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SQC (EQS_{sed}) – Proposal by the Ecotox Centre for: *4-tert-Octylphenol (4-(1,1,3,3-tetramethylbutyl)phenol)*

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Summary

SQC (EQS_{sed}): 12.1 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 generic SQC for 4-tert-octylphenol of 12.1 µg/kg d.w. is proposed for standard sediments with 1 % OC.

Zusammenfassung

SQK (EQS_{sed}): 12.1 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 4-tert-Octylphenol und unter Verwendung der Methode, die in der Technischen Richtlinie der EU zur Ableitung von Umweltqualitätsnormen beschriebenen wird, schlägt das Oekotoxzentrum einen allgemeines SQK für 4-tert-Octylphenol von 12.1 µg/kg TS für Standardsedimente mit 1 % OC vor.

Résumé

CQS (EQS_{sed}): 12,1 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 générique pour le 4-tert-octylphénole de 12,1 µg/kg p.s. est proposé pour les sédiments standards avec 1 % CO.

Sommario

CQS: 12,1 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 generico per il 4-tert-octilfenolo di 12,1 µg/kg p.s. è proposto per sedimenti standard con 1 % CO.

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1 General information

Selected information on the alkylphenol 4-tert-octylphenol relevant for sediment is presented in this chapter. Registration and EQS dossiers referred to are:

- EC octylphenols EQS dossier (EC 2005)
- Environmental Risk Evaluation Report: 4-tert-Octylphenol (Brooke et al. 2005)
- ECHA Information on Registered Substances (ECHA 2020)
- ECHA support document for identification of 4-(1,1,3,3-tetramethylbutyl)phenol, 4-tert-octylphenol, as substances of very high concern (ECHA 2011a)
- OSPAR Background document on octylphenol (OSPAR Commission 2006, 2009)

1.1 Identity and physico-chemical properties

As summarized in the UK risk assessment report on 4-tert-octylphenol (Brooke et al. 2005), “octylphenol” represents a large number of isomeric compounds of general formula C6H4(OH)C8H17. The octyl group may be branched or linear and can also be located at the 2-, 3- or 4-position of the benzene ring. Among the many possible octylphenol isomers, the European Alkylphenols and Derivatives Association (CEPAD) has identified “4-tert-octylphenol” (CAS No. 140-66-9) as the only isomer currently available commercially in Europe (Brooke et al. 2005). 4-tert-octylphenol is prepared from 2,2,4-trimethylpentane and phenol, resulting in only a single isomer product (Ferguson et al. 2001). In case the identity was not clear from the references cited below, “octylphenol” is used as generic term, while “4-tert-octylphenol” is reserved for cases were the substance was clearly identified.

The log K_{oc} reported for 4-tert-octylphenol are in the range of 3.44-8.76, while the most reliable log K_{ow} is 4.12[1] (Table 1), both triggering an effects assessment for sediments according to the EC TGD EQS (EC 2018).

Table 1 summarizes identity and physico-chemical parameters for 4-tert-octylphenol 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). Data in grey font were not used for EQS derivation.

Characteristics	Values	References
Common name	4-(1,1,3,3-tetramethylbutyl)phenol 4-tert-Octylphenol p-t-Octylphenol p-tert-Octylphenol	ECHA (2020)
IUPAC name	4-(2,4,4-trimethylpentan-2-yl)phenol	ECHA (2020)
Chemical group	Phenol	

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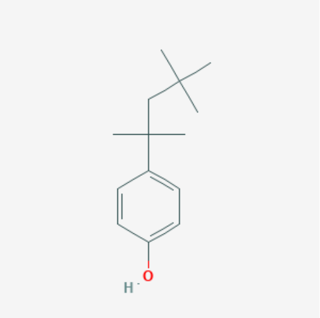
[1] “Nonyl- and Octylphenols do not follow the classical K_{ow} partition, because they can establish hydrogen bonds by the phenolic hydroxyl.” (EC 2010)

Characteristics	**Values**	**References**
Structural formula		PubChem (2019)
Molecular formula	$C_{14}H_{22}O$	Brooke et al. (2005)
CAS	140-66-9	Brooke et al. (2005)
EC number	205-426-2	Brooke et al. (2005)
SMILES code	Oc(ccc(c1)C(CC(C)(C)C)(C)C)c1	Brooke et al. (2005)
Molecular weight [g/mol]	206.33	Brooke et al. (2005)
Melting point [°C]	79 – 82 °C (exp.)	OECD SIDS Dossier (1994) cited in ECHA (2011b)
Boiling point [°C]	[1] 277 (exp.) [2] 280 – 283 (exp. pressure not indicated)	[1] Hüls AG and IUCLID Dossier (2000) cited in Brooke et al. (2005) [2] Sandoz Chemicals/OECD SIDS Dossier (1994) cited in Brooke et al. (2005)
Vapour pressure [Pa]	[1] 1 at 20 °C (exp.) [2] 0.21 at 20 °C (exp.)	[1] OECD SIDS Dossier (1994); IUCLID Dossier (2000), cited in Brooke et al. (2005) [2] Hüls AG cited and used in Brooke et al. (2005)
Henry's law constant [$Pa \cdot m^3/mol$]	[1] 0.52 (exp. at 298 K) [2] 0.46 - 0.70 (est.)	[1] Xie et al. (2004) cited in ECHA (2020) [2] EPISUITE (2004) cited in Brooke et al. (2005)
Water solubility [mg/L]	[1] 7 at 20 °C, pH = 6-7 (exp.) [2] (17-)19 at 22 °C (exp.)	[1] ECHA (2020) [2] SIDS (1994) cited and used in Brooke et al. (2005)
Dissociation constant (pK_a)	[1] ≥ 10.25 at pH = 5-9 (est.) [2] 10.33 at 25 °C (est.)	[1] ECHA (2020) [2] SIDS (1994) cited in Brooke et al. (2005)
Octanol-water partition coefficient (log K_{OW})	[1] 4.8 (exp. OECD 117, HPLC method, at 22 °C and pH 6.6) [2] 4.12 (exp. OECD 107, shake flask method, at 20.5°C) [3] 5.5 (exp., method unknown) [4] 5.28 (est., CAS 140-66-9) [5] 5.3 (exp., method unknown)	[1] ECHA (2020) [2] Ahel and Giger (1993) cited and used in Brooke et al. (2005) [3] Yamamoto and Liljestrand (2003) [4] KOWWIN™ v1.68 [5] EC (2010)
Organic carbon adsorption coefficient (log K_{OC})	[1] 3.54 – 4.27 (exp., river sediments)	[1] Johnson et al. (1998) cited in ECHA (2020)

Characteristics	Values	References
	[2] 5.18 (exp., coast embayment water and suspended matter) [3] 4.89 (4.74–5.07, exp., total humic substances, BKHS, from river sediment) [4] 4.85 (4.77–4.93, exp., high molecular weight humic substances, from river sediment) [5] 6.97 (±3.39) (exp., humic acid, commercial) [6] 8.76 (±2.46) (exp., Suwannee River humic acid) [7] 4.22 (±1.6) (exp., Suwannee River fulvic acid) [8] 3.43 (est. from log K_{ow} 4.12)	[2] Ferguson et al. (2001) [3, 4] Yeh et al. (2014) [5-7] Yamamoto and Liljestrand (2003) [8] see Appendix I
Sediment and sewage sludge adsorption coefficient (K_d [L/kg])	[1] 515 – 1559 (HPLC, sewage sludge) [2] 197 (est., sediment/water) [3] 126-1995 (mean 537) (exp., sediment/water) [4] 6-700 (exp., sediment/water)	[1] Clara et al. (2007) [2] calculated with FUGMOD V1.0 in OECD SIDS Dossier (1994) cited in Brooke et al. (2005) [3] Salgueiro-González et al. (2015) [4] Johnson et al. (1998)
Aqueous hydrolysis DT_{50}	Hydrolysis is believed to be a negligible removal process for 4-tert-octylphenol in the aquatic environment	Brooke et al. (2005), ECHA (2020)
Aqueous photolysis DT_{50}	[1] 7 -14 hours under continuous clear sky, noon, summer sunlight in surface layer of natural waters, photolysis rate in deeper layers is strongly attenuated, being approx. 1.5 times slower at depths of 20-25 cm than at the surface	[1] Ahel et al. (1994)
Biodegradation in aqueous environment DT_{50} [d]	[1] 8 – 71.2 (zero-order kinetics, 20 °C, river water) [2] 8.1 - 51 (first-order kinetics, 20 °C, river water) [3] 60 (aerobic degradation in seawater without air-bubbling) [4] 60 (20 °C, no air bubbling, sea water)	[1,2] Johnson et al. (2000) also cited in ECHA (2020) [3] Ying and Kookana (2003) also cited in ECHA (2020) [4] Ying and Kookana (2003)
Biodegradation in sediment DT_{50} [d]	[1] > 83 (river sediment, anaerobic conditions) [2] > 21 - 28 (marine sediment, aerobic conditions)	[1] Johnson et al. (2000) also cited in ECHA (2020) [2] Ying and Kookana (2003) also cited in ECHA (2020)
Biodegradation in soil DT_{50} [d]	No experimental data are available on the degradation of 4-tert-octylphenol in soil	Brooke et al. (2005), ECHA (2020)

