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

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

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Summary

SQC (EQS_{sed}): 0.102 mg/kg d.w. (generic) or 0.016 mg/kg d.w. (added to the local background)

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 SQC for mercury (Hg) of 0.016 mg/kg d.w. is obtained. Because this value is below the range of concentrations representative of background levels of Hg in Swiss sediments, a generic SQC of 0.102 mg/kg d.w. is proposed, calculated by adding the FOREGS (Forum of European Geological Surveys Geochemical database) mean value for Hg background concentrations of 0.086 mg/kg d.w. for floodplain sediments. The SQC can be derived for the local conditions by adding 0.016 mg/kg d.w. to the local Hg background concentration.

Zusammenfassung

SQK (EQS_{sed}): 0.102 mg/kg TS (allgemein) oder 0.016 mg/kg TS (zusätzlich zur lokalen Hintergrundkonzentration)

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 Grundlage der momentan verfügbaren wissenschaftlichen Literatur ergibt sich für Quecksilber (Hg) ein SQK von 0.016 mg/kg TS. Da dieser Wert unter dem typischen Konzentrationsbereich für die Hintergrundkonzentrationen von Hg in Schweizer Sedimenten liegt, wird ein allgemeines SQK von 0.102 mg/kg TS vorgeschlagen. Dieses wurde berechnet, indem zur Konzentration von 0.016 mg/kg TS der FOREGS (Forum of European Geological Surveys Geochemical database)-Mittelwert für Hintergrundkonzentrationen von Hg in Auensedimenten von 0.086 mg/kg TS addiert wird. Der standortspezifische SQK kann bestimmt werden, indem 0.016 mg/kg TS zur lokalen Hintergrundkonzentration für Hg addiert wird.

Résumé

CQS (EQS_{sed}): 0,102 mg/kg p.s. (générique) ou 0,016 mg/kg p.s. (ajouté au fond local)

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 pour le Mercure (Hg) de 0,016 mg/kg p.s. est dérivé. Étant donné que cette valeur est inférieure à la plage de concentrations représentatives des niveaux de fond de Hg dans les sédiments en Suisse, un CQS générique de 0,102 mg/kg p.s. est proposé, calculé en ajoutant la valeur moyenne FOREGS (Forum of European Geological Surveys Geochemical database) de 0,086 mg/kg p.s. pour les sédiments des plaines inondables. Le CQS peut être dérivé pour les conditions locales en ajoutant 0,016 mg/kg p.s. à la concentration de fond locale.

Sommario

CQS (EQS_{sed}): 0,102 mg/kg p.s. (generico) o 0,016 mg/kg p.s. (aggiunti alla concentrazione naturale di fondo locale)

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 per il mercurio (Hg) di 0,016 mg/kg p.s. è derivato. Poiché questo valore è inferiore alla gamma di concentrazioni rappresentative dei livelli di fondo di Hg nei sedimenti svizzeri, si propone un CQS generico di 0,102 mg/kg p.s. calcolato sommando il valore medio FOREGS (Forum of European Geological Surveys Geochemical database) di 0,086 mg/kg p.s. per i sedimenti delle pianure alluvionali. Il CQS può essere derivato per le condizioni locali aggiungendo 0,016 mg/kg p.s. alla concentrazione di fondo locale.

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1 General Information

The following assessment reports were used for the preparation of this EQS_{sed} dossier:

- EC 2005. Common Implementation Strategy for the Water Framework Directive. Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 21 Mercury and its Compounds CAS-No. 7439-97-6. Final version. Brussels.
- Euro Chlor 1999. Euro Chlor risk assessment for the marine environment. OSPARCOM region – North Sea. Mercury.

1.1. Identity and physico-chemical properties

Table 1 Information required for EQS derivation according to the TGD (EC 2011). Values not used in risk assessment are in grey font.

Characteristics	Value	References
IUPAC name	Mercury	EC 2005
Commercial name	Mercury	EC 2005
Chemical class	Metal	EC 2005
CAS number	7439-97-6 (elemental mercury)	Euro Chlor 1999
EINECS number	231-106-7	Euro Chlor 1999
Formula	Hg	EC 2005
Code SMILES	[Hg]	EC 2005
Molecular weight [g/mol]	200.59	Euro Chlor 1999
Melting point [°C]	-38.87	Euro Chlor 1999
Boiling point [°C]	356.58	Euro Chlor 1999
Vapor pressure [Pa]	0.25 (25°C; elemental mercury)	EC 2005
Henry's constant [Pa·m^3/mol]	1.3×10^{-3} (25°C)	Sander 2015
Water solubility [ng/L]	20-30 (elemental mercury)	EC 2005
Dissociation constant (pK_a)	$Hg^{2+} + H_20 \leftrightarrow HgOH^+ + H^+$ $pK_a = 3.4$ $Hg^{2+} + H_20 \leftrightarrow Hg(OH)_2^0 + 2H^+$ $pK_a = 6.17$	Essington 2015
Log K_{ow}	0.62 (25°C)	Okouchi and Sasaki 1985
Partition coefficients		
Kp [L/kg]	[1] 1.46×10^6 [2] 112 202 (sediment, batch and field studies); 169 824 (suspended matter, field studies)	[1] Agences de l'Eau 1999 cited in EC 2005 [2] Crommentuijn et al. 2000
Kd [m^3/m]	[3] 316 000 [4] 3981 to 630 957 (L/kg)	[3] Euro Chlor 1999 [4] Gascon-Diez et al. 2014
Kp $_{water\text{-}suspended}$ mater [L/kg]	[5] 100 000 (mean value) [6] 124 000 – 164 000 (suspended matter) [6] 57 000 [6] 250 000 – 330 000 [6] 5 000 – 900 000	[5] Schudoma et al. 1994 cited in EC 2005 [6] Different studies reviewed by Frimmel et al. 2001 cited in EC 2005
Bioaccumulation		
BCF fish:		
Oncorhynchus mykiss	1800 ($HgCl_2$, freshwater, whole body, 60 d) 85 700 ($HgCH_3Cl$, freshwater, whole body, 75 d)	Frimmel et al. 2001 cited in EC 2005
Pimephales promelas	4994 ($HgCl_2$, freshwater, whole body, 287 d)	
Salvelinus fontinalis	44 130-87 670 ($HgCH_3Cl$, whole body, 336 d)	
Riverine fish	11 000-33 000 ($HgCH_3Cl$, muscle, 273 d)	

