Vanadium and thallium exhibit biodilution in a northern river food web

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Abstract

Trophic transfer of contaminants dictates concentrations and potential toxic effects in top predators, yet biomagnification behaviour of many trace elements is poorly understood. We examined concentrations of vanadium and thallium, two globally-distributed and anthropogenically-enriched elements, in a food web of the Slave River, Northwest Territories, Canada. We found that tissue concentrations of both elements declined with increasing trophic position as measured by $\delta^{15}N$. Slopes of log [element] versus $\delta^{15}N$ regressions were both negative, with a steeper slope for V (-0.369) compared with Tl (-0.099). These slopes correspond to declines of 94% with each step in the food chain for V and 54% with each step in the food chain for Tl. This biodilution behaviour for both elements meant that concentrations in fish were well below values considered to be of concern for the health of fish-eating consumers. Further study of these elements in food webs is needed to allow a fuller understanding of biomagnification patterns across a range of species and systems.

Keywords: Trophic transfer, trace elements, fishes, invertebrates, periphyton, Slave River

Introduction

Biomagnification is a phenomenon whereby concentrations of a compound or element increase along the length of food chains, reaching highest concentrations in top predators. Given the potential for toxic effects to humans and wildlife that occupy high positions on food chains, biomagnification of pollutants is of key interest to scientists and regulators, and this is enshrined in its use as criteria in chemical evaluations alongside criteria for toxicity and persistence (Gobas et al. 2009). Determining biomagnification potential aids in risk assessments for natural and anthropogenically-derived releases of toxicants such as occurs from mine sites and industrial facilities (e.g. Burger 2008).

Trace elements exhibit variable biomagnification behaviour in food webs. While mercury, in its organic form, is known to biomagnify (Lavoie et al. 2013), other elements such as arsenic and lead show clear biodilution, decreasing in concentration with increased trophic position (Campbell et al. 2005a, Cui et al. 2011, Revenga et al. 2012). Elements such as copper, cadmium, selenium and zinc biomagnify in some but not all food chains (Croteau et al. 2005, Cui et al. 2011, Cardwell et al. 2013), in part depending on baseline concentrations, with lower biomagnification associated with higher baseline concentrations (DeForest et al. 2007). For some elements biomagnification behaviour has been examined only rarely and are less commonly included in a typical suite of analytes in inductively-coupled plasma mass spectrometry (Couture et al. 2011). To address this knowledge gap, we chose to examine two understudied but potentially toxicologically-important elements, vanadium (V) and thallium (Tl).

Vanadium is a trace element with a global distribution. The main anthropogenic source to the atmosphere is fossil fuel combustion, and human-caused releases to the environment likely exceed those from natural sources (Schlesinger et al. 2017). In the Slave River of northern Canada, total V concentrations often exceed interim guidelines of 6 ug/L for the protection of aquatic life (BC MOE 2006, Sanderson et al. 2012). However, much of the V carried by the river is bound to particulate matter, and dissolved concentrations (mean = 0.33 ug/L, Sanderson et al. 2012) are at or below values for other rivers worldwide where the range is typically 0.5 to 2.0 ug/L (Shiller and Boyle 1987, Huang et al. 2015). Elevated levels of V are a concern in the oil sands industry in the Athabasca River upstream from the Slave River (Timoney and Lee 2009), where it is leached in high concentrations from recovered coke that is used to treat oil-sands process waters (Schiffer and Liber 2017) and thus future development of the oil sands could increase V concentrations in the river. Prior work on V biomagnification in food webs is scarce and contradictory. Nfon et al. (2009) and Liu et al. (2018) report no significant relationships between [V] and $\delta^{15}N$ as an indicator of trophic position, and Campbell et al. (2005a) found higher concentrations in zooplankton relative to fish. But both Asante et al. (2008) and Ikemoto et al. (2008) report positive relationships between [V] and $\delta^{15}N$ in crustaceans in the East China Sea and the Mekong Delta, respectively, suggesting that V could biomagnify in subsets of the food web.

