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Less-Studied Technology-Critical Elements (Nb, Ta, Ga, In, Ge, Te) in the Marine Environment: Review on Their Concentrations in Water and Organisms

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The development in recent years of new technological and energy-related applications has increased the use and demand of a specific group of trace elements (Technology-Critical Elements, TCEs). Among the TCEs, there are a number of elements (Nb, Ta, Ga, In, Ge, Te) for which their biogeochemical cycles and their ecotoxicology and uptake by biota has been scarcely studied; they are known as Less-Studied TCEs (LSTCEs). Here we present a review on the concentrations of LSTCEs in marine waters and biota. We show that whereas oceanic profiles have been reported for all LSTCEs, and their geochemical behavior is well-constrained for some of them (e.g., Ga, In, Ge), only very few studies are available on the concentrations and behavior of these elements in estuarine and coastal waters which makes impossible the assessment of their status in environmentally impacted coastal areas. In marine biota, despite of the fact that concentrations have been reported in several organisms, information on the factors controlling the LSTCEs uptake or their potential to be biomagnified through the food web is mostly missing. It is therefore encouraged further research in order to have a better assessment on the impact of the uses of these metals on the concentrations of LSTCEs in such sensitive coastal zones, including their concentrations, bioavailability, thresholds for non-lethal endpoints and their capability of biomagnification.

Keywords: technology critical elements, seawater, organisms, concentrations, bioaccumulation

INTRODUCTION

The Earth's crust is composed of a great variety of igneous, metamorphic and sedimentary rocks, mainly dominated by a few elements (e.g., Si, Al, Fe, Ca, Na, K, Mg) and their oxides, comprising approximately 99.7% of the crust (Rudnick and Gao, 2003). The majority of the naturally occurring chemical elements (minor and trace elements) account only for the remaining 0.3%. The deleterious effects of some of the trace elements to living organisms have been well documented and have led to their concentrations in the aquatic environment to be regulated by protocols and directives (i.e., EU Water Framework Directive 2000/60/CE and 2008/56/CE) that determine their appropriate environmental concentrations.

A significant number of trace elements are, however, excluded in these studies. This is due to: (i) their low ambient concentrations, generally below the detection limits of the analytical procedures employed, and (ii) the absence of any significant industrial role in the past, thus having no apparent environmental implications (Cobelo-García et al., 2015). This situation is currently changing, since several of these non-regulated trace elements are now key components in the development of new technologies, including electronic displays, semiconductors, energy–related technologies or telecommunications technology. They are defined as Technology-Critical Elements (TCEs[1]), and include tellurium (Te), germanium (Ge), gallium (Ga), indium (In), niobium (Nb), tantalum (Ta), the platinum group elements (PGEs: Pt, Pd, Rh, Os, Ir, Ru) and the rare earth elements (REEs: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu). The extent of the environmental impact of the increasing anthropogenic use of these technology–critical elements needs therefore to be further assessed. Among the TCEs, the group of the less-studied TCEs (LSTCEs) – comprising Te, Ge, Ga, In, Nb and Ta – was defined by Filella and Rodríguez-Murillo (2017) for those TCEs for which, from an environmental perspective, have been less studied than the REEs or PGEs. A major reason for this scarcity in environmental studies of LSTCEs relies in the fact that their analytical determination is still challenging (e.g., Filella and Rodushkin, 2018).

Here we present a review on the available information existing to date on the concentrations of the LSTCEs in the marine environment, specifically in the water column and marine organisms. Based on the data collected, we provide an evaluation of the current gaps in our knowledge of these elements in marine systems and indicate directions for future research.

OCCURRENCE IN NATURE AND ANTHROPOGENIC APPLICATIONS

Niobium and Tantalum

Niobium and Ta are metals belonging to the Group 5 of the Periodic Table of Elements, and together with the adjacent metals Zr, Hf, Mo and W are known as 'high field strength elements' (HFSE; Rudnick and Gao, 2003). Both elements form compounds with a variety of oxidation states, but the + 5 is the only environmentally relevant (Filella, 2017). Niobium has only one natural stable isotope (^{93}Nb), but several artificial unstable isotopes that are found in radioactive wastes such as ^{95}Nb (35 days half-life) and ^{94}Nb (20,300 years half-life) (Astrom et al., 2008). Tantalum has two natural isotopes, the stable ^{181}Ta (99.988%) and the metastable ^{180}Ta (0.012%) (Filella, 2017). According to Rudnick and Gao (2003), the average concentrations of Nb and Ta in the upper continental crust are 12 and 0.9 μg g^{-1}, respectively. Niobium and Ta are considered as chemical twins due to their similar chemical properties (i.e., ionic charge and radius) generating a coherent behavior during magmatic differentiation; as a results, the Nb/Ta ratios are