Characteristics	Value	References
Fish	1000-15 000 (freshwater, muscle, natural environ.) 2000-10 000 (freshwater, muscle, natural environ.) 3 030 (OSPAR 1996; geometric mean for inorganic mercury) 3 640 (OSPAR 1996); 8 140 (Sloff et al. 1996); geometric means for methylmercury	Euro Chlor 1999 cited in EC 2005
<u>BCF mollusks:</u> *Mytilus edulis*	24-2 500 (derived from mean Hg in marine mollusks and mean dissolved Hg concentration in North sea estuaries) 3500 (mean BCF for organic Hg in mollusks) 190-5300 (BCF range of inorganic Hg; Slooff et al. 1995) 1750 (geometric mean, OSPAR 1996)	EC 2005
<u>Biomagnification</u> <u>BAF fish:</u> (field measurements; geometric means for methylmercury)	21 700 (Slooff et al. 1995) 1 600 000-6 800 000 (US EPA 1997) 120 000-27 000 000 (US EPA 2001) 200 000-78 000 000 (France 2004)	EC 2005

1.2. Regulation and environmental limits

In Switzerland the use, release and placing on the market of products containing mercury (Hg) is strictly regulated by the application of ordinances (ORRChim[1], OEaux[2]) resulting from federal laws including LEaux, LPE and LChim. At the international level, Switzerland is a signatory to the Minamata Convention[3], which aims to reduce emissions and anthropogenic releases of mercury and its compounds to protect human health and the environment.

Existing limit values for sediment remediation and management are not in place in Switzerland. The only reference values for sediments/suspended matter of application are the Target Values from the International Commission for the Protection of the Rhine (ICPR, see Table 2), which are most commonly applied to interpret concentrations in suspended matter. In the absence of values for sediments, the most common values used for sediment classification are the OSol values for soil.

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[1] https://www.admin.ch/opc/fr/classified-compilation/20021520/index.html

[2] https://www.admin.ch/opc/fr/classified-compilation/19983281/index.html

[3] http://www.bafu.admin.ch/chemikalien/01415/03112/index.html?lang=fr

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

Switzerland	
Suspended matter and sediment: Target Values - International Commission for the Protection of the Rhine (ICPR 2009)	- Target value (TV): 0.5 mg/kg d.w.; (pragmatic) limit for relevant sediment contamination is fixed to the fourfold target value, i.e. 2 mg/kg d.w.[4].
Soil: Threshold Values from the OFEV (OSol 1998)	- Indicative value: 0.5 mg/kg d.w. for soils with up to 15% organic matter. Considered as an equivalent to background value. - Threshold for investigation: proposal 0.5 mg/kg d.w. for food and forage crops (Portmann et al. 2013). Ensues an investigation to see if people, animals or plants are at risk. - Remediation value: proposal 20 mg/kg d.w. for food and forage crops (Portmann et al. 2013). According to OSol 1998, cantons should stop using the soil for certain uses and put measures to recover the levels to concentrations below. According to OSites, soil requires remediation.
Europe/elsewhere	
Surface water: EQS – European Commission (15.01.05)	- AA-QS protection against direct effects: $C_{background}$ + MPA (MPA = 0.05 µg/L; total dissolved Hg) - AA-QS protection against secondary poisoning: 20 µg/kg prey tissue (methyl-Hg) - MAC-QS: $C_{background}$ + MAC-MPA (MAC-MPA = 0.07 µg/L; total dissolved Hg)
Sediment: France (INERIS 2016)	- Proposal $QS_{sed,EqP}$: 3.6 mg/kg d.w. (proposal INERIS derived using the Equilibrium Partitioning approach using Rhine characteristics) - Proposal $QS_{sed,AF}$: 9.3 mg/kg d.w. (proposal INERIS derived using the Assessment Factor approach)
Sediment: Flanders, Belgium (based on de deckere et al. 2011)	- Proposal $QS_{sed,field}$: 0.55 mg/kg d.w. (Consensus 1 derived using field data from Flanders)
Sediment: Canada (CCME 1999)	- Interim Sediment Quality Guideline: 0.17 mg/kg d.w. (derived using field data from North America; below effects are rare) - PEL (probable effect level): 0.486 mg/kg d.w. (derived using field data from North America; above, adverse biological effects are frequent)

1.3. Use and emissions

Mercury is present naturally in the environment in magmatic rocks and volcanic regions. Having a large affinity for carbon, Hg is also present in crude oil, coal and shale.

Mercury has been used as a pesticide, a disinfectant, in measuring instruments (e.g. thermometers), in batteries, in dental fillings as well as in various industrial processes. It is still extensively used in several countries mainly for artisanal and small-scale gold mining. The worldwide anthropogenic emissions of Hg to the atmosphere are estimated at 1670 tonnes/year and mainly stem from the combustion of fossil fuels, mostly coal, for electricity and to a lesser extent from metal extraction and industrial operations such as cement production. The natural emissions are in the range of 500-900 tonnes/year (UNEP 2018). These emissions come from terrestrial geological activity (volcanoes) as well as from the evaporation in zones that are naturally enriched in mercury.

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[4] https://www.iksr.org/fileadmin/user_upload/DKDM/Dokumente/Fachberichte/EN/rp_En_0175.pdf

According to data from the Federal Office of the Environment (FOEN), 660 kg of mercury per year are released into the air in Switzerland and 70 kg into the water ((Ritscher et al. 2018), data for 2015). In Switzerland, the major contributors of emissions to the atmosphere are the combustion of fossil fuels and waste incineration (44%), industrial combustion mainly from the cement industry (27%) and industrial processes (12%). In surface waters, 15% of total mercury are estimated to come from point sources such as communal WWTPs and industry, and 85% from diffuse sources such as atmospheric deposition and soil erosion. The mercury release to the environment in Switzerland decreased sharply (approx. 85%) between 1985 and 2003 but since then has remained at a constant level[5].

2 Environmental fate

2.1. Speciation and sorption/desorption processes

Mercury is present in the environment in three general forms that can be converted to another (Krabbenhoft and Rickert 1995; UNEP 2018):

- As elemental mercury Hg(0), which is the only metal that is liquid at atmospheric temperature and pressure. In the air, mercury is mainly present as Hg(0) and can be transported over large distances. Mercury has limited solubility in water; in sediments, elemental Hg is typically a small fraction of total Hg and is not directly bioavailable to organisms.
- As inorganic Hg (mostly Hg^{2+}). Hg^{2+} is highly reactive and easily forms complexes with chloride/organic ligands or adsorbs to particles. Hg^{2+} is the most abundant form of Hg in contaminated sediments.
- As organic Hg, where Hg forms a bond with a carbon atom. Organic Hg compounds readily react with biologically important ligands such as sulfhydryl groups. Organisms easily take up organic Hg compounds because they are liposoluble. They bioaccumulate and are known to biomagnify (i.e. increase in concentration with each level of a food chain). The most important organic Hg compound is methylmercury, which is formed by microbial activity in water ecosystems.