Thallium is a toxic element present at low concentrations globally (John Peter and Viraraghavan 2005). Anthropogenic sources to the atmosphere include smelting and coal combustion (Belzile and Chen 2017). Waterborne Tl concentrations are elevated in tributaries draining oil sands operations upstream of the Slave River (Kelly et al. 2010) but it is unknown if this element is likely to become a concern in downstream waters, where total concentrations currently average 0.03 ug/L and dissolved concentrations average 0.01 ug/L (Sanderson et al. 2012). Biomagnification of Tl has been little studied. While Ikemoto et al. (2008) found no relationship between [Tl] and $\delta^{15}N$, Gantner et al. (2009) showed that larger Arctic charr with high $\delta^{15}N$ had higher Tl concentrations than smaller charr with low $\delta^{15}N$. Further, Asante et al. (2008, 2010) report a significant positive correlation between [Tl] and $\delta^{15}N$ of fish communities in oceanic waters. These latter findings provide some evidence that Thallium could also bioamagnify.

Here we examine concentrations of V and Tl in large and small fish, invertebrates and periphyton in the Slave River, NWT. We compare these concentrations against stable isotopes of nitrogen, known indicators of trophic position because ^{15}N increases predictably with each step in the food chain (Kidd et al. 1995), a mean increase of 3.4‰ (Post 2002). We conducted these analyses to understand biomagnification behaviour of these elements and to evaluate potential risks for people in this northern river, where fish consumption remains common in the human population and where concerns remain about upstream resource development and potential contamination (Mantyka-Pringle et al. 2017).

Methods

The Slave River drains a 616,400 km^2 basin that is formed by the confluence of the Peace and Athabasca rivers in northern Alberta. Mean annual discharge is 3,414 m^3/s with peak flows in spring associated with snowmelt. The river terminates at Great Slave Lake where it forms the Slave River Delta. Sedimentary records from a delta lake suggest consistent deposition of Tl over the past century, and a slightly increasing V concentration over the same time period (MacDonald et al. 2016). Consumption of fish and other aquatic food sources by the human population along the river remains above national averages (Halseth 2015).

We sampled at two locations in the river, one at Fort Smith, on the Alberta/NWT border, and the other in the Slave River Delta approximately 100 km downstream from Fort Smith (Carr et al. 2017). Sampling for sediment, periphyton, invertebrates and small fish occurred during August 2014, while large fish were collected during June, July and September 2014 and 2015. Periphyton was collected from submerged mud along the river margins in < 1m of water using a small coring device. The surface layer was scraped from this core into plastic bags, sealed and frozen (n = 20). Invertebrates were collected by sweeping with a D-frame kick net along vegetated shorelines and analysed as pooled samples at the family level. For snails, soft tissue was removed and shells were discarded. Although our sample size for isotope analysis was relatively large (n = 14), there was only enough material remaining for V and Tl analysis on a small subset (n = 3, one pooled sample each of corixids, amphipods and gastropods). Small fishes (shiners, *Notropis* spp.) were captured using daytime sets of gill nets with small mesh size (n = 11), and were analysed as skinless white muscle tissue. Large fish were caught with overnight gill net sets (n = 25). Species collected included walleye (*Sander vitreus*, n = 3), northern pike (*Esox lucius*, n = 12) and whitefish (*Coregonis clupeaformis*, n = 10) and these were also analysed as white muscle fillets.

In the laboratory, we oven-dried all samples at 60 ^{o}C prior to analysis. Samples were digested in nitric acid and hydrogen peroxide and analysed by inductively coupled plasma mass spectrometry (Triple Quad 8800, Agilent Technologies). Percent recovery of certified reference materials analysed alongside samples ranged from 86% (TORT-3, lobster hepatopancreas) to 123% (TORT-2, lobster hepatopancreas) for V and between 94% and 103% (1640, water) for Tl. The limit of detection ranged from 0.001 to 0.003 ng/g for both V and Tl.

