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Schweizerisches Zentrum für angewandte Ökotoxikologie  
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## **SQC (EQS<sub>sed</sub>) – Proposal by the Ecotox Centre for: *Lead (Pb)***

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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<sub>sed</sub>): 50.3 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 lead (Pb) of 50.3 mg/kg d.w. is proposed.

## Zusammenfassung

**SQK (EQS<sub>sed</sub>): 50.3 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 Blei (Pb) und unter Verwendung der Methode, die in der Technischen Richtlinie der EU zur Ableitung von Umweltqualitätsnormen beschrieben wird, schlägt das Oekotoxzentrum einen allgemeinen SQK für Pb von 50.3 mg/kg TS.

## Résumé

**CQS (EQS<sub>sed</sub>): 50,3 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 Plomb (Pb) de 50,3 mg/kg p.s. est proposé.

## Sommario

**CQS (EQS<sub>sed</sub>): 50,3 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 per il Piombo (Pb) di 50,3 mg/kg p.s. è proposto.



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## 1 General Information

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

- EC (2011). Common Implementation Strategy for the Water Framework Directive. Environmental Quality Standards (EQS) Substance Data Sheet. Priority Substance No. 20 Lead and its Compounds CAS-No. 7439-92-1. Brussels. (Update to the 2005 Substance Data Sheet).
- LDAI (2008). European Union Risk Assessment Report, Lead and its compounds.
- ECHA (2020) Information on Registered Substances: Lead, CAS number: 7439-92-1 <https://echa.europa.eu/it/substance-information/-/substanceinfo/100.028.273> Last modified: 06-Sept-2020.

### 1.1 Identity and physico-chemical properties

The Voluntary Risk Assessment Report (VRAR, LDAI 2008) for Lead and its compounds includes 13 CAS numbers<sup>1</sup>, including lead (Pb) and two inorganic Pb compounds (Pb oxide, Pb tetraoxide). The aquatic effects assessment in the VRAR (LDAI 2008) and the EQS Data Sheet (EC 2011) assumes that adverse effects on aquatic organisms are a consequence of exposure to the available Pb-ion, rather than the parent substances. This means that all Pb substances that dissociate or form the Pb-ion are similar from a hazard point of view (LDAI 2008). This dossier therefore describes general properties and characteristics for Lead metal (CAS 7440-66-6), and measured environmental concentrations and ecotoxicity data refer to total Pb concentrations if not otherwise stated.

Table 1 summarizes identity and physico-chemical parameters for Pb 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.

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<sup>1</sup> Lead metal [Pb]: CAS 7439-92-1  
 Lead oxide [PbO]: CAS 1317-36-8  
 Lead tetroxide [Pb<sub>3</sub>O<sub>4</sub>]: CAS 1314-41-6  
 Dibasic lead phthalate [C<sub>8</sub>H<sub>4</sub>O<sub>6</sub>Pb<sub>3</sub>]: CAS 69011-06-9  
 Basic lead sulphate [PbSO<sub>4</sub>]: CAS 12036-76-9  
 Tribasic lead sulphate [Pb<sub>4</sub>SO<sub>7</sub>]: CAS 12202-17-4  
 Tetrabasic lead sulphate [H<sub>8</sub>O<sub>8</sub>Pb<sub>5</sub>S<sub>2</sub>]: CAS 12065-90-6  
 Neutral lead stearate [Pb(C<sub>18</sub>H<sub>35</sub>O<sub>2</sub>)<sub>2</sub>]: CAS 1072-35-1  
 Dibasic lead stearate [2PbO.Pb (C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub>]: CAS 12578-12-0  
 Dibasic lead phosphite [H<sub>3</sub>O<sub>6</sub>PPb<sub>3</sub>]: CAS 12141-20-7  
 Polybasic lead fumarate [C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>Pb]: CAS 90268-59-0  
 Basic lead carbonate [(PbCO<sub>3</sub>)<sub>2</sub>·Pb(OH)<sub>2</sub>]: CAS 1319-46-6  
 Basic lead sulphite [PbSO<sub>3</sub>]: CAS 62229-08-7



Table 1 Information required for EQS derivation according to the TGD (EC 2018). Values not used in risk assessment in grey font.

Characteristics	Values	References
IUPAC name	Lead	ECHA (2020)
Chemical group	Metal	EC (2011)
Structural formula	Pb	ECHA (2020)
CAS	7439-92-1	ECHA (2020)
EC Number	231-100-4	ECHA (2020)
Molecular formula	Pb	ECHA (2020)
Code SMILES	[Pb]	ECHA (2020)
Molecular weight (g/mol)	207.2	EC (2011)
Melting point (°C)	326°C	ECHA (2020)
Boiling point (°C)	[1] No boiling point at atmospheric pressure up to the final temperature of 600 °C [2] 1740 °C	[1] ECHA (2020) [2] Haynes (2014)
Vapour pressure (Pa)	Metallic lead has a negligible vapour pressure at 20°C (vapour pressure recalculated through the Clausius-Clapeyron equation is $8.2 \times 10^{-7}$ Pa at the melting temperature of lead (326°C) assuming a vapour pressure of 133 Pa at a temperature of 1000 °C)	ECHA (2020)
Henry's law constant (Pa·m <sup>3</sup> /mol)	Not relevant	
Water solubility	Pb (metal powder): 185 mg/l (T 20°C, pH 10.96)  Transformation/ dissolution tests Pb (massive) loading 100 mg/l: 428.9 µg/l (7 d, pH 6), 109 µg/l (7 d, pH 7) Pb (massive) loading 1 mg/l: 0.28 µg/L (7 d, pH 8), 0.66 µg/l (28 d, pH 8) Pb (powder) loading 100 mg/l: 187.5 µg/l (24 h, pH 8). 607.0 µg/l (24 h, pH ), 3211.2 µg/l (24 h, pH 6)	ECHA (2020)  ECHA (2020)
pKa	Not relevant based on intrinsic chemical properties (substance with no relevant functional groups for which an assessment of the dissociation behaviour would provide information for risk assessment purposes)	ECHA (2020)
Octanol-water partition coefficient (log K <sub>ow</sub> )	Not relevant (the study does not need to be conducted because the substance is inorganic)	ECHA (2020)
K <sub>p</sub> <sub>sediment-water</sub> K <sub>p</sub> <sub>suspended matter-water</sub>	10 <sup>th</sup> -90 <sup>th</sup> percentile (50 <sup>th</sup> percentile) 35 481-707 946 (154 882) 50 119-1 698 244 (295 121)	LDAI (2008)



## 1.2 Regulatory context and environmental limits

Table 2 summarizes existing regulations and environmental limits in Switzerland, Europe and elsewhere for Pb.

Lead has been included in the candidate list of substances of very high concern (SVHC) and is fully registered in the EU as being manufactured and/or imported in the European Economic Area in 1 000 000 – 10 000 000 tons per year (ECHA 2020). Regarding the risk assessment for the sediment compartment, the voluntary risk assessment report prepared by the Lead Development Association International (LDAI 2008) concluded that there was no need for risk reduction for sediments related to local sewage treatment plants and generic local sites for the sector Pb oxide production for freshwater sediments. The same conclusion was obtained in the regional risk characterization for sediments. However, risk reduction measures were needed at some local sites for the sectors lead metal production, lead sheet production, battery production and lead crystal glass production and generic scenarios of rifle/shotgun shooting range and clay target shooting range. The local risk characterization for sediment at hunting and shooting areas could not be completed due to the difficulty in developing meaningful default scenarios. Local exposure and bioavailability parameters for the sediment compartment were needed to refine the assessment. Further sediment data for the marine environment were also necessary. The Scientific Committee on Health and Environmental Risks (SCHER) did not accept definitive conclusions on absence of risk or need for risk reduction methods due to the uncertainties associated with both exposure and effects for all compartments and at all levels, advocating for further work (SCHER 2009). The most critical point to develop according to the SCHER was the development of bioavailability for all compartments, and specifically biotic ligand models for the relevant aquatic organisms.

As a priority substance for the EU Water Framework Directive (Directive 2013/39/EU), EQS for Pb were derived in 2005 and further reviewed in 2011 following the VRAR (LDAI 2008) and the SCHER (2009) comments.

In Switzerland, Pb is regulated by the Water Protection Ordinance (WPO), the Contaminated Site Ordinance (CSO), the Soil Protection Ordinance, the Ordinance on Air Pollution Control (OAPC), the Ordinance on foreign substances in food product (OSEC), the Chemical Risk Reduction Ordinance (ORRChem), and the Register relating to Pollutant Release Ordinance (PRTRO). Limit values and maximum concentrations are included for Pb in different abiotic matrices (e.g. water, soil, air) as well as restrictions for use. No limit value or maximum concentration is available for the sediment compartment in Swiss regulations.