expected to be constant and of chondritic value ($\sim$17) in mantle and mantle-derived rocks (Hui et al., 2011; Niu, 2012). However, several studies have observed a large Nb/Ta fractionation in rocks from the world ocean floor; the causes for such unexpected fractionation are still under debate (Niu, 2012). The strongest fractionation observed for the Nb/Ta occurs in the aquatic environment, particularly in seawater; in general, the Nb/Ta ratios increase in the following order: continental crust < river water < coastal water < open ocean (Firdaus et al., 2008).

These elements are usually found together in nature, with coltan (short for columbite-tantalites) as the most commonly known ore of Nb–Ta. The world mine production for these metals has significantly increased in the past two decades, currently accounting for roughly 60,000 (Nb) and 1,200 (Ta) tons per year (Filella and Rodríguez-Murillo, 2017). Both elements are used in a variety of high-tech applications, including high-grade structural steel and superalloys (e.g., aerospace industry), and capacitors in several electronic devices (e.g., medical appliances, portable electronics, flat-screen TVs, etc.; Cobelo-García et al., 2015; Filella, 2017).

Gallium and Indium

Gallium and In are close neighbors in the periodic table and both have the + 3 as their only oxidation state in the environment. They have two natural isotopes each, ^{69}Ga (60.11%) and ^{71}Ga (39.89%), and ^{115}In (95.72%) and ^{113}In (4.28%). Their typical concentrations in the upper continental crust are 17.5 (Ga) and 0.056 (In) μg/g (Rudnick and Gao, 2003).

The use of Ga in semiconductors has made it a high-tech metal in the past decades. The two main application fields are integrated circuits and optoelectronic devices. The most commonly used Ga compound is gallium-arsenide (GaAs), followed by gallium-nitride (GaN); other compounds (e.g., gallium-antimonide – GaSb – and gallium-phosphide – GaP) are used in much smaller amounts. By mid-2010's, the global Ga consumption was around 285 t, representing a 70% increase compared to late 2000's, and an increasing demand is foreseeing during the coming years (Rongguo et al., 2016). The In production by mid-2010's was estimated to be around 1,500 t, being the liquid crystal display (LCD) industry in the manufacturing of flat-panel, touch-screen, and plasma displays for televisions, computers, and handheld electronic devices the main In application (>50% of the total consumption) in the form of ITO (Indium Tin Oxide). By 2020, the In demand is expected to increase over 2000 t (Lokanc et al., 2015).

Germanium

Germanium (Ge) has 5 naturally occurring isotopes: ^{70}Ge (20.8%), ^{72}Ge (27.5%), ^{73}Ge (7.7%), ^{74}Ge (36.3%), and ^{76}Ge (7.6%). This element shows a similar geochemical behavior to that of Si, as it has similar electronic configuration and ionic radii (Lewis et al., 1988), but unlike Si it has no known essential function for organisms (Höll et al., 2007). It has an abundance in the upper continental crust of $\sim$1.4 μg/g (Rudnick and Gao, 2003), and the common oxidation state in natural systems is +4, forming at natural pHs in solution the hydroxide Ge(OH)$_4$ as its main species.

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Germanium is used in fiber-optic systems, infrared optics and in electronics and solar electric applications. It is mainly obtained as a by-product during Zn mining and production; by mid-1990's, the Ge world production was ∼60 tons per year, and has increased since then to reach around 160 tons per year by 2015 (Filella and Rodríguez-Murillo, 2017).

