

2020

oekotoxzentrum
centre ecotox



Schweizerisches Zentrum für angewandte Ökotoxikologie
Centre Suisse d'écotoxicologie appliquée

**SQC (EQS_{sed}) – Proposal by the Ecotox
Centre for: *Bis(2-ethylhexyl) phthalate (DEHP)***

First proposal: 18.05.2020 (last bibliographic research)
12.11.2020 (implementation of the expertise)



Imprint

Publisher

Swiss Centre for Applied Ecotoxicology, 1015 Lausanne

Commissioned by

FOEN, Federal Office of the Environment, Water Quality Section, 3003 Bern

Authors

Carmen Casado-Martinez and Christina Thiemann, Swiss Centre for Applied Ecotoxicology

Scientific Support

Dr Karen Duis, ECT Oekotoxikologie GmbH, Böttgerstr. 2-14, D-65439 Flörsheim/Main, Germany

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

Contact

Carmen Casado: carmen.casado@centreecotox.ch

Citation Proposal

Carmen Casado-Martinez and Christina Thiemann. 2020. SQC (EQS_{sed}) – Proposal by the Ecotox Centre for: Bis(2-ethylhexyl) phthalate (DEHP). Lausanne (CH): Swiss Centre for Applied Ecotoxicology; 33 pp.

Oekotoxzentrum | Eawag | Überlandstrasse 133 | 8600 Dübendorf | Schweiz
T +41 (0)58 765 55 62 | info@oekotoxzentrum.ch | www.oekotoxzentrum.ch

Centre Ecotox | EPFL-ENAC-IIE-GE | Station 2 | CH-1015 Lausanne | Suisse
T +41 (0)21 693 62 58 | info@centreecotox.ch | www.centreecotox.ch



Summary

SQC (EQS_{sed}): 1.08 mg/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 DEHP of 1.08 mg/kg d.w. is proposed for standard sediments with 1 % OC.

Zusammenfassung

SQK (EQS_{sed}): 1.08 mg/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 Cypermethrin und unter Verwendung der Methode, die in der Technischen Richtlinie der EU zur Ableitung von Umweltqualitätsnormen beschrieben wird, schlägt das Oekotoxzentrum ein allgemeines SQK für DEHP von 1.08 mg/kg TS für Standardsedimente mit 1 % OC vor.

Résumé

CQS (EQS_{sed}): 1,08 mg/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 DEHP de 1,08 mg/kg p.s. est proposé pour les sédiments standards avec 1 % CO.



Sommario

CQS: 1,08 mg/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 DEHP di 1,08 mg/kg p.s. è proposto per sedimenti standard con 1% CO.



Table of content

| | |
|---|----|
| Summary | 2 |
| Zusammenfassung..... | 2 |
| Résumé..... | 2 |
| Sommario | 3 |
| 1 General Information..... | 5 |
| 1.1 Identity and physico-chemical properties | 5 |
| 1.2 Regulatory context and environmental limits | 8 |
| 1.3 Use and emissions..... | 10 |
| 1.4 Mode of action and sensitivity of taxonomic groups | 11 |
| 2 Environmental fate..... | 13 |
| 2.1 Stability and degradation products..... | 13 |
| 2.2 Sorption/desorption processes..... | 14 |
| 2.3 Bioavailability..... | 15 |
| 2.4 Bioaccumulation and biomagnification | 15 |
| 3 Analysis..... | 16 |
| 3.1 Methods for analysis and quantification limit | 16 |
| 3.2 Environmental concentrations..... | 16 |
| 4 Effect data (spiked sediment toxicity tests) | 18 |
| 4.1 Graphic representation of effect data | 23 |
| 4.2 Comparison between marine and freshwater species | 24 |
| 4.3 Overview of reliable and relevant long-term studies | 24 |
| 5 Derivation of QS_{sed} | 26 |
| 5.1 Derivation of $QS_{sed, AF}$ using the Assessment Factor (AF) method | 26 |
| 5.2 Derivation of $QS_{sed, SSD}$ using the species sensitivity distribution (SSD) method | 27 |
| 6 Derivation of $QS_{sed, EqP}$ using the Equilibrium Partitioning approach | 27 |
| 6.1 Selection of QS for water | 27 |
| 6.2 Selection of partition coefficient | 27 |
| 6.3 Selection of OC content for a reference sediment | 27 |
| 6.4 Derivation of $QS_{sed, EqP}$ | 27 |
| 7 Determination of QS_{sed} according to mesocosm/field data | 28 |
| 8 Toxicity of degradation products | 28 |
| 9 EQS_{sed} proposed to protect benthic species..... | 28 |
| 9.1 Protection of benthic organisms and uncertainty analysis..... | 29 |
| 10 References | 29 |
| Appendix I. Sediment-water partition coefficient (K_{oc}) coefficient..... | 33 |



1 General Information

Selected information on the plasticizer Bis(2-ethyl) phthalate (DEHP) relevant for sediment is presented in this chapter. Existing registration and dossiers for DEHP are:

- ECHA (2020). Substance name: Bis(2-ethylhexyl) phthalate. EC number: 204-211-0. CAS Nr 117-81-7. Online registration dossier : <https://echa.europa.eu/it/registration-dossier/-/registered-dossier/15358>
- EC (2008). Bis(2-ethylhexyl) phthalate (DEHP), Risk Assessment Report, pp. 1-588. (Literature Review from 2005)
- EC (2005). Common Implementation Strategy for the Water Framework Directive Environmental Quality Standards (EQS) Substance Data Sheet Priority Substance No. 12 Diethylhexylphthalate (DEHP) CAS-No. 117-81-7
- RIVM (Rijksinstituut voor Volksgezondheid en Milieu, Netherlands) (2001). Ecotoxicological Serious Risk Concentrations for soil, sediment and (ground)water: updated proposals for first series of compounds. Report 711701 020 (Verbruggen et al.), pp. 1-263.
- ECCC (Environment and Climate Change Canada, Health Canada) (2017). Risk Management Scope for 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester [DEHP] – Chemical Abstracts Service Registry Number (CAS RN): 117-81-7, pp. 1-20.
- Environment Canada and Health Canada (2017). Draft Screening Assessment, Phthalate Substance Grouping, pp. 1-228. (Literature Review from 2016)
- USEPA (2019). Proposed Designation of Di-Ethylhexyl Phthalate (DEHP) (1,2-Benzene-dicarboxylic acid, 1,2-bis (2-ethylhexyl) ester) (CASRN 117-81-7) as a High-Priority Substance for Risk Evaluation, pp. 1-64.

1.1 Identity and physico-chemical properties

DEHP, a colorless oily liquid, belongs to the class of phthalates and is used as a plasticizer.

Reliable log K_{oc} reported for DEHP are in the range of 5.41-5.95, estimated log K_{oc} is 6.18 (Table 1; Appendix 1). Reported experimental log K_{ow} is 7.5 (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 DEHP 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 EU TGD for EQS (EC 2018). Data not used in the EQS derivation are in grey font.

| Characteristics | Values | References |
|--------------------|--|------------|
| Common name | DEHP | |
| IUPAC name | Bis(2-ethylhexyl) phthalate | EC (2008) |
| Chemical group | Phthalates | EC (2008) |
| Structural formula | | EC (2008) |
| Molecular formula | C ₂₄ H ₃₈ O ₄ | EC (2008) |



| Characteristics | Values | References |
|---|--|--|
| CAS | 117-81-7 | EC (2008) |
| EC Number | 204-211-0 | EC (2008) |
| SMILES code | <chem>CCCCC(CC)COC(=O)C1=CC=CC=C1C(=O)OCC(CC)CCCC</chem> | ECHA (2020) |
| Molecular weight [g/mol] | 390.6 | EC (2008) |
| Melting point [°C] | [1] -50 | ECHA (2020) |
| Boiling point [°C] | [1] 374.15 (exp. atmospheric pressure) | ECHA (2020) |
| Vapour pressure [Pa] | [1] Between 1.8×10^{-5} and 3.4×10^{-5} Pa (room temperature 20-25°C; weight of evidence) [2] 2.52×10^{-5} | [1] ECHA (2020) [2] Cousins and Mackay (2000) cited in Net et al. (2015) |
| Henry's law constant [Pa·m ³ /mol] | 4.43 | EC (2008) |
| Water solubility [mg/l] | [1] 0.003 (exp. 20°C) [2] 0.00249 (est. 25°C, IUCLID) [3] 0.00362 (est. SPARC) [4] 0.34 (exp. 25 °C), colloidal water solubility | [1] Staples et al. (1997) cited in EC (2008) and ECHA (2020) [2] Cousin and Mackay (2000) cited in ECHA (2020) [3] Ellington and Floyd (1996) cited in ECHA (2020) [4] Howard et al. (1985) cited in ECHA (2020) |
| Dissociation constant (pK _a) | [1] no ionisable groups at environmentally relevant pH in the substance | [1] ECHA (2020) |
| Octanol-water partition coefficient (log K _{ow}) ^a | [1] 7.137 ± 0.153 (exp. OECD 123 slow stirring method) [2] 7.453 ± 0.061 (exp. OECD 123 slow stirring method) [3] 7.27 ± 0.04 (exp. OECD 123 slow stirring method) [4] 7.94 (exp. HPLC method) [5] 7.8 ± 1.4 (exp. HPLC method) [6] 7.54 (est. SPARC) [7] 7.73 (est. QSAR) | [1] Brooke et al. (1990) cited in ECHA (2020) [2] DeBruijn et al. (1990) cited in ECHA (2020) [3] Ellington et al. (1990) cited in ECHA (2020) [4] Howard et al. (1990) cited in ECHA (2020) [5] Klein et al. (1988) cited in ECHA (2020) [6] Ellington and Floyd (1996) cited in ECHA (2020) [7] Cousins and Mackay (2000) cited in ECHA (2020) |



