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

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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}): 99.7 mg/kg d.w. (generic) or 17.9 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 zinc (Zn) of 17.9 mg/kg d.w. is obtained. Because this value is below the range of concentrations representative of background levels of Zn in Swiss sediments, a generic SQC of 99.7 mg/kg d.w. is proposed, calculated by adding the FOREGS (Forum of European Geological Surveys Geochemical database) mean value for Zn background concentrations of 81.8 mg/kg d.w. for floodplain sediments. The SQC can be derived for the local conditions by adding 17.9 mg/kg d.w. to the local Zn background concentration.

Zusammenfassung

SQK (EQS_{sed}): 99.7 mg/kg TS (allgemein) oder 17.9 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 zinc (Zn) ein SQK von 17.9 mg/kg TS. Da dieser Wert unter dem typischen Konzentrationsbereich für die Hintergrundkonzentrationen von Zn in Schweizer Sedimenten liegt, wird ein allgemeines SQK von 99.7 mg/kg TS vorgeschlagen. Dieses wurde berechnet, indem zur Konzentration von 17.9 mg/kg TS der FOREGS (Forum of European Geological Surveys Geochemical database)-Mittelwert für Hintergrundkonzentrationen von Zn in Auensedimenten von 81.8 mg/kg TS addiert wird. Der standortspezifische SQK kann bestimmt werden, indem 17.9 mg/kg TS zur lokalen Hintergrundkonzentration für Zn addiert wird.

Résumé

CQS (EQS_{sed}): 99,7 mg/kg p.s. (générique) ou 17,9 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 zinc (Zn) de 17,9 mg/kg p.s. est dérivé. Étant donné que cette valeur est inférieure à la plage de concentrations représentatives des niveaux de fond de Zn dans les sédiments en Suisse, un CQS générique de 99,7 mg/kg p.s. est proposé, calculé en ajoutant la valeur moyenne FOREGS (Forum of European Geological Surveys Geochemical database) de 81,8 mg/kg p.s. pour les sédiments des plaines inondables. Le CQS peut être dérivé pour les conditions locales en ajoutant 17,9 mg/kg p.s. à la concentration de fond locale.

Sommario

CQS (EQS_{sed}): 99,7 mg/kg p.s. (generico) o 17,9 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 zinco (Zn) di 17,9 mg/kg p.s. è derivato. Poiché questo valore è inferiore alla gamma di concentrazioni rappresentative dei livelli di fondo di Zn nei sedimenti svizzeri, si propone un CQS generico di 99,7 mg/kg p.s. calcolato sommando il valore medio FOREGS (Forum of European Geological Surveys Geochemical database) di 81,8 mg/kg p.s. per i sedimenti delle pianure alluvionali. Il CQS può essere derivato per le condizioni locali aggiungendo 17,9 mg/kg p.s. alla concentrazione di fondo locale.

Table of content

1 General Information

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

- EU-RAR (EC 2010). European Union Risk Assessment Report CAS: 7440-66-6, EINECS No: 231-175-3, Zinc metal.
- ECHA (2020) Information on Registered Substances: Zinc, CAS number: 7440-66-6 https://echa.europa.eu/registration-dossier/-/registered-dossier/16146. Last modified:14-May-2020.
- UK EA (2010). Zinc EQS draft dossier (Brussels: United Kingdom Environment Agency).
- CCME (1999). Canadian Sediment Quality Guidelines for the Protection of Aquatic Life : Zinc.

1.1 Identity and physico-chemical properties

According to OECD Cooperative Chemicals Assessment Programme (CoCAP), the Zinc Category includes six CAS numbers[1] that are similar from a hazard point of view (OECD 2005). It is assumed that all Zn in the environment either dissociate or form the Zn cation that is responsible for the hazardous effects through several speciation or transformation reactions while counter ions do not significantly contribute to the major effects seen. This dossier therefore describes general properties and characteristics for Zinc Metal (CAS 7440-66-6) and measured environmental concentrations and ecotoxicity data refer to total Zn concentrations if not otherwise stated.

Table 1 summarizes identity and physico-chemical parameters for Zn required for EQS derivation according to the TGD (EC 2018). Where available, experimentally collected data is identified as (exp.) and estimated data as (est.). When not identified, no indication is available in the cited literature.

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

Characteristics	**Values**	**References**
Common name	Zinc	EU-RAR (EC 2010)
IUPAC name	Zinc	EU-RAR (EC 2010)
Chemical group	Metal	EU-RAR (EC 2010)
Structural formula	Zn	EU-RAR (EC 2010)
Molecular formula	Zn	EU-RAR (EC 2010)
CAS	7440-66-6	EU-RAR (EC 2010)
EC Number	231-175-3	EU-RAR (EC 2010)
SMILES code	[Zn]	EU-RAR (EC 2010)
Molecular weight [g/mol]	65.38	EU-RAR (EC 2010)
Melting point [°C]	420	EU-RAR (EC 2010)
Boiling point [°C]	908	EU-RAR (EC 2010)
Vapour pressure [Pa]	31 Pa at 450ºC	EU-RAR (EC 2010)
Henry's law constant [$Pa \cdot m^3 \cdot mol^{-1}$]	Not relevant	EU-RAR (EC 2010)
Water solubility [mg/l]	0.1 at 20 °C and pH 6.93 - 8.57	ECHA (2020)

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[1] Zinc metal [Zn]: CAS 7440-66-6
Zinc oxide [ZnO]: CAS 1314-13-2
Zinc distearate [C18H36O2.1/2Zn]: 557-05-1 / 91051-01-3
Zinc chloride [ZnCl2]: 7646-85-7
Zinc sulphate [ZnSO4]: 7733-02-0
Trizinc bis (orthophosphate) [Zn3(PO4)2 • 2-4H2O]: 7779-90-0

Characteristics	Values	References
Dissociation constant (pK_a)	Study not feasible	ECHA (2020)
Octanol-water partition coefficient ($\log K_{ow}$)	Scientifically unjustified	ECHA (2020)
Organic carbon adsorption coefficient ($\log K_{oc}$)	Not relevant	EU-RAR (EC 2010)
Sediment /soil adsorption coefficient (K_p [l/kg])	[1] 4 571 - 5 011 872 (freshwater suspended matter; geomean=59 196; N=20) [2] $K_p$sed = 88 794 (estimated as 1.5 × geomean of Kp for suspended matter, following EC 2010) [2] 1.4 – 320 000 (contaminated soils; median=1 731; mean=11 615; N=320)	[1] Appendix 1 [2] Estimated from Appendix 1 following EC (2010) [2] Sauvé et al. (2000)
Aqueous hydrolysis DT_{50}	Scientifically unjustified	ECHA (2020)
Aqueous photolysis DT_{50}	Scientifically unjustified	ECHA (2020)
Biodegradation in water environment DT_{50} [d]	Scientifically unjustified	ECHA (2020)
Biodegradation in sediment DT_{50} [d]	Scientifically unjustified	ECHA (2020)
Biodegradation in soil DT_{50} [d]	Scientifically unjustified	ECHA (2020)

1.2 Regulatory context and environmental limits

Zinc is a high production volume (HPV) chemical included in the OECD Cooperative Chemicals Assessment Programme (CoCAP), which published an initial assessment profile in 2005 (SIAP), 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 tonnes per year (OECD 2005). The associated risk assessment concluded that, for the sediment compartment, measured and predicted concentrations exceeded the predicted no effect concentration ($PNEC_{add,sediment}$ = 49 mg/kg d.w. to add to the background concentration) for a number of the production sites of Zn metal and a number of the processing scenarios of Zn metal, pointing to a potential risk for sediment-dwelling organisms. In addition, at some other production sites a risk may occur due to the possible existence of high regional background concentrations (OECD 2005).