Tellurium

Tellurium has eight natural isotopes (^{120}Te, ^{122}Te, ^{123}Te, ^{124}Te, ^{125}Te, ^{126}Te, ^{128}Te, ^{130}Te), the most abundant being ^{130}Te (34.1%) and ^{128}Te (31.7%). Tellurium (Te) belongs to the chalcogen group, which also includes O, S and Se. Unlike the other chalcogen elements, Te has not any known biological role (Nolan et al., 1991; Belzile and Chen, 2015). Te can exist in nature in various redox states: telluride (−2), elemental Te (0), tellurite (+ 4) and tellurate (+ 6). Under typical environmental conditions (e.g., oxygen, pH, etc.), the most abundant redox form of Te are Te^{4+} and Te^{6+} (Filella et al., 2019). They exist mainly as oxyanions and/or hydroxides, although their main chemical species are still a matter of controversy (Filella et al., 2019). The classical publications on elemental crustal abundance do not provide values for Te; values given for the Te terrestrial abundance display a range from 2 to 27 ng/g (Filella et al., 2019).

The main use of Te is for the production of cadmium–telluride (CdTe), which is used in semiconductor materials due to its optical and electrical properties especially in solar cells (Ramos-Ruiz et al., 2016). The solar cells industry is estimated to account for 40% of the global Te demand, followed by the thermoelectric production (30%; USGS, 2018). The estimation of the global Te production in 2017 was 410 tons, which is a 3–4 fold increase with respect to two decades ago – this increase being driven by its demand in the photovoltaic and thermoelectric applications (Filella et al., 2019).

CONCENTRATIONS AND BEHAVIOR IN THE MARINE ENVIRONMENT

Concentrations of dissolved Nb in the world's oceans range from ∼1 to 7 pmol/kg (**Table 1**), and from ∼ 0.02 to 0.3 pmol/kg for Ta. Both elements are depleted in surface waters and show a deep water enrichment (**Table 1**; Firdaus et al., 2011, 2018), indicating a removal in the photic zone by carrier phases and bottom water enrichment due to sediment resuspension (Firdaus et al., 2008). Contrary to open ocean waters, higher concentrations of Nb and Ta were observed in surface waters of coastal stations (Andaman Sea and Gulf of Thailand; Firdaus et al., 2018) and decreasing toward deep waters. This was attributed to the dissolution effect of atmospheric particles and riverine inputs (Firdaus et al., 2018).

The main dissolved inorganic forms of Ga and In in seawater are the hydroxylated species $Me(OH)_3^0$ and $Me(OH)_4^-$, as derived from thermodynamic calculations (Byrne et al., 1988). The hydrolysis products of trivalent metals display a significant particle-reactivity in the oceans, thus leading to short residence times (Alibo et al., 1999; Obata et al., 2007). Accordingly, Alibo et al. (1999) found the acid-soluble particulate fraction of In in the Mediterranean to average 47 ± 11% (n = 6), which is typical of other particle-reactive metals as Ce or Th. Thus, their concentrations are generally maintained at low concentrations due to removal from seawater by scavenging onto particles (Alibo et al., 1999). Both elements are geochemically similar to aluminum, although less particle-reactive (Al/Ga and Al/In in seawater are two orders of magnitude smaller than that of shale; Amakawa et al., 1996), and have the potential to provide information on dust input to the surface ocean that complements that obtained using Al as a tracer (Shiller and Bairamadgi, 2006).

Elevated In concentrations (up to 300 pM) compared to open ocean waters were reported for Japanese coastal waters (**Table 1**), especially those close to industrialized ports (Miyazaki et al., 2012). Also, evidence for In contamination was found in several estuaries in Japan (Tama, Ara, and Tone estuaries; Nozaki et al., 2000b); here dissolved In followed a smooth decrease with salinity and was significantly correlated with Gd – which presented a positive anomaly due to its use of Gd-DTPA as a medical agent in magnetic resonance imaging in hospitals. Nozaki et al. (2000b) suggested that In could be anthropogenically derived in a soluble form similar to that of Gd and pointed to the use of $In(DTPA)^{2-}$ as a diagnostic medical agent as a possible explanation. For Ga, concentrations of 11,000–19,000 pM were obtained for a coastal stream in Taiwan receiving wastewater treatment plant discharges impacted by a science park housing semiconductor, electronics and optoelectronic manufacturing (Hsu et al., 2011), and is therefore a potential Ga source to the neighboring coastal waters.