Our previous work examined mercury biomagnification in this food web by pairing mercury concentrations with stable isotope analyses (Carr et al. 2017). There, we found that many of the large-bodied fishes had isotope ratios indicative of foraging in the lake even though they were caught in the river. Therefore, for this investigation, we selected a subset of samples of large fish that were closely aligned with local riverine food sources. This ensured that we were representing trace element biomagnification in a well-defined food web (c.f. Chasar et al. 2009) and avoiding the confounding effect of mobile fish foraging elsewhere and undergoing differential exposure prior to sampling. Isotope data were generated as described in Carr et al. (2017), with analyses conducted by combusting samples in a PDZ Europa ANCA-GSL elemental analyser and delivering gases to a PDZ Europa 20-20 isotope ratio mass spectrometer. Precision of the analyses, based on mean differences in duplicate analyses, was 0.4‰ for $\delta^{13}C$ and 0.2‰ for $\delta^{15}N$. Only those fish with > 33% river-origin in a three source mixing model ($\delta^{34}S$ typically < 1.0‰) were included in the current analysis.

To compare concentrations among different compartments, we included sediment data from Doig et al. (2017) who sampled in the same locations in the river. Data for water were obtained from Sanderson et al. (2012) that included both total and dissolved concentrations from the Fort Smith location and a location approximately 40 km upstream at Fort Fitzgerald. To compare concentrations among compartments, we used an analysis of variance on log transformed concentrations. Data for V were normally distributed but had unequal variance, so we used Welch's test statistic, while data for Tl met both assumptions.

We calculated bioaccumulation factors for each compartment as [biota]/[water] and compared these to values previously reported in the literature. Biomagnification was assessed using the slope of the log [element] vs $\delta^{15}N$ regression, where a positive slope indicates biomagnification and a negative slope indicates biodilution. We used 95% confidence intervals around slope estimates to compare between the two trace elements.

Results

Isotope values fell within a relatively constrained range, with the majority of $\delta^{13}C$ values for all taxa falling between -28 and -24‰ (Figure 1). Large fish had the highest $\delta^{15}N$ values, averaging 10.8‰, approximately two trophic levels (~7‰) above invertebrates and periphyton that had similar values (3.5‰ and 2.8‰, respectively). Small fish, with $\delta^{15}N$ = 7.9‰, were one trophic level below large fish and one trophic level above invertebrates, suggesting they preyed upon invertebrates and were in turn eaten by large fish. The overall range of $\delta^{15}N$ values in our food web (maximum – minimum) was 11.7‰.

Both V and Tl showed decreasing tissue concentrations with increasing trophic position. Vanadium was highest in sediments (80 µg/g) and periphyton (17 µg/g) and lowest in large fish (0.02 µg/g) (Table 1). All groups were significantly different from one another ($F = 544.9$, $p < 0.001$), and concentrations declined in the order sediment > periphyton > invertebrates > small fish > large fish (Figure 2a). Thallium also had its highest concentrations in sediment (0.33 µg/g) and periphyton (0.18 µg/g), but the pattern in fish differed slightly. Like V, there were significant differences among all groups ($F = 164.4$, $p < 0.001$), but small fish had lower concentrations than large fish, meaning the rank from highest to lowest concentration was sediment > periphyton > invertebrates > large fish > small fish (Figure 2b).

Bioaccumulation factors for V ranged from >50,000 in periphyton to only 61 in large fish (Table 1). Thallium bioaccumulated less strongly at lower trophic levels, with BAFs ranging from 18,000 in periphyton to 900 in small fish.

