Biomagnification of Tantalum through Diverse Aquatic Food Webs

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Supporting Information

ABSTRACT: Tantalum (Ta) is a technology-critical element (TCE) that is growing in global demand because of its use in electronic and medical devices, capacitors, aircraft, and hybrid cars. Despite its economic relevance, little is known about its concentrations in aquatic food webs have not been studied. Invertebrates and fishes from coastal marine food webs representing different climatic zones in northwestern Chile, western Chilean Patagonia, and the Antarctic Peninsula were sampled and analyzed for Ta. The trophic level (TL) of species was assessed with nitrogen stable isotopes (δ15N), and carbon stable isotopes (δ13C) were used to trace energy flow in the food webs. Levels of Ta varied among taxa and sites, with the highest values found in fishes (0.53–44.48 ng g−1 dry weight) and the lowest values found in invertebrates (0.11–7.80 ng g−1 dry weight). The values of δ13C ranged from −11.79 to −25.66 ‰. Ta biomagnified in all four aquatic food webs, with slopes of log Ta versus TL ranging from 0.16 to 0.60. This has important implications as little is known about its potential toxicity and there may be increased demand for TCEs such as Ta in the future.

INTRODUCTION

Tantalum (Ta) is a rare transition element that is highly corrosion-resistant and stable at high temperatures,1,2 and it is increasingly used in technology related to renewable energies, electronics, the automotive and aerospace industries, and biomedicine.3,4 World production of Ta has increased over the last 2 decades, although its extraction remains low (ca. 1000 t per year) when compared to other elements.5 Although Australia, Brazil, Canada, Ethiopia and Nigeria have produced Ta, countries such as Burundi, Congo and Rwanda (65% of global production since 2014) have used it to finance illegal military operations during civil wars, dubbing it a “conflict mineral”.5,6 Nonetheless, it is estimated that new uses for Ta will increase global demand and production7 but its environmental concentrations and fate are poorly characterized.7

Published data on Ta levels in the environment are scarce, focusing mainly on mineralogical analysis and then abiotic matrices,7 with only a few reports on Ta in aquatic animals. Ascidians (Styela plicata) from Japanese waters had 100–410 μg g−1dw Ta (dw: dry weight) whereas marine organisms from coastal areas of southern England ranged from 0.009 in mollusks to 2.3 μg g−1dw in crustaceans.8 Chebotina et al.9 reported the bioconcentration of Ta from water to phytoplankton (>103) and zooplankton (>102). Despite evidence of Ta bioaccumulation in aquatic organisms, the factors affecting its concentrations in different species have not been examined.

Metals such as mercury, persistent organic pollutants and organotin compounds are known to biomagnify in diverse aquatic food webs to levels in upper-trophic-level fish that may pose a risk to fish consumers and the fish themselves.10–12 The trophic level (TL) of species is estimated from δ15N and frequently used to provide a measure of the relative trophic position of organisms within food webs.13 Levels of contaminants are regressed against TL to understand whether they biomagnify and these relationships can be compared...
among ecosystems differing in species composition, physical and chemical characteristics, and climatic zones.11,12

There is a lack of knowledge on the concentrations of Ta in biota and whether this element biomagnifies through aquatic food webs.7 This is important to address because of the likely increased use of Ta and the potential risk it may pose from dietary exposures.13 The objectives of the present study were to determine the concentrations of Ta and the relative trophic level of aquatic organisms from marine coastal food webs across three climatic zones in Antarctica and Chile. The results show for the first time that there is an increase in Ta concentrations with increasing trophic level, and that its biomagnification occurred at sites differing in their physical and biological characteristics.

■ MATERIAL AND METHODS

Field Collections. During the austral summer of 2015, four marine ecosystems with different climatic conditions were sampled in the following regions of the southern hemisphere (Figure 1): northwestern coast of Chile (Sector A), with a tropical hyper-desertic climate;14 western Chilean Patagonia (Sector B) with a climate classified as template hyper-oceanic,14 and the Antarctic Peninsula area (Sector C), which is classified as a cold desert.15 In northwestern Chile, samples were obtained from Pan de Azúcar Bay (26°09′ S, 70°40′ W). In Chilean Patagonia, samples were obtained from two sites: the first was off of La Leona Island (44°1′58″ W, 73°7′56″ W) and the second was at the mouth of the Marchant River (44°5′15″ S, 73°5′6″ W). In Antarctica, samples were obtained from Fildes Bay (62°12′ S, 58°58′ W).

