

Article

Bioaccumulation of Trace Elements in Myctophids in the Oxygen Minimum Zone Ecosystem of the Gulf of California

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Abstract: Myctophids are key members of mesopelagic communities with a world biomass estimated at 600 million tons. They play a central role in oceanic food webs and are known to perform diel vertical migrations, crossing the thermocline and reaching the oxygen minimum zone, however, very scarce information exists on trace element content in these organisms. Therefore, the trace elemental composition (Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd and Pb) of *Triphoturus mexicanus* and *Benthosema panamense* specimens was determined. Zinc (Zn) was the most common trace element for both species, *T. mexicanus* presented $39.8 \mu\text{g}\cdot\text{g}^{-1}$ dw and *B. panamense* $30.6 \mu\text{g}\cdot\text{g}^{-1}$ dw. Contrasting, for *T. mexicanus* the less abundant trace element was Ni ($0.332 \mu\text{g}\cdot\text{g}^{-1}$ dw) and for *B. panamense* was Pb ($0.236 \mu\text{g}\cdot\text{g}^{-1}$ dw). *T. mexicanus* exhibited significantly higher concentrations of Cr, Cu, Zn and Pb in comparison to *B. panamense*, and these differences seemed to be related to inherent physiological and/or ecological traits rather than environmental element availability. These diel vertical migrators are crucial in the energy transfer between the deep-sea and epipelagic zones (and vice-versa), and the estimation of the Biomagnification Factor (based on Cu, Zn, Cd and Pb) levels revealed that both *T. mexicanus* and *B. panamense* play a major role in trace element transfer to higher trophic levels in the pelagic food web of the Gulf of California.

Keywords: myctophids; *Triphoturus mexicanus*; *Benthosema panamense*; trace elements; bioaccumulation; Gulf of California

1. Introduction

Myctophids, also known as lanternfish, are the most widespread and diverse mesopelagic fish taxa with approximately 250 species distributed among 33 genera [1]. These small fish (2–15 cm, total length) account for as much as 65% of all deep-sea fish biomass, with an estimated global biomass of 600 million tons [2,3]. Myctophids also play a key role in the oceanic food web [1,4,5], by feeding majorly on zooplankton and larval and juvenile fishes [6], and serving as important prey items for

predators such as whales, dolphins, penguins and squids [4,5,7]. Moreover, myctophids constitute a major component of the deep scattering layer (DSL), a sound scattering layer in the water column resulting from the congregation of a variety of marine animals. The surface layer of the ocean is known as the epipelagic layer and extends from the surface to 200 m. Here enough light is available for photosynthesis. Below lies the mesopelagic layer, extending from 200 m to 1000 m. The mesopelagic layer is also known as the twilight zone as the light that penetrates this zone is extremely faint. DSL organisms are known to perform diel vertical migrations (DVM), moving from mesopelagic depths at day-time to food-rich epipelagic layers at night-time—in a reflection of their food tracking behavior [8,9]. Myctophids are able to dwell within the oxygen minimum zone (OMZ) [10], since they exhibit important adaptive mechanisms that cope with the radically reduced oxygen levels [11,12]. In this context, these ecologically-relevant fishes act as a key “biological pump”, delivering the organic matter consumed in the warm oxygenated photic zone, during the night, to colder hypoxic waters during the day [13].

Trace elements are persistent, prone to accumulation and have been detected in a wide range of environments and organisms e.g., [14–19]. Since the deep-sea bottom is the most typical environment of our planet (90% of the sea bottom), concerns over its potential to act as ultimate global sink for such elements are raising. However, surprisingly, the available data on trace elements of deep-sea organisms is very scarce. In this context, the objective of this study was to characterize, for the first time, the elemental composition of two abundant myctophid species (*Triphoturus mexicanus* and *Benthosema panamense*), and to better understand their relevance as potential vectors of trace elements in the pelagic food web of the Gulf of California.

2. Materials and Methods

2.1. Sampling

Myctophids (*T. mexicanus* and *B. panamense*) were collected in June 2012 at the Gulf of California (Guaymas basin, Figure 1) using an opening/closing Mother Tucker trawl with a 10 m² mouth.