As an inorganic substance, a PBT and vPvB assessment shall not be conducted. However, it is clarified that, as an essential metal, Zn is regulated and therefore is considered not to bioaccumulate or biomagnify. Although persistence does not apply either to metals, Zn is considered not persistent according to the documented removal from the water column, considered a surrogate for persistence.

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

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

Europe	
EU Priority substance list	Not identified as a priority substance in the field of the Water Framework Directive (Directive 2013/39/EU) 2^{nd} priority substance
REACH	Manufactured and/or imported in the European Economic Area in 1 000 000 - 10 000 000 tonnes per year
OECD	High Production Volume substance, included in the Cooperative Chemicals Assessment Programme (CoCAP)
Switzerland	
Water protection ordinance (WPO) (01.01.17)	Annex 2 Requirements on Water Quality : 20 µg/l Zn (total), 5 µg/l Zn (dissolved) (maximum concentrations) Annex 3 Requirements for the Discharge of Polluted Waste Water: 2 mg/l Zn (total, requirement for discharge into waters, 2 mg/l Zn (total, requirement for discharge into public sewers)
Contaminated site ordinance (CSO)(01.01.16)	Annex 2 Concentration values for assessing the impact of polluted sites on ground and surface waters (5 mg/l) Annex 3 Concentration for soil remediation 2000 mg/kg
Soil protection ordinance (12.04.16)	Annex 1 : Indicative values for soil remediation
Ordinance on Air Pollution Control (OAPC) (01.02.18)	Strictly regulated in several combustibles and industrial processes. Emission limits in place.
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)	Annex 2.2.1 Threshold in organic fertilisers, recycling fertilisers and farm manure Annex 2.8 Content in paints and varnishes

The $PNEC_{add,sediment}$ used in the EU RAR (EC 2010) is set at 49 mg/kg d.w. This PNEC is based on the added risk approach, and should be added to the local background concentration of Zn for risk assessment. This $PNEC_{add,sediment}$ was derived after applying an assessment factor of 10 to the lowest chronic effect concentration according to the TGD methodology (EC 2018). The $PNEC_{add, sediment}$ was derived from the lowest NOEC obtained in the 6-week test with *Hyalella azteca*, 488 mg/kg d.w. (Nguyen et al. 2005). This test was performed using sediment with a low OC content and, probably, a low content of acid-volatile sulphides. This NOEC was corrected for the background Zn concentration in the sediment, and a correction for bioavailability was performed for exposure concentrations in Tier 2 of the assessment (EC 2010).

Additional threshold values based on different approaches (mainly from laboratory tests and field data) summarized in Table 3 range from 129 to 140 mg/kg d.w. Only the Negligible Concentration from the Netherlands states clearly that it is derived for a standard sediment with 10 % TOC and 25 % clay.

Table 3 PNEC/quality standards 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
$PNEC_{add,sediment}$	49	Deterministic method (EC 2018): application of an Assessment Factor 10 to lowest NOEC	EU-RAR (EC 2010)
Negligible Concentration (Target Value) 10 % TOC, 25 % clay	140	Based on available information from laboratory tests and field data	Crommentuijn et al. (2000)
Class I-Class II boundary	139	Based on available information from laboratory tests and field data	Miljødirektoratet (2016)
ISQG	129	Based on available information from laboratory tests and field data	CCME (1999)

1.3 Use and emissions

In Europe, Zn is used in industry covering different domains like galvanizing (38.8 %), in brass (25.5 %), die casting alloy (12.4 %), and rolled/wrought Zn (11.8) (UK EA 2010). In Switzerland, the chemical industry accounts for 76.6 % of the total Zn released from point sources to wastewater whereas the production and processing of metals accounts for 22 % (data for 2016, OFEV 2016). In turn, wastewater accounts for 92.2 % of the total emission of Zn into water. Regarding emissions of Zn into the air, the production and processing of metals accounts for 95 % of the total Zn released into this environmental compartment, although emissions have decreased since 1990 by 40 to 60 % (OFEV 2016). No records of Zn release from diffuse sources are available for Switzerland but the main sources of Zn into water are airborne deposition (traffic, Sahara desert), urban runoff (roofing materials, anticorrosion paints, roads) and agriculture (manure, feed products, fertilizers and pesticides) (PPRC 2012). Zinc concentration in soils have remained relatively constant over the last 30 years except at zones with intensive grassland farm where soil protection values may be exceeded in 80-200 years according to present trends (OFEV 2017).

1.4 Mode of action and relative sensitivity of taxonomic groups

Zinc is an essential element for living organisms with a defined window of essentiality[2]. According to the substance profile available from ECHA (2020), it is essential for growth and development, neurological function, wound healing and immunocompetence. Excessive Zn exposure has been associated with neurodegenerative diseases and Zn deficiency adversely affect neurological function and immune competence. However, the exact mechanisms are not known.

Based on the existing information, ECHA (2020) concluded that there is no conclusive evidence for carcinogenic activity of any of the Zn compounds considered in the chemical safety report. The overall weight of the evidence from the existing in vitro and in vivo genotoxicity assays suggests that Zn compounds do not have biologically relevant genotoxic activity and no classification and labelling for mutagenicity is required. Regarding reproductive and developmental toxicity, there is no experimental evidence that would justify a classification of Zn compounds as hazardous for these effects according under the Dangerous Substance Directive 67/548/EEC or Regulation (EC) 1272-2008 on the

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[2] According to the EU-RAR (2010), the window of essentiality for an essential element is the range between the lowest and highest concentration that allows life.

classification, labelling and packaging of substances and mixtures. Experimental fertility data for mammals is, however, absent (ECHA 2020).

In fish, excess in Zn have been shown to interfere with Ca^{2+} homeostasis, provoking different lethal and sublethal effects like hypertrophy, hyperplasia, leukocyte infiltration and even suffocation (Hogstrand 2011). In aquatic invertebrates, Zn toxicity may induce sublethal effects like behavioral changes and changes in fecundity and growth, as well as loss in biodiversity and abundance in aquatic communities (CCME 1999; EC 2010). According to the effect data available for aquatic organisms (ECHA 2020), chronic effect concentrations available for fish species, invertebrates and microalgae fall within the same order of magnitude.

2 Environmental fate

2.1 Speciation and sorption/desorption processes

Zinc is the most abundant essential trace metal in the environment and has three different oxidation states: Zn^0, Zn^+ and Zn^{2+}. Under normal environmental conditions, inorganic Zn is present in the aquatic environment at the oxidation state Zn^{2+} (Cleven and Janus, 1993) and in many different forms, both in particulate form bound to different metal binding phases and in the dissolved phase. Its speciation is mainly dependent on pH and the presence and form of organic matter (OM), with Zn^{2+}, $ZnCO_3^0$, $ZnSO_4^0$, $ZnOH^+$, $Zn(OH)_2$, $ZnCl^+$, $Zn(Cl)_2^0$, $Zn(Cl)_3^-$, $ZnHPO_4$ and $Zn(Cl)_2^{-4}$ being the predominant forms (Hogstrand, 2011).