1.2 Regulation and environmental limits

Octylphenol (CAS 1806-26-4, EU 217-302-5) including isomer 4-(1,1',3,3'-tetramethylbutyl)-phenol (4-tert-octylphenol, CAS 140-66-9, EU 205-426-2) has been designated as a Water Framework Directive "priority substance" (DIRECTIVE 2013/39/EU), Environmental Quality Standards are given in Directive 2013/39/EU of 12 Augustus 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. 4-tert-octylphenol (CAS 140-66-9) is listed in the "Inclusion of Substances of Very High Concern in the Candidate List" (ED/77/2011) (ECHA 2011b).

The UK Environment Agency published an environmental risk evaluation report on octylphenol in April 2005 (Brooke et al. 2005) and a Risk Reduction Strategy was published (UK DEFRA 2008). The process stalled at European Union (EU) level because "it proposed a general restriction on the use of octylphenol followed by exemptions for the known uses. This approach was not supported because it was not sufficiently risk-based" (OSPAR Commission 2009).

In contrast to the decision at EU level, Switzerland has extended the ban of nonylphenol and its ethoxylates to the closely structurally related octylphenol (OP) and its ethoxylates (OPE). In comparison to the structurally related 4-nonylphenols, 4-tert-octylphenol is covered by less regulation.

Table 2 summarizes existing regulation and environmental limits in Switzerland, Europe and elsewhere for 4-tert-octylphenol.

Table 2 Existing regulation and environmental limits for 4-tert-octylphenol in Switzerland and Europe.

Europe	
Directive 2000/60/EC (Water Framework Directive) of the European Parliament and of the Council of 23 October 2000	Included as a "priority substance"
EQS – Water Framework Directive (inland waters)[2]	AA-EQS: 0.12 µg/L (inland surface waters) 0.012 µg/L (other surface waters covered by the WFD) MAC-EQS: not derived (AA-EQS considered protective enough) for CAS 1806-26-4 and 140-66-9
Switzerland	
Chemical Risk Reduction Ordinance (ORRChem), Annex 1.8	The placing on the market of octylphenol and its ethoxylates is prohibited for defined types of product if they contain 0.1 % or more of these substances.
Water protection ordinance (WPO) (01.06.18)	Annex 22, Additional requirements for groundwater which is used for drinking water or is intended as such: 0.1 µg/L per individual substance.

Table 3 summarizes available sediment quality guidelines (SQGs). The quality standard for sediments (named EQS_{sed} in Table 3) derived in EC (2005) using the Equilibrium Partitioning approach used the AA-QS of 0.122 µg/L but there are differences in the default values for the different parameters in the

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[2] Directive 2013/39/EU of 12 Augustus 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

TGD (EC 2018) from that used in previous versions of the TGD and used in EC (2005). Similarly, the quality standard derived in Norway used a AA-EQS of 0.1 µg/L but a K_{oc} of 2740 kg/L.

The most restrictive value is the VR proposed in the Netherlands (derivation method not reported). The most permissible SQG is that proposed in Denmark derived from spiked sediment effect data and an AF of 100, which adds an extra AF of 10 to account for potential endocrine effects.

Table 3 Sediment quality guidelines reported in the literature. foc = mass fraction of organic carbon for the sediment. In grey SQG for marine and other waters.

SQG description	Value [µg/kg d.w.]	Development method	Country/region and reference
EQS_{sed}	34 (5 % TOC, freshwater) 3.4 (5 % TOC, saltwater)	EqP method	EC (2005)
EQS_{sed}	3 (1 % TOC, freshwater) 15 (recalculated for 5 % TOC) 0.3 (1 % TOC, saltwater) 1.5 (recalculated for 5 % TOC)	EqP method	Norway, Arp et al. (2014)
MTR (maximum permissible) VR (negligible risk)	19 (10 % TOC, fresh and saltwater) 9.5 (5 % TOC, fresh and saltwater) 1.9 (10 % TOC, fresh and saltwater) 0.95 (5 % TOC, fresh and saltwater)	Method not reported	Netherlands, RIVM (2019 (accessed))
EQS_{sed}	39.3 x f_{oc} (196.5 for 5 % TOC, freshwater) 3.93 x f_{oc} (19.6 for 5 % TOC, other waters)	Method not reported	Denmark, Leth-Petersen and Westengaard Guldagger (2016)

1.3 Use and emissions

According to ECHA (2020), 4-tert-octylphenol is in the total range band of 10000 - 100000 tonnes per annum. 4-tert-Octylphenol (CAS no. 140-66-9) was reported a high production-volume substance (> 1000 t/a) with European Union (EU) consumption having been approximately 23000 tonnes in 2001 (Brooke et al. 2005). As recently summarized, 4-tert-octylphenol still qualifies as high production-volume chemical (Olaniyan et al. 2020). This substance is used as raw material for various industrial, agrochemical and domestic applications: It is a base compound for phenol formaldehyde resins and is used as surfactant for a wide range of products including carbonless copy paper, printing inks, detergents and personal care products. Phenolic resins accounted for 98 % of 4-tert-octylphenol usage and are used in rubber processing to make tyres (Brooke et al. 2005). Further, 4-tert-octylphenol is a breakdown product of alkylphenol polyethoxylates (APEOs; Brooke et al. 2005).

1.4 Mode of action

According to ECHA (2020) and Brooke et al. (2005), several in vivo studies in fish support the conclusion that 4-tert-octylphenol can exhibit oestrogenic effects on aquatic organisms. These studies triggered listing 4-tert-octylphenol as substance of very high concern for Authorization in December 2012 due to its endocrine effects to fish (ECHA 2011b). According to Brooke et al. (2005), the lowest reliable NOEC for oestrogenic effects for 4-tert-octylphenol is 12 µg/L, reported by Wenzel et al. (2001) for exposed fertilized eggs of zebrafish (*Dario rerio*) in flow through system, with significant effects in the time to first spawn, the total number of eggs per female per day and fertilization at exposure concentrations of 35 µg/L. This NOEC is lower than the EC_{50} of 28 µg/L reported by Segner et al. (2003)

for fertilization success in zebrafish life cycle tests. For rainbow trout (*Oncorhynchus mykiss*), NOECs for vitellogenin induction in adult males exposed for 21 d were reported by Jobling et al. (1996) at 1.6 µg/L, with no associated effect in gonadal size, and of 10 µg/L for rainbow trout and roach (*Rutilus rutilus*) by Routledge et al. (1998). Additional effect concentrations above these NOECs are available for juvenile brown trout (*Salmo trutta* EC_{50} based on vitellogenin induction in plasma of 7 µg/L and NOEC based on vitellogenin levels in the liver at 7.8 µg/L; Bjerregaard et al. 2008), guppies (*Poecilia reticulate*, significant effect in mortality, gonadopodium length, and gonadosomatic index in females at 149 µg/L but not at 11.7 µg/L in 6 day old fish exposed for 90 days; Toft and Baetrup 2001; Toft and Baetrup 2003), Japanese medaka (*Oryzias latipes*, NOEC of 6.94 µg/L based on assessment of testis-ova and vitellogenin levels after 60 d post hatch exposure of fertilized eggs; Gronen et al. 1999; Knörr and Braunbeck 2002; Seki et al. 2003), South American Cichlid (*Cichlasoma dimerus*, LOEC of 30 µg/L based on vitellogenin levels and 300 µg/L for testicular structure impairment in adults after 60 d exposure; Vazquez et al. 2009), the marine Sand Goby *(Pomatoschistus minutus*; NOEC of 20 µg/L based on vitellogenin levels after 28 d exposure; Robinson et al*.* 2004) and sheepshead Minnow (*Cyprinodon variegates*; NOEC of 11.5 µg/L based on vitellogenin levels in 8-9 month old fish exposed for 24 days; Karels et al. 2003). All the studies were considered reliable either by Brooke et al. (2005) or ECHA (2020).

