National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

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Proposal for an update according to the methodology of the Water Framework Directive

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RIVM letter report 2020-0024

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Colophon

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E.M.J. Verbruggen (author), RIVM
C.E. Smit (author), RIVM
P.L.A. van Vlaardingen. (author), RIVM

Contact:
Els Smit
Centre for Safety of Substances and Products
els.smit@rivm.nl

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Synopsis

Environmental quality standards for barium in surface water
Proposal for an update according to the methodology of the Water Framework Directive

RIVM is proposing new water quality standards for barium in surface water. These standards represent a safe concentration in water for aquatic organisms, for fish consumption by humans and for animals feeding on fish. The update is necessary because new information has become available on the effects of barium on humans, animals and plants. The health based risk limit has become less stringent. This risk limit indicates the intake level without harmful effects on human health.

Barium is a natural compound and humans may be exposed to it via food and drinking water. The amount of barium that humans can ingest daily without health risk is a known factor. This value was used to calculate the maximum allowable concentration in fish for daily lifetime consumption by humans.

Data from the scientific literature show that barium concentrations in fish and shellfish do not exceed this safe concentration for humans. Birds and mammals can be exposed to barium via consumption of aquatic vegetation, but negative effects are not expected for concentrations up to 93 microgram per litre water. This also applies to fish, water fleas and other aquatic organisms. Concentrations in Dutch surface water are generally below this value.

To determine the new standard, RIVM used recent literature on the environmental behaviour and effects of barium and the uptake of barium by plants and animals. The natural presence of barium in the environment was taken into account in calculating the new standard.

Keywords: water quality standard; barium; Water Framework Directive

Publiekssamenvatting

Milieukwaliteitsnormen voor barium in oppervlaktewater
Voorstel voor een herziening volgens de methodiek van de Kaderrichtlijn Water

Het RIVM stelt nieuwe waterkwaliteitsnormen voor de stof barium voor. Deze normen geven aan welke concentratie in het water veilig is voor planten en dieren die in het water leven, en voor mensen en dieren die vis uit dat water eten. De aanpassing is nodig omdat er nieuwe informatie is over de effecten van barium op mensen, dieren en planten. Zo is de gezondheidskundige risicogrens soepeler geworden. Deze risicogrens geeft aan hoeveel van een stof mensen mogen binnenkrijgen zonder schadelijke effecten voor hun gezondheid.

Barium komt van nature voor in het milieu. Mensen kunnen daarom barium binnenkrijgen via hun voedsel en drinkwater. Het is bekend hoeveel barium mensen dagelijks mogen binnenkrijgen zonder schadelijke gevolgen voor hun gezondheid. Met die waarde is berekend wat er maximaal in vis mag zitten als mensen tijdens hun hele leven elke dag vis zouden eten.

Gegevens uit de wetenschappelijke literatuur laten zien dat de concentraties van barium in vis en schaaldieren niet over die veilige waarde voor mensen heen gaan. Vogels en zoogdieren kunnen barium binnenkrijgen door waterplanten te eten, maar tot een concentratie van 93 microgram per liter water zijn er geen negatieve effecten te verwachten. Dit geldt ook voor vissen, watervlooien en andere dieren die in het water leven. De concentraties in het Nederlandse water zijn over het algemeen lager dan deze waarde.

Om de nieuwe norm te bepalen heeft het RIVM recente literatuur gebruikt over het gedrag en de effecten van barium in het milieu en over de hoeveelheid barium die planten en dieren opnemen. Bij de normafleiding is er rekening mee gehouden dat barium van nature in het milieu zit.

Kernwoorden: waterkwaliteitsnorm; barium; Kaderrichtlijn Water

Contents

Summary

In this report, RIVM proposes updated environmental quality standards (EQS) for barium in surface water in accordance with the methodology of the Water Framework Directive (WFD). Barium is a non-essential trace element that has a widely distributed natural occurrence. Barium and barium compounds are used for many purposes. The use in drilling mud and for production of ceramics, paint, glass and rubber are just a few examples. Barium enters the environment through weathering and anthropogenic releases.

The most recent scientifically derived annual average EQS is 9.3 μg/L, which is lower than the officially set background concentration of barium in Dutch freshwaters. Therefore, the current legal annual average EQS for barium in freshwater is set to the background value of 73 μg/L. During the past years, the human toxicological risk limit underlying the AA-EQS was updated and new information on bioaccumulation has become available. Furthermore, a new methodology for the derivation of water quality standards for secondary poisoning was developed and implemented in the European technical guidance for derivation of WFD-water quality standards.

The evaluation of human fish consumption and secondary poisoning is based on an extensive review of the scientific literature on barium accumulation. It is concluded that human fish consumption is not relevant for derivation of the EQS for barium, because concentrations in fish and other aquatic organisms would not lead to unacceptable exposure of humans. The uptake of barium by birds and mammals via consumption of water plants appears to be critical for the overall quality standard. However, when following the default methods for deriving safe levels for birds and mammals, the resulting safe concentration is much lower than ambient concentrations in Dutch surface water. This would mean that at present barium concentrations would severely hamper the maintenance of bird and mammal populations in the field, which is not a realistic assumption. It is concluded that the margin between toxicity and background concentrations is very small for barium, which is a reason not to apply the default assessment factors that are normally used to extrapolate toxicity data to the field situation. Based on the lowest no-effect level observed in animal studies, it is proposed to set the AA-EQS of barium in surface water to 93 μg/L. Because biomagnification is not expected, this value is also valid for marine waters.

The environmental behaviour of barium is complex, and the mechanisms that determine uptake, distribution and toxicity in biota are not fully understood. Bioavailability is of barium is reduced in the presence of sulfate and carbonate. Therefore, relevance of test conditions for the Dutch field situation was evaluated when deriving quality standards for direct ecotoxicity.

The proposed Maximum Acceptable Concentration-EQS for short term concentration peaks (MAC-$EQS_{fw, eco}$) is 1.1 mg/L, which is far above the concentration encountered in Dutch surface waters (maximum around 100 µg/L). The the chronic quality standard for direct ecotoxicity is also higher (620 µg/L). Direct effects on aquatic organisms are therefore not expected. Due to the absence of relevant data, it is not possible to derive a MAC-$EQS_{sw, eco}$ for marine waters.

1 Introduction

1.1 Background of this report

In this report a proposal is made for updated environmental quality standards (EQSs) for barium in surface water. Barium is included in Dutch national legislation in the context of the Water Framework Directive (WFD). The compound is listed as a specific pollutant in the Dutch decree on WFD-monitoring ('Regeling monitoring kaderrichtlijn water')[1]. Under the WFD, two types of EQSs are used to cover both long- and short-term effects on aquatic ecosystems:

- Annual Average EQS (AA-EQS) – a long-term standard, expressed as an annual average concentration and normally based on chronic ecotoxicity data. The AA-EQS should not result in risks due to secondary poisoning and/or risks for human health aspects. These aspects are therefore also addressed in the AA-EQS, when triggered by the characteristics of the compound (i.e. human toxicology and/or potential to bioaccumulate).
- Maximum Acceptable Concentration EQS (MAC-EQS) for aquatic ecosystems – the concentration protecting aquatic ecosystems from effects due to short-term exposure or concentration peaks. The MAC-EQS is derived for freshwater and saltwater ecosystems, and is based on direct ecotoxicity only.

In addition, a quality standard for protection of drinking water sources may be derived. Table 1 summarises the different types of WFD water quality standards.

The current legal AA-EQS for barium in freshwater is 73 µg/L. Until 2019, this was the officially set background concentration of barium in Dutch freshwaters. The most recent scientifically derived AA-EQS is 9.3 µg/L Van Vlaardingen & Verbruggen (2009). Because it is not reasonable to assume long term effects at levels below background, it was decided in the latest version of the monitoring decree to use the background concentration instead. The MAC-EQS is 148 µg/L dissolved barium, expressed as added concentration (Van Vlaardingen et al., 2005).

The AA-EQS of 9.3 µg/L is based on human exposure via fish consumption. Starting points was the Tolerable Daily Intake (TDI) of 0.020 mg/kg bodyweight per day (20 µg/kg bw/day) derived by Baars et al. (2001). Limited information on bioaccumulation of barium in fish was available to convert this human toxicological threshold into a water quality standard for human fish consumption. During the past decades, additional human toxicological assessments of barium were published, resulting in a higher TDI than used for derivation of the EQS (ASTDR, 2007; SCHER, 2012; US EPA, 1998-2005; Van Engelen et al., 2008).

[1] http://wetten.overheid.nl/BWBR0027502/2015-11-19

Table 1. Overview of the different types of WFD quality standards for freshwater (fw), saltwater (sw) and surface water used for drinking water (dw) considered in this report.

Type of QS	Protection aim	Terminology for temporary standard[a]	Notes	Final selected quality standard
long-term	Water organisms	$QS_{fw,\ eco}$ $QS_{sw,\ eco}$	Refers to direct ecotoxicity	lowest water-based QS is selected as $AA\text{-}EQS_{fw}$ and $AA\text{-}EQS_{sw}$
	Predators (secondary poisoning)	$QS_{biota,\ secpois,\ fw}$ $QS_{biota,\ secpois,\ sw}$ --- $QS_{fw,\ secpois}$ $QS_{sw,\ secpois}$	QS for fresh- or saltwater expressed as concentration in biota, converted to corresponding concentration in water	
	Human health (consumption of fishery products)	$QS_{biota,\ hh\ food}$ --- $QS_{water,\ hh\ food}$	QS for water expressed as concentration in biota, converted to corresponding concentration in water; valid for fresh- and saltwater[b]	
short-term	Water organisms	$MAC\text{-}QS_{fw,\ eco}$ $MAC\text{-}QS_{sw,\ eco}$	Refers to direct ecotoxicity; check with $QS_{fw,\ eco}$ and $QS_{sw,\ eco}$	$MAC\text{-}EQS_{fw}$ $MAC\text{-}EQS_{sw}$
dw	Human health (drinking water)		Relates to surface water used for abstraction of drinking water	$QS_{dw,\ hh}$

a: Note that the subscript "fw" refers to the freshwater, "sw" to saltwater; subscript "water" is used for all waters, including marine.
b: Although the biota standard for human fish consumption is the same for freshwater and salt water, the corresponding concentrations in water might differ if there is a difference in bioaccumulation potential for the freshwater and marine food chain.

Besides, more information on bioaccumulation in aquatic organisms has become available in the literature as indicated by the REACH-registration dossier of barium[2]. The higher TDI and additional bioaccumulation data will most likely lead to different quality standards for human fish consumption. In case of a substantially higher human-health based quality standard, the other routes (direct ecotoxicity and secondary poisoning) may become critical. The studies underlying the TDI are also input for the assessment of secondary poisoning and any additional information or change in endpoints will also affect this route.

[2] https://echa.europa.eu/registration-dossier/-/registered-dossier/19625/5/4/2

Furthermore, a new methodology for the derivation of water quality standards for secondary poisoning was developed (Verbruggen, 2014). It was therefore decided to perform a complete update according to the methodology of the WFD, in order to provide a sound basis for waterbody status assessments.

1.2 Methodology

The methodology for derivation of quality standards in the Netherlands is described in an on-line guidance document, available via the RIVM-website[3]. The methodology for surface water standards is in accordance with the European guidance document for derivation of environmental quality standards under the WFD (EC, 2018), further referred to as the WFD guidance. The methodology for derivation is briefly outlined below, details can be found in the respective chapters of this report.

1.2.1 Derivation of the $QS_{water,\ hh\ food}$

The methodology to derive human health based water quality standards for fish consumption includes two steps. The first one is to establish the concentration in fish without a negative impact on human health. This biota based standard is referred to as $QS_{biota,\ hh\ food}$. In the second step, the $QS_{biota,\ hh\ food}$ is converted to an equivalent concentration in water denoted as $QS_{water,\ hh\ food}$. The conversion is based on information on the accumulation of the contaminant in fish.

The starting point for derivation of the $QS_{biota,\ hh\ food}$ is a human toxicological threshold limit (TL_{hh}), such as the Acceptable or Tolerable Daily Intake (ADI, TDI), or Reference dose (RfD). The choice of the TL_{hh} is discussed in Chapter 3. It is based on human toxicological evaluations of barium by the United States Agency for Toxic Substances and Disease Registry (ASTDR, 2007), the United States Environmental Protection Agency (US EPA, 1998-2005) and the Scientific Committee on Health and Environmental Risks (SCHER) of the European Commission (SCHER, 2012). The TL_{hh} is converted to a $QS_{biota,\ hh\ food}$ using the default assumptions of the WFD guidance, i.e., a default body weight of 70 kg, a daily fish consumption of 1.63 g/kg_{bw}/d (= 115 g per person per day). The contribution of fish consumption to the total allowable intake is set at 20% of the TL_{hh}. In this way, the allocation factor takes into account that other exposure routes may contribute to total intake, such as drinking water or other food products. It is a conservative value to protect humans from adverse health effects caused by consuming contaminated fish and seafood (EC, 2018). The derivation of the $QS_{biota,\ hh\ food}$ is described in Section 3.5.

The next step is to convert the $QS_{biota,\ hh\ food}$ to an equivalent concentration in water, denoted as the $QS_{water,\ hh\ food}$. This conversion is based on information on the accumulation of contaminants in fish or fishery products such as mussels. Therefore, a literature search was performed to obtain information on barium accumulation in aquatic organisms.

[3] http://www.rivm.nl/rvs/Normen/Milieu/Milieukwaliteitsnormen/Handleiding_normafleiding

Papers on metal accumulation in general were also scanned for relevant information on barium. About 20 potentially relevant papers were retrieved and further evaluated to obtain field bioaccumulation factors (BAFs). The relevant studies are summarised in Appendix 1 and further discussed in Chapter 4.

1.2.2 *Derivation of the $QS_{fw, secpois}$ and $QS_{sw, secpois}$*

For secondary poisoning of predators, two biota based standards are derived, one for freshwater ($QS_{biota,secpois, fw}$) and one for marine or salt waters ($QS_{biota, secpois, sw}$). A distinction between fresh and marine water quality standards could be appropriate when fish-eating birds and mammals that serve at their turn as food for the marine top predators, are a more critical food item than fish. For derivation of the biota based QS for secondary poisoning, relevant data on mammalian toxicology were selected from the above mentioned human toxicological evaluations of barium (ASTDR, 2007; US EPA, 1998-2005). Where possible, the underlying studies were consulted to obtain the information necessary for derivation of the $QS_{biota,secpois, fw}$ and $QS_{biota, secpois, sw}$. Additional studies for birds were searched for as well. The results are discussed in Section 3.6.

Similar to the quality standard for human fish consumption, the BAF is used to express biota standards for secondary poisoning as equivalent water quality standards ($QS_{fw, secpois}$ and $QS_{sw, secpois}$). In this case, BAFs for several food sources could be relevant. Birds and mammals in the aquatic food chain have very diverse diets and fish, crustaceans, molluscs, insects and aquatic plants are all possible food sources for these species. The WFD-methodology for the assessment of secondary poisoning allows for this differentiation by accounting for differences in energy content between food sources. Therefore, bioaccumulation has been assessed for these different groups (see Chapter 4 and Section 6.2).

1.2.3 *Derivation of the quality standard for drinking water abstraction*

According to the WFD guidance, the quality standard for surface water intended for drinking water abstraction should be based on existing drinking water standards, where available (EC, 2018). Council Directive 98/83/EC[4] does not give a quality standard for barium in drinking water. A legal standard of 200 µg/L for surface water intended for drinking water abstraction is included in Dutch national WFD legislation[5]. The $QS_{water, dw}$ is therefore 200 µg/L. This standard specifically applies to drinking water intake points.

1.2.4 *Derivation of the QS_{eco} and MAC-QS_{eco} for direct ecotoxicity*

For the derivation of the quality standards for direct ecotoxicity, ecotoxicity data for aquatic species were collected. Starting with the dataset used by Van de Plassche et al. (1992) and Van Vlaardingen et al. (2005), a literature search was conducted to retrieve additional literature published since then. For this, the US EPA Database was searched for references on barium salts, and a broad literature search

[4] http://eur-lex.europa.eu/legal-content/NL/TXT/?uri=CELEX:31998L0083

[5] see Annex III to the Decree on Quality standards and monitoring water (Besluit kwaliteitseisen en monitoring water; BKMW, http://wetten.overheid.nl/BWBR0027061/

was performed using Scopus®. In addition, the REACH dossiers on barium compounds as published on the website of the European Chemical Agency (ECHA) were checked for relevant data. All studies, including those considered in 1992 and 2005, were evaluated according to the current quality criteria, but studies that were already disregarded in the previous reports were only briefly examined. Reliability indices (Ri) were assigned according to Klimisch et al. (1997), taking into account the criteria for reporting and evaluating ecotoxicity data as developed by Moermond et al. (2016). More information on specific issues considered in the evaluation of the ecotoxicity tests can be found in Chapter 5, the derivation of the QS_{eco} is described in Section 6.3.

1.2.5 Bioavailability

According to the WFD-guidance, the QS_{eco} and MAC-QS_{eco} are preferably derived using models that incorporate corrections for metal bioavailability. Since such models are available for few metals only, the 'added risk approach' (ARA) has been used since long as an alternative. The ARA was developed in the late 1990s by Struijs et al. (1997), and accounts for natural background concentrations and avoids setting regulatory standards below this background level. In this approach, the MAC- and QS_{eco} represent the maximum permissible additions that may be added to the local background concentration without adversely affecting the ecosystem. The ARA was applied in many EQS derivations for metals in the Netherlands, including those for barium (Crommentuijn et al., 1997; Van Vlaardingen et al., 2005; Van Vlaardingen & Verbruggen, 2009). It should be noted that the ARA only applies to the QS_{water} for direct ecotoxicity and not to the QS_{water} for secondary poisoning or human health, because the latter are derived using BAF values that include background exposure. Moreover, according to the current WFD guidance, the use of ARA in QS derivation is not preferred. The main reason is that the underlying assumption that the background concentration does not contribute to negative effects is no longer deemed scientifically justified. From a biological point of view, the distinction between naturally present and anthropogenically added metal is artificial, because the uptake and elimination of metals by organisms is not dependent on the origin of the metal.

2 Information on the substance

2.1 Regulatory status of barium

The available toxicological and ecotoxicological studies with barium are carried out with barium acetate, barium chloride, barium sulfate and barium nitrate. Except for barium acetate, these compounds are all registered under REACH. The website of ECHA contains a number of barium compounds, an overview of the most relevant ones is given below (Table 2). For the environmental effects assessment, all registration dossiers refer to barium chloride. This is considered a worst case approach considering metal ion availability.

Table 2. Overview of relevant barium compounds registered under REACH. Data from the ECHA-website[6].

Compound	CAS number	EC number	Total tonnage band [tonnes/year]
barium	7440-39-3	231-149-1	10-100
barium carbonate	513-77-9, 7440-39-3	208-167-3	100000 - 1000000
barium chloride	10326-27-9, 10361-37-2	233-788-1	10000 - 100000
barium hydroxide	12230-71-6, 17194-00-2	241-234-5	10000 - 100000
barium nitrate	10022-31-8	233-020-5	1000 - 10000
barium sulfate	7727-43-7	231-784-4	10000 - 100000

A harmonised classification and labelling according to CLP Regulation (EC) No 1272/2008 is available for barium carbonate (H302) and barium chloride (H301/332). There is also a group entry (H302/H332) for barium salts, with the exception of barium sulfate, salts of 1-azo-2-hydroxynaphthalenyl aryl sulfonic acid, and of salts specified elsewhere in Annex VI of the regulation. For compounds with BAF ≥ 100 L/kg, classification for H301/302 (toxic/harmful if swallowed) is a reason to include human fish consumption as relevant route (EC, 2018).

2.2 Occurrence, use and emission sources

Parts of the information provided in this section are taken from ASTDR (2007), US EPA (1998-2005), and Van Vlaardingen et al. (2005).

Barium is a non-essential trace element that has a widely distributed natural occurrence. Naturally occurring barium is a mix of seven stable isotopes. There are more than 20 known isotopes, but most of them are highly radioactive and have half-lives ranging from several milliseconds to several minutes. Barium metal oxidises readily in moist air and reacts with water, ammonia, oxygen, hydrogen, halogens and sulfur, and therefore occurs only as the divalent cation in combination with other elements.

[6] https://echa.europa.eu/information-on-chemicals.

In nature, it is found in fossil fuel, igneous rocks, feldspar and micas. Barium makes up 0.05% of the earth's crust and the two most prevalent naturally occurring barium sources are barite (barium sulfate) and witherite (barium carbonate) ores.

Barium and barium compounds are used for many purposes. One of the most important applications is the use as drilling muds in the oil and gas industries. Drilling muds facilitate drilling through rock by lubricating the drill. Barium compounds, such as barium carbonate, barium chloride, and barium hydroxide, are used to make ceramics. Barium compounds are also used to make paints, bricks, tiles, glass, and rubber, and as gas trapping agent due to its ability to bind oxygen, nitrogen and hydrogen. It is used as a pigment and as a loader for paper, soap, rubber and linoleum and as stabiliser for plastics. Barium sulfate is used to perform medical tests and X-ray examinations of the stomach and intestines.

Barium enters the environment through the weathering of rocks and minerals and through anthropogenic releases. Industrial emissions are the primary source of barium in the atmosphere. Fertilisers and soil amendments may be a source of barium in agricultural soils (ASTDR, 2007). Barium reaches surface water with industrial waste water and by run-off of soil with fly ash or sewage effluent in landfills. However, the latter routes are not relevant for the Netherlands, as fly ash storage and landfill do not occur here. Barium is occurring in most surface waters and in public drinking water supplies.

As indicated in the introduction, the official background concentration of dissolved barium in Dutch freshwater was 73 μg/L until recently. This value was set in 1998 based on measurements in relatively unburdened regions (Osté (2013), and references therein). However, recent monitoring data suggest that this background is rather high as measured concentrations in freshwater remain below this level (see Figure 1). There is no European harmonised method for establishing background concentrations for metals. After comparison of several methods, it was proposed to use the 10^{th} percentile of monitoring concentrations, although for elements with a relatively low anthropogenic load, a low percentile may be too strict (Osté, 2013). The 10^{th} percentile for barium was established as 22 μg/L by Osté & Altena (2019). From now on, this value will be used as the official background concentration of barium.

One reason for the discrepancy between the officially set background level (73 μg/L) and the 10^{th} percentile could be that the former was calculated from measurements of total barium, using partitioning coefficients (K_p) and assuming a default suspended matter concentration of 30 mg/L. This introduces a methodological uncertainty as both K_p-values and suspended matter concentrations can vary strongly (Osté, 2013). For the specific case of barium, other important factors should be considered as well, such as sulfate (see 2.3.2 below).

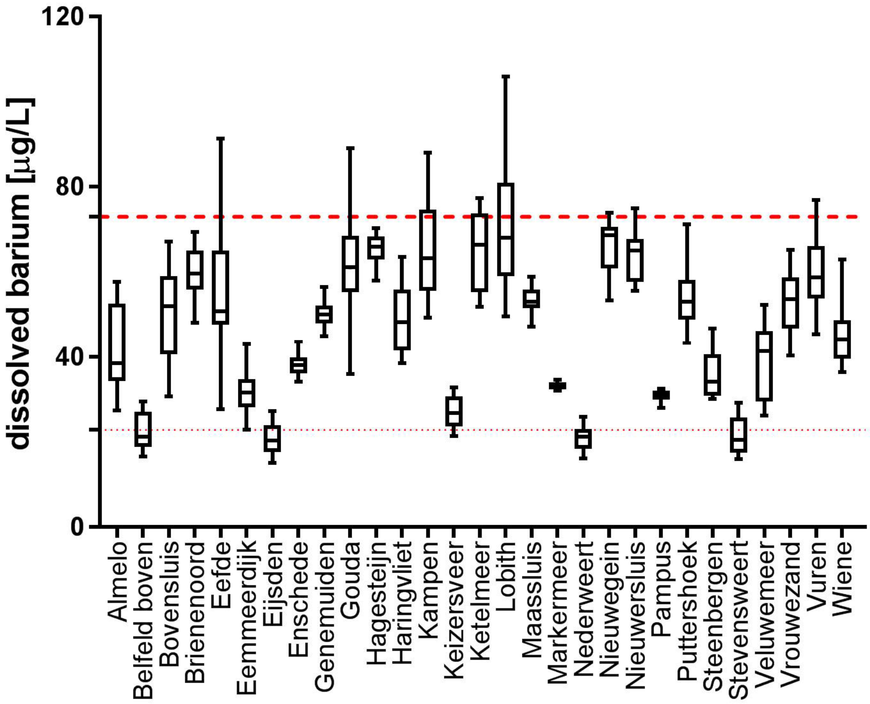

Figure 1. Dissolved barium concentrations [µg Ba/L] at freshwater monitoring locations in the Netherlands in 2016; weekly measurements for Eijsden, biweekly for Lobith and monthly for other locations. Boxes extend from the 25th to 75th percentiles, the line in the middle of the box is the median, and whiskers are minimum to maximum. The upper dotted red line is the previous background concentration of 73 µg/L, the lower one is the new background concentration of 22 µg/L.

2.3 Environmental behaviour of barium

As indicated above, barium sulfate and barium carbonate are often found in nature as underground ore deposits. These forms of barium have a low water solubility. Other barium compounds, such as barium acetate, barium chloride, barium hydroxide, barium nitrate, and barium sulfide dissolve more easily in water than barium sulfate and barium carbonate. Some of these are not commonly found in nature, but are manufactured from barium sulfate and only end up in the environment in case of emissions from industrial sites (ASTDR, 2007).

Barium adsorption to soil occurs onto metal oxides and hydroxides, and the concentration of barium in natural waters is next to precipitation with sulfate probably controlled by adsorption to metal oxides. The cation-exchange capacity is the main factor determining the non-specific sorption of barium, complexation to soil organic matter occurs to a limited extent. In most natural waters, barium does not occur in its free ionic form. The species and distribution of barium salts depend on the affinity to anions and their abundance, with the presence of sulfate ions as a dominant factor (Kravchenko et al., 2014; WHO, 2001). When soluble barium compounds, such as barium chloride, barium nitrate, or barium hydroxide, enter surface waters, dissolved barium quickly combines with naturally present sulfate or carbonate to form the less soluble barium sulfate and barium carbonate. These are the barium compounds that are most commonly found in soil and water (ASTDR, 2007). For the interpretation of aquatic ecotoxicity data, information on water hardness and the presence of sulfate are therefore considered of importance (see also Chapter 5). In general, barium solubility increases with decreasing pH although the scale of solubility depends on the ligand pair and/or the type of barium salt. Barium chloride is less influenced by pH than barium sulfate or carbonate (Kravchenko et al., 2014). Concentrations of barium in sediment are high as compared to water, due to precipitation of insoluble barium compounds (WHO, 2001).

2.3.1 *Dissolved and total concentrations: limited influence of sorption*

Monitoring data show that the range of dissolved and total concentrations of barium in Dutch freshwaters is quite similar. Figure 2 gives the data from 2016 for 27 freshwater locations for which both dissolved and total concentrations are available. Dissolved concentrations were determined after filtration over a 0.45 μm filter. At some individual time points, reported dissolved concentrations were equal to or higher than the concurrent total concentration. This shows that for barium, the difference between dissolved and total concentrations is often within the margins of the analytical variation.

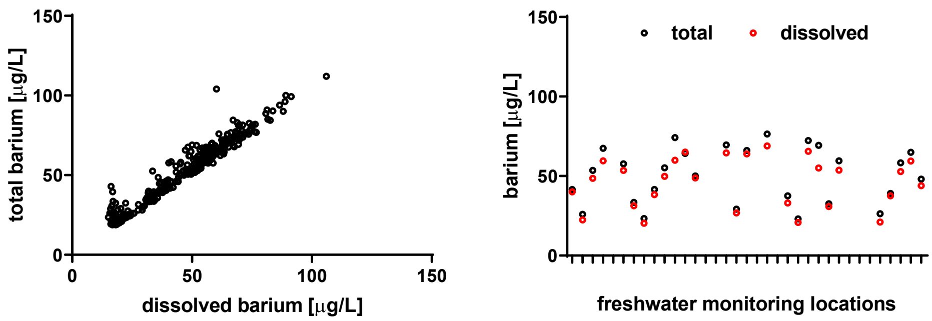

Figure 2. Dissolved and total concentrations of barium at Dutch freshwater monitoring locations in 2016. Left part: individual data. Right part: geometric means. For locations, see Figure 1. Data are monthly, weekly or biweekly measurements. Data retrieved via http://live.waterbase.nl/waterbase_wns.cfm?taal=nl.

