

Environmental Chemistry

Metal contaminants of emerging concern in aquatic systems

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Environmental context. There is potential for a range of metals being used in emerging industries to pose a risk if they reach aquatic environments. This is assessed by evaluating known environmental concentrations against available toxicity data. In most instances risks are low with current usage. Areas are identified where additional data are needed.

ABSTRACT

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The environmental concentrations and aquatic toxicity of a range of technology-critical metals comprising platinum group and rare earth group elements, together with gallium, germanium, indium, lithium, niobium, rhenium, tantalum, tellurium and thallium, have been reviewed to determine whether they pose a risk to aquatic ecosystem health. There is a reasonable body of toxicity data for most, but the quality is quite variable, and more data are required. Chronic toxicity EC10 or NOEC values are generally in the low mg L^{-1} range, far higher than the current environmental concentrations in the ng L^{-1} range, meaning that the existing risks to ecosystem health are extremely low. Missing are reliable toxicity data for niobium and tantalum, while confounding results for lanthanum toxicity need to be resolved. There is a likelihood that the currently low concentrations of most of these elements will increase in future years. Whether these concentrations are in bioavailable forms remains to be reliably determined. For most of the elements, measured speciation information is scarce, and unfortunately the thermodynamic data required to calculate their speciation are incomplete. In addition to this problem of uncertain speciation for some of these metals, notably those present in oxidation states of III or higher, there is also a need to explore the links between speciation and bioavailability for these higher valence metals. For circumneutral solutions, the calculated concentrations of the free metal ion tend to be very low for these metals and under such conditions the link between metal speciation and bioavailability is unclear.

Keywords: contaminant, gallium, germanium, indium, lithium, niobium, platinum group elements, rare earth elements, rhenium, tantalum, tellurium, thallium.

Introduction

The term 'emerging contaminant' is usually associated with new synthetic organic molecules that have been recently identified as environmental contaminants. Critical readers of the title of this article may well be wondering how an inorganic contaminant could qualify as 'emerging', given that we are necessarily constrained by the Periodic Table of the Elements. In effect, the use of the term 'emerging' here refers not to the element itself but rather to the new and emerging uses of the element and the concern that these pose in the aquatic environment. To quote from Gulley *et al.* (2018), 'While previous ages of human history can broadly be defined by a single metal or alloy (i.e. Iron Age or Bronze Age), the material compositions of today's emerging technologies encompass almost the entire periodic table and are constantly evolving.'

Over the past 50 years, when the issue of environmental concern for metal contaminants in waters and sediments was raised, those metals of primary concern were typically restricted to cadmium, copper, lead, zinc and mercury. Of secondary concern were chromium, cobalt, nickel and silver, largely related to their mining sources or to their subsequent use in industry. More ubiquitous metals such as iron, manganese and aluminium have also been investigated but only recently has their ecotoxicity been the subject of more detailed evaluations to allow derivation of water quality guideline values.

Recent publications have listed what are termed technology-critical elements (TCEs) (Cobelo-García *et al.* 2015), a term that includes those metals listed in Table 1. With the increasing use of these metals, attention is now focusing on the potential environmental impacts of elements that were previously minimally exploited. For the purposes of discussion, the TCEs have been subdivided into platinum group elements, rare earth elements and assorted other elements. An assessment of their environmental impact will require knowledge of their behaviour and fate in aquatic systems. This will include understanding their speciation in

 Table I.
 Some applications of technology-critical elements (adapted from Cobela-García et al. 2015).^A

Metal	Applications
Platinum group elements: Pt, Pd, Rh, Ru, Ir, Os	Assorted uses
Platinum, palladium, rhodium	Catalytic converters, chemotherapy
Platinum	Chemotherapy
Ruthenium, iridium, osmium	Electronics
Rare earth elements: Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu	Assorted uses
Cerium	Catalysts
La, Ce, Pr, Nd, Y, Eu, Gd, Lu, Dy	Ceramics
Neodymium, protoactinium, dysprosium	Magnets
Other elements	
Gallium	Smart phones, integrated circuits, solar cells
Germanium	Fibre optics, photovoltaics
Indium	Conductive thin-film coatings
Lithium	Batteries
Niobium	High-grade structural steel
Rhenium	Jet engines, turbines
Tantalum	Capacitors (automotive, computers, mobile phones)
Tellurium	Solar cells, thermal imaging
Thallium	Contrast agent in clinical screening, high-temperature superconductors

^ANote that the term 'critical' is sometimes used in an economic or geopolitical context, to include elements such as lithium, cobalt and copper for which the worldwide demand is projected to increase dramatically over the next 50 years but for which the known reserves are found only in a limited number of countries. In the present paper, we focus rather on data-poor elements for which the information needed to evaluate their potential environmental impacts is incomplete.

solution. There is a lack of thermodynamic data to input into speciation modelling, unlike the situation for the common metals listed above. Other laboratory or field-based measures of speciation have yet to be fully applied to TCEs. In addition, ecotoxicological studies are needed to better understand the bioavailability and toxicity of TCEs and the potential threats that they might pose to the aquatic environment.

In this review, we have focused on waterborne metals rather than those that are accumulated via dietary sources, noting that there are a number of papers (e.g. Amyot *et al.* 2017; Cardon *et al.* 2019) that cover the trophic transfer of TCEs in some detail, although this route appears to be less critical to the health of aquatic ecosystems than is the case for elements such as mercury and selenium. In the following pages, we first provide a brief overview of the data that would be needed to carry out a prospective ecological risk assessment of the TCEs and then review the available toxicity data and compare these with recent measured data on actual environmental concentrations to assess the current risk that is posed by these contaminants should they enter aquatic ecosystems.

Data needed for the environmental risk assessment of the TCEs

For most waterborne metals, there is good evidence that the free-metal ion concentration or activity is a good predictor of the metal's bioavailability, with due consideration of such toxicity modifying factors as water hardness and pH (Adams *et al.* 2020). To apply this approach to the TCEs, one would need to be able to measure the free metal ion concentration/ activity, or to calculate it using chemical equilibrium software. Unfortunately, as is discussed in the following sections, measured speciation results are very scarce and for many of the TCEs the thermodynamic data needed to calculate their speciation are incomplete.

In addition, the experimental evidence for the importance of the free-metal ion as a bioavailability predictor has been derived almost entirely for divalent cations (Cd^{2+} , Cu^{2+} , Ni²⁺, Pb²⁺, Zn²⁺) and there is good evidence that nonessential elements such as cadmium and lead can masquerade as essential metals and enter living cells in that manner (Bridges and Zalups 2005). However, as indicated in the following sections, many of the TCEs exist in higher oxidation states and little is known about how they enter cells. Additionally, in some cases the calculated free-ion concentration in aqueous solution for these higher oxidation states is vanishingly low - in such cases, does the free metal ion [M^{z+}] remain a useful bioavailability predictor? Indeed, in some cases toxicity may be induced by interaction of a metal at the surface of an epithelial cell surface (i.e. without involving trans-membrane transport). In such cases, the link between metal speciation and metal toxicity remains to be explored in detail.

Finally, the TCEs are also data-poor with respect to their intrinsic toxicity (Le Faucheur *et al.* 2021). This lack of reliable toxicological data reflects in part the recent surge in use of these elements and the accompanying lag time before the necessary toxicological data can be generated. However, another complicating factor is the limited aqueous solubility of many of the TCEs in the common toxicity test exposure media and the resulting limits on the concentration ranges that can be explored with the standard test protocols.