According to the review in Brooke et al. (2005) and ECHA (2020) only one reliable study is available for amphibians, reporting a NOEC of 50 µg/L based on effects on time to hatch, larval survival and snout-vent length for Streamside salamander (*Ambystoma barbouri*) eggs exposed for 35 days (Rohr et al. 2003). A considerably lower LOEC of 0.0021 µg/L was reported for tadpoles (*Rana pipiens*) by Croteau et al. (2009) based on the percent of individuals developing past the median stage. This study was classified as reliable with restrictions due to lacking measurements of exposed concentrations and information on purity and source of test chemical. Additional effect concentrations available for African clawed frog (*Xenopus laevis*), Bullfrog (*Rana catesbeiana*), Leopard frog (*Rana pipiens*), and Snapping turtle (*Chelydra serpentine*) were also classified as reliable with restrictions. Based on these results, ECHA (2011b) concluded that there is no evidence that amphibians are more sensitive than molluscs and fish to 4-tert-octylphenol.

A comprehensive review on the toxicity of 4-tert-octylphenol has recently been published (Olaniyan et al. 2020). Among others, inhibitory effects on photosynthesis in algae, delayed shedding of eggshells in crabs, and delayed growth in nauplius copepods are referenced. The latter two effects as well as effects on reproduction in amphibians (see summary in Olaniyan et al. (2020)) are attributed to the endocrine activity of 4-tert-octylphenol. Endocrine effects have also been reported in the mudsnail *Potamopyrgus antipodarum* but this study is classified as not reliable (Duft et al. 2003, Jobling et al. 2003). Effects on vascular plants – at much higher effect concentrations – have been reported upon exposure via liquid growth medium (Chen et al. 2013).

2 Environmental fate

2.1 Stability and degradation products

Abiotic degradation

Hydrolysis is believed to be a negligible removal process for 4-tert-octylphenol in the aquatic environment based on the chemical structure of octylphenol and observed stability of the substance in storage and in abiotic controls of biodegradation experiments (Brooke et al. 2005, ECHA 2020).

Photodegradation may occur according to Ahel et al. (1994) who reported a half-life of 7 -14 hours under continuous clear sky at noon/summer sunlight in the surface layer of natural waters. Photolysis rate in the deeper layers was strongly attenuated, being approximately 1.5 times slower at depths of 20-25 cm than at the surface.

Biodegradation

SIDS (1994) and IUCLID (2000) dossiers report results of standardized studies to assess inherent biodegradability of 4-tert-octylphenol (CAS No. 27193-28-8). In a OECD 302C study (non-GLP; MITI Test of oxygen consumption in close system), no degradation was observed with a mixed population of non-adapted microorganisms within 28 d. An additional GLP study according to ISO 10708 (biochemical oxygen demand in close system) showed 20 % biodegradation by non-adapted microorganisms in activated sludge after 28 d suggesting slow biodegradation (data owned by Hüls AG, 1991) (Brooke et al. 2005). By contrast, ready biodegradability of octylphenol (CAS N° 140-66-9 purity of 99.64 %) was assessed in a GLP study following OECD 301B (ready biodegradability: CO_2 evolution test; Gledhill 1999 cited in Brooke et al. 2005) with a domestic activated sludge from a waste water treatment plant (with high concentration of nonylphenolethoxylate). Octylphenol was extensively mineralized (≥ 60 % CO_2) during the 35 d study. Although these results classify octylphenol as readily biodegradable it fails the 10 day window, therefore suggesting that microorganisms may need an adaptation period. Despite of these contradictory results 4-tert-octylphenol is inherently biodegradable in water (ECHA 2020).

Several simulation tests are available addressing biodegradation of octylphenol in water and sediment from marine and continental environments, showing that the extend of degradation and resulting products depend on the physicochemical conditions and microbial community. In a kinetic study 4-tert-octylphenol biodegradation was assessed in 17 different water samples from 4 UK rivers, resulting in half-lives of 8 – 71.2 d (zero-order kinetics, 20 °C, river water) and 8.1 - 51 d (first-order kinetics, 20 °C, river water). In sediment from the same sites, no degradation was recorded during the 83 d of the study under anaerobic conditions (Johnson et al. 2000). Half-lives of 60 d were also reported in sea water (Southern Australia) without air bubbling, while 4-tert-octylphenol was quickly degraded within a week under aerobic conditions in marine sediment after an acclimation period of 21 days (Ying and Kookana 2003). It seems that 4-tert-octylphenol is persistent under anaerobic conditions.

Little information is available on **degradation pathways** and **degradation products** of octylphenol. The UK risk assessment report lists "ring cleavage, oxidation of alkyl chain" as degradation reactions (p. 172, Brooke et al. 2005). Due to similarity in molecular structure, it can be assumed that oxidative degradation of the alkyl side chain occurs as in nonylphenolpolyethoxylate isomeric mixtures (see degradation products in Di Corcia et al. 1998). For the latter, it has been observed that part of the intermediate breakdown products are hydrophilic and have been supposed to be carboxylated (Di Corcia et al. 1998). Hydrophilic breakdown products have also been reported for octylphenol, likewise suggesting carboxylation (Johnson et al. 2000).

Degradation including mineralization of the phenyl ring of 4-nonylphenol was also reported in seawater (Ekelund et al. 1993) and of octylphenoxyacetic acid by groundwater bacteria (Fujita and Reinhard 1997). In the latter study, the branched tert-octyl structure of the alkyl group was resistant to microbial degradation, and the alkyl chain persisted in the form of the tertiary alcohol. Among 3 river water samples, incomplete mineralization (up to 25 %) of the phenyl group of octylphenol (4-(1,1,3,3-tetramethylbutyl)-phenol) was detected in one sample within 56 d (Johnson et al. 2000).

The bacterial strains (*Stenotrophomonas* sp. strain IT-1 and *Sphingobium* spp. strains IT-4 and IT-5) isolated from the rhizosphere of *Phragmites australis* (common reed) were capable of utilizing 4-tert-octylphenol as a sole carbon source via type II *ipso*-substitution (or *ipso*-hydroxylation) which requires molecular oxygen (Toyama et al. 2011). Under aerobic conditions in spiked sediments, the three strains completely degraded 4-tert-OP within 5 d, but only slightly under anaerobic conditions (13.9 - 9.8 % removal within 21 d). One intermediate metabolite was identified as hydroquinone, another as potential octylhydroquinone.

2.2 Sorption/desorption processes

Experimental data and calculated partition coefficients suggest that 4-tert-octylphenol is strongly adsorbed to soils, sludge and sediments (Brooke et al. 2005, ECHA 2020). Given that 4-tert-octylphenol is a weak acid, pH might also have an effect on sorption. The pKa is ≥ 10.25, the substance will be present in the undissociated and hence more hydrophobic form (Brooke et al. 2005).