Mercury enters the aquatic environment primarily through atmospheric deposition, but also through runoff from Hg deposits in soil and rock. Mercury concentrations in the environment can vary considerably depending on the geological characteristics. The natural background concentrations in surface waters are generally lower than 0.1 µg/L.

Mercury's high affinity for organic ligands on particles and colloids means that Hg tends to sorb to various materials. Particles in water and in sediments therefore contain higher Hg concentrations than the water itself[6]. In sediments, inorganic Hg is the most abundant form, although microbial activity methylates Hg to some extent. Once deposited in sediments, Hg could partition (back) to the water column by dissolution equilibrium depending on pH, redox potential, organic matter, iron and manganese oxides or sulphide concentrations (Stordal et al. 1996).

The binding capacity of sediments is closely linked with their texture, whereas organic matter and sulphide are the main factors controlling Hg distribution and bioavailability (Boszke et al. 2004). Increasing concentrations of dissolved organic matter are associated with increasing dissolved Hg

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[5] OFEV, Thème produits chimiques, glossaire des polluants, mise à jour le 16.09.15.

[6] Suspended matter may contain from five to 25 times as much mercury as the water around it in areas of industrial pollution (https://pubs.usgs.gov/pp/0713/report.pdf)

concentrations, and increasing concentrations of Hg in suspended matter and sediments are generally associated with increasing organic content (Euro Chlor 1999).

2.2. Bioavailability

Under laboratory conditions, the major Hg bioavailable fraction to benthic invertebrates is that associated with iron and manganese oxides, while the least bioavailable is bound to organic matter (Zhong and Wang 2006).

Scientific evidence shows that sediment organic content has a negative effect on the accumulation of total Hg in deposit-feeders such as bivalves from sediment. However, efforts to express concentrations of Hg exposure on an organic carbon (OC) basis under the assumption that Hg bioavailability is controlled primarily by the amount of OC present in sediment have shown that this normalization does not reduce the variability in effect concentrations (Conder et al. 2015).

Mercury bioavailability is also influenced by redox potential, which can influence methylation and binding to sulfide. The SEM-AVS model suggests that a part of the metal will not be bioavailable when it is bound to the reactive solid sulfide present in sediments. The equation describing the equilibrium between the sulfide complexed metal and the free dissolved metal on a mole-to-mole basis:

$$\frac{2}{n}Me^{n+}_{(aq)} + FeS(s) <-> Me_{2/n}S\ (s) + Fe^{2+}_{(aq)}$$

$$\frac{2}{n}Me^{n+}_{(aq)} + MnS(s) <-> Me_{2/n}S\ (s) + Mn^{2+}_{(aq)}$$

Where Me^{n+}_{aq} is the aqueous form of a metal, MnS and FeS(s) are the insoluble Mn and Fe sulfide forms, $Me_{2/n}S$ is the insoluble metal sulfide form, and $Mn^{2+}_{(aq)}$ and $Fe^{2+}_{(aq)}$ are the soluble Mn and Fe forms.

Again, normalization against acid volatile sulfides (AVS) has not yield the same degree of success as for other divalent metals (Conder et al. 2015).

2.3. Bioaccumulation and biomagnification

Mercury is a non-essential element (EC 2011, table 2.1, p. 29) to biota and there is no metabolic function associated with it. Mercury bioaccumulates in aquatic organisms and eventually reaches a threshold level that ensues the cascade of toxic effects.

Concentrations of total Hg can vary five- to ten-fold among invertebrate species collected from a same environment, with bivalves being among the most efficient invertebrates at accumulating total Hg. Although invertebrates typically bioaccumulate lower proportions of methylmercury than do fish, invertebrates are of interest in Hg bioaccumulation because they act as a vector for transfer to higher trophic levels such as fish, which may suffer from secondary poisoning and in turn may become the major exposure route of Hg to humans.

The organisms most likely to accumulate the highest concentrations of Hg are birds, fish and mammals at the top of the food web.

Bioaccumulation factors (BCF) for marine mollusks derived from mean bioaccumulated Hg concentrations in mollusks and mean concentrations of dissolved Hg in North Sea estuaries (Table 1) range from 24 to 2500 (Euro Chlor 1999). The mean BCF for organic Hg is 3500 (Euro Chlor 1999). For fish, the geometric mean for inorganic Hg is 3030 and for methylmercury 3640 and 8140 (Euro Chlor 1999). For freshwater fish, the BCF for inorganic Hg range from 1000 to 15 000 from field measurements and from 1800 to 4994 under laboratory exposure (EC 2005). The BCF for methylmercury for fish under laboratory exposure range from 11 000 to 85 700 (EC 2005). To note that BCF for metals are not independent from external (water-) concentration and should not be used for assessing bioaccumulation, which should be assessed through other evidence (EC 2011).

Evidence shows that Hg can biomagnify, with an increase in concentration in subsequent trophic levels. High assimilation efficiencies from food and slow rate constants of loss lead to high bioaccumulation of methylmercury and allow preferential accumulation of the organic form of Hg in fishes and predators, with fish accumulating up to six orders of magnitude higher concentrations of methylmercury than the concentrations in the surrounding water (Luoma and Rainbow 2008). Uptake and loss, dietary exposure and trophic transfer are processes defining risks to fish and to humans from fish consumption. The EC (2005) concluded that biomagnification and secondary poisoning should be taken into consideration for Hg EQS derivation and a AA-QS at 20 µg/kg prey tissue (methyl-Hg) is proposed.

3 Analytics

3.1. Methods for analysis and quantification limit

Total mercury in dry sediments can be easily analyzed by Cold Vapour Atomic Absorption Spectrometry (CV-AAS). Automatic mercury analyzers are available commercially, such as the Altec Model AMA 254. The detection limit and working range is 0.01 and 0.05-600 ng, respectively.