| Characteristics | Values | References |
|---|---|--|
| Organic carbon adsorption coefficient ($\log K_{oc}$) | <p>[1] 5.48, 5.95, 5.41 (exp. Batch equilibrium method, freshwater sediment 0.15-1.88 % OC, 10.7, 25.8, 42.7 % clay)</p> <p>[2] 5.71 (exp. Batch equilibrium method, seawater sediment <1 % OC)</p> <p>[3] 4.94 (exp.)</p> <p>[4] 6.00 (exp.)</p> <p>[5] 5.60 (exp., suspended matter, St. Lawrence River)</p> <p>[6] 5.77 (exp., suspended matter, Lake Yssel and the Rhine River in the Netherlands).</p> <p>[7] 3.95 (exp. mean and median of 32 data, suspended matter, marine and freshwater in the Netherlands)</p> <p>[7] 5.77 (est. EUSES Model)</p> <p>[8] 5.22 (est. PCKOC Model)</p> | <p>[1] Williams et al. (1995)</p> <p>[2] Sullivan et al. (1982) cited in ECHA (2020)</p> <p>[3] Russell and MacDuffie (1986)</p> <p>[4] Furtman (1993) cited in Staples et al. (1997)</p> <p>[5] Germain and Langlois (1989) cited in Staples et al. (1997)</p> <p>[6] Ritsema et al. (1989) cited in Staples et al. (1997)</p> <p>[7] ECHA (2020)</p> <p>[8] Meylan (1992) cited in ECHA (2020)</p> |
| Sediment adsorption coefficient (K_d [l/kg]) | <p>[1] 452, 5860, 4830 (exp. Batch equilibrium method, freshwater sediment 0.15-1.88 % OC, 10.7-42.7 % clay)</p> | <p>[1] Williams et al. (1995)</p> |
| Aqueous hydrolysis DT_{50} | <p>[1] $10^6 d = \pm 2740$ years (est. worst case default half-life)</p> <p>[2] ± 2000 years (est.)</p> | <p>[1] EUSES cited in EC (2008)</p> <p>[2] Giam et al. 1984 cited in EC (2008) and USEPA (2019)</p> |
| Aqueous photolysis DT_{50} | <p>[1] $10^6 d = \pm 2740$ years (est. worst case default half-life)</p> <p>[2] 0 % (after 1h, river), 1.8 % (pond, after 30d), 1.4 % (eutrophic lake, after 200d), 13.7 % (oligotrophic lake, after 200d) (exp.)</p> | <p>[1] EUSES cited in EC (2008)</p> <p>[2] Wolfe et al. (1980) cited in EC (2008)</p> |
| Biodegradation in the aqueous compartment DT_{50} [d] | <p>[1] Readily biodegradable (exp. OECD 301 B Modified Sturm-test; aerobic conditions, sewage sludge).</p> <p>[2] 3.3 d (0.5 $\mu\text{g/g}$, pH 7, 30°C) to 16.1 days (1 $\mu\text{g/g}$, pH 5, 30°C) when tested in combination with DBP; 7 days when tested alone (30°C, pH 7 and 2 $\mu\text{g/g}$) (sewage, screening tests) (exp.)</p> <p>[3] 22-64 d (exp., eutrophic lake water, 29 °C, mineralization study)</p> <p>[4] 0 % mineralization (exp. oligotrophic water, after 60 d, 29 °C)</p> <p>[5] 30 d (exp. 20 °C, primary degradation, Mississippi river water)</p> <p>[6] 15 d (exp. 20 °C, primary degradation, Rhine water)</p> | <p>[1,2] ECHA (2020)</p> <p>[3,4] Subba-Rao et al. (1982) cited in ECHA (2020)</p> <p>[5] Saeger and Tucker (1976) cited in ECHA (2020)</p> <p>[6,7] Ritsema et al (1989) cited in ECHA (2020)</p> <p>[8,9] Furtmann (1993) cited in ECHA (2020)</p> <p>[10] ECHA (2020)</p> |



| Characteristics | Values | References |
|--|---|--|
| | [7] No primary degradation during 10 d (exp. 4°C, Rhine water) [8] 4.4 d (exp. 20° C, Rhine water) [9] No degradation at 4°C (exp. Rhine water) [10] 50 d (est. from Diefenbach (1994) for a temperature of 12 °C, as worst case). | |
| Biodegradation in sediment DT ₅₀ [d] | [1] 337 d (exp. similar to OECD 308; natural marine bulk sediment (aerobic surface layer, anoxic lower layers) and natural freshwater; 13 °C). MEHP (degradation product) was demonstrated to be degraded very rapid (DT50=26 hours at 22°C). [2] 33 d (exp. highly contaminated river in Taiwan, synthetic medium, 30°C and pH 7). 139.3 d (12°C, temperature adapted) [3] 300 d (exp. bulk sediment, aerobic + anaerobic; weight of evidence for 12°C) [4] Infinite DT50 for anaerobic sediment [5] 3000 d (sediment overall) | [1] Kickham (2010) cited in ECHA (2020) [2] Chang et al. (2005) cited in ECHA (2020) [3-5] Cited and used in ECHA (2020) |

^a data obtained from HPLC-based or unknown methods are in grey font and were not used for EQS derivation.

1.2 Regulatory context and environmental limits

Table 2 summarizes existing regulation and environmental limits in Switzerland, Europe and elsewhere for DEHP. Please note that these may have changed since finalization of this dossier.

Table 2 Existing regulation and environmental limits for DEHP in Switzerland and Europe.

| Europe | |
|---------------------------------|---|
| EU Priority substance list | PSR: priority substance under review according to Decision 2455/2001. |
| REACH Regulation (EC) 1907/2006 | Substance of very high concern (SVHC) included in the candidate list for authorization. Substance of very high concern requiring authorisation before it is used (Annex XIV, Entry N° 4) <ul style="list-style-type: none"> - Sunset date¹ 21/02/2015 - Exceptions: Uses in the immediate packaging of medicinal products covered under Regulation (EC) No 726/2004, Directive 2001/82/EC, and/or Directive 2001/83/EC. |

¹ Date from which the placing on the market and the use of that substance shall be prohibited unless an exemption applies or an authorisation is granted, or an authorisation application has been submitted before the application date also specified in Annex XIV, but the Commission decision on the application for authorisation has not yet been taken.



| | |
|--|---|
| | <p>Status under Article 57 (c): Identified as a CMR (toxic for reproduction)</p> <p>Status under Article 57 (f): as substance of very high concern due to its endocrine disrupting properties for which there is scientific evidence of probable serious effects to human health and the environment which give rise to an equivalent level of concern to those of other substances listed in paragraph(s) (a) to (e) of that Article (Commission implementing decision of 4.7.2017)</p> <p>Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles (Annex XVII of REACH, entry N° 51 for DEHP, DBP, BBP and DIBP):</p> <ul style="list-style-type: none"> - Use as substances or in mixtures in toys and childcare articles - Placing toys and childcare articles containing BBP, DBP and DEHP on the market <p>< 0.1 % individually or in combination (Effective July 7, 2020)</p> |
| <p>Annex I to Directive 67/548/EEC (Index Number: 607-317-00-9)</p> | <p>Human health:</p> <ul style="list-style-type: none"> - Classified as toxic to reproduction (Repr. Cat. 2, R60-61: may impair fertility, may cause harm to the unborn child) - Needs labelling on medical devices that come in contact with human body (initially defined in Council Directive 93/42/EEC (1993)) <p>Environment:</p> <ul style="list-style-type: none"> - none |

According to the high partitioning of DEHP to sediments, a PNEC_{sed} was derived in the EU RAR (EC 2008). This value, > 100 mg/kg d.w., was derived from a NOEC >1000 mg/kg d.w. for amphibians with an assessment factor of 10 (because effect studies were available for organisms from 3 trophic levels) and is also reported as PNEC/QS_{sed} by INERIS (INERIS 2018). Supportive studies with microorganisms indicated an effect at around 1 mg/kg d.w. but these were not used in the PNEC_{sed} derivation. The EU RAR (EC 2008) concluded that there was a need for further information and/or testing because there was concern for sediment dwelling organisms as a consequence of exposure to DEHP. However, implementation of risk management measures to address the risks identified for other environmental compartments would eliminate the need for further information on sediment dwelling organisms.

The EQS data sheet (EC 2005) derived a QS_{sed} of 100 mg/kg d.w. as in the EU RAR (EC 2008). Additionally an EQS_{SPM,sec.pois.} for protection from secondary poisoning to top predators of 17.2 mg/kg d.w. for freshwater and 20.4 mg/kg d.w. for marine water are derived from the biota QS of 3.2 mg/kg (tissue of prey, wet weight) corresponding to EQS of 1.3 µg/l and back-calculated for suspended matter using the equilibrium partitioning.



The limit values derived in the Netherlands by van Wezel et al. (1999) and Verbruggen et al. (2001) were one order of magnitude lower, with a Serious Risk Concentration (SRC) set at the NOEC from the study with amphibians of 10 mg/kg d.w. (Larsson and Thurén 1987), a Maximum Permissible Concentration (MPC) of 1.0 mg/kg d.w. derived after the application of safety factor of 10 and a Negligible Concentration (NC) of 0.01 mg/kg.

Table 3 PNEC/quality standards available from authorities and reported in the literature for DEHP. All values for sediments in mg/kg d.w. if not otherwise stated.

| Water | | | |
|---|---|---|-------------------------------|
| Description | Value [$\mu\text{g/l}$] | Development method | References |
| EQS | 1.3 | Derived to protect from secondary poisoning, derivation of EQS for pelagic organisms not suitable. All types of surface waters | EC (2005) EU RAR (EC 2008) |
| Sediment | | | |
| Description | Value [mg/kg d.w.] | Development method | References |
| $EQS_{SPM, sec. pois.}$ | 17.2 (freshwater) 20.4 (saltwater) | Derived from the biota QS of 3.2 mg/kg (tissue of prey, wet weight) corresponding to EQS of 1.3 $\mu\text{g/l}$ | EC (2005) |
| QS_{sed} | 100 | Derived from a NOEC >1000 mg/kg d.w. for amphibians with an assessment factor of 10 | EC (2005) |
| $PNEC_{sediment}$ | > 100 | | EU RAR (EC 2008) |
| SRC = Serious Risk Concentration | 10 | For 10 % OC and 25 % clay. From the NOEC for study with amphibians of 10 mg/kg d.w. (Larsson and Thurén 1987) | Verbruggen et al. (2001) |
| MPC = Maximum Permissible Concentration | 1.0 | For 10 % OC and 25 % clay. NOEC for study with amphibians of 10 mg/kg d.w. (Larsson and Thurén 1987) with application of safety factor of 10. An additional MPC of 6.9 is derived through the EqP with the MPC_{water} and $\log K_p$ of 3.42 | |
| $ERL_{sediment}$ | 1.0 | For 10 % OC, in mg/kg fresh weight. Effect data was not normalized for OC but OC was between 5 and 13 % fresh weight | van Wezel et al. (1999) |
| NC = Negligible Concentration | 0.01 | For 10 % OC, in mg/kg fresh weight. Effect data was not normalized for OC but OC was between 5 and 13 % fresh weight | |

1.3 Use and emissions

DEHP is a medium-chain phthalate and the most common member of the class of phthalates, which are used as plasticizers in polymer products to make plastic soft and malleable. Originally, plasticizers were used to increase the flexibility and workability mainly of poly(vinyl chloride) (PVC) (EC 2008; Net et al. 2015). ECHA (2008) reports a content of DEHP in flexible PVC at around 30 %. Flexible PVC, which accounts for over 80 % of world plasticizer consumption (OECD 2018) is used in manufacturing a wide variety of consumer products, such as packed food and beverages, soft plastic products such as toys, building and furniture materials such as vinyl flooring, cables, roofs, as well as medical products like blood bags, dialysis equipment, catheters (EC 2008, OECD 2018).



DEHP was identified as high production volume chemical (HPVC) by the OECD (OECD HPVC list 2007). The biggest market for phthalates globally is the People's Republic of China, accounting for around 45% of all use, while Europe and the United States together account for around 25 % of use, with the remainder widely spread around the world (IHS Markit 2015 cited in OECD 2018). Production volume of DEHP in 2015, as reported to US EPA in 2016, ranged between 100 million pounds and 250 million pounds (ca. 45 000 -113 400 tones). This is the annual production volume reported from 1986 to 2015 (US EPA 2019). No figure could be located for Europe or Switzerland.