Johnson et al. (1998) studied the sorptive behaviour of 4-tert-octylphenol in sediments and suspended matter from three English rivers with contrasting water quality following the batch equilibrium method (OECD 196: Adsorption - Desorption Using a Batch Equilibrium Method). Distribution coefficients (K_d) for bed sediments were 6–700 L/kg and organic carbon normalised partition coefficients (K_{oc}) 3500–18000 L/kg, with the highest sorption in sediments with the highest total organic carbon and proportion of clay and silt particles. Suspended sediments also showed 5-35 times higher sorbed 4-tert-octylphenol than the corresponding sediments. Sediments from industrial sites, predominantly organic aggregates, showed higher sorption capacity than sediments from rural sites, predominantly composed of algae.

Ferguson et al. (2001) studied the distribution in sediments, water and suspended matter in a urbanized estuarine environment in the US, reporting a log K_{oc} for suspended sediments of 5.18 (mean of 5 measurements at three stations). As these authors argue, the K_{oc} values derived from field studies were comparatively higher than those derived from batch experiments in the laboratory (Johnson et al. 1998) and that estimated from K_{ow}, which could be due to the different levels of concentrations used in laboratory experiments compared to field studies or the binding to more resistant (to desorption) phases on sediments or detritus in the field compared to the lab.

To understand the specificity of the sorption process, Yeh et al. (2014) tested specific sorption of octylphenol to humic substances extracted from sediment and separated into high molecular weight (HMHS 0.45 µm-1 kDa) and low molecular weight (LMHS < 1 kDa) humic substances. No adsorption to low molecular weight humic substances was detected, while a log K_{HMHS} of 4.77–4.93 for HMHS was determined. Arya et al. (2017) found that the sediment concentrations of 4-tert-octylphenol correlated with sediment total organic carbon content at all sampling sites in the streams Cameron Run, Hunting Creek, Potomac River in Virginia, USA. Given that the K_{oc} values derived for humic and fulvic acids are higher than those derived with sediments and that the TGD for EQS lacks guidance concerning sorption data derived using humic and fulvic acids, these values are excluded in the derivation of the geometric mean K_{oc} value that is taken forward.

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).

Specific information on the bioavailability of octylphenol is scarce. Based on the sorption behavior of octylphenol to organic carbon, it is expected that bioavailability in soil and sediment is influenced by the amount and type of organic carbon present. In line with this assumption, the presence of colloidal humic acid reduced bioavailability of octylphenol in algae toxicity tests (Kim et al. 2016).

2.4 Bioaccumulation and biomagnification

One laboratory study has described the accumulation of 4-tert-octylphenol in killifish (*Oryzias latipes*) during 168 h accumulation and 24 h excretion (Tsuda et al. 2001). The bioconcentration factor (BCF) reached a plateau after 48 h, resulting in BCF of 261 ± 62 (whole body wet weight). This BCF is similar to the bioaccumulation factor (BAF) of 297±194 (n=3) in ayu fish (*Plecoglossus altivelis*) collected from eight rivers once every 2 months for ten consecutive months by these same authors (Tsuda et al. 2001). In Ferreira-Leach and Hill (2001), bioaccumulation in tissues of rainbow trout (*Oncorhynchus mykiss*) reached steady state concentrations within the fish after 4 days of exposure, leading to BCF in the whole fish of 470 (n=4). According to these BCF, 4-tert-octylphenol is not bioaccumulative because it does not fulfil the criteria for “bioaccumulative (B)” or “very bioaccumulative (vB)” (BCF below 2000 or 5000, respectively).

The bioaccumulation of 4-tert-octylphenol was studied in mussels *Mytilus trossulus* from the Gulf of Gdansk (Southern Baltic), yielding a mean tissue concentration of 0.0306 µg/g d.w. (median: 0.0166) (Staniszewska et al. 2017). While bioaccumulated concentrations in mussels were not linearly correlated with concentrations in water, phytoplankton and sediment (water and sediment concentrations were presented in separate publications: Koniecko et al. (2014), Staniszewska et al. (2014)), cluster analysis indicated that concentrations in phytoplankton had the greatest influence on the observed variability of 4-tert-octylphenol concentrations. The derived BAF based on measured 4-tert-octylphenol concentrations in phytoplankton was 4.7 (0-129.5).

Concerning the risk of benthic invertebrates to transfer toxic and bioaccumulative substances to higher trophic levels, the EFSA scientific opinion for sediment risk assessment proposes to perform spiked sediment bioaccumulation tests with benthic invertebrates for substances that show significant bioaccumulation in fish (BCF ≥ 2000) 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). 4-tert-octylphenol does not meet these criteria and thus it is concluded that benthic invertebrates probably do not contribute to the risk to higher organisms through trophic transfer. Tissue concentrations of 4-tert-octylphenol in the freshwater clam *Corbicula fluminea*, filter-feeder that also deposit-feeds, were assessed in samples from the Minho River estuary (Northwestern Iberian Peninsula) and ranged from 0.0199 to 0.0397 µg/g d.w. Sediment concentrations in 22 sediment samples taken across the estuary ranged from 0.0093 and 0.0745 µg/g d.w. The calculated BAF was 439 ± 161 L/kg, the calculated BSAF was 1.56 ± 0.43 (Salgueiro-González et al. 2015).

3 Analysis

3.1 Methods for analysis and quantification limit

Different methods to analyze 4-tert-octylphenol in sediment exist, each with different detection limits. A selection of reported methods for various matrices was published by Acir and Guenther (2018). Detection limits of approx. 1.4 µg/kg d.w. are achieved by solid-phase extraction followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) and of approx. 0.2 µg/kg d.w. by gas chromatography-mass spectrometry. Lower limits of quantification (0.08 µg/kg d.w.) have been reported for HPLC-fluorescence analysis.

Table 4 Methods for 4-tert-octylphenol 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
1.4	40	LC-MS/MS	Loyo-Rosales et al. (2003)
0.2	0.5	GC-MS	Oketola and Fagbemigun (2013)
n.a.	0.08	HPLC-fluorescence	Koniecko et al. (2014)

3.2 Environmental concentrations

Measured environmental concentrations (MEC) in sediments for Switzerland are available for 18 small streams from monitoring campaigns in August 2018 (Table 5). 4-tert-octylphenol was only detected at 3 of the 18 sites, with concentrations ranging from < 1 to 2.53 µg/kg d.w.

Additional data has been collected for other European countries and elsewhere around the world (Table 5). Overall, higher concentrations are measured close to wastewater treatment plants and in urbanized and industrialized areas. No trend regarding marine and coastal sediments vs. freshwater sediments was observed.

Table 5 Measured environmental concentrations (MEC) of 4-tert-octylphenol in Switzerland, Europe, and elsewhere. All concentrations expressed as µg/kg d.w. for sediment if not indicated. n.d. not detected

Country	MEC (min-max)	No. of sites	Comments	Reference
Switzerland	< LOQ (1) – 2.54	18	4-tert-octylphenol, sampling in August 2018, fraction < 2 mm, small streams	Ecotox Centre, unpubl. data
Portugal/Spain	9.3 – 74.5	22	4-tert-octylphenol, May 2012, upper 4 cm of freshwater sediment (Minho River estuary)	Salgueiro-González et al. (2015)
USA	~2 - 8 (only graphical information available)	38	4-tert-Octylphenol, 2014, upper 2-4 cm, Cameron Run river and Hunting Creek (Virginia, USA)	Arya et al. (2017)
China	85 – 421	14	octylphenol, upper 5 cm, Sept 2007, Shaying River	Zhang et al. (2013)
China	2.7 - 42	7	octylphenol, upper 5 cm, July 2013, Pearl River	Zhong et al. (2017)
China	n.d.* – 38 (summer) n.d.* – 29 (winter)	49	4-tert-octyphenol, 2015, Hanjiang River *LOD 0.3–1.5 µg/kg	Hu et al. (2019)
Italy	30-70	1	para-tert-octylphenol, sampling once per year between 2009-2013, upper 5 cm of marine sediment (North Adriatic Sea)	Moschino et al. (2016)