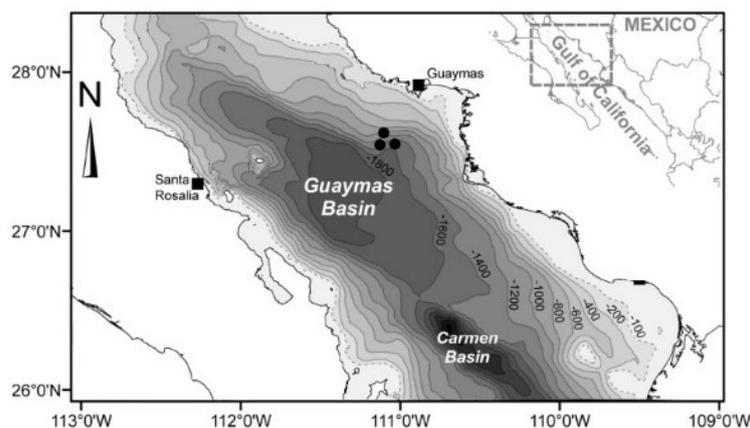


Figure 1. Study area in the Gulf of California, Mexico (between Santa Rosalia and Guaymas). Sampling locations are represented with black dots.

The semi-enclosed Gulf of California (GC) is a marginal sea on the Pacific coast of Mexico and encompasses one of the world’s five most productive and diverse ecosystems, being an important feeding ground for a wide variety of marine organisms [20,21]. The Guaymas Basin, in the GC, is characterized by the presence of a hydrothermal vent that has an organic-rich sedimentary cover enriched in Mn provided by the Colorado River runoff [22,23]. These fluids are strongly diluted by seawater during their mixing [24]. The sediments herein have abundant concentrations of metal sulfites [25]. The GC is also characterized by the presence of mining complexes and other industrial and urban activities along the coast, responsible for releasing high amounts of metals into this ecosystem

(especially Cd, Cu, Fe, Pb and Zn) [24,26]. García-Rico et al. [26] found high levels of Cd, Pb and Zn in the dissolved fraction, while detecting high levels of Cu, Fe and Mn in the particulate fraction. The Partition coefficients of Fe, Mn and Cu were found in high levels, suggesting high metal adsorption onto sediments.

Increasing the knowledge on the elemental composition of key constituents of this food web, such as the myctophids, is therefore imperative to evaluate potential impacts on the living resources that depend on such important and rich ecosystem.

The fishing net was equipped with a 30-L thermally protecting cod end that reduced mechanical damage and heat shock to animals during recovery [12,27,28]. Trawls were conducted at depths between 300 and 400 m during the day and between 40 and 50 m of depth during night-time. Ship speed was kept very low (0.5–1 kn) to decrease turbulence and abrasion in the net and to reduce the number of animals collected in the cod end. Upon reaching the surface, specimens were immediately transferred to liquid nitrogen. *T. mexicanus* total length measured 3.22 ± 0.2 cm and *B. panamense* measured 3.31 ± 0.3 cm.

2.2. Trace Element Analysis

Nine pooled samples per species (5 whole adult fish specimens of the same size per pool, i.e., comprising a total of 45 specimens per species) of *T. mexicanus* and *B. panamense* were freeze-dried, ground and homogenized for the analytical procedures. Trace elements were determined in samples after digestion with the mixture of HNO₃ (sp, 65% v/v) and H₂O₂ (sp, 30% v/v) according to the method described in Ferreira et al. [29]. Prior to digestions all labware was decontaminated with HNO₃ (20%) for two days and rinsed with Milli-Q water (18.2 MΩ.cm). Procedural blanks were prepared using the analytical procedure and reagents indicated above. Concentrations of Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd and Pb were determined by quadrupole ICP-MS (Thermo Elemental, X-Series). The accuracy of the analytical method was assessed through analysis of international certified materials (IAEA—452, scallop (*Pecten maximus*) sample, DORM-4, fish protein and DOLT-4, fish liver). The results obtained did not differ significantly ($p > 0.05$) from the certified values (Table 1).

Procedural blanks always accounted for less than 1% of the total element concentration in the samples. All measured values were above detection limits. Results are given in microgram per gram of tissue dry weight ($\mu\text{g}\cdot\text{g}^{-1}$, dw).