Table 2 Existing regulation and environmental limits for Pb in Switzerland and Europe. Environmental limits for sediment are presented in Table 3.

Europe	
EU Priority substance list	Identified as a priority substances in the field of the Water Framework Directive (Directive 2013/39/EU) but not as a hazardous priority substance. Priority Substance No. 20
EU WFD EQS	Directive 2013/39/EU AA-EQS (Inland surface waters): 1.2 µg/l AA-EQS (Other surface waters): 1.3 µg/l MAC-EQS (Inland and other surface waters): 14 µg/l



REACH	Manufactured and/or imported in the European Economic Area in 1 000 000 – 10 000 000 tons per year
OECD	High Production Volume substance Declaration on Risk Reduction for Lead adopted the 20 <sup>th</sup> of February 1996
<b>Switzerland</b>	
Water Protection Ordinance (WPO) (07.02.17)	Annex 2 Requirements on Water Quality : 0.01 mg/l Pb (total), 0.001 mg/l Pb (dissolved) (maximum concentrations) Annex 3 Requirements for the Discharge of Polluted Waste Water: 0.5 mg/l Pb (total)
Contaminated Site Ordinance (CSO) (01.01.16)	Annex 2 Threshold concentration values for assessing the impact of polluted sites on ground and surface waters (0.05 mg/l) Annex 3 Concentration for assessing the need of soil remediation: - Sites used for agricultural or horticultural purposes: 2000 mg/kg d.w. Sites in private gardens and allotments, children's playgrounds and other facilities where children play regularly: 1000 mg/kg d.w.
Soil Protection Ordinance (12.04.16)	Annex 1 Indicative value for soil remediation (50 mg/kg d.w.)
Ordinance on Air Pollution Control (OAPC) (01.08.16)	Strictly regulated in liquid fuels and petrol, and industrial processes
Ordinance on foreign substances in food product (OSEC) (01.10.15)	Annex 2 List of maximal permissible concentration for metals and metalloids
Register relating to Pollutant Release Ordinance (PRTRO) (15.12.06)	Annex 2 Threshold value for reporting obligation to water and to land
Chemical Risk Reduction Ordinance (ORRChem) (01.02.17)	Use restriction in packaging Use restriction in vehicle construction material Annex 2.18 Use restriction in electronics Annex 2.8 Interdiction in paint and varnish Annex 2.2.1 Threshold in organic fertilizers, recycling fertilizers and farm manure Annex 2.17 Threshold in wood-based materials

Available limit values and predicted no effect concentrations (PNEC) for sediments are summarized in Table 3. The most relevant values are the  $QS_{sed,total}$  of 131 mg/kg d.w. derived using the species sensitivity distribution (SSD) approach and an assessment factor (AF) of 4, and the  $QS_{sed,bioavailable}$  of 41 mg/kg d.w. derived using the deterministic approach and an AF of 10 applied to the lowest effect datum after bioavailability (acid volatile sulphide –AVS- concentration) correction. In addition,  $EQS_{sed}$  or indicative values for Pb are available from different EU countries. Norway, Sweden and Denmark have  $EQS_{sed}$  for total Pb of 66, 130 and 163 mg/kg d.w., respectively. For France, a preliminary  $QS_{sed}$  of 53.4 mg/kg d.w. was derived as Maximum Permissible Addition through the Equilibrium Partitioning (EqP), which should be added to the background concentration. The EqP was also used to derive a Maximum Permissible Concentration of 530 mg/kg d.w. in the Netherlands (10 % TOC, 25 % clay) and a Target Value of 85 mg/kg d.w.



The VRAR (LDAI 2008) proposed a  $PNEC_{total}$  freshwater sediment of 174 mg/kg d.w. derived from the SSD method and the application of an AF of 3. ECHA (2020) refers to a  $PNEC_{sed}$  of 186 mg/kg d.w. obtained from the same derivation method. Additionally, the VRAR (LDAI 2008) proposes a  $PNEC_{bioavailable}$  of 81 mg/kg d.w. derived after normalization of effect data for the content of AVS in test sediments. The  $PNEC_{bioavailable}$  should be compared with sediment concentrations expressed as bioavailable Pb (see section 2.2)

Table 3  $PNEC$ /quality standards for sediments available from authorities and reported in the literature (additional sediment quality standards based on field data are summarized in Section 8).

Description	Value [mg/kg d.w.]	Development method	References
$QS_{sed,total}$	131	SSD method: application of an assessment factor 4 to the HC5.	EC (2011)
$QS_{sed,bioavailable}$	41	Deterministic method: application of an assessment factor of 10 to lowest effect concentration expressed as bioavailable Pb (with AVS/SEM correction).	
$EQS_{sed}$	163	$EQS_{sed}$ for Denmark, Inland and other surface waters. No information on derivation.	MFVM (2017)
$EQS_{sed}$	66	$EQS_{sed}$ for Norway, Inland waters. Class I-Class II boundary. Based on available information from laboratory tests and field data	Miljødirektoratet (2016)
$EQS_{sed}$	130	$EQS_{sed}$ for Sweden, Inland waters.	HVMFS 2015:4
MPA	53.4	Maximum Permissible Addition, derived through the Equilibrium Partitioning; exposure through contact or ingestion cannot be excluded, an additional factor of 10 is applied. $QS_{sed}$ calculated as MPA + Background Concentration.	INERIS (2018)
MPC (10 % TOC, 25 % clay) Target Value (10 % TOC, 25 % clay)	530 85	Maximum Permissible Concentration, derived through the modified Equilibrium Partitioning.  Based on available information from laboratory tests and field data.	Crommentuijn et al. (2000)
$PNEC_{total}$	186	SSD method: application of an assessment factor 3 to the HC5.	
$PNEC_{bioavailable}$	81	SSD method: application of an assessment factor 3 to the HC5. Derived after normalization of effect data for the content of acid volatile sulphides in test sediments. To be compared with sediment concentrations expressed as bioavailable.	LDAI (2008)



### 1.3 Use and emissions

80 % of the worldwide use of Pb is for batteries production (ILA 2017). In addition, Pb is used in cable covering, plumbing, paints, ammunitions and radioactive absorbers (Haynes 2014). In Switzerland, Pb is no longer authorized or is strictly regulated in cable covering, plumbing and painting. According to the Federal Office of the Environment (FOEN), emissions have sharply decreased in the country since the reduction of Pb in gasoline in 1970 (OFEV 2016a).

According to the Swiss Pollutant Release and Transfer Register (SwissPRTR database, OFEV 2016b) 97.67% of Pb emissions into water for the period 2007-2015 came from diffuse sources. The main sources of Pb to surface waters are household and wastewater treatment plants while agriculture (manure) and shooting facilities are the main sources of Pb to soil (EC 2011). Approximately 3800 shooting facilities were included in the registry of polluted sites in Switzerland as of 2015 (OFEV 2015).

### 1.4 Mode of action

Lead is not an essential element for the biosphere but it can use the same routes as essential elements to enter into the cell using active transport (i.e. ATP-mediated  $Ca^{2+}$  transport) as well as passive transport (carrier-mediated transport (Bressler et al. 2004)).

Once in the cell, Pb can bind sulphur residues in proteins and replace essential elements complexed in metalloproteins such as  $Zn^{2+}$  and  $Ca^{2+}$  and disrupt their function. Respiratory organs are a main target tissue (EC 2011). In higher organisms such as fish, Pb can reduce  $Ca^{2+}$  ATPase activity in acute exposure and induce neurotoxicological and hematological effects like anemia in chronic exposure (Alsop et al. 2016).

In invertebrates,  $Na^+$  homeostasis appears to be disrupted in response to chronic Pb exposure in pulmonate snails (*Lymnaea stagnalis*) displaying a biphasic pattern, with elevated whole-body  $Na^+$  concentrations at the lowest Pb concentrations and reduced whole-body  $Na^+$  concentrations at the higher Pb concentrations (Grosell et al. 2006). The authors argued that it could reflect a chronic respiratory or metabolic acidosis at low Pb concentrations that is partly compensated by increased exchange of  $H^+$  and  $Na^+$ , in agreement with observations of elevated haemolymph  $Na^+$  concentrations and reduced pH (acidosis) in *L. stagnalis* held in acidic water. Reduced whole-body  $Na^+$  concentrations at the higher Pb concentrations could be due to direct effects on  $Na^+$  transport proteins such as those previously observed in rainbow trout, showing reduced  $Na^+$  uptake and plasma  $Na^+$  concentrations, and may reflect inhibition of  $Na^+/K^+$  adenosine triphosphatase activity (Rogers et al. 2003 cited in Grosell et al. 2006).