Figure 3 shows the individual data for barium concentrations as a function of suspended solids (left) and sulfate (right) measured in the same sample. From this figure it appears that there is no correlation between the barium concentrations and the content of suspended solids.

Together with the very small difference between filtered and total concentrations (Figure 2), it can be concluded that barium is not adsorbing to suspended matter in significant amounts. Sorption of barium to suspended solids cannot explain the differences in barium concentrations in the filtered water samples among freshwater locations. Filtered water samples would be expected to contain dissolved barium only. Therefore, the correlation between barium concentration and sulfate would be expected to be limited by the contour that is defined by the solubility product of barium sulfate (barite), with no barium concentrations above this line.

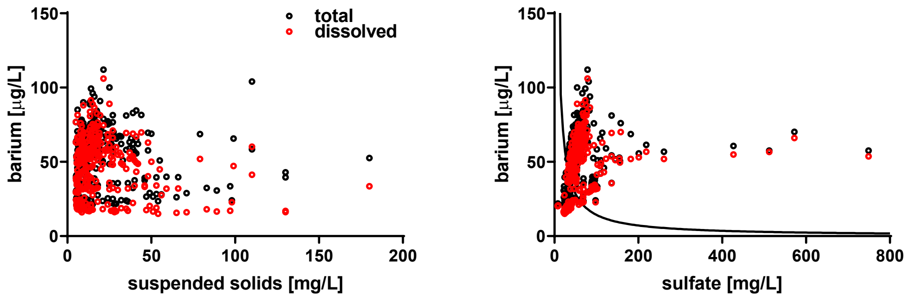

Figure 3. Dissolved and total concentrations of barium at Dutch freshwater monitoring locations in 2016 as a function of suspended solids (left) and sulfate (right). Reporting (lower) limit of suspended solids is 5 mg/L. Data below the reporting limit and data points where dissolved concentrations were higher than total are omitted. Drawn line in right figure represents the solubility product of barium sulfate (barite).

However, it is observed that this is not the case, with many experimental data exceeding the water solubility of barite. A conclusion could be that filtered water samples do not represent the dissolved fraction only. Instead there seems to be a positive correlation between barium and sulfate concentrations, which is a strong indication that a large part of the barium in the surface water filtrates is actually present as finely dispersed barite.

It was tested whether the excess of barium above the solubility of barite in filtered water samples could be due to sorption to dissolved organic carbon (DOC). For this purpose, the excess of barium above the solubility limit of barite was considered associated with the measured concentration of DOC in each sample. It appeared that the partition coefficients of barium to DOC (K_{oc}) had to be unrealistically high to explain the amount found in the filtered water samples (log K_{oc} = 5.31 ± 0.66 for freshwater and 6.71 ± 0.50 for saltwater). There was a significant difference between log K_{oc} for freshwater and saltwater, which indicates that there is no single value for log K_{oc} to describe the observed differences. Also within small domains of sulfate concentrations, there is no correlation between the excess amount of barium and the concentrations of dissolved organic matter. It is therefore concluded that barium concentrations above the solubility limit of barium sulfate can at most to a very limited extent be explained by sorption to dissolved organic carbon. Finally, both dispersed barite as well as barium sorbed to dissolved organic carbon should be considered as not bioavailable.

2.3.2 *Influence of sulfate*

Dissolved barium concentrations in saltwater are generally lower than in freshwater, the highest geometric mean dissolved concentration of saltwater monitoring locations in 2016 is around 50 µg/L, while this is around 70 µg/L for freshwater. Saltwater has higher sulfate concentrations of around 2 g/L, whereas most freshwaters have sulfate concentrations in the range of 40 to 60 mg/L. Exceptions are Lake Veluwe and the Markermeer, which have higher sulfate levels of around 100 mg/L, and the Nieuwe Waterweg at Maassluis with sulfate levels between 109 and 749 mg/L. Despite the lower barium concentrations, also for saltwater the solubility product of barite is exceeded in all samples, thus suggesting the presence of dispersed barite in the filtered water samples.

Speciation modelling shows that the concentration of truly dissolved barium is never much higher than concentrations that follow from the solubility product (Golding et al., 2018). At low barium concentrations, the modelled concentrations of barium and sulfate are only slightly higher than the solubility product that would follow from the reported solubility of barite of 0.0025 g/L. This might be the result of not exactly the same input data for the solubility of barite in the used speciation model in this study (Visual MINTEQ). In this study, dissolved barium concentrations were also determined by filtering the water over a 0.45 µm-filter. The experimental, filtered water concentrations were generally close to the modelled concentrations, but especially at the low barium concentrations (0.1, 1 mg/L) more than a factor of two higher than the modelled concentrations. Another observation from this study was that although the measurement of the dissolved fraction after filtration confirmed the formation of precipitate, this precipitate was not visible by eye up to total barium concentrations of 10 mg/L. The combination of these two observations support the hypothesis that at low barium concentrations finely dispersed barite is present in water samples filtered over a 0.45 µm-filter.

The study by Golding et al. (2018) also shows that availability of barium differs between higher and lower barium concentration, depending on the sulfate content of the water. By adding barium to the medium, the modelled dissolved barium concentrations stay constant because of regulation by the sulfate concentration of the medium. As a result, the fraction freely dissolved barium declines accordingly. However, at the point where the sulfate concentration becomes depleted, the dissolved barium concentration increases with further addition, increasing the fraction of the free concentration. In the synthetic soft water medium with 84 mg/L sulfate the modelled concentration dissolved barium changes from 0.19 mg/L at 100 mg/L total barium, to 180 mg/L at 300 mg/L barium, i.e. a change in the dissolved fraction from 0.19‰ to 60% in one concentration step in a toxicity experiment. This huge difference was also verified by the experimentally determined, filtered water concentrations.

3 Biota standards: human health and secondary poisoning

3.1 Toxicity mechanism

Barium is not considered an essential element for humans as cited in Kravchenko et al. (2014) and WHO (2016). The mechanism of barium toxicity is not fully clear. Observed effects, such as heart rate disorder, hyper- or hypotension, muscle weakness and paralysis are most likely due to increased intracellular potassium levels (ASTDR, 2007). Barium is a competitive antagonist for potassium channels, and it can block the passive efflux of intracellular potassium, resulting in the increase of intracellular potassium with a consequent decreased resting membrane potential. The muscle fibres become electrically unexcitable leading to paralysis (SCHER, 2012). The ability of barium to substitute calcium is also mentioned to cause toxicity by stimulation of the smooth muscles of the gastro-intestinal tract, cardiac muscle, and voluntary muscles (CCME, 2013). Magnesium and calcium suppress the uptake of barium in the pancreatic islets, but low barium levels stimulate calcium uptake by these cells. It is suggested that barium stimulates insulin release by displacement of calcium, but the experimental data are not sufficient to determine the significance for human health (ASTDR, 2007).

3.2 Uptake and excretion of barium

For humans, ingestion of barium through drinking water and food are the main routes of exposure. Inhalation of barium associated with particles may also occur, but little information is available on the absorption of barium by this route (WHO, 2001). In humans, 5-30% absorption from the gastro-intestinal tract is reported by Kravchenko et al. (2014), while ASTDR (2007) and SCHER (2012) mention a range of 3 to 60%. Differences can be explained with differences in experimental design and methodology used, e.g., duration, age, fasting status of the animals, and calculation of absorption vs. the background levels (SCHER, 2012). ASTDR (2007) and SCHER (2012) cite studies with rats which show that younger animals (≤ 22 days old) absorb about 10 times more barium chloride from the gastrointestinal tract than older animals, and absorption was higher in fasted adults than in fed animals.

Barium is primarily excreted in the feces. In human studies, 90-98% of the barium was excreted in feces at normal intake levels of barium from food, water, and air, excretion in urine accounts for 2-5% (WHO, 2001). Of the barium that stays in the body, about 90% is found in bone, only 1-2% is found in muscle, skin, fat and connective tissue (Kravchenko et al., 2014; WHO, 2001). Studies with rats indicate that apart from the skeleton, barium may end up in heart, eyes, muscle, kidney, blood and liver (ASTDR, 2007; McCauley & Washington, 1983).

It should be noted that absorption is often measured as the net difference between intake and excretion, and it should be noted that between these events internal processes may have taken place, including uptake and subsequent excretion. The actual absorption can thus be higher than the reported values. Further, as explained below, also the dose might be a crucial factor leading to different results for absorption.

3.3 Absorption efficiency and influence of chemical form on uptake

According to many authors, the chemical form of barium is the most important factor determining its uptake (Kravchenko et al., 2014). Barium toxicity is assumed to be caused by the free cation, and the solubility of the barium compound to which an individual is exposed is the crucial factor affecting the onset of adverse health effects (SCHER, 2012). It is generally assumed that insoluble forms of barium, such as barium sulfate, are non-toxic because they are an inefficient source of barium ions. It is hypothesised that insoluble forms such as barium carbonate, may release barium ions in the acid environment of the stomach (ASTDR, 2007; SCHER, 2012; WHO, 2001).
However, as the solubility of barium salts is not strongly dependent on pH (Menzie et al., 2008; Van Tilborg, 2020), this is not likely to occur. It could be hypothesised that at low doses the sulfate (and to a lesser extent carbonate) concentrations in body fluids and gastrointestinal tract play an important role in mediating the uptake of barium, irrespective of the form in which it is administered. Concentrations of sulfate in the gastrointestinal tract are 0.06 to 0.15 mM in saliva, 4.0 mM in bile and pancreatic juice and 1,0 mM in succus entericus (intestinal juice) (Van Tilborg, 2020). These sulfate concentrations are higher than those resulting from the solubility of barite at different pH and hence the sulfate concentrations in the digestive tract will effectively control the solubility of barium in these digestive fluids, regardless of pH and the form in which barium is taken up (Van Tilborg, 2020).
The availability to mammals and humans could be dependent on the dose, with low doses leading to the highest availability due to the relative larger fraction of dissolved barium (Menzie et al., 2008). Also the dissolution kinetics of barium salts could play a role in the uptake of barium, as the absorbed dissolved barium might be replenished by dissolution of the salts. Here, the particle size of mainly barite and the residence time in the digestive tract become important parameters. More finely dispersed barium salts will dissolute quicker and large herbivorous animals have longer digestive residence times than small carnivorous species (Menzie et al., 2008).

Indeed, a few experimental studies with rats on the uptake of different forms of barium show that the chemical form of barium is relatively unimportant for the uptake of barium in the organism. However, even for a small species as the rat (with an assumed low digestive residence time), the absorption efficiency is rather high and would not be anticipated from the expected low solubility in the digestive tract. These studies are summarised and discussed below.

McCauley & Washington (1983) exposed male rats orally to either barium chloride or barium sulfate at 50 µg Ba/kg_{bw}, and found almost no difference in uptake. However, barium carbonate in a vehicle of 0.8 M sodium bicarbonate was adsorbed by 45% relative to barium chloride. The authors hypothesised that gastric acid solubilises inavailable barium complexes such as barium sulfate, and that sodium bicarbonate has a buffering capacity in the uptake of barium carbonate in this case. It is also hypothesised by the authors that the dose might be a relevant factor in this as well, i.e. lower uptake at higher doses. They argue that small finely divided particles of barium sulfate and barium carbonate, relevant for chronic exposure, are more easily solubilised and taken up than large doses (McCauley & Washington, 1983). It can be reasoned that even at this low dose, only a small amount will be present as free barium in the digestive fluids and the pH will not change the bioavailability (Van Tilborg, 2020). Concentrations in blood, eye, heart, liver, kidney and muscle at 24 hours after dosing are presented. With default values for the relative organ weights of the rat, as for example used in PBPK modelling (Law et al., 2017), it can be concluded from the data presented that 30% of the administered single dose could be retrieved from these organs after 24 hours. Given the fact that these tissues only make up 53% of the total body weight and that other tissues like bones are not accounted for, the total absorption efficiency will be even higher and could be in the order of 50% or higher.

Stoewsand et al. (1988) made a comparison between the uptake of barium added as barium chloride, and barium naturally present in Brazilian nuts (*Bertholletia excelsa*), mixed through the diet in a proportion of 25%. The diet contained in both cases 249 mg Ba/kg_{diet}, was isocaloric and isonitrogenous. The control diet without additional barium chloride contained 24.7 mg Ba/kg_{diet}. The control diet contained barium in a concentration of 10% that of the two barium dosed groups. This basal rat diet contained 40 times less barium than the Brazilian nuts. The diets were fed for 29 days to male weanling rats. In this case there was no difference in uptake between barium added as barium chloride or occurring naturally in Brazilian nuts. The rats fed the diet with nuts or barium chloride consumed over 100 mg Ba in 29 days versus 10 mg Ba in the rats fed with the control diet. No effects were observed on growth between the control group, the group with barium chloride diet and the group with Brazilian nuts diet. The amount of barium that is included in the skeleton after 29 days of exposure was 0.65 to 0.70% in the exposed groups, in contrast to only 0.25% in the control group fed with standard diet (Stoewsand et al., 1988).

It has to be noted that the weight of the skeleton is only 4.15% of the total body weight (Law et al., 2017) and from the study by McCauley & Washington (1983) it appears that a significant part of a single dose is found in other tissues. Further, the amount found in the body after 29 days does not reflect the absorption efficiency, as a significant amount of the absorbed amount might be excreted by urine of feces in the meantime. The data from the study are not sufficient to construct a mass balance. However, based on the reported concentrations of barium in the urine and feces of the rat (Stoewsand et al., 1988) and estimates for daily urine and feces excretion (Bellamy et al., 1970), it is estimated that less than 10% of the total barium intake is excreted via these routes. This is most likely an underestimation of the excretion, because after an intraperitoneal injection of a trace amount of barium, 6.6% and 22.7% were excreted after 48 hours by urine and feces, respectively (Bauer et al., 1956). However, it is still a strong indication that at least a significant amount of barium is retained in the body after 29 days of exposure.

3.4 Dose dependent deposition in bones

The presented results for skeletal barium by Stoewsand et al. (1988) are in line with what has been found in in femur bone of rats from the control group and the highest dose of barium chloride in the 15 month interim evaluation of the chronic study of the National Toxicology Program (NTP, 1994). From the amount of barium for the control diet from Stoewsand et al. (1988), a concentration in the skeleton of 3 mg Ba/kg can be estimated. The control diet in the NTP study contained less than 20 mg Ba/kg_{diet}. This lead to concentrations in three parts of the femur bone of 3.4 to 3.7 mg Ba/kg for male rats and 2.1 to 5.5 mg Ba/kg for female rats. From the study of Stoewsand concentrations in the skeleton of around 90 mg Ba/kg can be estimated resulting from the diets with Brazilian nuts or added barium chloride. The dose that can be estimated for these diets is around 20 mg/kg_{bw}/d. In the high dose of the NTP study, the concentrations in the femur bone varied from 1221 to 1685 mg Ba/kg for male rats and 1114 to 1464 mg Ba/kg for female rats. The doses for this level were 63 and 74 mg/kg_{bw}/d, for males and females. It can be concluded that the higher the dose, the higher the concentration in the bones is, but not in a proportionate way. At higher doses the deposition of barium in the bones is relatively higher. In the NTP study (NTP, 1994), also the plasm levels were measured after 15 months of exposure. The plasm levels were contrary to the concentrations in femur bones only slightly dependent on the dose. Over the entire range of doses the concentration in plasma levels increased by less than a factor of two in both sexes of rats and less than a factor of three in both sexes of mice. This could be the result of the fact that the dissolved concentrations in plasm are determined by solubility due to the presence of sulfate and other anions.

3.5 Human toxicological risk limit and $QS_{biota,\ hh\ food}$

As indicated in Section 1.1, the previously used human toxicological risk limit was derived by Baars et al. (2001). For soluble barium compounds, they proposed to maintain the TDI of 20 µg/kg_{bw}/d that was derived earlier by Vermeire et al. (1991). This TDI was derived from a study with human volunteers that were exposed to barium in drinking water with 0.2 mg/kg_{bw}/d as the lowest dose. Although no clear No Observed Effect Level (NOEL) was found in this study, the TDI was derived using an uncertainty factor of 10 (Baars et al., 2001).

In 2012, the Scientific Committee on Health and Environmental Risks (SCHER) of the European Commission adopted an opinion on the TDI of barium in the context of the Toys Safety Directive (SCHER, 2012). The SCHER acknowledges that human data are considered a more relevant basis for deriving a TDI, but concludes that the previously used human studies had important flaws. In this opinion, the SCHER therefore followed the approach of the United States Agency for Toxic Substances and Disease Registry (ASTDR, 2007). The ASTDR performed a benchmark analysis of the incidence data for nephropathy in mice as observed in a chronic study with drinking water exposure performed by the National Toxicology Program (NTP, 1994), and derived a benchmark dose (BMD) of 80.06 mg Ba/kg_{bw}/d for a 5% increase in the incidence of nephropathy. Instead of the 10% incidence, which is generally used as a benchmark, the 5% level was chosen because of the marked severity of nephropathy and increased mortality seen at the LOAEL, as a consequence to the steepness of the dose-response curve. The 95% lower confidence limit on the BMD (BMDL05) was 61.13 mg Ba/kg$_{bw}$/d. An assessment factor of 300 was applied to this value, 100 to account for inter- and intraspecies variability and a conservative, additional factor of 3 to account for deficiencies in the data base, leading to a TDI of 0.2 mg Ba/kg$_{bw}$/day.

The US EPA used the same method to derive an oral reference dose (RfD) for barium of 0.2 mg Ba/kg$_{bw}$/d (US EPA, 1998-2005). Also using the BMDL-approach, but applying an assessment factor of 100, a TDI of 0.6 mg Ba/kg$_{bw}$/d was proposed by RIVM (Van Engelen et al., 2008). Although published later, this report was already finalised before the publication of the ASTDR-assessment.

Recent research published after the opinion of the SCHER reports that exposure to barium may lead to aural impairment. After two weeks of exposure to barium chloride in drinking water, mice exposed to 0.14 and 1.4 mg Ba/kg$_{bw}$/d showed hearing loss compared to controls in a dose-dependent manner. This was confirmed by further analysis of the inner ears of mice exposed to the same levels of barium for two months (Ohgami et al., 2012). The correlation between exposure to barium and hearing loss is probably also relevant for humans, because in an epidemiological follow-up study there was a significant correlation between hearing loss at 8 and 12 kHz and barium concentrations in hair and toes of humans (Ohgami et al., 2016). The WHO did not find the evidence of the findings of rats for the relevance for humans strong enough to base their guideline value on these studies and used nearly the same TDI as proposed by SCHER (WHO, 2016). However, the epidemiological study was not yet available at that time and thus not taken into account. It should be noted that it is unclear if hearing loss should be included in the human toxicological risk assessment, and which assessment factors are appropriate if this effect would be taken into account.

In the present report, the opinion of the SCHER is followed and the TDI of 0.2 mg Ba/kg$_{bw}$/d is used for further calculations. This value is a factor of 10 higher than used previously in Van Vlaardingen & Verbruggen (2009). Using the WFD-methodology (see Section 1.2.1), the QS$_{biota,\ hh\ food}$ is calculated as 0.2 x 0.2 / 0.00163 = 24.5 mg/kg$_{wwt\ food}$. Because of the 10-fold increase in TDI and the increase in the allocation factor from 10 to 20%, the QS$_{biota,\ hh\ food}$ is 20 times higher than the value used by Van Vlaardingen & Verbruggen (2009)

3.6 Effects on birds and mammals

For the derivation of the QS$_{biota,\ secpois}$, the lowest energy-based concentration is used as a starting point. The most critical studies for three species (chickens, mice and rats) are discussed below. Almost all toxicological studies with mammals have been performed with barium chloride or barium acetate in drinking water and might reflect worst case exposure conditions regarding barium ion availability.

3.6.1 *Chickens*

Female chickens were exposed from 1 day of age until 4 weeks of age to either barium acetate or barium hydroxide in their diet. The effects of barium were rather independent of the compound administered. At 8000 mg Ba/kg_{diet} in both series more than half of the chickens died and at higher concentrations of 16000 and 32000 mg Ba/kg_{diet} all chickens died. The endpoint growth was more sensitive and the authors conclude that 1000 mg Ba/kg_{diet} is tolerated, but that at 2000 mg Ba/kg_{diet} there was a slight suppression in growth, while at 4000 mg Ba/kg_{diet} growth was significantly decreased. In the same study the lethal single dose for 50% of the chickens (LD_{50}) was determined as 623 mg Ba/kg_{bw} for 7-w old male chickens of 943 ± 44 g bodyweight dosed orally with barium hydroxide. The results from another experiment with 1-w old male and female chickens dosed with barium hydroxide for three weeks are in accordance with the results from the 4-w experiment. No significant mortality or decreased growth was found in diet concentrations up to 1280 mg Ba/kg_{diet} (Johnson et al., 1960).

From the presented mortality data from the 4-w experiment, a log-logistic dose-response curve was constructed. The lethal dietary concentration for 10 and 50% of the species was estimated, yielding an LC_{10} 5300 mg/kg_{diet} and an LC_{50} of 7400 mg/kg_{diet}. The same was done for chick growth during the 4-w exposure period. The controls for the barium hydroxide group grew slightly faster than in the control group for barium acetate. However, this difference seems most likely caused by chance as in some of the unaffected low doses, the barium acetate groups grew slightly faster than the groups exposed to barium hydroxide. Indeed, all data together fit well to a single dose-response curve. From this curve, the dietary concentrations with 10 and 50% effect on growth were estimated, yielding an EC_{10} of 3400 mg Ba/kg_{diet} and an EC_{50} of 8100 mg Ba/kg_{diet}. The onset of growth reduction is indeed observed before significant mortality occurs, making this the more sensitive endpoint.

As indicated in the introduction (see 1.2.2), different food sources are considered in the assessment of secondary poisoning. An energy based approach is followed to select the food source that will drive the QS. For this, the endpoints for birds and mammals have to be converted to energy normalised values, expressed as mg Ba per kJ_{diet} The WFD-guidance provides two methods for calculating energy normalised endpoints (EC, 2018). In the first method, energy based endpoints are calculated from the daily dose and daily energy expenditure (DEE; kJ/d) of the species of interest (method A in the guidance). The DEE is strongly correlated with body weight, with small animals expending relatively more energy than larger animals and the WFD-guidance presents the allometric functions for birds and mammals. In the other method, dietary concentrations are recalculated into energy-based values using the caloric content of the feed (method B in the guidance). Because sufficient information is present, both methods are applied here.

Method A. The dose at each level can be estimated from the presented results. The total feed consumption at each level can be accurately calculated from the ratio of the growth and the weight increase per consumed mass of feed. The average body weight (BW) from day 1 until 4 weeks of age, is estimated by assuming that the chickens are around 40 g at hatching and growth is linear. The daily food consumption is then around 11% of the body weight. This is in reasonable agreement with the default factor of 8 kg_{bw}/kg_{food}/d for chickens (=12.5% of the body weight each day). However, for young birds and mammals this factor might change over time. The reported data on body weight gain and food consumption refer only to the difference between the start and end of the exposure period, which means that the dose might change over time. Expressed as average daily dose, the resulting LD_{10} is 540 mg Ba/kg_{bw}/d and the LD_{50} 770 mg Ba/kg_{bw}/d, which is even slightly higher than the LD_{50} of 623 mg Ba/kg_{bw}/d after a single dose. This could be an indication that mortality is not strongly dependent on exposure time. For growth reduction, the ED_{10} and ED_{50} are 390 and 860 mg Ba/kg_{bw}/d.

The DEE for chickens was estimated using the allometric function for birds from the guidance. The energy normalised LC_{10} and EC_{10}-values were subsequently calculated from the dietary dose, BW and DEE (as dose x BW/DEE). This results in an LC_{10} of 0.46 mg Ba/kJ_{diet} for mortality and and EC_{10} of 0.36 mg Ba/kJ_{diet} growth reduction.

Method B. The composition of the feed is given in detail. Therefore, an assessment of the caloric content of the food can be made. The three main constituents in the feed are ground yellow corn (61.56%), soybean oil meal (44% protein) (31%), and menhaden fish meal (3%). The remaining 4.5% are mainly minerals and a minor amount of vitamins and these are assumed not to contain significant metabolisable energy. The metabolisable energy content of these three main constituents are tabulated and are 3390, 2240 and 2950 kcal/kg_{diet}, respectively (Batal, 2011). This renders the energy content of the food to be 12,000 kJ/kg_{diet}. Based on energy content, the LC_{10} is 0.44 mg Ba/kJ_{diet} and the EC_{10} for growth reduction is 0.29 mg Ba/kJ_{diet}.

Both methods to calculate energy normalised endpoints are completely independent, but still result in very similar values. More weight is given to the effect concentrations based on the actual energy content of the food (method B) because of the uncertainties in the exact body weights and exposure time, and the fact that the chickens are fast growing during the exposure period. As a consequence DEE, body weight and dose (which are input to method A) might have changed continuously.

3.6.2 *Mice*

In 15-days subacute, 13-weeks subchronic and 2-years chronic studies, mice were exposed to barium chloride dihydrate in drinking water (NTP, 1994). Drinking water consumption and weight of the mice were tabulated, mostly per week. Barium doses were given as mg Ba/kg_{bw}/d. However, the reported doses seem to be rounded to increments of 5. Especially for the lower doses the difference with the dose calculated from the weight of the mice and the corresponding water consumption is large and could be significant (i.e., 20 to 30%). Therefore, all doses were recalculated with the reported weight, water consumption and average verified water concentrations.

In the 15-d study, five water concentrations (24-390 mg Ba/L) were tested and calculated doses were 3.9 to 71 mg Ba/kg_{bw}/d for males and 3.5 to 85 mg Ba/kg_{bw}/d for females. No effects on body weight, growth or survival were observed.

In the 13-w study, barium chloride dihydrate was tested at five water concentrations (70, 280, 560, 1100, and 2200 mg Ba/L). The No Observed Adverse Effect Concentration (NOAEC) for effects on growth and survival was 1100 mg Ba/L. Severe effects (more than 50% mortality and no weight gain or even decrease) were observed at the next higher drinking water concentration of 2200 mg Ba/L. In the groups exposed to 1100 mg Ba/L, the actual dose decreased from 230 to 120 mg Ba/kg_{bw}/d for males and from 250 to 110 mg Ba/kg_{bw}/d for females due to growth over time in combination with a reduced water consumption. In the high concentration of 2200 mg Ba/L, growth was almost absent and the calculated dose changed only little over time, from 360 to 330 mg Ba/kg_{bw}/d for males and from 580 to 550 mg Ba/kg_{bw}/d for females.

In the 2-y study, concentrations of 280, 710 and 1400 mg Ba/L were tested. No effects on growth and survival were observed at the two lower drinking water concentrations of 280 and 710 mg Ba/L. Effects on growth and survival were observed in the highest drinking water concentration of 1400 mg Ba/L, with an onset of effects after about 15 weeks. Especially for mortality of females, this effect was well in excess of 10% throughout the study. Growth was reduced by about 10% for both females and males at the highest concentration. Calculated doses decreased until halfway the study and then slightly increased again over time. The time-weighted average doses corresponded well with the reported doses and are considered as reasonable average dose for the complete study duration. The No Observed Adverse Effect Level (NOAEL) for growth and mortality was 77 and 91 mg Ba/kg_{bw}/d, for males and females, respectively. The Lowest Observed Adverse Effect Level (LOAEL) was 160 and 200 mg Ba/kg_{bw}/d, for males and females, respectively.

Because exposure was via drinking water, method A has to be applied to recalculate the endpoints into energy normalised values. With the body weights and dose reported over the entire study, time-weighted average energy normalised NOECs were calculated as 0.033 mg Ba/kJ_{diet} for males and 0.038 mg Ba/kJ_{diet} for females. The energy normalised Lowest Observed Effect Concentrations (LOECs) are 0.068 mg Ba/kJ_{diet} for males and 0.085 mg Ba/kJ_{diet} for females. Due to the limited number of concentrations and the absence of effects in all but one concentration, a dose-response relationship is difficult to establish for growth. For both males and females, the EC_{10} for growth reduction is in the order of the LOEC, while for mortality the LOEC corresponds to a higher effect than 10% mortality, especially for females. The LC_{10} for survival probability until the end of the study is only 0.036 mg Ba/kJ_{diet} for males, which is very close to the NOEC, while the LC_{10} for females of 0.057 mg Ba/kJ_{diet} is slightly higher than the NOEC.

3.6.3 *Rats*

A similar study as with mice was performed with rats, which were exposed to barium chloride dihydrate in drinking water in a 15-d subacute, 13-w subchronic and 2-y chronic study (NTP, 1994). Similar as with the study for mice, the recalculated doses differ from the reported doses, especially for the lower doses. Again, all doses were recalculated with the reported weight, water consumption and average verified water concentrations.