Zinc adsorption plays a predominant role in the fate and transport of Zn in aquatic systems, with a relatively high proportion of Zn (40-90 %) present in adsorbed form (Cleven and Janus 1993). Zinc binds the particulate phases through iron and manganese oxyhydroxides, particulate organic carbon (OC) and under reducing condition it forms stable complexes with acid volatile sulfide (AVS) (Chapman et al. 1998; Cleven and Janus 1993).

Adsorption of metals to the solid fraction of sediment or particulate matter is dependent on many variables such as cation exchange capacity (CEC), OM and clay content, pH, or redox potential. Adsorption (and therefore K_p) increases at increasing pH, while at low pH most metals are dissolved assuming that H^+ replaces metals sorbed on particles. Sauvé et al. (2000) showed that pH is the factor that explained the highest variability in the large database of K_p for contaminated soils (56 % of the variability of K_p values; N=320). There is also an apparent increase of K_p values at decreasing total Zn concentrations (higher adsorption to sediments and suspended matter in uncontaminated systems), increasing OM content and decreasing size of sediment particles (Cleven et al. 1993). For contaminated soils, OM and total Zn concentration explained little variability in K_p values (Sauvé et al. 2000).

According to a non-exhaustive review of available literature (Table 1 and Appendix 1), Zn partitioning coefficients for suspended matter from field studies in freshwater bodies range from 4 571 to 5 011 872 l/kg (log K_p 3.4-6.9), resulting in a geomean of 59 196 l/kg (N=20) (log K_p=4.80). According to the EU RAR (EC 2010), the Zn partitioning coefficients for sediments ($K_p$sed) is estimated from that for particulate matter, as follows: $K_p$sed = $K_p$susp / 1.5, based on the average difference in concentrations of Zn and other metals in both media. The estimated $K_p$sed is 88 794 l/kg. The difference in metal concentration in particulate matter and sediment is attributable to the difference in adsorption capacity, mainly due to the difference in clay and OM content (particulate matter: 40 % clay and 20 % OM; sediment: 25 % clay and 10 % OM; standard values used for Dutch surface waters (Stortelder et al. 1989 cited in EC 2010)).

An exhaustive review of partitioning coefficients for contaminated soils (Sauvé et al. 2000) reported a range of K_p values of 1.4-320 000 l/kg, with mean and median of 11 615 (log K_p=4.06) and 1 731 l/kg (log K_p=3.24) respectively (N=320). The range of values for soils are lower than the range of values reported for suspended matter (Table 1 and Appendix 1). Values for soils are considered less relevant than those for suspended matter and are therefore not used here for sediment EQS derivation. The value used here for EQS derivation is the estimated $K_p$sed value following the EU RAR (EC 2010).

2.2 Bioavailability

The bioavailability of divalent metals such as Zn to benthic organisms is driven by physicochemical and geochemical characteristics of the water-sediment system such as AVS, CEC, Fe/Mn oxyhydroxides, OC, particle size, water hardness and pH, and biological traits such as the feeding behavior and exposure route of a given organisms (Luoma and Rainbow 2008).

In aerobic sediments, OC and FeOOH content have the greatest influence on bioavailability by driving exposure of organisms to free ions in porewater and overlying water when this is the major exposure route (Chapman et al. 1998). This exposure pathway may be the major exposure route for tube-dwellers (oligochaetes) and large benthic crustaceans due to their bioturbation activities (Chapman et al. 1998). Depending on environmental and physiological conditions, diet-borne Zn may become the major exposure route (Nguyen et al. 2012a).

In anaerobic sediments, Zn (and divalent metals in general) can bind and form stable complexes with AVS by replacing either Fe and Mn sulfides in soluble forms to form more insoluble Zn sulfide (Chapman et al. 1998). The Simultaneously Extracted Metals (SEM)-AVS model suggests that a part of the metal will not be bioavailable when it is bound to the reactive solid sulfide present on the surface of the sediment. The following equation summarizes the equilibrium between the sulfide-complexed metal and the free dissolved metal on a mol-to-mol 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 forms, and $Mn^{2+}_{(aq)}$ and $Fe^{2+}_{(aq)}$ are the soluble Mn and Fe forms.

The SEM-AVS model showed to be a good predictor of non-toxicity in sediments when the SEM_{zn}-AVS difference was lower than zero (Nguyen et al. 2012b; Sibley et al. 1996; Vandegehuchte et al. 2013).

Bioavailability corrections based on normalized concentrations are historically considered a feasible approach to regulation (Chapman et al. 1998). A 2-tiered approach has been recommended for sediment risk assessment (Bodar et al. 2005), with a first tier including a region or site specific risk assessment that uses $PEC_{add}/PNEC_{add}$[3] ratio corrected for background concentrations because *"background concentration may affect the sensitivity or tolerance of individual organisms, but this effect is relatively small compared with the larger variety of toxicity observed in multiple species"* (p.304

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[3] PEC_{add}: Predicted Environmental Concentration, expressed as added concentration to the regional or site specific background concentration; $PNEC_{add}$: Predicted No Effect Concentration, expressed as added concentration to the regional or site specific background.

Bodar et al. 2005). A second tier that includes bioavailability correction for SEM/AVS was considered in the EU RAR (EC 2010), but using a default factor of 0.5 to correct exposure concentrations.

According to the EU TGD (EC 2018), this approach could be used as a line of evidence in the weight of evidence to predict the absence of metal toxicity in compliance checking under the EU Water Framework Directive (EU TGD pp. 117-118, EC 2018). Normalization of effect data used in EQS derivation was not considered feasible here.

2.3 Bioaccumulation and biomagnification

As an essential element, Zn accumulates to some degree in all organisms to maintain biological functions. This results in relatively high bioaccumulation factors at low exposure concentrations. At increasing exposure concentrations, most organisms are capable of regulating Zn internal concentrations to some extent (Luoma and Rainbow 2008).

According to available bioaccumulation data (Table 4), fishes and crustaceans accumulate Zn to a lower extent than algae and benthic organisms (Cleven and Janus 1993). Accumulation through the food chain decreases from algae to fishes, therefore it can be concluded that Zn does not biomagnify and secondary poisoning is not relevant (Cleven and Janus 1993; EC 2010).

Table 4 Summary of bioaccumulation factors (BCF) values from data search on ECOTOX Knowledgebase (U.S. EPA 2016)

Taxonomic Group	Median (25th-75th percentile)	n
Fish	100 (7-1000)	291
Crustaceans	470 (3-1945)	180
Worms	1000	3
Algae, moss, fungi	750 (213-1800)	182

3 Analytics

3.1. Methods for analysis and quantification limit

Zinc 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 0.001 µg/l for ICP-MS to 5 µg/l for ICP-OES. Expressed in terms of concentration in sediments, the range of LOD is 0.002-2.5 mg/kg d.w. Extraction can be performed on a greater amount of sediment to decrease the LOD.

3.2. Environmental concentrations

The ambient concentration of Zn in sediments is 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 background concentrations in sediments in order to develop EQS_{sed} relevant for the region of application. A review of available data is provided in Table 5. For comparison, ambient concentrations are also provided for fine sediments (< 63 µm) and for total sediment (< 2 mm).

No field campaign or project has been dedicated specifically to develop natural (background) concentrations of Zn in Swiss sediments. Thus, two different types of data relevant for evaluating the natural contribution to Zn 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 values are ideally those measured in the layer dated ca. 1850.
- Concentrations that are statistically representative of environmental concentrations not affected by anthropogenic sources of pollution, including the concentrations in stream sediments and floodplain sediments reported for Switzerland in the atlas of the Forum of the European Geological Surveys[4], which has been most commonly used as default background concentration.