3.2. Environmental concentrations

No field campaign or project has been dedicated specifically to develop natural (background) concentrations of mercury in Swiss sediments. Thus, two different types of data relevant for evaluating the natural contribution to mercury concentrations in Swiss sediments have been reviewed (Table 3)[7]:

- *Historical concentrations in sediments*: these correspond to natural (background) concentrations measured in (pre-industrial) sediments from lakes, most commonly quantified in sediment cores. The concentrations retained as background values were ideally those measured in the layer dated ca. 1850.
- *Current concentrations in sediments*: these correspond to concentrations that are statistically representative of environmental concentrations not affected by anthropogenic sources of pollution. Current concentrations include the concentrations in stream sediments (fraction <150 µm) and floodplain sediment (fraction < 2 mm) reported for Switzerland in the atlas of the Forum of the European Geological Surveys[8], which has been most commonly used as default values, and current monitoring data.

Overall, the concentrations of Hg relevant for the estimation of background concentrations range over one order of magnitude. Mercury in pre-industrial lake sediments range from 0.03 to 0.2 mg/kg d.w., with a mean and median of 0.08 and 0.05 mg/kg d.w. (Casado-Martinez et al. 2016). In the low range of pre-industrial lake sediments are the concentration estimated by the FOREGS for Switzerland for stream sediment (fraction <150 µm, mean 0.037 mg/kg d.w.) and for floodplain sediments (fraction < 2 mm, mean 0.086 mg/kg d.w.), the 5th and 10th percentile of all available current monitoring data

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[7] EU TGD (EC 2011, p. 104): The definition of the natural background levels of metals in sediments is similar to that for water. Again, the default procedure will be to search for baseline levels in pristine or close to pristine areas. Unlike the situation for water, the analysis of deeper, undisturbed bed sediments, combined with radio-isotopic techniques, may allow one to estimate historical ambient concentrations, and thus to judge «pre-industrial» levels. Other possibilities are to: -to gather information from national or international databases. For example, FOREGS Geological Baseline Programme… ».

[8] www.gsf.fi/publ/foregsatlas

(fraction < 63 µm, 0.03 and 0.04 mg/kg d.w.), and the background concentration reported for Swiss rivers from the Lemanic basin (0.05 mg/kg d.w.). The median value derived by Pardos et al. for Swiss large rivers at sites far from contamination sources (< 63 µm, 0.14 mg/kg d.w.) falls in the high range.

According to the EU TGD for EQS development (p. 64) “sample results with elevated concentrations from known point sources discharges or pollution events” should be removed from current monitoring data for the derivation of background concentrations. This could not be performed for the available databases reviewed in the absence of the necessary information on known point sources discharges or pollution events. The integration of different types of historical and current monitoring data and the good agreement between the different databases is considered sufficient for the purpose of estimating background concentrations until specific programs are implemented. The mean value for floodplain sediments (fraction < 2 mm) of the FOREGS database of 0.086 mg/kg d.w. is taken forward in the EQS derivation.

Table 3 Measured environmental concentrations of mercury in Switzerland. All concentrations expressed as mg/kg d.w. for sediment. n.d. not detected.

Database	Value	Comments	Reference
Current monitoring data	Mean: 0.25 Median: 0.12 Min-Max: LOD[9]-7.80 5th Percentile: 0.03 10th Percentile: 0.04	N=559 Most data from fraction < 63 µm	See review Casado-Martinez et al. 2016
Pre-industrial concentrations in lakes	Min-Max: 0.03-0.2	N=7 Most data refer to total sediment	See review Casado-Martinez et al. 2016
Ambient concentrations in Swiss large rivers	Median: 0.14	N=80 Data refer to < 63 µm	Pardos et al. 2003
FOREGS Stream sediment	Mean: 0.037 Median: 0.028	N=10 Stream sediment (fraction < 150 µm)	www.gsf.fi/publ/foregsatlas
FOREGS Floodplain sediment	Mean: 0.086 Median: 0.049	N=10 Stream sediment (fraction < 2 mm)	www.gsf.fi/publ/foregsatlas
Swiss rivers, Lemanic basin	0.05		Faverger et al. 1990

4 Effect data (spiked sediment toxicity tests)

According to EU TGD (EC 2011), PNECs derived within published Risk Assessment Reports should be normally adopted as QS because the assessments and associated data have undergone thorough peer review, promoting consistency between chemical assessment and control regimes. The following documents are relevant for EQS$_{sed}$ development:

- Common Implementation Strategy for the Water Framework Directive, Environmental Quality Standards (EQS), Substance Data Sheet Priority Substance No. 21, Mercury and its compounds, CAS-No. 7439-97-6, Final version 15 January 2005
- Euro Chlor Risk Assessment for the Marine Environment OSPARCOM Region – North Sea. Mercury- August 1999

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[9] Data comes from several sources, limit of detection most often not available.

Relevant data from these reports were reviewed for reliability when studies where available. A literature search was performed for new ecotoxicity data to complete the effect data already included in the EQS Sheet, which dates back to 2005. New effect data was assessed for reliability and relevance according to the CRED methodology (Moermond et al. 2016) modified for assessing effect data from sediment toxicity test (Casado-Martinez et al. 2017).

For substances for which the bioavailability is dependent on the organic carbon (OC) content of the sediment, the bioavailability introduced by the presence of toxicity values generated at different OC concentrations can be accounted for by normalizing each toxicity test result to OC and then express all results in sediment with a standard organic carbon content of 5% (EC 2011, p. 103).

There is enough scientific evidence of the decrease in bioavailability of Hg to benthic organisms at increasing OC concentrations (Mason and Lawrence 1999; Boeing 2000; Lawrence and Mason 2001), although a recent review found that normalizing effect data from a heterogeneous database of laboratory and field studies did not reduce the variability in effect concentrations (Conder et al. 2015).

The OC content of the sediments from the literature database varied between virtually no OC, 2% and 7%, with one effect concentration per species corresponding to the low OC value and one effect concentration per species corresponding to the high OC. Normalization against OC content decreased differences in effect concentrations for *H. curvispina*, which were obtained from a same study from Peluso et al. (2013). The effect concentrations (NOECs) available were normalized to 5% OC and the geometric mean of these two NOECs is used for EQS derivation.

Normalization did not explain the differences between the effect concentrations for *C. riparius* emergence inhibition, which were obtained from different studies. This could be due to differences in other physico-chemical properties affecting mercury bioavailability (e.g. AVS), aging duration after sediment spiking, or differences in the sensitivity of the test organisms that cannot be further addressed in the absence of the full study by Thompson et al. 1998 (partially reported in Eurochlor 1999). For *C. riparius*, the two effect concentrations (NOECs) were not averaged.