Platinum group elements

The environmental impacts of platinum group elements (PGEs) have been comprehensively reviewed by both Fortin et al. (2011) and Zereini and Wiseman (2015). Mining is a significant localised source of PGEs, as indicated by a limited number of reports of high measured concentrations (Rauch and Fatoki 2015). More widespread sources include their use as automotive catalysts for emission control, while their medical usage (anticancer drugs, implanted medical devices) represents 3-12% of the automotive source (Rauch and Peucker-Ehrenbrink 2015). Particulate emissions eventually reach aquatic systems as documented in the many papers by Rauch and coworkers (e.g. Rauch and Morrison 1999, 2000, 2008; Rauch et al. 2004, 2005). The use of PGEs as automobile catalysts dates back to the 1970s in Europe with adoption in other jurisdictions happening later in the 1980s and 1990s. There is evidence that environmental concentrations are increasing (Fortin et al. 2011).

Environmental concentrations and speciation

Little is known of the routes by which particulate emissions are transformed to soluble ionic, complexed or adsorbed forms in aquatic environments (Fortin *et al.* 2011). Analytical data indicate that aqueous concentrations are normally extremely low ($< 1 \text{ ng L}^{-1}$) and are only elevated as a consequence of anthropogenic activities, e.g. in areas with high vehicular traffic. Sediment concentrations are high in such areas, suggesting that many of the PGEs are transported there, possibly in relatively unavailable forms. A good discussion of the speciation of platinum in natural waters has been provided by Reith *et al.* (2014).

Dissolved platinum concentrations in a pristine Croatian river were found to be as low as 0.03 ng L^{-1} (Padan *et al.* 2020) and in East Asian rivers at a median concentration of 0.10 ng L⁻¹ (Soyol-Erdene and Huh 2012). In freshwaters, platinum is largely present as the Pt(OH)₂⁰ complex, but in estuarine and marine waters, Pt^{IV} becomes dominant, predicted to be largely as PtCl₅(OH)²⁻ (Cobelo-García *et al.* 2013). Dissolved platinum concentrations increased with salinity and in estuarine areas of Tokyo Bay were as high as 7 ng L⁻¹ (Obata *et al.* 2006). Needless to say, detection of

picomolar platinum concentrations has required the development of specialised analytical detection methods (e.g. Obata *et al.* 2006; Padan *et al.* 2020).

Few measurements have been reported for palladium and rhodium in waters, although these too are used in automotive catalysts. Liu et al. (2021) discuss the transport of atmospheric sources of palladium via rainfall leading to dissolved concentrations near 5 ng L^{-1} in receiving waters and decreasing to 2.3 ng L^{-1} in downstream estuarine waters near the city of Haikou in Hainin Province, China, not dissimilar to the concentrations found for platinum. In an earlier report, Hu et al. (2005) reported respective concentrations of 5.2, 4.1 and 1.9 ng L^{-1} for platinum, palladium and rhodium in an unspecified Chinese river's water. In the water column, the concentrations of particle-associated platinum group metals (expressed as ng L^{-1}) are typically lower than the dissolved concentrations (Fortin et al. 2011). Bioaccumulation mostly occurs from waters via dissolved forms although the links with dissolved metal speciation need further investigation (Fortin et al. 2011).

Like platinum, palladium exists as Pd^{II} and Pd^{IV} although in natural waters the former is dominant (Cobelo-Garcia *et al.* 2007). Rhodium is present only as Rh^{III} so its chemistry and adsorptive behaviour will be different.

Aquatic toxicity

There are quite a few reports of aquatic toxicity testing of platinum group metals, although many of these are based only on acute toxicity (as 50% lethal concentration, LC_{50} , values) rather than the chronic 10% effective concentration (EC_{10}) data that are favoured for the development of water quality guideline values, as summarised by Fortin *et al.* (2011) and Sures *et al.* (2015). These and more recent data are shown in Table 2.

Chronic toxicity to the crustacean *Hyalella azteca* in soft water varied in the order Pt > Pd > Rh (Borgmann *et al.* 2005), whereas for *Daphnia magna*, acute toxicity in a similar freshwater followed the order $Pd > Pt \gg Rh$ (Zimmermann *et al.* 2017). For the nematode *Caenorhabditis elegans*, chronic toxicity was significantly greater for palladium than platinum (Schertzinger *et al.* 2017). The order of sensitivity of palladium and platinum could be a function of organism type and the mechanism of toxicity. The oxidation state of these metals could also affect their toxic response, but the oxidation state prevailing under the conditions of the toxicity tests was not always clearly indicated in the publications.

Many of the tests in Table 2 report nominal rather than measured concentrations, so the quoted toxicity values may be in error. In toxicity tests with a freshwater alga, *Chlamydomonas reinhardtii*, losses of metals from test solutions were shown to be a major concern by Roy (2009), with up to 50% loss over 96 h. The data reported by Roy (2009) for the toxicity of palladium to *C. reinhardtii*, revealed a very low IC₅₀ value and a steep dose–response curve from which a

Table 2. Selected toxicity data for platinum group elements.

Metal ^A	Test organism	Test medium ^B	Acute/ chronic	Test duration	Effect	Endpoint	Value (µg L ⁻¹)	Reference
Pt	Hyalella azteca (crustacean)	Soft water (150 mg L ⁻¹)	Chronic	7 days	Mortality	LC ₅₀	220	Borgmann et al. (2005)
Pd	Hyalella azteca (crustacean)	Soft water (150 mg L^{-1})	Chronic	7 days	Mortality	LC ₅₀	570	Borgmann et al. (2005)
Rh ^{III}	Hyalella azteca (crustacean)	Soft water (150 mg L ⁻¹)	Chronic	7 days	Mortality	LC ₅₀	980	Borgmann et al. (2005)
Pt ^{IV}	Daphnia magna (crustacean)	Soft water (45 mg L ⁻¹)	Chronic	21 days	Reproductive impairment	EC16	14	Biesinger and Christensen (1972)
Pt ^{IV}	Daphnia magna (crustacean)	Soft water (45 mg L ⁻¹)	Chronic	21 days	Reproductive impairment	EC ₅₀	520	Biesinger and Christensen (1972)
Pt ^{IV}	Daphnia magna (crustacean)	Hard water (240 mg L ⁻¹)	Acute	48 h	Immobility	EC ₅₀	110	Zimmermann et al. (2017)
Pd ^{II}	Daphnia magna (crustacean)	Hard water (240 mg L ⁻¹)	Acute	48 h	Immobility	EC ₅₀	13	Zimmermann et al. (2017)
Rh ^{III}	Daphnia magna (crustacean)	Hard water (240 mg L ⁻¹)	Acute	48 h	Immobility	EC ₅₀	12 300	Zimmermann et al. (2017)
Pt ^{II}	Caenorhabditis elegans (nematode)	Soft water	Chronic	96 h	Reproduction	EC10	381	Schertzinger et al. (2017)
Pd ^{II}	Caenorhabditis elegans (nematode)	Soft water	Chronic	96 h	Reproduction	LOEC	10	Schertzinger et al. (2017)
Pd ^{II}	Pseudokirchneriella subcapitata (green alga)	Soft water	Chronic	72 h	Growth	LOEC	30	Vannini et al. (2011)
Pd ^{II}	Chlamydomonas reinhardtii (green alga)	Soft water	Chronic	72 h	Cell density	IC ₁₀ C	5.7	Roy (2009)
Pt ^{I∨}	Chlorella kessleri (green algae)	Milli-Q + medium	Chronic	96 h	Growth	IC ₅₀	1890	Fujiwara et al. (2008)
Pd ^{II}	Chlorella kessleri (green algae)	Milli-Q + medium	Chronic	96 h	Growth	IC ₅₀	1420	Fujiwara et al. (2008)
Rh ^{III}	Chlorella kessleri (green algae)	Milli-Q + medium	Chronic	96 h	Growth	IC ₅₀	885	Fujiwara et al. (2008)
Pt ^{I∨}	Cypris subglobosa (ostracod)	Hard water (245 mg L ⁻¹)	Acute	48 h	Mortality	LC ₅₀	95	Khangarot and Das (2009)
Pd ^{IV}	Cypris subglobosa (ostracod)	Hard water (245 mg L ^{-I})	Acute	48 h	Mortality	LC ₅₀	195	Khangarot and Das (2009)
Pt"	Dreissena polymorpha (zebra mussel)	Soft water	Chronic	35 days	Metallothione- in induction	LOEC	0.25	Frank et al. (2008)

^AOxidation state indicated if stated in the reference.