In the 15-d study, five water concentrations of 70-1100 mg Ba/L were tested, calculated doses were 6.7 to 100 and 8.6 to 110 mg Ba/kg_{bw}/d for males and females, respectively. No effects on growth and survival were observed. Growth was reduced by 18% in males exposed at the highest concentrations, but this did not seem to be significant.

In the 13-w study five test concentrations were included (70, 280, 560, 1100, and 2200 mg Ba/L). No effects on growth and survival were observed with drinking water concentrations up to 1100 mg Ba/L. Onset of effects were observed at drinking water concentrations of 2200 mg Ba/L, but these were less severe than those observed for mice (a significant reduction in growth, which amounted to approximately 10% for both males and females, and 30 and 10% mortality for males and females, respectively). Due to the growth and reduced water consumption over time by the rats that were exposed to non-toxic concentrations, the dose at 1100 mg Ba/L decreased over time from 170 to 61 mg Ba/kg_{bw}/d for males and from 150 to 64 mg Ba/kg_{bw}/d for females. In the high concentration of 2200 mg Ba/L, the calculated dose changed over time from 270 to 100 mg Ba/kg_{bw}/d for males and from 230 to 130 mg Ba/kg_{bw}/d for females.

In the 2-y study with test concentrations 280, 710 and 1400 mg Ba/L, survival was not negatively affected up to the highest concentration. Effects on the final body weight for males were reported in the highest drinking water concentration of 1400 mg Ba/L only, starting at 18 weeks with a gradual increase of effects over the entire study. For females, both 710 and 1400 mg Ba/L were reported to result in lower final body weights. However, also in males the lower dose of 710 mg Ba/L seems to result in small effects. When growth over the entire study is considered, the reduction is 3 and 5% for males and 9 and 15% for females, at 710 and 1400 mg Ba/L respectively. Calculated doses decreased until halfway the study and then stayed more or less constant. The calculated time-weighted average doses differed slightly from the reported doses (up to 20%). The doses are considered as reasonable average dose for complete study duration. The NOAELs for growth were 35 and 18 mg Ba/kg_{bw}/d, for males and females, respectively. The LOAELs were 63 and 45 mg Ba/kg_{bw}/d, for males and females, with 5% and 6% lower final body weight compared to the controls, respectively. For mortality, the NOAEL was ≥63 and ≥74 mg Ba/kg_{bw}/d for males and females, respectively.

Time-weighted average energy normalised endpoints were calculated with the body weights and dose reported over the entire study. The NOEC for growth was 0.029 and 0.013 mg Ba/kJ_{diet} for males and females, respectively. The LOECs were 0.052 and 0.032 mg Ba/kJ_{diet}, respectively. Fitting a dose-response curve through the data, EC_{10}-values for growth were estimated as 0.091 and 0.036 mg Ba/kJ_{diet} for males and females, respectively.

3.7 Biota based quality standard for secondary poisoning

The critical food item (e.g. fish, molluscs, crustaceans, plants) follows from the ratio of the bioaccumulation potential in different food items and the quality standard in the food items. The relevant quality standards for secondary poisoning in different food items from the aquatic environment are derived from the lowest value for birds and mammals as follows.

For the three species for which data were available, a quality standard for biota was derived by dividing the lowest EC_{10} by an assessment factor for exposure duration (Table 3). Although the QS_{biota} for chickens is lowest, the three values are very similar and if the NOEC for growth instead of the EC_{10} is taken as preferred endpoint, rats would be the most sensitive species.

Table 3. Lowest endpoint per species and derivation of biota standard.

Species	Lowest EC_{10} [mg Ba/kJ_{diet}]	Exposure	AF	QS_{biota} [mg Ba/kJ_{diet}]
Chicken	0.28	Subchronic	100	0.0028
Mouse	0.036	Chronic	10	0.0036
Rat	0.036	Chronic	10	0.0036

The quality standard based on energy content can be recalculated in different food items that are relevant for the aquatic food chain. The energy contents of fish, crustaceans, aquatic vegetation and bivalves are 5523, 4953, 2790 and 1602 kJ/kg_{wwt}, respectively (Smit, 2005; Verbruggen, 2014). Based on the QS_{biota} of 0.0028 mg/kJ_{diet}, this leads to biota standards of 16, 14, 8.0 and 4.6 mg Ba/kg_{wwt}, respectively. The accumulation of barium in these four groups determines which of these values is critical for the overall quality standard in water. This is further described in Section 6.2.

4 Bioaccumulation of barium in aquatic organisms

4.1 Field monitoring studies

Bioaccumulation data on barium were obtained from field monitoring studies and field studies with caged organisms. The available studies are summarised in Appendix 1. Bioaccumulation factors (BAFs) were derived from these studies for a range of taxa, including fish, amphibians, molluscs, crustaceans, insects, zooplankton, phytoplankton and plants. No information could be found on the uptake and excretion mechanisms of barium in water organisms. Bones, together with liver and skin, were demonstrated as the major sink in amphibians (Marques et al., 2011), while in fish highest concentrations were observed in spleen (Le Guernic et al., 2016), kidney and gills (Gagnaire et al., 2015). All individual BAFs are listed in Appendix 2. Below, the data are further discussed.

4.2 Use of dissolved or total concentrations

In most studies it was indicated that water was filtered before analysis, but in some other studies this was not the case. For these studies, it was assumed that reported levels refer to total concentrations. As indicated in Section 2.3, the presence of sulfate and carbonate is expected to influence the partitioning of barium, because of the formation of precipitates. However, large precipitates will transfer to sediment and will not influence the measured concentration in the water column. Sorption to suspended solids may also contribute to the difference between total and dissolved concentrations, but little information is available on this from bioaccumulation studies.

Nakamoto & Hassler (1992) report concentrations with and without filtration for Merced River and Salt Slough in the San Joaquin Valley (see Appendix 1, study 15). Dissolved concentrations were 79 and 64% of total for Merced River and Salt Slough, respectively, while filterable residue and turbidity differed by a factor 9 between the two rivers. In the study of Hope et al. (1996), mean concentrations of total and dissolved barium were the same in two ponds on the banks of James River, Virginia (see Appendix 1, study 18), but no information is given on the concentration of suspended solids or other water characteristics. Measured concentrations and bioaccumulation factors in *Libella* sp., Chironominae and crayfish from the Savannah River Project (see Appendix 1, study 17) do not show large differences between sites, despite differences in turbidity (Cherry et al., 1979).
Some additional information on the lack of influence of suspended solids on bioavailability may be obtained from Wang (1986a), who tested the response of duckweed to barium chloride in deionised water, filtered and unfiltered river water with 110 mg/L suspended solids. Toxicity in deionised water was highest, whereas the difference between filtered and unfiltered river water was small. From these experiments, it was concluded that other characteristics than particulate matter play a role, and the presence of sulfate in the river water was stated to be the determining factor. However, measurements of total and dissolved barium are not presented in this study.

If suspended solids would influence the availability of barium, BAFs based on total concentrations would be lower than those based on dissolved, because the available concentration in the water phase is overestimated. However, a meaningful comparison of BAFs based on dissolved or total concentrations can only be made for fish muscle, crustaceans and plants, because for the other taxa too few data are available for one or the other group. For fish, BAFs for total concentrations tend to be lower than those for dissolved concentrations (mean log BAF 0.66 vs. 0.78), but the difference is not significant. For crustaceans and plants, BAFs for total concentrations are even larger than those for dissolved concentrations. For crustaceans and insects, the variation in the BAFs for total concentrations is higher than for dissolved concentrations, despite the larger number of data. These differences in BAFs are probably not related to bioavailability, but are due to species or location specific differences.

As shown in Section 2.3, the difference between total and dissolved concentration in Dutch surface waters is generally small and often within the margins of the analytical variation. Sorption may become important probably only at fairly high suspended solid concentrations. Therefore, the BAFs are used irrespective if they refer to filtered or unfiltered water, which leads to an increase in the number of available BAF data.

4.3 Range of concentrations in biota

Figure 4 shows the data on barium concentrations in biota per taxon. The data originate from the studies summarised in Appendix 1. Biota concentrations were converted to wet weight values where necessary. The concentrations in biota span several orders of magnitude, with molluscs, crustaceans, insects and plants showing the highest levels. Wet weight concentrations in fish muscle are significantly lower than those in whole fish, and fish whole body or muscle concentrations are significantly lower than those for molluscs, crustaceans, insects and plants. Concentrations in crustaceans, molluscs, insects and plants are not significantly different from each other (Tukey’s test on log-transformed data, $p < 0.05$).

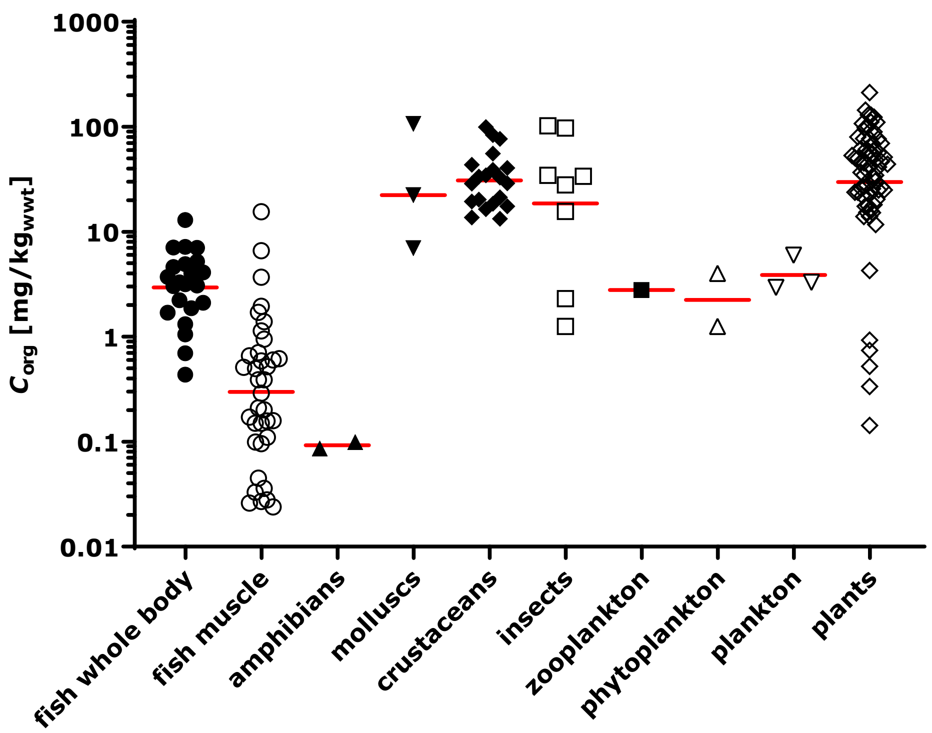

Figure 4. Range of barium concentrations observed in organisms, grouped per taxon. Concentrations are given in mg Ba/kg$_{wwt}$. Red lines represent the geometric mean per taxon.

4.4 Relationship with external concentrations

Figure 5 shows the concentrations in organisms as a function of barium concentrations in water, both log-transformed. Linear regression (GraphPad Software Inc., 2017) shows that the slopes of the regression lines are significantly deviating from zero for fish muscle (P 0.02), insects (P 0.0018) and plants (P<0.001), indicating that there is a relationship between external and internal concentration. For fish (whole body) and crustaceans, the slope is not significantly different from zero. Too few data are available for the other taxa. For insects and aquatic plants, a positive correlation between the concentration in the organisms and the concentration in water was found. For aquatic plants there is a highly significant relationship between external and internal concentrations that even is slightly distorted by the three relatively low data from one study (Samecka-Cymerman & Kempers, 2001), which are statistically identified as outliers. For insects, the relevance of this finding can be questioned due to the low number of data. For fish muscle, the relationship is negative, which would mean that at higher external water concentrations, the concentration in fish becomes lower. This is hard to explain from a biological point of view, and the relevance of this significance could be questioned as well.

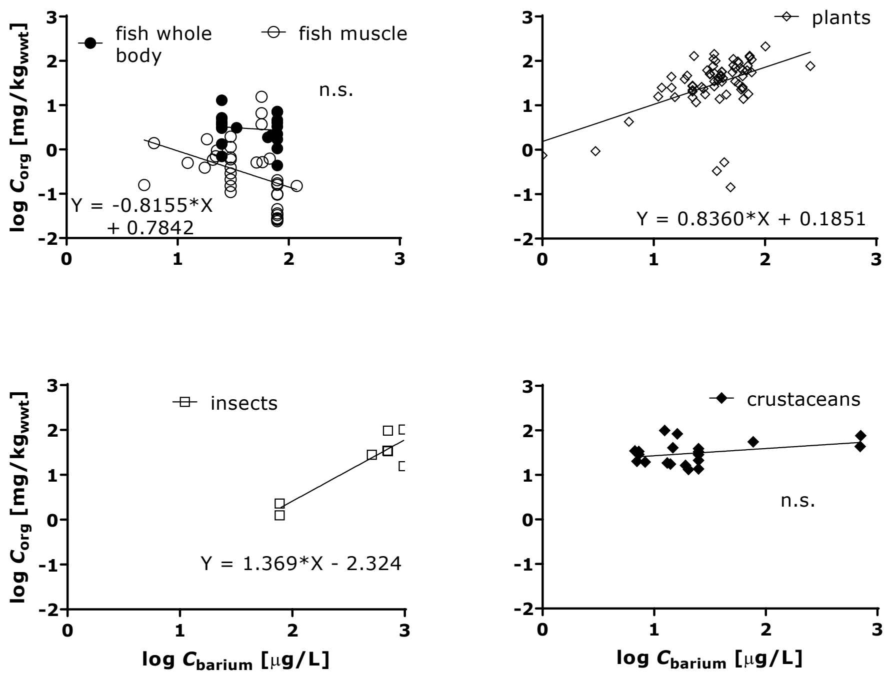

Figure 5. Wet weight based barium concentrations in fish, plants, insects and crustaceans as a function of barium concentrations in water, both log-transformed. Note that the scales of X- and Y-axis differ between figures. Slopes significantly different from zero are indicated by the equation, n.s. = not significant.

Figure 6 shows the results of the regression analysis for the log BAF as a function of log barium concentration in water. For plants and insects, the slopes of the lines are not significantly different from zero. The three data points for aquatic plants that deviate most strongly from the rest, originate from one study (Samecka-Cymerman & Kempers, 2001), as described above. These three data are identified as outliers in the set of 68 BAF values for plants and are therefore discarded for further analyses.

For fish, there is a negative relationship (slope significantly different from zero) between the BAFs based on both whole body and muscle and the external concentration. The slopes of these two regression lines are not significantly different: the pooled slope is -1.552, which is an exceptional value. If a compound is perfectly regulated, constant concentrations in biota are expected over a large range of external concentrations. In that case the slope of the log-log regression line would be -1. A larger negative slope (values < -1) indicates that internal concentrations decrease with external concentrations, which is hard to explain from a biological point of view as mentioned above.

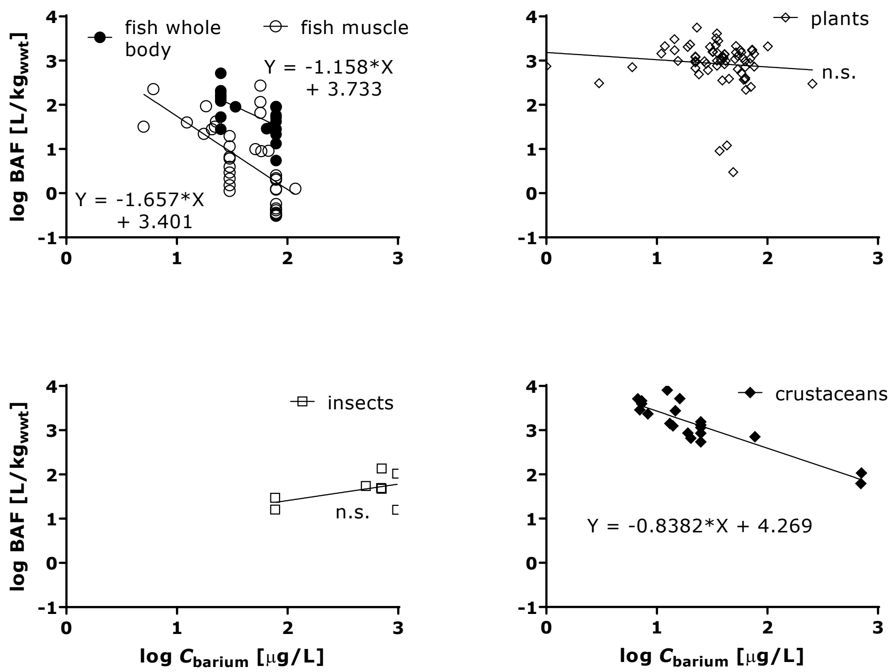

Figure 6. Wet weight based BAFs in fish, plants, insects and crustaceans as a function of barium concentrations in water, both log-transformed. Note that the scales of X- and Y-axis differ between figures. Relationships significantly different from zero are indicated by the equation, n.s. = not significant.

4.5 Difference between freshwater and saltwater

According to the WFD guidance document, freshwater and saltwater toxicity data for metals should not be combined unless it can be demonstrated that there is no significant difference between the two data sets. Although it is not explicitly mentioned that bioaccumulation data should be treated the same way, it seems logical to perform a comparison between freshwater and saltwater bioaccumulation data too.

Data for saltwater or brackish water are available from two studies with plants from the Thessaloniki Gulf in Greece (Malea et al., 2015; Malea & Kevrekidis, 2013), one study with fish (whole body), crustaceans and phytoplankton from the Mekong delta in Vietnam (Ikemoto et al., 2008), one study with fish (muscle) in a salt lake and in Plata River estuary in Argentina (Avigliano et al., 2015), and one study with molluscs and phytoplankton in the Pará River estuary in Brasilia (Vilhena et al., 2016).

For fish (whole body) there is a significant difference in bioaccumulation factors between the data for freshwater and saltwater (P=0.003). However, it should be noted that the data are from a few experimental studies with lower external barium concentrations in saltwater than in the freshwater studies. If internal whole body concentrations are compared instead of BAFs, there is no difference between the two data sets (P=0.61). This finding indicates that the concentrations of barium in fish are regulated at environmental levels, but that there is no difference between freshwater and saltwater fish. Data for saltwater fish muscle are limited (two samples from two sites in Argentina), but both BAF and internal concentrations are in the range of freshwater data and follow their trend. The same is observed for aquatic plants and crustaceans. For molluscs there only three data points for which the one saltwater species has a higher BAF and internal concentration than the two freshwater species. However, no conclusion can be drawn for this small data set for molluscs.

In general data appear to be very similar between freshwater and saltwater species. Therefore, it is considered justified to combine the data from freshwater and saltwater. The final values for secondary poisoning and human fish consumption are thus applicable to both freshwater and saltwater environment.

4.6 Relationship with trophic level

Donald (2017) concludes that barium shows trophic dilution throughout the food chain (see Appendix 1, study 5), because internal barium concentrations decrease with increasing $\delta^{15}N$ values. The explanation is sought in the gradient from benthic to pelagic food sources, because barium concentrations are significantly higher in invertebrates and fish associated with benthic substrates compared with those associated with pelagic environments. This is consistent with the observed high concentrations of barium in sediment relative to water (Donald, 2017). Campbell et al. (2005) measured stable isotopes and elements in algae, zooplankton, Arctic cod (*Boreogadus saida*), ringed seals (*Phoca hispida*) and eight species of seabirds in an Arctic food web in Baffin Bay, Canada. Using data for invertebrates, Arctic cod and vertebrate muscle, they found a significant negative relationship between $\delta^{15}N$-values and barium concentrations. According to the authors, this was due to the fact that concentrations in zooplankton were much higher than in vertebrates. For benthic organisms in deep water of the East China Sea, Asante et al. (2008) also found significant negative correlations between $\delta^{15}N$ and barium concentrations. In a food web study in Patagonia, Arribére et al. (2010) concluded that an increase in carnivory (trophic level) was related to a decrease in barium concentration. In the study of Ikemoto et al. (2008), however, regressions between barium concentrations and $\delta^{15}N$ values in crustaceans and fish were not significant (see Appendix 1, study 19). Fletcher et al. (2014) measured stable isotopes and elements in fish and herbivorous invertebrates in the Beaver Dam Creek (part of the Savannah River site, see Appendix 1, study 17), but could not perform further statistical analysis for barium because the proportion of non-detects was >60%.

Kravchenko et al. (2014) cites references showing that barium levels are lower in high-order animals, because the amount of barium that incorporates into the body decreases as nutrients move through the food chain by a process known as 'biopurification'. Biopurification is the tendency of an organism to preferentially assimilate calcium in preference to barium and strontium (Burton et al., 1999). Biopurification leads to a reduction in the organism's Ba/Ca and Sr/Ca ratios, relative to dietary ratios, which is reflected in bone. As a result, herbivores have lower ratios than the plants they consume, and carnivores similarly have lower ratios than their diet, which might include omnivores and other carnivores as well as herbivores (Burton et al., 1999). The observed decline in concentrations with increasing trophic level results from specific interactions with other elements. It is therefore probably not correct to consider this phenomenon as the opposite of biomagnification, because the latter is based on different mechanisms. The accumulation data collected in this report generally support the observation that accumulation is higher in plants and crustaceans than in fish and indeed concentrations seems to be effectively regulated in fish (see) see also. Molluscs also tend to have higher concentrations, but too few data are available to draw firm conclusions.

4.7 Relationship with fish weight

For fish, the above mentioned biopurification may play a role in the observed pattern, but fish weight may be a contributing factor as well. The raw data of Donald (2017) indicate a trend towards decreasing concentrations in whole body with increasing body weight. A similar trend is seen for muscle tissue in some, but not all species. Fletcher et al. (2014) also suggest an effect of size on bioaccumulation of barium in muscle for largemouth bass (*Micropterus salmoides*), based on the observation that all fish with detectable barium levels were small fish (<150 mm). Figure 7 shows the concentrations in fish and BAFs as a function of fish weight, both on a log scale. An F-test after performing linear regression shows that for muscle tissue, there is a significant relationship between fish weight and concentrations (P = 0.03) and BAF (P = 0.0004). However, the relationship is not significant for whole fish (see Figure 7).

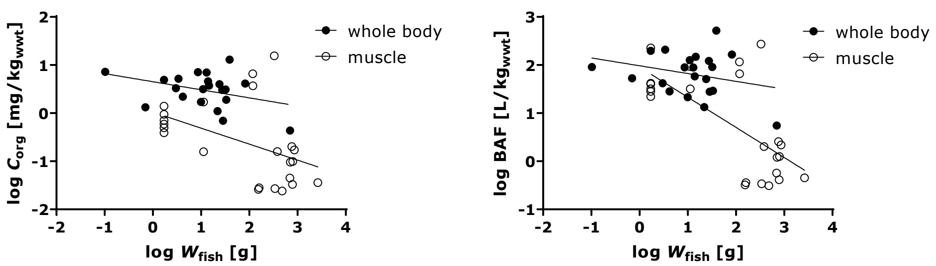

Figure 7. Barium concentrations in fish and fish bioaccumulation factors (BAFs) as a function of fish weight. Data for whole body (closed circles) and muscle (open circles) from Donald (2017), Gagnaire et al. (2015), Ikemoto et al. (2008), Le Guernic et al. (2016), (Léopold et al., 2015), and Nakamoto & Hassler (1992). Data from Hope et al. (1996) and Avigliano et al. (2015) are not included as no information on fish weight was given in these studies.

Because of the relatively low number of studies, the (absence or presence of) correlations could be coincidental, e.g., in one study at concentration X, fish are systematically smaller than in the other at concentration Y. However, there is no study-related association between fish weight and external concentrations. Fish weight is 1.71 and 11.3 g in the studies with the lowest concentrations (Gagnaire et al., 2015; Le Guernic et al., 2016), 0.7–82 g in the study of Ikemoto et al. (2008), and 0.1-700 g in the study with the highest concentration (Donald, 2017). Therefore, it must be concluded that the observed relationship between external concentration and BAF cannot be explained solely by fish weight as a confounding factor and regulation of internal concentrations is a more plausible explanation. It should be noted, however, that the number of studies included in the analyses for fish is relatively low: for whole fish there are four studies with 22 data points over five different concentrations between 24.98 and 79 µg Ba/L. For muscle there are also four studies, with 23 data points over 10 concentrations between 5 and 79 µg Ba/L.

4.8 Summary of the findings and choice of the BAF

Table 4 shows the summary statistics of the bioaccumulation data per taxon. Differences between the BAFs per taxon were analysed using a Tukey multiple comparison test (α = 0.05).

Table 4. Summary statistics of bioaccumulation data for barium per taxon. BAFs expressed as log-transformed values.

Taxon	Summary statistics of log BAF [L/kg_{wwt}]						
	#	Min	Max	Median	Mean	95% CI of mean	
fish whole	22	0.741	2.71	1.86	1.77	1.56	1.99
fish muscle	36	-0.509	2.44	0.693	0.740	0.447	1.03
amphibians	2	0.903	1.38	1.14	1.14	-1.89	4.17
molluscs	3	2.37	3.67	2.46	2.83	1.03	4.63
crustaceans	20	1.79	3.91	3.14	3.13	2.88	3.38
insects	8	1.20	2.14	1.69	1.64	1.36	1.93
zooplankton	1	1.56	1.56	1.56	1.56		
phytoplankton	2	1.70	2.24	1.97	1.97	-1.47	5.41
plankton	3	1.54	1.84	1.59	1.66	1.26	2.06
plants	65	2.34	3.75	3.04	3.03	2.96	3.10

The following conclusions and observations are made:

- BAF in whole fish are significantly higher than in fish muscle.
- BAF in whole fish is more relevant for secondary poisoning than BAFs for fish muscle. For humans, whole fish is relevant in case of small fish (anchovy, sardines). However, in most cases, humans consume filet from larger fish and thus fish muscle is more relevant than whole fish for the endpoint human fish consumption.
- BAF in whole fish are significantly lower than in crustaceans and aquatic plants.
- There are only three values for molluscs, these are in the range of the crustacean data.
- Crustaceans are relevant for human fish consumption; aquatic plants are relevant for secondary poisoning in particular.
- The only significant and biologically meaningful relationship between external and internal concentration was found for aquatic plants. This means that only for plants a biota standard can be recalculated to an equivalent water concentration.
- For the other taxonomic groups a comparison will be made of reported concentrations in biota with the biota standard.
- No differences between freshwater and saltwater data were observed for groups of species (fish, crustaceans, aquatic plants). Bioaccumulation data can thus be used for both the freshwater and saltwater environment.

5 Ecotoxicity of barium to aquatic organisms

5.1 Considerations on reliability assessment

A total of 39 studies from the open literature and three REACH dossier summaries were evaluated. Detailed information is tabulated in Appendix 3. Most of the open literature studies were performed decades ago and many of these do not meet recent guidelines and/or current standards for experimentation and reporting. A major deficiency in most studies is the lack of adequate chemical analysis. In the majority of cases no analytical measurement was carried out at all, while in some studies only total barium concentrations in unfiltered water were determined. For chemicals in general and metals in particular, the dissolved fraction is considered as the relevant entity for ecotoxicological assessment. For barium, the determination of the dissolved fraction is of major importance, considering that soluble barium compounds, such as barium chloride or barium nitrate, can quickly precipitate in the presence of sulfate and carbonate. In Section 4.2 it was argued that for the field bioaccumulation studies, it is expected that large precipitates are sedimented and are not present in the water column anymore. This may be different for ecotoxicity studies, which are performed immediately after preparing the test solutions. Precipitation was reported for a number of studies, and because of the relatively small volume of most test systems, precipitates may have been present in samples that were analysed for barium without filtration.

The presence of sulfate is indicated by some authors as a major factor modifying barium availability and toxicity. In Section 4.2, the study of Wang (1986a) was mentioned, who tested the response of duckweed to barium chloride in plant nutrient medium prepared in deionised water, filtered and unfiltered river water, respectively. River water had a suspended solids concentration of 100 mg/L. Toxicity in deionised water medium was highest, whereas the difference between filtered and unfiltered river water was small. From these experiments, it was concluded that other characteristics than particulate matter play a role, and the presence of sulfate in the river water was stated to be the determining factor. Further experiments with a series of natural waters indicated that differences in sulfate concentrations may indeed explain differences in barium toxicity (Wang, 1988). The reported data show a tendency of decreasing toxicity with increasing hardness, but because hardness and sulfate are correlated, this may in reality be an effect of sulfate. There is no clear correlation with pH, but the pH-range in the study was rather narrow (6.32-8.34).