According to available chronic data for pelagic organisms normalized to account for differences in bioavailability among studies (Table 7.4 in EC 2011, with NOEC and  $EC_{10}$  values based on the concentration of dissolved Pb), the taxa most sensitive to Pb are molluscs and in particular pulmonate snails (represented by *L. stagnalis*, NOEC/ $EC_{10}$  of 1.7  $\mu g/l$ ), followed by algae (*Pseudokirchneriella subcapitata*, NOEC/ $EC_{10}$  of 8.42  $\mu g/l$ ) and *Hyalella azteca* (a species of amphipod crustacean, NOEC/ $EC_{10}$  of 8.2  $\mu g/l$ ). Fish appear to be relatively insensitive to Pb compared to invertebrates, especially mollusks. Plants and chironomid larvae are the most insensitive taxa in the species sensitivity distribution (EC 2011).



## 2 Environmental fate

### 2.1 Speciation and sorption/desorption processes

Lead has three different oxidation states, Pb<sup>0</sup>, Pb<sup>2+</sup> and Pb<sup>4+</sup>. At normal environmental conditions, inorganic Pb is present at the oxidation state Pb<sup>2+</sup> (Baxter and Frech 1995). Its speciation in water depends mainly on pH, salinity, dissolved organic carbon and hardness. Its free form is dominant at pH below 6.5 (VRAR, LDAI 2008) whereas Pb is mainly present in form of carbonated complex at pH above 7 (US EPA 1999).

Powell et al. (2009) presents a more comprehensive review of Pb speciation. Complex formation between Pb<sup>2+</sup> and the common environmental inorganic ligands, Cl<sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>, can be significant in natural waters with low concentrations of organic matter (OM). In weakly acidic fresh water systems, the speciation of Pb<sup>2+</sup> is similar to that of Cu<sup>2+</sup>. In the absence of organic ligands, Pb<sup>2+</sup> speciation is dominated by Pb<sup>2+</sup>(aq), with PbSO<sub>4</sub>(aq) as a minor species. In weakly alkaline solutions, 8.0 - 9.0, the speciation is dominated by the carbonate species PbCO<sub>3</sub>(aq) and Pb(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>. In weakly acidic saline systems, the speciation is dominated by PbCl<sub>n</sub><sup>(2-n)+</sup> complexes, (n= 0–3), with Pb<sup>2+</sup>(aq) as a minor species. In saline systems, the speciation contrasts with that of Cu because of the higher stability of the Pb<sup>2+</sup>-chlorido- complexes, with speciation clearly dominated by the uncharged species PbCO<sub>3</sub>(aq) with a significant contribution from Pb(CO<sub>3</sub>)Cl<sup>-</sup> and minor contributions from PbCl<sub>n</sub><sup>(2-n)+</sup> and Pb(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>.

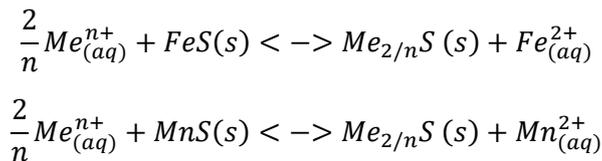
In anoxic conditions, Pb binds to sulfur groups present in sediments to form insoluble sulfide forms. According to measurements of Pb concentrations in spiked-sediment toxicity tests with Pb (Nguyen et al. 2012), when simultaneously extracted metals exceeding AVS, (SEM<sub>Pb</sub>-AVS) < 0, no correlation between (SEM<sub>Pb</sub>-AVS) and dissolved Pb was noted, while at (SEM<sub>Pb</sub>-AVS) > 3 mmol/kg d.w. in bulk sediment dissolved Pb increased with increasing (SEM<sub>Pb</sub>-AVS) demonstrating the influence of AVS on Pb partitioning. After copper, Pb has the second highest affinity for sulfur compared to other trace metals. In oxic conditions, Pb adsorption is influenced mainly by Cation Exchange Capacity (CEC) and then pH. Organic matter and clay content are the main drivers for CEC. The presence of anions like carbonates, sulfates and chlorides decreases Pb adsorption to the solid phase (Di Toro et al. 1990, LDAI 2008, US EPA 1999).

According to the review performed for the VRAR (LDAI 2008), the partitioning coefficients for suspended matter K<sub>p</sub><sup>suspended matter-water</sup> values from field studies for Pb used were 50 119 and 1 698 244 l/kg (10<sup>th</sup> and 90<sup>th</sup> percentile, 50<sup>th</sup> percentile of 295 121 l/kg). The partitioning coefficients for sediments were lower than for suspended matter, of 35 481 l/kg and 707 946 l/kg (10<sup>th</sup> and 90<sup>th</sup> percentile, 50<sup>th</sup> percentile 154 882 l/kg). These values are also reported in the EQS datasheet for Pb (EC 2011). No additional values have been searched, these values are used for QS<sub>sed,EqP</sub> derivation.

### 2.2 Bioavailability

Metal bioavailability and toxicity for sediment organisms depend on the concentration in sediment, porewater and overlaying water. Which compartment is most relevant depends on the organisms (feeding behavior, exposure route, etc.), type of metal and geochemistry (Luoma and Rainbow 2008). The measurable parameters that have shown to influence sediment metal bioavailability include AVS, SEM, CEC, Fe/Mn oxyhydroxides, organic carbon, particle size, hardness and pH (Tarazona et al. 2014).

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 is (LDAI 2008):



Where  $Me_{aq}^{n+}$  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  $Mn_{(aq)}^{2+}$  and  $Fe_{(aq)}^{2+}$  are the soluble Mn and Fe forms.

Hansen et al. (2005) reviewed available acute and chronic toxicity tests results for different metals, species and endpoints and concluded that the SEM-AVS  $\leq 0.0$  (or SEM-AVS  $\geq 1$ ) approach was useful in prediction of the absence of toxicity. The same exercise was performed specifically for Pb in the VRAR (LDAI 2008), concluding that the SEM-AVS model works “reasonably well” for Pb in predicting non-toxicity of sediments when the AVS exceed the SEM<sub>Pb</sub>.

However, AVS and SEM alone are not sufficient to describe the complexity of metal bioavailability in sediments. The SEM-AVS model may not be appropriate for benthic organisms living in oxygenated burrows (Fairbrother et al. 2007), experimental studies have shown that bioavailability of sediment-bound metals may be higher from oxic sediments than anoxic sediments (Chong and Wang 2000), and metals bound to AVS have also been found to be bioavailable to deposit feeders (Lee et al. 2000). According to the SCHER review of the VRAR for Pb (SCHER 2009), organic carbon (OC) content and phosphate and carbonate precipitation should be also considered for explaining Pb bioavailability (SCHER 2009). An alternative proposed to the SEM-AVS model is the organic carbon-normalized excess SEM ((SEM-AVS)/f<sub>OC</sub>), which is based on the theoretical foundation of equilibrium partitioning (Hansen et al. 2005; Vandegehuchte et al. 2013). Such bioavailability models for EQS<sub>sed</sub> derivation and implementation are however difficult to implement.

### 2.3 Bioaccumulation and biomagnification

According to the most recent review performed for the EQS derivation (EC 2011), bioaccumulation factors (wet weight) range from 7 to 15 400 l/kg, with mean and median values of 1 554 and 440 l/kg respectively. It was noted that one third of the values that were greater than values due to water concentrations being less than the limit of detection were treated as actual values. Alternatively, the mean and median would be 1 256 l/kg and 41 l/kg. It was also noted that BAFs derived from unfiltered water concentrations were considerably lower than those from filtered water. According to EC (2011), BAFs (wet weight) for fish range from 10 to 237 l/kg derived from unfiltered water concentrations while reported BAFs derived from filtered (0.45  $\mu$ m) water concentrations range from 260 to 1 032 l/kg. For crustaceans, BAFs range from 495 to 15 400 l/kg (from filtered water concentrations), for molluscs the range goes from 550 to > 3 850 l/kg (filtered) and from 7 to 18 l/kg (unfiltered, all BAFs for the mussel *Dreissena polymorpha*) while for insects the range spans from >440 to >5 310 l/kg (filtered).

According to ECHA (2020), based on median BAFs the highest bioaccumulation of Pb in typical environmental concentrations (0.18-15  $\mu$ g/l) was attributed to crustaceans (3 440 l/kg, n=7), followed by insects (1 830 l/kg, n=7), molluscs (675 l/kg, n=11) and fish (23 l/kg, n=16) (ECHA 2020). It is also noted that BAFs derived using both filtered (< 0.45  $\mu$ m) and unfiltered water concentrations were used, although BAFs derived from unfiltered water sample concentrations are lower than those from filtered ones.

Secondary poisoning was taken into consideration for setting the EQS for Pb, resulting in a QS<sub>freshwater, sec.pois.</sub> of 2.3  $\mu$ g/l for mammals and 10.8  $\mu$ g/l for birds from a QS<sub>biota</sub> of 3.6 and 16.9  $\mu$ g/kg biota w.w.,



respectively (EC 2011). However, it is assumed that Pb does not tend to biomagnify through the food chain (EC 2011).