2.3. Statistical Analyses

Trace element concentrations were initially tested for normality and homogeneity of variances. Non-compliance of parametric assumptions led to the application of the Mann-Whitney non-parametric test to evaluate differences between element concentrations in the two species. All statistical analyses were performed for a significance level of 0.05, using STATISTICA™ 12 software (Statsoft, Inc., Tulsa, OK, USA).

2.4. Biomagnification Factor

The Biomagnification Factor (BMF) is a useful and advantageous measure in toxicology and environmental chemistry reflecting the ability of a chemical substance to be accumulated over different levels of a food web [30,31]. BMF was calculated in accordance to [32–35] as following:

$$\text{BMF} = ((C_{\text{predator}}) / (C_{\text{prey}})) / ((\text{TL}_{\text{predator}}) / (\text{TL}_{\text{prey}})). \quad (1)$$

The compound is considered to be biomagnified when the $\text{BMF} > 1$ [30].

The BMF was calculated to assess the role of *T. mexicanus* and *B. panamense* as potential vectors of trace elements. The calculation of the BMF was restricted to four trace elements, two essential - Cu and Zn [36,37], and two toxic—Cd and Pb [38,39], to allow comparison with published data. Pauly et al. [40] calculated the Trophic Level (TL) of *S. longirostris*, *P. catodon* and *E. robustus*. For *D. gigas* it was used the TL obtained by Field et al. [41], while for *T. mexicanus* and *B. panamense* TL values were obtained from the Fishbase database [42,43].

Table 1. Median and standard deviation concentrations of Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd and Pb ($\mu\text{g}\cdot\text{g}^{-1}$, dry weight) in a scallop (*Pecten maximus*) sample (IAEA-452), in fish protein (DORM-4) and fish liver (DOLT-4) obtained in the present study and certified values. Indicative values are indicated by asterisk (*).

		Cr	Mn	Co	Ni	Cu	Zn	As	Se	Cd	Pb
		$(\mu\text{g}\cdot\text{g}^{-1}, \text{DW})$									
IAEA - 452	Obtained	-	250 ± 6.0	1.79 ± 0.30	-	11 ± 1.5	165 ± 30	18.5 ± 3.6	7.7 ± 0.3	31.7 ± 4.4	-
	Certified	-	273 ± 34	1.62 ± 0.20	-	10.8 ± 1.3	166 ± 21	17.5 ± 2.2	6.55 ± 0.82	29.6 ± 3.7	-
DORM-4	Obtained	2.2 ± 0.85	-	-	1.4 ± 0.36	16 ± 2.9	55 ± 13	7.4 ± 1.5	4.2 ± 1.5	0.31 ± 0.058	0.32 ± 0.10
	Certified	1.87 ± 0.16	-	-	1.36 ± 0.22	15.9 ± 0.9	52.2 ± 3.2	6.80 ± 0.64	3.56 ± 0.34	0.306 ± 0.015	0.416 ± 0.053
DOLT-4	Obtained	1.2 ± 0.69	-	0.23 ± 0.03	0.71 ± 0.28	32 ± 3.8	125 ± 12	9.1 ± 1.8	9.1 ± 1.1	24 ± 3.9	0.22 ± 0.15
	Certified	1.4^*	-	0.25^*	0.97 ± 0.11	31.2 ± 1.1	116 ± 6	9.66 ± 0.62	8.3 ± 1.3	24.3 ± 0.8	0.16 ± 0.04

3. Results

Median concentrations of Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd and Pb ($\mu\text{g}\cdot\text{g}^{-1}$, dry weight) in *T. mexicanus* and *B. panamense* captured in the Gulf of California are presented in Figure 2.

