measured concentration, not relevant for EQS derivation).

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 2018). 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 $QS_{sed, AF}$ is determined using assessment factors (AFs) applied to the lowest credible datum from long-term toxicity tests.

The lowest reliable and relevant effect datum available for HCBD is the NOEC of 2.4 mg/kg d.w. (1 % OC) for the survival of *Hyalella azteca* (Table 7).

Table 7 Most sensitive relevant and reliable data summarized from Table 6.

Species	Exposure duration [d]	Endpoint	$NOEC/EC_{10}$ [µg/kg d.w.]	OC [%]
Hyalella azteca	10 d	Survival	2 400	1

If only results from short-term tests with sediment-dwelling organisms are available, an assessment factor of 1000 is applied to the lowest reliable value.

The application of an AF of 1000 to the lowest credible datum results in a $QS_{sed,AF}$ of 2.4 µg/kg d.w. for 1 % OC representing a worst case scenario for Switzerland, which corresponds to 12 µg/kg d.w. for a sediment with 5 % OC.

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 $NOECs/EC_{10}s$, from different species covering at least eight taxonomic groups (EC (2018), 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

When only short-term tests are available the Equilibrium Partitioning (EqP) should be used to estimate the $QS_{sed,EqP}$. The lowest value among the $QS_{sed,AF}$ and $QS_{sed,EqP}$ would be proposed.

6.1. Selection of QS for water

Several environmental risk limits and quality standards are available for HCBD in water (section 1.2). For the derivation of the $EQS_{sed,EqP}$, a PNEC for the aquatic freshwater environment derived with a methodology similar to the procedure described in the TGD for deriving the AA-EQS for freshwater (e.g. with regard to the AF) should be used.

The $QS_{FW\text{-}ECO}$ used for the calculation of the $QS_{sed,EqP}$ based on direct toxicity using the equilibrium partitioning approach is 0.44 µg/L (AA-QS, EC 2005). Additionally, the EQS of 0.1 µg/L (EC 2005) consistent with the existing EQS in Council Directive 86/280/EEC is used for harmonization among compartments.

The $QS_{FW\text{-}ECO}$ used for the calculation of the $QS_{sed,EqP}$ based on secondary poisoning using the equilibrium partitioning approach is 0.003 µg/L (EQS, EC 2005).

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. K_d, 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 2018).

Estimates of the organic carbon normalised partition coefficient (K_{OC}) are available from three studies, plus one value estimated from K_{OW} (4.84). The average (geometric mean) K_{OC} value is 146 249 (log K_{OC} 5.17). The $K_{sed\text{-}water}$ value calculated from this K_{OC} value is 3 657 for a sediment with 5 % organic carbon, and 732 for a sediment with 1 % organic carbon.

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 2018). 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.

Table 8 summarized the derivation of the $QS_{sed,EqP}$ for the different water quality standards and organic carbon values. For highly liphophilic substances (log K_{OW} > 5), equilibrium may not be achieved, so a correction for exposure through food is added with the additional AF of 10. With an average K_{OW} of 4.84 this correction is not applied.

The $QS_{sed,EqP,eco}$ for HCBD based on direct toxicity in a sediment with 1 % organic carbon is 644.4 µg/kg d.w. and in a sediment with 5 % organic carbon is 3 218 µg/kg d.w., which translate into 146.4 µg/kg d.w. for 1 % organic carbon and 731.4 µg/kg d.w. for 5 % organic carbon when using the EQS for surface waters from the EU WFD (EC 2005).

The $QS_{sed,EqP,sec.pois.}$ for HCBD based on secondary poisoning in a sediment with 1 % organic carbon is 4.39 µg/kg d.w., and in a sediment with 5 % organic carbon is 21.9 µg/kg.

Table 8 Derived $QS_{sed,EqP}$ for a mean K_{OC} based on Appendix I and the PNEC for water (see section 6.1). The partition coefficient solid-water sediment (Kp_{sed}) is estimated for a sediment with 5 % OC (standard EC TGD sediment) and 1 % TOC (worst-case scenario in Switzerland).

	K_{OC} [l/kg]	Kp_{sed} [l/kg]	$K_{sed-water}$ [m³/m³]	$PNEC_{water}$ [µg/l]	$QS_{sed,EqP}$ [µg/kg w.w.]	$QS_{sed,EqP}$ [µg/kg d.w.]
Rounded value, direct toxicity						
1 % OC	146 249	1 462.5	732	0.1	56.3	**146.4**
5 % OC	146 249	7 312.5	3 657	0.1	281.3	**731.4**
Direct toxicity						
1 % OC	146 249	1 462.5	732	0.44	247.8	**644.2**
5 % OC	146 249	7 312.5	3 657	0.44	1 238	**3 218**
Secondary poisoning						
1 % OC	146 249	1 462.5	732	0.003	1.69	**4.39**
5 % OC	146 249	7 312.5	3 657	0.003	8.44	**21.9**

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

No field or mesocosm studies that provide effect concentrations of HBCD in sediment are available, thus, no QS_{sed} based on mesocosm data has been derived.