^BHardness value indicated if reported. ^CEstimated from dose–response curve.

low IC_{10} could be estimated. This alga was far more sensitive than *Chlorella kessleri* tested by Fujiwara *et al.* (2008), as shown in Table 2.

From Table 2, the results for palladium indicate that concentrations above $6 \mu g L^{-1}$ might be a concern for some sensitive species, while for platinum, that value might be $10 \ \mu g \ L^{-1}$. There is some evidence that hardness may protect against platinum and palladium toxicity (Fortin et al. 2011), but the data in Table 2 are largely derived for low hardness samples. There were very few data for marine waters, particularly chronic data for sensitive species, and these results have not been tabulated here. Based on these limited data, the overall findings to date are that environmental concentrations in the low ng L⁻¹ range are well below concentrations that are likely to affect sensitive aquatic biota. So saying, it is notable that sub-chronic biomarker responses have been seen in the high ng L^{-1} range. For example, Frank et al. (2008) reported metallothionein induction in the freshwater zebra mussel Dreissena polymorpha following exposure to platinum(II) at a lowest observed effect concentration (LOEC) value of 250 ng L^{-1} . It follows that although a reliably determined water quality guideline value could be as low as $\geq 1 \mu g L^{-1}$, there might be a concern if dissolved platinum metal concentrations increased above 100 ng L^{-1} .

Clearly there is a need for more toxicity testing, with careful quality control, for a range of taxonomic groups and for chronic endpoints. Equally important would be more mechanistic information regarding the uptake pathways exploited by the various platinum group elements.

The overall findings to date are that environmental concentrations are well below concentrations that are likely to affect sensitive aquatic biota. Toxicity data suggest that palladium is more toxic than platinum and rhodium, however, these data are very preliminary and many more results are required before reliable predicted no-effect concentration (PNEC) or water quality guideline values can be determined.

Rare earth elements

Environmental concentrations and speciation

Rare earth elements (REEs) comprise the 15 lanthanide elements: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu, together with yttrium and scandium. These are wellknown constituents of soils and sediments as a consequence of their natural geological abundance, and their weathering and dissolution is the source of their presence in fresh and marine waters. The distributions of lanthanide element concentrations in soils and waters decrease in a log-linear fashion with atomic number, but due to the Oddo–Harkins effect, elements with even atomic numbers are more abundant than adjacent odd numbered elements, forming a saw-tooth pattern (Byrne and Sholkovitz 1996). Well-described anomalies arise for both cerium and europium due to differences in chemical behaviour. A negative anomaly for cerium is thought to be due to oxidation of Ce^{III} to the less soluble Ce^{IV} . A positive europium anomaly arises from the reduction of Eu^{III} to the more mobile Eu^{II} .

While the above behaviour is a function of rare earth mineralogy, distortion of the log-linear distribution can be seen due to anthropogenic impacts. Rare earth elements are increasingly used in consumer products including catalysts, magnets, phosphors and alloys as well as in fertilisers (Yin et al. 2021). The effects of this increased use are seen for example in southern San Francisco Bay, where total dissolved rare earth concentrations have increased relatively uniformly from 1993 (35 ng L^{-1}) to 2013 (201 ng L^{-1}) (Hatie et al. 2016). Since the late 1980s, gadolinium has been increasingly used as a contrast agent in medical imaging, with the result that temporal records of waters near high technology industrial and medical establishments have shown anomalously high and variable dissolved concentrations of gadolinium chelates (up to 1640 ng L^{-1}) (Ebrahimi and Barbieri 2019)). A similar anthropogenic anomaly was seen for effluent waters from a wastewater treatment plant in waters in northern Australia (Lawrence et al. 2006). Such treatment plants are unable to remove the refractory forms of complexed gadolinium, such as gadolinium DTPA (diethylenetriamine pentaacetate) used in medical imaging (Hatje et al. 2016).

Mining activities can accelerate the release of dissolved rare earths to rivers by many orders of magnitude, as shown for rivers in China (Liang *et al.* 2014) (Table 3). As can be seen for sites removed from the mining activities, background concentrations are typically very low, < 0.2 ng L⁻¹. Pristine rivers in Australia had values < 5 ng L⁻¹, similar to those in Japan. The Japanese rivers which emptied into Tokyo Bay showed evidence of colloidal species, excluded using 0.04 µm filtration. Gadolinium concentrations decreased by a factor of up to six further upstream, where concentrations were extremely low. Lower concentrations were also found in Tokyo Bay, approaching those in surface waters of the Atlantic Ocean.

The speciation of rare earth elements has received limited consideration. Most (e.g. La and Gd) exist only in oxidation state (III), whereas elements such as cerium exist in both states (III) and (IV). In solution, in addition to the free ion, complexation takes place with carbonate, hydroxide and phosphate, but the low solubility product of $LaPO_4(s)$ limits the soluble concentrations of phosphate complexes (Khan *et al.* 2017). El-Akl *et al.* (2015) undertook useful laboratory investigations of cerium speciation and found that while at below pH 6, cerium(m) is bound to carbonate and hydroxide, at pH 7, colloidal species, most likely as cerium(m) are dominant.

In addition to these inorganic ligands, the rare earth elements also tend to bind to fulvic and humic acids. This complexation with natural organic matter has been studied in the laboratory, using capillary electrophoresis, fluorescence

Site	La	Ce (µg L ⁻¹)	Gd	Reference
Yellow River, China	0.10	0.22	0.028	Liang et al. (2014)
Kundulun River, China	140	152	7.2	Liang et al. (2014)
Sidaosha River, China	988	1150	763	Liang et al. (2014)
Southern Yellow River, China	0.065	0.135	0.022	Liang et al. (2014)
Amazon River	0.074	0.212	-	Liang et al. (2014)
Pioneer Creek, Qld, Australia	0.0028	0.0028	0.00063	Lawrence et al. (2006)
Pioneer Creek, Qld, Australia	0.0031	0.0043	0.00086	Lawrence et al. (2006)
Lake Drummond, Virginia, USA	0.66	1.78	0.23	Johannesson et al. (2004)
Tone River, Japan ^A	0.0025	0.0034	0.0092	Nozaki et al. (2000)
Tamu River, Japan ^A	0.0047	0.0131	0.0022	Nozaki et al. (2000)
Tokyo Bay, Japan	0.0021	0.0034	0.00025	Nozaki et al. (2000)
Atlantic Ocean (surface)	0.0026	0.0016	0.00064	De Baar et al. (1985)
Atlantic Ocean (1000 m)	0.0049	0.0011	0.0014	De Baar et al. (1985)

Table 3. Environmental concentrations of selected rare earth elements in waters.

 $^{A}0.04\,\mu m$ filtration; all others 0.45 μm filtered.

quenching, ion-exchange or partial ultrafiltration (Stern *et al.* 2007; Leguay *et al.* 2016; Nduwayezu *et al.* 2016). These data have been incorporated into the Windermere Humic Aqueous Model (WHAM VII: Tipping *et al.* 2011), however, there are relatively few actual measurements of REE speciation in natural waters and it is difficult to judge the accuracy of the model output. Marsac *et al.* (2021) provide a useful overview of the capacity of the WHAM VII model to predict REE speciation in synthetic solutions containing natural organic matter and other cations.