According to the European Pollutant Release and Transfer Register (E-PRTR), the major diffuse source of DEHP to waters are urban waste water treatment plants, contributing with 96.3 % of the total release to waters or 17 493.54 tones in 2017 (last year available). The second main contributor is the production of pig iron or steel, contributing 1.4 % of the total, and disposal or recovery of hazardous waste 1.3 % (or 230.63 tones). Landfills only account for 0.7 % or 118 tones to DEHP released from diffuse sources to waters in Europe. In 2007, first year of record in the E-PRTR, urban waste water was also the main contributor to DEHP released to surface waters from diffuse sources but it accounted for 82.5 % of the total release and only 5 128.5 tones. Industrial scale production of organic chemicals also contributed with 10.5 % or 665.69 tones, sector that is no longer appearing as releasing DEHP in the registry.

According to the EU RAR (EC 2008), while the general information on manufacture and use of DEHP as a PVC plasticizer was envisaged to be well documented, information on the use of DEHP in formulation and processing of PVC polymers by down-stream industries (off-site; small industries) was not available with respect to the number and size of the sites and it was not known whether the import volumes used in the RAR were representative. It may be that the import volumes are underestimated. In addition, there is no detailed information on formulation/processing of DEHP in non-PVC polymers nor in non-polymer uses and neither on the use of these products.

1.4 Mode of action and sensitivity of taxonomic groups

DEHP is officially recognized in the EU as toxic to reproduction, listed in the Harmonized Classification and Labelling (Harmonized C&L) and in the Candidate list of Substances of Very High Concern (SVHC), and is classified as Endocrine Disrupting (Candidate list of SVHCs) (ECHA 2020).

According to the most recent assessment report from Environment Canada and Health Canada (2017)², at acute exposure levels phthalates act in vertebrates through diester toxicity, a non-specific mode of action similar to baseline (non-polar) narcosis and polar narcosis, but resulting in slightly higher toxicity. Under longer-term exposure, many phthalates also act in vertebrates through specific modes of action, mainly androgen-dependent effects affecting development of the male reproductive tract, as documented in mammalian studies (Health Canada 2015 cited in Environment Canada and Health Canada (2017). Adverse effects in the endocrine system of mammals have been reported in *in vivo* studies through reduced fetal testosterone, results further substantiated mechanistically in down-regulation of genes in the steroidogenic biosynthesis pathway in *in vivo* studies (ECHA 2014)². Adverse effects observed in studies with rats include increased nipple retention, decreased anogenital distance, genital malformations, reduced number of spermatocytes and testicular changes including multinucleated gonocytes, tubular atrophy and Leydig cell hyperplasia, all negative effects on reproduction that can lead to long term negative effects at the population level (ECHA 2014).

² Conclusions and the studies they were based on have not been assessed for reliability and relevance here due to time constraints.



In aquatic organisms, different apical and non-apical effects have been observed in experimental studies with exposures to short- and a number of medium-chain phthalates including DEHP. While non-apical responses related to development, reproduction, and cellular stress have been identified for certain short- and medium-chain phthalates, for well-studied phthalates such as DEHP there is variability or inconsistency among studies and observed effects or responses, such as changes in vitellogenin (VTG) levels or model estimates of receptor binding affinities making it difficult to elucidate the precise mode of toxic action (Environment Canada and Health Canada 2017). According to ECHA (2014), available data indicate that DEHP exposure leads to effects in the sex ratio and reproductive output in fish, and several studies indicate the estrogenic mode of action of DEHP in fish. Corradetti et al. (2013) cited in Environment Canada and Health Canada (2017) reported impaired reproduction in zebrafish by inducing a number of changes, including reduced embryo production at a concentration of 2×10^{-4} mg/l DEHP. Histological changes in fish spermatozoa and gonads (indication of intersex) and retardation of oocyte development following exposure to DEHP have also been reported (Ye et al. 2013, Kim et al. 2002, Norman et al. 2007 cited in Environment Canada and Health Canada 2017). For Environment Canada and Health Canada (2017), non-apical effects for DEHP have been linked to androgen-mediated pathways while estrogen-mediated pathways have produced conflicting data while no data was located for thyroid-mediated pathways at the time of the review (Environment Canada and Health Canada 2017, p. 21). In silico predictions of estrogen receptor (ER) and androgen receptor (AR) binding capabilities of phthalates (Environment Canada and Health Canada 2017, p. 22) showed no binding affinity of DEHP for rainbow trout ER (ERES version 3) but binding affinity for rodent ER while not for AR receptor (TIMES 2014).

According to available data reviewed by Environment Canada and Health Canada (2017), DEHP as other medium-chain phthalates with side-chain backbones of six or fewer carbons—i.e., DBP, BBP, DCHP and B79P—are highly hazardous to fish, invertebrates, and algae, with effects such as behavioral abnormalities in fish, reproductive effects in daphnids, and effects on biomass in algae observed at exposure concentration of less than 1 mg/l. However, most toxicity data comes from studies with test levels that are above the very low water solubility of DEHP of approx. 3 µg/l, causing problems when testing and interpreting the results. At higher concentrations than the water solubility emulsions of microdroplets and surface films are formed that can produce direct physical effects in test organisms such as entrapment. Furthermore, test solutions are unstable and the bioavailable fraction is lower than the nominal concentration, therefore the exposure of the organisms cannot be correctly quantified. Because DEHP had not shown toxic effects at concentrations up to and markedly exceeding the water solubility, neither the solubility predicted from the physico-chemical properties nor the apparent solubility as observed in toxicity tests with daphnids which indicates problems at concentrations > 0.1 mg/l, a PNEC_{water} was not derived in the EQS sheet for DEHP (2005).



2 Environmental fate

2.1 Stability and degradation products

According to ECHA (2020), DEHP shows very slow hydrolysis at neutral pH, leading to mono(2-ethylhexyl)phthalate (MEHP) and 2-ethylhexanol, with an estimated half-life of approximately 2 000 years (Giam et al. 1984).

Similarly, loss via photolysis (simulation using Exposure Analysis Modelling System EXAMS, Wolfe et al. 1980 cited in EC 2008) is estimated at 0 % in river water over a period of 1 hour and 1.8 % in a pond over a period of 30 days. The estimated loss for a period of 200 days was 1.4 % for a eutrophic and 13.7 % for an oligotrophic lake (Wolfe et al. 1980 cited in EC 2008).

According to ECHA (2020), DEHP is readily biodegradable in aerobic conditions by sewage sludge based on the key study that followed OECD 301 B (Modified Sturm-test), showing 82 % degradation (20.3 mg/l initial concentration) after 28 d at 20-22 °C (EC 2008) and several supporting studies showing similar results. A lag phase demonstrates adaptation of microorganisms, however testing with unexposed sludge becomes difficult due to the widespread presence of phthalates in the environment. The biodegradation rate in sewage treatment plants is set to the default value of 1 (h^{-1}) (i. e. DT_{50} -STP = 0.029 d; EC 2008). Under anaerobic conditions, two experimental studies have reported no significant anaerobic degradation in municipal sewage sludge during a 32 d study at several test concentrations (Ziogou et al. cited in ECHA 2020) and during 92 d at 37 °C (Ejlertsson et al. 1997 cited in ECHA 2020). Additional studies showed complete biodegradation with petrochemical sludge under anaerobic conditions with half-lives (disappearance of parent) ranging from 3.3 days to 16.1 days at much lower initial concentrations.

Three studies are cited in ECHA (2020) on primary degradation of DEHP in different surface waters. Degradation of DEHP was observed in eutrophic water (35 – 71 % was mineralised at 29 °C after 40 days), whereas in oligotrophic water no mineralization was observed during 60 days (Subba-Rao et al. 1982 cited in ECHA 2020). In addition to nutrient enrichment, degradation rate in waters is highly temperature-dependent, with no degradation of DEHP at 4°C in Rhine water (Ritsema et al. 1989 and Furtmann 1993 cited in ECHA 2020) and considerable degradation at >20 °C (Ritsema et al. 1989, Furtmann 1993, Subba-Rao et al. 1982 cited in ECHA 2020). Since the main metabolite MEHP is considered ecotoxicologically relevant as being more toxic than the parent compound, ECHA (2020) concludes that the estimation of the biodegradation rate should preferably not be based on primary degradation. According to the results of screening tests on biodegradability from Diefenbach (1994) resulting in a half-life of 15 days in surface water and considering the variability of the degradations observed in test simulating natural conditions, a half-life for DEHP in surface waters of 50 days (at 12°C) is cited in ECHA (2020) as a conservative approach taking due account of data pointing to lower degradation rates at lower temperatures in line with EU-RAR (EC 2008).

Four studies are cited in ECHA (2020) investigating degradation of DEHP in sediments. In a synthetic medium, Chang et al. (2005, cited in ECHA 2020) reported a DT_{50} of 33 d (139.3 d for 12°C according to temperature correction) for whole system (sediment from a highly contaminated river of Taiwan and synthetic medium under anaerobic conditions at 30°C and pH 7) in a modified OECD 311 biodegradation study of 84 days duration. Kickham (2010) performed a test similar to OECD 308 transformation study with marine sediment spiked with DEHP plus overlying bottom water from a depth of approximately 5 m for 144 days incubation time at 13 °C. Concentrations of DEHP declined slowly in test sediment over the incubation period, with approximately 85 % of the original amount of DEHP remaining at the end of the test. A half-life of 337 d was estimated for natural marine bulk



sediment (aerobic surface layer, anoxic lower layers) through first order kinetics while the DEHP metabolite MEHP increased from 48 to 162 $\mu\text{g}/\text{kg}$ d.w. over the first 12 days of incubation, declining and stabilizing at 25-30 $\mu\text{g}/\text{kg}$ d.w. until end of study. Primary biodegradation of MEHP was demonstrated to be very rapid ($DT_{50}=26$ hours at 22°C). The much lower half-life estimated by Chang et al. (2005) compared to the study of Kickham (2010) was attributed to the use of synthetic medium instead of natural water, pre-adapted microorganisms due to the heavy pollution of the river, higher temperature, as well as freshwater conditions which may be more favorable for degradation. Using two supportive studies, ECHA (2020) proposes a conservative half-life (DT_{50}) for DEHP of 300 days for bulk sediment (aerobic and anaerobic) and an infinite DT_{50} for anaerobic sediment for 12°C using a weight of evidence, leading to a final DT_{50} for bulk sediment (overall sediment) of 3 000 days (ECHA 2020), deviating from the initial EU RAR (EC 2008).

2.2 Sorption/desorption processes

With a log K_{ow} of 7.29, DEHP is expected to be strongly adsorbed to organic matter. This is further enhanced by bonding (van der Waals type bonds) between mineral surfaces and the benzene rings and carbonyl groups in DEHP. Although this suggests that the mobility of DEHP in soil would be low, DEHP adsorption to organic acids (especially humic substances) and to non-humic matter such as proteins suggest that colloidal matter may also enhance subsurface transport of contaminants in soils (ECHA 2020). Together with its low water solubility, DEHP is expected to be sorbed to suspended matter and sediments.

Williams et al. (1995) calculated log K_{oc} values ranging from 5.48 to 5.95, with mean 5.68 for freshwater sediment following US EPA batch equilibrium method (EPA OTS 796.2750, Sediment and Soil Adsorption Isotherm). Sullivan et al. (1982) observed that DEHP dissolved in seawater rapidly adsorbed onto and desorbed from three clay minerals (montmorillonite, kaolite, calcium montmorillonite). Average corrected partitioning coefficients for calcite in seawater ranged from 130 000 to 1 270 000 l/kg. Reported K_{oc} values from a marine sediment/water system ranged from 794 000 to 1 260 000 l/kg (Sullivan et al. 1982). Extensive to complete desorption of DEHP was found for all clay minerals and calcite while DEHP showed significant irreversibility of adsorption to sediment, which suggests that marine sediment may act as final repository of DEHP. This is in agreement with field studies and fugacity model results showing that DEHP consistently shows stronger net adsorption to sediments compared to other phthalates such as DBP (Lee et al. 2019).