Criteria continuous concentrations (CCC) for Ga and In – defined as the highest concentration of a toxicant to which aquatic organisms can be exposed indefinitely without causing unacceptable effects –were predicted by use of quantitative ion characteristic-activity relationships-species sensitivity distributions (QUICAR-SSD; Mu et al., 2014; Qie et al., 2017); this method, used to predict the biological activity of metal ions, is based on the assumption that similar electronic configurations should have similar functions and therefore several physico-chemical descriptors are applied for such calculations. For In, the calculated CCC of 5 nM (Qie et al., 2017) to 120 nM (Mu et al., 2014) are at least one order of magnitude higher than the highest dissolved In observed in the marine environment (0.3 nM in Japanese coastal waters, see above). In the case of Ga, a predicted CCC of 200 nM was reported (Mu et al., 2014). However, based on chronic toxicity data for several marine species, van Dam et al. (2018) proposed a marine water quality guideline (WQG) for this element of 11.5 μM, i.e., 2 orders of magnitude higher than the value proposed by Mu et al. (2014). In any case, the highest reported Ga concentrations in impacted estuarine-coastal areas (<20 nM; see above) are below both guideline values.

The Ga/In ratios in seawater are in the range of those in shale, indicating a similar chemical reactivity in the oceans, although some fractionation during takes place during scavenging resulting in different vertical profiles (Amakawa et al., 1996). Both Ga and In show a large interoceanic variation, with concentrations in the Atlantic considerably higher than in the Pacific (**Table 1**; Alibo et al., 1999; Shiller and Bairamadgi, 2006). Solubilization of In from aeolian dust – rather than riverine

TABLE 1 | Concentrations (pmol/kg) of dissolved TCEs in natural seawater samples.

Element	Location	Depth	Concentration	References
Niobium	North East Pacific	0–5000 m (range)	2.6–4.2	Sohrin et al., 1998
		0–200 m (average)	3.0 ± 0.3 ($n = 10$)	
		>2000 (average)	3.8 ± 0.1 ($n = 5$)	
	Western North Pacific	0–5000 (range)	4.0–7.2	Firdaus et al., 2008
		0–200 m (average)	4.8 ± 0.5 ($n = 31$)	
		>2000 (average)	6.4 ± 0.4 ($n = 28$)	
	North Atlantic	0–5000 m (range)	0.9–3.1	Firdaus et al., 2018
		0–200 m (average)	1.3 ± 0.2 ($n = 5$)	
		>2000 (average)	2.8 ± 0.2 ($n = 10$)	
Tantalum	North East Pacific	0–5000 m (range)	0.06–0.29	Sohrin et al., 1998
		0–200 m (average)	0.12 ± 0.03 ($n = 7$)	
		>2000 (average)	0.20 ± 0.06 ($n = 5$)	
	Western North Pacific	0–5000 (range)	0.08–0.29	Firdaus et al., 2008
		0–200 m (average)	0.11 ± 0.02 ($n = 31$)	
		>2000 (average)	0.20 ± 0.03 ($n = 28$)	
	North Atlantic	0–5000 m (range)	0.024–0.088	Firdaus et al., 2018
		0–200 m (average)	0.033 ± 0.007 ($n = 5$)	
		>2000 (average)	0.071 ± 0.011 ($n = 10$)	
Indium	Chao Phraya Estuary (Thailand)	Surface (range)	0.03–0.42*	Nozaki et al., 2000a
	Tone, Tama and Ara Estuaries (Japan)	Surface (range)	1.0–14.7*	Nozaki et al., 2000b
	Coastal Waters of Japan	Surface (range)	2–300	Miyazaki et al., 2012
		Surface (average)	25 ± 55 ($n = 38$)	
	Western North Pacific	0–3500 m (range)	0.047–0.101	Amakawa et al., 1996
		0–200 m (average)	0.069 ± 0.031 ($n = 2$)	
		>2000 (average)	0.064 ± 0.003 ($n = 3$)	
	North Atlantic	0–2100 m (range)	0.59–1.62	Alibo et al., 1999
		0–200 m (average)	0.65 ± 0.07 ($n = 3$)	
		>2000 (average)	1.56 ± 0.09 ($n = 2$)	
	Mediterranean Sea	0–2000 m (range)	3.2–4.7	
		0–2000 m (average)	3.8 ± 0.6 ($n = 8$)	
	Eastern Indian Ocean and SE Asian Seas	0–5500 m (range)	0.06–3.4*	Obata et al., 2004
		0–200 m (average)	1.2 ± 0.6* ($n = 30$)	
		>2000 m (average)	1.3 ± 0.6* ($n = 65$)	
	Japan Sea and Sea of Okhotsk	0–3500 m (range)	0.05–0.58*	Obata et al., 2007
		0–200 m (average)	0.27 ± 0.15* ($n = 15$)	
		>2000 m (average)	0.13 ± 0.06* ($n = 19$)	
Gallium	North East Pacific	0–5300 m (range)	2–30	Orians and Bruland, 1988
		0–200 m (average)	9.5 ± 4.7 ($n = 24$)	
		>2000 m (average)	17 ± 7 ($n = 16$)	
	South and Central Atlantic	0–5200 m (range)	6–40	Shiller and Bairamadgi, 2006
		0–200 m (average)	25 ± 6 ($n = 45$)	
		>2000 m (average)	33 ± 4 ($n = 40$)	
	North West Pacific	0–4500 m (range)	3–30	
		0–200 m (average)	14 ± 5 ($n = 44$)	
		>2000 m (average)	22 ± 5 ($n = 8$)	
Germanium[a]	Western Indian	0–5000 m (range)	2–99	Froelich et al., 1989
		0–200 m (average)	7 ± 4 ($n = 24$)	
		>2000 m (average)	92 ± 6 ($n = 26$)	
	North Atlantic	0–5400 m (range)	<4–37	
		0–200 m (average)	<4 ($n = 2$)	
		>2000 m (average)	22 ± 7 ($n = 8$)	
	South Pacific	0–5300 m (range)	5–97	
		0–200 m (average)	8 ± 3 ($n = 6$)	