The slope of the log [element] vs. $\delta^{15}N$ regression was significant and negative for both V ($r^2 = 0.89$, $F = 457.5$, $p < 0.001$, Figure 3a) and Tl ($r^2 = 0.47$, $F = 49.7$, $p < 0.001$, Figure 3b). The slope was significantly steeper for V (-0.369 ± 0.034 95% C.I.) than for Tl (-0.099 ± 0.028 95% C.I.). Assuming a $\delta^{15}N$ increase of 3.4‰ with each trophic level, these slopes correspond to 94% and 54% declines with each trophic level for V and Tl, respectively.

Discussion

Our findings suggest that V and Tl biodilute in aquatic food webs. This adds to a growing list of trace elements for which this biodiluting behaviour is documented, including chromium, cobalt, copper, arsenic, nickel and lead (Campbell et al. 2005a, Revenga et al. 2012, Ward et al. 2012, Guo et al. 2016). Few trace elements exhibit consistent biomagnification, with only mercury, and perhaps cesium and rubidium, showing regular increases with trophic position (Rowan et al. 1998, Campbell et al. 2005b, Gantner et al. 2009, Lavoie et al. 2013). These results offer guidance on risk assessments for most metals, and show how exposure may be greatest for organisms that are low on the food chain as opposed to humans and charismatic wildlife that occupy high trophic positions.

Trophic transfer of metals is dictated by the balance between elimination rates and assimilation efficiency, with the proportion of the metal found in the soluble fraction of the cell largely responsible for efficiency of transfer (Reinfelder and Fisher 1991, Reinfelder et al. 1998, Cheung and Wang 2005). The percentage of Tl in the cell that can be found in trophically-available fractions varies from ~30% to >50%, and assimilation efficiency by predators can range from as low as 17% to as high as 70% (Dumas and Hare 2008, Lapointe and Couture 2009), suggesting that trophic transfer should occur for this element, albeit at a far lower efficiency than that for mercury which also has an extremely slow rate of elimination (Reinfelder et al. 1998). Our results suggest that these moderate values for trophic availability and assimilation efficiency lead to modest Tl biodilution in food webs. For V, cellular fractionation, assimilation efficiency and elimination rates in aquatic organisms are unknown, but the strong biodilution observed here would suggest that the elimination rate is high or assimilation efficiency is low.

Although biomagnification of these elements does not occur, there is evidence for bioconcentration, defined as a higher concentration in an organism relative to the water in which it resides. Thallium is taken up through both waterborne and dietary pathways (Lapointe and Couture 2009). Field-based bioconcentration factors (BCFs) for amphipods, calculated using caging studies and a biotic ligand model, were > 1 for Vanadium and > 10 for Thallium and associated with a low LC50 for the latter element (Borgmann et al. 2007, Couillard et al. 2008). These are congruent with the high BCFs observed in our study, with high concentrations recorded in periphyton despite low concentrations in water (Table 1). The V concentrations we observed in periphyton were lower than those reported by Pederson and Vaultonburg (1996). Periphyton in that study in the Embarras River, Illinois had concentrations between 30 and 108 ppm, and were collected from artificial substrates after incubation in waters with concentrations near 0.005 mg/L. This would correspond to approximately similar BCFs for periphyton (~10,000) as the current study. For invertebrates and small fishes, our BAFs were higher than those reported earlier by Bellante et al. (2016), who calculated BAFs for V between 13 and 133 for filter-feeders. It is unknown if toxic effects are occurring at lower trophic levels where concentrations were high, in part because most toxicity data is derived from waterborne exposures for both V and Tl (Pickard et al. 2001, Schiffer and Liber 2017). While our waterborne concentrations were well below the hazard concentration (HC_5) for V of 0.05 mg/L for chronic endpoints (Schiffer and Liber 2017) and the inhibition concentration (IC_{25}) for Tl of 0.10 mg/L for *Ceriodaphnia dubia* (Pickard et al. 2001), this could underestimate potential toxicity to invertebrates because it does not consider dietary exposure from ingesting periphyton with high concentrations of these metals.