As regards benthic organisms, the diversity of living and feeding modes makes it very difficult to generalize when describing metal bioaccumulation processes. Deposit or detritus feeders living in the sediment surface may be mainly exposed via sediment particles thus sediment-based food chains might be an important pathway for metal exposure (Luoma and Rainbow 2008). Lead accumulation in *Chironomus riparius* was better predicted through total Pb concentration in sediment (Roulier et al. 2008), suggesting that the ingestion of particles is an important route for Pb uptake. However, Vink (2009) found better predictions for metal uptake in *Chironomus riparius* and the oligochaete *Limnodrilus* spp. through the free metal ion concentrations. For the oligochaete *Tubifex tubifex* Méndez-Fernandez et al. (2014) showed that sediment Pb concentration was the best predictor for Pb bioaccumulation. However, AVS was not relevant for metal uptake in a range of field-collected sediments. Filter feeders living in the water-sediment interface may also assimilate more efficiently metals taken up from food than from water according to high residence time of ingested particles in the digestive tracts, being metal bioaccumulation independent of AVS concentrations found in sediments (de Jonge et al. 2010).

### 3 Analytics

#### 3.1 Methods for analysis and quantification limit

Lead can be analyzed after extraction by either inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma - optical emission spectrometry (ICP-OES) or atomic absorption spectrometry (AAS). The limits of detection (LOD) range from 0.005 µg/l for ICP-MS to 50 µg/l for ICP-OES. For solid phases, LOD is 0.01 to 25 mg/kg d.w. Extraction can be performed on a greater amount of sediment to decrease the LOD.

#### 3.2 Environmental concentrations

An overview of measured concentrations of Pb in sediments from Swiss water bodies is provided in Table 4. Pb concentrations in sediments range over three orders of magnitude (reviewed in Casado-Martinez et al. 2016), with higher concentrations reported in fine sediments according to the tendency of metals to accumulate in this sediment fraction.

Metal concentrations in sediments are dependent on geological and anthropogenic inputs in each watershed. Due to geochemical differences, the natural contribution to metal concentrations in sediments may vary from one region to another. It is therefore necessary to estimate the natural concentrations in sediments in order to develop  $EQS_{sed}$  relevant for the region of application. No field campaign or project has been dedicated specifically to develop natural (background) concentrations of Pb in Swiss sediments. Thus, two different types of data relevant for evaluating the natural contribution to Pb concentrations in sediments are included:

- Natural (background) concentrations measured in pre-industrial sediments from lakes, most commonly quantified in sediment cores. The concentrations retained as background concentrations are ideally those measured in the layer dated ca. 1850, which range from 10 to 50 mg/kg d.w. for the main lakes in Switzerland.
- Concentrations that are statistically representative of environmental concentrations not affected by anthropogenic sources of pollution, including the concentrations in stream



sediments <150  $\mu\text{m}$  and floodplain sediments < 2mm reported for Switzerland in the atlas of the Forum of the European Geological Surveys (FOREGS)<sup>2</sup>, which has been most commonly used as default background concentration. FOREGS reported a geochemical baseline concentration for Switzerland of 48 mg/kg d.w. for stream sediment < 150  $\mu\text{m}$  and 38 mg/kg d.w. for floodplain sediment < 2mm based on average of 10 sampling points. From the database of measured Pb concentrations performed between 2003 and 2010 in sediments from canton Bern a 10<sup>th</sup> percentile of 13 mg/kg d.w. was estimated (R. Ryser, pers. comm.).

It is noted that the FOREGS value is slightly above the median of measured environmental concentration of 36 mg/kg d.w. estimated from the cantonal database of measured ambient concentrations in Swiss sediments (N=559, mainly referring to sediments < 63  $\mu\text{m}$ ; Casado-Martinez et al. 2016). Pardos et al. (2003) reported values from large rivers in Switzerland ranging from 13.3 to 90 mg/kg d.w., with a median of 26.7 mg/kg d.w.

Table 4 Measured environmental concentrations (MEC) of Pb in Switzerland. All concentrations expressed as mg/kg d.w. for sediment.

Database / water body	Concentration	Comments	Reference
<i>Natural environmental concentrations</i>			
FOREGS database	Stream sediment: Average: 48 Min: 8 Max: 343 Median 12.5	N=10 Fraction < 150 $\mu\text{m}$ Aqua regia extraction	<a href="http://www.gtk.fi/publ/foregsatlas">http://www.gtk.fi/publ/foregsatlas</a>
	Floodplain sediment: Average: 38 Min: 12 Max: 164 Median 26	N=10 Whole sediment Aqua regia extraction	
Ecotox Centre database	Average: 55.8 Min: 4.6 Max: 1287 Median: 36 10 <sup>th</sup> percentile: 14.4	N=593 Mostly fraction < 63 $\mu\text{m}$ and extraction with aqua regia	Casado-Martinez et al. (2016)
Large rivers	26.7	Median of 80 data of sediments and suspended matter	Pardos et al. (2003)
Swiss rivers, Lemanic basin	50	Reference concentration, from ca. 400 data	Faverger et al. (1990)
Water bodies in canton Bern	10 <sup>th</sup> percentile: 13	2003-2010	R. Ryser, personal communication in Casado-Martinez et al. (2016)
<i>Background concentrations estimated in lakes</i>			
Constance	10, 20	Dated cores	Reviewed in Casado-Martinez et al. (2016)
Lucerne	22, 40		

<sup>2</sup> <http://www.gtk.fi/publ/foregsatlas>



Database / water body	Concentration	Comments	Reference
Zurich	10	Most data refer to total sediment and extraction with HNO <sub>3</sub> /HClO <sub>4</sub> /HF	
Geneva	20-30	Dated cores HNO <sub>3</sub> /HClO <sub>4</sub> /HF	Thevenon et al. (2011)

#### 4 Effect data (spiked sediment toxicity tests)

Effect data for benthic organisms up to 2006 was collected in the VRAR for Pb (LDAI 2008). Relevance (“C” score in the table below) and reliability (“R” score in the table below) of studies were evaluated according to the CRED-criteria (Moermond et al. 2016, Casado-Martinez et al. 2017) based on information reported in the VRAR (LDAU 2008) and the ECHA website (ECHA 2020) when full study reports were not available. A complementary bibliographic search was performed in the U.S. Ecotox Data Base (US EPA 2017). Among the 5856 entries for aquatic data on Pb toxicity, only 14 data were attributed to the sediment compartment. A key word research on the database Scopus for publications newer than 2006 (the most recent reference in the LDAI (2008)) was also performed, resulting in 855 entries.

As is stated in the TGD for EQS, for metals freshwater and saltwater datasets are separated and should only be combined if there is no demonstrable difference in sensitivity. Effect data for estuarine / marine organisms are classified as relevant with restrictions, pending further sensitivity comparisons.

According to the EU TGD (EC 2018) “*What is considered chronic or acute is very much dependent on 1) the species considered and 2) the studied endpoint and reported criterion*”. The effect database is composed of data within the EFSA criterion for true chronic tests, 28-65 d (EFSA 2015), and is therefore relevant for EQS derivation. Additional effect concentrations from 21 d tests are classified as relevant without restrictions (Nguyen et al. 2012) according to the endpoint considered.

For some of the species, both NOECs and EC<sub>10</sub> were available. The EC<sub>10</sub> were chosen in the VRAR (LDAI 2008) and the EQS datasheet (EC 2011) when an interval of confidence was given and when a clear dose response curve was obtained. When EC<sub>10</sub> could not be judged reliable due to the quality of data and information provided, the lowest value was chosen (the NOEC in all cases; LDAI 2008 and EC 2011). As recognized in the TGD (p. 155), the choice between the NOEC and EC<sub>x</sub> point estimates is subject to continuing debate. The most recent recommendations for judging whether using EC<sub>10</sub> or NOEC for risk assessment by EFSA (2019) include additional requirements such as the goodness of fit, the normalized width of the confidence interval, or the relationship between EC<sub>10</sub> and EC<sub>20</sub>/EC<sub>50</sub>. After internal discussion on the use of EC<sub>10</sub> or NOEC values, the NOECs are used here for EQS derivation.

According to the EU TGD (EC 2018), the concentration in the overlying water during the equilibration period should be measured in semi-static and static sediment toxicity tests and testing should preferably only be initiated when the metal concentration is stable. When overlying water was not monitored in semi-static or static tests before testing or the test was initiated after a short equilibration period without additional measurements of overlying and porewater, results are considered not suitable for EQS derivation and are therefore classified as not reliable. The test with *Tubifex tubifex* (Nguyen et al. 2003 cited in EC 2020) was initiated after a short equilibration period (14 d) but measurements in all relevant compartments were performed and concentrations in overlying and porewater were relatively low. The test is therefore classified as reliable with restrictions (R2).