The small available database does not allow assessing the relevance of a bioavailability correction for other factors such as AVS. However, the lowest effect data for each species and endpoint in the database (Table 4) corresponds to artificial sediments, where AVS-dependent bioavailability is maximized thus representing a worst case scenario.

Table 4 Sediment effect data for mercury. Data were evaluated for relevance and reliability according to the CRED criteria adapted for sediments (Casado-Martinez et al. 2017) based on Moermond et al. (2016). All concentrations in mg/kg d.w. if not otherwise stated. Data not used in EQS derivation are in grey font.

Substance	Species	Taxonomic group	Test duration [d]	Effect parameter	End-point	NOEC [mg/kg d.w.]	NOEC [5% OC]	Exposure concentration	Dose – response	Adminis-tration of substance	OC [%]	Sediment type	Equili-bration time [d]	Reference	Validity
Mercury chloride	*Chironomus riparius*	Diptera Chironomidae	14	Survival	NOEC	2.4	4.8	Measured	Yes	Static renewal	2.5	Artificial OECD: AVS < 0.06 µmol/g	7 d	Chibunda 2009	C3
Mercury chloride	*Chironomus riparius*	Diptera Chironomidae	14	Growth, as dry weight	NOEC	0.93	1.86	Measured	Yes	Static renewal	2.5	Artificial OECD: AVS < 0.06 µmol/g	7 d	Chibunda 2009	C3
Mercury chloride	*Chironomus riparius*	Diptera Chironomidae	15	Survival	NOEC	> 5	> 10	Not reported	One test concen-tration	Static	2	Natural sediment: clay 75-80%	5 d	Odin et al. 1994	R3,C3
Mercury chloride	*Chironomus riparius*	Diptera Chironomidae	15	Growth	NOEC	> 5	> 10	Not reported	One test concen-tration	Static	2	Natural sediment: clay 75-80%	5 d	Odin et al. 1994	R3,C3
Mercury chloride	*Hyalella curvispina*	Amphipoda	21	Survival	NOEC	≥ 10.7	≥ 26.8	Measured[1]	Yes	Spiked sediment	2	Artificial OECD: AVS 0.05 µmol/g d.w.[2]	7 d	Peluso et al. 2013	R2,C1
Mercury chloride	*Hyalella curvispina*	Amphipoda	21	Survival	NOEC	> 9.4	> 6.7	Measured[1]	Yes	Spiked sediment	7	Natural sediment	7 d	Peluso et al. 2013	R2,C1
Mercury chloride	*Hyalella curvispina*	Amphipoda	21	Survival	NOEC	**4.5**	--	Measured[1]	Yes	Spiked sediment	0	Artificial OECD, no organic matter	7 d	Peluso et al. 2013	C3
Mercury chloride	*Hyalella curvispina*	Amphipoda	21	Growth, as length	NOEC	**4.5**	--	Measured[1]	Yes	Spiked sediment	0	Artificial OECD, no organic matter	7 d	Peluso et al. 2013	C3
Mercury chloride	*Hyalella curvispina*	Amphipoda	21	Growth, as length	NOEC	**2.0**	**4.9**	Measured[1]	Yes	Spiked sediment	2	Artificial OECD: AVS 0.05 µmol/kg d.w.[2]	7 d	Peluso et al. 2013	R1,C1
Mercury chloride	*Hyalella curvispina*	Amphipoda	21	Growth, as length	NOEC	**4.3**	**3.1**	Measured[1]	Yes	Static renewal	7	Natural sediment	7 d	Peluso et al. 2013	R1,C1
					Geometric mean		**3.9**								
Mercury chloride	*Chironomus riparius*	Diptera Chironomidae	28	Emergence	NOEC	**2.4**	**4.8**	Measured	Yes	Static renewal	2.5	Artificial OECD: AVS < 0.06 µmol/g d.w.	7 d	Chibunda 2009	R2,C1
Mercury chloride	*Chironomus riparius*	Diptera Chironomidae	28	Emergence	NOEC	**930.0**	**801.7**	Measured	Yes	Static renewal	5.8	Natural sediment	n.a.	Thompson et al. 1998, in Eurochlor 1999	R1,C1

[1] Mean concentration derived from reported values of measured concentrations in sediments on day 0 and day 21; [2] Not reported, quantified in other studies for same composition of artificial sediment.

4.1. 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*".

Chronic toxicity test results for two different sediment-relevant species are available (Table 5): the amphipod *Hyalella curvispina* (four individual NOEC values) and the insect *Chironomus riparius* (two individual NOEC values).

Hyalella curvispina: there are values of NOECs for two different endpoints derived from one chronic study (21 d). The NOECs for survival is > 11 mg/kg d.w. for an artificial sediment with 2.03% OC and > 9.4 mg/kg d.w. for a natural sediment with 6.96% OC. For growth, NOECs are of 2.0 mg/kg d.w. and 6.0 mg/kg d.w. for an artificial sediment with 2.03% OC and natural sediment with 6.96% OC. Normalized to a standard sediment of 5% OC the NOECs for growth are of 4.9 mg/kg d.w. and 4.3 mg/kg d.w., respectively.

Chironomus riparius: there are values of NOECs for the endpoint growth derived from two chronic studies. One study reported a 28 d NOEC for emergence success of 2.4 mg/kg d.w. for an artificial sediment with 2.5% OC while another study reported a NOEC of 930 mg/kg d.w. for a natural sediment with 5.8% OC. After normalization, the corresponding NOECs for a standard sediment of 5% OC are 4.8 mg/kg d.w. and 801.7 mg/kg d.w.

Table 5 Most sensitive endpoint from relevant and reliable chronic studies from Table 4.

Species	**Exposure duration [d]**	**Endpoint**	**NOEC [mg/kg d.w. 5% OC]**	**NOEC [mg/kg d.w. 1% OC]**	**Reference**
Hyalella curvispina	21	Growth, as length	<u>3.9</u>	0.78	Geometric mean (N=2)
Chironomus riparius	28	Emergence	4.8	0.96	Chibunda 2009

5 Derivation of QS_{sed}

According to the EC TGD for EQS, sediment toxicity tests, aquatic toxicity tests in conjunction with equilibrium partitioning (EqP) and field/mesocosm studies are used as several lines of evidence to derive QS_{sed} (EC 2011). Thus, in the following, the appropriateness of the deterministic approach (AF-Method), the probabilistic approach (SSD method) and the EqP approach were examined.