Country	MEC (min-max)	No. of sites	Comments	Reference
Poland	< LOQ (0.08 µg/kg d.w.) — 48.88	12	4-tert-octylphenol, spring, summer and autumn 2011 and 2012, upper 5 cm of marine sediment (Gulf of Gdańsk)	Koniecko et al. (2014)
Spain	20.1 – 35.3	5	4-tert-octylphenol, upper 5 cm of marine sediment (off the Galician coast), 4-octylphenol not detected	Salgueiro-González et al. (2014)
USA	n.d.* - 45	10	4-tert-octylphenol, 1998, upper 2 cm sediment from Jamaica Bay, Long Island, NY *exact LOD not stated	Ferguson et al. (2001)
China	8 – 9.3 (YS) 7 – 11.1	66	octylphenol, upper 2 cm, Yellow Sea (YS) and East China Sea (ECS) inner shelf	Duan et al. (2014)

4 Effect data (spiked sediment toxicity tests)

A non-filtered bibliographic search was performed for 4-tert-octylphenol in the US Ecotox Data Base (U.S. EPA 2016) which did not yield data on sediment organisms. Likewise, a search in the German Environmental Office database ETOX did not yield any relevant results. A key word search performed on Scopus (octylphenol + sediment + toxicity, no restriction regarding publication date) resulted in 26 publications, only two were actually based on spiked sediment tests. Potentially unpublished data was searched for in registration dossiers, risk assessment dossiers and EQS dossiers (Brooke et al. 2005, EC 2005, ECHA 2020, OSPAR Commission 2006).

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

In a joined effort by the Italian National Research Council and Danish Environmental Protection Agency, three chronic studies on *Lumbriculus variegatus* (number, biomass, reproduction, growth, mortality) *Chironomus riparius* (emergence, development) and *Hyalella azteca* (survival, growth, reproduction) were conducted (Kamper 2015, Valsecchi et al. 2015a, 2015b). The reported endpoints are considered relevant without/with restrictions and reliable without/with restrictions (see Table 6 and section 4.3).

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). Therefore, effect data from 10 d tests with *Chironomus riparius* were considered as acute effect data. Acute effect data considered reliable and relevant cannot be used directly to derive EQS_{sed} but are retained as they can be used as supporting information for example when choosing the assessment factor (AF).

In addition, data from chronic exposure of the freshwater mudsnail *Potamopyrgus antipodarum* are available (Duft et al. 2003). Endpoints considered were the total number of embryos and the number of new (unshelled) embryos after 14, 28 and 56 d. For this assessment, only data from 28 d exposures were used as effect concentrations could not be calculated for 14 and 56 d exposures.

Table 6 Sediment effect data collection for 4-tert-octylphenol 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 assessed as not relevant and/or not reliable is in grey font. Data used for QS development is underlined. Abbreviations: n. a. = not available.

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Value (Confidence limits) [mg /kg d.w.]	Sediment type	Normalized value [mg /kg d.w. 1 % OC]	Normalized value [mg/kg d.w. 5 % OC]	Chem. analysis	Note	Validity	References
Acute toxicity data in freshwater															
Insecta	*Chironomus riparius*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Larval survival	10 d	EC_{10}	17 (10-30)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.7, 1.98±0.07% TOC	8.5	42.5	Measured^{1}	Highest test concentration elicited <50 % of the effect	R2, C2	Valsecchi et al. (2015b)
Insecta	*Chironomus riparius*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Larval survival	10 d	EC_{50}	336 (251-450)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.7, 1.98±0.07% TOC	169.7	848.5	measured^{1}	Highest test concentration elicited <50 % of the effect	R2, C2	Valsecchi et al. (2015b)
Insecta	*Chironomus riparius*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Larval growth	10 d	EC_{10}	>302	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.7, 1.98±0.07% TOC	>152.5	>762.5	measured^{1}	Highest test concentration elicited no effect	R2, C2	Valsecchi et al. (2015b)
Insecta	*Chironomus riparius*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Larval growth	10 d	EC_{50}	>302	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.7, 1.98±0.07% TOC	>152.5	>762.5	measured^{1}	Highest test concentration elicited no effect	R2, C2	Valsecchi et al. (2015b)
Acute toxicity data in marine water															
No data available															
Chronic toxicity data in freshwater															
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Survival	42 d (28 d exposure, 14 d in clean water)	NOEC	20	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5 % TOC	10	50	Measured^{2}	Highest test concentration elicited <50 % of the effect	R2, C2	Kamper (2015)
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Survival	42 d (28 d exposure, 14 d in clean water)	EC_{10}	8.7 (4.9-13.5)	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5% TOC	4.35	21.75	Measured^{2}	Highest test concentration elicited	R2, C2	Kamper (2015)

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Value (Confidence limits) [mg /kg d.w.]	Sediment type	Normalized value [mg /kg d.w. 1 % OC]	Normalized value [mg/kg d.w. 5 % OC]	Chem. analysis	Note	Validity	References
													<50 % of the effect		
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Growth	42 d (28 d exposure, 14 d in clean water)	NOEC	>50	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5 % TOC	>25	>125	Measured^2	Highest test concentration elicited <50 % of the effect	R2, C2	Kamper (2015)
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Reproduction	42 d (28 d exposure, 14 d in clean water)	NOEC	>50	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5 % TOC	>25	>125	Measured^2	Highest test concentration elicited <50 % of the effect	R2, C2	Kamper (2015)
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Survival	35 d (28 d exposure, 7 d in clean water)	NOEC	20	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5 % TOC	10	50	Measured^2	Highest test concentration elicited <50 % of the effect	R2, C1	Kamper (2015)
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Survival	35 d (28 d exposure, 7 d in clean water)	EC_{10}	8.9 (4.9-14-1)	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5 % TOC	4.45	22.25	Measured^2	Highest test concentration elicited <50 % of the effect	R2, C1	Kamper (2015)
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Survival	28 d	NOEC	20	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5 % TOC	10	50	Measured^2	Highest test concentration elicited <50 % of the effect	R2, C1	Kamper (2015)
Crustacea (Amphipoda)	*Hyalella azteca*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, renewal of overlying water	3 d at test conditions	Survival	28 d	EC_{10}	8.4 (5.6-11.6)	Artificial (OECD218), 5% peat, 20% kaolin clay, 75% quartz sand; pH 7, 2±0.5 % TOC	4.2	21	Measured^2	Highest test concentration elicited <50 % of the effect	R2, C1	Kamper (2015)
Insecta	*Chironomus riparius*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Emergence ratio	28 d	EC_{10}	15 (6-36)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.7, 1.98±0.07% TOC	7.6	37.9	Measured^1		R2, C1	Valsecchi et al. (2015b)
Insecta	*Chironomus riparius*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Development rate	28 d	EC_{10}	>302	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1%	>152.5	>762.5	Measured^1	Highest test concentrat	R2, C2	Valsecchi et al. (2015b)