The geometric mean of valid experimentally determined K_{oc} values and one K_{oc} value estimated from the K_{ow} (Table 1) is 5.71 (Appendix 1). This value is used here for EQS derivation.

Additional log K_{oc} values calculated from suspended matter and water concentrations measured in field studies range from 4.94 to 6.00 as reported by Staples et al. (1997). These values are not considered here for QS derivation due to the non-accessibility of the studies as they were not included in the risk assessments of DEHP (EC 2008, ECHA 2020). Peijnenburg and Stuijs (2006) also reported a mean and median log K_p value of 3.95 from 32 pairs of suspended matter and water concentrations in freshwater and marine samples from the Netherlands (no OC for normalization included). However, a strong positive correlation between sediment OC or OM and DEHP is observed from field study results, according to the high hydrophobicity of DEHP (e.g. Arfeinia et al. 2019, Lee et al. 2019, Zhang et al. 2020). In addition, although particle size also shows a negative correlation with DEHP concentration in sediment in field studies, the distribution of DEHP concentrations is mostly affected by organic content of sediments rather than the size of particles (Arfaeinia et al. 2019).



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). However, it has been argued that substances with very low water solubility are likely to be less bioavailable in the environment through direct water uptake, with more likely exposure through the diet (Environment Canada and Health Canada 2017). No studies are available to discern the contribution of dissolved water versus food/sediment ingestion in aquatic or benthic organisms.

According to a study on the bioaccumulation of five phthalates in the earthworm *Eisenia fetida* (Hu et al. 2005), phthalates that were more hydrophobic were assimilated slower by earthworms according to their higher affinity for soil organic matter (OM). Consequently, this resulted in lower desorption and diffusion of phthalates in the soil solution and lower uptake via dermis. It is noted that only two of the four phthalate studied were detected earthworms. Kinetic BSAF (calculated from uptake and efflux rate constants as K_u/K_e) for DEHP was higher for soil with lower organic matter compared to BSAF for high organic matter (0.244 for sediment with 1.35 % OM compared to 0.073 for 4.53 % OM). This circumstance is as well attributed to the lower desorption, which presumably decreases bioavailability of DEHP in pore water and bioavailability of DEHP from ingested sediment. Aging of DEHP in soils also leads to a decrease in the bioaccumulation and therefore bioavailability, according to the lower extractability of DEHP from soil (Hu et al. 2005).

Lee et al. (2019) also attributed a low bioavailability from sediments for phthalates with high $\log K_{ow}$ according to the positive correlation between \log BAFs (calculated from water concentrations and fish sampled at the Asan Lake of Korea) and $\log K_{ow}$ and negative correlation between \log BSAF values and $\log K_{ow}$. The authors concluded that higher molecular weight phthalates are more strongly adsorbed to sediments than low molecular weight ones. Thus, relatively low bioaccumulation happens into fish compared to high levels of phthalates in the sediment (Lee et al. 2019). This study also found higher concentrations of phthalates in benthic compared to pelagic fishes, suggesting a contribution of sediments in DEHP bioaccumulation through aquatic food webs.

2.4 Bioaccumulation and biomagnification

According to ECHA (2020), 3 studies are available that studied bioconcentration of DEHP using the radioactive parent compound (DEHP). Mayer and Sanders (1973) exposed fathead minnows to a DEHP concentration of 1.9 $\mu\text{g/l}$ during 56 days followed by a depuration phase of 28 days in freshwater. The calculated BCF was 1380 presumably for total weight with a plateau after 28 d of exposure. Depuration reached 50 % of the accumulated DEHP after 7 days in clean freshwater. However, in a later study by Mehrle and Mayer (1976), adult fathead minnows were exposed to 0.9, 2.5, 4.6, 8.1, 14, 30 and 62 $\mu\text{g/l}$ DEHP for 56 days at 25°C in a flow-through system followed by a depuration phase of 28 days. Here, the BCF values based on ^{14}C -DEHP were between 582 and 614 and between 737 and 891 when based on total ^{14}C which is much less than in the study of Mayer and Sander (1973). BCF values that were calculated with the computer program BIOFAC resulted in a mean BCF of 842 ± 105 based on total ^{14}C .

Several studies on the bioaccumulation of DEHP in invertebrates are available from ECHA (2020) (e.g. Sanders et al. 1973, Mayer and Sanders 1973, Streufert et al. 1980, Brown and Thompson 1980 cited



in ECHA 2020) that were used in the EU RAR (EC 2008). The BCFs obtained in these studies, which encompassing from laboratory water-only exposures to mesocosm studies with water and sediment, suggested that DEHP bound to colloids were more bioavailable, resulting a significant exposure route of DEHP to filter feeders such as *Mytilus edulis* and *Mulina lateralis* (EC 2008). The update in ECHA (2020) concludes that these BCFs are not reliable because exposure concentrations are much higher than water solubility of DEHP and all are based on total radioactivity instead of DEHP only.

BAFs and BSAFs from field studies have been recently derived for several species of fish collected at Asan Lake, a lake in South Korea surrounded by industrial complex and farmland, sampled in 2016 and 2017. The concentrations of DEHP were the highest among other phthalates, with concentrations ranging from 6.7 $\mu\text{g}/\text{kg}$ d.w. in bluegill to 140 and 141 $\mu\text{g}/\text{kg}$ d.w. in crucian carp and skygager, corresponding to BAFs of 61 and 1 273, respectively. BSAFs calculated as the average concentration of DEHP in fish in $\mu\text{g}/\text{kg}$ d.w. divided by the average concentration in sediment in $\mu\text{g}/\text{kg}$ d.w. ranged from 0.001 to 0.0086. Higher accumulation is observed in fishes with benthic compared to pelagic life habits.

Mackintosh et al. (2004) studied the distribution of phthalate esters in a marine aquatic food web consisting of eighteen species (pelagic and benthic) that represented approximately four trophic levels at three different locations in False creek, Vancouver. DEHP food-web magnification factors (FWMFs) of 0.32 (0.14-0.71, 95 % CI, based on stable isotope) and 0.34 (0.18-0.64, 95 % CI, based on trophic position) indicate that DEHP does not biomagnify in the studied aquatic food web. It rather undergoes trophic dilution, with high molecular weight phthalates and the lipid equivalent concentrations significantly declining with increasing trophic position.

3 Analysis

3.1 Methods for analysis and quantification limit

DEHP can be analyzed together with other phthalates using several analytical techniques, with different limits of quantification (Table 4).

Limits of quantification in the low $\mu\text{g}/\text{kg}$ d.w. can be achieved for sediments by Gas Chromatography - Tandem Mass Spectrometry (GC-MS/MS) conducted by service and research laboratories (LABERCA, Personal Communication; Loizeau et al. 2017; Lee et al. 2019). DEHP can be also analyzed by Liquid chromatography–mass spectrometry (LC-MS) but detection and quantification limits are in the range of tens to hundreds $\mu\text{g}/\text{kg}$ d.w. (Nagorka and Koschorreck 2020).

Table 4 Methods for DEHP analysis in sediments and corresponding limits of detection (LOD) and limits of quantification for sediment samples (LOQ) ($\mu\text{g}/\text{kg}$ d.w.). n.a. means not reported.

| LOD | LOQ | Analytical method | Reference |
|------|------|-------------------|--|
| 43 | 130 | LC/MS | Nagorka and Koschorreck (2020) |
| n.a. | 1 | GC-MS/MS | LABERCA, Personal Communication; Loizeau et al. (2017) |
| 0.92 | 2.75 | GC-MS/MS | Lee et al. (2019) |

3.2 Environmental concentrations

Measured environmental concentrations (MEC) of DEHP in sediments are summarized in Table 5. The concentrations are presented for recent sampling campaigns. In sediments from small streams in Switzerland collected in August 2018, DEHP concentrations ranged from < 1 (LOD) to 525.6 $\mu\text{g}/\text{kg}$ d.w.



in sediments sieved at < 2 mm, and from 21.4 to 1 197.5 $\mu\text{g}/\text{kg}$ d.w. in sediments sieved at < 63 μm , with means of 209.1 and 311.6 $\mu\text{g}/\text{kg}$ d.w. respectively. These results indicate that DEHP is preferentially accumulated in the fine fraction at contaminated sites. The concentrations in Lake Geneva measured in 2016 ranged from 30 to 7 080 $\mu\text{g}/\text{kg}$ d.w., with a median concentration of 90 $\mu\text{g}/\text{kg}$ d.w. and peak concentrations close to the WWTP in the Bay of Vidy (Loizeau et al. 2017). The concentrations in Lake Geneva were slightly lower but on average within the same range as those measured in 2007 (Edder et al. 2008). These concentrations are in the same range as those measured in Lake Asan, a large lake surrounded by an industrial complex and farmland (Lee et al. 2019), although the median concentration determined in Lake Asan is by a factor of approx. 10 higher than the median concentration determined in Lake Geneva.

In Germany, analysis of suspended matter from several rivers reported concentrations ranging from 488 to 6 720 $\mu\text{g}/\text{kg}$ d.w. in stored samples from 2005 and 2006. In 2017, concentrations had decreased and ranged from 225 to 2 080 $\mu\text{g}/\text{kg}$ d.w., showing an overall decreasing trend in DEHP concentrations in suspended matter and an increasing trend for other phthalates used as substitutes for DEHP (Nagorka and Koschorrek 2020).

Table 5 Measured environmental concentrations (MEC) of DEHP in Switzerland and elsewhere. All concentrations expressed as $\mu\text{g}/\text{kg}$ d.w. for sediment if not indicated otherwise. n.d. not detected

| Country | MEC (min-max) | Nr sites | Comments | Reference |
|-------------|---|----------|--|---|
| Switzerland | Sediment < 2 mm: 209.1 (mean) (<1-525.6) Sediments < 63 μm : 311.6 (mean) (21.4-1197.5) | 18 | Small streams sampled in August 2018. Different levels and sources of pollution. Detection frequency ca. 100 % | Centre Ecotox, unpubl. data |
| Switzerland | 90 (median) (30-7 080) | 31 | Lake sediment sampled in 2016. Maximum concentration close to WWTP. Detection frequency 100 % | Loizeau et al. (2017) |
| Germany | 2 005-2 006: 488-6 720 | 11 | Suspended matter from German rivers. Detection frequency 100 % | Nagorka and Koschorrek (2020) |
| | 2017: 225-2 080 | 13 | | |
| | 2009: 278, 867 | 2 | Danube suspended matter | |
| Germany | 2002: 700 (median) (210-8 440) | 35 | German surface waters (rivers, lakes, channels) | Fromme et al. (2002) cited in Leschber (2006) |
| | 2002-2010: 500-10 000 | n.a. | Particle bound phthalates (DEHP and DBP) in Bavarian surface waters | LfU (2014, Landesamt für Umwelt Bayern) |
| USA | 1 800 (average concentration) | 10 | 39.2 % of collected sediments showed stated concentration, sediments from Mud Dump Sites in the New York Bight | Friedman et al. (2000) cited in Leschber (2006) |
| South Korea | 3.6-8 326 (median: 1 020, mean: 2 056) | 47 | Sediment from Asan Lake sampled in 2016 and 2017, surrounded by industrial complex and farmland | Lee et al. (2019) |



4 Effect data (spiked sediment toxicity tests)

A non-filtered bibliographic search was performed for DEHP (by CAS number) in the US Ecotox Data Base (U.S. EPA 2016) which yielded two publications on sediment organisms: Call et al. (2001) and Brown et al. (1996). A search in the German Environmental Office database ETOX did not yield any relevant results. A key word search performed on Scopus (DEHP + sediment + toxicity, no restriction regarding publication date) resulted in 468 publications, none of which were based on spiked sediment tests – except the Call et al. (2001) publication.