Fishes and invertebrates were collected from each of the locations by SCUBA to ensure the collection of the selected species, as well as to minimize any impacts of sampling. At Pan de Azúcar Bay in northwestern Chile, 8 species of macroinvertebrates and 6 species of fishes were collected (N = 61; Table S1). In Chilean Patagonia, 4 species of macroinvertebrates and 3 species of fishes were collected at the mouth of the Marchant River (N = 31), and 4 species of macroinvertebrates and 3 species of fishes were sampled at La Leona Island (N = 28; Table S2). At Fildes Bay in Antarctica, 9 of both macroinvertebrate and fish species were sampled (N = 55; Table S3). Fish were anaesthetized with BZ-20 (Veterquímica), sacrificed by severing the spinal cord, and sampled for muscle tissues. Soft tissues of mollusks were collected and whole bodies of other macroinvertebrates were retained. All...
specimens were stored at −20 °C until processed in the laboratory.

**Laboratory Analyses.** Individual fish muscle and soft invertebrate tissues were freeze-dried until dry masses were constant and then were homogenized into a fine powder using a glass mortar and pestle precleaned with 2% Conrad solution (Merck) for 24 h, washed with deionized water and HCl 1 M and rinsed with distilled water. Subsamples (0.2 g) were placed into 50 mL Teflon beaker with 5 mL of ultrapure nitric acid and heated (at 110 °C) until almost dry (about 3 h). Then 5 mL of ultrapure nitric acid and 1 mL of hydrogen peroxide were added, and the mixture was heated again to near dryness (about 3 h). The residue was dissolved in 5 mL of 1% ultrapure nitric acid, filtered with glass fiber filter (<0.45 μm), and then transferred to a centrifuge tube. This digestion and filtration were repeated four times so to obtain a final volume of 25 mL. Total Ta was determined by mass spectrometry coupled with a plasma inducter (ICP-MS, NexION-350D, PerkinElmer) at the Environmental Health Science Laboratory, Toyo University (Japan).

To ensure the quality of the Ta measurements, a seven-point calibration curve was made and a median response factor used to calculate sample concentrations. The detection limits and quantification limits were 0.0019 and 0.036 ng g$^{-1}$dw respectively for each batch of samples calculated as 3X and 5X the standard deviation of the blanks (n = 12). A certified reference material (CRM) for Ta in biological materials is not available. Instead, a Custom Claritas PPT grade Tantalum for ICP-MS (CLTA9-1BY) by SPEXertificate (n = 12) and Multielement Calibration Standard 5 by PerkinElmer (n = 12) were used. The internal standard was In (stable isotope of Ga) respectively for each batch of samples calculated as 3X and 5X the standard deviation of the blanks (n = 12). All Ta values are expressed on a dw basis.

**Quantification of Stable Isotopes.** Tissues (1 mg) were analyzed for carbon and nitrogen (δ$^{13}$C and δ$^{15}$N) isotope using an elemental mass spectrometer Costech 4010 interfaced with Delta XP at the Stable Isotopes in Nature Laboratory (SINLAB) at the University of New Brunswick (Canada). The stable isotope measurements were reported in delta notation (δ) and in parts per thousand (%). Two reference materials, N-2 (n = 6) and CH-7 (n = 6), both certified by the International Atomic Energy Agency (IAEA) for isotope values were used as well as certified standards of commercially available elements, acetonilide (n = 18) and nicotinamide (n = 18). In addition, three laboratory standards, bovine liver (n = 18), muskellunge muscle (n = 42) and protein (n = 18), were used and they had an average deviation of 0.03% for the long-term values. Replicates were performed of every 10th sample and the accuracy was 0.28 ± 0.29 ng g$^{-1}$ for Ta (n = 54). All Ta values are expressed on a dw basis.

δ$^{15}$N values were adjusted by subtracting the average δ$^{15}$N of primary consumers from each site, thus obtaining δ$^{15}$Nadj values. Raw and lipid-adjusted δ$^{15}$N data were used to ensure organisms were energetically linked, and details are given in Tables S7–S12. Consumer δ$^{15}$N values were also converted to trophic levels (TL) according to the following equation:

$$T_{\text{consumer}} = \frac{(\delta^{15}N_{\text{consumer}} - \delta^{15}N_{\text{baseline}})}{\Delta \delta^{15}N + \lambda}$$  

where, λ is the trophic level of the baseline organism, herein 2 for primary consumers. $T_{\text{consumer}}$ is the trophic level of a given consumer, and $\delta^{15}N_{\text{consumer}}$ and $\delta^{15}N_{\text{baseline}}$ are raw δ$^{15}$N values of a given consumer and the baseline organism for each site (see Tables S7–S9). A trophic discrimination factor for δ$^{15}$N (Δ$^{15}$N) of 3.4‰ was used as in Lavoie et al.11