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Value (Confidence limits) [mg /kg d.w.]	Sediment type	Normalized value [mg /kg d.w. 1 % OC]	Normalized value [mg/kg d.w. 5 % OC]	Chem. analysis	Note	Validity	References
									quartz sand; pH 6.7, 1.98±0.07% TOC				ion elicited no effect		
Oligochaeta	*Lumbriculus variegatus*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Total number of worms	28 d	EC_{10}	17 (7-44)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.5-6.8, 2.24±0.04% TOC	7.6	37.9	Measured^1		R1, C1	Valsecchi et al. (2015a)
Oligochaeta	*Lumbriculus variegatus*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Biomass	28 d	EC_{10}	60 (39-92)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.5-6.8, 2.24±0.04% TOC	26.8	133.9	Measured^1		R1, C1	Valsecchi et al. (2015a)
Oligochaeta	*Lumbriculus variegatus*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Increase in number of worms (reproduction)	28 d	EC_{10}	8.8 (2.7-28.9)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.5-6.8, 2.24±0.04% TOC	3.9	19.6	Measured^1		R1, C1	Valsecchi et al. (2015a)
Oligochaeta	*Lumbriculus variegatus*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Increase of total biomass (growth)	28 d	EC_{10}	58 (22-153)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.5-6.8, 2.24±0.04% TOC	25.9	129.5	Measured^1		R1, C1	Valsecchi et al. (2015a)
Oligochaeta	*Lumbriculus variegatus*	4-tert-Octylphenol (CAS 140-66-9)	Whole-sediment, static	14 d at test conditions	Mortality	28 d	EC_{10}	87 (not determined)	Artificial (OECD 218), 4±1% peat, 20±1% kaolinite clay, 76±1% quartz sand; pH 6.5-6.8, 2.24±0.04% TOC	38.8	194.2	Measured^1		R1, C3	Valsecchi et al. (2015a)
Mollusca	*Potamopyrgus antipodarum*	*4-tert-octylphenol*	Whole-sediment, static	5 d in darkness at test conditions	Number of new (unshelled) embryos	28 d	NOEC	< 0.001	Artificial, 95% quartz sand, 5% beech leaves; 2.3% TOC; mean grain size 180 µm	< 0.0005	< 0.0025	-	EC based on nominal concentrations, increase in number of embryos	R4, C2	Duft et al. (2003)
Mollusca	*Potamopyrgus antipodarum*	*4-tert-octylphenol*	Whole-sediment, static	5 d in darkness at test conditions	Total number of embryos	28 d	NOEC	0.01	Artificial, 95% quartz sand, 5% beech leaves; 2.3% TOC; mean grain size 180 µm	0.005	0.05	-	EC based on nominal concentrations, increase in number of embryos	R4, C1	Duft et al. (2003)
Mollusca	*Potamopyrgus antipodarum*	*4-tert-octylphenol*	Whole-sediment, static	5 d in darkness at test conditions	Total number of embryos	28 d	EC_{10}	0.00211 (0.00089-0.00291)	Artificial, 95% quartz sand, 5% beech leaves; 2.3% TOC;	0.00092	0.00459	-	EC based on nominal concentrat	R4, C1	Duft et al. (2003)

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Value (Confidence limits) [mg /kg d.w.]	Sediment type	Normalized value [mg /kg d.w. 1 % OC]	Normalized value [mg/kg d.w. 5 % OC]	Chem. analysis	Note	Validity	References
									mean grain size 180 µm				ions, increase in number of embryos		
Mollusca	*Potamopyrgus antipodarum*	*4-tert-octylphenol*	Whole-sediment, static	5 d in darkness at test conditions	Total number of embryos	56 d	NOEC	< 0.001	Artificial, 95% quartz sand, 5% beech leaves; 2.3% TOC; mean grain size 180 µm	< 0.0005	< 0.0025	-	EC based on nominal concentrations, increase in number of embryos	R4, C2	Duft et al. (2003)
Chronic toxicity data in marine water															
No data available															

[1] Derived from measured highest and lowest concentrations.

[2] Derived from measured concentrations at start of test. Concentrations in sediments during exposure to spiked-sediment (28 d) remained constant.

4.1 Graphic representation of effect data

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

Before OC-normalization, the EC_{10} for survival of amphipods (*Hyalella azteca*, 8.4 mg/kg d.w.) is the lowest effect datum followed by reproduction of oligochaetes (*Lumbriculus variegatus*, 8.8 mg/kg d.w.) and emergence ration for insects (*Chironomus riparius*, 15 mg/kg d.w.). After normalization, the lowest effect datum was reproduction of oligochaetes (3.9 mg/kg d.w.) followed by survival of amphipods (4.2 mg/kg d.w.).

The ratio of relevant acute to chronic data for insects (EC_{10} 10 d survival and EC_{10} 28 d emergence) is 1.13, and 22.4 for EC_{50} 10 d survival and EC_{10} 28 d emergence.

Reproductive effects in molluscs (*Potamopyrgus antopodarum*) occurred at concentrations 3 orders of magnitude lower than the lowest reliable/relevant EC_{10}. These effect data cannot be used for EQS derivation due to limited reliability of the study. However, in water-only tests 4-tert-octylphenol led to similar increases in reproduction of *P. antopodarum* at 5 µg/L (Jobling et al. 2004, 9 weeks exposure) and in other gastropod species, inducing 'superfemales' and imposex at a LOEC of 10 µg/L (nominal) in the freshwater snail *Marisa cornuarietis* and the marine prosobranch *Nucella lapillus* (Oehlmann et al. 2000).

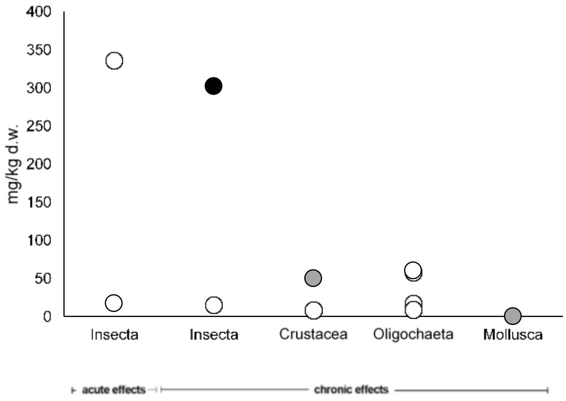

Figure 1a Graphical representation of acute and chronic effect data from spiked sediment toxicity tests with 4-tert-octylphenol. Data not normalized for OC. Filled symbols: unbounded data. Grey symbols: Non-relevant/non-reliable data.

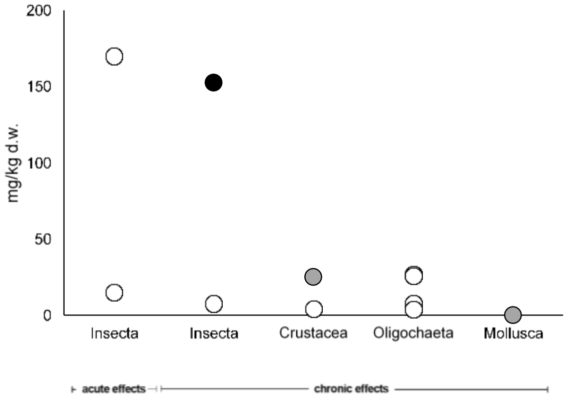

Figure 1b Graphical representation of acute and chronic effect data from spiked sediment toxicity tests with 4-tert-octylphenol. Data normalized for OC. Filled symbols: unbounded data. Grey symbols: Non-relevant/non-reliable data.

4.2 Comparison between marine and freshwater species

No marine effect data were available for 4-tert-octylphenol.

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

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*".

The chronic effect data for *L. variegatus* (number, biomass, reproduction, growth, mortality) have been evaluated as R1/C1. The chronic effect data for *C. riparius* (emergence ratio, development rate) and *H. azteca* (survival, growth, reproduction) as R2/C1 or R2/C2. In the following section, the studies on *L. variegatus* and *H. azteca* assessed as R1/C1, lowest chronic effect concentrations after OC normalization, are summarized.

Valsecchi et al. (2015a): Sediment-water toxicity test on *L. variegatus* using sediment spiked with 4-tert-octylphenol.