In a recent study, Golding et al. (2018) showed that removal of sulfate from standard ecotoxicity media increases the proportion of dissolved barium. In standard OECD algal medium with nominal barium chloride concentrations of 0.1 to 100 mg Ba/L, measured dissolved barium concentrations were 0.3 to 52% of total barium. Replacing sulfate in the medium by chloride resulted in >96% solubility over the range of 0.1 to 10000 mg Ba/L, despite the presence of carbonate in the medium. As expected, the toxicity to *Ceriodaphnia dubia* could be explained best by dissolved concentrations. However, the response of the alga *Chlorella* sp. in the presence of sulfate could not be explained by the dissolved fraction. For this species, clear concentration-response relationships were obtained when exposure was expressed as total barium[7] concentrations. Toxicity was higher in the presence of sulfate. The authors suggest that precipitated barium sulfate contributes to the toxicity, by shading, physical smothering or interference with nutrients. Referring to the above mentioned study by Wang (1988), Golding et al. (2018) note that their observations on algae are not in line with other studies with plants in which a detoxifying effect of sulfate was seen. Because the physical or indirect effects may be related to the specific conditions of the test system, the total-based values for *Chlorella* sp. are not further used.

In a test with embryos of the marine California mussel (*Mytilus californianus*), Spangenberg & Cherr (1996) observed abnormal morphology and apparent developmental delay after 48-hours exposure to barium acetate at concentrations between 0.2 and 0.8 mg Ba/L. Corresponding measured barium concentrations in filtered samples after 48 h ranged from 0.23 mg/L at 0.2 mg Ba/L (107% of nominal) to 0.46 mg/L at 0.8 mg Ba/L (64% of nominal). At nominal levels of 1 mg Ba/L and higher, measured soluble barium concentrations were similar to background levels and no significant effects on larval development were observed.

The information above clearly indicates that the interpretation of aquatic ecotoxicity studies with barium is rather complex. Therefore, for the present report, only studies with analytical measurements are accepted. Preference is given to study results expressed on the basis of dissolved concentrations, *i.e.* in filtered water. However, if for a species the lowest result is based on concentrations in unfiltered water, or if these are the only results available for this species, they may be used provided that the conditions in the ecotoxicity study are relevant for the Dutch situation (see Section 5.3).

5.2 Overview of accepted ecotoxicity tests

Table 5 shows the test results for freshwater species based on measured, dissolved concentrations. The only reliable marine study is the above mentioned study with Californian mussels by Spangenberg & Cherr (1996), who report a NOEC of 0.1 mg/L dissolved barium for embryonic development (Table 6). The authors showed that effects of barium occur between 16 and 32 hours post-fertilisation. Exposure before or after this period did not result in abnormal development.

[7] Note that 'total' in this context means the total added concentration in unfiltered water, the medium did not contain barium as background.

Table 5. Summary of accepted ecotoxicity tests for barium with freshwater organisms.

	Hardness [mg $CaCO_3$/L]	**Sulfate [mg/L]**	**Criterion**	**Value [mg/L]**	**Remark**
Acute					
Algae					
Chlorella sp. 12	80-90	0	EC_{50}	240	dissolved
Pseudokirchneriella subcapitata	110	98.7	EC_{50}	>1.2	dissolved; 1.1% inhibition of growth rate
Crustacea					
Ceriodaphnia dubia	80-90	0	EC_{50}	17	dissolved
Daphnia magna	250	48.1	EC_{50}	11	unfiltered; no other data available
Hyalella azteca	18	3.4	LC_{50}	>1.1	dissolved; 93% survival
Pisces					
Danio rerio	171-179	24	LC_{50}	>3.5	dissolved; no mortality
Macrophyta					
Lemna minor	54-78	2.8	EC_{50}	95	unfiltered; lowest value in natural water with relevant hardness and sulfate, low turbidity[8]
Chronic					
Algae					
Chlorella sp. 12	80-90	0	EC_{10}	40	dissolved
Pseudokirchneriella subcapitata	110	98.7	EC_{10}	>1.2	dissolved; 1.1% inhibition of growth rate
Crustaceans					
Ceriodaphnia dubia	40	7.7	EC_{10}	8.3	unfiltered; no other data available
Pisces					
Danio rerio	164-182	24	NOEC	≥1.26	dissolved
Macrophyta					
Lemna minor			EC_{10}	6.2	unfiltered; no information on test medium

Table 6. Summary of accepted ecotoxicity tests for barium with marine organisms.

	Salinity [‰]	**Sulfate [mg/L]**	**Criterion**	**Value [mg/L]**	**Remark**
Chronic					
Mollusca					
Mytlius californianus	33		NOEC	0.1	filtered; development

[8] measured barium was 95% of nominal, therefore background concentrations are considered to be negligible

5.3 Relevant sulfate and hardness conditions for the Netherlands

Monitoring data on sulfate and hardness in fresh surface waters were retrieved from Rijkswaterstaat. For 2016, data were available for 36 locations, daily measurements for locations Lobith and Eijsden and monthly measurements for the other locations. Geometric mean sulfate concentrations in 2016 ranged from 33 mg SO_4^{2-}/L in the Twentekanaal to 131 mg SO_4^{2-}/L in Lake Veluwe. The overall mean concentration was 61 mg/L, the 5th percentile 40 mg/L. For hardness, data from 34 locations were available, with geometric mean values between 134 and 276 mg $CaCO_3$/L, an overall mean of 209 mg $CaCO_3$/L and a 5th percentile of 175 mg $CaCO_3$/L. Considering that low sulfate levels and low hardness represent critical conditions with respect to barium availability, the 5th percentile values are chosen to judge whether or not the conditions in the ecotoxicity studies are relevant for the Dutch situation. In summary, ecotoxicity tests performed in media with hardness around 175 mg/L or lower and sulfate around 40 mg/L or lower are considered relevant.

6 Derivation of water quality standards

6.1 Derivation of the $QS_{water,\ hh\ food}$

Figure 8 shows the wet weight based concentrations in biota from the field studies discussed in Chapter 3 for those species / taxa that are considered relevant for human consumption (fish, molluscs and crustaceans). The data are the same as in Figure 4. For crustaceans all data are included, assuming that almost all these species are suitable for human consumption (prawns, shrimps, crabs, crayfish and lobster). As can be seen from this graph, the $QS_{biota,\ hh\ food}$ of 24.5 mg/kg is not reached in fish and the geometric means of the concentrations found in molluscs and crustaceans are just at the critical level for humans. For all these groups no significant increase of the concentrations was observed with increasing exposure concentrations (see Section 4.4). Considering the fact that the default value for fish consumption represents a worst case for the Netherlands, and taking into account that the average diet will not consist of molluscs or crustaceans only, it is concluded that barium exposure via fish or seafood will most likely not lead to risks for humans. Therefore, derivation of the $QS_{water,\ hh\ food}$ is not considered relevant.

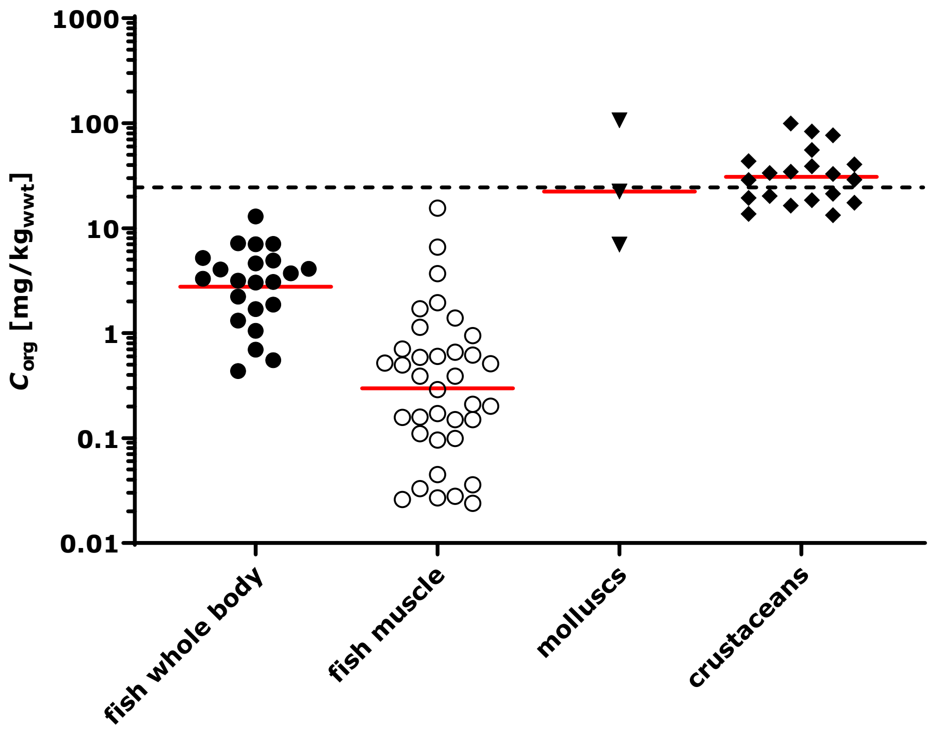

Figure 8. Concentrations of barium in biota relevant for human consumption based on the field studies summarised in Section 3. Concentrations are given in mg Ba/kg$_{wwt}$. Red lines represent the geometric mean per taxon. The dotted line is the $QS_{biota,\ hh\ food}$ of 24.5 mg Ba/kg$_{food}$ (see 3.5).

6.2 Derivation of the $QS_{water, secpois}$

A similar assessment as done above for the quality standard for the endpoint human health can be made for the endpoint secondary poisoning. Figure 9 shows the wet weight based concentrations in biota from the field studies and the dotted lines represent the $QS_{biota, secpois}$ for derived in Section 3.7. For fish, the same situation is observed as for the endpoint human fish consumption. The concentrations in fish from the monitoring studies are below the $QS_{biota, secpois}$ for fish of 16 mg Ba/kg_{wwt} (upper dashed line in Figure 9). However, for the aquatic arthropods (crustaceans and insects), aquatic plants and bivalves most data are above the $QS_{biota, secpois}$ for these taxonomic groups (14, 8.0 and 4.6 mg Ba/kg_{wwt}, respectively; second, third and fourth line in Figure 9).

Only for aquatic plants a significant positive relationship could be established between concentrations in the organism and concentrations in water (see Section 4.4). As the BAF values for plants do not depend on the water concentrations, a geometric mean of all BAF data for aquatic plants can be used. This value is 1068 L/kg_{wwt}. With the $QS_{biota, secpois}$ of 8.0 mg/kg_{wwt} for aquatic vegetation, the $QS_{fw, secpois}$ becomes 8.6 µg/L. This value is well below background concentrations (Section 2.2).

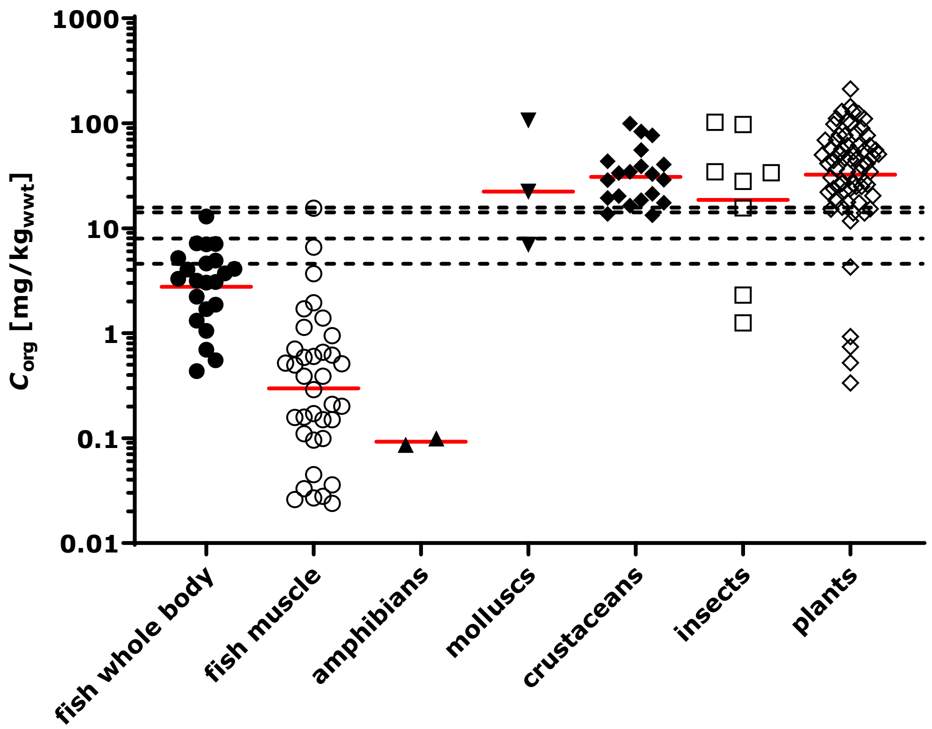

Figure 9. Barium concentrations in biota of monitoring data relevant for secondary poisoning based on the field studies summarised in section 3. Concentrations are given in mg Ba/kg_{wwt}. Red lines represent the geometric mean per taxon. The dotted lines represent the increasing $QS_{biota, secpois}$ of 4.6, 8.0, 14 and 16 mg/kg_{wwt} for bivalves, aquatic vegetation, freshwater arthropods and fish, respectively (see Section 3.7).

It can thus be concluded that both the biota standards for aquatic arthropods, bivalves and aquatic vegetation, as well as the equivalent water concentration for aquatic vegetation are not useful as quality standard.

The question arises whether barium administered in the toxicity studies is more toxic than barium in food from the field. Several studies mention that barium sulfate and other poorly soluble forms of barium are not available for uptake and that most of the barium in nature is in similar unavailable forms. However, the validity of this statement is arguable, mostly because these statements are not backed up by references to experimental verification. Moreover, in the studies that are available it seems that there is little difference in the uptake of different forms of barium (see Section 3.3). From these studies, it can be concluded that the form in which barium is added to the food does most likely not influence the uptake of barium very strongly. Therefore, an assumed high availability of barium in the toxicity studies is most likely not a good explanation for the observed exceedance of the quality standard by biota samples. This can be further underpinned by theoretical considerations of the influence of gastrointestinal fluids on the solubility of barium in the gastrointestinal tract. From that perspective, it seems plausible that also well soluble barium salts become less available in the gastrointestinal tract.

Instead of differences in availability between laboratory and field, a more plausible explanation is that the margin between toxicity and background concentrations is very small for barium. The application of an assessment factor of only 10 is enough to extrapolate NOEC concentrations that are at the upper end of the monitored biota concentrations, to levels for the quality standards that are below these observed biota concentrations. Moreover, the absence of a significant relationship between barium concentrations in biota and water for most taxonomic groups makes the derivation of quality standard for water even more complicated. However, because such a relationship does exist for aquatic vegetation and some birds and mammals do consume mainly aquatic vegetation, the assessment of the water concentration for these species is still meaningful. The species with the lowest effect concentration is the mouse with an EC_{10} of 0.036 mg/kJ. With the energy content of aquatic vegetation this corresponds to 99 mg/kg_{wwt}. With a geometric mean BAF of 1068 L/ kg_{wwt}, the EC_{10} leads to a water concentration 93 µg/L. It seems reasonable to state that a quality standard for water should not be higher than this value.

6.3 Derivation of the QS_{eco} for direct ecotoxicity

6.3.1 Derivation of the MAC-EQS$_{eco}$

Acute toxicity data are available for the base set (algae, *Daphnia*, fish), but part of these are censored data. The lowest uncensored value is the EC_{50} of 11 mg/L for *Daphnia magna*, based on measured barium concentrations in unfiltered test medium. Hardness and sulfate in this study were both higher than the relevant conditions for the Netherlands, which may indicate that toxicity is underestimated. Based on the sulfate concentration of 48.1 mg/L, precipitation of barium sulfate is expected to occur at the level of the EC_{50}. On the other hand, a slightly higher

EC_{50} of 17 mg/L dissolved barium was obtained for the related species *Ceriodaphnia dubia* under more critical conditions in the absence of sulfate. Application of an assessment factor of 10 on the lowest uncensored toxicity value of 11 mg/L is therefore considered justified, and a $MAC\text{-}EQS_{fw,\ eco}$ of 1.1 mg/L is proposed. This value is protective for the crustacean *Hyalella azteca* for which an LC_{50} of >1.1 mg/L was obtained, because <10% effect was observed at this concentration.

The current $MAC\text{-}EQS_{fw,\ eco}$ is 148 µg/L, expressed as maximum acceptable addition of dissolved barium. This value is based on a 240 h LC_{50} of 14.8 mg/L[9] for the flatworm *Dugesia tigrina* with an assessment factor of 100 because the BAF for barium was higher than 100 L/kg. This study is no longer considered valid in the present evaluation, and a lower acute EC_{50} is used instead. Because bioaccumulation is no longer considered in the current WFD assessment factor scheme, the proposed $MAC\text{-}EQS_{fw,\ eco}$ value is higher.

Because only one test with marine species is available, derivation of the $MAC\text{-}EQS_{sw,\ eco}$ is not possible.

6.3.2 *Derivation of the chronic QS_{eco}*

Chronic toxicity values are available for algae, invertebrates and fish. The lowest uncensored EC_{10} is 6.2 mg/L for growth of *Lemna minor* in a 96-hour test. The EC_{10} is based on total (not filtered) concentrations and the composition of the medium is not known. The next higher value is the EC_{10} of 8.3 mg/L for *Ceriodaphnia dubia* in a 7-day test. This value is also based on concentrations in unfiltered water, but hardness and sulfate are low and represent critical conditions compared to the Dutch situation. In view of the data, an assessment factor of 10 on the lowest value is considered protective. Therefore, a $QS_{fw,\ eco}$ of 620 µg/L is proposed.

Van Vlaardingen & Verbruggen (2009) derived a $QS_{fw,\ eco}$ of 29 µg/L, expressed as added concentration of dissolved barium. This value is based on a 21-day NOEC of 2.9 mg/L for *Daphnia magna*. An assessment factor of 100 was used, because the taxon with the then lowest LC_{50} (flatworms, see above) was not represented in the chronic dataset. In the current data set, this does no longer apply, since species with lower $L(E)C_{50}$ values than the 14.5 mg/L for the flatworm *D. tigrina* are now present (both crustacean species) and these species are also represented in the chronic data set. Following the rules applicable at that time, the NOEC of 2.9 mg/L was calculated as $EC_{16}/2$, but the EC_{10} can be calculated based on the reported effect concentrations and is 5.3 mg/L (see Appendix 3).

This chronic *Daphnia* study is now disregarded due to the absence of analytical measurements and other deficiencies, but the EC_{10}-value of the currently accepted chronic study with a crustacean is in the same range. However, in the current QS derivation, a lower assessment factor can be applied, resulting in a higher $QS_{fw,\ eco}$.

[9] In the main text of the reports, a rounded value of 15 mg/L is given (Van Vlaardingen et al., 2005; Van Vlaardingen & Verbruggen, 2009)

Because only one test with marine species is available, derivation of $QS_{sw,\ eco}$ is not possible. The data suggest that early life stages of marine mussels may be sensitive to barium. As indicated in Section 2.3, the highest measured dissolved concentrations at saltwater monitoring stations in the Netherlands are around 50 µg/L, which is below the NOEC for mussels.

6.3.3 *Expression of the MAC-EQS$_{fw,\ eco}$ and QS$_{fw,\ eco}$*

As indicated in the introduction (see Section 1.2.5), previous assessments used the 'added risk-approach' for derivation of the MAC-and $QS_{fw,\ eco}$. In the updated WFD-guidance, background concentrations are not included as part of the EQS-derivation. Since the proposed MAC-$EQS_{fw,\ eco}$ and $QS_{fw,\ eco}$ of 1.1 mg/L and 620 µg/L are far above the levels encountered in Dutch surface waters (see Figure 1), they should be used as including the background concentrations and be compared with measured total dissolved barium concentrations.

7 Discussion and conclusions

Both the environmental behaviour and the internal distribution of barium in organisms are complex. Major factors are the concentrations of sulfate and to a lesser extent carbonate. The low fraction of dissolved barium can have strong effects on the observed toxicity of barium. Toxicity tests of birds and mammals that are used for derivation of the $QS_{biota,\ secpois}$ mostly use well soluble forms of barium and often administered in the drinking water instead of food, because this route is most relevant for humans. In experiments performed with rats, it was shown that barium in the form of barite or naturally incorporated in Brazilian nuts was taken up in similar levels as barium chloride. This indicates that the availability of barium for birds and mammals is rather independent of form in which barium is administered. It is still possible that uptake from food is less efficient at higher concentrations of barium, and maybe in presence of larger crystalline forms of barite and other poorly soluble forms of barium.

The QS values for the routes secondary poisoning and human fish consumption, translated to water, have their basis in field bioaccumulation data for which the availability in water is not particularly high. The BAF values obtained from field studies are determined at low concentrations in the presence of natural amounts of sulfate and carbonate. Despite filtration, it is likely that a considerable fraction of the lower barium concentrations in water samples still represents finely dispersed barite. This may be the reason that for many of the taxonomic groups no relationship between internal and external barium concentrations was observed. Whether or not regulation of internal barium concentrations by organisms themselves also plays a role is not clear from the data, although this is plausible as well. The only meaningful correlation was found between the concentration in aquatic plants and the surrounding water.

Because of the absence of meaningful relationships between the water concentration and the concentration in biota, only the $QS_{biota,\ secpois}$ for plant eating animals can be recalculated to water concentrations. For the other food items (fish, molluscs, crustaceans, insects) a qualitative assessment was made by comparing the biota standards with ambient biota concentrations found in field studies from around the world.

Fish, larger crustaceans and molluscs are considered as relevant food sources for humans. Of these, fish is considered most important, and all concentrations in field caught fish are below the biota based human toxicological risk limit ($QS_{biota,\ hh\ food}$). For larger crustaceans and molluscs concentrations are at the level of the TDI, but these food sources are not considered to fill 100% of the total consumption of fishery products. Thus, for the endpoint human fish consumption it can be concluded that the toxicological endpoints are above levels observed in the field studies. For secondary poisoning, the opposite is observed. Only for fish the concentrations observed in the field study are below the derived biota based risk limit for secondary poisoning ($QS_{biota,\ secpois}$). For invertebrates and aquatic plants however, barium concentrations are higher and most of them exceed the $QS_{biota,\ secpois}$ derived for these groups individually. A correlation exists between water concentrations and the concentration in aquatic plants. For this group a translation of the $QS_{biota,\ secpois}$ to water could be made, which resulted in a $QS_{fw,\ secpois}$ of 7.5 µg/L, based on the EC_{10} for chickens and an assessment factor of 100. Ambient concentrations in the Netherlands exceed this value on a large scale.

In a regular EQS derivation, an assessment factor of 10 is applied to extrapolate from the most sensitive bird or mammal species in the toxicity tests, to all birds and mammals in the whole ecosystem. Additional assessment factors are applied to account for the limited test duration, as would be done for the test with chickens in this case. Application of these assessment factors leads to biota concentrations that are below ambient background concentrations as observed in the bioaccumulation studies for invertebrates and aquatic plants. Contrary to that, all NOECs for chickens, mice and rats are above these levels in biota. The default assessment factors are too high for extrapolation and not applicable in this case, because the margin between toxicity and background concentrations is very small for barium. Using the lowest EC_{10} for mice without an assessment factor, and the BAF for aquatic plants, an equivalent concentration of 93 µg/L in surface water is calculated (expressed as dissolved concentration). Because biomagnification is not expected, this value is also valid for marine waters. It is proposed to use this value as the overall AA-EQS for fresh and marine waters. This value is slightly above the range of monitoring values in the Netherlands.

Many of the ecotoxicity studies with barium are performed in test media with relatively low sulfate concentrations, representing conditions with a relatively high availability compared to field samples. Still, barium might be present as fine dispersion of barite, while in other experiments precipitates were observed. Moreover, a direct relationship between dissolved barium concentrations and toxicity is sometimes missing in the ecotoxicity studies. Despite the potentially high bioavailability in the laboratory studies, the derived values for the $MAC\text{-}EQS_{fw,\ eco}$ of 1.1 mg/L and the $QS_{fw,\ eco}$ of 620 µg/L are far above the dissolved concentrations observed in Dutch surface waters and much higher than the proposed AA-EQS based on secondary poisoning.

8 References

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Appendix 1. Summary of field monitoring studies

Bioaccumulation data on barium were obtained from field monitoring studies and field studies with caged organisms. The available studies are summarised below, an overview of the BAFs is given in Appendix 2. Starting point for selection of BAFs was the availability of measured barium concentrations in matching pairs of organisms and water samples from the same site and representative time interval. If for a particular location multiple samples of the same species were reported, the geometric mean BAF was calculated and taken forward. BAFs are expressed on a wet weight basis. If concentrations in organisms were given in dry weight, these were converted using the reported moisture content if available, otherwise default moisture contents from Smit (2005) were used.

1. Argentina
Avigliano et al. (2015) determined concentrations of over 25 elements in water and muscle of silverside (*Odontesthes bonariensis*) sampled in August 2011 at four commercial fishing sites at the Argentinian east-coast. The Adela Lagoon and the Barrancas Lagoon are freshwater sites with salinities of <1‰, the de la Plata River is an estuary with salinity ranging from 0.04 to 27‰, and the Chasicó Lake is an inland saltwater lake with salinity above 27‰. Dissolved barium concentrations in water were 67.6, 58.2, 51.4 and 118 µg Ba/L for Adela, Barrancas, de la Plata and Chasicó, respectively. As water samples were acidified before filtration, these concentrations may include total barium. Corresponding average concentrations in fish muscle were 0.62, 0.52, 0.51 and 0.15 mg/kg_{wwt} (*n*=3-5), respectively, leading to wet weight based BAFs of 9.2, 8.9, 9.9 and 1.3 L/kg.

2. Brazil, Pará River estuary
Vilhena et al. (2016) sampled water and pearl oysters (*Paxyodon ponderosus*) and phytoplankton (diatoms and algae; *Aulacoseira granulata*, *Coscinodiscus rothii*, *Polymyxus coronalis*, *Coscinodiscus* sp.) near Barcarena County, a mid-sized urban center with aluminum ore processing industries and a cargo terminal. Water and biota were analysed for 17 elements. The water is freshwater most of the year, but slightly brackish between August and November. Sampling was done in January, April, August and November. Concentrations of dissolved barium in the river water were 22.6 and 23.4 µg Ba/L in the rainy and dry season, respectively, BAFs were based on the average concentration of 23.0 µg Ba/L. The authors report average BAFs of 56022 L/kg_{dwt} for oysters (*n*=33; sampled at 2 locations) and 4348 L/kg_{dwt} for phytoplankton (average of 4 locations). Using default moisture contents of 91.7% for molluscs and 96% for plankton (Smit, 2005), the corresponding wet weight based BAFs are 4641 and 174 L/kg_{wwt}.

3. Cameroon, Lake Yaounde
Léopold et al. (2015) determined concentrations of 16 elements in muscle and gills of three fish species, nile tilapia (*Oreochromis niloticus*), mango tilapia (*Sarotherodon galilaeus*), and catfish (*Clarias* sp.) from the Yaounde Municipal Lake, Cameroon. Fish were sampled in April

2007, dissolved concentrations of barium in water are reported by Kwon et al. (2012), for August 2006 and August 2007 these ranged from 34 to 90 µg/L and 30 to 106 µg/L, respectively, with average values of 53 and 58 µg/L. The average concentration is reported as 57 µg Ba/L by Léopold et al. (2015). Using this concentration and the reported barium concentrations in fish, BAFs for muscle tissue were calculated as 12.8-897 L/kg_{wwt} for nile tilapia (n=8), 10.7-689 L/kg_{wwt} for mango tilapia (n=6) and 89.8-897 L/kg_{wwt} for catfish (n=4). No relationship was present between fish weight and BAFs. Geometric mean BAFs are 116, 66 and 272 L/kg_{wwt} for nile tilapia, mango tilapia and catfish, respectively. It has to be noted that individual fish samples varied widely within each species.