(Continued)

TABLE 1 | Continued

Element	Location	Depth	Concentration	References
		>2000 m (average)	84 ± 9 (*n* = 23)	
	Northwest Pacific	0–5900 m (range)	5–117	
		0–200 m (average)	7 ± 3 (*n* = 2)	
		>2000 m (average)	107 ± 5 (*n* = 16)	
	Southwest Pacific	0–4100 m (range)	0.7–97	Sutton et al., 2010
		0–200 m (average)	1.6 ± 0.7 (*n* = 20)	
		>2000 m (average)	87 ± 8 (*n* = 9)	
	Atlantic	0–4800 m (range)	1.5–45	
		0–200 m (average)	4 ± 2 (*n* = 18)	
		>2000 m (average)	32 ± 6 (*n* = 15)	
	Southern Ocean	0–4000 m (range)	0.4–106	
		0–200 m (average)	3 ± 2 (*n* = 7)	
		>2000 m (average)	86 ± 13 (*n* = 12)	
Tellurium	Pacific Ocean	0–300 m	1.39 ± 0.19 (*n* = 7)	Yoon et al., 1990
		301–1000 m	1.01 ± 0.10 (*n* = 7)	
		1001–2000 m	0.67 ± 0.12 (*n* = 4)	
		2001–4000 m	0.46 ± 0.08 (*n* = 6)	
	Atlantic Ocean	0–1000 m	1.03 ± 0.12 (*n* = 10)	
		1001–2000 m	0.74 ± 0.03 (*n* = 5)	
		2001–3000 m	0.64 ± 0.05 (*n* = 4)	
		3001–5000 m	0.56 ± 0.04 (*n* = 7)	
	Atlantic Ocean	Surface water	~1.3–1.7	Lee and Edmond, 1985
		>2500 m	~0.5–0.6	

*A filtration through 0.04 μm was reported instead of the more commonly used 0.2 or 0.45 μm. [a]Concentrations refer to inorganic Ge only.

and/or coastal waters – has been suggested as the main source of In to the oceans, and would explain the elevated concentrations observed in the Mediterranean Sea (**Table 1**) due to the higher dust flux in this basin. Aeolian dust deposition also represents the main Ga delivery to the surface ocean at a global scale, although inputs from river plumes may be important in certain coastal areas (e.g., Columbia river plyme; McAlister and Orians, 2012).