The biodilution slope for V was steeper than those reported for chromium, cobalt and arsenic in a Patagonian lake (Revenga et al. 2012). This resulted in V concentrations in large fish at the top of the food chain that were very low, similar to values reported for largemouth bass from a lake in Alabama, USA (<0.01 mg/kg wet weight, Ikem et al. 2003), juvenile northern pike from a boreal lake (0.112 mg/kg dry weight, Kelly and Janz 2009) and fish communities in the Caspian Sea (0.008 to 0.064 mg/kg dry weight, Anan et al. 2005). These were much lower than croaker *Johnius belangerii* analyzed from the Persian Gulf, where concentrations were between 0.9 and 5.9 mg/kg wet weight (Fard et al. 2015) and fishes from an Iranian wetland (1.6 to 9.6 mg/kg, Hosseini Alhashemi et al. 2012). The latter values are due to a high water concentration in the area (0.234 mg/L) that led to low BAF values (7 to 41 L/kg) that were similar to what we observed for this element (Table 1). The former values are difficult to interpret because another study from the same region reported concentrations between 0.001 and 0.015 mg/kg wet weight for five fish species (Agah et al. 2009), much more in line with our findings. .

Our Tl biodilution slope was shallower than that for chromium, cobalt and arsenic (Revenga et al. 2012), but concentrations in fishes were low nonetheless. Our measured concentrations in pike, walleye and whitefish (mean = 0.005 mg/kg wet weight) are similar to those reported for Arctic char from a northern lake (range among years 0.005 to 0.017 mg/kg, Gantner et al. 2009) and fishes from the Caspian Sea (<0.001 to 0.006 mg/kg dry weight, Anan et al. 2005). They are lower than those for lake trout *Salvelinus namaycush* from Lake Michigan that had concentrations = 0.14 ± 0.11 mg/kg wet weight (Lin et al. 2001). Thallium BAFs for small and large fishes (180 and 500 L/kg, Table 1) were similar to those calculated for juvenile Atlantic salmon under controlled conditions (Zitko et al. 1975), but much lower than the measured value for lake trout from Lake Michigan (~10,000, Lin et al. 2001). While the overall change in concentration with trophic level was negative, there was an increase in [Tl] with increasing $\delta^{15}N$ for the fishes, with large fish having almost three times greater concentration than small fish. This may point to accumulation with age in older fish because pike, walleye and whitefish have lifespans of > 20 years as opposed to the shiner species that live < 5 years. However, Lin et al. (2001) found no relationship between fish age and [Tl]. Instead, differences in concentrations between small and large fishes in the Slave may be due to cellular partitioning in prey items for the two groups (invertebrates for the former and fish for the latter) and subsequent assimilation efficiency (Couture et al. 2011). If fish partition Tl in a more bioavailable form relative to invertebrates, it could lead to higher trophic transfer to piscivores such as pike and walleye.

Our results suggest no concerns for human exposure to these two elements associated with fish consumption. The reference dose for Tl is 5 µg for a 70 kg adult (US EPA 1992). Based on our mean concentration of 5 ng/g wet weight, exposure would amount to only 0.6 µg daily even for a person consuming a 230 g portion of fish every second day. These calculated exposure values are lower than those for lake trout from Lake Michigan (Lin et al. 2001). For V, the minimal risk level (MRL) value for intermediate duration exposure has been set at 0.01 mg V/kg/day, or 700 µg for a 70 kg adult (ATSDR 2012). Given that mean concentrations in large fishes ranged from 0.01 to 0.11 µg/g wet weight, it is impossible for someone to reach the MRL even if they ate three portions of fish per day.

Together, our findings suggest that increasing concentrations of V and Tl owing to fossil fuel combustion and smelting of ores (Couture et al. 2011, Schlesinger et al. 2017) are likely to have only modest effects on concentrations in top predators because of strong biodilution in food webs. The very low concentrations in fish in this region imply a very low risk to fish-eating consumers that would change little with increasing inputs, but higher concentrations elsewhere warrant concern for humans and wildlife with high rates of fish consumption. Additional food web work on these elements is needed to reveal why V and Tl concentrations are high in some geographic locations, separating out the effects of inputs at the base of the food web from biomagnification and biodilution patterns within the food web.