Zinc concentrations in pre-industrial lake sediments range from 50 to 100 mg/kg d.w. for the main lakes in Switzerland. FOREGS reports concentrations for 10 sites for stream sediments referring to sediments <150 µm and floodplain sediment < 2 mm after aqua regia extraction. These correspond to a mean of 76.1 mg/kg d.w. and 81.8 mg/kg d.w., respectively. The concentrations in floodplain sediments are higher likely due to some anthropogenic influence compared to stream sediments.

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

Natural concentrations	Concentrations	Comments	Reference
Generic value			
FOREGS database	76.1	N=10 Fraction < 150 µm Aqua regia extraction Bed sediments	http://www.gtk.fi/publ/foregsatlas
	81.8	N=10 Fraction < 2 mm Aqua regia extraction Bed sediments	
Lakes			
Constance	53-58	Dated cores Most data refer to total sediment and extraction with HNO3/HClO4/HF	Reviewed in Casado-Martinez et al. (2016)
Lucerne	100		
Zurich	50		
Geneva	80	Dated cores $HNO_3/HClO_4/HF$	Thevenon et al. (2011)
Ambient concentration	**Concentrations [mg/kg d.w.]**	**Comments**	**Reference**
Fine sediment (< 63 µm)			
Ecotox Centre database	209 (Mean) 148 (Median) 13.3-3658 (Min-Max) 68.9 (10th percentile) 378 (90th percentile)	N=593 Mostly fraction < 63 µm and extraction with aqua regia	Casado-Martinez et al. (2016)
Total sediment (< 2 mm)			
Low-middle impacted sites			
Lienne St.-Léonard	40-80		Ecotox centre (unpubl. data)
Jona nach Rüti	45		

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[4] http://www.gtk.fi/publ/foregsatlas

Doubs	47-57	Bed sediment Extraction with aqua regia	
Birse Reconvilier	50		
Sihlsee	76		
High impacted sites			
Klausbach	208	Bed sediment Extraction with aqua regia	Ecotox centre (unpubl. data)
Wiese	307		
Birs	288		
Seegraben	208		

4 Effect data (spiked sediment toxicity tests)

Effect data for benthic organisms up to 2008 was collected from the extensive review performed for the European Union Risk Assessment Report for Zinc metal (EC 2010). 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 Annex 3.3.2.D of the EU-RAR (EC 2010).

A complementary bibliographic search was performed in the U.S. Ecotox Data Base (U.S. EPA 2016) as well as a key word search on Scopus for publications from 2008. The search returned 229 references.

Table 6 summarises effect data as total concentration and added concentration. Most of the studies were performed with natural sediment, AVS and OC content are reported in Table 6 when available.

According to the EU TGD (EC 2018) "*What is considered chronic or acute is very much dependent on 1) the species considered and 2) the studied endpoint and reported criterion*". According to EFSA, true chronic tests should cover a range of 28-65 d when half-life of a pesticide in sediment is >10 d (EFSA 2015). Here, results of 10 d toxicity tests are considered short-term tests and therefore not relevant for sediment EQS derivation.

According to the UE TGD (EC 2018), the concentration in the overlying water should be measured in semistatic 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 semistatic or static tests before testing or test was initiated after a short equilibration period (study with *Chaenorabditis elegans*, Haegerbaeumer et al. (2016) and study with *Tubifex tubifex*, Farrar and Bridges (2003) cited in EC 2010) results are considered not suitable for EQS derivation and are therefore classified as not reliable. The test with *C. elegans* was classified as not reliable and not retained for EQS derivation due to the short equilibration period and absence of measurements of concentrations in water and sediment. The study with *T. tubifex* was not retained for EQS derivation but was used as supportive information because of the long equilibration time and measurement of concentrations.

Additionally effect data for three estuarine and marine species were available: the amphipods *Corophium volutator* and *Melita plumosa* and the polychaete *Arenicola marina*. Effect data for *C. volutator* and *A. marina* are considered not relevant for sediment EQS derivation as acute toxicity data and not reliable due to the low equilibration period before starting the test. The study for *M. plumosa* returned reliable without restriction NOEC for growth, a reliable with restriction NOEC for reproduction due to the high variability among consecutive tests and potential impact of feeding regime during the test, and two additional L/EC_{50} assessed as not relevant for EQS sediment derivation. As is stated in section 4.2 of the EQS_{sed} proposal, it is recommended in the TGD for EQS that for metals freshwater and saltwater datasets should be kept separate and should only be combined, if there is no demonstrable difference in sensitivity. Data for freshwater and estuarine / marine organisms are presented separately in different subsections of the table.

AVS values in test sediments ranged from 0.5 to 37 mmol/kg d.w., with AVS in reliable and relevant chronic studies performed on sediments ranging from 2.1 to 10 mmol/kg d.w. Normalization of effect data against AVS has not been performed before EQS derivation, in line with the EU Cu-RAR (ECI 2008) and the EU RAR for Zn (EC 2010). For EQS derivation, test data in which bioavailability is maximized are preferred. The EU Cu-RAR derived a PNEC from the effect data retained after excluding data from sediments for which bioavailability of Cu was limited due to the presence of AVS, i.e. NOEC values generated with sediments that had AVS concentration higher than 0.77 mmol/kg d.w. This AVS value corresponds to the 10th percentile of the AVS concentrations derived from a Flemish dataset and is assumed to be representative of oxic conditions (ECI 2008). Here, all effect data was considered for EQS derivation. However, AVS values in head streams from South Switzerland reported by Burton et al. (2007) ranged from 0.006 to 0.02 mmol/kg d.w. Thus, it should be noted that the effect data used in EQS derivation were not representative of worst-case scenarios where bioavailability is maximized although it is representative for anoxic, depositional sediments where Zn is accumulated preferentially rather than erosional, oxic sediments.

Table 6 Sediment effect data for Zn. Data were evaluated for relevance and reliability according to the CRED criteria for sediments (Casado-Martinez et al. 2017) adapted based on Moermond et al. (2016). Total concentration: effect concentration derived from measured concentrations in test system. Cb: background concentration of Zn in test sediments before spiking. Added: effect concentration expressed as added (total-Cb), i.e. subtracting the background from the total measured concentration. All concentrations in mg/kg d.w. if not otherwise stated. Data not used in EQS derivation in grey.