Potentially unpublished data was searched for in registration information, risk assessment dossiers and EQS dossiers (Environment Canada 2017, RIVM 2001, EC 2008). The EU risk assessment report on DEHP lists six toxicity tests performed with benthic organisms exposed via spiked sediment (EC 2008).

One of the original reports (Wennberg et al. 1997 cited in ECHA 2020) is not available but is documented as indicated in EC (2008) and ECHA (2020). It is considered not reliable according to ECHA (2020) assessment on reliability being compromised by spiking with ethanol.

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).

According to the (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). Available data that originate from ≥ 26 d tests are considered as “chronic” endpoints while effect data from 10 d tests are considered here as acute, independently of the measured endpoint.

Proposed SQC (EQS_{sed}) for Bis(2-ethylhexyl) phthalate (DEHP)



Table 6 Sediment effect data collection for DEHP 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 not reliable is in grey font.

| Group | Species | Test compound | Exposure ^a | Equilibration time | Endpoint | Test duration | Temperature | Effect concentration | Value [mg/kg d.w.] | Sediment type | Normalized value [mg/kg d.w., 1% OC] | Normalized value [mg/kg d.w., 5%OC] | Chem. Analysis ^b | Note | Validity | References |
|--|---|--------------------|-----------------------|------------------------------|------------------|---------------|-------------|----------------------|--------------------|--|--------------------------------------|-------------------------------------|-----------------------------|--|----------|----------------------|
| Acute toxicity data in freshwater | | | | | | | | | | | | | | | | |
| Insecta | <i>Chironomus tentans</i> (10-12d old larvae) | DEHP (99 % purity) | T | 1 d (mixing 6 d in rotation) | Survival | 10 d | 23 °C | NOEC (unbound) | ≥ 3 000 | Uncontaminated, natural sediment from Airport Pond and West Bearskin Lake, 4.8 % TOC, 46.9 % sand, 30.2 % silt, 2.34 % coarse clay, 20.5 % fine clay | ≥ 625 | ≥ 3 125 | nom-i | Limit test. Sediment, porewater and overlying water analysed at day 0 and 10, mean recovery 86.4%. Additional details in companion paper Call et al. 2001b | R2/C2 | Call et al. (2001a) |
| Insecta | <i>Chironomus tentans</i> (10-12d old larvae) | DEHP (99 % purity) | T | “ | Growth | 10 d | “ | NOEC (unbound) | ≥ 3 000 | “ | ≥ 625 | ≥ 3 125 | nom-i | “ | R2/C2 | Call et al. (2001a) |
| Amphipoda | <i>Hyalella azteca</i> (7-14d old) | DEHP (99 % purity) | T | “ | Survival | 10 d | “ | NOEC (unbound) | ≥ 3 000 | “ | ≥ 625 | ≥ 3 125 | nom-i | “ | R2/C2 | Call et al. (2001a) |
| Amphipoda | <i>Hyalella azteca</i> (7-14d old) | DEHP (99 % purity) | T | “ | Growth | 10 d | “ | NOEC (unbound) | ≥ 3 000 | “ | ≥ 625 | ≥ 3 125 | nom-i | “ | R2/C2 | Call et al. (2001a) |
| Acute toxicity data in marine water | | | | | | | | | | | | | | | | |
| No data available | | | | | | | | | | | | | | | | |
| Chronic toxicity data in freshwater | | | | | | | | | | | | | | | | |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | 5 d (mixing 7 d) | Hatching success | 26 d | 10 °C | NOEC (unbound) | ≥ 845 | Natural coarse sediment, TOC 16.0 | ≥ 52.8 | ≥ 263.9 | m-t | 3 test concentrations at 2 temperatures. Only results for 10°C reported, low reliability of results at 5°C. Recovery at start <80% attributed to non-homogeneous sediments | R2/C1 | Solyom et al. (2001) |

Proposed SQC (EQS_{sed}) for Bis(2-ethylhexyl) phthalate (DEHP)



| Group | Species | Test compound | Exposure ^a | Equilibration time | Endpoint | Test duration | Temperature | Effect concentration | Value [mg/kg d.w.] | Sediment type | Normalized value [mg/kg d.w., 1% OC] | Normalized value [mg/kg d.w., 5%OC] | Chem. Analysis ^b | Note | Validity | References |
|----------|--|--------------------|-----------------------|--------------------|----------------------------------|---------------|-------------|----------------------|--------------------|--|--------------------------------------|-------------------------------------|-----------------------------|---|----------|---|
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | 5 d (mixing 7 d) | Hatching success | 26 d | 10 °C | NOEC (unbound) | ≥ 1 165 | Natural fine sediment with TOC 17.3 | ≥ 67.3 | ≥ 336.4 | m-t | " | R2/C1 | Solyom et al. (2001) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Survival | 26 d | 10 °C | NOEC (unbound) | ≥ 845 | Natural coarse sediment, TOC 16.0 | ≥ 52.8 | ≥ 263.9 | m-t | " | R2/C1 | Solyom et al. (2001) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Survival | 26 d | 10 °C | NOEC (unbound) | ≥ 1 165 | Natural fine sediment with TOC 17.3 | ≥ 67.3 | ≥ 336.4 | m-t | " | R2/C1 | Solyom et al. (2001) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Visual morphological deformation | 26 d | 10 °C | NOEC (unbound) | ≥ 845 | Natural coarse sediment, TOC 16.0 | ≥ 52.8 | ≥ 263.9 | m-t | " | R2/C1 | Solyom et al. (2001) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Visual morphological deformation | 26 d | 10 °C | NOEC (unbound) | ≥ 1 165 | Natural fine sediment with TOC 17.3 | ≥ 67.3 | ≥ 336.4 | m-t | " | R2/C1 | Solyom et al. (2001) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Growth | 26 d | 10 °C | NOEC (unbound) | ≥ 845 | Natural coarse sediment, TOC 16.0 | ≥ 52.8 | ≥ 263.9 | m-t | " | R2/C1 | Solyom et al. (2001) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Growth | 26 d | 10 °C | NOEC (unbound) | ≥ 1 165 | Natural fine sediment with TOC 17.3 | ≥ 67.3 | ≥ 336.4 | m-t | " | R2/C1 | Solyom et al. (2001) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | Not reported | Hatching (measured after 14d) | 29 d | 10 °C | NOEC (unbound) | ≥ 433 | Natural sediment with OM 22.5 % measured as loss of ignition, converted to 13.2 % OC with factor 1.7 | ≥ 32.8 | ≥ 166 | m | 7 concentrations tested, one concentration tested with 3 different sediments | R3/C1 | Wennberg et al. 1997 cited in ECHA (2020) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Survival | 29 d | 10 °C | NOEC (unbound) | ≥ 433 | " | ≥ 32.8 | ≥ 166 | m | " | R3/C1 | Wennberg et al. 1997 cited in ECHA (2020) |
| Amphibia | <i>Rana arvalis</i> (eggs) | DEHP | R | " | Growth | 29 d | 10 °C | NOEC (unbound) | ≥ 433 | " | ≥ 32.8 | ≥ 166 | m | " | R3/C1 | Wennberg et al. 1997 cited in ECHA (2020) |
| Amphibia | <i>Rana arvalis</i> (field collected eggs) | DEHP (97 % purity) | S | 7 d | Hatching success | 60 d | | NOEC | 27.08 | Natural sediment from pond, dry weight = 25-40 % (mean 32.5 %), OM = 21-33% (mean 27%) | 1.69 | 8.46 | m | NOEC from Table 1 (8.8 mg/kg w.w.) converted to d.w. using 32.5 % mean dw, estimated 16 % OC (27 % OM/1.724 | R4/C1 | Larsson and Thuren (1987) |
| Amphibia | <i>Rana arvalis</i> | DEHP, 97 % purity | S | 7 d | Survival | 60 d | | NOEC (unbound) | ≥ 2 415 | " | ≥ 151 | ≥ 755 | m | NOEC from Table 1 (784.8 mg/kg w.w.), further details see above | R4/C1 | Larsson and Thuren (1987) |
| Amphibia | <i>Rana arvalis</i> | DEHP, 97 % purity | S | 7 d | Median hatching time | 60 d | | NOEC (unbound) | ≥ 2 415 | " | ≥ 151 | ≥ 755 | m | " | R4/C1 | Larsson and Thuren (1987) |

Proposed SQC (EQS_{sed}) for Bis(2-ethylhexyl) phthalate (DEHP)



| Group | Species | Test compound | Exposure ^a | Equilibration time | Endpoint | Test duration | Temperature | Effect concentration | Value [mg/kg d.w.] | Sediment type | Normalized value [mg/kg d.w., 1% OC] | Normalized value [mg/kg d.w., 5%OC] | Chem. Analysis ^b | Note | Validity | References |
|---------------------|--|--|-----------------------|--|---|--|-------------|----------------------|--------------------|---|--------------------------------------|-------------------------------------|-----------------------------|---|----------|---------------------------|
| Amphibia | <i>Rana arvalis</i> | DEHP (97 % purity) | S | 7 d | Development | 60 d | | NOEC (unbound) | ≥ 2 415 | " | ≥ 151 | ≥ 755 | m | " | R4/C1 | Larsson and Thuren (1987) |
| Insecta | <i>Aeshna sp</i> | DEHP | S | 5 d (3 d plus 2 d in test beakers before water addition) | Predatory efficiency (measured as successful strikes of labium extensions) | 63 d (21 d acclimatization to test exposure plus 40 d observation) | | NOEC ^c | 780 | Natural sediment from eutrophic pond, 40 % dw at 105°C, OC estimated from related study (loss of ignition at 530°C = 23 %) (Larsson et al. 1986) | 60 | 300 | m | LOEC w.w. converted to d.w. with factor 2.6 from EC TGD (2018); normalized OC values estimated with 13% OC (23% OM /1.724, out boundaries for normalization 0.2-10% OC) | R3/C1 | Woin and Larsson (1987) |
| Insecta | <i>Chironomus riparius</i> (<24h post-hatch) | DEHP (mixed radiolabelled, -99.5 % and stable 93.3 % purity) | R | Overnight (18 h mixing) | Time to first emergence | 28 d | 20°C | NOEC (unbound) | ≥ 10 000 | Natural sediment from river Frome, wet:dry ratio = 2.35, LOI (550°C) = 8.6% w.w., TOC = 3.6 % w.w. (estimated as 42 % of the organic matter by the authors), 23.6 % coarse sands, 40.6 % medium/very fine sands, 35.8 % silt/clay | ≥ 2'778 | ≥ 13'889 | nom | Recovery of DEHP in sediment: 100-140% (start), 110-130% (end). NOEC derived from nominal | R2/C1 | Brown et al. (1996) |
| Insecta | <i>Chironomus riparius</i> (<24h post-hatch) | " | R | Overnight (18 h mixing) | Time to 50 % emergence | 28 d | 20°C | NOEC (unbound) | ≥ 10 000 | " | ≥ 2 778 | ≥ 13 889 | nom | " | R2/C1 | Brown et al. (1996) |
| Insecta | <i>Chironomus riparius</i> (<24h post-hatch) | " | R | Overnight (18 h mixing) | Emergence at 28 d | 28 d | 20°C | NOEC (unbound) | ≥ 10 000 | " | ≥ 2 778 | ≥ 13 889 | nom | " | R2/C1 | Brown et al. (1996) |
| Insecta | <i>Chironomus riparius</i> (<24h post-hatch) | " | R | Overnight (18 h mixing) | Sex distribution | 28 d | 20°C | NOEC (unbound) | ≥ 10 000 | " | ≥ 2 778 | ≥ 13 889 | nom | " | R2/C1 | Brown et al. (1996) |
| Microbial community | | DEHP | R | n.a. (most probably overnight) | Oxygen demand (measured at two times: after 100h to 1 week, and after 1 to 2 weeks) | 4 weeks | 5°C | NOEC | 43.42 | Natural sediment and overlying water from eutrophic lake, LOI (550°C) = 23 % w.w., TOC = 13.5 % (as LOI/1.7), converted from w.w. to d.w. using conversion factor of 2.6 (EC 2018). | 3.22 | 16.1 | m | Measured at end of test in top 5 cm sediment, while DEHP injected at sub-surface layer therefore measured concentrations | R3/C1 | Larsson et al. (1986) |