4. Canada, Ontario, 12 lakes
Shuhaimi-Othmani et al. (2006) analysed water and amphipods (*Hyalella azteca*) from 12 lakes between Sudbury and North Bay in Ontario, Canada. Four lakes were within 12 km of the Sudbury area where copper smelters are located, 4 lakes were at an intermediate distance of 32–52 km and 4 reference lakes were 94–154 km from the smelters. Three pooled samples of 10 animals per lake were analysed for 10 metals, except for Lake Raft, where only 2 animals were found and treated as a single sample. Barium concentrations in the lakes ranged from 6.73 to 20.3 µg Ba/L, most likely measured as total concentrations. Concentrations in pooled samples of *H. azteca* ranged from 50.3 to 375.9 mg/kg_{dwt}. Based on the reported average moisture content of 73.7%, wet weight based BAFs of 657 to 8033 L/kg_{wwt} are calculated. Linear regression with GraphPad Prism (GraphPad Software Inc., 2017) indicates that the relationship between concentration and BAF is not significant.

5. Canada, Lake Diefenbaker
Donald (2017) investigated barium dynamics in the aquatic ecosystem of Lake Diefenbaker, Saskatchewan, Canada. Zooplankton, clams (*Lampsilis radiata*), insects (diving beetles and water boatsmen), crustaceans (crayfish *Oronectes virilis*), nine fish species and fry were sampled. Fish sampling took place between 2008 and 2010, invertebrate sampling is not specified, but most likely during late spring. Individual data on barium concentrations in whole tissue were obtained from the author upon request. Dissolved barium concentration in water was 77.3 µg Ba/L from May to July, this value is used to calculate BAFs for invertebrates because these were collected during that period. The average dissolved concentration from 2000 to 2010 was 79 ± 10.2 µg Ba/L, with little variation throughout the year, this value was used to calculate BAFs for fish that were sampled over multiple years. The highest BAF of 717 L/kg_{wwt} was found for crayfish, BAFs for zooplankton, clams, diving beetles and water boatsmen were 36, 290, 30 and 16 L/kg_{wwt}, respectively. The lowest whole body BAF was found for walleye (*Sander vitreus*), with a geometric mean value of 5.51 L/kg_{wwt} (*n*=38; range 1.0-19.9 L/kg_{wwt}), whole body BAFs for other fish species ranged from 13.3 L/kg_{wwt} for quillback (*Carpoides cyprinus*) to 89 L/kg_{wwt} for silver redhorse (*Moxostoma anisurum*) and sauger (*Sander canadensis*). Additional data for barium concentrations in fish muscle were also supplied by the author. Geometric mean concentrations in muscle ranged from 24.5 ng/g in cisco (*Coregonus*

artedi) to 202 ng/g in quillback. Based on these data, muscle based BAFs ranged from 0.310 to 2.56 L/kg_{wwt}. Concentrations in muscle and corresponding BAFs are much lower than those for whole body. In mammals, barium accumulates in bones (ASTDR, 2007; SCHER, 2012; US EPA, 1998-2005; WHO, 2001) and this was also observed in amphibians (Marques et al. (2011), see study 12). This may also be the case for fish, which would explain the lower concentrations found in muscle as compared to whole body. There was a tendency towards lower whole body barium concentrations with increasing trophic position as determined by stable isotope analysis. Barium concentrations in the top predator walleye were lowest. According to the author, the trophic dilution may be explained by a pelagic to benthic food source gradient feeding behaviour. The observed correlation may be influenced by the large differences in sample size, with 38 samples for walleye and single or duplicate samples for the other species. Fish weight and differences in the proportion of muscle and bone may also be confounding factors. This is further discussed in Section 4.6.

6. Czech Republic/Germany, River Nysa basin
Vazquez et al. (2004) analysed water and apical parts of common water moss (*Fontinalis antipyretica*) from 12 locations in the Nysa river and its tributaries for 24 elements. Barium concentrations in water ranged from 11.0 to 256 µg/L, measured as total concentrations, since water was acidified before analysis. Concentrations in moss were between 74.9 and 593.4 mg/kg_{dwt}, resulting dry weight based BAFs range from 1609 to 17200 L/kg_{dwt}. Using the default moisture content of 81.4% for aquatic vegetation (Smit, 2005), wet weight based BAFs range from 299 to 3199 L/kg_{wwt}. The authors report that there was no correlation between concentrations in water and accumulation by *F. antipyretica*. However, the lack of correlation seems to be influenced by the sampling point with the highest barium concentration of 256 µg/L. This concentration seems to be very high in comparison with the other locations with concentrations of 11 to 39.2 µg Ba/L.

7. Germany, Ore Mountains and Bavaria
Samecka-Cymerman et al. (2002) determined the concentration of 11 metals and three macro nutrients in water and the aquatic mosses that were sampled in 35 streams in the Erzgebirge (Ore Mountains, eastern Germany). The area was intensively used for mining and additionally suffered from industrial emissions of air pollutants. Five reference locations were sampled in the West Bavarian Alps. Samples of water and long-beaked water feathermoss (*Platyhypnidium riparioides*), liverwort (*Scapania* sp.), and common water moss (*Fontinalis antipyretica*) were taken in triplicate. Dissolved barium concentrations in water were between 1 and 45 µg/L in the Bavarian reference streams, and between 19 and 101 µg/L in the Ore Mountains. Concentrations in moss ranged from 4 to 94 mg/kg_{dwt} at the reference locations, and from 75 to 1140 mg/kg_{dwt} in the Ore Mountains. Corresponding dry weight based BAFs were 1667-4000 L/kg dwt (Bavaria) and 1172-30174 L/kg_{dwt} (Ore Mountains). Using the default moisture content of 81.4% for aquatic vegetation (Smit, 2005), wet weight based BAFs range from 310 to 744 L/kg in Bavaria and from 218 to 5612 L/kg_{wwt} in the Ore Mountains. The authors observed significant positive correlations between barium in water and plants. They also performed multiple regressions for

relationships between elements in plants and water, but barium in plants is not included as variable.

8. France, Cantal and Haute Vienne
Le Guernic et al. (2016) studied biomarker response and accumulation of metals in stickleback (*Gasterosteus aculeatus*) after exposure in reference ponds, and ponds contaminated by uranium mining in the Cantal and Haute-Vienne regions. One-year old fish from a breeding culture were exposed in cages in April-May 2013, and muscle, spleen and livers were analysed after 28 days. Only muscle data are presented here. Dissolved barium concentrations in water were measured after 14 and 28 days, the geometric means are used here for further calculations and were 12.32 and 17.52 µg Ba/L for the U-mining ponds and between 6.14 and 22.95 µg Ba/L for the reference ponds. Concentrations in fish muscle were 1.89 and 1.48 mg Ba/kg$_{dwt}$ in the reference ponds and ranged from 2.24 to 5.3 mg Ba/kg$_{dwt}$ in the contaminated ponds. Using a default moisture content of 73.5% for fish (Smit, 2005), wet weight based BAFs between 22.2 and 41.9 L/kg$_{wwt}$ are calculated for five ponds. The highest concentration in fish muscle (5.3 mg/kg$_{dwt}$) was obtained for the reference pond with the lowest barium concentration (6.14 µg/L), resulting in a much higher BAF of 227 L/kg$_{wwt}$ for this pond as compared to the other locations. As for the previous study, it is not clear if the exposure duration of 28 days was sufficient to reach equilibrium.

9. France, Vincou
Gagnaire et al. (2015) studied biomarker response and accumulation of metals in roach (*Rutilus rutilus*) that were exposed in cages for 28 days in a reference pond and a pond receiving discharge from a former uranium mining site. Fish (2 years old) were obtained from a commercial breeder. Dissolved barium concentration in the reference pond was below the limit of detection (LOD 10 µg/L), concentrations in the other pond were 21.7±0.2 µg/L on day 14, and 18.4±0.2 µg/L on day 28 (±SD; *n*=3). Barium concentrations in muscle were not detectable after 14 days (LOD not given), and were 0.6 and 6.5 mg/kg dwt after 28 days for the reference and contaminated pond, respectively. Using 5 µg/L (LOD/2) as barium concentration in water for the reference pond and a default moisture content for fish of 73.5% (Smit, 2005), 28-days BAFs of 32 and 93 L/kg$_{wwt}$ are calculated for the reference and mining pond, respectively. Considering that concentrations in fish muscle increased between 14 and 28 days, it is questionable if the exposure duration has been long enough to reach equilibrium.

10. Greece, Thessaloniki Gulf
Malea & Kevrekidis (2013) and Malea et al. (2015) studied the seasonal fluctuations in concentrations of 12 trace elements in seagrass (*Cymodocea nodosa*), sea lettuce (*Ulva intestinalis*, *Ulva rigida*), green sea fingers (*Codium fragile*) and seaweed (*Gracilaria gracilis*) at a sampling station in eastern part of the Gulf of Thessaloniki, Greece. In both studies, monthly samples were taken. Malea & Kevrekidis (2013) report annual mean BAFs for seagrass leave compartments of 6394 to 6408 L/kg$_{dwt}$, BAFs calculated from the reported mean concentrations in Malea et al. (2015) are 5286, 4893, 6645 and 3647 L/kg$_{dwt}$ for *U. intestinalis*, *U. rigida*, *C. fragile* and *G. gracilis*, respectively. Using the

default moisture content of 81.4% for aquatic vegetation (Smit, 2005), wet weight based BAFs range from 678 to 1236 L/kg$_{wwt}$.

11. Western Poland, Zielona Gora
Samecka-Cymerman & Kempers (2001) studied accumulation of 13 metals and three macro nutrients in several plant species from nine anthropogenic lakes near Zielona Gora, West Poland. These lakes are the result of open cut mining of brown coal which took place until 1974. Two reference lakes were included in the study as well. Lake water, sediment and plants were sampled in triplicate during the full growing season in July (year not specified). The reference lakes and three anthropogenic lakes had more or less neutral pH, the others were acidic (pH 2.9-3.5). Dissolved barium concentrations in the reference lakes A and B were 28 and 37 µg/L, the other lakes had dissolved barium concentrations between 35 (lake 6) and 59 µg/L (lake 7). In reference lake A, leaves of common reed (*Phragmites australis*) and water lily (*Nymphaea alba*) contained 17 and 1.8 mg Ba/kg dwt. In reference lake B, lakeshore bulrush (*Schoenoplectus lacustris*), lesser bulrush (*Typha angustifolia*) and water pepper (*Polygonum hydropiper*) were sampled, leaves contained 4.3, 4.6 and 46 mg Ba/kg$_{dwt}$, respectively. Resulting dry weight based BAFs ranged from 48.6 to 1643 L/kg. In the other lakes, dry weight based BAFs per species were as follows: 93.3 L/kg for bushgrass (*Calamagrostis epigeios*), 1371 and 1667 L/kg for remote sedge (*Carex remota*), 24.5 L/kg for Kneiff's Hook- moss (*Drepanocladus aduncus*), 34.9 L/kg for yellow iris (*Iris pseudoacorus*), 24.4-214 L/kg for bulbous rush (*Juncus bulbosus*), 32.4-124 L/kg for common rush (*Juncus effusus*), 47.5 and 371 L/kg for reed canary grass (*Phalaris arundinacea*), 69.5-595 L/kg for common reed (*Phragmites australis*) and 65.1 L/kg for broad-leaved pondweed (*Potamogeton natans*). Using a default moisture content of 81.4% for aquatic vegetation (Smit, 2005), corresponding wet weight based BAFs range from 4.54 to 310 L/kg. However, except for water lily, Kneiff's Hook-moss and broad-leaved pondweed, the sampled plants are not true water plants but rather wetland species located on lakeshores, which makes the relevance of a BAF questionable. Moreover, the default moisture content for aquatic vegetation may not be applicable, therefore, only the true water living species are taken into account. There does not seem to be a relationship between pH and BAF. The authors investigated the correlations between metals in plants, water and sediment, but barium concentrations in plants were not significantly correlated with levels of other elements in water or sediment. The BAF values from this study are much lower than the other values for plants and are identified as outliers in the set of 68 BAF values for plants. Therefore, they are discarded for further analyses.

12. Portugal, Mangualde
Marques et al. (2011) studied accumulation of 20 metals and biomarker response in Iberian green frogs (*Pelophylax perezi*, formerly *Rana perezi*). Animals were captured in a pond at a deactivated uranium mining site and at a reference location, the Vouga river, near Mangualde, central Portugal, and metals were analysed in liver, kidney, bones, muscle and skin. Total concentrations of barium in water were 4.09 µg/L for the reference river and 10.94 µg/L for the mining site pond. Corresponding concentrations in frog muscle were 0.47 ± 0.12

and 0.41 ± 0.14 mg/kg_{dwt} (± SE; *n*=5), much higher concentrations were found in bones (25.57 and 13.27 mg/kg dwt), liver (12.37 and 14.39 mg/kg_{dwt}) and skin (31.92 and 27.95 mg/kg_{dwt}), concentrations in kidney were not detectable. Based on the reported concentrations, dry weight based BAFs for muscle tissue were calculated as 115 and 37 L/kg for the reference and mining site, respectively. Smit (2005) does not report moisture contents for amphibians, Stocking Brown & Brown (2014) mention a value of 78.9% for 14 fully hydrated species. Using this value, wet weight based BAFs for the two sites amount to 24.2 and 7.91 L/kg.

13. Serbia, West Morava River basin
Đikanović et al. (2016) measured concentrations of 16 metals in fish species from different trophic levels caught in 2012 in the Međuvršje Reservoir in the West Morava River basin, Serbia. Samples of liver, muscle and gills from the following fish species were analysed: common nase (*Chondrostoma nasus*), roach (*Rutilus rutilus*), freshwater bream (*Abramis brama*), barbel (*Barbus barbus*), Prussian carp (*Carassius gibelio*), chub (*Squalius cephalus*), European perch (*Perca fluviatilis*), wels catfish (*Silurus glanis*) and northern pike (*Esox lucius*). Concentrations in gills were highest, followed by liver and muscle; only the latter are considered for this report. The barium concentration in water was 30 µg/L, most likely measured as total concentration. Concentrations in fish muscle ranged from 0.11 mg Ba/kg dwt for northern pike to 1.95 mg Ba/kg_{dwt} for roach, wet weight based BAFs as reported by the author range from 1.12 to 19.7 L/kg_{wwt}. Only few significant correlations between element concentration and fish size were found, and these did not include barium.

14. Turkey, Yeniçağa Lake
Saygı & Yiğit (2012) determined concentrations of 14 metals in water, sediment and plankton from the Yeniçağa Lake in the Western Black Sea region in Turkey. The lake receives nutrient-rich water via domestic wastewater and discharge from a slaughterhouse, and also receives input from artesian wells. Samples were taken monthly from March 2008 to February 2009 at three locations, two in the front of inlet creeks and one at a municipal waste water outlet. Plankton was collected with a 30 µm mesh net, the fraction >0.45 µm was used for analysis. Yearly average dissolved concentrations of barium at the three locations were similar with 86.1, 85.1 and 85.3 µg/L, but there were large fluctuations in monthly values. Concentrations in plankton ranged from not detected in October 2008 and February 2009 to 721 mg/kg_{dwt} in February 2008, the yearly averages were 157, 86.7 and 77.8 mg/kg_{dwt} for the respective sampling locations. The monthly average concentrations per sampling time cannot be used for calculation of BAFs, because they are means of the three different locations. Based on the reported yearly averages per location, dry weight based BAFs were 1813, 1019, and 912 L/kg_{dwt}. A default moisture content for plankton is not available in Smit (2005), but a value of 96.2% is reported in Ikemoto et al. (2008). Using this value, BAFs of 69.3, 38.7 and 34.7 L/kg_{wwt} are calculated for the three sampling locations. In view of the observed high seasonal variation, the use of yearly averages may be considered as less relevant. On the other hand, in most other studies only spot sampling is applied and no information on the variation is available either.

15. USA, San Joaquin Valley
Nakamoto & Hassler (1992) sampled water and bluegill sunfish (*Lepomis macrochirus*) from Merced River and Salt Slough, in San Joaquin Valley, California. Salt Slough receives tile and surface irrigation return flows, Merced River does not receive tile drainage water. Water and fish (ovaries, testes and remaining carcasses) were analysed for 20 trace elements. Barium concentrations in filtered water were 34 and 65 μg/L for Merced River and Salt Slough, respectively, corresponding total concentrations were 43 and 101 μg Ba/L. Barium concentrations in carcass were 12.9 and 11.9 mg/kg$_{dwt}$ for male and female fish from Merced River, and 8.2 and 7.0 mg/kg$_{dwt}$ for males and females from Salt Slough (*n*=4 for males and 6 for females). Weighted means for combined males and females are 12.30 and 7.48 mg/kg$_{dwt}$, respectively. Using the reported concentrations in filtered water and the average moisture content of 75%, weighted mean BAFs for carcasses are calculated as 90.4 and 28.8 L/kg$_{wwt}$ for Merced River and Salt Slough, respectively. Since only the ovaries and tested were removed, the BAFs for carcasses are considered as whole body BAFs in further calculations.

16. USA, Times Beach Disposal Facility
Roper et al. (1996) studied the composition and toxicity of water and sediment from the Times Beach Confined Disposal Facility (CDF) in Buffalo, New York. The site was used until 1976 to dispose material dredged from Buffalo River. They exposed caged zebra mussels (*Dreissena polymorpha*) from a nearby reference site *in-situ* at four locations in the study area, and at the reference site. Mussels were placed in the water at sediment level and in the water column in October 1993, and edible tissue was analysed for PAHs, PCBs and 8 metals on day 0 and after 34 days. Barium concentration in water was 30 μg/L for 16 CDF-locations combined, most likely expressed as total concentration. Baseline concentration in mussels collected on day 0 was 2.40±1.62 mg Ba/kg$_{wwt}$ (*n*=4). The concentration was 1.25 mg Ba/kg$_{wwt}$ after 34 days of exposure at the reference site (*n*=4), and 7.00±1.62 mg Ba/kg$_{wwt}$ at the CDF-site (*n*=26; 4 locations). Using the water concentration of 30 μg/L, this latter value gives a BAF of 233 L/kg$_{wwt}$. Because the concentration of barium in water at the reference site is not presented, a comparison between the sites cannot be made. It is not clear if the exposure duration of 34 days was enough to reach equilibrium.

17. USA, Savannah River Project
Cherry et al. (1976), Cherry et al. (1979) and Guthrie & Cherry (1979) report studies at the Savannah River Project in South California, a drainage system that received high coal ash concentration at one end and thermal discharges at the other end. The data in Cherry et al. (1976) and Guthrie & Cherry (1979) are less usefull, because reported water concentrations are 15 months' means for different sampling stations, while the data in Cherry et al. (1979) indicate that barium concentrations differ between sampling locations. Moreover, some values in Guthrie & Cherry (1979) seem to be taken from Cherry et al. (1979). These authors sampled an ash basin A with 980 μg Ba/L, an ash influenced swamp D (700 μg Ba/L), a site beyond major ash influence E (710 μg Ba/L) and a site without ash discharge F (510 μg Ba/L), concentrations most likely refer to unfiltered water. Damselflies

(*Enallagma* sp.) were collected at site A, crayfish at sites D and E, midges (Chironominae) at site A and E, and dragonflies (*Libellula* sp.) at sites E, D and F. Based on the reported concentrations in the organisms, wet weight based BAFs were 15.9 L/kg_{wwt} for damselflies, 108 and 62.1 L/kg_{wwt} for crayfish, 104 and 137 L/kg_{wwt} for midges and 47.5-54.8 L/kg_{wwt} for dragonflies .

18. USA, James River
Hope et al. (1996) studied uptake and trophic transfer of barium in a terrestrial ecosystem on the banks of the James River near Lynchburg, Virginia. Water, soil, vegetation, soil dwelling insects, small mammals, and sunfish (*Lepomis* sp.) from two onsite ponds were sampled in July 1994. Total and dissolved concentration of barium in water was 70 ± 100 µg/L (± SD; *n*=33), concentration in fish was 2.1±1.1 mg/kg (*n*=13, pooled into 4 samples). The authors mention that based on barium concentrations of 0.07 mg/L in water and 2.1 mg/kg_{wwt} in fish, the BCF is 129 L/kg_{wwt}. It is not clearly specified if concentration in fish are based on wet or dry weight, but because the reported concentrations in fish and water lead to a BAF of 30 L/kg, the concentration in fish seems to refer to wet weight and the reported BAF to dry weight (i.e. moisture content of 77% which is close to the default moisture content of 73.7%).

19. Vietnam, Mekong Delta
Ikemoto et al. (2008) report the concentrations of 21 trace elements in water and in the various biota in the main stream of the Mekong Delta near Can Tho, South Vietnam. Whole samples of phytoplankton, crustaceans (prawns *Metapenaeus tenius* and 5 species of *Macrobrachium*) and nine fish species were analysed, and stable isotopes were analysed. The dissolved barium concentration in water was 24.98 µg/L (geomean of 2 samples). The concentration of barium in phytoplankton was 33 mg/kg_{dwt}, prawn contained 55-130 mg/kg_{dwt} and concentrations in fish ranged from 2.7 mg/kg_{dwt} for rice paddy (*Pisodonophis boro*) to 56 mg/kg_{dwt} in duskyfin glassy perchlet (*Parambassis wolffii*). Wet weight based BAFs were calculated using reported moisture contents and amounted to 50.2 L/kg_{wwt} for phytoplankton, 546-1551 L/kg_{wwt} for prawn and 27.9-518 L/kg_{wwt} for fish. Regressions between barium concentrations and $\delta^{15}N$ values in crustaceans and fish were not significant.

Appendix 2. Bioaccumulation factors derived from field studies

Table A1.2. Summary of barium concentrations in water and tissue and wet weight bioaccumulation factors (BAFs) obtained from field monitoring studies and studies with caged organisms. In case of multiple samples per species, the range of tissue concentrations and geometric mean BAF is presented. BAF values in grey are excluded in final calculations (see text in Appendix 1 and Chapter 4).

Legend to column headings	
WT	water type: fw = freshwater; sw = marine water; bw = brackish water; trans = transitional water
Tax	taxonomic group: pisc = fish; crust = crustacean; moll = mollusc; ins = insects; phyto = phytoplankton; zoo = zooplankton; plank = plankton; plant = plantae
MC	moisture content [%] used for conversion to wet weight based BAF
A	analysis method
Cw	concentration in water [ng/L]; italics indicate unfiltered samples
Corg	concentration in organism [ng/g]
Based on	expression of C_{org}: wwt = wet weight; dwt = dry weight; mu = muscle; wh = whole body/plant; ed = edible; lea = leaf; bl = blades; sh = sheats
log BAF	log bioaccumulation factor based on wet weight [L/kg]
N	notes
Ref	reference

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
ARG, Adela Lagoon	fw	pisc	*Odontesthes bonariensis*		August 2011	IPC-MS	*67.6*	0.62	wwt; mu	0.962	1	Avigliano et al. (2015)
ARG, Barrancas Lagoon	fw	pisc	*Odontesthes bonariensis*		August 2011		*58.2*	0.52	wwt; mu	0.951	2	
ARG, Chasico Lake	sw	pisc	*Odontesthes bonariensis*		August 2011		*118*	0.15	wwt; mu	0.104	3	
ARG, de la Plata River estuary	trans	pisc	*Odontesthes bonariensis*		August 2011		*51.4*	0.51	wwt; mu	0.997	4	
BRA, Pará River estuary, Barcarena city	fw/bw	moll	*Paxyodon ponderosus*	91.7	January, April, August, November	ICP-MS/ OES	23	1286	dwt; wh	3.667	5	Vilhena et al. (2016)