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Total concentration	Sediment type	Added	Chem. analysis	Note	Validity	References
Marine and estuarine														
Acute														
Crustacean Amphipoda	*Corophium volutator*	ZnSO$_4$ – 7H$_2$O	Static	48 h	Survival	10 d	LC$_{50}$	31.87	Natural clean sediment, sandy. Cb: 7.5 mg/kg; salinity 32 ‰	24.37	Measured	Concentrations measured at the end of test in the fine fraction	R2/C3	Bat and Rafaelli (1998)
Polychaeta	*Arenicola marina*		Static	48 h	Survival	10 d	NOEC	23	Natural clean sediment, sandy. Cb: 7.5 mg/kg; salinity 32 ‰	15.5			R2/C3	
Chronic														
Crustacean Amphipoda	*Melita plumosa*	n.a.	Static	14 d	Reproduction	42 d	NOEC	730	Natural marine sediment (64% water, 99% particles <63µm, AVS 0.5 mmol/kg, pore-water salinity 29‰ and pH 7.3), Cb: 240 mg/kg	490	Measured		R2/C1	Gale et al. (2006)
					Survival		LC$_{50}$	>1645		>1405		Average of two tests	R1/C3	
					Gravidity		EC$_{50}$	>1770		>1530			R1/C3	
					Growth		NOEC	1280		1040			R1/C1	
Freshwater														
Acute														
Insecta Diptera	*Chironomus tentans*	n.a.	n.a.	n.a.	Growth	10 d	EC$_{10}$	80	Lake sediment from Canada, Cb: 26, 38 and 253 mg/kg d.w. not attributed to specific test sediments	n.a.	Measured	Classified as R1 in ECHA (2020)	R4/C3	ECHA (2020)
Chronic														
Insecta Diptera	*Chironomus tentans*	ZnCl$_2$	Static-renewal	14 d	Survival	20 d	NOEC	850	Lake sediment; Cb: 55 mg/kg d.w. (SEM-Zn), AVS 3.9 mmol/kg d.w., SEM 1.0 mmol/kg d.w., SEM-Zn 0.84-41 mmol/kg d.w., corresponding to 45 mg Zn/kg d.w., no TOC or clay information	795	Measured	NOECs expressed as arithmetic mean between measurements on day 20 and 56 of top sediment layer. Monitoring of equilibration through porewater measurements	R2/C1	Sibley et al. (1996)
					Growth	20 d	NOEC	850		795			R2/C1	
					Emergence	56 d	NOEC	850		795			R2/C1	
					Reproduction	56 d	NOEC	850		795			R2/C1	
Insecta Diptera	*Chironomus tentans*	ZnCl$_2$	Static-renewal	30 d	Growth	20 d	NOEC	639	Pond sediment; Cb: 30 mg/kg d.w., AVS 37	609	Measured	Expressed as arithmetic	R1/C1	Farrar and Bridges 2002

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Total concentration	Sediment type	Added	Chem. analysis	Note	Validity	References
					Survival	20 d	NOEC	2420	mmol/kg d.w., total Zn 0.47 mmol/kg d.w., SEM-Zn 0.14 mmol/kg d.w., 1.0% TOC	2390		mean between measured concentrations on day 0 and 20	R1/C1	cited in EU-RAR (EC 2010)
Insecta Ephemeroptera	*Ephoron virgo*	$ZnCl_2$	Static-renewal	40 d	Growth	21 d	EC_{10}	204	Stream sediment; Cb: 25 mg/kg d.w., AVS 2.1-4.5 mmol/kg d.w., 1.5 % TOC, 8 % clay	179	Measured	Time average concentration between day 0 and day 21, AVS concentration is time average in top sediment layer	R1/C1	Vandegehuchte et al. (2013)
Insecta Ephemeroptera	*Hexagenia sp.*	n.a.	n.a.	n.a.	Growth	21 d	EC_{10}	608	Lake sediment; Cb are 26, 38 and 253 mg/kg but result cannot be attributed)	n.a.	Measured	Classified as R1 in ECHA (2020)	R4/C1	ECHA (2020)
Crustacean Amphipoda	*Hyalella azteca*	$ZnCl_2$	Static-renewal	35 d	Survival	28 d	NOEC	347	Stream sediment; Cb: 47.6 mg/kg d.w., AVS 3-10 mmol/kg d.w., SEM 0.5 mmol/kg d.w.; 1.5-2.5% TOC, 8% clay	299.4	Measured	Time averaged concentrations between day 0 and day 28, additional overlying water concentrations measured	R1/C1	Nguyen et al. (2012a)
					Growth	28 d	NOEC	347		299.4			R1/C1	
Crustacean Amphipoda	*Hyalella azteca*	$ZnCl_2$	Static-renewal	40 d	Growth	28 d	NOEC	≥ 1000	Stream sediment, Cb: 55 mg/kg d.w., AVS 5.5 mmol/kg d.w., SEM-Zn 0.84 mmol/kg d.w.; 1.3% TOC controls 1.6-1.7% TOC treatments, 8% clay	≥ 945[a]	Measured	Arithmetic mean day 0-28	R2/C1	Nguyen et al. 2005 cited in EU-RAR (EC 2010)
					Reproduction	42 d	NOEC	≥ 1000		≥ 945[a]		Arithmetic mean of measured concentrations on day 0 and day28. 28 d exposure to spiked sediment and 14 d in clean water.	R2/C1	
					Survival	42 d	NOEC	510		455[a]			R1/C1	
Crustacean Amphipoda	*Gammarus pulex*	$ZnCl_2$	Static-renewal	40 d	Survival	35 d	NOEC	418	Stream sediment; Cb: 34 mg/kg d.w., AVS 6.3 mmol/kg d.w., 1.5% TOC, 8% clay	384	Measured	Time average concentration between day 0 and day 35. AVS concentration is time average in top sediment layer	R1/C1	Vandegehuchte et al. (2013)

Group	Species	Test compound	Exposure	Equilibration time	Endpoint	Test duration	Effect concentration	Total concentration	Sediment type	Added	Chem. analysis	Note	Validity	References
Oligochaeta	*Lumbriculus variegatus*	$ZnCl_2$	Static-renewal	40 d	Biomass per replicate	28 d	EC_{10}	730	Stream sediment; Cb: 34 mg/kg d.w., AVS 4.2-6.9 mmol/kg d.w., 1.5% TOC, 8% clay	696	Measured	Time average concentration between day 0 and day 28. AVS concentration is time average in top sediment layer	R1/C1	Vandegehuchte et al. (2013)
Oligochaeta	*Tubifex tubifex*	$ZnCl_2$	Static	30 d	Reproduction	28 d	NOEC	1135	Pond sediment; Cb: 34 mg/kg d.w., total SEM 0.57 mmol/kg d.w., Zn SEM 19 mg/kg.d.w.; 1-2% TOC	1101	Measured	Arithmetic mean of measured concentrations on day 0 and day28.	R3/C1	Farrar and Bridges 2003 cited in EU-RAR (EC 2010)
					Survival	28 d	NOEC	2610		2576			R3/C1	
Nematoda	*Caenorhabditis elegans*	$ZnCl_2$	Static	None	Reproduction	96 h	EC_{20}	94.7	Natural sandy stream sediment; Cb: <10	84.7	Nominal	No measured concentrations in overlying water or sediments	R3, C1	Haegerbaeumer et al. (2016)
Higher plant	*Avicennia marina*	$ZnCl_2$	*Static*	14 d	Emergence	6 months	NOEC	250	Artificial sediment (50% silty clay loam, 20% washed river sand, 30% organic peat moss) in 20% seawater, Cb assumed 0 mg/kg	250	Nominal		R2/C3	MacFarlane and Burchett (2002)
					Growth									

[a] The EU RAR (EC 2010) reports a Cb of 22 mg/kg d.w. in Table 3.3.2.e. while a Cb of 55 mg/kg d.w. is reported in the study summary.

4.1 Graphic representation of effect data

There is no specific group that is significantly more sensitive to Zn according to the reliable data from chronic tests (Fig. 1[5]).

Considering all chronic data in the data set, nematodes show the greatest sensitivity but the study is considered not reliable due to absence of measured concentrations in water and sediments and short equilibration time, which may cause the high effect concentrations in this study. Effect concentrations derived from acute tests for Polychaeta and Crustacea may be also low due to the sandy nature of sediments and very short equilibration time, leading to relatively high bioavailability. The additional chronic effect concentration available for marine Crustacea (amphipods) does not highlight differences in sensitivity between marine and freshwater species.