**Data Analysis.** Levels of Ta were log$_{10}$-transformed to meet the assumptions of normality and biomagnification was examined with linear regressions as in Lavoie et al.11 and Yoshinaga et al.10 using the following equations:

$$\log_{10}[Ta] = b\delta^{15}N_{adj} + a$$ (2)

$$\log_{10}[Ta] = b \text{TL} + a$$ (3)

where b in eq 2 is known as the trophic magnification slope (TMS) and the antilog of the slope in eq 3 as the trophic magnification factor (TMF). Analysis of Covariance (ANCOVA) was used to determine whether Ta biomagnification was significantly different in the four food webs. Statistical analyses were performed using JMP from SAS.

**RESULTS AND DISCUSSION**

The trophic levels of species sampled in northwestern Chile showed TL ranged between 2.21 ± 0.16 and 4.81 ± 0.11; *Crucibulum scutellatum* had the lowest TL and *Hemichthus macrorynchus* had the highest TL. In contrast, in Chilean Patagonia at the Marchant River Mouth *Fissurella* spp. (2.48 ± 0.69) had the lowest trophic level and *Graus nigra* (4.69 ± 0.06) had the highest trophic level. At Leona Island, *Aulacomya ater* (2.21 ± 0.13) and *Pinguipes chilensis* (4.23 ± 0.27) were the species with the lowest and highest TL, respectively. Finally from the Antarctic Peninsula, the TL values ranged from 2 (*Cenmidocarpa verrucosa*) to 4.13 (*Pagodinithia borshchewinikii*). Across all three climatic regions, Ta levels in macroinvertebrates were consistently lower than those in fishes (Tables S4–S6). In macroinvertebrates from the northwestern coast of Chile, the lowest mean Ta level was in sea snails (*Crucibulum scutellatum*, 0.17 ng g$^{-1}$), a benthic grazer, whereas the highest was in sea stars (*Furcipula* spp., 0.83 ng g$^{-1}$), a benthic predator. In fishes, the lowest and highest mean Ta levels were found in *Pinguipes chilensis* (a benthic-pelagic predator, 2.09 ng g$^{-1}$) and *Trachurus symmetricus murphyi* (a pelagic predator, 2.86 ng g$^{-1}$), respectively, and they were 12.3 to 17.6 times higher than the lowest levels found in macroinvertebrates from this location. In western Chilean Patagonia at Marchant River, mean Ta levels ranged from 1.05 ng g$^{-1}$ in the filter-feeding mollusk (*Aulacomya ater*) to 1.51 ng g$^{-1}$ in crabs (*Cancer coronatus*), benthic predators. In fishes, mean Ta was 2.08 ng g$^{-1}$ in *Genypterus chilensis* (a benthic predator) and 2.48 ng g$^{-1}$ in *Eleginops maclovinus* (a benthic-pelagic predator), over 2 times higher than those in mollusks from the same location. Similarly for La Leona Island, the lowest Ta levels were found in macroinvertebrates, and ranged from 0.23 ng g$^{-1}$ in mollusks (*Aulacomya ater*), to 0.37 ng g$^{-1}$ in mollusk (*Concholepas concholepas*), a benthic predator. In fishes from this location, the lowest and highest Ta levels were in *Pinguipes chilensis* (0.61 ng g$^{-1}$) and *Sebastes capensis* (1.84 ng g$^{-1}$), a benthic predator, respectively. Finally, from the Antarctic Peninsula, the lowest and highest mean Ta levels of all macroinvertebrates were in sea urchin (*Arbatus agassizii*, 0.43 ng g$^{-1}$), which is a benthic forager, and starfish (*Odontaster validus*, 7.8 ng g$^{-1}$), a predator. Fishes from Antarctica had the highest Ta of all sites examined herein, with mean levels ranging from 2.23 ng g$^{-1}$ in *Pagodinithia hansoni* to 14.0 ng g$^{-1}$ in *Notothrissa kempfi*, both are benthic predators.
For those taxa collected at several sites, the levels of Ta varied but not consistently across the climatic gradient. More specifically, *Aulacomya ater* had Ta levels at Marchant River Mouth that were 4.5 and 2 times lower than the levels found at nearby La Leona Island and the most northerly site Pan de Azúcar Bay, respectively. In contrast, *Fissurella* spp. had lower Ta levels at Pan de Azúcar Bay (0.31 ng g\(^{-1}\)) than at Marchant River Mouth (1.4 ng g\(^{-1}\)). Finally, *Concholepas concholepas* showed similar Ta levels of 0.26 ng g\(^{-1}\) at Pan de Azúcar Bay and 0.38 ng g\(^{-1}\) at La Leona Island; similarly, *Genypterus chilensis* had Ta levels of 1.83 and 2.08 ng g\(^{-1}\) from La Leona Island and Marchant River Mouth, respectively. Although nothing is known about the dynamics of Ta in organisms and the factors that affect its uptake and storage, these data suggest that site specific factors may be relevant in determining its environmental fate.