According to the key role of AVS in driving bioavailability, effect data used in EQS derivation should report SEM and AVS concentrations if natural sediment is used in spiked-sediment toxicity testing (EU TGD, EC 2018). Artificial sediment has very low or no AVS representing worst-case scenarios and effect data can be used for EQS sediment derivation even when AVS and SEM are not reported. All effect data in the Pb data set came from spiked sediment toxicity tests performed with natural sediments and reported AVS content. The AVS content in test sediments range from 3.94 to 10 mmol/kg d.w., with the highest AVS value of 42 mmol/kg d.w. reported for the test with *Chironomus tentans* (Farrar and Bridges 2003 cited in ECHA 2020). It is noted, as highlighted by SCHER (2009), that all sediments used in the tests from which effect data for Pb were produced had AVS concentrations above the 10<sup>th</sup> percentile of the AVS concentrations assumed to be representative of oxic conditions (i.e. 0.77 mmol/kg d.w.; ECI 2008). The SCHER (2009) recommended performing additional tests with artificial sediments where AVS are low or virtually absent but at the time of completing this report such studies are not yet available.

Here, all effect data was used for EQS derivation except the NOEC for survival of *C. tentans*, which was considered not relevant for EQS derivation due to high AVS concentration. It is recognized that the AVS values of test sediments are representative for anoxic, depositional sediments where metals are preferentially accumulated but they do not correspond to worst-case scenarios where bioavailability is maximized. To note here that AVS values at head streams from South Switzerland reported by Burton et al. (2007) range from 0.006 to 0.02 mmol/kg d.w., concentrations much lower than the lowest AVS concentration in the test sediments. The derived EQS based on total Pb would not be protective.



Table 5 Sediment effect data collection for Pb 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. Abbreviations: n. a. = not available; Cb = background concentration; LOI = loss of ignition.

Group	Species	Test compound	Exposure	Equilibration	Endpoint	Test duration	Effect concentration	Value (mg/kg d.w.)	Sediment type	SEM-AVS (mmol/kg d.w.)	SEM-AVS/foc (mmol/kg d.w.)	Chem. analysis	Note	Validity	References
<b>Chronic toxicity data in freshwater</b>															
Crustacean Amphipoda	<i>Hyalella azteca</i>	PbCl <sub>2</sub>	static renewal	30 d, no information on water renewal during equilibration, stability of metal concentrations in overlying water or pH at the end of equilibration	Survival	28 d	NOEC	<u>1 390</u>	Field sediment, sieved to <300 µm. Cb 13.6-58.7 mg/kg d.w., AVS 8.5 mmol/kg d.w.	-2/4.2	n.a.	measured	AVS: 1.8 mmol/kg d. w. (AVS levels indirectly derived); no additional information provided neither in LDAI (2008) nor ECHA (2020).	R2/C1	Farrar and Bridges, 2003 cited in ECHA (2020)
Crustacean Amphipoda	<i>Hyalella azteca</i>	PbCl <sub>2</sub>	static renewal	"	Survival	28 d	EC10	1 416	"	"	n.a.	"	"	R2/C1	Farrar and Bridges, 2003 cited in ECHA (2020)
Crustacean Amphipoda	<i>Hyalella azteca</i>	PbCl <sub>2</sub>	Static	n.a.	Survival	28 d	LC <sub>10</sub>	1 844	Natural sediment, not uncontaminated but appropriate for amphipod survival, Cb 113 mg Pb/kg d.w., 101 mg Cu/kg d.w., 1 204 mg Zn/kg d.w. OM 3% (LOI).	n.a.	n.a.	measured		R3/C1	Borgmann and Norwood, 1999 cited in LDAI (2008)
Crustacean Amphipoda	<i>Gammarus pulex</i>	PbCl <sub>2</sub>	static renewal	35 d. overlying water renewed every week, pH, conductivity and concentration in overlying water monitored and stabilized before test initiation	Survival, growth	35 d	NOEC	<u>1 699</u>	Field sediment, Cb 20 mg/kg d.w., AVS 5-10 mmol/kg d.w., SEM 0.5 mmol/kg d.w., SEM/AVS 0.05-0.1 mmol/kg d.w. sand 56%, silt: 36%, clay 8%, TOC 1.5%	7.95 <sup>a</sup>	450 (surface)	measured	Sediment and porewater measurements at start and end of test, overlying water before renewal. AVS and SEM measured at start and end in surface and whole sediment. Concentrations expressed as time average.	R1/C1	Vandegehuchte et al. (2013)
Crustacean Amphipoda	<i>Gammarus pulex</i>	PbCl <sub>2</sub>	static renewal	"	Growth	35 d	EC10	2 541	"		660.5 (surface)	measured	"	R1/C1	Vandegehuchte et al. (2013)
Oligochaeta	<i>Lumbriculus variegatus</i>	PbCl <sub>2</sub>	static renewal	"	Growth (biomass per replicate)	28 d	NOEC	<u>1 736</u>	Field sediment, Cb 20 mg/kg d.w., AVS 5-10 mmol/kg d.w., SEM 0.5 mmol/kg d.w., SEM/AVS 0.05-0.1 mmol/kg d.w. sand 56%, silt: 36%, clay 8%, TOC 1.5%	5.6 <sup>a</sup>	295 (surface)	measured	Sediment and porewater measurements at start and end of test, overlying water before	R1/C1	Vandegehuchte et al. (2013)

Proposed SQC (EQS<sub>sed</sub>) for Lead



Group	Species	Test compound	Exposure	Equilibration	Endpoint	Test duration	Effect concentration	Value (mg/kg d.w.)	Sediment type	SEM-AVS (mmol/kg d.w.)	SEM-AVS/foc (mmol/kg d.w.)	Chem. analysis	Note	Validity	References
													renewal. AVS and SEM measured at start and end in surface and whole sediment		
Oligochaeta	<i>Lumbriculus variegatus</i>	PbCl <sub>2</sub>	static renewal	"	Growth (biomass per replicate)	28 d	EC10	1 870	"		528 (surface)	measured	Sediment and porewater measurements at start and end of test, overlying water before renewal. AVS and SEM measured at start and end in surface and whole sediment	R1/C1	Vandeghechuchte et al. (2013)
Oligochaeta	<i>Tubifex tubifex</i>	Pb(NO <sub>3</sub> ) <sub>2</sub>	static renewal	14 d	Survival	28 d	NOEC	> 4 719	Field sediment, Cb 20 mg/kg d.w., AVS: 3.94 mmol/kg d.w., SEM/AVS: 0.16, TOC 1.95%	n.a.		measured	Concentrations in sediment, porewater and overlying water at start and end of the test	R2/C1	Nguyen et al. 2003 cited in ECHA (2020)
Oligochaeta	<i>Tubifex tubifex</i>	Pb(NO <sub>3</sub> ) <sub>2</sub>	static renewal	14 d	Growth rate	28 d	NOEC	860	"	n.a.		measured	Concentrations in sediment, porewater and overlying water at start and end of the test Additional LOEC of 1101 mg/kg d.w.	R2/C1	Nguyen et al. 2003 cited in ECHA (2020)
Oligochaeta	<i>Tubifex tubifex</i>	Pb(NO <sub>3</sub> ) <sub>2</sub>	static renewal	14 d	Reproduction	28 d	NOEC	<u>503</u>	"	2.39		measured	Concentrations in sediment, porewater and overlying water at start and end of the test Additional LOEC of 860 mg/kg d.w. (4.51 SEM-AVS mg/kg d.w.)	R2/C1	Nguyen et al. 2003 cited in ECHA (2020)
Oligochaeta	<i>Tubifex tubifex</i>	Pb(NO <sub>3</sub> ) <sub>2</sub>	static renewal	14 d	Reproduction	28 d	EC10	573	"	n.a.		measured	Concentrations in sediment, porewater and overlying water at start and end of the test	R2/C1	Nguyen et al. 2003 cited in ECHA (2020)
Insecta Ephemeroptera	<i>Hexagenia limbata</i>	Pb(NO <sub>3</sub> ) <sub>2</sub>	static renewal	35 d. overlying water renewed every week	Survival, growth	21 d	NOEC	<u>≥ 2 903</u>	Field sediment, Cb 20 mg/kg d.w., AVS 3-10 mmol/kg d.w., SEM 3-10 mmol/kg d.w., SEM-AVS (-2.5)-(-9.5), sand 56%, silt: 36%, clay 8%, TOC 1.5-2.5%	11.81 (surface)	739.5 (surface)	measured	Concentrations in sediment, porewater and overlying water at start and end of the test	R2/C1	Nguyen et al. (2012)
Insecta Ephemeroptera	<i>Ephoron virgo</i>	Pb(NO <sub>3</sub> ) <sub>2</sub>	static renewal	35 d. overlying water	Survival	21 d	NOEC	<u>1126</u>	"	3.89 (surface)	262.8 (surface)	measured	"	R1/C1	Nguyen et al. (2012)