There is not enough information to explaining the lowest effect concentration reported for *C. tentans* in acute rather than in chronic tests.

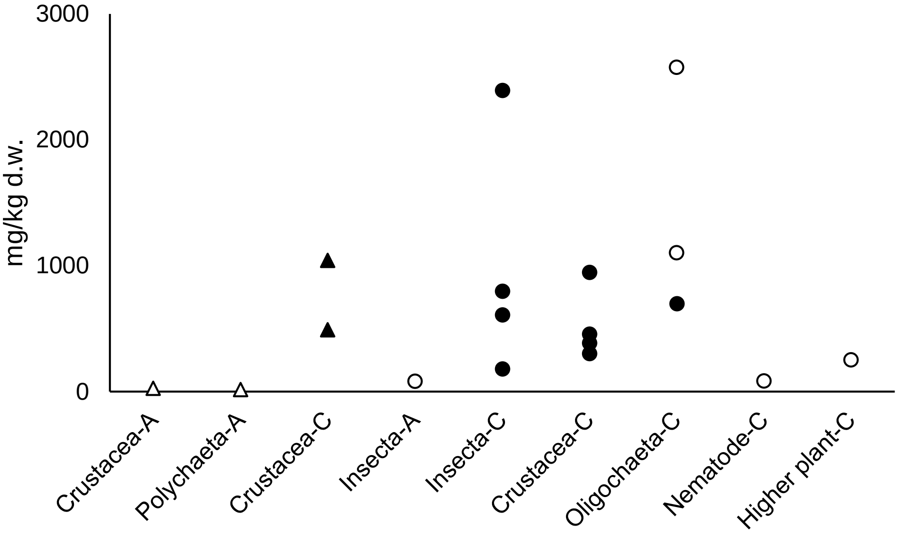

Figure 1 Graphical representation of acute (A) and chronic (C) effect data from spiked sediment toxicity tests with Zn for marine /estuarine and freshwater organisms. Empty symbols are data that are not used for EQS derivation according to reliability and relevance assessment. Triangles: effect data for marine / estuarine species; circles: effect data for freshwater species.

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 priory and should only be combined when there is no demonstrable difference in sensitivity. According to the limited number of reliable and relevant data, freshwater and marine data has been kept separated and only effect data for freshwater species is used in EQS derivation.

4.3 Overview of reliable and relevant long-term studies

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

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[5] Only added (total – background) effect concentrations. Similarly, graphical representation of OC-normalized data is not presented because it did not provide additional information to that presented.

Relevant and reliable chronic data is available for 5 species (Table 7), with additional effect data for other 2 freshwater species.

There are values (NOECs) for four different endpoints, derived from two chronic studies with *Chironomus tentans*. The geometric mean of NOECs for growth is 696 mg/kg d.w. total (609 mg/kg d.w. added), the geometric mean of NOECs for survival is 1434 mg/kg d.w. total (1378 mg/kg d.w. added), and there is a single NOEC for emergence of 850 mg/kg d.w. total (795 mg/kg d.w. added) and a single NOEC for reproduction of 850 mg/kg d.w. total (795 mg/kg d.w. added). The geometric mean value of 696 mg/kg d.w. total (609 mg/kg d.w. added) for growth is selected for use in EQS derivation.

There are values (NOECs) for three different endpoints, derived from two chronic studies with *Hyalella azteca*. The geometric mean of NOECs for survival is 421 mg/kg d.w. total (385 mg/kg d.w. added), the geometric mean of NOECs for growth is 589 mg/kg d.w. total (532 mg/kg d.w. added), and there is a single NOEC for reproduction of >1 000 mg/kg d.w. total (945 mg/kg d.w. added). The geometric mean value of 421 mg/kg d.w. total (385 mg/kg d.w. added) for survival is selected for use in EQS derivation.

There are single NOEC values ($NOEC/EC_{10}$) from chronic studies with *Ephoron virgo*, *Lumbriculus variegatus* and *Gammarus pulex*.

Table 7 Most sensitive endpoint from relevant and reliable chronic studies from Table 6.

Species	**Exposure duration [d]**	**Endpoint**	**$NOEC/EC_{10}$ Total [mg/kg d.w.]**	**$NOEC/EC_{10}$ Added [mg/kg d.w.]**	**Reference**
Chironomus tentans	20	Growth	696	609	Geometric mean (N=2)
Ephoron virgo	21	Growth	<u>204</u>	179	Vandegehuchte et al. (2013)
Hyalella azteca	28[a]	Survival	421	385	Geometric mean (N=2)
Gammarus pulex	35	Survival	418	384	Vandegehuchte et al. (2013)
Lumbriculus variegatus	28	Biomass per replicate	730	696	Vandegehuchte et al. (2013)

[a] Survival in the Nguyen et al. 2005 cited in EU-RAR (EC 2010) study is assessed after 28 d of exposure to spiked sediment followed by 14 d exposure to clean water (standard reproduction test).

5 Derivation of QS_{sed}

According to the EC TGD for EQS, sediment toxicity tests, aquatic toxicity tests in conjunction with equilibrium partitioning (EqP) and field/mesocosm studies are used as several lines of evidence to derive QS_{sed} (EC 2018). Thus, in the following, the appropriateness of the deterministic approach (AF-Method), the probabilistic approach (SSD method) and the EqP approach were examined.

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

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

The lowest long-term effect datum available for Zn is the NOEC of 204 mg/kg d.w. total or 179 mg/kg d.w. added after correction for background concentration (1.5 % OC, Table 6) for the growth 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)).

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

$$QS_{sed,AF,total} = \frac{204\ \left(\frac{mg}{kg}\right)}{10} = 20.4\ \left(\frac{mg}{kg}\right)$$

$$QS_{sed,AF,added} = \frac{179\ \left(\frac{mg}{kg}\right)}{10} = 17.9\ \left(\frac{mg}{kg}\right)$$

The application of an AF of 10 to the lowest credible chronic datum results in a $QS_{sed,AF,total}$ of 20.4 mg/kg d.w. or $QS_{sed,AF,added}$ of 17.9 mg/kg d.w.

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 EU-RAR 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 the whole set of available effect data for Zn (Table 6), including effect data 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 reliable and relevant total and added effect concentrations for freshwater species in Table 6 (including data with restrictions) to check the effects that these different treatments have on the derived value. The results of the SSD are included in Fig. 2 for total effect data and Fig. 3 for added effect data and Appendix 2.

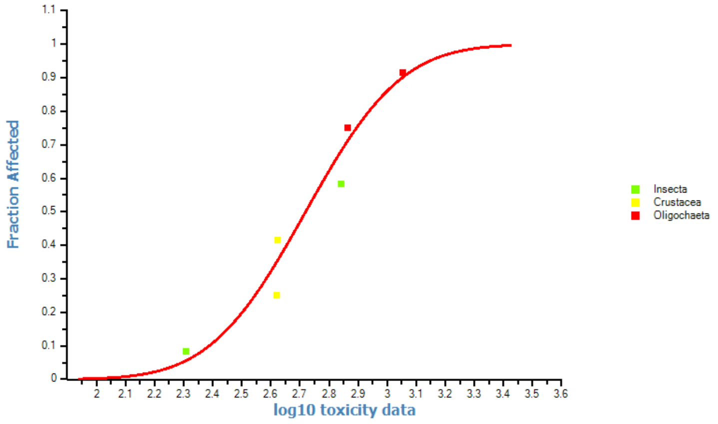

Figure 2 Species sensitivity distribution (SSD) of the chronic effect concentrations of all species for total Zn generated with ETX 2.2. Number of data points (n) = 6; requirements for normal distribution according to van Vlaardingen et al. (2005) were met.