Aquatic toxicity

Several studies have reviewed the aquatic toxicity of rare earth elements (Gonzalez *et al.* 2014, 2015; Malhotra *et al.* 2020). While there are considerable data for impacts on biota in freshwaters, studies of marine species are limited. A selection of freshwater toxicity data is presented in Table 4.

The toxicity of lanthanum has been thoroughly reviewed by Herrmann *et al.* (2016) and Rogowska *et al.* (2018). A number of deficiencies in the published data were identified including a failure to adequately describe the test media and the use of nominal rather than measured concentrations. The importance of reporting measured concentrations was highlighted by Weltje *et al.* (2002, 2003), with losses due to adsorption to container surfaces and membrane filters being significant loss pathways.

The need to report measured concentrations is particularly important for toxicity studies with algae. Because lanthanide phosphates are relatively insoluble, the addition of a lanthanide to the test medium may lead to its precipitation as a phosphate with effects on algal growth

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that are due to nutrient limitation, not lanthanide toxicity (Herrmann et al. 2016). Such precipitation reactions will of course also reduce the true lanthanide concentration in the exposure medium. As a consequence, significant variations in endpoint concentrations are seen in reported algal tests. Aharchaou et al. (2020) discussed this point and suggested that a medium free of inorganic phosphates would be desirable to avoid both precipitation and loss of dissolved lanthanides and possible nutrient limitation. Some algae are able to utilise organic sources of phosphorus, and for such species an organophosphate such as glycerol-2phosphate can be used as a phosphorus source (Nys et al. 2014). Alternatively, algae that are able to perform luxury uptake and store the excess phosphate intracellularly can be used for the toxicity test since they are able to grow for several days in the absence of an extracellular source of phosphorus.

Several laboratory studies using microalgae have identified calcium as a competitor with lanthanides that limits their internalisation by algal cells (Yang et al. 2014; El-Akl et al. 2015; Yang and Wilkinson 2018; Aharchaou et al. 2020). In simple test media, acidity also attenuates the uptake of lanthanides, likely due to the proton binding to the membrane transport site and inhibiting the binding and uptake of the lanthanide ion. Complexation of lanthanides by organic ligands would also be expected to limit their bioavailability, and indeed, in laboratory experiments with simple monomeric organic ligands such as malate, iminodiacetate and nitrilotriacetate, this has been demonstrated (Aharchaou et al. 2020). Similarly, the toxicity of the gadolinium-DPTA complex to algae was significantly lower than the toxicity of dissolved inorganic Gd (Gonzalez et al. 2015) (Table 4). However, with natural organic matter

Metal	Test organism	Test medium	Test duration	Effect	End-point	Value (mg L ⁻¹)	Reference
La	Scenedesmus subspicatis (alga)		72 h	Growth	EC10	1.40	Bogers (1995a)
La	Raphidocelis subcapitata (alga)		72 h	Growth	NOEC	0.13	Stauber and Binet (2000)
La	Scenedesmus obliquus (alga)	WC medium	72 h	Growth	NOEC	2.5	Oosterhout and Lürling (2013)
La	Chlorella fusca (alga)	Modified high salt medium	100 h	Growth	EC ₂₀	32	Aharchaou et al. (2020)
La	Daphnia magna (crustacean)	WC medium	14 days	Reproduction	NOEC	1.0	Lürling and Tolman (2010)
La	Ceriodaphnia dubia (crustacean)		7 days	Reproduction	NOEC	0.05	Stauber and Binet (2000)
La	Cyprinus carpio (fish)		21 days		NOEC	0.26	Boger (1995b)
Ce	Chlorella fusca (alga)	Modified high salt medium	100 h	Growth	EC ₂₀	56	Aharchaou et al. (2020)
Ce	Chlamydomonas reinhardtii (alga)	USEPA medium	72 h	Growth	NOEC	2	Taylor et al. (2016)
Ce	Daphnia magna(crustacean)	ISO medium	48 h (acute)	Reproduction	EC ₅₀	0.30	Gonzalez et al. (2015)
Ce	Raphidocelis subcapitata (alga)	ISO medium	72 h	Growth	IC ₁₀	1.31	Gonzalez et al. (2015)
Gd	Raphidocelis subcapitata (alga)	ISO medium	72 h	Growth	IC ₁₀	1.38	Gonzalez et al. (2015)
Gd	Desmodesmus subspicatus (alga)		72 h	Growth	NOEC	4.9	Neubert et al. (2008)
Gd DTPA	Desmodesmus subspicatus (alga)		72 h	Growth	NOEC	>100	Neubert et al. (2008)
Gd	Daphnia magna (crustacean)	ISO medium	48 h (acute)	Reproduction	EC ₅₀	0.69	Gonzalez et al. (2015)
Lu	Daphnia magna (crustacean)	ISO medium	48 h (acute)	Reproduction	EC ₅₀	0.85	Gonzalez et al. (2015)
Lu	Raphidocelis subcapitata (alga)	ISO medium	72 h	Growth	IC ₁₀	1.53	Gonzalez et al. (2015)

Table 4. Selected chronic toxicity data for selected rare earth elements in fresh waters.

(NOM) as the complexing ligand, the limited experimental data are equivocal on this point. For example, uptake of cerium and samarium by *C. reinhardtii* in the presence of NOM was markedly reduced (El-Akl *et al.* 2015; Rowell *et al.* 2018). However, in similar work with lanthanum and a different alga, *Chlorella fusca*, uptake of the lanthanide was enhanced rather than attenuated in the presence of NOM and the EC_{50} value expressed as dissolved lanthanum was lower in the presence of the NOM (Rahal 2018).

Given the relative scarcity of toxicological data for the rare earth elements, as well as the experimental challenges of working with these elements in traditional toxicity testing media, no reliable PNEC or guideline values have yet been derived for lanthanum, or indeed any other rare earths. Herrmann *et al.* (2016) reported a PNEC value for lanthanum of 4 μ g L⁻¹, but this was based on an assessment factor approach rather than the preferred species sensitivity distribution method. More reliable estimates of PNEC values for cerium, gadolinium and lutetium were estimated by Gonzalez *et al.* (2015) as 54, 57 and 5.8 μ g L⁻¹ respectively, leading them to conclude that toxicity increases with atomic number. This certainly was not the case for the alga *Raphidocelis subcapitata* exposed to the same elements (Table 4).

Other elements

Lithium

The move to electric vehicles and associated lithium-ion batteries is creating greatly increased worldwide demands for lithium. As such, it is now considered as an emerging contaminant. Sources include lithium mining and associated tailings, lithium-rich brines and used lithium-containing products, in particular batteries (Aral and Vecchio-Sadus 2008; Bibienne *et al.* 2020).

Environmental concentrations and speciation

Surface water lithium concentrations are typically $< 40 \ \mu g \ L^{-1}$, mostly in the range 1–10 $\mu g \ L^{-1}$ while seawater has 170 $\mu g \ L^{-1}$ (Aral and Vecchio-Sadus 2008). Given its status as a Class A or hard monovalent cation, the speciation of lithium in fresh waters is very simple, similar to that of Na⁺ and K⁺, with the free Li⁺ ion predominating. Similarly, because of its marked tendency to form ionic rather than covalent bonds and its weak affinity for reduced sulfur, its predicted toxicity is low.