Group	Species	Test compound	Exposure	Equilibration	Endpoint	Test duration	Effect concentration	Value (mg/kg d.w.)	Sediment type	SEM-AVS (mmol/kg d.w.)	SEM-AVS/foc (mmol/kg d.w.)	Chem. analysis	Note	Validity	References
				renewed every week											
Insecta Ephemeroptera	<i>Ephoron virgo</i>	Pb(NO3)2	static renewal	"	Growth	21 d	NOEC	≥2071	"	8.35 (surface)	468.6 (surface)	measured	2 Concentrations in sediment, porewater and overlying water at start and end of the test	R1/C1	Nguyen et al. (2012)
Insecta Diptera	<i>Chironomus tentans</i>	PbCl <sub>2</sub>	static renewal	30 d	Survival	20 d	NOEC	<u>3 390</u>	Field sediment, sieved at sieved to <300 µm, Cb 13.6-58.7 mg/kg d.w., AVS 42 mmol/kg d.w.	-28/-228		measured	AVS: 1.8 mmol/kg dry weight (AVS levels indirectly derived)	R2/C3	Farrar and Bridges, 2003 cited in ECHA (2020)
<b>Chronic toxicity data in marine water</b>															
Crustacean Amphipod	<i>Leptocheirus plumulosus</i>	PbCl <sub>2</sub>	static renewal	7 d	Survival, reproduction	28 d	NOEC	3 980	Field sediment sieved to < 300µm, Cb: 12.8 mg/kg d.w. AVS 12.5 mmol/kg d.w., total SEM 1.79 mmol/kg d.w.	8.13			Pb measured in sediment, not in pore water or overlying water, at day 0.	R3/C2	Farrar and Bridges, 2003 cited in ECHA (2020)
Crustacean Amphipod	<i>Leptocheirus plumulosus</i>	PbCl <sub>2</sub>	static renewal	7 d	Growth rate	28 d	NOEC	931	"	-1.01	n.a.	measured	"	R3/C2	Farrar and Bridges, 2003 cited in ECHA (2020)
Crustacean Amphipod	<i>Leptocheirus plumulosus</i>	PbCl <sub>2</sub>	static renewal	7 d	Growth rate	28 d	EC10	1 291	"		n.a.	measured	"	R3/C2	Farrar and Bridges, 2003 cited in ECHA (2020)
Polychaete	<i>Neanthes arenaceodentata</i>	PbCl <sub>2</sub>	static renewal	7 d	Survival	28 d	NOEC	3 180	Field sediment sieved to < 300µm, Cb: 23.8 mg/kg d.w. SEM 11.9 mg Pb/kg d.w. AVS 12.5 mmol/kg d.w., total SEM 1.79 mmol/kg d.w.	-4.82	n.a.	measured	Pb measured in sediment, not in pore water or overlying water, at day 0.	R3/C2	Farrar and Bridges, 2003 cited in ECHA (2020)
Polychaete	<i>Neanthes arenaceodentata</i>	PbCl <sub>2</sub>	static renewal	7 d	Growth	28 d	NOEC	801	"	-14.89	n.a.	"	"	R3/C2	Farrar and Bridges, 2003 cited in ECHA (2020)
Polychaete	<i>Neanthes arenaceodentata</i>	PbCl <sub>2</sub>	static renewal	7 d	Growth	28 d	EC10	801	"	-14.89	n.a.	"	"	R3/C2	Farrar and Bridges, 2003 cited in ECHA (2020)

<sup>a</sup> Calculated from publication for surface sediment concentrations in Table 2, as time-average SEM-AVS.



#### 4.1 Graphic representation of effect data

According to the effect data available from spiked sediment toxicity tests with Pb expressed as total Pb concentrations, there is no specific group that is significantly more sensitive to Pb according to the reliable data from chronic tests (Fig. 1). The lowest effect concentrations available are for oligochaetes, but they are in the same order of magnitude than effect concentrations for insects and crustacean amphipods.

According to effect concentrations in spiked water tests with Pb and supportive field data used in EQS derivation (EC 2011 and references therein), the most sensitive taxa to Pb are molluscs (represented by *Lymnaea stagnalis* in the effect dataset), followed by algae (*Pseudokirchneriella subcapitata*) and *Hyalella azteca*. It should be noted that effect data for molluscs lack in the present sediment toxicity dataset. Chironomid larvae were the most insensitive taxa in the species sensitivity distribution (EC 2011) although the test was performed with high AVS values and no OC content for test sediment was reported. Field data indicates that mayflies (Ephemeroptera) are more sensitive than chironomids, in agreement with the effect data for *E. virgo* and *C. tentans* in spiked sediment toxicity testing. *T. tubifex* was also more sensitive in acute spiked water toxicity testing than chironomids.

Although according to SCHER (2009), EC (2011) and the EU TGD for EQS (EC 2018, p. 108) effect concentrations based on bioavailable Pb should be considered as far as possible, normalization of data as presented in Table 5 (SEM-AVS and SEM-AVS/foc) did not decrease the variability of effect data (graphic representation not shown).

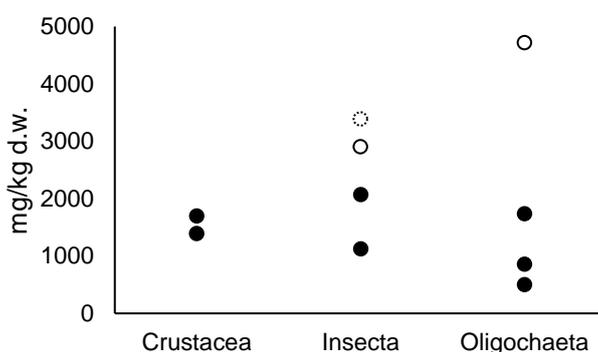


Figure 1 Graphical representation of chronic effect data from spiked sediment toxicity tests with Pb expressed as total measured sediment concentration for freshwater organisms. Empty symbols are unbounded ( $\geq$ ) data; full symbols are reliable and relevant (R1-R2/C1) data; dotted lines represent data not used in EQS derivation after reliability and relevance assessment.

#### 4.2 Comparison between marine and freshwater species

According to the EU TGD p. 39 (EC 2018), freshwater and saltwater data for metals should be separated a priori and should only be combined when there is no demonstrable difference in sensitivity. According to the limited number of reliable and relevant data for marine species, freshwater and marine data are separated and only effect data for freshwater species are used in EQS derivation.

#### 4.3 Overview of reliable and relevant long-term studies

According to the EU TGD p. 25 (EC 2018): “All available data for any taxonomic group or species should be considered, provided the data meet quality requirements for relevance and reliability”. Relevant and reliable chronic data is available for 5 species (Table 6), with additional effect data for other 2



freshwater species. Table 6 includes effect concentrations (NOECs) expressed as total Pb and added Pb, these last NOECs derived by subtracting the background concentration in the test sediment to the NOEC expressed in total Pb. Because all tests were performed with natural sediments the background Pb concentrations ranged from 12.6 to 58.7 mg/kg d.w.

There are values (NOECs) for three different endpoints, derived from one 28 d chronic study with *Tubifex tubifex*. The NOEC for the most sensitive endpoint, reproduction, of 503 mg/kg d.w. total Pb is used for EQS derivation.

There are values (NOECs) for two different endpoints, derived from one 21 d chronic study with *Ephoron virgo*. The NOEC derived the most sensitive endpoint, growth, of 1 126 mg/kg d.w. total Pb is used for EQS derivation.

There is one NOEC value for one endpoint derived from one 28 d chronic study with *Hyalella azteca*. The NOEC derived for survival of 1 390 mg/kg d.w. total Pb is used for EQS derivation.

There are values (NOECs) for two different endpoints, derived from one 28 d chronic study with *Gammarus pulex*. The NOEC derived for survival and growth of 1 699 mg/kg d.w. total Pb is used for EQS derivation.

There is one NOEC value for one endpoint derived from one 28 d chronic study with *Lumbriculus variegatus*. The NOEC derived for biomass per replicate of 1 736 mg/kg d.w. total Pb is used for EQS derivation.

There is one unbounded NOEC value for two endpoints derived from a chronic 21 d study with *Hexagenia limbata*. The unbounded NOEC derived for survival and growth > 2 903 mg/kg d.w. total Pb is used for EQS derivation.

Table 6 Most sensitive endpoint for each species from relevant and reliable chronic studies for freshwater organisms from Table 5.