The resulting $HC_{5,total}$ is 184.6 mg/kg d.w. (lower and upper 90 % confidence limits 57.5-311.1 mg/kg, standard deviation of the $\log_{10}$ transformed values = 0.26).

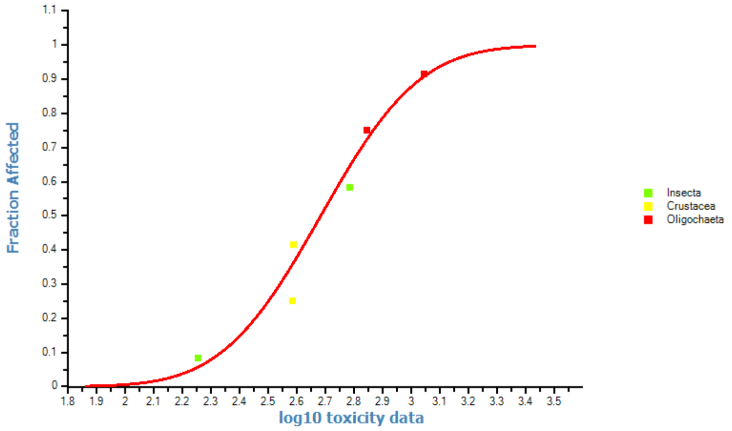

Figure 3 Species sensitivity distribution (SSD) of the chronic effect concentrations of all species for added Zn generated with ETX 2.2. Number of data points (n) = 6; requirements for normal distribution according to van Vlaardingen et al. 2005 were met.

The resulting $HC_{5,added}$ is 160.9 mg/kg d.w (lower and upper 90 % confidence limits 47.3-278.2 mg/kg, standard deviation of the $\log_{10}$ transformed values = 0.27).

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 Zn.

An AF of 5 is used as default:

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

$$QS_{sed,SSD,total} = \frac{184.6\left(\frac{mg}{kg}\right)}{5} = 36.9\left(\frac{mg}{kg}\right)$$

$$QS_{sed,SSD,added} = \frac{160.9\left(\frac{mg}{kg}\right)}{5} = 32.2\left(\frac{\mu g}{kg}\right)$$

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

The EqP model has been applied using the $PNEC_{add,aquatic}$ derived in the EU-RAR (EC 2010) of 7.8 µg/l for dissolved Zn in freshwater. This concentration is based on the 5th percentile value of the Species Sensitivity Distribution (HC_5) that includes 18 NOECs covering 7 taxonomic groups. An assessment factor of 2 was applied on the concentration of 15.6 µg/l to account for remaining uncertainties. The effect data for the water phase used in this report to derive this $PNEC_{add,aquatic}$ were not evaluated for relevance and reliability as it was performed in the EU RAR (EC 2010).

6.2 Selection of partition coefficient

One of the main factors influencing the application of the EqP model is the choice of the partition coefficient. It is stipulated in the ECHA 2017 guideline (p. 143, ECHA (2017)) that "To increase the reliability of PNEC sediment screen derived using the EqP, it is imperative that a conservative but realistic partitioning coefficient (e.g. K_d, K_{oc}, K_{ow}) is chosen. A clear justification must be given for the chosen coefficient and any uncertainty should be described in a transparent way."

The EC EQS TGD prefers measured K_p values for sediment/suspended matter for freshwater, estuarine and marine water bodies respectively (EC 2018). Preference is given to field measurements and not laboratory sorption or toxicity experiments.

The K_p estimated for Zn selected here for deriving a $QS_{sed,EqP}$ for comparison purposes is 88 794 l/kg (Table 1).

6.3 Derivation of $QS_{sed,EqP}$

The derivation of $QS_{sed,EqP}$ is summarized in Table 8, resulting in 692.6 mg/kg d.w.

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.

Table 8 Derived $QS_{sed,EqP}$ according to estimated $K_p$sed based on Appendix 1 and Table 1, and the PNEC for water derived by (EU-RAR; EC 2010). No additional AF was applied.

$K_p$sed [l/kg]	**$K_{sed\text{-}water}$ [m³/m³]**	**$PNEC_{water}$ [mg/l]**	**$QS_{sed,EqP}$ [mg/kg w.w.]**	**$QS_{sed,EqP}$ [mg/kg d.w.]**	**Additional AF**
88 794	44 398	0.0078	266.4	**692.6**	--

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

7.1 Overview of available mesocosm/microcosm studies

The effect of Zn to a natural nematode assemblages was assessed in a microcosm study performed during 180 days (Haegerbaeumer et al. 2016). The ratios of sensitive nematodes species divided by all species identified (NemaSPEAR $[\%]_{metal}$) were determined at start of test (day 0), and after 30, 90 and 180 days of exposure. The treatments included a nominal concentration of 10 mg/kg d.w. and 100 mg/kg d.w., the highest concentration corresponding to the effect concentration on reproduction for nematodes in spiked sediment toxicity tests. The results showed a clear dose-response effect. Nematodes species composition was affected already after 30 days and up to 180 days at a measured concentration between 13 to 19 mg/kg Zn d.w. (0.02 and 0.03 mg/l in porewater). This NOEC can be considered added according to the negligible background concentration in test sediment. Although water quality parameters and Zn concentration in overlying water, porewater and sediment were measured, a proper equilibration period between the addition of the overlying water and the start of the test was not included. The reliability of the study is therefore limited and is not used for sediment EQS derivation.

7.2 Available sediment quality guidelines from field data

Sediment quality guidelines (SQG) derived from field data mainly based on macrozoobenthos for total Zn range between 120 and 129 mg/kg d.w. These SQGs are close to the lowest effect concentration from spiked sediment toxicity testing and the HC_5 obtained from the SSD approach. The lowest SQG derived from field data are those describing effects in oligochaete communities, which are within a factor 2.5 below other SQGs from field studies considering mainly macrozoobenthos. These SQG include indirectly the background concentration found in the areas where these sediments were collected and are therefore considered as total concentrations.

Table 9 Sediment quality guidelines available in the literature based on field data.

SQG	Value [mg/kg d.w.]	Reference	Description
Threshold effect level (TEL)	123	Smith et al. (1996)	Sediments are considered to be clean to marginally polluted. No effects on most sediment-dwelling organisms expected below this concentration.
Lileky effect level (LEL)	120	Persaud et al. (1993)	Concentration below which adverse effects are expected to occur only rarely.
Environmental risk limit (ERL)	120	Long and Morgan (1991)	Chemical concentration below which adverse effects would be rarely observed.
Lowest effect level (LEL)	129	de Deckere et al. (2011)	Concentration below which adverse effects on macrozoobentos is rarely observed. A SEL of 1 300 mg/kg d.w. describes concentration above which macrozoobentos is likely affected.
Threshold effect level (TEL_{oligo})	46.9	Vivien et al. (2020)	Concentration below which oligochaete communities are rarely affected. A PEL_{oligo} of 88.1 mg/kg d.w. describes concentrations above which oligochaete communities are likely affected.
Threshold effect concentration (TEC)	121	MacDonald et al. (2000)	Threshold effect concentration for benthic organisms.