In natural waters dissolved Ge is present as inorganic Ge (Ge_i) in the form of $Ge(OH)_4$, monomethyl germanium (MMGe) and dimethylgermanium (DMGe) (Lewis et al., 1988). The geochemical behavior of Ge_i closely resembles that of Si, showing a strong correlation (Froelich et al., 1989; Santosa et al., 1997; Ellwood and Maher, 2003), as they are cycled in seawater by diatoms. However, fractionation between Si and Ge has been observed during uptake by and regeneration from phytoplankton, which may explain the slight positive Ge intercepts seen for the global Ge versus Si relationships (Ellwood and Maher, 2003; Sutton et al., 2010). In estuaries, Ge_i displays a non-conservative behavior, showing both net inputs and removal following the seasonal Si cycle (Andreae et al., 1983; Froelich et al., 1985a,b). Unlike Ge_i, MMGe and DMGe display and apparent stable and inert behavior, producing conservative profiles in estuaries and the ocean (Lewis et al., 1988) in contrast with methylated species for other metals such as As (e.g., monomethylarsonic acid and dimethylarsinic acid) which show maximum concentrations in surface waters (Santosa et al., 1997). Experiments conducted by Lewis et al. (1989) suggested that methylgermanium species are produced on the continents during

methanogenensis and derived to the oceans where they remain unreactive; however, Ge_i enrichment and methylgermanium depletion was observed in marine anoxic waters indicating that anaerobic processes are capable of demethylating marine organogermanium (Lewis et al., 1989).

Ge_i concentrations typically range from 0.5 to 120 pM, with lower concentrations in the surface layers reflecting diatom uptake. For MMGe and DMGe, a global average concentration of 330 ± 15 pM (MMGe) and 120 ± 20 pM (DMGe) has been proposed, and account for more than 70% of total dissolved Ge in seawater (Lewis et al., 1988). In estuaries, conservative behavior of MMGe and DMGE – reflecting their unreactive characteristics – was observed, with low concentrations in the freshwater end-member compared to seawater. For Ge_i, its distribution in estuaries is non-conservative (Froelich et al., 1985a,b) and also showing a similar behavior to Si as observed for the ocean.

A criteria continuous concentrations (CCC; see above) around 1 μM was predicted for Ge in the marine environment (Mu et al., 2014). Concentrations reported for Ge_i in estuaries and coastal areas (Andreae et al., 1983; Froelich et al., 1985a,b) are in the range of those found for the ocean, and are thus several orders of magnitude lower that these quality limits. Elevated Ge concentrations in coastal watersheds were only reported in areas impacted by effluents by the leather industry, which contains high amounts of Ge (Zhang and Zhang, 2007).

The only two studies reporting an oceanic Te profile provided a total dissolved Te ranging from ~0.4 to ~2 pM (**Table 1**),

showing a scavenged-type behavior profile in the water column. The two studies cited in **Table 1** were published in 1985 and 1990 (no other oceanic profiles has been reported since) and, as noted in the extensive review of Filella et al. (2019), their reported concentrations are 2–3 orders of magnitude lower than those provided in more recent studies for seawater. Accordingly, a total Te concentration of 305 pM was given for a coastal water in the English Channel (Biver et al., 2015), with 70% as Te(VI). Concentrations of 85–263 pM were obtained for coastal seawater close to cities in China, with Te(VI) representing 70–87% of total Te (Huang and Hu, 2008). For the Changjiang Estuary and nearby coastal waters, Wu et al. (2014) reported concentrations of Te(IV) ranging from 3 to 60 pM, and from 5 to 330 for Te(VI), observing a predominance of Te(IV) in surface waters and Te(VI) in bottom waters. A similar Te(VI) predominance over Te(IV) was found throughout the water column of the Atlantic and Pacific oceans (Yoon et al., 1990). Te(IV) predominance over Te(VI) was observed at the redox boundary of the Saanich Inlet (Canada) indicating that the reduced form may prevail under oxygen-depleted conditions; however, these inorganic Te forms were not the dominant species in this basin, and accounted only less than 30% of total Te, which suggests the formation of organotellurium species in these waters (Yoon et al., 1990).