5.1. Derivation of $QS_{sed, A}$F using the Assessment Factor (AF) method

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

The lowest credible datum classified as reliable and relevant is the 21 d NOEC derived for the amphipod *H. curvispina* (Peluso et al. 2013). When normalized for the OC content and expressed for a standard sediment with 5% OC the lowest credible datum is 3.9 mg/kg d.w.

In case of long term tests (NOEC or EC_{10}) being available for two species representing different living and feeding conditions, the EU TGD recommends the application of an assessment factor of 50 on the lowest credible datum.

$$QS_{sed,AF} = \frac{lowest\ EC10\ or\ NOEC}{AF}$$

$$QS_{sed,AF,total} = \frac{3.9\left(\frac{mg}{kg}\right)}{50} = 0.078\left(\frac{mg}{kg}\right)$$

The application of an AF of 50 to the lowest credible chronic datum results in a $QS_{sed,AF}$ of 0.078 mg/kg d.w. for 5% OC or $QS_{sed,AF}$ of 0.016 mg/kg d.w. for 1% OC.

5.2. Derivation of $QS_{sed,SSD}$ using the species sensitivity distribution (SSD) method

The minimum data requirements recommended for the application of the SSD approach for EQS water derivation is preferably more than 15, but at least 10 NOECs/EC_{10}s, from different species covering at least eight taxonomic groups (EC 2011). 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 $QS_{sed,EqP}$. 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 0.05 µg/L (total dissolved Hg) for the protection against direct effects on pelagic species (EC 2005). This AA-QS, proposed as Maximum Permissible Addition (MPA)[10], was derived by statistical extrapolation (SSD) from freshwater and saltwater NOECs (29 individual NOECs) and after application of an assessment factor of 3 (EC 2005):

$$MPA_{water,SSD}\ [\mu g/L] = 0.142\ [\mu g/L])\ /\ AF\ (3) = 0.047\ \mu g/L$$

6.2. Selection of partition coefficient

The TGD (EC 2011, p. 104) states: "When using the EqP approach for metals, measured Kd values for sediment/suspended solids from freshwater, estuarine and marine waterbodies respectively can be used. Preference is given to Kd values derived from field measurements and not laboratory sorption or toxicity experiments. However, large variations in Kd are often observed even among different field-based measurements and therefore, for freshwater sediments, the QS derived from EqP may be refined by using Kds, modeled from WHAM speciation models (Tipping 1994). It should be noted however that the only solid phase that can be estimated by WHAM is organic carbon. Before using this approach, the validity of organic carbon determined WHAM Kd values should be checked, as other factors may contribute to partitioning."

Taking in consideration that the EqP method is only required when no spiked-sediment toxicity test data is available or when only acute data is available, two different partitioning coefficients were used here for $QS_{sed,EqP}$ derivation for comparison purposes:

- A generic empirically-derived partition coefficient (Crommentuijn et al. 2000):

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[10] A maximum permissible addition is used when the added risk approach is recommended. This occurs when the derived QS < relevant background concentration (TGD 2011, p.56), which was the case for Hg EQS for the water phase.

Log Kp_{sed} = 5.05, which corresponds to Kp_{sed} of 112 202 L/kg.

- Local empirically-derived coefficient values for Lake Geneva (Gascon-Diez et al. 2014): Log Kd range from 3.6 to 5.8, which correspond to Kd values from 3981 to 630 957 L/kg.

6.3. Derivation of $QS_{sed,EqP}$

The calculated $QS_{sed,EqP}$ using the different partitioning coefficient are included in Table 6. According to the EC TGD (EC 2011, p. 98): "When the $QS_{sediment}$ has been calculated using the EqP and log Kow >5 for the compound of interest, $QS_{sediment}$ is divided by 10. This correction factor is applied because EqP only considers uptake via the water phase. Extra uncertainty due to uptake by ingestion of food should be covered by the applied assessment factor of 10."

For mercury, scientific evidence shows that uptake by ingestion of food is an important (if not major) source of mercury to benthic organisms (Williams et al. 2010; Taylor et al. 2014). In addition, the EQS fact sheet (EC 2005) states that "Mercury can lead to biomagnification with an increase in concentration in subsequent trophic levels. Mercury, and methylmercury in particular, can also be accumulated to a large extent from food which leads to higher mercury levels under field conditions than expected on the basis of theoretical BCF-values. This should be taken into account for higher trophic levels (secondary poisoning)". An extra AF of 10 is therefore applied.

The derived $QS_{sed,EqP}$ after the application of an extra AF of 10 are 0.53 mg/kg d.w. (generic) and 0.02-2.97 mg/kg d.w. (local).

Table 6 $QS_{sed,EqP}$ derived from equilibrium partitioning approach using the AA-QS for water (EC 2005).

Case		**AA-EQS** [µg/L]	**Kp_{sed}** [L/kg]	**$K_{sed\text{-}water}$** [m^3/m^3]	**$QS_{sed,EqP}$** [mg/kg w.w.]	**$QS_{sed,EqP}$** [mg/kg d.w.]	**$QS_{sed,EqP}/10$** [mg/kg d.w.]
Generic		0.047	112 202	56 102	2.03	5.27	0.53
Local	Low	0.047	3981	1991	0.07	0.19	0.02
	High	0.047	630 957	315 479	11.41	29.66	2.97

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

7.1. Overview of available mesocosm/microcosm studies

No mesocosm studies as defined in OECD (2006) that include sediments have been found that assess mercury effects on structural and functional endpoints on benthic taxonomic groups.

Klaus et al. (2016) performed field exposures of newly-colonised periphyton to a concentration series of $HgCl_2$ spiked sediment with the objective of measuring net methylmercury production and accumulation of methylmercury and total Hg in the newly established colonies. At the end of the incubation, organic content and metabolic activity measured as net primary production and respiration were assessed as endpoints for toxicity, showing no effect at the exposure concentrations and for the sediments tested. Based on nominal concentrations (measured concentrations at the end of exposure were > 85% of nominal), a NOEC > 20 mg/kg d.w. derived for sandy sediments with low OC content was estimated for periphyton organic content and metabolic activity. This study, however, is not retained for EQS_{sed} derivation because it is not in agreement with OECD (2006).

7.2. Available sediment quality guidelines from field data

Several threshold concentrations have been derived for total mercury from field studies (EC TGD 2011, p. 101-102). Table 7 summarizes threshold concentrations referring to concentrations where biological effects are unlikely to occur, which "are preferred over thresholds associated with a significant biological impact" (EC TGD 2011, p. 102). According to what stated in the TGD, the relevant thresholds are those that specify that not more than 20-25% of samples should display a toxic effect, and none of these thresholds should be used without a thorough assessment of the reliability of the data and their relevance.