Proposed SQC (EQS_{sed}) for Bis(2-ethylhexyl) phthalate (DEHP)



| Group | Species | Test compound | Exposure ^a | Equilibration time | Endpoint | Test duration | Temperature | Effect concentration | Value [mg/kg d.w.] | Sediment type | Normalized value [mg/kg d.w., 1% OC] | Normalized value [mg/kg d.w., 5%OC] | Chem. Analysis ^b | Note | Validity | References |
|-------|---------|---------------|-----------------------|--------------------|----------|---------------|-------------|----------------------|--------------------|---------------|--------------------------------------|-------------------------------------|-----------------------------|--|----------|------------|
| | | | | | | | | | | | | | | is most probably an underestimation. Recovery 76-134 %. LOEC estimated from measured (134% nominal), converted into a NOEC as LOEC/2 because effect is <20 % (EC 2018) | | |

^a S: static; R: static renewal; T: flow-through

^b m: based on measured concentration at the test end; nom: based on nominal concentrations; nom-i: based on nominal concentrations, in case recovery was 80-120 %; m-t: time-averaged measured concentrations at start and end of the test.

^c NOEC estimated as LOEC/2 according to EU TGD p. 154.



4.1 Graphic representation of effect data

All available data have been plotted independently of their relevance and reliability before and after normalization to a standard sediment with 5 % OC content (Figures 1a and 1b, respectively).

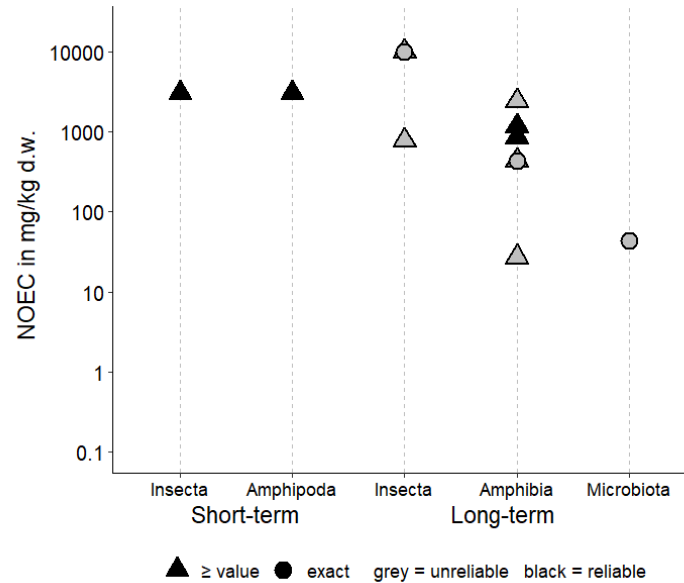


Figure 1a Graphical representation of short- and long-term effect data from spiked sediment toxicity tests with DEHP. Data are not normalized for OC.

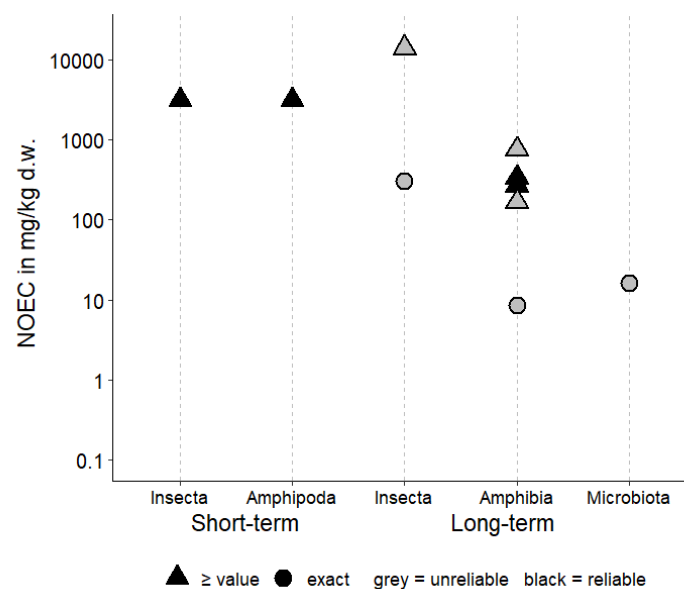


Figure 1b Graphical representation of short- and long-term effect data from spiked sediment toxicity tests with DEHP, normalized to 5 % OC content of the sediment used.

All relevant and reliable short- and long-term effect concentrations are unbounded values (all values below are normalized to 5 % OC):

- (a) the acute NOECs of $\geq 3\ 125$ mg/kg d.w. for *C. riparius* and *H. azteca* (Call et al. 2001), and



- (b) the chronic NOECs of ≥ 263.9 mg/kg d.w. for *R. arvalis* (Solyom et al. 2001) and $\geq 13\,899$ mg/kg dw for *C. riparius* (Brown et al. 1996).

For unbounded (\geq) NOEC values, the choice of the range of test concentrations influences the NOEC and therefore no sound conclusions can be drawn regarding the sensitivity of different test organisms. Overall, the tested DEHP concentrations do not appear to have a toxic effect on the tested organisms.

4.2 Comparison between marine and freshwater species

No marine data was available.

4.3 Overview of reliable and relevant long-term 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”.

Effect data for *Rana arvalis* (several endpoints) from Solyom et al. (2001) were evaluated as R2/C1. The chronic effect data for *Chironomus riparius* from Brown et al. (1996) were also evaluated as R2/C1. These studies are summarized below.

Solyom et al. (2001) « Further investigations on the influence of sediment associated phthalate esters (DEHP and DINP) on hatching and survival of the moorfrog *Rana arvalis*”.

- Species: *Rana arvalis*.
- No standardised guideline was followed, and the study was not conducted according to the principles of GLP.
- Exposure was started with eggs with intact jellycoat and continued for 35 d at 5°C and 26 d at 10°C. Only data from 10°C exposures is considered reliable due to 5°C exposures adversely affecting test organisms.
- Experimental sediment: 2 types of sediments: fine sediment (mostly degraded material, particles > 2mm = 0.1 % d.w., TOC = 17 % d.w.) and coarse sediment (contained undegraded material, particles > 2mm = 4.7 % d.w., TOC = 16 % d.w.).
- Spiking and equilibration time: DEHP was spiked with acetone as solvent, directly into dried sediment, followed by evaporation of acetone under reduced pressure in an evaporator. The dry, spiked sediment was then mixed with wet sediment for 7 d on a shaking board. Afterwards, sediment-water systems were set up, left for 5 days equilibration with added lake water then eggs were added.
- Bioassay: 3 nominal exposure concentrations: 100, 300, and 1 000 mg/kg d.w.; tested in 5 replicates for each temperature/sediment combination, 50 eggs per replicate. Control and solvent control were run in parallel. Photoperiod of 12h light and 12h darkness, beakers were gently aerated.
- Daily measurements of temperature, oxygen, and pH; at least weekly measurements of ammonia and nitrite; in 15 beakers representing all treatments. Temperature variations <0.5°C, oxygen levels always >70 %. pH values decreased below 6.5, addition of NaHCO₃ to maintained appropriate pH levels on days 9, 14 and 18. Ammonia and nitrite levels at levels appropriate for the species. No bacteria/fungi infections in none of the beakers.
- Measured DEHP concentrations: at start and end of experiment, ranged between 73 and 118% of nominal concentrations, except lowest concentration (100 mg/kg d.w.) in the fine sediment tested at 5°C: 242 % of nominal (242 mg/kg d.w.). Relevant media were monitored for DEHP concentrations before and during exposures. Effect concentrations expressed as time-average due to variation in measured versus nominal at start of the test.



- Endpoints: median hatching time (monitored on day 9, 12, 16 and 21): approx. 12 d at 10°C and ± 24d at 5°C. Hatching success: 92-95 % at 10°C and 73-86 % at 5°C in all controls and concentrations. Mortality of tadpoles: 0-3 % for both temperatures at all concentrations. Deformation of tadpoles (retarded tail): 0-2.3 % for both temperatures at all treatments.
- No statistically significant differences between controls and exposure concentrations.
- Results: Hatchability of eggs and survival of tadpoles NOEC ≥ 1 000 mg/kg d.w. (nominal concentration), corresponding to ≥ 1 165 mg/kg d.w. time-averaged measured concentrations in fine sediment and ≥ 845 mg/kg d.w. time-averaged measured concentrations in coarse sediment.

Brown et al. (1996) "The effect of phthalate ester plasticisers on the emergence of the midge (*Chironomus riparius*) from treated sediments".