It is possible to make only limited comparisons of the Ta levels in marine species from Chile and Antarctica to data from other regions. Ta values in the current study are much lower than those reported in macroinvertebrates from southern England (ranging from 0.1 to 2 ppm dw),\(^9\) and those in the ascidian *Styela plicata* collected off the coast of Japan (between 100 and 410 ppm dw).\(^8\) It was not possible to find other studies on Ta in fishes.

**Trophic Transfer of Ta.** In general, in all the food webs studied here (Tables S7–S9 and Figure S1), fishes had \(\delta^{13}C\) values that were between those of the macroinvertebrates, indicating reliance on both pelagic and benthic energy sources, as observed in temperate lake food webs.\(^{20}\) Ta levels increased with the TL of the organisms, showing biomagnification of this element (Table S13 and Figure S2). The TMS ranged from 0.05 at Marchant River Mouth in Chilean Patagonia to 0.18 at Fildes Bay in Antarctica (Table 1 and Figure 2). The slopes of log Ta versus TL were significantly different across sites (site * TL, \(p < 0.001\)) and translated into TMF values of 2.29 in northwestern Chile, 2.00 and 1.45 at the sites in Chilean Patagonia and 3.98 in Antarctica, indicating that Ta does not consistently biomagnify across sites and that the highest trophic transfer of Ta occurred at the coldest latitude. Indeed, the slope for Antarctica was significantly higher than for all other sites and this may be because these marine food webs are simple and clearly defined on the basis of benthic and pelagic populations,

<table>
<thead>
<tr>
<th>Sector</th>
<th>Location</th>
<th>Slope</th>
<th>Intercept</th>
<th>(R^2)</th>
<th>(p)-value</th>
<th>(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(^a)</td>
<td>Pan de Azúcar Bay</td>
<td>0.36 ± 0.04</td>
<td>−1.50 ± 0.17</td>
<td>0.52</td>
<td>&lt;0.0001</td>
<td>61</td>
</tr>
<tr>
<td>B(^b)</td>
<td>La Leona Island</td>
<td>0.30 ± 0.07</td>
<td>−1.34 ± 0.25</td>
<td>0.39</td>
<td>0.0004</td>
<td>28</td>
</tr>
<tr>
<td>B(^b)</td>
<td>Marchant River Mouth</td>
<td>0.16 ± 0.07</td>
<td>−0.42 ± 0.23</td>
<td>0.15</td>
<td>0.02</td>
<td>34</td>
</tr>
<tr>
<td>C(^b)</td>
<td>Fildes Bay</td>
<td>0.60 ± 0.10</td>
<td>−1.72 ± 0.35</td>
<td>0.39</td>
<td>&lt;0.0001</td>
<td>55</td>
</tr>
</tbody>
</table>

\(^a\)See Figure 2. Letters indicate significant differences among trophic magnification slopes (TMS). \(^b\)A = northwestern coast of Chile; B = western Chilean Patagonia; C = south Shetland Island (Antarctic Peninsula area).
which are strongly coupled with each other. The Ta biomagnification slopes for the food webs of Pan de Azúcar Bay and La Leona Island fell between those of the Marchant River and Antarctica sites and were not statistically different from one another (p = 0.46). In contrast, Marchant River Mouth had the lowest TMF and a slope that was significantly lower than those at all other sites (p < 0.012). The lower biomagnification of Ta may be the result of the large inputs of nutrients and other elements from the river to the coast, suggesting that Ta biomagnification be examined in other diverse food webs to develop a broader understanding of how ecosystem characteristics affect the fate of this element.

There is no published information on Ta toxicity in aquatic animals. In mammals, Ta₂O₅ inhalation can cause bronchitis and interstitial pneumonitis. So far, there is a general consensus that Ta does not play a biological role but it is unclear whether the biomagnification of Ta observed herein poses a risk to upper-trophic-level consumers. This becomes important considering that the production and use of Ta will likely increase with the growing demand for new technologies and, as such, is an issue that needs more investigation.

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