CONCENTRATIONS AND UPTAKE BY MARINE ORGANISMS

There are few data on Nb and Ta concentrations in marine organisms, although there is some evidence of a high accumulation coefficient for these elements by zooplankton in aquatic systems (Chebotina et al., 2011). Sánchez-Rodríguez et al. (2001) reported Ta concentrations ranging from 5 to 350 ng/g in different seaweed species collected in Loreto Bay (Gulf of California, Mexico). Using a dissolved Ta concentration in surface coastal waters of ∼0.2 pmol/kg (0.036 ng/kg), results in an enrichment factor (EF) of 10^5–10^7, indicating an elevated accumulation of this element by seaweed. Concentrations of Ta in invertebrates and fishes from coastal zones of Chile representing different climatic zones were reported by Espejo et al. (2018). In macroinvertebrates they found concentrations ranging from 0.17 to 7.8 ng/g, with a median value of 0.51 ng/g ($n = 24$), whereas for fishes ranged from 0.61 to 14.0 ng/g and a median of 2.4 ng/g ($n = 22$). Importantly, they observed a correlation between the Ta concentrations and the trophic levels for each of the coastal areas sampled indicating a Ta biomagnification through the aquatic food webs. In mussels (*Mytilus Galloprovincialis*) cultivated in rafts from the Galician rias (NW Iberian Peninsula), concentrations up to 211 ng/g were obtained, although average values were normally below the detection limit (<8 ng/g; Costas-Rodríguez et al., 2010). In this same study, average Nb concentrations ranged from <6 to 29 ng/g, with values as high as 235 ng/g observed. In the CRM DORM-2 (dog-fish muscle), Engström et al. (2004) provided a concentration of 2.8 ± 0.3 ng/g.

For In, we only found one published study reporting concentrations in marine organisms, namely the marine mussel

tissue CRM NIST2976 (24 ± 5 ng/g; Krishna and Arunachalam, 2004) – probably reflecting the analytical difficulties in its determination and the fact that this metal is commonly used as an internal standard during the analytical determination by ICPMS. The situation is somewhat different for Ga, for which there are several studies reporting concentrations in biota. For example, Costas-Rodríguez et al. (2010) obtained concentrations ranging from 20 to 580 ng/g in mussels (*Mytilus Galloprovincialis*), with average values from 60 (Pontevedra Ria) to 240 ng/g (Vigo Ria). In two species of clams collected in the coastal Ganzirri Lake (Messina, Italy), Di Bella et al. (2013) reported concentrations of 610 ± 370 ng/g (range 380–1500 ng/g) for *Venerupis aurea laeta* and 370 ± 300 ng/g (range 140–880 ng/g) for *Cerastoderma edule glaucum*, with no significant differences in the concentrations between both species. In 32 fish species from the French market, Guérin et al. (2011) obtained an average Ga concentration of 2 ± 1 ng/g, and an average of 7 ± 12 ng/g in other seafood and products ($n = 20$). It is interesting noting that the value obtained by Guérin et al. (2011) for mussels (3 ng/g) is 1–2 orders of magnitude than those obtained from the Galician rias (Costas-Rodríguez et al., 2010); suggesting possible geographical or species-specific reasons explaining such differences in concentrations, although analytical bias cannot be excluded.

In fish from Malaysian coastal waters, Agusa et al. (2005) obtained Ga concentrations ranging from 9 to 469 ng/g in liver, and from <1 to 104 ng/g in muscle; here, the authors observed a strong positive correlation between concentrations in liver and muscle. Gallium concentrations in liver samples of dolphins collected in the Brazilian coast reported by Kunito et al. (2004) were 5 ± 2 ng/g ($n = 20$; *Sotalia guianensis*) and 3 ± 4 ng/g ($n = 23$; *Pontoporia blainvillei*), with no significant differences between both species and between immature and mature specimens. Campbell et al. (2005) analyzed a range of trace elements in a pelagic Arctic marine food web (North water Polynya, Baffin Bay, Canada), including primary organisms (e.g., ice algae), invertebrates, fish (cod), seabirds and mammals (ringed seal); for Ga they observed no relationship in its concentrations with the trophic position indicating that it was not biomagnified or biodiluted through the food web. They found, however, significant correlations of Ga between liver and muscle in ringed seals and seabirds – in accordance with the results given by Agusa et al. (2005) for fish –, indicating that this element is proportionally distributed throughout the body tissues.

Germanium concentrations in fish and seafood from French market ranged from 1 to 5 ng/g (Guérin et al., 2011), with an average value of 2 ± 2 ng/g ($n = 52$). One order of magnitude higher concentration (68 ± 5 ng/g) was reported for the marine mussel tissue CRM NIST2976 (Krishna and Arunachalam, 2004). For Te, Guérin et al. (2011) reported concentrations from 1 to 12 ng/g, with a mean value of 2–3 ng/g ($n = 52$) in fish. These values are in the range of those observed for mussels from the Galician rias, with concentration ranging from <1.4 to 5.9 ng/g (Costas-Rodríguez et al., 2010). Similar concentrations were reported in an historical Te record (1984–2017) in wild oysters from the Gironde Estuary (France); here Gil-Díaz et al. (2019) obtained an average concentration of 2.08 ng/g, with values ranging from

1.33 to 2.89 ng/g with no clear temporal trend unlike other anthropogenically released metals (e.g., Cd, Ag, Pt). These values are within those obtained in wild oysters for the Arcachon Bay (France; 1.18 ± 0.52 ng/g, $n = 20$) or the Bilbao Estuary (Spain; 3.48 ± 1.39 ng/g, $n = 20$) (Gil-Díaz et al., 2019).