Aquatic toxicity

Although relatively little work has been published on the ecotoxicity of lithium, there is no doubt that it is biologically active. Its effects on humans are well documented and it has been used for over 70 years as a mood stabiliser (Bibienne *et al.* 2020). Several comprehensive reviews have captured what little is known about the toxicity of lithium in natural water systems (Kszos and Stewart 2003; Aral and Vecchio-

Sadus 2008) and the general conclusion is that the toxicity of lithium is low, similar to that of other hard cations (Na⁺, K^+ , Mg^{2+} , Ca^{2+}). An important finding was the antagonistic effect of sodium (Kszos et al. 2003). Chronic toxicity tests were conducted using Ceriodaphnia dubia (7-days reproduction), the snail Elimia clavaeformis (feeding rate) and fathead minnow, Pimephales promelas (larval growth). Kszos et al. (2003) reported an IC₂₅ of 0.38 mg Li L⁻¹ for C. dubia reproduction in a low sodium (2.85 mg L^{-1}) control demineralised water, compared to 3.33 mg Li L⁻¹ in a creek water with 17 mg Na L^{-1} , and 100% survival in 40 mg Na L^{-1} water containing at least 4 mg Li L⁻¹. Their tests of sodium antagonism on C. dubia showed that no toxicity was seen when the natural log of the molar ratio of sodium to lithium exceeded 1.63. These findings have important implications as in many natural waters the presence of sodium will be sufficient to prevent lithium toxicity.

The overall verdict for lithium is that it is inherently highly available (negligible complexation by natural ligands) but also intrinsically not very toxic. Realistically, it should not be of environmental concern except in areas where it is being extracted from brines or mined, or possibly in areas where used batteries are being discarded. However, given an anticipated increase in the recycling of lithium from used batteries (Ambrose and Kendall 2020), this endof-life source should decline with time.

Gallium

Gallium is finding extensive use as both gallium arsenide and gallium nitride semiconductors in microelectronics. It occurs as a by-product in the processing of bauxite, where its similar ionic radius leads to it replacing aluminium in the mineral. To a lesser degree, it replaces zinc in the zinc sulfide mineral, sphalerite (Foley *et al.* 2017).

Environmental concentrations and speciation

In uncontaminated fresh waters, gallium is present at extremely low concentrations. In their recent review of gallium geochemistry, Yuan *et al.* (2021) provided a range of 0.07–18 ng Ga L⁻¹ for rivers in the USA; Foley *et al.* (2017) suggested a slightly broader range for world rivers (1–120 ng Ga L⁻¹). Concentrations recorded for thermal waters are higher but still low (2–25 µg L⁻¹). Groundwaters associated with semiconductor manufacturing areas were contaminated up to 40 µg L⁻¹ (Chen 2006). In surface oceanic waters, concentrations are < 3 ng L⁻¹, sourced largely from aeolian transport (Shiller 1998).

Unsurprisingly, the geochemistry of gallium is similar to that of aluminium. In aqueous solution, it forms a series of hydroxo-complexes $(Ga(OH)_n^{(3-n)+})$; as a function of pH, the speciation shifts from Ga^{3+} in very acidic solutions to Ga $(OH)_4^-$ at pH values above 4.5 (Wood and Samson 2006). As the aqueous gallium concentration increases, metastable polynuclear species form, eventually leading to precipitation

Test organism	Test medium	Test duration	Effect	Endpoint	Value (mg L ⁻¹)	Reference
Desmodesmus subspicatus (alga)	OECD growth medium (method 201)	72	Growth	EC ₁₀	0.46	ECHA (2021 <i>a</i>)
Daphnia magna (crustacean)	OECD Method 202	48 h	Mortality	LC ₅₀	15.0	ECHA (2021a)
Macrobrachium nipponense (freshwater shrimp)	Dechlorinated tap water	96 h	Mortality	LC ₅₀	2.8	Yang et al. (2014)
Danio rerio (zebra fish)	Dechlorinated tap	96 h	Mortality	LC ₅₀	9.1	Yang and Chen (2018)
	water			NOEC	4.0	
Rhodeus ocellatus (fish)	Dechlorinated tap	96 h	Mortality	LC ₅₀	10.7	Yang and Chen (2018)
	water			NOEC	6.0	
Nitzschia closterium (alga)	Seawater (32°C)	72 h	Growth	IC ₁₀	0.86	Harford et al. (2011)
Isochrysis galbana (alga)	Seawater (28°C)	72 h	Growth	NOEC	> 6	Trenfield et al. (2015)
Nassarius dorsatus (snail)	Seawater (28°C)	96 h	Larval growth	EC10	3.8	Trenfield et al. (2016)
Coenobita variabilis (crab)	Seawater (28°C)	6 days	Larval development	EC10	6.0	van Dam et <i>al</i> . (2018)
Amphibilanus amphitrite (barnacle)	Seawater (29°C)	96 h	Nauplii transition	EC10	5.1	van Dam et <i>al</i> . (2016)
Acropora tenuis (coral)	Seawater (27°C)	18 h	Metamorphosis	EC10	1.2	Negri et al. (2011)

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of amorphous $Ga(OH)_3(s)$. The influence of these speciation shifts on gallium bioavailability has not been investigated. However, it is known that, in some bacteria, Ga^{III} can compete with Fe^{III} for the same transmembrane transporter, this presumably being a reflection of their very similar ionic radii (0.62 Å for Ga^{III} and 0.62 Å for Fe^{III}); the known antimicrobial effects of gallium have been attributed to this Ga–Fe antagonism (Kaneko *et al.* 2007).

Aquatic toxicity

Selected data for the aquatic toxicity of gallium are shown in Table 5. Overall, gallium exhibits low toxicity in both fresh and marine waters. Of the species tested to date, algae were the most sensitive but with EC_{10} values above 460 µg L⁻¹. Acute tests with *Daphnia magna* in freshwater gave an extremely insensitive LC₅₀ of 15 mg L⁻¹, surely approaching the solubility limit. Yang *et al.* (2014) noted that the order of acute toxicity to the zebrafish *Danio rerio* followed the order Sb^{III} > Ga^{III} > In^{III}.

Given that environmental concentrations of gallium in natural waters are in the ng L^{-1} range, it can be reliably concluded that the current risks from gallium to the health of aquatic biota are insignificant, although this may change if the predicted rapid growth in its use in photovoltaics and clean energy technologies occurs (Foley *et al.* 2017).

Germanium

Germanium is a metalloid that is mainly used in semiconductor applications, with additional applications in the fibre optics and telecommunications sectors. It occurs mainly in zinc sulfide ores (Holl *et al.* 2007) but because its ionic radius is similar to that of silicon, it is also commonly found dispersed in silicate minerals (Rosenberg 2009; Shanks *et al.* 2017). The overall geochemical behaviour of germanium closely resembles that of silicon, to the extent that it is taken up by siliceous organisms and incorporated into the cell wall of diatoms. Although germanium exists largely as Ge^{IV} in the natural environment, divalent forms are produced synthetically and used in industry.

Environmental concentrations and speciation

Germanium has been measured in the concentration range 0.05–0.1 μ g L⁻¹ in freshwaters, where it is predicted to be present as Ge(OH)₄⁰ at pH values below 8 (Rosenberg 2009). In surface oceanic waters, dissolved germanium concentrations have been measured as low as 0.3 ng L⁻¹ (Ellwood and Maher 2003) but averaged over a range of depths values they lay between < 0.07 and 8.3 ng L⁻¹ (Romero-Freire *et al.* 2019). Concentrations were up to 100 μ g L⁻¹ in coal mine waters, especially as a result of its enrichment in coal seams (Holl *et al.* 2007). Coal combustion has been identified as the largest industrial source of germanium emissions to the environment (Shanks *et al.* 2017).