- Species: *Chironomus riparius*.
- No standardised guideline was followed, and the study was not conducted according to the principles of GLP.
- The study set-up comprised a semi-static soft-bottom water-sediment study. Each breaker (borosilicate 400-mL cylinders) had a bottom layer of 94 g w.w. homogenized natural sediment spiked with DEHP in acetone.
- Origin of test organisms: continuous laboratory culture.
- Experimental sediment: natural river sediment with a wet:dry ratio of 2.35. Loss on ignition of dried sediment at 550°C for ±1h showed an organic content of 8.6 % w/w and an estimated organic carbon content of 3.6 % w/w based on the assumption that 42 % of the organic matter are organic carbon. The sediment was analyzed for grain size in a particle size analyzer (Malvern 3600E) and sieving for fractions >0.5mm: 23.6 % coarse sands (0.5-2mm), 40.6% medium/very fine sands (0.0625-0.5mm), 35.8 % silt/clay (<0.0625mm).
- Spiking and equilibration time: spiking via addition of 4 mL DEHP acetone solution to an oven dried portion of the sediment (34 g d.w. [20 % of total spiked sediment]), dried at 60°C for >48h). Sediment and acetone solution were mixed in a glass bottle, acetone left to evaporate, and 320 g wet sediment (equating 170 g d.w.) plus 46 mL dilution water added afterwards. 40 g d.w. were placed into test vessels after spiked sediment was left for mixing at 20 rpm for 18h (at 20°C). Dilution water was added up to the 300 mL-mark and the system left to equilibrate overnight before addition of test organisms.
- Overlying water: glass-distilled water with added NaHCO₃ (96 mg/l), CaSO₄·2H₂O (60 mg/l), MgSO₄·7H₂O (122.7 mg/l), and KCl (4 mg/l); pH of 8.25. Aerated for >2h before use.
- Bioassays: the animals were exposed to DEHP in a semi-static soft-bottom water-sediment study. Each beaker (borosilicate 400 mL cylinders) had a bottom layer of 94 g w.w. homogenized natural sediment. Water temperature was 20±1°C. Throughout the exposure period, light regime followed a 16h light and 8h dark cycle with a 15 min transition time. 70 % of overlying water was replaced after 14 d. The experiment consisted of 5 test conditions (two control series and three DEHP exposure series – nominally 100, 1 000 and 10 000 mg/kg d.w.), with 3 replicates, each containing 20 larvae. Test vessels were randomly allocated.
- Test endpoints: emergence and sex ratio after 28 d – with no effects on both endpoints.
- Measured DEHP concentrations: sediments were dried prior to methanol extraction. Thanks to the fraction of radio labelled DEHP in some of the tested concentrations, analysis could be achieved using liquid scintillation counting (with a Beckmann LS5801 liquid scintillation spectrometer). For non-labelled extracts, radio thin layer chromatography with both normal and reverse phase was used (with a Bioscan System 200 imaging scanner). Measurements at start showed 100-140 % recovery and at end 110-130 %. Results are expressed as measured concentrations for EQS derivation.



- Statistics: moving average angle analysis (time to 50 % emergence), one-way ANOVA on arcsine square root proportion of females (sex ratio).
- Results: time to first emergence, time to 50 % emergence and total emergence at 28 d, and sex ratio NOEC $\geq 10\ 000$ mg/kg d.w. (nominal concentration) corresponding to 13 889 mg/kg d.w.

5 Derivation of QS_{sed}

According to the EU 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 chronic effect datum available for DEHP is the unbounded NOEC of ≥ 289 mg/kg d.w. (5 % OC) for *R. arvalis*.

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

| Species | Exposure duration (d) | Endpoint | NOEC/EC ₁₀ [mg/kg d.w.] | OC [%] | NOEC/EC ₁₀ [mg/kg d.w. 5 % OC] |
|----------------------------|-----------------------|--|------------------------------------|--------|---|
| <i>Rana arvalis</i> | 26 d | Hatching success, survival, growth, visual morphological deformation | ≥ 845 | 16.0 | ≥ 269 |
| <i>Chironomus riparius</i> | 28 d | Emergence | $\geq 10\ 000$ | 4.8 | $\geq 13\ 889$ |

In case of long-term NOECs or EC₁₀s being available for two species the TGD recommends the application of an assessment factor of 50 on the lowest credible datum (Table 11 in EC (2018)).

$$QS_{sed, AF} = \frac{\text{lowest EC}_{10} \text{ or NOEC}}{AF}$$

$$QS_{sed, AF} = \frac{269 \left(\frac{mg}{kg} \right)}{50} = 5.38 \left(\frac{mg}{kg} \right)$$

The application of an AF of 50 to the lowest datum results in a $QS_{sed, AF} = 5.38$ mg/kg d.w. for a standard sediment with 5 % OC, which corresponds to 1.08 mg/kg d.w. for a sediment with 1 % OC representing a worst case scenario in Switzerland.

According to the TGD for EQS (section A1.3.2.9, p. 144), unbounded effect concentrations cannot be used to derive an EQS value. Since for DEHP, all relevant and reliable effect concentrations are



unbounded values, it appears a pragmatic approach to use the lowest of these values for EQS derivation. However, the derived $QS_{sed, AF}$ are designated as tentative value.

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 NOEC/EC₁₀, 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

According to the EU EQS datasheet (EC 2005) and the EU RAR (EC 2008, ECHA 2020) an EQS of 1.3 µg/l was derived based on protection of top predators for secondary poisoning, which is used for deriving a QS using the EqP for comparison purposes.

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

The valid log K_{oc} reported for DEHP are in the range of 5.41-5.95 (Table 1, Appendix 1). Reported experimental log K_{ow} for DEHP is 7.29 (Table 1), estimated log K_{oc} is 6.00. The geometric mean Log K_{oc} of 5.71 is used for EQS derivation via EqP.

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 for EQS 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 $QS_{sed, EqP}$ (Table 8), the partition coefficient between water and sediment has been estimated as the fraction of organic carbon multiplied by organic carbon partition coefficient ($K_p = f_{oc} * K_{oc}$) 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.



An additional AF of 10 should be applied to the resulting $QS_{sed,EqP}$ for substances with $\log K_{ow} > 5$. According to the experimental $\log K_{ow} > 5$ the additional AF of 10 is warranted.

Table 8 Derived $QS_{sed,EqP}$ for a mean K_{OC} based on Appendix I and the EQS from the EU EQS datasheet (EC 2005). The partition coefficient solid-water sediment (Kp_{sed}) is estimated for a sediment with 5 % OC (standard EC TGD sediment) and 1% OC (worst case scenario in Switzerland).

| | K_{OC} [l/kg] | Kp_{sed} [l/kg] | $K_{sed-water}$ [m ³ /m ³] | $PNEC_{water}$ [µg/l] | $QS_{sed,EqP}$ [µg/kg w.w.] | $QS_{sed,EqP}$ [µg/kg d.w.] | Included AF |
|--------|--------------------|----------------------|--|--------------------------|--------------------------------|--------------------------------|----------------|
| 5 % OC | 512 716 | 25 635.8 | 12 818.7 | 1.3 | 12 820 | 3 333 | 10 |
| 1 % OC | 512 716 | 5 127.2 | 2 564.4 | 1.3 | 2 777 | 667 | 10 |

Given the analytical challenges in DEHP analysis in surface waters, DEHP is most often monitored within the EU WFD in suspended particulate matter. Accordingly, the EU EQS datasheet (EC 2005) proposed a $QS_{SPM,EqP}$ of 17.2 mg/kg d.w. for suspended matter derived using a Kp of 16 500 l/kg and a concentration of suspended particulate matter in freshwater environments of 15 mg/l. The differences in the derived $QS_{sed,EqP}$ and the $QS_{SPM,EqP}$ are therefore attributed to the different calculation methods for suspended matter (EC 2005) compared to those for sediments in the EU TGD (EC 2018) and the additional AF of 10 for this last one.

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

No field or mesocosm studies that provide effect concentrations of DEHP are available on benthic invertebrates or amphibians.

8 Toxicity of degradation products

According to the EU RAR (EC 2008), the degradation product Mono-2-ethylhexyl phthalate (MEHP) is formed during biodegradation. MEHP causes reproductive toxic effects in studies on mammals (EC 2008, Net al. al. 2015) but other ecotoxicological properties of MEHP are unknown. The extent of formation of MEHP in the environment was also unknown at the time of completing the DEHP RAR (EC 2008). However, the large amount of DEHP observed in DEHP-related technological processes was expected to be a considerable potential for formation and distribution of MEHP. The fate of this metabolite can be expected to differ from DEHP's fate due to different chemical and physical properties. Therefore, the EU RAR concluded that it was not possible based on available data to estimate the environmental (and human) risks of MEHP formed in the environment (EC 2008).

It is concluded that the lack of (a) information on environmental behavior of MEHP and (b) information on their ecotoxicity is the reason that the present EQS_{sed} proposal does not include a specific risk assessment for the degradation products of DEHP.

9 EQS_{sed} proposed to protect benthic species

The different QS values for each derivation method included in the EU TGD for EQS are summarized in Table 9. According to the EU TGD for EQS, 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 for EQS and their corresponding AF. All concentrations expressed as mg/kg d.w.

| | Sediment 5 % TOC | Sediment 1 % TOC | AF |
|--|---------------------|---------------------|----|
| $QS_{sed,SSD}$ | -- | -- | -- |
| $QS_{sed,EqP}$ | 3.33 | 0.67 | 10 |
| $QS_{sed,AF}$ | 5.38 | 1.08 | 50 |
| Proposed EQS_{sed} | 5.38 | 1.08 | |

A EQS_{sed} of 1.08 mg/kg (1 % OC) for DEHP including the application of an AF of 50 is thus suggested.

9.1 Protection of benthic organisms and uncertainty analysis

According to the critical data used in EQS sediment derivation and additional supportive information, the proposed EQS for sediment should protect amphibians as well as benthic invertebrates from general toxicity as they appear to be less sensitive to DEHP than amphibians in spiked sediment toxicity tests. The proposed EQS_{sed} is also lower but within the same order of magnitude than the estimated NOEC for microbial activity that is not used in EQS derivation due to lower reliability.

According to the TGD for EQS (section A1.3.2.9, p. 144), unbounded effect concentrations cannot be used to derive an EQS value. Since for DEHP, all relevant and reliable effect concentrations are unbounded values, it appears a pragmatic approach to use the lowest of these values for EQS derivation. However, the derived $QS_{sed, AF}$ is designated as tentative value.

DEHP is known for its endocrine effects but this endpoint is not considered in the EQS_{sed} . However, the derived $QS_{sed,EqP}$ based on protection of top predators for secondary poisoning, which is within the same order of magnitude of the proposed EQS_{sed} , includes endpoints in its derivation that are related to endocrine effects. The EQS_{sed} should partially be protective against this endpoint.

It is noted here that recently Environment Canada and Health Canada (2017) derived a PNEC for surface waters within the context of the draft screening risk assessment of phthalates of 0.07 $\mu\text{g/l}$ based on a 21 d EC_{90} for zebrafish of 0.2 $\mu\text{g/l}$ (Corradetti et al. 2013) and an assessment factor of 3. The derivation procedure is not in line with that in the EU TGD (EC 2018) and the effect data used in this recent draft screening assessment have not been assessed here for reliability and relevance. However the estimated $QS_{sed,EqP}$ based on this PNEC water would be two orders of magnitude lower than the proposed EQS_{sed} .

In addition, it is noted that DEHP occurs in sediments together with other phthalates, the need for assessing phthalates as a mixture is not within the scope of this report but should be further evaluated.

The proposed EQS_{sed} does not involve analytical challenges.

10 References

- Arfaenia H, Fazlzadeh M, Taghizadeh F, Saeedi R, Spitz J, Dobaradaran S. (2019). Phthalate acid esters (PAEs) accumulation in coastal sediments from regions with different land use configuration along the Persian Gulf. *Ecotox Environ Saf* 169: 496-506.
- Brown D, Thompson RS, Stewart KM, Croudace CP, Gillings E. (1996). The effect of phthalate plasticizers on the emergence of the midge (*Chironomus riparius*) from treated sediments. *Chemosphere* 32: 2177–2187.