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 EQS TGD (EC 2018) are summarized in Table 10. 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. The $QS_{sed,SSD}$ is not taken forward due to the limited number of effect data used in its derivation.

Given the essentiality of Zn and the background levels found in Swiss sediments (Table 5), a $EQS_{sed,added}$ of 17.9 mg/kg for Zn including the application of an AF of 10 is proposed. According to available measured concentrations in Swiss sediments (Table 5), an $EQS_{sed,total}$ of 99.7 mg/kg d.w. is proposed, using the FOREGS value of 81.8 mg/kg d.w. for floodplain sediments.

Table 10 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.

	Total Zn concentration	**Added Zn concentration**	**AF**
$QS_{sed,SSD}$[a]	36.9	32.2	5
$QS_{sed,AF}$	20.4	17.9	10
$QS_{sed,EqP}$[a]	692.6		--
Field SQG	46.9-129	--	--
Proposed EQS_{sed}	**99.7**	**17.9**	

[a] Derived for comparison purposes.

9.1 Protection of benthic organisms and uncertainty analysis

The proposed $EQS_{sed,added}$ and $EQS_{sed,total}$ 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 Zn concentrations, is higher than the derived $QS_{sed,AF,added}$ but lower than the $EQS_{sed,total}$. Because a) the TEL_{oligo} was derived from field data for small and medium water bodies and background concentrations for total sediment (< 2 mm) are not available for this type of water bodies to assess whether the proposed $EQS_{sed,added}$ would be protective for oligochaete communities at these sites, and b) according to Table 6 oligochaetes were not among the most sensitive organisms, it is concluded that there is not enough evidence to modify the proposed $EQS_{sed,added}$. It is however noted that oligochaete communities, and in particular sensitive oligochaete species, may not be protected when using the $EQS_{sed,total}$.

The derivation took into consideration the added risk approach but did not consider bioavailability corrections in its derivation. As noted in section 4, AVS values in sediments from the effect data base may not be representative of worst-case scenarios where bioavailability is maximized. Following recommendations from the EU TGD (EC 2018), the SEM-AVS approach could be used as a line of information in the weight of evidence to predict the absence of toxicity for compliance check.

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Appendix I. Suspended matter-water partition coefficient (K_p)

Water body	Log K_p	K_p [l/kg]	Reference/Source
Mero River (ES) (range 1.6-8.1)	5.60	398107	Palleiro et al. (2013)
Rio Grande (US)	4.28	19055	Popp, Laquer (1980) cited in EU-RAR (EC 2010)
Rio Puerco (US)	4.48	30200	Popp, Laquer (1980) cited in EU-RAR (EC 2010)
Rio Salado (US)	3.43	2692	Popp, Laquer (1980) cited in EU-RAR (EC 2010)
Hudson River (US)	4.00	10000	Li et al. (1984) cited in EU-RAR (EC 2010)
Hudson River + sea water (US)	3.66	4571	Li et al. (1984) cited in EU-RAR (EC 2010)
Netherlands median of 4 locations fresh surface water; 1983-1986	5.04	109648	Stortelder et al. (1989) cited in EU-RAR (EC 2010)
Netherlands 3 locations fresh surface water; 1992-1994	4.73	53703	Koelmans and Radovanovic (1997) cited in EU-RAR (EC 2010)
North sea, Wadden sea; 1995	5.04	109648	Yland, Smedes (1996) cited in EU-RAR (EC 2010)
Rhine	4.92	84000	Venema (1994) cited in EU-RAR (EC 2010)
Meuse	5.25	176000	Venema (1994) cited in EU-RAR (EC 2010)
Scheldt	4.75	56000	Venema (1994) cited in EU-RAR (EC 2010)
Lake IJssel	5.13	134000	Venema (1994) cited in EU-RAR (EC 2010)
Haringvliet	5.16	146000	Venema (1994) cited in EU-RAR (EC 2010)
Nieuwe Waterweg	4.81	64000	Venema (1994) cited in EU-RAR (EC 2010)
Northsea Canal	4.93	85000	Venema (1994) cited in EU-RAR (EC 2010)
Rhine (at Lobith, mean 1983-86)	4.91	81000	UBA (1994) cited in EU-RAR (EC 2010)
Rhine (91-863 km section, 1988)	5.05	113000	UBA (1994) cited in EU-RAR (EC 2010)
Deûle River (FR) (median, range 4.96-5.15 N=5)	5.08	120000	Lesven et al. (2009)
Day River (municipal waste, Vietnam) (median, range 4.3-5.8)	5.20	158489	Duc et al. (2013)
Rhine	4.0-5.2		Golimowski et al. (1990) cited in Cleven and Janus (1993)
Waal	4.0-5.3		Golimowski et al. (1990) cited in Cleven and Janus (1993)
Meuse	4.9-5.4		Golimowski et al. (1990) cited in Cleven and Janus (1993)
Lake Balaton (Hungary)	4.3-5.4		Nguyen et al. (2005)

Water body	**Log K_p**	**K_p [l/kg]**	**Reference/Source**
Estuarine (Australia)	4.4-6.7		Munksgaard and Parry (2001) cited in Nguyen et al. (2005)
Six Estuaries, Texas	3.8-6.0		Benoit et al. (1994) cited in Nguyen et al. (2005)
Scheldt Estuary	4.3-4.6		Paucot et al. (1997) cited in Nguyen et al. (2005)
Scheldt Estuary	4.5-4.8		Baeyens et al. (1998) cited in Nguyen et al. (2005)
Brahmaputra River, India (N=10)	3.5-6.9		Gogoi et al. 2016
Geomean	**4.8**	**59 196**	

Values in grey are not used, only ranges reported.

Appendix 2. Goodness-of-fit of toxicity data from ETX SSD results

Total concentrations

Anderson-Darling test for normality					
Sign. level	Critical	Normal?			
0.1	0.631	Accepted			
0.05	0.752	Accepted		AD Statistic:	0.288111
0.025	0.873	Accepted		n:	6
0.01	1.035	Accepted			
Kolmogorov-Smirnov test for normality					
Sign. level	Critical	Normal?			
0.1	0.819	Accepted			
0.05	0.895	Accepted		KS Statistic:	0.517231
0.025	0.995	Accepted		n:	6
0.01	1.035	Accepted			
Cramer von Mises test for normality					
Sign. level	Critical	Normal?			
0.1	0.104	Accepted			
0.05	0.126	Accepted		CM Statistic:	0.02862
0.025	0.148	Accepted		n:	6
0.01	0.179	Accepted			

For added concentrations

Anderson-Darling test for normality					
Sign. level	Critical	Normal?			
0.1	0.631	Accepted			
0.05	0.752	Accepted		AD Statistic:	0.255765
0.025	0.873	Accepted		n:	6
0.01	1.035	Accepted			
Kolmogorov-Smirnov test for normality					
Sign. level	Critical	Normal?			
0.1	0.819	Accepted			
0.05	0.895	Accepted		KS Statistic:	0.53773
0.025	0.995	Accepted		n:	6
0.01	1.035	Accepted			
Cramer von Mises test for normality					
Sign. level	Critical	Normal?			
0.1	0.104	Accepted			
0.05	0.126	Accepted		CM Statistic:	0.022424
0.025	0.148	Accepted		n:	6
0.01	0.179	Accepted			