As is the case for other elements in Group 14 (previously Group IVA) (e.g. Sn, Pb), germanium also forms strong covalent bonds to carbon. Provided the number of such covalent bonds does not exceed three, the resulting organo-germanium compounds tend to be soluble in natural waters, with hydroxide groups occupying the remaining coordination positions about the central germanium atom. Some of these organo-germanium compounds are synthesised industrially, but an additional source appears to be natural biomethylation. Methylgermanium and dimethylgermanium have been detected in natural waters, and since there is no known anthropogenic source of these methylated forms, it would appear that they must result from biomethylation (Thayer 2002). Their concentrations in freshwater are much lower than in seawater (where methylated forms account for 70% of dissolved germanium) (Romero-Freire *et al.* 2019). In the ocean, the methylated forms appear to be conservative, showing no change in concentration with depth, which has led biogeochemists to conclude that they do not participate actively in the germanium biogeochemical cycle.

Aquatic toxicity

Inorganic Ge^{IV} is known to enter or leave cells passively through protein-lined pores that allow the neutral solutes to traverse cell membranes (Nodulin 26-like intrinsic channel proteins or 'NIPs') (Pommerrenig *et al.* 2015). However, very few data exist on the aquatic toxicity of germanium. Especially given its limited solubility (Wood and Samson 2006; Rosenberg 2009), toxicity is expected to be low. A very early study by Lewin (1966) on 10 marine diatom species found on average an IC₅₀ value of 0.69 mg Ge L⁻¹ following exposure for 12 days. Testing used GeO₂ dissolved in a NaOH solution and then neutralised. The formation of diatom frustules was inhibited in all but the most-weakly silicified diatom, *Phaeodactylum tricornutum*. The effect of germanium on silicate utilisation was reversed by the addition of more silica.

Given the low concentrations of germanium in natural waters, the risks posed to aquatic biota are likely to be extremely low.

Indium

The principal uses of indium are in electrically conducting thin film coatings on glass, solar cells and in semiconductor materials. It is a trace constituent in many minerals, especially those of tin, and is a major by-product of the refining of zinc ores (Schroll 1998; Jorgenson and George 2005; Shanks *et al.* 2017).

Environmental concentrations and speciation

In river waters, indium concentrations have been reported in the range from 0.003 to 0.05 ng L^{-1} in the Chao Praya River in Thailand compared to somewhat higher concentrations (0.11–1.7 ng L^{-1}) in some Japanese rivers (Nozaki *et al.* 2000). The higher values were attributed to the presence of a medical waste product, In(DTPA)^{2–}. The weathering of sulfidic tailings and the development of acid mine drainage would be expected to favour the mobilisation of indium; White *et al.* (2017) reviewed published values for indium in such drainage and suggested a concentration range from 0.02 to 500 μ g L⁻¹. In contaminated groundwaters, concentrations as high as 20 μ g In L⁻¹ have been reported (Chen 2006). In marine waters, concentrations ranged from 0.006 to 0.5 ng L⁻¹ (Florence *et al.* 1974; Obata *et al.* 2007 and references therein), the highest values being found in surface waters.

Indium exists in both the (I) and (III) oxidation states, the latter being the more stable. Indium is somewhat softer than its congeners in the Periodic Table (Al, Ga) and it does show appreciable affinity for chloride and sulfide, but nevertheless $In(OH)_3^0$ is predicted to be the dominant inorganic form in the pH range 5–9 (Wood and Samson 2006).

Aquatic toxicity

Very few data are available for indium toxicity to aquatic biota and these have been largely limited to acute testing in both fresh and marine waters (Table 6). The Daphnia test of Brun et al. (2019) was extended to 21 days to obtain a chronic endpoint, but specific values were not reported. These data suggest that indium is not particularly toxic, with all endpoints at high mg L^{-1} concentrations. Solubility is a potential limitation at such concentrations, as is the possible formation of transient polynuclear species. Although such species probably do not play an important role in the aqueous transport of indium (Wood and Samson 2006), their presence in toxicity test media may well have a bearing on our ability to determine the toxicity of the metal. Olivares et al. (2016) evaluated indium toxicity to the zebrafish Danio rerio in the presence of citrate (citrate/indium molar ratio of 3.75:1) in an attempt to overcome solubility problems; no mortality was observed at the highest tested concentration (103 mg In L^{-1}). The researchers did not provide any speciation data, but citrate would be expected to complex indium and reduce its bioavailability. Indeed, these results are inconsistent with those of Yang and Chen (2018), who reported toxicity to two fish species at much lower concentrations (Table 6). In this work, indium was marginally more toxic than gallium to D. rerio and R. ocillatus.

In summary, it would appear that indium poses minimal risks to aquatic biota at its current usage rates.

Thallium

Thallium is found in the environment associated with sulfide minerals (Karbowska 2016; Belzile and Chen 2017; Zhuang and Song 2021), entering the environment as a product of mining operations, mineral smelting and coal burning. It has a range of uses, including in electronics and specialty glasses.

Environmental concentrations and speciation

The concentrations of thallium in both marine and freshwaters have been summarised in several publications (Couture *et al.* 2011; Karbowska 2016; Belzile and Chen 2017). In seawater, concentrations range from 1.3 to 20 ng L⁻¹

Test organism	Test medium	Test duration	Effect	Endpoint	Value (mg L ⁻¹)	Reference
Daphnia magna (crustacean)	Artificial Daphnia medium	96 h	Mortality	LC ₅₀	55	Brun et al. (2019)
Danio rerio (zebra fish)	Dechlorinated tap	96 h	Mortality	LC ₅₀	15.4	Yang and Chen (2018)
	water			NOEC	6.0	
Rhodeus ocellatus (fish)	Dechlorinated tap	96 h	Mortality	LC ₅₀	14.0	Yang and Chen (2018)
	water				8.0	
Oreochromis mossambicus (fish)	Freshwater	96 h	Mortality	LC ₅₀	20	Lin and Hwang (1998)
Oreochromis mossambicus (fish)	Freshwater	16 days	Larval growth	EC10	> 20	Lin and Hwang (1998)
Macrobrachium niþþonense (crustacean)	Freshwater	96 h	Mortality	LC ₅₀	6.9	Yang (2014)
Americamysis bahia (crustacean)	Seawater	96 h	Mortality	LC ₅₀	30.5	Onikura et al. (2008)
Brachionus plicatilis (rotifer)	Seawater	24 h	Mortality	LC ₅₀	24	Onikura et al. (2008)
Artemia salina (shrimp)	Seawater	48 h	Mortality	LC ₅₀	51	Onikura et al. (2008)

Table 6. Acute aq	uatic toxicity	data for indium.
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(Belzile and Chen 2017), while in river waters concentrations cover a similar range. Zhuang and Song (2021) also compiled data for contaminated waters, with freshwaters in the 20–50 ng L^{-1} range and coastal waters from 80 to 3500 ng L^{-1} . Concentrations as high as 1000 µg L^{-1} have been reported for rivers near mining areas (Belzile and Chen 2017).

Thallium occurs in the environment in two oxidation states: Tl^I and Tl^{III}. Batley and Florence (1975) were among the first to show that in seawater and some fresh waters, thallium was present as Tl^{III}, contrary to thermodynamic predictions. This dominance was later attributed to a combination of photo-oxidation and microbial oxidation (Twining *et al.* 2003; Li *et al.* 2005).

Chemical equilibrium calculations suggest that thallium(I) is largely present as the free ion in fresh waters, but its affinity for chloride is such that in seawater the monochloro TlCl⁰ complex is predicted to be of similar importance. Thallium(III) would be expected to form hydroxo complexes in aqueous solutions, but there is some disagreement in the literature regarding the relevant thermodynamic constants (Couture *et al.* 2011). Similarly, the trivalent state would be expected to bind to humic and fulvic acids, but the extent of this complexation is also uncertain. Finally, Tl^{I} is subject to microbial oxidation and biomethylation, yielding dimethylthallium, (CH₃)₂Tl⁺, which has been detected in seawater where it accounted for 3–48% of the total dissolved thallium (Belzile and Chen 2017).