Species	Exposure duration [d]	Endpoint	NOEC Total Pb [mg/kg d.w.]	NOEC Added Pb [mg/kg d.w.]	Reference
<i>Tubifex tubifex</i>	28	Reproduction	503	483	Nguyen et al. 2003 cited in ECHA (2020)
<i>Ephoron virgo</i>	21	Growth	1 126	1 106	Nguyen et al. (2012)
<i>Hyalella azteca</i>	28	Survival	1 390	1 331-1 376	Farrar and Bridges, 2003 cited in ECHA (2020)
<i>Gammarus pulex</i>	35	Survival	1 699	1 679	Vandegheuchte et al. (2013)
<i>Lumbriculus variegatus</i>	28	Biomass per replicate	1 736	1 716	Vandegheuchte et al. (2013)
<i>Hexagenia limbata</i>	21	Survival/growth	> 2 903	> 2 883	Nguyen et al. (2012)



## 5 Derivation of $QS_{sed}$

According to the EU TGD for EQS derivation, 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.

Because bioavailability could have been reduced by AVS concentrations in the test sediments from the effect data set, the SCHER (2009) considered that environmental quality criteria derived from total (not normalized) effect data originated from sediment containing high AVS content as those used in the spiked sediment toxicity tests was of “little relevance” and should not be used. Furthermore, the opinion of SCHER (2009) regarding LDAI (2008) was that a generic sediment PNEC, i.e. a PNEC based on total Pb, without considering bioavailability, was of little relevance. The VRAR (LDAI 2008) therefore followed the simultaneously extracted metal/acid volatile sulphide (SEM/AVS) approach to derive a bioavailable PNEC for sediment risk assessment. EC (2011) in the EU EQS dossier followed two approaches for  $EQS_{sed}$  derivation (a) based on total Pb using an SSD, and (b) using the lowest unbounded NOEC based on bioavailable Pb (i.e. Pb in excess of available AVS), to which an AF of 10 was applied. As stated in EC (2011), the uncertainty associated with both  $EQS_{sed}$  values was high and, as noted, although the SCHER Opinion (2009) agreed that Pb sediment bioavailability should be accounted for, it did not agree with the methodology taken mainly due to the limitations in the dataset in regard to the estimation of the bioavailable PNEC.

Here, all effect data was used for EQS derivation based on total Pb without bioavailability correction except the NOEC for survival of *C. tentans*, which was considered not relevant for EQS derivation due to high AVS concentration. It is recognized that the AVS values of test sediments are representative for anoxic, depositional sediments where metals are preferentially accumulated but they do not correspond to worst-case scenarios where bioavailability is maximized.

### 5.1 Derivation of $QS_{sed,AF}$ 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 long-term effect datum available for total Pb is the NOEC of 503 mg/kg d.w. for reproduction of *Tubifex tubifex*.

The lowest long-term effect datum available for bioavailable Pb (Pb in excess) is the NOEC of 262.8 mmol/kg d.w. for survival of *Ephoron virgo*.

In case of long term tests (NOEC or  $EC_{10}$ ) being available for three species representing different living and feeding conditions, the EU TGD recommends the application of an assessment factor of 10 on the lowest credible datum (Table 11 in EC (2018)).

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

$$QS_{sed,AF,total} = \frac{503 \left( \frac{mg}{kg} \right)}{10} = 50.3 \left( \frac{mg}{kg} \right)$$



$$\begin{aligned}
 QS_{sed,AF,bioav} &= \frac{262.8 \left( \frac{\text{mmol excess Pb}}{\text{kg}} / f_{oc} \right)}{10} = 26.28 \left( \frac{\text{mmol excess Pb}}{\text{kg}} / f_{oc} \right) \\
 &= 54.5 \frac{\text{mg}}{\text{kg}} (1\% OC)
 \end{aligned}$$

The application of an AF of 10 to the lowest credible chronic datum results in a  $QS_{sed,AF,total}$  of 50.3 mg/kg d.w.

For comparison purposes only, when bioavailability is taken into consideration and the lowest credible chronic datum is expressed in excess Pb, the application of an AF of 10 results in a  $QS_{sed,AF,bioav}$  corresponding to 54.5 mg/kg d.w. (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 NOEC/ $EC_{10}$ , from different species covering at least eight taxonomic groups (EC (2018), p. 43). Specific recommendations for the sediment compartment are only available to some extent in the ECHA Proceedings of the Topical Scientific Workshop Principles for Environmental Risk Assessment of the Sediment Compartment (ECHA 2018) but further recommendations on the minimum data requirements are not fixed.

The SSD approach has been previously applied for the derivation of sediment PNECs in the VRAR for Copper (ECI 2008) with 6 data from 6 species (trimmed data set of 63 NOECs), and recently a Danish draft report for sediment EQS derivation with effect data for Zn for 12 species representing 6 systematic groups: insects were represented by two different orders as Diptera and Ephemeroptera have widely different ecology and feeding strategies, Macrophyta, Oligochaeta, Polychaeta, Amphipoda (Crustacea), Diptera and Ephemeroptera.

The minimum data requirements are not met for the use of the SSD approach. However, the SSD approach is used here for comparison purposes. The SSD was performed using total effect concentrations for freshwater species in Table 6. The results of the SSD are included in Fig. 2 and Appendix 1.

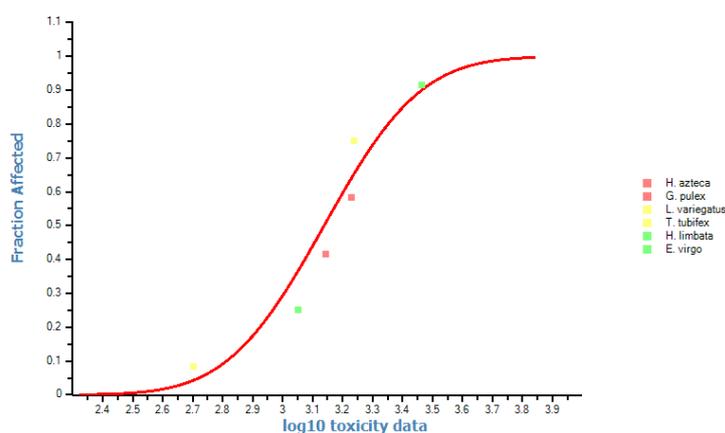


Figure 2 Species sensitivity distribution (SSD) of the chronic effect concentrations of all species for total Pb generated with ETX 2.2. Number of data points ( $n$ ) = 6; requirements for normal distribution according to van Vlaardingen et al. 2005 were met. Color code: orange crustacean Amphipoda, yellow Oligochaeta, green insect.



The resulting HC<sub>5,total</sub> is 494.0 mg/kg d.w. (lower and upper 90 % confidence limits 157.3-824.2 mg/kg d.w., standard deviation of the log<sub>10</sub> transformed values = 0.25).

According to the EU TGD for EQS, an SSD should be based on the most sensitive groups of species (EC 2018). From the effect data base available for benthic organisms, there is no indication of a group that is particularly sensitive to Pb.

An AF of 5 is used as default:

$$QS_{sed,SSD} = \frac{HC5}{AF}$$

$$QS_{sed,SSD,total} = \frac{494 \left(\frac{mg}{kg}\right)}{5} = 98.8 \left(\frac{mg}{kg}\right)$$

## 6 Derivation of QS<sub>sed,EqP</sub> using the Equilibrium Partitioning approach

If no reliable sediment toxicity data are available, the Equilibrium Partitioning (EqP) can be used to estimate the QS<sub>sed,EqP</sub>. This approach, developed for non-ionic substances, is used here for comparison purposes.

### 6.1 Selection of QS for water

An Annual Average Quality Standard (AA-EQS) has been proposed by the European Commission which set a value of 1.2 µg/l for the protection of pelagic species after the application of an AF of 2 on the HC<sub>5</sub> of the SSD<sub>water</sub> (EC 2011). The effect data for the water phase used in the EQS dossier for the development of the EQS<sub>water,SSD</sub> were not evaluated for relevance and reliability.

### 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<sub>d</sub>, K<sub>oc</sub>, K<sub>ow</sub>) is chosen. A clear justification must be given for the chosen coefficient and any uncertainty should be described in a transparent way.”

The K<sub>p</sub> values reported in the VRAR (LDAI 2008) range from 35 481 to 707 946 (154 882) l/kg for sediment and from 50 119 to 1 698 244 (295 121) l/kg for suspended matter (10<sup>th</sup>-90<sup>th</sup> percentile (50<sup>th</sup> percentile)). Here the K<sub>p</sub> values for sediments are used for sediment EQS derivation. No additional values have been searched.

### 6.3 Derivation of QS<sub>sed,EqP</sub>

According to the TGD (EC 2018), the calculation of the QS<sub>sed,EqP</sub> for sediment is derived as follows:

$$QS_{sed,EqP} \left(\frac{mg}{kg} \text{ wet weight}\right) = \frac{K_{sed-wat}}{\rho_{sed}} * AA - EQS_{water}$$

where

AA-EQS<sub>water</sub>: Annual Average Environmental Quality Criteria for freshwater derived by EU (EC 2011).