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Table 1. Bioaccumulation factors (BAF, [biota]/[water]) for vanadium and thallium in various compartments of the Slave River food web.

Element	Dissolved water concentration (mg/L) (range)	Compartment	Conc. (mg/kg d.w.) (n)	BAF (L/kg)
V	0.00033	periphyton	17.29 ± 5.38 (20)	52394
		invertebrates	6.40 ± 5.38 (3)	19394
		small fish	0.08 ± 0.08 (11)	242
		large fish	0.02 ± 0.02 (20)	61
Tl	0.00001	periphyton	0.18 ± 0.05 (20)	18000
		invertebrates	0.08 ± 0.05 (3)	8000
		small fish	0.01 ± 0.01 (11)	900
		large fish	0.03 ± 0.01 (20)	2500

Figure 1. Stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope values for biota in the Slave River, NWT. Circles = large fishes, diamonds = small fishes, triangles = invertebrates, squares = periphyton.

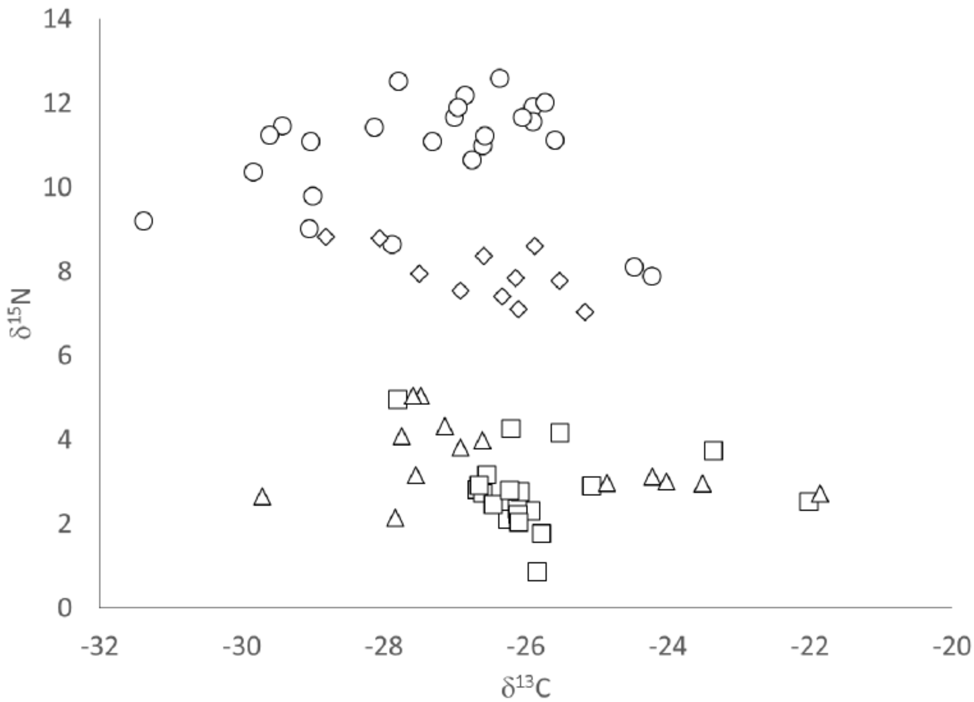

Figure 2. Concentrations of vanadium (A) and thallium (B) in various ecological compartments in the Slave River, NWT, illustrating the general decline in concentration with increasing trophic level for both elements.