Aquatic toxicity

Toxicity data evaluations are complicated by the differing toxicities of Tl^{I} and Tl^{III} . Early studies by Puddu *et al.* (1988) suggested that Tl^{I} exhibited greater toxicity to marine algae than Tl^{III} . This is supported by other more recent toxicity data in Table 7. Ralph and Twiss (2002) showed that based on the modelled free ion concentration, Tl^{3+} was 50 000 times more toxic than Tl^+ to the freshwater alga *Chlorella* sp., although no toxicity values (EC_x) were reported. However, because the Tl^{III} in their toxicity tests was predicted to be almost entirely in the form of TI (OH)₃⁰, supposedly of low bioavailability, the total dissolved thallium concentrations that resulted in comparable reductions in algal growth rates were similar for both oxidation states. They could not, however, eliminate the possibility of Tl^{III} reduction and they recommended that water quality guidelines be based on Tl^{I} .

Toxicity assessment is further complicated by the confounding effects of potassium. There is now considerable evidence that Tl^I, having a similar ionic radius to K⁺, is taken up by organisms via potassium transport channels in the cell membrane (Hassler et al. 2007; Couture et al. 2011). An elegant study by Zhang and Rickaby (2020) demonstrated that differences in phytoplankton responses to thallium could be related to differences in potassium transporters. Cyanobacteria and haptophytes were the least affected by thallium while chlorophytes were the most affected. None were impacted at environmental concentrations < 100 ng Tl L⁻¹. Potassium influences both the uptake and toxicity of thallium. This was demonstrated for Hyalella azteca by Borgmann et al. (1998) and for other biota by Rickwood et al. (2015), who showed that both Tl^I and Tl^{III} toxicities were affected by potassium (Table 7) and also noted an inhibitory effect of Ca^{2+} .

The test species that is most sensitive to thallium appears to be the crustacean, *Daphnia magna*. Nagel *et al.* (2021) used a moderately hard water (containing 3.1 mg K L^{-1}) and

Test organism	Test medium	Test duration	Effect	Endpoint	Value (µg L ⁻¹)	Reference
Raphidocelis subcapitata	M4 exposure medium	72 h	Growth	IC ₂₅	160 (TI ^I)	Rickwood et al. (2015)
(alga) ^A					332 (TI ^{III})	
Raphidocelis subcapitata (alga)	Freshwater	72 h	Growth	IC ₂₅	90 ^E	Pickard et al. (2001)
Chlorella sp. (alga)	Modified Fraquil medium	72 h	Cellular chlorophyll	EC ₂₀	9 ^F	Hassler et al. (2007)
Ceriodaphnia dubia	M4 exposure medium	7 days	No. of	IC ₂₅	160 (TI ^I)	Rickwood et al. (2015)
(crustacean) ⁵			neonates		285 (TI ^{III})	
Ceriodaphnia dubia (crustacean)	Dilute mineral water	7 days	Reproduction	IC ₂₅	100 ^E	Pickard et al. (2001)
Daphnia magna (crustacean)	Moderately hard water	21 days	Growth	NOEC	0.9 (T ^I)	Nagel et al. (2021)
Pimephales promelas (fish)	Dechlorinated municipal	7 days	Larval survival	IC ₂₅	201 (TI ^I)	Rickwood et al. (2015)
	water				159 (TI ^{III})	
Hyalella azteca (amphipod)	Tap water	28 days	Survival	LC ₂₅	10 (TI ^I) ^C	Borgmann et al. (1998)
Lemna gibba (duckweed)	Modified Steinberg medium	7 days	Frond no.	EC10	141 (TI ^I)	Naumann et al. (2007)
Oncorhynchus mykiss (fish)	Dilute mineral water	96 h	Survival	LC ₅₀	4270 ^E	Pickard et al. (2001)
Phaeodactylum tricornutum	Seawater	72 h	Growth	LOEC	57 (TI ^I)	Puddu et al. (1988)
(marine alga)					90 (TI ^{III})	
Dunaliella tertiolecta	Seawater	72 h	Growth	LOECD	33 (TI ^I)	Puddu et al. (1988)
(marine alga)					74 (TI ^{III})	

Table 7.	Selected	aquatic	toxicity	data	for	thallium.

^AValues respectively 35 and 46 μg L^{-1} if K depleted and 189 and 8.3 if Ca depleted. ^BValues respectively 4.6 and 9.8 μg L^{-1} if K depleted and 182 and 226 if Ca depleted.

 $^{C}2.5 \ \mu g \ L^{-1}$ in artificial medium without K.

^DLOEC values converted to IC_{10} by dividing by 2.5.

^EForm of TI not stated.

^FToxicity reduced by added K.

derived a NOEC of $0.9 \,\mu g \, L^{-1}$ for growth. Reproduction was a less sensitive endpoint and the authors were unable to calculate a 21-days LC_{50} , although it lay between 424 (no mortality) and 702 μ g L⁻¹ (100% mortality). We note that there was an order of magnitude gap in concentrations from 0.9 to the next highest concentration of $9 \mu g L^{-1}$. The authors concluded that there are differences in mechanisms of toxicity for different crustacean species (cf. Ceriodaphnia dubia), and between acute and chronic exposures.

In their algal work, Zhang and Rickaby (2020) also determined the subcellular distribution of thallium in the different algal species and noted that it was consistently found largely in the cytosolic fraction. Similar work on juvenile yellow perch (Perca flavescens) collected along a metal contamination gradient in the field, also indicated that hepatic thallium tended to concentrate in the cytosol and that it remained there even after a heat-denaturation step (Caron et al. 2018). However, unlike silver and cadmium, which as expected were bound to metallothionein in the heat-stable fraction, thallium was associated with an

unidentified cytosolic ligand of much lower molecular weight (< 0.12 kDa).

In deriving water quality guideline values, the confounding effects of both potassium and calcium need to be taken into consideration, as well as the differing toxicities of the two oxidation states. Based on the results in Table 7 and the above discussion, depending on the solution chemistry, the toxicity of thallium could be considered comparable to common metal toxicants such as copper and cadmium. There is hence the possibility that waste streams contaminated with thallium could reach concentrations that could affect sensitive biota such as algae. More data are required to better define the behaviour of thallium in natural waters and to permit derivation of water quality guideline values of higher reliability for both oxidation states.

Niobium and Tantalum

Niobium and tantalum are both members of Group 5 (previously Group VA) of the periodic table (along with vanadium)

and as such have very similar physical and chemical properties. In the minerals where they occur (typically oxide and hydroxide minerals), they are found together (Schulz *et al.* 2017). Niobium is mainly used in microalloyed steel but is finding increasing use in superconducting magnets (for magnetic resonance imaging) (Schulz *et al.* 2017). Tantalum is largely used by the electronics industry in capacitors for energy storage and release. Brazil is the largest source of both niobium and tantalum.

Environmental concentrations and speciation

In the environment, both elements exist in the (V) oxidation state. In seawater, niobium is suggested to exist as Nb $(OH)_6^-$ and to a lesser extent Nb(OH)₅, while for tantalum, $Ta(OH)_5$ is said to dominate over $Ta(OH)_6^-$ (Koschinsky and Hein 2003). Measured concentrations of niobium and tantalum in natural waters have been summarised by Firdaus et al. (2008). In river waters, world average concentrations have been reported as 1.7 and $1.1 \text{ ng } L^{-1}$ respectively, with the Uji River in Japan having 7.0 and 0.7 ng L^{-1} respectively. Reported values for coastal seawater were respectively 0.7 and 0.05 ng L^{-1} . A more recent study by Poehle and Koschinsky (2017) examined niobium concentrations in Atlantic and Pacific Ocean waters finding values near 0.3 ng L^{-1} in surface waters, increasing only slightly with depth. There was no evidence of a significant colloidal fraction.