ρ<sub>sed</sub>: bulk density of sediment default value 1300 kg/m<sup>3</sup> (EC 2018)

K<sub>sed-wat</sub>: partition coefficient between sediment and water



Where:

$$K_{sed-water} = Fair_{sed} * K_{air-water} + Fwater_{sed} + Fsolid_{sed} * \frac{Kp_{sed}}{1000} * \rho_{solid}$$

Where

$Fair_{sed}$  : fraction air in sediment ( $\sim=0$ )

$K_{air-water}$  : air-water partition coefficient

$Fwater_{sed}$  : fraction water in sediment default value 0.8 for sediment (EC 2018)

$Fsolid_{sed}$  : fraction of solids in sediment default value 0.2 for sediment (EC 2018)

$\rho_{solid}$  : density of the solid phase default value 2500 kg/m<sup>3</sup> (EC 2018)

The  $QS_{sed,EqP}$  (dry weight) is transform from a wet weight basis to a dry wet basis by multiplying the  $QS_{sed,EqP}$  (wet weight) and a conversion factor of:

$$CONV_{sed} = \frac{\rho_{sed}}{Fsolid_{sed} * \rho_{solid}} = 2.6$$

The resulting  $QS_{sed,EqP}$  are 42.6 and 849.5 mg/kg d.w. for the 10<sup>th</sup> and 90<sup>th</sup> percentile values of  $Kp$ , and 158.9 mg/kg d.w. for the 50<sup>th</sup> percentile.

An additional AF of 10 should be applied to the resulting  $QS_{sed,EqP}$  for substances with  $\log K_{ow} > 5$ . No additional AF was applied.

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

### 7.1 Overview of available mesocosm studies

No mesocosm studies were found for Pb.

### 7.2 Available sediment quality guidelines from field data

Sediment quality guidelines (SQG) derived from field data mainly based on macrozoobenthos for total lead range between 19 and 35.8 mg/kg d.w. (Table 7). These SQGs are of the same order of magnitude as the different  $QS_{sed}$  based on spiked sediment toxicity tests, one order of magnitude below the effect concentrations from spiked sediment toxicity testing available for Pb. The SQG derived from field data are close the  $QS_{sed,EqP}$  derived using the lowest  $Kp_{sediment-water}$ . The threshold for effects derived from altered oligochaete communities in field studies is 12.3 mg/kg d.w., the lowest among these values. The main criticism of field SQG is that they do not account for causality because are derived from field data where co-occurring contaminants were also present.



Table 7 Sediment quality guidelines available in the literature based on field data.

SQG	Value [mg/kg d.w.]	Reference	Description
Threshold effect level (TEL)	35	Smith et al. (1996)	Sediments are considered to be clean to marginally polluted. No effects on most sediment-dwelling organisms expected below this concentration.
Likely effect level (LEL)	31	Persaud et al. (1993)	Concentration below which adverse effects are expected to occur only rarely.
Environmental risk limit (ERL)	35	Long and Morgan (1991)	Chemical concentration below which adverse effects would be rarely observed.
Lowest effect level (LEL)	19	De Deckere et al. (2011)	Concentration below which adverse effects on macrozoobentos is rarely observed. A SEL of 167 mg/kg d.w. describes concentration above which macrozoobentos is likely affected.
Threshold effect level ( $TEL_{oligo}$ )	12.3	Vivien et al. (2020)	Concentration below which oligochaete communities are rarely affected. A $PEL_{oligo}$ of 23.9 mg/kg d.w. describes concentrations above which oligochaete communities are likely affected.
Threshold effect concentration (TEC)	35.8	MacDonald et al. (2000)	Threshold effect concentration for benthic organisms. Derived from different field and laboratory effect data.

## 8 Toxicity of degradation products

Not relevant for metals.

## 9 $EQS_{sed}$ proposed to protect benthic species

The different QS values for each derivation method included in the EC EQS TGD (EC 2018) are summarized in Table 8. According to the TGD, the most reliable extrapolation method for each substance should be used (EC 2018). In all cases, data from spiked sediment toxicity tests and thus the  $QS_{sed,AF}$  are preferred over the EqP approach. An  **$EQS_{sed}$  of 50.3 mg/kg d.w.** is proposed.

According to available data (Table 4), the proposed  $EQS_{sed}$  is above the background and lowest range natural concentrations in Swiss sediments. Therefore, the  $EQS_{sed}$  is considered total<sup>3</sup>.

Table 8  $QS_{sed}$  derived according to the three methodologies stipulated in the EU-TGD and their corresponding AF. All concentrations expressed as mg/kg d.w. <sup>a</sup> Derived for comparison purposes.

	Total Pb concentration	AF
$QS_{sed,SSD}^a$	98.8	5
$QS_{sed,AF}$	50.3	10
$QS_{sed,EqP}^a$	42.6-850	--
Field SQG	12.3-35.8	--
<b>Proposed <math>EQS_{sed}</math></b>	<b>50.3</b>	

<sup>3</sup> When the derived QS is < background concentration, the Added Risk Approach (ARA) can be used, adding the  $EQS_{sed}$  to the background concentration for compliance check.



## 9.1 Protection of benthic organisms and uncertainty analysis

The proposed  $EQS_{sed}$  is in the lowest range of EQS derived in other EU countries and the PNEC used for risk assessment. In all cases, these EQS are set as total Pb except the  $EQS_{sed}$  proposed in France, which is close to the  $EQS_{sed}$  derived here but is derived using the Equilibrium Partitioning approach and is proposed as Maximum Permissible Concentration and should be applied following the Added Risk Approach by adding to the background concentration.

The following considerations and uncertainties related to the proposed  $EQS_{sed}$  here are highlighted:

- 1) Field SQGs are lower than the proposed  $EQS_{sed}$ , providing uncertainty on the level of protection for benthic communities and macrozoobenthos. The effect data base does not include studies on effects in benthic molluscs and microalgae, which were the most sensitive in water-only toxicity tests compared to the crustacean *H. azteca*. Although the  $QS_{sed,EqP}$  should protect against adverse effects to these organisms through exposure in the pelagic environment, it is lower than the proposed  $EQS_{sed}$  based on spiked-sediment toxicity tests data. These two groups of organisms are also relevant for the benthic compartment and may be exposed to additional exposure routes. Additional effect concentrations from spiked sediment toxicity tests for these group would be beneficial.
- 2) The threshold effect concentration for oligochaete communities is lower than the proposed  $EQS_{sed}$ , close to the lowest available background and environmental concentrations in Switzerland. Although the lowest effect concentrations from spiked sediment toxicity tests available in the effect database are for oligochaetes, these are one order of magnitude higher than the threshold effect concentration for oligochaete communities.
- 3) The proposed  $EQS_{sed}$  is close to the high range background concentrations available in Switzerland. Increasing the AF or setting the  $EQS_{sed}$  based on the  $QS_{sed,EqP}$  should be considered as Maximum Permissible Concentration, to be added to the background concentration and therefore would result in a similar value to the proposed  $EQS_{sed}$ .
- 4) Remaining uncertainties also relate to the use of effect concentrations from studies with test sediments with AVS concentrations not corresponding to worst-case scenarios such as head streams in Switzerland. Normalization against this factor is possible but still challenging for implementation.

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## Appendix 1. Goodness-of-fit of toxicity data from ETX SSD results

Parameters of the normal distribution						
Name	Value	Description				
mean	3.138119	mean of the log toxicity values				
s.d.	0.253894	sample standard deviation				
n	6	sample size				
<b>HC5 results</b>						
Name	Value	log10 (Value)	Description			
LL HC5	157.3111	2.196759	lower estimate of the HC5			
HC5	493.954	2.693686	median estimate of the HC5			
UL HC5	824.1744	2.916019	upper estimate of the HC5			
sprHC5	5.239137	0.71926	spread of the HC5 estimate			
<b>FA At HC5 results</b>						
Name	Value	Description				
FA lower	0.246	5% confidence limit of the FA at standardised median logHC5				
FA median	5	50% confidence limit of the FA at standardised median logHC5				
FA upper	27.737	95% confidence limit of the FA at standardised median logHC5				
<b>HC50 results</b>						
Name	Value	log10 (Value)	Description			
LL HC50	849.6794	2.929255	lower estimate of the HC50			
HC50	1374.417	3.138119	median estimate of the HC50			
UL HC50	2223.218	3.346982	upper estimate of the HC50			
sprHC50	2.616537	0.417727	spread of the HC50 estimate			
<b>FA At HC50 results</b>						
Name	Value	Description				
FA lower	25.09482	5% confidence limit of the FA at standardised median logHC50				
FA median	50	50% confidence limit of the FA at standardised median logHC50				
FA upper	74.90518	95% confidence limit of the FA at standardised median logHC50				