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
BRA, Pará River estuary, Barcarena city	fw/bw	phyto	*Aulacoseira granulata, Coscinodiscus rothii, Polymyxus coronalis, Coscinodiscus sp.*	96			23	100	dwt; wh	2.24	6	
CMR, Lake Yaounde	fw	pisc	*Clarias sp.*		April 2007, water August 2006 and 2007	ICP-AES	57	15.5	wwt; mu	2.435	7	Léopold et al. (2015)
CMR, Lake Yaounde	fw	pisc	*Oreochromis niloticus*		April 2007, water August 2006 and 2007	ICP-AES	57	6.6	wwt; mu	2.063	8	
CMR, Lake Yaounde	fw	pisc	*Sarotherodon galilaeus*		April 2007, water August 2006 and 2007	ICP-AES	57	3.7	wwt; mu	1.817	9	
CND, Ontario, Lake McFarlane	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	20.3	50.3	dwt; wh	2.817	10	Shuhaimi-Othmani et al. (2006)
CND, Ontario, Lake Kakakiwaganda	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	7.3	108.9	dwt; wh	3.597	10	
CND, Ontario, Lake Lower Sturgeon	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	6.73	130.1	dwt; wh	3.71	10	
CND, Ontario, Lake Nepewassi	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	7	76.2	dwt; wh	3.46	10	
CND, Ontario, Lake Nosbonding	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	8.3	73.2	dwt; wh	3.369	10	
CND, Ontario, Lake Raft	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	14.7	153.3	dwt; wh	3.441	11	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
CND, Ontario, Lake Ramsey	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	19.1	62.1	dwt; wh	2.935	12	
CND, Ontario, Lake Restoule	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	16.1	315.5	dwt; wh	3.715	12	
CND, Ontario, Lake Richard	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	14	65.9	dwt; wh	3.096	12	
CND, Ontario, Lake Talon	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	13.1	70	dwt; wh	3.151	12	
CND, Ontario, Lake Tomiko	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	12.4	375.9	dwt; wh	3.905	12	
CND, Ontario, Lake Trout	fw	crust	*Hyalella azteca*	73.5	August 2008	ICP-MS	7.29	126.8	dwt; wh	3.664	12	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Coregonus artedi*		2008-2010	ICPSFMS	79	0.0245	wwt; mu	-0.509	13	Donald (2017)
CND, Saskatchewan, Lake Diefenbaker	fw	moll	*Lampsilis radiata*		May-July	ICPSFMS	77.3	22.4	wwt; wh	2.462	14	
CND, Saskatchewan, Lake Diefenbaker	fw	crust	*Oronectes virilis*		May-July	ICPSFMS	77.3	55.4	wwt; wh	2.853	15	
CND, Saskatchewan, Lake Diefenbaker	fw	ins	*Dytiscidae*		May-July	ICPSFMS	77.3	2.3	wwt; wh	1.474	16	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Notropis atherinoides*		2008-2010	ICPSFMS	79	2.23	wwt; wh	1.452	17	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Hiodon alosoides*		2008-2010	ICPSFMS	79	0.0268	wwt; mu	-0.469	18	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Coregonus clupeaformis*		2008-2010	ICPSFMS	79	0.0449	wwt; mu	-0.245	19	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Catostomus catostomus*		2008-2010	ICPSFMS	79	0.0957	wwt; mu	0.083	20	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Hiodon tergisus*		2008-2010	ICPSFMS	79	0.0255	wwt; mu	-0.490	21	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Hiodon tergisus*		2008-2010	ICPSFMS	79	1.7	wwt; wh	1.333	22	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Esox lucius*		2008-2010, 2012-2014	ICPSFMS	79	0.0356	wwt; mu	-0.346	23	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Carpiodes cyprinus*		2008-2010	ICPSFMS	79	1.1	wwt; wh	1.124	24	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Carpiodes cyprinus*		2008-2010	ICPSFMS	79	0.202209	wwt; mu	0.408	25	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Notropis blennius*		2008-2010	ICPSFMS	79	3.3	wwt; wh	1.621	26	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Sander canadensis*		2008-2010	ICPSFMS	79	0.0285	wwt; mu	-0.443	27	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Sander canadensis*		2008-2010	ICPSFMS	79	7.07	wwt; wh	1.952	28	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Moxostoma macrolepidotum*		2008-2010	ICPSFMS	79	0.159	wwt; mu	0.304	29	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Moxostoma macrolepidotum*		2008-2010	ICPSFMS	79	4	wwt; wh	1.709	30	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Moxostoma anisurum*		2008-2010	ICPSFMS	79	0.172	wwt; mu	0.338	31	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Moxostoma anisurum*		2008-2010	ICPSFMS	79	7	wwt; wh	1.949	32	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc			2008-2010	ICPSFMS	79	7.2	wwt; wh	1.96	33	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Sander vitreus*		2008-2010	ICPSFMS	79	0.0325	wwt; mu	-0.385	34	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Sander vitreus*		2008-2010	ICPSFMS	79	0.435	wwt; wh	0.741	35	
CND, Saskatchewan, Lake Diefenbaker	fw	ins	*Corixidae*		May-July	ICPSFMS	77.3	1.26	wwt; wh	1.206	36	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Catostomus commersoni*		2008-2010	ICPSFMS	79	0.099	wwt; mu	0.098	37	
CND, Saskatchewan, Lake Diefenbaker	fw	pisc	*Catostomus commersonii*		2008-2010	ICPSFMS	79	4.6	wwt; wh	1.766	38	
CND, Saskatchewan, Lake Diefenbaker	fw	zoo			May-July	ICPSFMS	77.3	2.78	wwt; wh	1.556	39	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	11.0	85.2	dwt; lea	3.159	40	Vazquez et al. (2004)
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	11.8	134.2	dwt; lea	3.325	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	14.4	237.7	dwt; lea	3.487	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	14.5	134.2	dwt; lea	3.236	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	15.5	82.4	dwt; lea	2.995	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	30.2	332.7	dwt; lea	3.312	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	34.2	411.3	dwt; lea	3.35	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	34.5	593.4	dwt; lea	3.505	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	39.2	74.9	dwt; lea	2.551	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	54.1	371.4	dwt; lea	3.106	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	56.9	527	dwt; lea	3.236	40	
CZE, River Nysa basin	fw	plant	*Fontinalis antipyretica*	81.4	June 1997	ICP-OES/ ICP-MS	256	411.8	dwt; lea	2.476	40	
DEU, Bavaria	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	3	5	dwt; wh	2.491	41	Samecka-Cymerman et al. (2002)
DEU, Bavaria	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	1	4	dwt; wh	2.872	42	
DEU, Bavaria	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	6	23	dwt; wh	2.853	43	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
DEU, Bavaria	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	24	63	dwt; wh	2.689	44	
DEU, Bavaria	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	45	94	dwt; wh	2.589	45	
DEU, Erzgebirge	fw	plant	*Fontinalis antipyretica*	81.4		ICPES	32	269	dwt; wh	3.194	46	
DEU, Erzgebirge	fw	plant	*Fontinalis antipyretica*	81.4		ICPES	35	772	dwt; wh	3.613	47	
DEU, Erzgebirge	fw	plant	*Fontinalis antipyretica*	81.4		ICPES	58	163	dwt; wh	2.718	48	
DEU, Erzgebirge	fw	plant	*Fontinalis antipyretica*	81.4		ICPES	52	597	dwt; wh	3.329	49	
DEU, Erzgebirge	fw	plant	*Fontinalis antipyretica*	81.4		ICPES	76	578	dwt; wh	3.151	50	
DEU, Erzgebirge	fw	plant	*Fontinalis antipyretica*	81.4		ICPES	73	698	dwt; wh	3.25	51	
DEU, Erzgebirge	fw	plant	*not clear*	81.4		ICPES	63	128	dwt; wh	2.577	52	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	63	243	dwt; wh	2.856	53	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	69	330	dwt; wh	2.949	54	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	63	330	dwt; wh	2.989	55	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	32	273	dwt; wh	3.201	56	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	32	277	dwt; wh	3.207	46	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	35	144	dwt; wh	2.884	47	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	28	128	dwt; wh	2.93	57	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	40	259	dwt; wh	3.081	58	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	38	198	dwt; wh	2.986	59	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	58	480	dwt; wh	3.187	48	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	40	242	dwt; wh	3.051	49	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	36	542	dwt; wh	3.447	60	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	41	310	dwt; wh	3.148	61	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	42	222	dwt; wh	2.993	62	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	41	183	dwt; wh	2.919	63	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	29	95	dwt; wh	2.785	64	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	27	140	dwt; wh	2.984	65	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	19	209	dwt; wh	3.311	66	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	20	250	dwt; wh	3.366	67	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	23	694	dwt; wh	3.749	68	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	51	299	dwt; wh	3.038	69	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	35	187	dwt; wh	2.997	70	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	38	223	dwt; wh	3.038	71	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	52	429	dwt; wh	3.186	72	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	101	1140	dwt; wh	3.322	73	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	54	186	dwt; wh	2.807	74	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	60	374	dwt; wh	3.064	75	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	73	662	dwt; wh	3.227	51	
DEU, Erzgebirge	fw	plant	*Platyhypnidium riparioides*	81.4		ICPES	76	299	dwt; wh	2.864	52	
DEU, Erzgebirge	fw	plant	*Scapania sp.*	81.4		ICPES	63	138	dwt; wh	2.61	53	
DEU, Erzgebirge	fw	plant	*Scapania sp.*	81.4		ICPES	61	122	dwt; wh	2.571	54	
DEU, Erzgebirge	fw	plant	*Scapania sp.*	81.4		ICPES	41	305	dwt; wh	3.141	55	
DEU, Erzgebirge	fw	plant	*Scapania sp.*	81.4		ICPES	35	286	dwt; wh	3.182	70	
DEU, Erzgebirge	fw	plant	*Scapania sp.*	81.4		ICPES	70	416	dwt; wh	3.044	76	
DEU, Erzgebirge	fw	plant	*Scapania sp.*	81.4		ICPES	71	97	dwt; wh	2.405	77	
DEU, Erzgebirge	fw	plant	*Scapania sp.*	81.4		ICPES	64	75	dwt; wh	2.338	78	
FR, Cantal	fw	pisc	*Gasterosteus aculeatus*	73.7	March-April	ICP-MS/ ICP-AES	12.32	1.89	dwt; mu	1.606	79	Le Guernic et al. (2016)
FR, Cantal	fw	pisc	*Gasterosteus aculeatus*	73.7	March-April	ICP-MS/ ICP-AES	20.8	2.24	dwt; mu	1.452	80	
FR, Cantal	fw	pisc	*Gasterosteus aculeatus*	73.7	March-April	ICP-MS/ ICP-AES	22.59	3.6	dwt; mu	1.622	81	
FR, Haute Vienne	fw	pisc	*Gasterosteus aculeatus*	73.7	March-April	ICP-MS/ ICP-AES	6.14	5.3	dwt; mu	2.356	82	
FR, Haute Vienne	fw	pisc	*Gasterosteus aculeatus*	73.7	March-April	ICP-MS/ ICP-AES	17.52	1.48	dwt; mu	1.347	83	
FR, Haute Vienne	fw	pisc	*Gasterosteus aculeatus*	73.7	March-April	ICP-MS/ ICP-AES	22.05	2.68	dwt; mu	1.505	84	
FR, Vincou river area	fw	pisc	*Rutilus rutilus*	73.7	March-April	ICP-MS/ ICP-AES	5	0.6	dwt; mu	1.499	85	Gagnaire et al. (2015)
FR, Vincou river area	fw	pisc	*Rutilus rutilus*	73.7	March-April	ICP-MS/ ICP-AES	18.4	6.5	dwt; mu	1.968	86	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
GRC, Thessaloniki Gulf	sw	plant	*Cymodocea nodosa*	81.4	monthly February 2007-January 2008	ICP-MS	22.38	143.1	dwt; bl	3.075	88	Malea & Kevrekidis (2013)
GRC, Thessaloniki Gulf	sw	plant	*Codium fragile*	81.4	early spring to mid summer 2007-2008	ICP-MS	22.38	148.7	dwt; sh	3.092	87	Malea et al. (2015)
GRC, Thessaloniki Gulf	sw	plant	*Gracilaria gracilis*	81.4	late spring to early autumn 2007-2008	ICP-MS	22.38	81.63	dwt; sh	2.832	89	
GRC, Thessaloniki Gulf	sw	plant	*Ulva intestinalis*	81.4	winter and spring 2007-2008	ICP-MS	22.38	118.3	dwt; sh	2.993	90	
GRC, Thessaloniki Gulf	sw	plant	*Ulva rigida*	81.4	early spring, mid-summer to winter 2007-2008	ICP-MS	22.38	109.5	dwt; sh	2.959	91	
POL, Zielona Gora	fw	plant	*Calamagrostis epigeios*	81.4	July	ICPES	45	4.2	dwt; lea	1.24	92	Samecka-Cymerman & Kempers (2001)
POL, Zielona Gora	fw	plant	*Carex remota*	81.4	July	ICPES	35	48	dwt; lea	2.407	93	
POL, Zielona Gora	fw	plant	*Carex remota*	81.4	July	ICPES	45	75	dwt; lea	2.491	92	
POL, Zielona Gora	fw	plant	*Drepanocladus aduncus*	81.4	July	ICPES	49	1.2	dwt; wh	0.658	94	
POL, Zielona Gora	fw	plant	*Iris pseudoacorus*	81.4	July	ICPES	43	1.5	dwt; lea	0.812	95	
POL, Zielona Gora	fw	plant	*Juncus bulbosus*	81.4	July	ICPES	41	1	dwt; lea	0.657	96	
POL, Zielona Gora	fw	plant	*Juncus bulbosus*	81.4	July	ICPES	45	6.2	dwt; lea	1.409	92	
POL, Zielona Gora	fw	plant	*Juncus bulbosus*	81.4	July	ICPES	35	7.5	dwt; lea	1.601	93	
POL, Zielona Gora	fw	plant	*Juncus effusus*	81.4	July	ICPES	37	1.2	dwt; lea	0.78	97	
POL, Zielona Gora	fw	plant	*Juncus effusus*	81.4	July	ICPES	59	2.2	dwt; lea	0.841	98	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
POL, Zielona Gora	fw	plant	*Juncus effusus*	81.4	July	ICPES	51	2.9	dwt; lea	1.024	99	
POL, Zielona Gora	fw	plant	*Juncus effusus*	81.4	July	ICPES	39	3.8	dwt; lea	1.258	100	
POL, Zielona Gora	fw	plant	*Juncus effusus*	81.4	July	ICPES	45	5.6	dwt; lea	1.364	92	
POL, Zielona Gora	fw	plant	*Nymphaea alba*	81.4	July	ICPES	37	1.8	dwt; lea	0.957	101	
POL, Zielona Gora	fw	plant	*Phalaris arundinacea*	81.4	July	ICPES	59	2.8	dwt; lea	0.946	98	
POL, Zielona Gora	fw	plant	*Phalaris arundinacea*	81.4	July	ICPES	35	13	dwt; lea	1.839	93	
POL, Zielona Gora	fw	plant	*Phragmites australis*	81.4	July	ICPES	59	4.1	dwt; lea	1.111	98	
POL, Zielona Gora	fw	plant	*Phragmites australis*	81.4	July	ICPES	35	4.7	dwt; lea	1.398	93	
POL, Zielona Gora	fw	plant	*Phragmites australis*	81.4	July	ICPES	43	7.3	dwt; lea	1.499	95	
POL, Zielona Gora	fw	plant	*Phragmites australis*	81.4	July	ICPES	37	17	dwt; lea	1.932	101	
POL, Zielona Gora	fw	plant	*Phragmites australis*	81.4	July	ICPES	37	22	dwt; lea	2.044	97	
POL, Zielona Gora	fw	plant	*Polygonum hydropiper*	81.4	July	ICPES	28	46	dwt; lea	2.485	102	
POL, Zielona Gora	fw	plant	*Potamogeton natans*	81.4	July	ICPES	43	2.8	dwt; lea	1.083	95	
POL, Zielona Gora	fw	plant	*Schoenoplectus lacustris*	81.4	July	ICPES	28	4.3	dwt; lea	1.456	102	
POL, Zielona Gora	fw	plant	*Typha angustifolia*	81.4	July	ICPES	28	4.6	dwt; lea	1.485	102	
PRT, Mangualde, reference site	fw	amph	*Pelophylax perezi*	78.9	spring	ICP-MS	*4.09*	0.47	dwt; mu	1.385	103	Marques et al. (2011)
PRT, Mangualde, U mine effluent	fw	amph	*Pelophylax perezi*	78.9	spring	ICP-MS	*10.94*	0.41	dwt; mu	0.898	103	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Abramis brama*	73.7	June, August 2012	ICP-OES	*30*	0.66	wwt; mu	0.824	104	Đikanović et al. (2016)
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Barbus barbus*	73.7	June, August 2012	ICP-OES	*30*	0.6	wwt; mu	0.786	104	
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Carassius gibelio*	73.7	June, August 2012	ICP-OES	*30*	0.21	wwt; mu	0.333	104	
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Chondrostoma nasus*	73.7	June, August 2012	ICP-OES	*30*	1.14	wwt; mu	1.061	104	
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Esox lucius*	73.7	June, August 2012	ICP-OES	*30*	0.11	wwt; mu	0.05	104	
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Perca fluviatilis*	73.7	June, August 2012	ICP-OES	*30*	0.15	wwt; mu	0.181	104	
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Rutilus rutilus*	73.7	June, August 2012	ICP-OES	*30*	1.95	wwt; mu	1.295	104	
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Silurus glanis*	73.7	June, August 2012	ICP-OES	*30*	0.39	wwt; mu	0.6	104	
SRB, West Morava Riverbasin, Međuvršje Reservoir	fw	pisc	*Squalius cephalus*	73.7	June, August 2012	ICP-OES	*30*	0.29	wwt; mu	0.47	104	
TUR Yeniçağa Lake	fw	plank		96.2	March 2008-February 2009	ICP-MS	86.1	157	dwt	1.841	105	Saygı & Yiğit (2012)
TUR Yeniçağa Lake	fw	plank		96.2	March 2008-February 2009	ICP-MS	85.1	86.7	dwt	1.588	106	
TUR Yeniçağa Lake	fw	plank		96.2	March 2008-February 2009	ICP-MS	85.3	77.8	dwt	1.54	107	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
USA, CA, Merced River	fw	pisc	*Lepomis macrochirus*		May-June 1988	ICAP	34	12.3	dwt; wh	1.956	108	Nakamoto & Hassler (1992)
USA, CA, Salt Slough	fw	pisc	*Lepomis macrochirus*		May-June 1988	ICAP	65	7.5	dwt; wh	1.459	109	
USA, NY, Times Beach Disposal Facility	fw	moll	*Dreissena polymorpha*		1993	ICAP	30	7	wwt; ed	2.368	110	Roper et al. (1996)
USA, SC, Savannah River Project	fw	crust	*Astacidae*			NAA	710	76.43	wwt; mu	2.032	111	Cherry et al. (1979)
USA, SC, Savannah River Project	fw	crust	*Astacidae*			NAA	700	43.5	wwt; mu	1.793	112	
USA, SC, Savannah River Project	fw	ins	*Chironominae sp.*			NAA	980	102	wwt; mu	2.017	113	
USA, SC, Savannah River Project	fw	ins	*Chironominae sp.*			NAA	710	97	wwt; mu	2.136	111	
USA, SC, Savannah River Project	fw	ins	*Enallagma sp.*			NAA	980	15.6	wwt; mu	1.202	113	
USA, SC, Savannah River Project	fw	ins	*Libellula sp.*			NAA	710	33.75	wwt; mu	1.677	111	
USA, SC, Savannah River Project	fw	ins	*Libellula sp.*			NAA	700	34.6	wwt; mu	1.694	112	
USA, SC, Savannah River Project	fw	ins	*Libellula sp.*			NAA	510	27.93	wwt; mu	1.739	114	
USA, Virginia, James River	fw	pisc	*Lepomis*		1994		70	2.1	wwt; wh	1.477	115	Hope et al. (1996)
VNM, Mekong Delta	bw	crust	*Macrobrachium equidens*	73.9	April 2004	ICP-MS	24.98	110	dwt; wh	3.06	116	Ikemoto et al. (2008)
VNM, Mekong Delta	bw	crust	*Macrobrachium rosenbergii*	70.2	April 2004	ICP-MS	24.98	130	dwt; wh	3.191	117	

Location	WT	Tax	Latin name	MC	Sampling date	A	Cw	Corg	Based on	log BAF	N	Ref
VNM, Mekong Delta	bw	crust	*Macrobrachium sp.*	71.4	April 2004	ICP-MS	24.98	115	dwt; wh	3.119	118	
VNM, Mekong Delta	bw	crust	*Macrobrachium sp.*	78.7	April 2004	ICP-MS	24.98	100	dwt; wh	2.931	119	
VNM, Mekong Delta	bw	crust	*Macrobrachium tenuis*	75.2	April 2004	ICP-MS	24.98	55	dwt; wh	2.737	120	
VNM, Mekong Delta	bw	phyto		96.2	April 2004	ICP-MS	24.98	33	dwt; wh	1.701	121	
VNM, Mekong Delta	bw	pisc	*Clupeoides sp.*	81.9	April 2004	ICP-MS	24.98	7.3	dwt; wh	1.723	122	
VNM, Mekong Delta	bw	pisc	*Cyclocheilichthys armatus*	74.3	April 2004	ICP-MS	24.98	16	dwt; wh	2.216	123	
VNM, Mekong Delta	bw	pisc	*Cynoglossus sp.*	79.5	April 2004	ICP-MS	24.98	24	dwt; wh	2.294	124	
VNM, Mekong Delta	bw	pisc	*Eleotris melanosoma*	75.7	April 2004	ICP-MS	24.98	13	dwt; wh	2.102	125	
VNM, Mekong Delta	bw	pisc	*Glossogobius aureus*	76.7	April 2004	ICP-MS	24.98	16	dwt; wh	2.174	126	
VNM, Mekong Delta	bw	pisc	*Parambassis wolffii*	76.9	April 2004	ICP-MS	24.98	56	dwt; wh	2.714	127	
VNM, Mekong Delta	bw	pisc	*Pisodonophis boro*	74.2	April 2004	ICP-MS	24.98	2.7	dwt; wh	1.445	128	
VNM, Mekong Delta	bw	pisc	*Polynemus paradiseus*	79.2	April 2004	ICP-MS	24.98	25	dwt; wh	2.318	129	
VNM, Mekong Delta	bw	pisc	*Puntioplites proctozysron*	74.7	April 2004	ICP-MS	24.98	12	dwt; wh	2.085	130	

Notes

1 n=3; adult, 26.0 cm; water samples in triplicate; acidified before filtration, most likely total concentrations; recovery of reference water 108%; 6 g muscle sample per fish, measured in dried samples, corrected to wwt with conversion factor of 0.58%

2 n=3; adult, 27.8 cm; water samples in triplicate; acidified before filtration, most likely total concentrations; recovery of reference water 108%; 6 g muscle sample per fish, measured in dried samples, corrected to wwt with conversion factor of 0.58%

3 n=4; adult, 31 cm; water samples in triplicate; acidified before filtration, most likely total concentrations; recovery of reference water 108%; 6 g muscle sample per fish, measured in dried samples, corrected to wwt with conversion factor of 0.58%

4 n=5; adult, 30.1 cm; water samples in triplicate; acidified before filtration, most likely total concentrations; recovery of reference water 108%; 6 g muscle sample per fish, measured in dried samples, corrected to wwt with conversion factor of 0.58%

5 n=33; 5-12 cm; 2 river locations P1B and P3B; water concentration is geometric mean of rainy season (22.6 µg/L) and dry season (23.4 µg/L); water is fw most of the year, slightly brackish between August and November; ICP-MS for water, ICP-OES for tissues; BAF is mean value reported by authors, BAF calculated from reported mean concentration in water and oysters is 55922; no significant difference among seasons

6 4 river locations; 20 μm mesh; water concentration is geometric mean of rainy season (22.6 μg/L) and dry season (23.4 μg/L); water is fw most of the year, slightly brackish between August and November; ICP-MS for water, ICP-OES for phytoplankton; BAF calculated from reported mean concentration in phytoplankton
7 n=4; 30.5-38 cm; 235-391 g; BAF is geometric mean of 4 individual fish; water concentration is average reported by Kwon et al. (2012), range 30-106 μg/L
8 n=8; 16-21 cm; 82.5-208 g; BAF is geometric mean of 8 individual fish; water concentration is average reported by Kwon et al. (2012), range 30-106 μg/L
9 n=6; 16-21.5 cm; 71.3-171 g; BAF is geometric mean of 6 individual fish; water concentration is average reported by Kwon et al. (2012), range 30-106 μg/L
10 3 pooled samples of 10 animals; water concentration most likely expressed as total
11 n=1; water concentration most likely expressed as total
12 3 pooled samples of 10 animals; water concentration most likely expressed as total
13 n=2; 382-608 g; BAF based on geometric mean concentration of 2 individual values; raw data obtained from author
14 33.7 g; raw data obtained from author
15 n=4; 5-12 g; BAF is geometric mean of 4 individual datapoints obtained from author
16 0.225 g; raw data obtained from author
17 n=2; 3.1-5.6 g; BAF is geometric mean of 2 individual datapoints obtained from author
18 n=65; 47-986 g; BAF based on geometric mean concentration of 65 individual values; raw data obtained from author
19 n=38; 451-2374 g; BAF based on geometric mean concentration of 38 individual values; raw data obtained from author
20 n=15; 234-1659 g; BAF based on geometric mean concentration of 15 individual values; raw data obtained from author
21 n=51; 50-416 g; BAF based on geometric mean concentration of 51 individual values; raw data obtained from author
22 10 g; raw data obtained from author
23 n=27; 61-11144 g; BAF based on geometric mean concentration of 27 individual values; raw data obtained from author
24 22 g; raw data obtained from author, concentration in fish is also mentioned in text
25 n=7; 308-1352 g; BAF based on geometric mean concentration of 7 individual values; raw data obtained from author
26 3 g; raw data obtained from author
27 n=24; 13-995 g; BAF based on geometric mean concentration of 24 individual values; raw data obtained from author
28 8.6 g; raw data obtained from author, concentration in fish is also mentioned in text
29 n=18; 83-748 g; BAF based on geometric mean concentration of 18 individual values; raw data obtained from author
30 24 g; raw data obtained from author
31 n=32; 13-2982 g; BAF based on geometric mean concentration of 32 individual values; raw data obtained from author
32 13 g; raw data obtained from author
33 multispecies composite sample; mean 0.103 g; raw data obtained from author, concentration in fish is also mentioned in text
34 n=50; 107-5566 g; BAF based on geometric mean concentration of 49 individual values; raw data obtained from author
35 n=38; 38-5566 g; BAF is geometric mean of 38 individual datapoints obtained from author
36 2 composite samples; sampling year not given, invertebrates supposed to be sampled in May-June, BAF is geometric mean of 2 individual datapoints obtained from author
37 n=33; 38-1569 g; BAF based on geometric mean concentration of 33 individual values; raw data obtained from author
38 14 g; raw data obtained from author
39 raw data obtained from author
40 apical parts; not clear if water samples were filtered; authors report lack of significant correlation between concentrations in moss and water
41 n=3; site 36; uncontaminated area
42 n=3; site 37; uncontaminated area
43 n=3; site 38; uncontaminated area
44 n=3; site 39; uncontaminated area
45 n=3; site 40; uncontaminated area

46 n=3; site 13; ore deposit/mining area
47 n=3; site 14; ore deposit/mining area
48 n=3; site 2; ore deposit/mining area
49 n=3; site 33; ore deposit/mining area
50 n=3; site 36; ore deposit/mining area
51 n=3; site 8; ore deposit/mining area
52 n=3; site 1; ore deposit/mining area; plant code given as "C", probably "F" for Fontinalis is meant
53 n=3; site 1; ore deposit/mining area
54 n=3; site 10; ore deposit/mining area
55 n=3; site 11; ore deposit/mining area
56 n=3; site 12; ore deposit/mining area
57 n=3; site 15; ore deposit/mining area
58 n=3; site 16; ore deposit/mining area
59 n=3; site 17; ore deposit/mining area
60 n=3; site 21; ore deposit/mining area
61 n=3; site 22; ore deposit/mining area
62 n=3; site 23; ore deposit/mining area
63 n=3; site 24; ore deposit/mining area
64 n=3; site 25; ore deposit/mining area
65 n=3; site 26; ore deposit/mining area
66 n=3; site 27; ore deposit/mining area
67 n=3; site 28; ore deposit/mining area
68 n=3; site 29; ore deposit/mining area
69 n=3; site 3; ore deposit/mining area
70 n=3; site 30; ore deposit/mining area
71 n=3; site 31; ore deposit/mining area
72 n=3; site 32; ore deposit/mining area
73 n=3; site 35; ore deposit/mining area
74 n=3; site 4; ore deposit/mining area
75 n=3; site 7; ore deposit/mining area
76 n=3; site 34; ore deposit/mining area
77 n=3; site 5; ore deposit/mining area
78 n=3; site 6; ore deposit/mining area
79 caged 1 y old fish from breeding culture, 5.24 cm, 1.71 g; n=10; exposure in March-April for 28 d in U mining contaminated pond Saint-Pierre; water concentration is geomean of t=14 and 28 (16.2 and 9.2 µg/L)
80 caged 1 y old fish from breeding culture, 5.24 cm, 1.71 g; n=10; exposure in March-April for 28 d in reference pond Etang-Noir water concentration is geomean of t=14 and 28 (21.2 and 20.4 µg/L)
81 caged 1 y old fish from breeding culture, 5.24 cm, 1.71 g; n=10; exposure in March-April for 28 d in reference pond Madic; water concentration is geomean of t=14 and 28 (40.5 and 12.6 µg/L)
82 caged 1 y old fish from breeding culture, 5.24 cm, 1.71 g; n=10; exposure in March-April for 28 d in reference pond Malessard; water concentration is geomean of t=14 and 28 (6.4 and 5.9 µg/L)
83 caged 1 y old fish from breeding culture, 5.24 cm, 1.71 g; n=10; exposure in March-April for 28 d in U mining contaminated pond Pontabrier; water concentration is geomean of t=14 and 28 (18.5 and 16.6 µg/L)
84 caged 1 y old fish from breeding culture, 5.24 cm, 1.71 g; n=10; exposure in March-April for 28 d in reference pond Jonchère-Saint-Maurice; water concentration is geomean of t=14 and 28 (6.4 and 5.9 µg/L)

85 caged adults from commercial breeder, 2 y old, 10 cm, 11.3 g; exposure in March-April for 28 d in pond Sauvage upstream from U mining discharge; mortality 10%; water: LOD 10 µg/L for ICP-MS and 10 ng/L for ICP-AES, not clear which method is used

86 caged adults from commercial breeder, 2 y old, 10 cm, 11.3 g; exposure in March-April for 28 d in pond Pontabrier downstream from U mining discharge; mortality 6.3%; not clear if equilibrium is reached

87 water concentration is mean, same values for mean and CV as in Malea & Kevrekidis 2013, but different SE is reported; large variation in water concentrations over sampling period, peak in October; concentration in Codium is mean concentration, SE 12.23 µg/g

88 n=3 per sampling; water concentration is mean, large variation in water concentrations over sampling period, range 6.96-147.68 µg/L, peak in October (see Malea et al 2015); concentration in blades is mean concentration, range 27.9-298.1 µg/g

89 water concentration is mean, same values for mean and CV as in Malea & Kevrekidis 2013, but different SE is reported; large variation in water concentrations over sampling period, peak in October; concentration in Gracillaria is mean concentration, SE 20.37 µg/g

90 water concentration is mean, same values for mean and CV as in Malea & Kevrekidis 2013, but different SE is reported; large variation in water concentrations over sampling period, peak in October; concentration in Ulva is mean concentration, SE 13.41 µg/g

91 water concentration is mean, same values for mean and CV as in Malea & Kevrekidis 2013, but different SE is reported; large variation in water concentrations over sampling period, peak in October; concentration in Ulva is mean concentration, SE 11.67 µg/g

92 lake 8; anthropogenic lakes resulting from brown coal mining

93 lake 6; anthropogenic lakes resulting from brown coal mining

94 lake 5; anthropogenic lakes resulting from brown coal mining; moss is reported to be the only species in the most acidic lake (pH 2.8), but lowest pH 2.6 is reported for lake 6 instead of lake 5

95 lake 1; anthropogenic lakes resulting from brown coal mining

96 lake 9; anthropogenic lakes resulting from brown coal mining

97 lake 3; anthropogenic lakes resulting from brown coal mining

98 lake 7; anthropogenic lakes resulting from brown coal mining

99 lake 2; anthropogenic lakes resulting from brown coal mining

100 lake 4; anthropogenic lakes resulting from brown coal mining

101 natural lake A

102 natural lake B

103 n=5; male adults; 6.8 cm; 27.88 g; water most likely not filtered;

104 n=10; BAFs are those reported by author, values are in reasonable agreement with those calculated on the basis of reported concentrations in water and biota, difference most likely due to dwt-wwt conversion

105 30 µm mesh; plankton > 0.45 µm; average for sampling station B1; water SD ± 34.3 µg/L, plankton SD ± 336 µg/g

106 30 µm mesh; plankton > 0.45 µm; average for sampling station B2; water SD ± 39.0 µg/L, plankton SD ± 179 µg/g

107 30 µm mesh; plankton > 0.45 µm; average for sampling station B3; water SD ± 34.7 µg/L, plankton SD ± 115 µg/g

108 n=10; m/f; 8-130 g; BAF is weighted mean of males and females; BAFs calculated using reported concentrations in filtered water and fish; wwt-based values calculated with reported moisture content; author reports BAFs based on unfiltered water, recalculation with reported concentration in fish and water lead to similar results

109 n=10; m/f; 11-110 g; BAF is weighted mean of males and females; BAFs calculated using reported concentrations in filtered water and fish; wwt-based values calculated with reported moisture content; author reports BAFs based on unfiltered water, recalculation with reported concentration in fish and water lead to similar results

110 n=26; caged mussels from uncontaminated site; 1.6 cm; not clear if water is filtered; mussels from relatively uncontaminated site were exposed for 34 days in cages; tissue concentration at collection site 1.25 mg/kg, not clear if equilibrium is reached, day 0 values 2.4 mg/kg

111 site beyond major ash influence (E); data refer most likely to average of samples taken over 15 months; not clear if water is filtered

112 ash influenced swamp (D); data refer most likely to average of samples taken over 15 months; not clear if water is filtered

113 ash basin (A); data refer most likely to average of samples taken over 15 months; not clear if water is filtered

114 site without ash discharge (F); data refer most likely to average of samples taken over 15 months; not clear if water is filtered

115 n=13, pooled into 4 samples; expression of fish concentration not clear, most likely wwt; author reports that BCF = 129 L/kg based on water concentration 0.07 ppm and whole body fish concentration of 2.1 ppm

116 n=7; 41.5 mm; 2.2 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
117 n=5; 98.8 mm; 34.5 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
118 n=2; 79.7 mm; 11.5 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
119 n=3; 33.0 mm; 0.7 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
120 n=1; 52.7 mm; 1.9 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
121 water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
122 n=1; 35.8 mm; 0.7 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
123 n=1; 153.4 mm; 82.1 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
124 n=1; 56.4 mm; 1.7 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
125 n=1; 71.9 mm; 11 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
126 n=5; 81.5 mm; 14.6 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
127 n=1; 102.3 mm; 39.0 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
128 n=2; 429.9 mm; 28.6 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
129 n=3; 53.6 mm; 3.4 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content
130 n=1; 89.1 mm; 27.4 g; water concentration is geometric mean of two samples: 24 and 26 µg/L; wwt-based values calculated using reported moisture content

Appendix 3. Detailed ecotoxicity data

Legend to column headings	
A	analysed Yes/No; only studies with analytical measurements are accepted
Test subst.	test substance: Cl2 = $BaCl_2$ (or hydrated); NO3 = $Ba(NO_3)_2$; SO4 = $BaSO_4$; Ac = $Ba(CH_3COOH)_2$
Test type	S = static; R = renewal
Pur.	purity: ag = analytical grade; rg = reagent grade
WT	water type: am = artificial medium; nw = natural water; dw = deionised water; dtw = dechlorinated tap water; rw = reconstituted water; sw = synthetic seawater
$CaCO_3/SO_4$	Hardness as mg $CaCO_3$/L, sulfate in mg/L
T	temperature
Based on	N = nominal; U = measured in unfiltered water; F = measured in filtered water
N U F	effect value based on nominal, unfiltered or filtered concentrations
Ri	Reliability index; studies with Ri1 or 2 are accepted, non-reliable Ri3 studies are not used and indicated in grey Ri *: result is taken over from another study, Ri refers to original reference
N	notes
Ref	reference

Table A2.1. Summary of acute ecotoxicity studies in freshwater.