Nb/Ta concentration ratios have been shown to exist in a narrow range in most rocks but have been shown to differ in the order: open ocean seawater > coastal seawater > river water > crustal abundance (Firdaus *et al.* 2008). The authors indicated how these can be used to understand the fate of these elements in the aquatic environment.

Aquatic toxicity

A thorough literature search revealed only one study of the ecotoxicology of niobium and tantalum. This was a study of 7-day mortality of 63 metals to *Hyalella azteca* in both hard and soft waters (Borgmann *et al.* 2005). LC_{50} values for niobium were 26 and 1640 µg L⁻¹ in soft and hard waters respectively, while for tantalum, the respective values were 2 and 1980 µg L⁻¹. Based on this single report, the toxicity of niobium appears significant, at least in soft waters. However, as niobium and tantalum were of minor interest in the Borgmann *et al.* study and in the absence of other data, it is presently difficult to draw conclusions as to the risks posed by these metals, although given their chemical inertness and extremely low aqueous solubilities (Schulz *et al.* 2017), risks could be expected to be low.

Rhenium

Rhenium is an extremely rare metal, being found as a byproduct of copper mining, largely associated with molybdenite (John *et al.* 2017). Chile is the source of more than 50% of rhenium worldwide. Rhenium is mainly used in hightemperature superalloys and in catalysts for the petrochemical industry (John *et al.* 2017).

Environmental concentrations and speciation

Rhenium exists in the (VII) oxidation state as the perrhenate ion ReO_4^- in natural waters. Tagami *et al.* (2006) used an anion exchange resin separation to demonstrate that, in seawater, rhenium was 100% in that form and completely dissolved. They measured concentrations ranging from 6.1 to 7.4 ng L⁻¹ in Japanese coastal waters, similar to the 7.6 ng L⁻¹ reported by Dickson *et al.* (2020) for Atlantic Ocean surface waters. Tagami and Uchida (2008) measured rhenium in 45 Japanese rivers finding concentrations in the range from 0.12 to 8.7 ng L⁻¹ (mean of 0.81 ng L⁻¹). A strong correlation with sulfate concentrations suggested an origin as sedimentary sulfides, such as ReS₂.

Aquatic toxicity

Only one study (Stolte et al. 2015) could be found that had investigated the aquatic toxicity of rhenium. Results were reported for four species using ammonium perrhenate as the test compound. A chronic IC_{50} of $> 280 \text{ mg L}^{-1}$ was measured after only 24 h for growth of the alga Raphidocelis subcapitata in a synthetic soft water culture medium. For the crustacean, Daphnia magna, the acute 48-h LC₅₀ value was > 466 mg L^{-1} . The duckweed *Lemna minor* grown in Steinberg medium for 7 days had an EC_{50} of 78 mg L^{-1} , whereas inhibition of bioluminescence by the marine bacterium Vibrio fischeri gave an EC_{50} of > 2.0 g L⁻¹. Little detail was provided on QA/QC for these tests, but the data as presented indicate that rhenium has extremely low toxicity. Coupled with the extremely low environmental concentrations, this low toxicity suggests that risks to aquatic biota are very low.

Tellurium

Tellurium is another extremely rare metalloid. It is frequently found in association with gold, as well as in porphyry copper and sulfide minerals. Volcanogenic sulfides on the sea floor are a further source of tellurium (Goldfarb *et al.* 2017). Its major uses are in photovoltaic solar cells and in alloys for thermoelectric cooling products (Goldfarb *et al.* 2017; Filella *et al.* 2019).

Environmental concentrations and speciation

Tellurium has a very low crustal abundance and consequently occurs at low environmental concentrations. Its chemistry parallels that of selenium, a fellow member of Group 16 (previously Group VIA) in the periodic table. Thus, it exists in four oxidation states (-II, 0, IV and VI) (Filella *et al.* 2019). Although it is not a biologically essential element, tellurium does form a variety of organo-tellurium compounds where it has replaced sulfur or selenium in the normal biochemical cycle of these essential elements (Ogra 2017).

The concentrations of tellurium in natural waters have been comprehensively reviewed by Belzile and Chen (2015) and by Filella et al. (2019). A number of studies used techniques to separately determine values for Te^{IV} and Te^{VI} in addition to total dissolved tellurium. In surface seawater samples from the South Atlantic Ocean, Lee and Edmond (1985) found Te^{VI} to comprise some 70% of 0.15 ng L^{-1} of total dissolved tellurium. Similar total concentrations have been found by several studies, but there are a few that quote seawater concentrations as high as 29 ng L^{-1} (e.g. Huang and Hu 2008; Najafi et al. 2010), again with over 70% TeVI. River water concentrations were typically below 50 ng L^{-1} total dissolved tellurium, but speciation analyses were rarely carried out (Filella et al. 2019). These authors expressed concern about the reliability of results where pre-concentration was required, especially in the absence of certified reference materials.

Aquatic toxicity

Very few references were found to tellurium toxicity to either freshwater or marine biota. ECHA (2021*b*) reported wonly three results. For the freshwater alga *Raphidocelis subcapitata*, a chronic EC₁₀ value of 2.7 mg Te L⁻¹ was quoted, based on testing of the water-accommodated fraction of tellurium dioxide based on its limited solubility, i.e. a saturated solution of TeO₂ was diluted to provide a range of exposure concentrations. For the crustacean *Daphnia magna*, a 24-h acute immobilisation EC₅₀ was 5.8 mg Te L⁻¹. For the rainbow trout (*Oncorhynchus mykiss*), a 96-h LC₅₀ was > 37 mg Te L⁻¹. These results indicate a low risk of toxicity given that chronic effects are seen at concentrations some six orders of magnitude above natural environmental concentrations.

Conclusions

In the foregoing text, where we have considered individual metals or groups of metals, the recurring themes have included: the limited solubility of many of the higher valence metals; the regrettable use of nominal rather than measured concentrations; the absence of speciation measurements in the toxicity test media; the focus on waterborne metals; and the scarcity of chronic toxicity data covering a full range of taxonomic groups. Clearly, there is a need for better communication between aquatic geochemists and toxicologists, particularly with respect to the design and implementation of toxicity tests for TCEs.

In our review, we have catalogued the concentrations observed in pristine environments and in severely contaminated waters and have compared these concentrations with those that have been shown to cause adverse effects in test organisms. In many cases, the severely contaminated waters have been collected downstream from mines that are extracting metals from sulfidic ores and have mismanaged their pyrite-rich tailings. This leads us to the general observation that for many of the TCEs, the major impact will probably not be from the individual metal finding its way into the receiving environment at the point of use, but rather from the mining activities that are needed to unearth and process the ores from which the TCEs are extracted.

A second general observation is that the previous generation of environmental chemists, who were largely working on divalent cations (Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}), benefitted greatly from the careful work that had been carried out by analytical chemists around the world, establishing stability constants for the complexation reactions of these metals with model ligands. Unfortunately, this type of work has fallen out of favour and very few new data are being generated. For example, the US National Institute of Standards and Technology database of 'Critically Selected Stability Constants of Metal Complexes' was unceremoniously discontinued in 2004. As a result, the thermodynamic data needed to predict the speciation of many of the TCEs are incomplete.

Sediments are an obvious repository for many of the elements being studied here and sediment pore waters may well represent an ecologically significant exposure medium. Further investigation of this pathway is recommended. We also suggest that, as a complement to the monitoring of TCE concentrations in receiving waters, the use of biomonitor organisms should be explored. We are using the term biomonitor in a limited sense, meaning the analysis of sessile, long-lived and widespread organisms to determine whether bioavailable TCE concentrations are in fact increasing in the aquatic environment.

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