The set of threshold concentrations from field data range between 0.15 and 0.23 mg/kg d.w. The Threshold Effect Concentration (TEC) of 0.18 mg/kg d.w. from MacDonald et al. (2000) was derived as the geometric mean of different sediment quality guidelines and is used extensively around the world as concentration below which adverse effects would be rarely observed. The TEC from MacDonald et al. (2000) is considered the most relevant and reliable threshold concentration that is derived mainly from field data. The lowest Threshold Effect Level derived from field data is the one related to effects in oligochaete communities, which is one order of magnitude below the other sediment quality guidelines from field studies considering mainly macrozoobenthos.

Table 7 Field thresholds (co-occurrence sediment quality values; mg/kg dw) for freshwater sediments referring to concentrations where biological effects are unlikely to occur (from Conder et al. 2015).

Threshold name	Value	Reference	Description
Interim Sediment Quality Guideline (ISQG)	0.174	CCME 1999, Smith et al. 1996	Sediments are considered to be clean to marginally polluted. No effects on the majority of sediment-dwelling organisms are expected below this concentration.
Lowest Effect Level (LEL)	0.2	Persaud et al. 1993	Concentration below which adverse effects are expected to occur only rarely.
Effect Range Low (ERL)	0.15	Long and Morgan 1991	Concentration below which adverse effects would be rarely observed.
Consensus 1	0.23	de Deckere et al. 2011	Average between concentration below which adverse effects would be rarely observed in benthic communities (0.28 mg/kg dw) and that below which toxicity to *Hyalella azteca* in 10 day acute toxicity test is rarely observed (0.18 mg/kg dw).
Consensus Based Threshold Effect Concentration (TEC)	0.18	MacDonald et al. 2000	Represents the concentration below which adverse effects are expected to occur only rarely.
Threshold effect level (TEL_{oligo})	0.0218	Vivien et al. 2020	Concentration below which oligochaete communities are rarely affected. A PEL_{oligo} of 0.054 mg/kg d.w. describes concentrations above which oligochaete communities are likely affected.

8. Toxicity of degradation products

Not relevant for metals.

9. EQS_{sed} proposed to protect benthic species

The QS_{sed} derived using the different methods included in the TGD (EC 2011) are summarized in Table 8. According to the TGD, the most reliable extrapolation method for each substance should be used (EC 2011, p. 39). In all cases, data from spiked sediment toxicity tests are preferred over the EqP approach thus the $QS_{sed,AF}$ prevail over the $QS_{sed,EqP}$.

Regarding the use of field data, the EU-TGD (p. 102) states that reliable data arising from field studies can be used to influence the derivation of the QS_{sed} as follows in relation to $QS_{sed,AF}$:

1. Field threshold ≥ $QS_{sed,AF}$: use $QS_{sed,AF}$ or reduce AF applied to laboratory data if field data are reliable and relevant to a wide range of European (or national) conditions.
2. Field threshold < $QS_{sed,AF}$: increasing AF size if field data is reliable.

Because the field thresholds that are based on macrozoobenthos are higher than the $QS_{sed,AF}$, either the $QS_{sed,AF}$ is used or the AF applied is decreased if field data are reliable and relevant to a wide range of European/national conditions. Available field thresholds were obtained from studies of field-collected sediments that measured Hg concentrations along with concentrations of other chemicals, and associated biological effects of North America and Flanders. These studies most commonly represent a wide range of concentrations of Hg, types of sediment, and mixtures of chemicals. Their reliability is unknown, as well as their relevance as they have not been validated for Switzerland. The TEL_{oligo} was derived from field data from small and medium water bodies in Switzerland, and is close to the $QS_{sed,AF}$ derived for 1% OC, a worst case scenario for Switzerland and relevant for the type of water bodies considered in the derivation of the TEL_{oligo}. The TEL_{oligo} is also close to the $QS_{sed,EqP}$ derived using the lowest Kd value for lake Geneva.

The derived $QS_{sed,AF}$ of 0.016 mg/kg d.w. (1% OC) is below the background concentrations in Swiss sediments. In this case, the EU-TGD (p. 61) recommends using the Added Risk Approach, which allows accounting for natural background concentrations. Taking the FOREGS value of 0.086 mg/kg d.w. for floodplain sediments, a generic EQS_{sed} of **0.102 mg/kg d.w.** is proposed.

Table 8 QS_{sed} derived according to the different methodologies stipulated in the EU TGD (EC 2011) and their corresponding AF. All concentrations expressed in mg/kg dw.

	Derived value [mg/kg d.w.]	**AF**
$QS_{sed,AF}$		50
5% OC	0.078	
1% OC	0.016	
$QS_{sed,EqP}$		10
Generic	0.53	
Local	0.02-2.97	
Background		
Range	0.03-0.2	
FOREGS Floodplain sediment (<2 mm)	0.086	
Proposed EQS_{sed}	**0.102**	

10. Protection of benthic organisms and uncertainty analysis

The proposed EQS_{sed} are lower or close to existing sediment quality guidelines and thresholds based on field data, thus they should be protective for benthic communities and macrozoobenthos.

The TEL_{oligo}, which is derived from total Hg concentrations, is higher than the derived $QS_{sed,AF,added}$ but lower than the $EQS_{sed,total}$. Accordingly, it is also below the background concentrations reported in Swiss sediments. No effect concentration for oligochaetes was available in the database, so it cannot be concluded whether oligochaetes are particularly sensitive to Hg.

The derivation took into consideration the added risk approach. According to the EQ TGD (EC 2011) p.56 "The ARA should not be used in combination with bioavailability correction". Here the $QS_{sed,AF}$ was derived for 1% OC, which is considered a worst-case scenario for Switzerland because OC normalization reduced variability in the effect databased. Bioavailability corrections may be considered in higher tier assessments when the proposed EQS_{sed} is exceeded.