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	N U F	Ri	N	Ref
Protozoa																	
Tetrahymena pyriformis	1e4 cells/ mL	N	S	Cl2		am			28	3 h	IC50	cell prolif.	585	N	3	1	Sauvant et al. (1995b)
										6 h			415		3	1	
										9 h			330		3	1	
Tetrahymena pyriformis	1e4 cells/ mL	N	S	Cl2		am			28	9 h	IC50	cell prolif.	350	N	3	2	Sauvant et al. (1995a)
Algae																	
Chlorella sp. 12	2-4e3/mL; lab culture originally from lake	Y	S	Cl2	ag	am	80-90/ 84	7.2-8.5	27	48 h	EC50	growth	10	U	3	3	Golding et al. (2018)
							80-90/0	7.5-8.2					240	U/F	2	4	
Chlorococcales		N		Cl2						24 h	EC50	ass. eff.	>1000	N	3	5	Krebs (1991)

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Pseudokirch-neriella subcapitata	SAG 61.81; 0.5E4/mL	Y	S	Cl2		am	110/98.7	5.8-6.1	22.9	72 h	EC50	growth rate	>1.2	F	1	6	ECHA (2018)
													>30.1	U	1	7	
Platyhelminthes																	
Dugesia tigrina	20 d, 11-12 mm	N	S	NO3	ag	am	105/-	7.2-8.2	18-22	96 h	LC50	mortality	51	N	3	8	Piontek (1999)
Dugesia tigrina	20 d, 11-12 mm, cut ind.	N	S	NO3	ag	am	105/-	7.2-8.2	18-22	240 h	LC50	mortality	7.8	N	3	9	Piontek (1999)
Crustacea																	
Austropotamobius pallipes	19-32 mm	Y		Cl2		nw		7	16	96 h	LC50	mortality	46	U	3	10	Boutet & Chaisemartin (1973)
Ceriodaphnia dubia	lab culture originally from lake; <24 h old	Y	S	Cl2	ag	am	80-90/0	7.3-8.4		48 h	EC50	immobility	17	U/F	2	11	Golding et al. (2018)
							-/5.5	7.8-8.5					38	F	2	12	
							-/5.5						39	U	2	12	
		N		SO4	ag	am	-/5.5						116.7	N	3	13	
Ceriodaphnia dubia	neonates	Y	R	BaCO3		dtw	40/7.7	7.9	26±1	7 d	LC50	mortality	147	U	2	14	Brix et al. (2010)
Daphnia magna		N	S	NO3	>99	rw				24 h	LC50	mortality	109	N	3	15	Calleja et al. (1993)
Daphnia magna		N	S	NO3	>97	rw				24 h	LC50	mortality	110	N	3	16	Calleja et al. (1994)
Daphnia magna				NO3						24 h	EC50	immobility	70.3		4*	17	Martins et al. (2007)
													108.5		4*	18	
Daphnia magna	<24 h; neonate	N	S	NO3	rg	fw	200/14.4	7.6	21	24 h	EC50	immobility	70.3	N	3	19	Lilius et al. (1994)

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Daphnia magna	<24 h; neonate	N	S	NO3	rg	fw	200/14.4	7.6	21	24 h	EC50	immobility	70.3	N	3*	19	Lilius et al. (1995)
Daphnia magna	females <24 h old	Y	S	Cl2	>99.	ftw	250/48.1	6.5-8.5	21	48 h	EC50	immobility	11	U	2	20	Okamoto et al. (2015)
Daphnia magna	field collected	N	S	SO4	rg	nw	240/-	7.2-7.8	11.5-14.5	48 h	LC50	mortality	32	N	3	21	Khangarot & Ray (1989)
Daphnia magna	<24 h old	N	S	Cl2	rg	nw	44-53	7.4-8.2	18	48 h	LC50	mortality	14.5	N	3	22	Biesinger & Christensen (1972)
Daphnia magna	<24 h	N	S	Cl2		nw	200/-	7.5		48 h	EC50	immobility	170	N	3	23	Bringmann & Kühn (1959)
Daphnia magna		N	S		>80	am	173/-	7.4-9.4	22	48 h	LC50	mortality	410	N	3	24	LeBlanc (1980)
Daphnia magna	4-8 h			Cl2		nw				64 h	EC50	immobility	19	N	3	25	Anderson (1948)
Echinogammarus berilloni	10-20 mm; field collected	N		Cl2		nw	277/-	7.7	19	96 h	LC50	mortality	122	N	3	26	Vincent et al. (1986)
							27/-						129		3	27	
Gammarus pulex		N		Cl2			277/-	7.7	19	96 h	LC50	mortality	238		3	26	
							27/-						227		3	27	
Hyalella azteca	1-11 d old	Y	S	Cl2		dw/dt	18/3.4	7.39	24-2	7 d	LC50	mortality	>1.1	F	2	28	Borgmann et al. (2005)
		N				dtw	124/32	8.21				mortality	>3.15	N	3	29	
Streptocephalus proboscideus	2-3rd instar	N	S	NO3	>99	am	85/81.3		25	24 h	LC50	mortality	353	N	3	30	Calleja et al. (1993)
Streptocephalus proboscideus	2-3rd instar	N	S	NO3	>97	am	85/81.3		25	24 h	LC50	mortality	372	N	3	31	Calleja et al. (1994)
Rotifera																	
Brachionus calyciflorus	larvae	N	S	NO3	>97	am	85/-		25	24 h	LC50	mortality	370	N	3	32	Calleja et al. (1993)
Brachionus calyciflorus	larvae	N	S	NO3	>97	am	85/-		25	24 h	LC50	mortality	372	N	3	33	Calleja et al. (1994)
Ostracoda																	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Cypris subglobosa	field collected	N	R	SO4	rg	nw	245/-	7.4-7.7	20-22	48 h	EC50	immobility	798	N	3	34	Khangarot & Das (2009)
Annelida																	
Tubifex tubifex	field collected	N	R	SO4	rg	nw	245/-	7.6		24 h	LC50	mortality	45.0	N	3	35	Khangarot (1991)
										48 h			33.7	N	3	35	
										96 h			33.7	N	3	35	
Mollusca																	
Bulinus contortus		N	S	Cl2						48 h	LC10	mortality	9.4	N	3	36	Bijan & Deschiens (1956)
				NO3									10.5	N	3	37	
Potamopyrgus jenkinsi	field coll., adults, summer gen.	N	S	BaCl2		nw	267/-	8		96 h	LC50	mortality	1.74	N	3	38	Vareille-Morel & Debord (1990)
													1.10	N	3	39	
							42/-	7		96 h	LC50	mortality	1.45	N	3	40	
													1.29	N	3	41	
	field coll., adults, winter gen.	N	S	BaCl2		nw	267/-	8		96 h	LC50	mortality	1.78	N	3	38	
													0.33	N	3	40	
	field coll., juveniles summer gen.	N	S	BaCl2		nw	267/-	8		96 h	LC50	mortality	0.93	N	3	38	
													0.45	N	3	40	
Planorbis glabratu		N		Cl2						48 h	LC10	mortality	7.3	N	3	42	Bijan & Deschiens (1956)
				NO3									10.5	N	3	37	
Pisces																	
Carrassius auratus		N	S	Cl2							LC0	mortality	9.4	N	3	43	Bijan & Deschiens (1956)
				Cl2							LC10	mortality	132	N	3	43	
				NO3							LC0	mortality	105	N	3	44	
Danio rerio	0.12 g; 2.69 cm	Y	S	Cl2		rw	171-179/ 24	7.1-7.5	21.3-22.4	96 h	LC50	mortality	>3.5	F	2	45	ECHA, 2018
Gambusia affinis	adult	N	S	Cl2	rg	nw		7.1-7.6	18-20	96 h	LC50	mortality	1082	N	3	46	Wallen et al. (1957)
				BaCO3				7.6-8.5	17-20				>6959	N	3	47	
Leuciscus idus melanotus	1.5 g; 5-7 cm	N	S	Cl2		tw	270/-	7-8	20	48 h	LC50	mortality	570	N	3	48	Juhnke & Lüdemann (1978)

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Pimephales promelas	cells in vitro	N	S	Cl2		am				2 h	EC50	survival	398	N	3	49	Brandão et al. (1992)
Salmo trutta	yearling	N	S	Cl2		dtw	100/-	7.6-8	15	48 h	LC50	mortality	150	N	3	50	Woodiwiss & Fretwell (1974)
Macrophyta																	
Lemna minor	field collected; 20 colonies 40 fronds	N	S	Cl2	rg	am		7.5	27 ± 2	96 h	EC50	growth rate	32	N	3	51	Wang (1986b)
Lemna minor	eld collected; 40 fronds	N	S	Cl2	rg	am		7.6	27 ± 2	96 h	EC50	growth inhibition	23	N	3	52	Wang (1986a)
						nw	215/-	7.8					>50	N	3	53	
						nw	215/100	7.8					>50	N	3	54	
Lemna minor	15 colonies 30 fronds	Y	S	Cl2	rg	am			25-28	96 h	EC50	# fronds	25	U	3	55	Wang (1988)
Lemna minor	15 colonies 30 fronds	Y	S	Cl2	rg	nw	274-400/ 294	7.64-	25-28	96 h		# fronds	>400	U	2	56	Wang (1988)
							245-320/ 44.7	8.00-					314	U	2	57	
							290-318/ 64.0	8.13-					146	U	2	58	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
							37-38/ 21.5	6.32-					97	U	2	59	
							54-78/ 2.8	6.92-					95	U	2	60	
							232-364/ 94.4	7.85-					232 to >400	U	2	61	
							252-257/ 57.5	7.80-					310, >400	U	2	62	
							140-146/ 38.1	7.95-					119	U	2	63	
							84-87/ 49.0	7.32-					174	U	2	64	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
							185-298/ 70.4	7.95-					330, >400	U	2	65	
							237-242/ 35.0	8.08-					136	U	2	66	
							308-311/ 99.5	7.85-					354	U	2	67	
							82-256/ 26.2	7.57-					111	U	2	68	
							225-265/ 116	7.95-					331, 400	U	2	69	
							160-310/ 45.5	8.05-					133	U	2	70	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Lemna minor	15 colonies 30 fronds	Y	S	Cl2	rg	nw	80-129/ 12.6	7.30-	25-28	96 h	EC50	# fronds	97	U	2	71	Wang (1988)
							126-314/ 24.7	7.48-					193	U	2	72	
							244-325/ 69.5	7.82-					259	U	2	73	
Scapania undulata	field coll.; stream 1	N	S	Cl2		nw			14	16 d	EC50	mortality	223	N	3	74	Samecka-Cymerman (1988)
	field coll.; stream 4												195	N	3	74	
	field coll.; stream 6												193	N	3	74	
	field coll.; stream 7												183	N	3	74	
	field coll.; stream 9												220	N	3	74	
	field coll.; stream 10												197	N	3	74	
	field coll.; stream 12												226	N	3	74	
	field coll.; stream 13												172	N	3	74	
	field coll.; stream 18												201	N	3	74	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Scapania undulata	field coll.; stream 1	N	S	Cl2		nw			14	16 d	EC50	gametophyte length	186	N	3	74	Samecka-Cymerman (1988)
	field coll.; stream 4												108	N	3	74	
	field coll.; stream 6												62	N	3	74	
	field coll.; stream 7												79	N	3	74	
	field coll.; stream 9												152	N	3	74	
	field coll.; stream 10												125	N	3	74	
	field coll.; stream 12												177	N	3	74	
Scapania undulata	field coll.; stream 13	N	S	Cl2		nw			14	16 d	EC50	gametophyte length	99	N	3	74	Samecka-Cymerman (1988)
	field coll.; stream 18												138	N	3	74	
Scapania undulata	field coll. stream 1	N	S	Cl2		nw			14	16 d	EC50	length lateral branches	109	N	3	74	Samecka-Cymerman (1988)
	field coll.; stream 4												19	N	3	74	
	field coll.; stream 6												82	N	3	74	
	field coll.; stream 7												34	N	3	74	
	field coll.; stream 9												3.1	N	3	74	
	field coll.; stream 10												7.1	N	3	74	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
	field coll.; stream 12												133	N	3	74	
	field coll.; stream 13												105	N	3	74	
	field coll.; stream 18												136	N	3	74	
Scapania undulata	field coll. stream 1	N	S	Cl2		nw			14	16 d	EC50	number lateral branches	15	N	3	74	Samecka-Cymerman (1988)
	field coll.; stream 4												99	N	3	74	
	field coll.; stream 6												110	N	3	74	
	field coll.; stream 7												38	N	3	74	
	field coll.; stream 9												156	N	3	74	
	field coll.; stream 10												59	N	3	74	
	field coll.; stream 12												61	N	3	74	
	field coll.; stream 13												84	N	3	74	
	field coll.; stream 18												153	N	3	74	

Notes
1 number of test concentrations not given, most likely 5 concentrations were tested; IC50 is estimated by linear regression of the ratio of cell number at t=x and t=0, versus concentration, but it is not clear if the effect on cell multiplication is indeed linear
2 number of test concentrations not given; IC50 is estimated by linear regression of the relative doubling time versus concentration, but it is not clear if the effect on cell multiplication is indeed linear; results are most likely based on the data from the previous study
3 synthetic soft water with sulfate present (84 mg/L); reference toxicant CuSO4; validity criterion used was 1.9 doublings/day in control and copper reference EC50 within internal database limits (2.6 ± 1.6 µg/L) and pH drift <1; analysis in filtered water; precipitation of barium sulfate; speciation calculated with Visual Minteq 3.1; measured dissolved barium 0.073-0.22 mg/L at total concentrations 0.1-100 mg/L, corresponding modelled Ba2+(aq) concentrations were 0.032-0.19 mg/L; EC50 expressed as total barium; no relationship between algal growth and dissolved barium up to total concentration 333 mg/L; authors suggest that precipitate contributes to toxicity, possibly by indirect effects (smothering, reduction in light, nutrient depletion); relevance for field situation is not clear

4 synthetic soft water with chloride instead of sulfate; reference toxicant CuSO4 and chloride control; validity criterion used was 1.9 doublings/day in control and copper reference EC50 within internal database limits (2.6 ± 1.6 µg/L) and pH drift <1; analysis in total and filtered water; measured dissolved concentrations represent >96% of total concentrations at 0.01-10000 mg/L; at total concentrations of 0.01-1000 mg/L, >98% of total barium predicted to be present as Ba2+(aq); NOEC of chloride control equivalent to 320 mg Ba/L, indicating that effects are due to barium; concentration-response curves for total and dissoled barium not significantly different; EC50 expressed as total and dissolved barium

5 disregarded in previous evaluation; non-standard endpoint

6 data from REACH dossier BaCl2/BaCl2.2H2O; test reportedly according to OECD 201, but medium according to Kuhl & Lorenzen (1964), hardness and sulfate calculated from reported composition; test item not specified, but reported calculation from Ba to test item indicates that BaCl2.2H2O is tested; test concentrations 0, 1.0, 2.2, 10, 31.6 and 100 mg test item/L; controls n=6, treatments n=3; analysis at start and end in solutions with algae, total Ba after acidification, dissolved Ba after filtration over 0.45 µm; inhibition of growth rate max 4.6% at 10 mg/L, 1.1% inhibition at 100 mg/L, EC50 reported as >1.15 mg/L (geomean of dissolved barium) and ≥ 30.1 mg/L (geomean total barium); EC50 >1.2 mg/L calculated by evaluator based on reported dissolved barium concentrations

7 data from REACH dossier BaCl2/BaCl2.2H2O; test reportedly according to OECD 201, but medium according to Kuhl & Lorenzen (1964), hardness and sulfate calculated from reported composition; test item not specified, but reported calculation from Ba to test item indicates that BaCl2.2H2O is tested; test concentrations 0, 1.0, 2.2, 10, 31.6 and 100 mg test item/L; controls n=6, treatments n=3; analysis at start and end in solutions with algae, total Ba after acidification, dissolved Ba after filtration; geomean of measured total Ba at t=0 and t=72: 0, 0.25, 0.24, 3.4, 4.3, 30.1 mg/L, geomean of measured dissolved calculated by evaluator as 0, 0.087, 0.15, 0.48, 1.3, 1.2 mg Ba/L; Ba at 100 mg/L at t=72 without algae was 1.12 mg/L (diss) and 30.1 mg/L (total); inhibition of growth rate max 4.6% at 10 mg/L, 1.1% inhibition at 100 mg/L.

8 test water according to ISO-guidelines, hardness taken over from previous evaluation; LC50 calculated by author using probit analysis; reported value 96.7 mg/L as barium nitrate

9 test water according to ISO-guidelines, hardness taken over from previous evaluation; LC50 calculated by author using probit analysis; reported value 14.8 mg/L as barium nitrate; test with cut organisms considered less relevant

10 test based on American guidelines; test water from natural pond; no information on characteristics; concentrations measured with AAS; most likely static

11 synthetic soft water with chloride instead of sulfate; mobility in controls 93-100%, mobility in chloride controls 80-100%, NOEC chloride control equivalent to 1000 mg Ba/L; analysis in total and 0.45 µm filtered water; measured dissolved concentrations represent >96% of total concentrations at 0.01-10000 mg/L; at total concentrations of 0.01-1000 mg/L, >98% of total barium predicted to be present as Ba2+(aq); same effect concentration expressed as total or dissolved

12 mineral water (Perrier) diluted with Millipore (20% v/v) with low sulfate (5.5 mg/L); analysis in total and 0.45 µm filtered water; dissolved barium >86% of total at nominal concentrations of 0.1-1000 mg/L; precipitate at 10 mg/L and higher; predicted Ba2+(aq) more than 9 times lower than measured dissolved barium, probably due to unknown mineral composition of mineral water; effect concentrations expressed as total or dissolved almost similar

12 mineral water (Perrier) diluted with Millipore (20% v/v) with low sulfate (5.5 mg/L); analysis in total and 0.45 µm filtered water; dissolved barium >86% of total at nominal concentrations of 0.1-1000 mg/L; precipitate at 10 mg/L and higher; predicted Ba2+(aq) more than 9 times lower than measured dissolved barium, probably due to unknown mineral composition of mineral water; effect concentrations expressed as total or dissolved almost similar

13 mineral water (Perrier) diluted with Millipore (20% v/v) with low sulfate (5.5 mg/L); control mobility 95%; range finding study; EC50 calculated by evaluator based on reported data in Supplemental Information (Table S3); calculated EC50 much higher than water solubility

14 standard 7 d test according to US EPA 2002; test concentrations 50-1000 µM Ba2+ (6.9-137.3 mg/L); test concentrations were analytically verified, but further information not provided, most likely expressed as total; survival data read from figure: no mortality up to 100 µM, full mortality at 200 and 500 µM, no partial mortality; LC50 estimated as geometric mean of highest test concentration with 100% survival and lowest with 0% survival, concentrations read from graph; this study is referred to by Golding et al (2018) as testing a mixture of dissolved and precipitated BaSO4 and BaCO3 because of presumed high sulfate concentration (77 mg/L), but test sulfate concentration is reported as 0.08 mM = 7.7 mg/L

15 test according to OECD 202 (1984), no further details on test water and other conditions; mean of at least 3 replicate tests; reported logEC50 2.90 µmol/L as bariumnitrate

16 test according to OECD 202 (1984), no further details on test water and other conditions; mean of at least 3 replicate tests; LC50 calculated from reported EC50 801 µmol/L
17 cited value from Lilius et al 1995
18 cited from Lilius et al 1995, who in turn refer to Calleja et al 1993
19 test according to OECD 202; hardness and sulfate calculated from reported medium composition; EC50 is mean of at least 3 tests, reported as 0.512 mM; visual determination of immobility which is not in accordance with guideline
19 test according to OECD 202; hardness and sulfate calculated from reported medium composition; EC50 is mean of at least 3 tests, reported as 0.512 mM; visual determination of immobility which is not in accordance with guideline
20 test according to OECD 202 (2004); 5 concentrations, spacing factor 2; charcoal filtered tap water; hardness and sulfate calculated by evaluator from composition of OECD-medium (also mentioned by Golding et al 2018)
21 disregarded in previous evaluation; filtered aerated tubewell hardwater; precipitation within 3-5 h
22 natural water from Lake Superior; background concentration 8-22 µg Ba/L
23 test in water from Havel river, which is indicated as mesotrophic and moderately affected; hardness calculated from reported German degrees; no information on background concentrations
24 according to text, the chemicals were tested on an active ingredient basis and concentrations are reported as milligrams (mg) of test material per liter (L) of diluent water; results table gives 'barium' as test substance, but test substance not indicated
25 disregarded in previous evaluation; test in Lake Erie water; test duration too long
26 test in high calcium water from a natural stream; test concentrations 150-1500 mg/L; result reported as mg Ba/L; background concentrations not reported
27 test in low calcium water from a natural source; reported test concentrations 150-1500 mg/L; result reported as mg Ba/L; background concentrations not reported
26 test in high calcium water from a natural stream; test concentrations 150-1500 mg/L; result reported as mg Ba/L; background concentrations not reported
27 test in low calcium water from a natural source; reported test concentrations 150-1500 mg/L; result reported as mg Ba/L; background concentrations not reported
28 test solution prepared from 1 g Ba/L AAS standard in 2% HCl; buffer added to correct pH; test in 10/90% dechlorinated tapwater/Millipore water; animals fed during test; 84 and 93% survival at 0.315 and 1 mg/L; measured concentration in filtered samples 1.1 mg/L at 1 mg/L nominal
29 test solution prepared from 1 g Ba/L AAS standard in 2% HCl; buffer added to correct pH; 89% survival at 1 mg/L; animals fed during test
30 standard testkit Streptoxkit; testwater EPA synthetic freshwater; details on test methods in Calleja & Persoone 1992; reported logLC50 3.41 µmol/L as barium nitrate
31 standard testkit Streptoxkit; testwater EPA synthetic freshwater; details on test methods in Calleja & Persoone 1992; LC50 reported as 2710 µmol/L
32 standard testkit Rotoxkit; testwater EPA synthetic freshwater; details on test methods in Calleja & Persoone 1992; reported logLC50 3.43 µmol/L as bariumnitrate
33 standard testkit Rotoxkit; testwater EPA synthetic freshwater; details on test methods in Calleja & Persoone 1992; reported LC50 2710 µmol/L as bariumnitrate
34 well water; precipitation observed within a few hours
35 tubewell water; precipitation observed within 2-3 h
36 six snails together with one fish and waterplants, mortality at 1 to 70000; assumed that this refers to 1 g/70 L
37 six snails together with one fish and waterplants, mortality at 1 to 50000; assumed that this refers to 1 g/50 L
38 molluscs collected from stream with 107 mg Ca/L tested in their natural water; hardness calculated from reported Ca-content; result given as log(LC50);
39 molluscs collected from stream with 17 mg Ca/L tested in high calcium natural water; hardness calculated from reported Ca-content (107 mg/L); result given as log(LC50);
40 molluscs collected from stream with 107 mg Ca/L tested in low calcium natural water; hardness calculated from reported Ca-content (17 mg/L); result given as log(LC50);

41 molluscs collected from stream with 17 mg Ca/L tested in their natural water; hardness calculated from reported Ca-content; result given as log(LC50);
42 six snails together with one fish and waterplants, mortality at 1 to 90000; assumed that this refers to 1 g/90 L
43 one fish together with snails and waterplants; test duration unknown; no mortality at 1 to 70000, mortality at 1 to 5000; assumed that this refers to 1 g/70 L and 1 g/5 L, respectively
44 one fish together with snails and waterplants; test duration unknown; no mortality at 1 to 5000; assumed that this refers to 1 g/5 L
45 data from REACH dossier BaCl2/BaCl2.2H2O; test according to OECD 203; test concentrations 0, 66 and 100 mg Ba/L (100, 152 mg BaCl2/L, 117-178 mg BaCl2.2H2O/L); test solutions prepared by direct weighing, appearance milky suspensions; test water reconstituted water (OECD 203) mixed 1:1 with deionised water and 1% artificial seawater; measured dissolved (0.45 µm filtered): t=0: 1.44 and 3.35 mg Ba/L, t=96 h: 1.42 and 3.68 mg Ba/L; measured total t=0: 62 and 100 mg Ba/L, t=96 h: 64 and 95 mg Ba/L; sulfate concentration calculated from OECD 203, taking 1:1 dilution with deionised water into account; no mortality, LC50 >3.5 mg Ba/L (dissolved) and >97.5 mg Ba/L (total)
46 test in turbid pond water from a farm; initial tubidity 100 mg/L, decreased to <25 mg/L by the end of the test; LC50 reported as 1640 mg/L for test substance
47 test in turbid pond water from a farm; initial tubidity 380 mg/L, decreased to 140 mg/L by the end of the test; LC50 reported as >10000 mg/L for test substance
48 hardness previously indicated as 255 mg CaCO3/L, present value based on required hardness of 15 °d; LC50 reported as 870 mg/L for bariumchloride; test duration too short
49 disregarded in previous evaluation; cell survival is measured as neutral red uptake inhibition; test duration is contact time with toxicant
50 test in soft water, composition not given; test duration too short
51 test in algal nutrient solution, characteristics unknown; medium prepared from deionised water previously kept in sunlight or fluorescent light for >7 d because initial toxicity was observed in control water; author reports EC50 26 mg/L; EC50 for specific growth rate of 32 mg/L was calculated by evaluator according to OECD 221, using data on frond number increase read from digitised graph; doubling time in control 2.6 d, current validity criterion of OECD 221 is 2.5 or less; barium compound not given, but next study indicates that BaCl2 was tested
52 Lemna collected from unpolluted groundwater recharge pit; 4 replicates; test medium deionised water with plant nutrients; EC50 reported as 26 mg/L by author, probably based on same experiment as previous study; EC50 for growth inhibition of 23 mg/L was calculated by evaluator, using data on growth inhibition read from digitised graph
53 Lemna collected from unpolluted groundwater recharge pit; 4 replicates; test in unfiltered river water with 350 mg/L dissolved solids and 110 mg/L suspended solids, and 100 mg/L sulfate
54 Lemna collected from unpolluted groundwater recharge pit; 4 replicates; test in filtered river water with 100 mg/L sulfate
55 double strength algal medium, composition could not be retrieved; concentrations between 5.5 and 200 mg/L; # fronds in control 65 after 96 h, equivalent to daily growth rate of 0.19, which is lower than specified in current OECD 221; recovery of barium concentrations 95% of nominal; IC50 is average of 7 tests; 95 CI 18-33 mg/L
56 disregarded in previous evaluation; natural water; Beaucoup Creek; turbidity 50-114 NTU; dissolved solids 995 mg/L, possibly influenced by oil drilling; 2 tests; measured barium within 95% of nominal; copper, lead and zinc reported <10, <70 and <50 µg/L
57 Embarras River; turbidity 6-70 NTU; EC50 is geometric mean of 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L
58 natural water; Fox River; turbidity 17-26 NTU; EC50 is geometric mean of 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L
59 natural water; Hayes Creek; turbidity 3-11 NTU; EC50 is geometric mean of 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L
60 natural water; Horseshoe Lake; turbidity 11-21 NTU; EC50 is geometric mean of 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L
61 disregarded in previous evaluation; natural water; Illinois River; turbidity 33-105 NTU; 13 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L
62 disregarded in previous evaluation; natural water; LaMoine River; turbidity 14-16 NTU; 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

63 natural water; Lake Michigan; turbidity 0-137 NTU; EC50 is geometric mean of 4 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

64 natural water; Rend Lake; turbidity 29-54 NTU; EC50 is geometric mean of 3 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

65 disregarded in previous evaluation; natural water; Sangamon River; turbidity 54 NTU; 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

66 natural water; Lake Geneva; turbidity 3-4 NTU; EC50 is geometric mean of 3 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

67 natural water; Kankakee River; turbidity 13-16 NTU; EC50 is geometric mean of 3 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

68 natural water; Mississippi River; turbidity 70-109 NTU; EC50 is geometric mean of 3 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

69 disregarded in previous evaluation; natural water; Missouri River; turbidity 38-258 NTU; 3 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

70 natural water; Rock River; turbidity 8-28 NTU; EC50 is geometric mean of 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

71 natural water; Salt River; turbidity 14-246 NTU; EC50 is geometric mean of 3 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

72 natural water; Skunk River; turbidity 57-414 NTU; EC50 is geometric mean of 2 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

73 natural water; Wabash River; turbidity 26-156 NTU; EC50 is geometric mean of 3 tests; measured barium within 95% of nominal, therefore background considered to be low; copper, lead and zinc reported <10, <70 and <50 µg/L

74 plants and water collected from mountain forest streams in the Sudetic Mountains; exposure to 11 different Ba-concentrations between 1 and 250 mg/L; EC50 estimated by non-linear regression of reported effect percentages setting top to 100 and bottom to 0; background concentration of barium not known

Table A2.2. Summary of chronic ecotoxicity studies in freshwater.