Data on Te for two CRMs have been reported; accordingly, Engström et al. (2004) provided a concentration of 1.8 ± 0.1 ng/g for DORM-2 (dog-fish muscle) and Filella et al. (2019) a value of 5.5 ± 0.9 ng/g for BCR-414 (plankton). Tellurium was also analyzed in different tissues of the squid Todarodes pacificus in the Korean East Coast (Waska et al., 2008), with concentrations of ($n = 10$) 0.9 ± 0.6 ng/g in muscle, 2.4 ± 4.1 ng/g in stomach, 0.9 ± 0.1 ng/g in gills and 3.4 ± 2.5 ng/g in hepatopancreas. These results indicate a moderate Te bioaccumulation, with values in the range of 6×10^3 to 2×10^4 (Waska et al., 2008).

CONCLUSION AND FUTURE RESEARCH PRIORITIES

Research on the biogeochemical cycles of the less-studied technology-critical elements (Nb, Ta, Ga, In, Ge, Te) and their ecotoxicology and uptake by biota has been, in general, scarce to date. Therefore the are still important open questions on their environmental behavior and potential impact. The absence of a known biological role for these LSTCEs and the common time-consuming and complicated analytical procedures employed to analyze their trace to ultra-trace concentrations – and the presence of salt normally adds another issue, especially when using spectroscopic techniques – have greatly discouraged marine scientists working on trace elements to include them in their studies. The recent use of these LSTCEs in a number of new technologies – e.g., electronic displays, semiconductors, energy–related technologies or telecommunications technology – has considerably increased the production of these metals at a global scale. Therefore, studies on their biogeochemical behavior and ecotoxicology are expected to increase in the coming years (e.g., Cobelo-García et al., 2015) especially if new analytical procedures, making easier their determination, are developed (e.g., Poehle et al., 2015). Such studies would greatly benefit from the availability of appropriate certified reference materials (in water and biota), which do not exist at present for these elements, in order to guarantee the quality and, therefore, the comparability of the results provided by different authors.

Oceanic profiles have been reported for all the LSTCEs, especially for those that display similar geochemical behavior than 'key' oceanic elements. For example, Ga and In have the potential to provide information on the dust input to the surface ocean complementing that obtained using Al, whereas interest in Ge relies on its close similarity with Si as both are subject to cycling by diatoms. From an environmental perspective it is surprising, however, that only very few studies – especially in the recent years – are available on the concentrations and behavior of LSTCEs in estuarine and coastal waters which makes impossible the assessment of their status in environmentally impacted coastal areas. From the available literature, contamination has been observed in waters close to industrialized areas in Japan (In) and Taiwan (Ga), although their concentrations are still below the predicted WQGs for these elements. In marine biota, despite of the fact that concentrations have been reported in several organisms (with the exception of In), information on the factors controlling the LSTCEs uptake (e.g., metal speciation) or their potential to be biomagnified through the food web is mostly missing; accordingly, only two papers reported a study on the trophic transfer – specifically for Ga and Ta – showing a significant biomagnification for Ta but not for Ga.

A scientific effort is therefore encouraged regarding the determination of LSTCEs in different estuarine and coastal areas under varying degrees of anthropogenic influence in order to provide: (i) a better assessment on the impact of the uses of these metals on the concentrations of LSTCEs in such sensitive zones. (ii) Information on the bioavailability of the different chemical forms (e.g., speciation) of the LSTCEs to marine biota, and the factors controlling such speciation (i.e., pH, salinity). (iii) A determination of concentration thresholds for non-lethal endpoints (e.g., stress markers). (iv) A degree of biomagnification through the aquatic food web in order to evaluate potential long-term effects.

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AR-F and PN made the bibliographic search and the first draft of the manuscript. JS-E and AC-G critically revised the manuscript. AC-G made the final revision and English editing.

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