Effect data from a dilution study using field contaminated sediments were reported by Fuchsman et al. (2000), consisting of 29 sediment samples including six sediment dilution series and five additional undiluted sediment samples. Sediment samples were collected at three locations in Bayou d'Inde (a tributary to the Calcasieu River, LA, USA) and seven locations in an industrial discharge canal. Concentrations ranged from 0.04 to 350 µg/kg d.w. Other chemicals detected in the majority of samples included several metals and chlorinated benzenes, as well as bis(2-ethylhexyl)phthalate and pyrene (concentrations not reported). Detectable concentrations of volatile organic compounds were generally limited to two sediment samples and their dilutions, and were considered elevated. When these samples are eliminated from the database, HCBD concentrations ranged from 0.04 to 8.5 µg/kg d.w. Physical characteristics of the diluent sediment (3.39 % TOC, 57 % fines) were within the range of the samples to be diluted (1.41–7.41 % TOC, 29–84 % fines). Sediments were tested for survival and growth of *Hyalella azteca* and *Leptocheirus plumosus* in standard ASTM 10 d toxicity tests similar to the test from which effect data for EQS derivation were obtained.

The relationship between HCBD concentrations and test organism responses was quantified through nonlinear regression analysis after removal from the data set of nine HCBD concentrations that were considered biased through logistic equations. The estimated effects threshold defining organism survival or biomass of 80 % normalized to control performance for *H. azteca* was 0.63 mg/kg d.w. for both survival and growth and 1.6 mg/kg d.w. for survival and 3.2 mg/kg d.w. for growth of *L. plumulosus* (all for 1 % OC). It was noted that most of the samples containing more than 3 mg/kg d.w. HCBD also contained other chemicals that might have contributed to the observed toxicity while all sediments with less than 3 mg/kg d.w. had no chemicals other than HCBD identified as potentially significant contributors to toxicity. These threshold values were used to confirm the results of the spiked sediment study used in $QS_{sed,AF}$ derivation but do not provide further evidence to reduce the assessment factor applied to derive the $QS_{sed,AF}$ because effect concentrations are obtained for the same species included in the data set and refer to short-term studies.

8. Toxicity of degradation products

Detailed information on the toxicity of HBCD degradation products was not available.

9. EQS_{sed} proposed to protect benthic species

The different QS values for each derivation method included in the EC EQS TGD (EC 2018) are summarized in Table 9. According to the TGD, the most reliable extrapolation method for each substance should be used (EC 2018). When only short-term tests are available the Equilibrium Partitioning (EqP) should be used to estimate the $QS_{sed,EqP}$. The lowest value among the $QS_{sed,AF}$ and $QS_{sed,EqP}$ would be proposed. A preliminary EQS_{sed} of 2.4 µg/kg (1 % OC) is proposed for HCBD, including the application of an AF of 1000.

Table 9 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**
$QS_{sed,SSD}$	-	-	-
$QS_{sed,EqP,eco}$	146.4	731.4	-
$QS_{sed,EqP,sec.pois.}$	4.39	21.9	-
$QS_{sed,AF}$	2.4	12	1000
Proposed EQS_{sed}	**2.4**	**12**	

9.1. Uncertainty analysis

The proposed EQS_{sed} is derived from a very limited dataset of effect concentrations from spiked sediment toxicity tests but it is supported by the use of the equilibrium partitioning and the EQS for pelagic organisms which include long-term chronic data for fish, daphnia and algae, short-term acute data for fish, crustaceans and one mollusc species (EC 2005). The resulting $QS_{sed,EqP}$ is orders of magnitude higher than the proposed EQS_{sed}, therefore the later should be protective for effects from direct toxicity to other benthic invertebrates. Key benthic invertebrates absent in the dataset are insects and oligochaetes. However, Fuchmans et al. (2000) indicate that tests performed with the midge *Chironomus tentans* (P. Fuchsman, unpublished data) showed greater sensitivity to HCBD for *H. azteca* (complete *H. azteca* mortality at 9.5 mg/kg d.w. 1 % OC) than for *C. tentans* (survival of 62 % and biomass of 27 %, relative to the unspiked reference). The proposed EQS_{sed} should be protective for secondary poisoning in top predators according to the $QS_{sed,EqP,sec.pois.}$

It is noted that the K_{OC} value used here was derived from field contaminated sediments, where bioavailability may be reduced due to slow desorption. Using the worst case log K_{OC} value proposed by EuroChlor (2002) and EC (2005) of 3.95 would result in a $QS_{sed,EqP,sec.pois.}$ of 1.40 and 0.28 µg/kg d.w. for 5 % and 1 % OC, respectively and a $QS_{sed,EqP,eco.}$ of 46.8 and 9.49 µg/kg d.w. for 5 % and 1 % OC.

The proposed EQS_{sed} is considered preliminary and should not be used alone for risk assessments. It is also noted that the EQS_{sed} may also entail analytical problems depending on the analytical methods used for quantification.

10. References

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Appendix I. Sediment-water partition coefficient (K_{OC}) coefficient

Sediment type	**Log K_{OC}**	**K_{OC}**	**Reference/Source**
Desorption experiment, historically contaminated lake sediment, large fraction of fine particles, 4.1 % OC	5.44	275 423	Chen et al. 1999
Sorption/desorption experiment, mean of values for two historically contaminated lake sediment 4.1 and 1.5 % OC	5.1	125 893	Chen et al. 2000
Field study, freshwater suspended matter. Mean (range 5.5-6.4, n=9).	6.1	1 260 000	Lau et al. 1989
Estimated from K_{OW} (4.78)	4.02	10 471	Log K_{OC}=0.81*log K_{OW}+0.10 (EC 2018)
	5.17	**146 249**	**Geomean**