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Cyanobacteria																	
Anacystis nidulans	1e7 cells/mL	N	S	Cl2		am	65/60	7.9		7 d	EC10	growth rate	75	N	3	1	Lee & Lustigman (1996)
Anacystis nidulans	1e7 cells/mL	N	S	Cl2		am	65/60	7.9		7 d	EC10	growth rate	52	N	3	2	Lee & Lustigman (1996)
Algae																	
Chlorella sp. 12	2-4e3/mL; lab culture originally from lake	Y	S	Cl2	ag	am	80-90/84	7.2-8.5	27	48 h	EC10	growth	3.5	U	3	3	Golding et al. (2018)
							80-90/0						40	U/F	2	4	Golding et al. (2018)
Nannochloropsis sp.	UTEX# LB 2291	Y	S	Cl2	ag	am				10 d	NOEC	growth rate	≥ 0.37	F	3	5	Theegala et al. (2001)
Pseudokirchneriella subcapitata	UTEX# 1648												≥ 0.37	F	3	6	
Pseudokirchneriella subcapitata	SAG 61.81; 0.5E4 cells/mL	Y	S	Cl2		am	110/98.7	5.8-6.1	22.9	72 h	NOEC	growth rate	≥1.2	F	1	7	ECHA (2018)
													≥30.1	U	1	8	
Scenedesmus quadricauda		N	S	Cl2		nw	214	7.5	24	96 h	NOEC	growth	34	N	3	9	Bringmann & Kühn (1959)
Scenedesmus subspicatus	UTEX# 2594	Y	S	Cl2	ag	am				7 d	NOEC	growth rate	≥ 0.37	F	3	6	Theegala et al. (2001)
Crustacea																	
Austropotamobius pallipes	19-32 mm	Y		Cl2		nw		7	16	30 d	LC50	mortality	43	U	3	10	Boutet & Chaisemartin (1973)

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Ceriodaphnia dubia	neonates	Y	R	CO3		dtw	40/ 7.7	7.9	26± 1	7 d	EC10	reproduction	8.3	U	2	11	Brix et al. (2010)
Daphnia magna	<24 h old	N	R	Cl2	rg	nw	44-53	7.4-8.2	18	21 d	EC10	reproduction	5.3	N	3	12	Biesinger & Christensen (1972)
Orconectes limosus	19-32 mm	Y		Cl2		nw		7	16	30 d	EC50	mortality	61	U	3	10	Boutet & Chaisemartin (1973)
Pisces																	
Danio rerio	embryos	Y	R	Cl2		rw	164-182/ 24	7.2-7.6	23.4 - 26.2	33 d	NOEC	mortality, hatching, growth, deform.	≥1.26	F	2	13	ECHA (2018)
Macrophyta																	
Elodea canadensis		N	S	Cl2						15 d	LC100	mortality	6.6	N	3	14	Bijan & Deschiens (1956)
				NO3									5.2	N	3	14	
Lemna minor	field collected; 20 colonies/ 40 fronds	N	S	Cl2	rg	am		7.5	27 ± 2	96 h	EC10	growth rate	7.6	N	3	15	Wang (1986b)
Lemna minor	field collected; 40 fronds	N	S	Cl2	rg	am		7.6	27 ± 2	96 h	EC10	growth rate	5.5	N	3	16	Wang (1986a)
Lemna minor	15 colonies/ 30 fronds	Y	S	Cl2	rg	am			25-28	96 h	EC10	# fronds	6.2	U	2	17	Wang (1988)
Myriophyllum spicatum	apex, 4 cm	N	S			am	95.9		20	32 d	EC10	root weight	41.2	N	3	18	Stanley (1974)
											EC50	shoot weight	103	N	3	19	
											EC50	root length	113	N	3	19	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
											EC50	shoot length	83.8	N	3	19	
Scapania undulata	field coll. stream 1	N	S	Cl2		nw			14	16 d	EC10	mortality	199	N	3	20	Samecka-Cymerman (1988)
	field coll.; stream 4												168	N	3	20	
	field coll.; stream 6												168	N	3	20	
	field coll.; stream 7												160	N	3	20	
	field coll.; stream 9												199	N	3	20	
	field coll.; stream 10												175	N	3	20	
Scapania undulata	field coll.; stream 12	N	S	Cl2		nw			14	16 d	EC10	mortality	200	N	3	20	Samecka-Cymerman (1988)
	field coll.; stream 13												172	N	3	20	
	field coll.; stream 18												181	N	3	20	
Scapania undulata	field coll. stream 1	N	S	Cl2		nw			14	16 d	EC10	gametophyte length	149	N	3	20	Samecka-Cymerman (1988)
	field coll.; stream 4												44	N	3	20	
	field coll.; stream 6												9.1	N	3	20	
	field coll.; stream 7												28	N	3	20	
	field coll.; stream 9												99	N	3	20	
	field coll.; stream 10												61	N	3	20	
	field coll.; stream 12												130	N	3	20	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
	field coll.; stream 13												42	N	3	20	
	field coll.; stream 18												82	N	3	20	
Scapania undulata	field coll. stream 1	N	S	Cl2		nw			14	16 d	EC10	length lateral branches	33	N	3	20	Samecka-Cymerman (1988)
	field coll.; stream 4												0.18	N	3	20	
	field coll.; stream 6												26	N	3	20	
	field coll.; stream 7												0.63	N	3	20	
	field coll.; stream 9												<1	N	3	20	
	field coll.; stream 10												<1	N	3	20	
	field coll.; stream 12												51	N	3	20	
Scapania undulata	field coll.; stream 13	N	S	Cl2		nw			14	16 d	EC10	length lateral branches	43	N	3	20	Samecka-Cymerman (1988)
	field coll.; stream 18												58	N	3	20	
Scapania undulata	field coll. stream 1	N	S	Cl2		nw			14	16 d	EC10	# lateral branches	0.21	N	3	20	Samecka-Cymerman (1988)
	field coll.; stream 4												48	N	3	20	
	field coll.; stream 6												54	N	3	20	
	field coll.; stream 7												2.2	N	3	20	
	field coll.; stream 9												79	N	3	20	
	field coll.; stream 10												7.4	N	3	20	
	field coll.; stream 12												3.3	N	3	20	

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	CaCO3/ SO4 [mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NU F	Ri	N	Ref
	field coll.; stream 13												21	N	3	20	
	field coll.; stream 18												80	N	3	20	

Notes

1 medium with 1% EDTA; test concentrations 50, 100, 250, 500, 750 and 1000 mg/L; hardness and sulfate calculated by evaluator for test medium D of Kratz & Myers (1955), as this contains EDTA; test duration 21 d, but clear decrease in control growth after 7 d; EC10 estimated as 114 mg/L from a logistic dose-response relationship, using data from digitised graph, most likely expressed as BaCl2

2 medium without EDTA; test concentrations 50, 100, 250, 500, 750 and 1000 mg/L; hardness and sulfate calculated by evaluator for test medium D of Kratz & Myers (1955), as this contains EDTA; test duration 21 d, but clear decrease in control growth after 7 d; EC10 estimated as 79 mg/L from a logistic dose-response relationship, using data from digitised graph, most likely expressed as BaCl2

3 synthetic soft water with sulfate present (84 mg/L); reference toxicant CuSO4; validity criterion used was 1.9 doublings/day in control and copper reference EC50 within internal database limits (2.6 ± 1.6 µg/L) and pH drift <1; analysis in filtered water; precipitation of barium sulfate; speciation calculated with Visual Minteq 3.1; measured dissolved barium 0.073-0.22 mg/L at total concentrations 0.1-100 mg/L, corresponding modelled Ba2+(aq) concentrations were 0.032-0.19 mg/L; EC10 expressed as total barium; no relationship between algal growth and dissolved barium up to total concentration 333 mg/L, but concentration response relationship with total barium indicating that precipitate contributes to toxicity, possibly by indirect effects (smothering, reduction in light); relevance for field situation is not clear

4 synthetic soft water with chloride instead of sulfate; reference toxicant CuSO4 and chloride control; validity criterion used was 1.9 doublings/day in control and copper reference EC50 within internal database limits (2.6 ± 1.6 µg/L) and pH drift <1; analysis in total and filtered water; measured dissolved concentrations represent >96% of total concentrations at 0.01-10000 mg/L; at total concentrations of 0.01-1000 mg/L, >98% of total barium predicted to be present as Ba2+(aq); NOEC of chloride control equivalent to 320 mg Ba/L, indicating that effects are due to barium; concentration-response curves for total and dissoled barium not significantly different; EC10 expressed as total and dissolved barium

5 tapwater with Guillard's F/2 nutrient medium, sterilised with bleach, excess chlorine removed by addition of 4 drops of a commercial chlorine remover, containing sodium thiosulfate and sodium carbonate; 4 test concentrations 0.25-5 mg Ba/L; barium concentrations determined in filtered water and adsorbed on/accumulated in algae; total barium concentrations calculated as sum of both are in line with nominal, but concentrations in filtered water 0.20, 0.20, 0.38 and 0.37 mg/L; no information on medium without algae; slower growth at 1 and 5 mg/L; differences in growth rate not significant; irregular growth pattern, no growth from day 1-3

6 tapwater with Guillard's F/2 nutrient medium, sterilised with bleach, excess chlorine removed by addition of 4 drops of a commercial chlorine remover, containing sodium thiosulfate and sodium carbonate; 4 test concentrations 0.25-5 mg Ba/L; barium concentrations determined in filtered water and adsorbed on/accumulated in algae; total barium concentrations calculated as sum of both are in line with nominal, but concentrations in filtered water 0.20, 0.20, 0.38 and 0.37 mg/L; no information on medium without algae; lowest growth in control, highest growth at 0.25 and 0.5 mg/L; differences in growth rate not significant; irregular growth pattern, no exponential growth in control

7 data from REACH dossier BaCl2/BaCl2.2H2O; test reportedly according to OECD 201, but medium according to Kuhl & Lorenzen (1964), hardness and sulfate calculated from reported composition; test item not specified, but reported calculation from Ba to test item indicates that BaCl2.2H2O is tested; test concentrations 0, 1.0, 2.2, 10, 31.6 and 100 mg test item/L; controls n=6, treatments n=3; analysis at start and end in solutions with algae, total Ba after acidification, dissolved Ba after filtration over 0.45 µm; analysis results reported; inhibition of growth rate max 4.6% at 10 mg/L nominal, 1.1% inhibition at 100 mg/L nominal; NOEC reported as ≥ 1.15 mg/L (geomean of dissolved barium); NOEC ≥1.2 mg/L calculated by evaluator based on reported dissolved barium concentrations

8 data from REACH dossier BaCl2/BaCl2.2H2O; test reportedly according to OECD 201, but medium according to Kuhl & Lorenzen (1964), hardness and sulfate calculated from reported composition; test item not specified, but reported calculation from Ba to test item indicates that BaCl2.2H2O is tested; test concentrations 0, 1.0, 2.2, 10, 31.6 and 100 mg test item/L; controls n=6, treatments n=3; analysis at start and end in solutions with algae, total Ba after acidification, dissolved Ba after filtration over 0.45 µm; analysis results reported; inhibition of growth rate max 4.6% at 10 mg/L, 1.1% inhibition at 100 mg/L, NOEC reported as ≥ 30.1 mg/L (geomean total barium)

9 test in water from Havel river, which is indicated as mesotrophic and moderately affected; hardness calculated from reported German degrees; no information on background concentrations

6 tapwater with Guillard's F/2 nutrient medium, sterilised with bleach, excess chlorine removed by addition of 4 drops of a commercial chlorine remover, containing sodium thiosulfate and sodium carbonate; 4 test concentrations 0.25-5 mg Ba/L; barium concentrations determined in filtered water and adsorbed on/accumulated in algae; total barium concentrations calculated as sum of both are in line with nominal, but concentrations in filtered water 0.20, 0.20, 0.38 and 0.37 mg/L; no information on medium without algae; lowest growth in control, highest growth at 0.25 and 0.5 mg/L; differences in growth rate not significant; irregular growth pattern, no exponential growth in control

10 disregarded in previous evaluation; test duration chronic but only EC50 reported; test based on American guidelines; test water from natural pond; no information on characteristics; concentrations measured with AAS; most likely static

11 standard 7 d test according to US EPA 2002; test concentrations 50-1000 µM Ba2+ (6.9-137.3 mg/L); EC25 reported as 73 µM, EC10 estimated by non-linear regression of reproduction data from digitised figure as 60.79 nM (= 8.3 mg/L); test concentrations were analytically verified, but further information not provided, most likely expressed as total; referred to by Golding et al 2018 as mixture of dissolved and precipitated BaSO4 and BaCO3 because of presumed high sulfate concentration (77 mg/L), but test sulfate concentration is reported as 0.08 mM = 7.7 mg/L

12 natural water from Lake Superior; weekly transfer to new medium; test with food; EC10 calculated from EC50 8.9 mg/L and EC16 5.8 mg/L; previously reported as 2.9 mg/L, calculated as EC16/2; background concentration 8-22 µg Ba/L, 2-20 µg Cr/L, 1-26 µg Al/L, 1-2.7 µg Zn/L, 0.3-3.2 µg Cu/L, 7-20 µg Pb/L; effects of other metals cannot be ruled out

10 disregarded in previous evaluation; test duration chronic but only EC50 reported; test based on American guidelines; test water from natural pond; no information on characteristics; concentrations measured with AAS; most likely static

13 data from REACH dossier BaCl2/BaCl2.2H2O; test according to OECD 210; test concentrations 6.25, 12.5, 25.0, 50.0, and 100 mg test item/L; cloudy white precipitate in stock solution, intense stirring applied when preparing test solutions; analysis on day 0, 7, 14, 16, 28 and 30 of the test period; test water reconstituted water (OECD 203) mixed 1:1 with deionised water and 1% artificial seawater; no significant differences for any parameter; NOEC ≥100 mg/L (nominal), equivalent with ≥61.1 mg BaCl2/L (geomean measured total) and ≥1.91 mg BaCl2/L; endpoint summary in REACH dossier presents equivalent dissolved concentration as 1.26 mg Ba/L, results of analysis not presented in summary; sulfate concentration calculated from OECD 203, taking 1:1 dilution with deionised water into account

14 plant together with 12 snails and one fish, mortality at 1 to 100000; assumed that this refers to 1 g/100 L

14 plant together with 12 snails and one fish, mortality at 1 to 100000; assumed that this refers to 1 g/100 L

15 test in algal nutrient solution, characteristics unknown; medium prepared from deionised water previously kept in sunlight or fluorescent light for >7 d because initial toxicity was observed in control water; author reports EC50 26 mg/L; EC10 for specific growth rate of 7.6 mg/L was calculated by evaluator according to OECD 221, using data on frond number increase read from digitised graph; doubling time in control 2.6 d, current validity criterion of OECD 221 is 2.5 or less; barium compound not given, but next study indicates that BaCl2 was tested

16 Lemna collected from unpolluted groundwater recharge pit; 4 replicates; medium was deionised water with plant nutrients; EC10 based on non linear regression of data read from digitised graph by Van Vlaardingen et al 2005, data most likely based on same experiment as previous study

17 double strength algal medium, composition could not be retrieved; concentrations between 5.5 and 200 mg/L; # fronds in control 65 after 96 h, equivalent to daily growth rate of 0.19, which is lower than specified in current OECD 221; recovery of barium concentrations 95% of nominal; EC10 is average of 7 tests, obtained by Van Vlaardingen et al 2005 using non-linear regression of datapoints obtained from digitised graph

18 barium compound not given, result presented as Ba2+; hardness calculated from reported concentrations of Ca and Mg; according to materials and methods, three incubations were performed: 1) with toxicant added to soil substrate, 2) with toxicant added to water but soil substrate present, 3) with toxicant added to water and ferric silicate present as substrate; it is not fully clear to which treatment the results refer, but abstract suggests that it is the treatment with inert substrate; ratio of EC90 and EC50 is 34, EC90 is 1401 mg/L; EC10 calculated from EC90 and EC50

19 barium compound not given; hardness calculated from reported concentrations of Ca and Mg; according to materials and methods, three incubations were performed: with toxicant added to soil substrate, with toxicant added to water but soil substrate present, with toxicant added to water and ferric silicate present as substrate, but it is not clear to which treatment the results refer
19 barium compound not given; hardness calculated from reported concentrations of Ca and Mg; according to materials and methods, three incubations were performed: with toxicant added to soil substrate, with toxicant added to water but soil substrate present, with toxicant added to water and ferric silicate present as substrate, but it is not clear to which treatment the results refer
19 barium compound not given; hardness calculated from reported concentrations of Ca and Mg; according to materials and methods, three incubations were performed: with toxicant added to soil substrate, with toxicant added to water but soil substrate present, with toxicant added to water and ferric silicate present as substrate, but it is not clear to which treatment the results refer
20 plants and water collected from mountain forest streams in the Sudetic Mountains; exposure to 11 different Ba-concentrations between 1 and 250 mg/L; EC10 estimated by non-linear regression of reported effect percentages setting top to 100 and bottom to 0; background concentration of barium not known, variation in Ba accumulation between locations indicates different background levels
20 plants and water collected from mountain forest streams in the Sudetic Mountains; exposure to 11 different Ba-concentrations between 1 and 250 mg/L; EC10 estimated by non-linear regression of reported effect percentages setting top to 100 and bottom to 0; background concentration of barium not known, variation in Ba accumulation between locations indicates different background levels

Table A2.3. Summary of acute ecotoxicity studies in saltwater.

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	salinity/ SO4 [‰/mg/L]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NUF	Ri	N	Ref
Bacteria																	
Vibrio fischerii		N	S	NO3	>97	am				5-15 min	EC50	luminescence	>52600	N	3	1	Calleja et al. (1994)
Vibrio harveyi		N	S	Cl2		am	2.5‰	7.0	23	1 h	EC50	luminescence	>100	N	3	2	Thomulka et al. (1997)
Crustacea																	
Artemia salina	2-3rd instar	N	S	NO3	>99	am	35‰ 6127		25	24 h	LC50	mortality	4762	N	3	3	Calleja et al. (1993)
Artemia salina	2-3rd instar	N	S	NO3	>97	am	35 ‰ 6127		25	24 h	LC50	mortality	4738	N	3	3	Calleja et al. (1994)
Pisces																	
Cyprinodon variegatus	14-28 d; 8-15 mm	N	S		>80	nsw	10-31‰		25-31	96 h	EC50	mortality	>500	N	3	4	Heitmuller et al. (1981)
Fundulus heteroclitus				Cl2		nw	7‰ 22‰		20	96 h	LC50	mortality	>1000	N	3	5	Dorfman (1977)

Notes
1 disregarded in previous evaluation; standard test according to Microtox protocol; testwater synthetic seawater, no further information; EC50 reported as >383000 μmol/L
2 disregarded in previous evaluation; value is reported to be cited from Thomulka et al (1993), but is not in accordance with the cited source
3 standard testkit Artoxkit; test in synthetic seawater; details on test methods from Calleja & Persoone 1992; sulfate calculated from reported medium composition (9.06 g/L Na2SO4); reported logEC50 4.54 in μmol/L as bariumnitrate
3 standard testkit Artoxkit; test in synthetic seawater; details on test methods from Calleja & Persoone 1992; sulfate calculated from reported medium composition (9.06 g/L Na2SO4); EC50 reported as 34500 μmol/L
4 disregarded in previous evaluation; barium compound unknown; test in filtered seawater
5 disregarded in previous evaluation; test in natural water, diluted with aged tap water to obtain salinity; no information on water characteristics; not clear if expressed on the basis of BaCl2 or barium
5 disregarded in previous evaluation; test in natural water, diluted with aged tap water to obtain salinity; no information on water characteristics; not clear if expressed on the basis of BaCl2 or barium

Table A2.4. Summary of chronic ecotoxicity studies in saltwater.

Species	Species properties	A	Test type	Test subst.	Pur. [%]	WT	salinity [‰]	pH	T [°C]	Exp. time	Crit.	Effect	Value Ba [mg/L]	NU F	Ri	N	Ref
Crustacea																	
Cancer anthonyi	embryos, 4-lobed stage	N	R	Cl2	ag	sw	34	7.8	20	7 d	EC10	mortality	50.0	N	3	1	MacDonald et al. (1988)
												hatching	12.1	N	3	2	
				SO4								mortality	228	N	3	3	
												hatching	85.9	N	3	4	
Mollusca																	
Mytilus californianus	embryos,20 hpf	Y	S	Ac		sw	33	7.8	15	48 h	NOEC	develop-ment	0.100	F	2	5	Spangenberg & Cherr (1996)
	embryos, 0 hpf								15	48 h	EC10		0.288	F	2	6	
	embryos, 20 hpf gastrula								15	28 h	EC10		0.308	F	2	7	
	embryos, 32 hpf trochophore								15	16 h	NOEC		≥ 0.5	F	2	8	

Notes
1 filtered seawater; background concentration dissolved barium 13.5 μg/L, test solutions not analysed; 4 test concentrations 1-1000 mg/L; control mortality 5.9%; 5.0 to 50.6% at 1 to 1000 mg/L nominal; significant mortality at 100 and 1000 mg/L; EC10 calculated using control corrected mortality and adding background concentration to nominal test concentrations
2 filtered seawater; background concentration dissolved barium 13.5 μg/L, test solutions not analysed; 4 test concentrations 1-1000 mg/L; control hatching 91.1%; 87.6, 91.9, 60.1 and 44.6% at 1 to 1000 mg/L nominal; significant difference at 100 and 1000 mg/L; EC10 calculated using control corrected hatching rate and adding background concentration to nominal test concentrations
3 disregarded in previous evaluation; filtered seawater; background concentration dissolved barium 13.5 μg/L, test solutions not analysed; 4 test concentrations 1-1000 mg/L; control mortality 5.9%; no mortality at 1 and 100 mg/L, 9.5 and 51.5% at 100 and 1000 mg/L nominal; significant mortality at 1000 mg/L; EC10 calculated using control corrected mortality and adding background concentration to nominal test concentrations; incomplete dissolution reported
4 disregarded in previous evaluation; filtered seawater; background concentration dissolved barium 13.5 μg/L, test solutions not analysed; 4 test concentrations 1-1000 mg/L; control hatching 91.1%; 91.6, 82.6, 83.1 and 46.4% at 1 to 1000 mg/L nominal; significant difference at 1000 mg/L; EC10 calculated using control corrected hatching rate and adding background concentration to nominal test concentrations; incomplete dissolution reported
5 short term test but considered as chronic in view of the life stage considered; filtered seawater (0.2 μm), background concentration 0.03 mg/L (detection limit); concentrations 0.2-20 mg/L; no significant effects on morphology or development of larvae below 0.2 mg/L and above 0.9 mg/L; measured barium concentrations in filtered samples were between 88 and 111% of nominal at 0.2, 0.4 and 0.6 mg/L, dropped to 64 and 5% at 0.8 and 1 mg/L and were <0.03 mg/L at higher test concentrations; results expressed relative to control; NOEC based on nominal because intermediate concentrations were not analysed; no information on control performance
6 short term test but considered as chronic in view of the life stage considered; filtered seawater (0.2 μm), background concentration 0.03 mg/L (detection limit); concentrations 0-500 μg/L; results expressed relative to control, no information on control performance; data read from Figure 4, figures for continous exposure

7 short term test but considered as chronic in view of the life stage considered; filtered seawater (0.2 µm), background concentration 0.03 mg/L (detection limit); concentrations 0-500 µg/L; results expressed relative to control, no information on control performance; exposure from gastrula stage (20-48 hpf); data read from Figure 4; legend does not match with text, based on Fig 3, gastrula stage is affected

8 short term test but considered as chronic in view of the life stage considered; filtered seawater (0.2 µm), background concentration 0.03 mg/L (detection limit); concentrations 0-500 µg/L; results expressed relative to control, no information on control performance; exposure from trochophore stage (32-48 hpf); data read from Figure 4; legend does not match with text, based on Fig 3, trochophore stage is not affected

Erratum RIVM Letter report 2020-0024

Date: 28 January 2021
Report number: 2020-0024
Report title: Environmental quality standards for barium in surface water. Proposal for an update according to the methodology of the Water Framework Directive.

Correction: In the legend to Appendix 2 page 69, the units for Cw and Corg are mistakenly given as ng/L and ng/g. The correct units are Cw µg/L and Corg µg/g.

The correct legend is presented below.

Erratum RIVM briefrapport 2020-0024
Datum: 28 januari 2021
Rapportnummer: 2020-0024
Rapporttitel: Environmental quality standards for barium in surface water. Proposal for an update according to the methodology of the Water Framework Directive.

Correctie: In de legenda van Appendix 2 op pagina 69 staan de eenheden voor Cw en Corg per abuis vermeld als ng/L en ng/g. De juiste eenheden zijn Cw µg/L en Corg µg/g.

De juiste legenda staat hieronder.

Legend to column headings	
WT	water type: fw = freshwater; sw = marine water; bw = brackish water; trans = transitional water
Tax	taxonomic group: pisc = fish; crust = crustacean; moll = mollusc; ins = insects; phyto = phytoplankton; zoo = zooplankton; plank = plankton; plant = plantae
MC	moisture content [%] used for conversion to wet weight based BAF
A	analysis method
Cw	concentration in water [µg/L]; italics indicate unfiltered samples
Corg	concentration in organism [µg/g]
Based on	expression of C_{org}: wwt = wet weight; dwt = dry weight; mu = muscle; wh = whole body/plant; ed = edible; lea = leaf; bl = blades; sh = sheats
log BAF	log bioaccumulation factor based on wet weight [L/kg]
N	notes
Ref	reference

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