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Appendix 1. Overview of available spiked sediment toxicity studies

Peluso et al. 2013

- Species: *Hyalella curvispina.*
- Origin: laboratory culture.
- Experimental sediment: Artificial OECD (2004) sediment with 3.5% organic matter and 75% quartz sand, 20% kaolinite and 5% sphagnum moss peat and calcium carbonate. One additional test sediment consisting of artificial OECD with virtually no organic matter was used but effect data was not included in the derivation according to its low relevance. A stream sediment with 12% organic matter was also used. Background Hg concentrations are <0.05 mg Hg/kg dw. No AVS measurements, for OECD (2004) AVS can be assumed to be approx. 0.05 mmol/kg. Sediment measurements included pH, loss of ignition at 550°C and mercury concentrations.
- Spiking and equilibration time: dried sediments rehydrated to 30% water, then mercury additions done from a stock solution of 1 g/L prepared from HgCl2 (Anedra®) in distilled water. The corresponding volume was added, and then stirred manually. Seven days of equilibration at same light and temperature as toxicity testing following Simpson et al. (2004). Spiked nominal concentrations are: 0, 1.7, 3.0, 6.0, 7.5, 9.6 and 12 mg/kg d.w. for the artificial sediment, and 6.0, 7.5, 9.6 and 12 mg/kg d.w. for the natural sediment.
- Overlying water: dechlorinated tap water. Dissolved oxygen, pH, conductivity, ammonia, hardness and alkalinity at the beginning and end of test.
- Overlying water quality measurements: Hg analyses after acid digestion by cold vapour atomic absorption spectrometry with hydride generator. One replicate for chemical analyses at start and end of test for each exposure concentrations and control. Controls <0.05 mg/kg d.w.; artificial sediment six concentrations ranging from 1.6 and 1.3 mg/kg d.w. to 11.8 and 9.5 mg/kg d.w. at start and end of the test, respectively. Natural sediment with four concentrations ranging from 4.5 and 4.0 mg/kg d.w. to 10.2 and 8.5 mg/kg d.w. at start and end of test, respectively. Concentrations in overlying water increasing with increasing sediment concentrations from <0.001 to 0.008 mg/L and from start to end of test. Higher concentrations in overlying waters in the artificial sediment than in the natural sediment for a same sediment concentration, in agreement with organic carbon concentrations in sediments. Concentrations measured in overlying waters always below the 96 h LC10 derived in the same study.
- Bioassays: 7-14 d old juveniles. Seven replicates per concentration, 10 organisms per replicate. 21 d of exposure at 21°C on 16:8 light:dark. Organisms fed fish food and boiled lettuce *ad libitum* one every five days, before renewal of water. One third of overlying water renewed every five days. Each exposure chamber comprises 100 mL sediment and 175 mL overlying water.
- Test endpoints: survival and growth (length).
- Statistics: normality and homoscedasticity tested using Shapiro_Wilk's and Barlett's tests. One way ANOVA followed by Dunnet's test. Data arcsine-transformed for % survival and log-transformed for length data. Statistical significance established at p<0.05.

→ Data are accepted as R1/C1. Information not provided in the publication was communicated by the authors upon request. Effect data from artificial sediment with virtually no organic matter considered not relevant.

Chibunda 2009

- Species: *Chironomus riparius*
- Origin: laboratory culture at Laboratory of Animal Physiology and Toxicology at Sokoine University of Agriculture (Tanzania), originated from Ghent University, at 20°C and 12:12 dark: light.
- Experimental sediment: Artificial OECD (2004) sediment with 2.5% TOC and 75% sand, 20% kaolin clay and 5% sphagnum moss peat and calcium carbonate pH 7.0. AVS < 0.06 µmol/g d.w.
- Spiking and equilibration time: dried sediments rehydrated to 30-50% water, then mercury additions from a stock solution of $HgCl_2$ reagent grade (Merck-Germany) to reach the concentrations then mixed thoroughly. Addition of distilled and double deionized water 1:3 sediment: water ratio and left for 7 days at 4°C in the dark. Then overlying water discarded. Nominal spiked concentrations: 0, 1, 1.8, 3.2, 5.6, 10 and 18 mg/kg d.w.
- Overlying water: EPA-medium, moderately hard water with a hardness of 85 mg/L as $CaCO_3$. Temperature, dissolved oxygen, pH, ammonia, hardness measured 3 times per week, before water change, at approx. 1 cm of sediment surface.
- Metal and other analyses during the test: Hg analyses after acid digestion by atomic absorption spectrometry with cold vapour generator technique. One replicate for chemical analyses at end of test for each exposure concentration and control and measurements at start of test. Measured concentrations reported for day 0: controls <0.02 mg/kg d.w.; artificial sediment six concentrations ranging from 0.59 and 12.68 mg/kg d.w., not reported if time-weighted. Concentrations in pore water increasing with increasing sediment concentrations from <0.00002 to 0.8 mg/L. Pore water concentration at the NOEC is 0.142 mg/L.
- Bioassays: following OECD 2018 (2004). 48 h old juveniles. Eleven replicates per concentration: five replicates for 14 d survival and growth, five replicates for survival, growth and emergence at 28d, and one replicate for chemical analysis. Ten organisms per replicate. 28 d of exposure at 20°C on 12:12 light: dark. Organisms fed fish food daily at 0.5 mg first 10 days, 1 mg afterwards. Water renewal (75%) three times a week. Test chambers consist of 800 mL glass beakers with 175 mL EPA-medium and 100 g spiked sediment, prepared 1 d before test start.
- Test endpoints: survival, growth (dry weight), emergence success.
- Statistics: data arcsine square root transformed before analysis. Normality and homogeneity using Shapiro_Wilkinson tests. One way ANOVA followed by Fisher LSD test. $p<0.05$

→ Data at 28 d are accepted as R2/C1 because concentrations in overlying water were not measured but pore waters were quantified. Survival and growth at 14 d are considered C3 as they are considered short-term exposures.

<u>Thompson et al. 1998 cited in Euro Chlor 1999</u>

- Species: *Chironomus riparius*
- Origin: laboratory culture
- Experimental sediment: natural sediment with 5.8% organic carbon. No gran size or AVS measurements.
- Spiking and equilibration time: $HgCl_2$. No information on spiking and equilibration.
- Overlying water: no information, only Hg concentrations.
- Metal and other analyses during the test: Five concentrations and control measured at start, middle and end of test. Concentrations ranging from 81-94% of nominal. Concentrations in

overlying water maximal at start of 0.0062 mg/L at the highest sediment concentration, with no clear relationship. At 14 and 28 d concentrations < 0.001 mg/L.

- Bioassays: <24 h post-hatching juveniles. Triplicates, no information on number of organisms per replicate. 28 d of exposure at 20°C, partial renewal at day 14. No further information.
- Test endpoints: emergence
- Statistics: no information

→ Data are accepted as R1/C1 according to acceptance in the two master references (Euro Chlor 1999, EC 2005).