- Protocol: OECD Guideline for Testing of Chemicals No. 225 "Sediment-Water *Lumbriculus* Toxicity Test Using Spiked Sediment"
- Species: *Lumbriculus variegatus*
- Origin: in house culture, originally obtained from Dr. Matti Leppänen, Department of Biology, University of Eastern Finland, Joensuu (FIN). Worms were synchronized 17 days before the test, and were adapted to test conditions 14 d before the test.
- Experimental sediment: artificial sediment according to OECD 225, containing 0.4-0.5 % of Urtica powder.
- Spiking: a "stock sediment" (1.0 mg/g wet weight, nominal concentration) was produced by adding 0.1 g (wet weight) of 4-tert-octylphenol manually to 10 g of artificial sediment, then homogenized with 90 g (wet weight) of artificial sediment and further mechanically homogenized by mixing overnight (at 300 rpm). The appropriate quantity of stock sediment was then diluted in artificial sediment to obtain seven final test concentrations. Each test sediment was mechanically mixed (300 rpm) for 1 hour and divided into the required number of replicates.
- Overlying water: reconstituted water according to OECD Guideline 225 (set to pH 7.6, total water hardness 275 mg/L as $CaCO_3$). Over time, pH ranged from 8.0 to 8.5, O_2 concentrations ranged from 68 to 95 %, temperature ranged from 20.0 to 20.4 °C, $N\text{-}NH_4$ concentrations ranged from 0.04 to 3.53 mg/L, and total hardness ranged from 292 to 402 mg/L as $CaCO_3$. The respective validation requirements for the OECD 225 test were thus met (the pH of the overlying water should be between 6 and 9 throughout the test; the O_2 concentration in the overlying water should not be below 30 % of air saturation value at test temperature during the test).
- Bioassays: The 28 d toxicity test was performed in line with OECD Guideline for Testing of Chemicals No. 225 "Sediment-Water *Lumbriculus* Toxicity Test Using Spiked Sediment". The test was performed in 250-mL glass bottles (inner diameter: 6 cm) with 55 mL sediment (75 g; 2 cm depth) and 220 mL water (8 cm depth). Ten individuals were tested per vessel with 3 replicates per treatment and control. 6 control replicates are recommended in the guideline, but the minimum of 3 is considered sufficient. Separate vessels (control, the highest and lowest concentration) were prepared to verify test substance concentration in the sediment

and partitioning of the tested chemical in the water-sediment system. Overlying water was not changed, evaporation compensated with deionized water if necessary. Overlying water was aerated with a Pasteur pipette (one bubble a second). Light/dark cycle was 16 h light, 8 h dark. Organisms were not additionally fed. All relevant water parameters were measured.

- Test endpoints: total number of worms, biomass as ash free dry weight, increase in number (reproduction), and increase in biomass (growth) after 28 d are considered relevant and reliable, the endpoint mortality was only presented based on estimates for interpreting the other effect concentrations and is not part of the OECD 225 test.
- Measured 4-tert-octylphenol concentrations: 4-tert-octylphenol concentrations were determined by liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) coupled to a turbulent flow chromatography for the on-line purification of the extracts. Concentrations were measured in sediment, overlying water and pore waters. Sediments were measured for all tested concentrations at the end of the mixing time, and for the control, lowest and highest tested concentrations at the start before adding the test organisms, and at the end of the test in additional test replicates prepared for this purpose. In pore water and in overlaying water, concentrations were always below the limit of detection (0.5 mg/L). The 4-tert-octylphenol sediment concentration of the test control was always below 0.5 µg 4-tert-octylphenol/g sediment dry weight. 4-tert-octylphenol sediment concentrations after mixing ranged between 77 and 140 % of the nominal concentration. 4-tert-octylphenol sediment concentrations during the test (Start and Day 28) ranged between 69 and 117 %. All the measured concentrations were interpolated from a linear regression relationship between nominal and measured concentrations.
- Statistics: Effect concentrations (E(L)Cx) were determined by using the Toxicity Relationship Analysis Program (TRAP) Version 1.22 (US EPA, 2013).
- Results: The derived effect concentrations are within the range of the test concentrations (nominal: 4-154 µg/kg dry weight, measured: 4.2-175 µg/kg dry weight). An estimate of the dry weight of the worms at start of exposure was obtained by measurement of the ash-free dry weight of 3 representative sub-samples (N=10) of the batch of synchronised worms used for the test (mean of 4.3 ± 0.2 mg dry weight). The validity criterion of average number of living *L. variegatus* per control replicate increasing by a factor of ≥ 1.8 during test duration was met.

Kamper (2015): Sediment-water toxicity test on *H. azteca* using sediment spiked with 4-tert-Octylphenol.

- Protocol: US EPA No. 600/R-99/064: Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates, Second Edition, 2000, Section 14, Test Method 11.
- Species: *Hyalella azteca.*
- Origin: *H. azteca* purchased from Aquatic Research Organisms, Inc., Hampton, NH, USA and delivered to DHI 24 hours before test start. At test start the *Hyalella* amphipods were 7-8 days old.
- Experimental sediment: artificial sediment according to OECD 118, containing 5 % peat.
- Spiking and equilibration time: a stock solution (A) of 3.0 g/L in acetone was prepared. A series of 20-mL stock solutions (B) in acetone with different concentrations of the test item was prepared from stock solution (A). A series of sand (160 g) was spiked with 20 mL of the different B stock solutions, one for each final test concentration. The control with acetone was made by adding 20 mL acetone to 160 g sand. When the acetone had evaporated, the final test mixtures

were made by mixing the spiked sand with wet artificial sediment (1040 g dry weight) to a total of 1200 g dry weight. An equilibration period of 72 hours before introducing the test organisms to the test system was applied under test conditions.

- Test concentrations: nominal 2.5, 4, 6.5, 11, 18, 30 and 50 mg/kg d.w. and an acetone control.
- Overlying water: reconstituted water.
- Bioassays: the 28 d exposure to spiked sediment-water followed by 14 d exposure to clean water was performed in line with US EPA No. 600/R-99/064: "Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates". The test was performed in 300 mL high-form lipless glass beaker, with stainless steel net, with 100 mL which equals 160 g wet sediment and 200 mL water in the sediment exposure from Day 0 to Day 28 and 300 mL in the water only exposure from Day 28 to Day 42. Ten individuals were tested per vessel with 3 replicates per treatment and 4 for controls ending on Day 28 and additional 3 replicates per treatment and 4 for controls ending on Day 42. Two separate series of test vessels were prepared for 4-tert-octylphenol concentrations, one series collected at the start of the test and one with addition of organisms collected on Day 28. Overlying water renewal performed on flow through system at 2 volume additions/d; automatic system giving one volume addition every 12 h. Overlying water was not aerated unless dissolved oxygen in overlying water dropped below 2.5 mg/L. Light/dark cycle was 16 h light, 8 h dark. Organisms fed daily 1.0 mL per test chamber with YCT food (1800 mg SS/L). All relevant water parameters were measured.
- Test endpoints: 28 d survival and growth. Additional endpoints considered C2 due to exposure in clean water during Day 28 and Day 42 include 35 d survival; and 42 d survival, growth, reproduction, and number of adult males and females on day 42.
- Measured 4-tert-octylphenol concentrations: concentrations were measured in sediment, overlying water and pore waters. Sediments were measured for all tested concentrations at the start of the test, and for the control, 11 and highest tested concentrations at the end of the test in additional test replicates prepared for this purpose. Pore water and overlying water concentrations measured at start and end in the acetone control, 11 and 50 mg/kg d.w. treatment. Concentrations in waters and sediment in the acetone control were always below the limit of detection. 4-tert-octylphenol sediment concentrations at start of the test ranged between 80 and 120 % of the nominal concentration. The measured concentrations were used as basis for interpolation to estimated concentrations where no measurements were made.
- Statistics: NOEC, LOEC and EC values estimated on the effect parameters survival and growth by use of Dunnett's procedure /6/ and TOXEDO /5/. The effect on the growth of the amphipods was calculated on the basis of the mean larvae length in each test concentration compared to controls by a student's t-test. The reproductive output (mean number of live offspring per live female) for each replicate was calculated and the effect concentrations (NOEC, LOEC, EC10 and EC_{50}) were determined by use of Dunnett's procedure /6/ and TOXEDO /5/.
- Results: the derived effect concentrations were within the range of the test concentrations (nominal: 2.5-50 mg/kg d.w., measured: 2.8-50 mg/kg d.w.). Test acceptability criteria were met.

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

The lowest long-term effect datum available for 4-tert-octylphenol is the EC_{10} of 8.8 mg/kg d.w. before OC normalization or 3.92 mg/kg d.w. for 1 % OC (2.24 ± 0.04 % OC, Table 7) for the increase in number of individuals (reproduction) in *Lumbriculus variegatus*.