- Call DJ, Cos DA, Geiger DL, Genisot, KI, Markee TP, Brooke LT, Polkinghorne CN, Vandeventer FA, Gorsuch JW, Robillard KA, Parkerton TF, Reiley MC, Ankley GT, Mount DR. (2001a). An assessment of the toxicity of phthalate esters to freshwater benthos. 2. Sediment exposures. *Environ Toxicol Chem* 20(8):1805–1815.
- Call DJ, Cos DA, Markee TP, Geiger DL, Brooke LT, Vandeventer FA, Cox DA, Genisot, KI, Robillard KA, Gorsuch JW, Parkerton TF, Reiley MC, Ankley GT, Mount DR. (2001b). An assessment of the toxicity of phthalate esters to freshwater benthos. 2. Aqueous exposures. *Environ Toxicol Chem* 20(8): 1798–1804.
- Casado-Martinez MC, Mendez-Fernandez L, Wildi M, Kase R, Ferrari BJD, Werner I. (2017) Incorporation of sediment specific aspects in the CRED evaluation system: recommendations for ecotoxicity data reporting. SETAC Europe 27th Annual Meeting, Brussels.
- Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR. (1991) Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ Toxicol Chem* 10(12): 1541-1583.
- EC (2018). Technical Guidance for Deriving Environmental Quality Standards Environment, Guidance Document No. 27, Updated version 2018, Document endorsed by EU Water Directors at their meeting in Sofia on 11-12 June 2018.
- EC (2008). Bis(2-ethylhexyl) phthalate (DEHP), Risk Assessment Report, pp. 1-588. (Literature Review from 2005)
- EC (2005). Common Implementation Strategy for the Water Framework Directive Environmental Quality Standards (EQS) Substance Data Sheet Priority Substance No. 12 Diethylhexylphthalate (DEHP) CAS-No. 117-81-7
- ECHA (2014). Principles for environmental risk assessment of the sediment compartment: proceedings of the topical scientific workshop. Helsinki (FI): ECHA. 81 p.
- ECHA (2014). Substance Name: Bis(2-ethylhexyl) phthalate (DEHP), EC Number: 204-211-0, CAS Number: 117-81-7. Support document to the opinion of the member state Committee for identification of Bis(2-ethylhexyl) phthalate (DEHP) as a substance of very high concern because of its endocrine disrupting properties which cause probable serious effects to human health and the environment which give rise to an equivalent level of concern to those of CMR and PBT/vPvB substances. Available at https://echa.europa.eu/documents/10162/21833221/svhc_msc_opinion_support_document_dehp_20141211_en.pdf
- ECHA (2017) Guidance on Information Requirements and Chemical Safety Assessment; Chapter R.7b: Endpoint specific guidance.
- ECHA (2020). Substance name: Bis(2-ethylhexyl) phthalate. EC number: 204-211-0. CAS Nr 117-81-7. Online registration dossier : <https://echa.europa.eu/it/registration-dossier/-/registered-dossier/15358>
- ECCC (Environment and Climate Change Canada, Health Canada) (2017). Risk Management Scope for 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester [DEHP] – Chemical Abstracts Service Registry Number (CAS RN): 117-81-7, pp. 1-20.
- Edder P, Ortelli D, Klein A, Ramseier S. (2008). Métaux et micropolluants organiques dans les eaux et sédiments du Léman. Rapp Comm int prot eaux Léman contre pollut, Campagne 2007: 57-84.
- EFSA (2015) Scientific Opinion on the effect assessment for pesticides on sediment organisms in edge-of-field surface water (PPR Panel). *EFSA Journal* 13(7), 4176.
- Environment Canada and Health Canada (2017). Draft Screening Assessment, Phthalate Substance Grouping, pp. 1-228. (Literature Review from 2016)
- Hu X-Y, Wen B, Zhan S, Shan X-Q. (2005). Bioavailability of phthalate congeners to earthworms (*Eisenia fetida*) in artificially contaminated soils. *Ecotoxicol Environ Saf* 62(1): 26-34.
- INERIS (2018) Portail Substances Chimiques: DEHP. CAS : 117-81-7. <https://substances.ineris.fr/fr/substance/nom/dehp>. Last accessed: 22.07.2020.
- Larsson P, Thurén A. (1987) Di-2-ethylhexylphthalate inhibits the hatching of frog eggs and is bioaccumulated by tadpoles. *Environ Toxicol Chem* 6: 417-422.



- Larsson P, Thurén A, Gahnström G. (1986) Phthalate esters inhibit microbial activity in aquatic sediments. *Environ Poll (Series A)* 42: 223-231.
- Lee YM, Lee JE, Choe W, Kim T, Lee JY, Kho Y, Choi K, Zoh KD. (2019). Distribution of phthalate esters in air, water, sediments, and fish in the Asan Lake of Korea. *Environ Int* 126: 635-643.
- Leschber R. (2006). Evaluation of the relevance of organic micro-pollutants in sewage sludge. In: Background values in European soils and sewage sludges. Results of a JRC-coordinated study on background values. Ed: BM Gawlik and G Bidoglio. ISBN 92-79-02120-6.
- LfU (Landesamt für Umwelt Bayern) (2014). Stoffinformationen Phthalate. https://www.lfu.bayern.de/analytik_stoffe/doc/abschlussbericht_svhc.pdf
- Loizeau J-L, Makri S, Arpagaus P, Ferrari B, Casado-Martinez C, Benejam T, Marchand P. (2017). Micropolluants métalliques et organiques dans les sédiments superficiels du Léman. Rapport scientifique de la Commission internationale pour la protection des eaux du Léman contre la pollution (CIPEL), Campagne 2016, pp 143-198.
- Mackintosh CE, Maldonado J, Hongwu J, Hoover N, Chong A, Ikonomou MG, Gobas FA. (2004) Distribution of phthalate esters in a marine aquatic food web: comparison to polychlorinated biphenyls. *Environ Sci Technol* 38(7): 2011-20.
- Mayer FL, Sanders HO. (1973) Toxicology of phthalic acid esters in aquatic organisms. *Environ Health Perspect* 3: 153-157.
- Moermond CTA, Kase R, Korkaric M, Ågerstrand M. (2016) CRED: Criteria for reporting and evaluating ecotoxicity data. *Environ Toxicol Chem* 35(5): 1297-1309.
- Nagorka R and Koschorrek J. (2020). Trends for plasticizers in German freshwater environments – Evidence for the substitution of DEHP with emerging phthalate and non-phthalate alternatives. *Environ Poll* 262: 114237
- Net S, Rabodonirina S, Sghaier RB, Dumoulin D, Chbib C, Tlili I, Ouddane B. (2015). Distribution of phthalates, pesticides and drug residues in the dissolved, particulate and sedimentary phases from transboundary rivers (France-Belgium). *Sci Total Environ* 521-522: 152-159.
- OECD (2018). Socio-Economic assessment of phthalates was prepared for the SACAME workshop in Ottawa, Canada of 30-31 August 2017, by Mike Holland, EMRC.
- Peijnenburg W, Struijs J. (2006). Occurrence of phthalate esters in the environment of the Netherlands. *Ecotox Environ Saf* 63(2): 204-215.
- RIVM (Rijksinstituut voor Volksgezondheid en Milieu, Netherlands) (2001). Ecotoxicological Serious Risk Concentrations for soil, sediment and (ground)water: updated proposals for first series of compounds. Report 711701 020 (Verbruggen et al.), pp. 1-263.
- Solyon P, Remberger M, Viktor T. (2001). Further investigations on the influence of sediment-associated phthalate esters (DEHP and DINP) on hatching and survival of the moorfrog *Rana arvalis*. IVL Swedish Environmental Research Institute Ltd. Report B1417 for CEFIC.
- Staples CA, Peterson DR, Parkerton TF, Adams WJ (1997). The environmental fate of phthalate esters. A literature review. *Chemosphere* 35(4): 667-749.
- Sullivan KF, Atlas EL, Giam CS (1982). Adsorption of phthalic acid esters from seawater. *Env Sci Technol* 16: 428-432.
- USEPA (2019). Proposed Designation of Di-Ethylhexyl Phthalate (DEHP) (1,2-Benzene- dicarboxylic acid, 1,2-bis (2-ethylhexyl) ester) (CAS RN 117-81-7) as a High-Priority Substance for Risk Evaluation, pp. 1-64.
- Van Wezel AP, Van Vlaardingen P, Posthumus R, Crommentuijn GH, Sijm DTHM. (1999). Environmental risk limits for two phthalates, with special emphasis on endocrine disruptive properties. *Ecotoxicol Environ Saf* 46: 305-321.
- Verbruggen EMJ, Posthumus R, van Wezel AP. (2001). Ecotoxicological Serious Risk Concentrations for soil, sediment and (ground)water: updated proposals for first series of compounds. RIVM (Rijksinstituut voor Volksgezondheid en Milieu, Netherlands) report 711701 020.
- Warren N, Allan IJ, Carter JE, House WA, Parker A. (2003). Pesticides and other micro-organic contaminants in freshwater sedimentary environments—A Review. *Appl Geochem* 18: 159-194.



- Williams MD, Adams WJ, Parkerton TF (1995). Sediment sorption coefficient measurements for four phthalate esters: experimental results and model theory. *Environ Toxicol Chem* 4 (9): 1477-1486.
- Woin P, Larsson P (1987) Phthalate esters reduce predation efficiency of dragonfly larvae, Odonata; Aeshna. *Bull Environ Contam Toxicol* 38: 220-225.
- Zhang ZM, Zhang Jm Zhang HH, Shi XZ, Zou YW, Yang GP. (2020). Pollution characteristics, spatial variation, and potential risks of phthalate esters in the water–sediment system of the Yangtze River estuary and its adjacent East China Sea. *Environ Pollut* 265(Part A): 114913.



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

Values in grey font are not used in EQS derivation.

| TOC, type | | Log K_{oc} | K_{oc} [L/kg] | Reference/Source |
|---|------|--------------|-----------------|---|
| Batch equilibrium study, freshwater sediment OC 0.15 % pH 8.32 clay 10.7% | exp. | 5.48 | 301000 | Williams et al. (1995) |
| Batch equilibrium study, freshwater sediment OC 0.66 % pH 7.76 clay 25.8% | exp. | 5.95 | 888000 | Williams et al. (1995) |
| Batch equilibrium study, freshwater sediment OC 1.88 % pH 7.6 clay 42.7% | exp. | 5.41 | 257000 | Williams et al. (1995) |
| Batch equilibrium study, marine sediment OC ≤ 1 % clay 30.4% | exp. | 5.71 | 510000 | Sullivan et al. (1982) cited in ECHA (2020) |
| Soil 1.59 % OC, and freshwater sediments 0.26 % OC | exp. | 4.94 | 87420 | Russell and MacDuffie (1986) |
| | | 6.00 | 1000000 | Furtman (1993) cited in Staples (1997) |
| Field study | exp. | 5.60 | 398000 | Germain and Langlois (1989) cited in Staples (1997) |
| Field study | exp. | 5.77 | 583000 | Ritsema et al. (1989) cited in Staples (1997) |
| EUSES Model | est. | 5.77 | 589000 | EUSES model, cited in ECHA (2020) |
| Pckoc Model | est. | 5.22 | 165000 | Meylan (1992) cited in ECHA (2020) |
| Estimated from K_{ow} , see Table 1 | | 6.00 | 1011347 | $\log K_{oc} = 0.81 \cdot \log K_{ow} + 0.10$ |
| Geomean | | 5.74 | 554494 | Geomean |