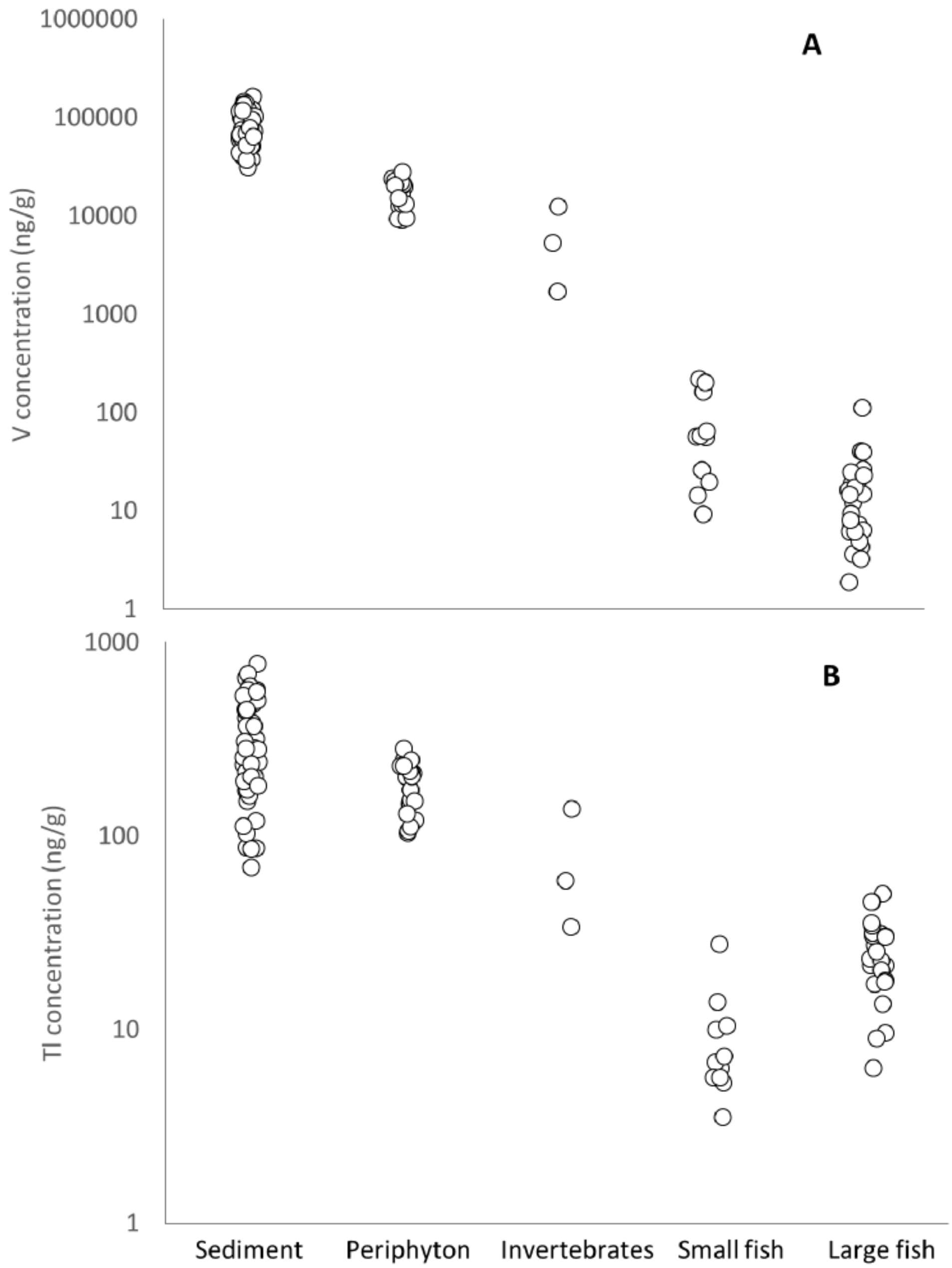

Figure 3. Concentrations of vanadium (A) and thallium (B) versus $\delta^{15}N$ for periphyton (squares), invertebrates (triangles), small fishes (diamonds) and large fishes (circles) in the Slave River, NWT.