Table 7 Most sensitive relevant and reliable chronic data summarized from Table 5.

Species	**Exposure duration [d]**	**Endpoint**	**EC_{10} [mg/kg d.w.]**	**OC [%]**	**EC_{10} [mg/kg d.w. 1 % OC]**
Chironomus riparius	28 d	Emergence ratio	15	1.98±0.07	7.6
Hyalella azteca	28 d	Survival	8.4	2±0.5	4.2
Lumbriculus variegatus	28 d	Increase in number of worms (reproduction)	8.8	2.24±0.04	3.92

In case of long term tests (NOEC or EC_{10}) being available for three species representing different living and feeding conditions, the TGD recommends the application of an assessment factor of 10 on the lowest credible datum (Table 11 in EC (2018)). The application of this AF would lead to a $QS_{sed,AF}$ of 1960 µg/kg d.w. for 5 % OC or 392 µg/kg d.w. for 1 % OC as 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/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

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 European Commission which sets a value of 0.122 µg/L (freshwater) for the protection of pelagic species based on the deterministic approach and "traditional toxicity" (not endocrine) effects (EC 2005). The QS is based on a 60 d NOEC (growth) for rainbow trout (*Oncorhynchus mykiss*) (6.1 µg/L) and an AF 50. Concentrations of 4-tert-octylphenol eliciting endocrine effects are very close to concentrations causing general toxicity therefore EC (2005) stated that the AA-QS of 0.122 µg/L is a “precautionary value targeted to prevent the occurrence of endocrine effects”.

No AA-EQS specifically derived for Swiss surface waters is currently available. As no more sensitive endpoints than used for the assessment published by the EC in 2005 were found in the literature, the corresponding AA-EQS is used in the application of the EqP.

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).

A geomean K_{oc} of 9736.61 kg/L derived from the experimental K_{oc} values and the K_{oc} value estimated from the most reliable K_{ow} of 4.12 (list of K_{oc} is provided in Appendix I) was used as basis for $QS_{sed,EqP}$ derivation (6.4, Table 7).

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.

The derived $QS_{sed,EqP}$ ranges between 12.1 µg/kg d.w. for the worst case scenario (sediment with 1 % OC) to 59.6 µg/kg d.w. for the standard sediment in the TGD (with 5 % OC; Table 8).

An additional AF of 10 should be applied to the resulting $QS_{sed,EqP}$ for substances with log K_{ow} >5. Reported log K_{ow} for 4-tert-octylphenol and isomeric mixtures range from 3.7-5.5, with a geometric mean of 4.58 (Table 1). The most reliable K_{ow} derived by the shake flask method (OECD 107) is 4.12, thus, application of the additional AF is not warranted (Table 8).

Table 8 Derived $QS_{sed,EqP}$ for a geometric mean K_{OC} based on Appendix I and the AA-EQS for water derived by EC (2005) (0.122 µg/L). The solid-water partition coefficient for 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]	$K_{sed\text{-}water}$ [m^3/m^3]	$QS_{sed,EqP}$ [µg/kg w.w.]	$QS_{sed,EqP}$ [µg/kg d.w.]	Additional AF
1 % OC	9736.61	97	49.5	4.6	**12.1**	-
5 % OC	9736.61	487	244.2	22.9	**59.6**	-

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

No field or mesocosm studies that provide effect concentrations of the active substance 4-tert-octylphenol in sediment are available, thus, no QS_{sed} based on field data or mesocosm data has been derived.

8 Toxicity of degradation products

As detailed in section 2.1, suggested degradation pathways are heterogeneous, depending on the microorganism or microbial community tested and on physicochemical conditions.

The ECHA support document on 4-tert-octylphenol (ECHA 2011a) does not mention toxicity of 4-tert-octylphenol degradation products. The UK risk assessment report on 4-tert-octylphenol (Brooke et al. 2005) discusses the potential endocrine activity of “other ethoxylate breakdown products” of octylphenolethoxylates (p. 135/136). It is concluded that “Based on the limited evidence currently available, the OPEs and carboxylate derivatives appear to be less toxic than the parent alkylphenol”. However, as also stated in the report, these molecules are neither made from 4-tert-octylphenol nor are they degradation products, thus do not strictly qualify for risk assessment in this context.

Against this background, a risk assessment for degradation products of 4-tert-octylphenol in sediment is not conducted.

9 EQS_{sed} proposed to protect benthic species

The different QS values for each derivation method included in the EC EQS TGD 2018 are summarized in Table 9. According to the TGD, the most reliable extrapolation method for each substance should be used (EC 2018). In all cases, data from spiked sediment toxicity tests are preferred over the EqP approach.

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**
$QS_{sed,SSD}$	-	-	-
$QS_{sed,EqP}$	12.1	59.6	-
$QS_{sed,AF}$	392	1960	10
EC EQS_{sed}	-	34[a]	-
Proposed EQS_{sed}	**12.1**	59.6	

[a] tentative value as derived by EqP method

9.1 Uncertainty analysis

According to the TGD, an AF of 10 is foreseen for $EQS_{sed,AF}$ in case of long term tests (NOEC or EC_{10}) being available for three species representing different living and feeding conditions. The spiked sediment toxicity database available for 4-tert-octylphenol includes three taxonomic groups highly relevant for sediment assessment.

Endocrine effects of 4-tert-octylphenol have been reported (see section 1.4) and the available database includes endpoints related to reproduction for the three species represented. In addition to these, endocrine effects have been reported in mollusks (Duft et al. 2003, Jobling et al. 2003). The EC_{10} for increase in unshelled (new) embryos in *Potamopyrgus antipodarum* after 4 weeks was 0.004 µg/kg d.w. (Duft et al. 2003), which is orders of magnitude lower than the $QS_{sed,AF}$ derived using the AF of 10. The EC_{10} was extrapolated far below the tested range (LOEC = 1 µg/kg d.w.) and no chemical analysis was performed to determine actual exposure concentrations. However, additional studies in spiked waters are available (e.g. Jobling et al. 2003) supporting the conclusion that prosobranch snails may be highly sensitive to endocrine effects from 4-tert-octylphenol, including an additional EC_{50} of 40.7 µg/kg d.w. reported in Durf et al. (2007) for a 4 week experiment with *Nassarius reticulatus* (original study (Tillmann 2004 cited in Durf et al. 2007) not available). The database available for $QS_{sed,AF}$ does not include any reliable and relevant data for amphibians, taxonomic group for which the potential of exposure through sediment is high and with similar apparent sensitivity to molluscs and fish.

Given that the AA-EQS used in the derivation of the $QS_{sed,EqP}$ is a "precautionary value targeted to prevent the occurrence of endocrine effects", it is proposed to set the EQS_{sed} at the level of the $QS_{sed,EqP}$ assuming that this value should be also protective for preventing the occurrence of endocrine effects from contaminated sediments. Because the $QS_{sed,EqP}$ is backed up by three relevant benthic invertebrates, this EQS_{sed} is proposed as definitive rather than tentative or preliminary.

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

TOC, type	Log K_{oc}	K_{oc}	Reference/Source
2.42 %, river sediment	4.02	10373	Johnson et al. (1998)
7.02 %, river sediment	4.00	10071	Johnson et al. (1998)
0.12 %, river sediment	4.03	10833	Johnson et al. (1998)
5.71 %, river sediment	4.01	10193	Johnson et al. (1998)
0.09 %, river sediment	3.83	6722	Johnson et al. (1998)
0.08 %, river sediment	4.27	18500	Johnson et al. (1998)
1.76 %, river sediment	3.54	3466	Johnson et al. (1998)
2.88 %, river sediment	3.60	3958	Johnson et al. (1998)
Industrial estuarine water-suspended sediment	5.16	144544	Ferguson et al. (2001)
Estimated from K_{ow}, see Table 1	3.43	2692	Log K_{OC}=0.57*log K_{OW}+1.08 Formula : EC (2018)
		9736.61	**Geometric mean**