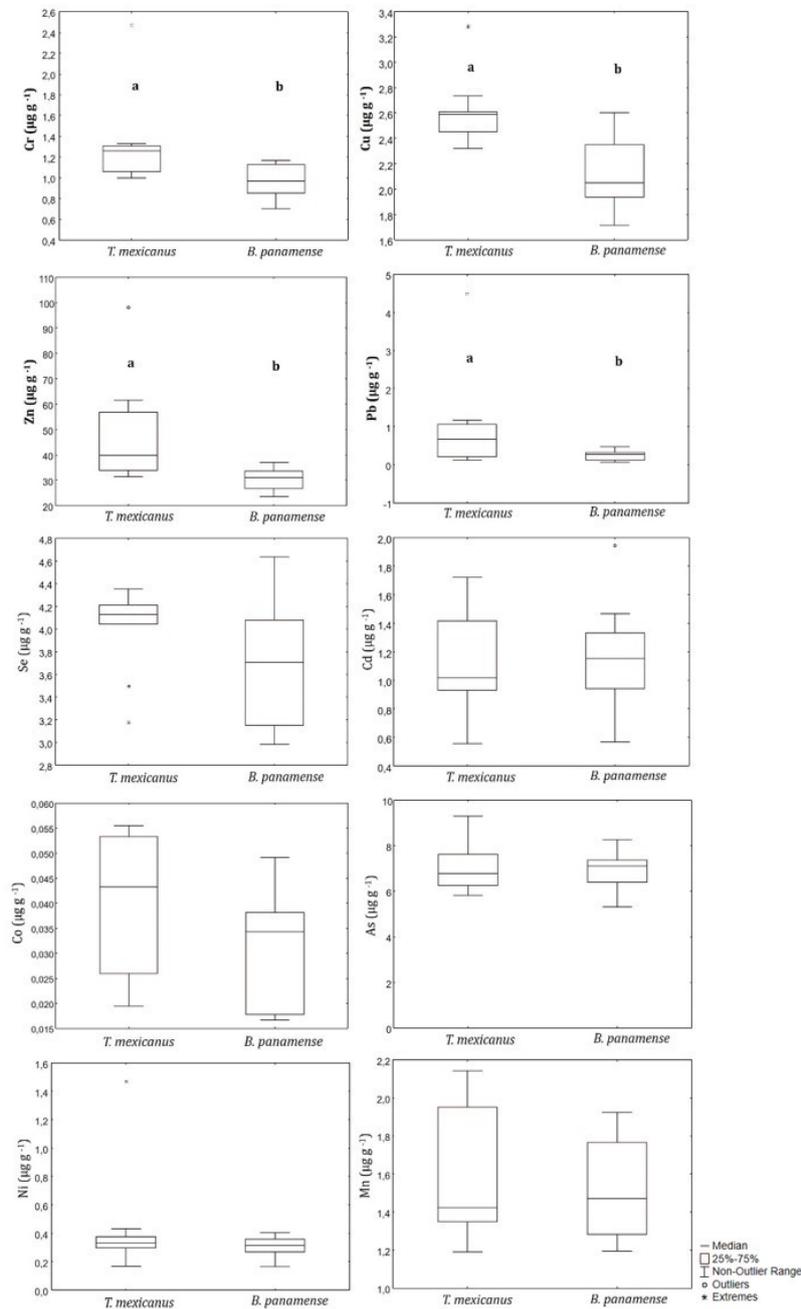


Figure 2. Element concentrations of Cr, Cu, Zn, Pb, Se, Cd, Co, As, Ni, and Mn ($\mu\text{g}\cdot\text{g}^{-1}$, dry weight) in *Triphoturus mexicanus* and *Benthosema panamense*. Different letters represent significant differences between species ($p < 0.05$).

Zinc was by far the most abundant element in both species, followed by arsenic. Concentrations of Zn ranged between 31 and 98 $\mu\text{g}\cdot\text{g}^{-1}$ in *T. mexicanus* while *B. panamense* presented significantly lower levels, varying in a narrower interval (24–37 $\mu\text{g}\cdot\text{g}^{-1}$). Content of As was similar in both species, ranging between 5.8 and 9.3 $\mu\text{g}\cdot\text{g}^{-1}$ in *T. mexicanus* and 5.3–8.3 $\mu\text{g}\cdot\text{g}^{-1}$ in *B. panamense*. Cobalt was the less abundant element in both myctophids, with median levels almost negligible, varying in the range

of $0.009\text{--}0.055\ \mu\text{g}\cdot\text{g}^{-1}$ in *T. mexicanus* and $0.017\text{--}0.049\ \mu\text{g}\cdot\text{g}^{-1}$ in *B. panamense*. Regarding interspecific differences, *T. mexicanus* exhibited significantly higher concentrations of Cr, Cu, Zn and Pb ($p < 0.05$; Figure 2) than *B. panamense*.

BMF's for Zn, Cu, Pb and Cd of *T. mexicanus* top predators are presented in Figure 3A and *B. panamense* top predators are presented in Figure 3B.

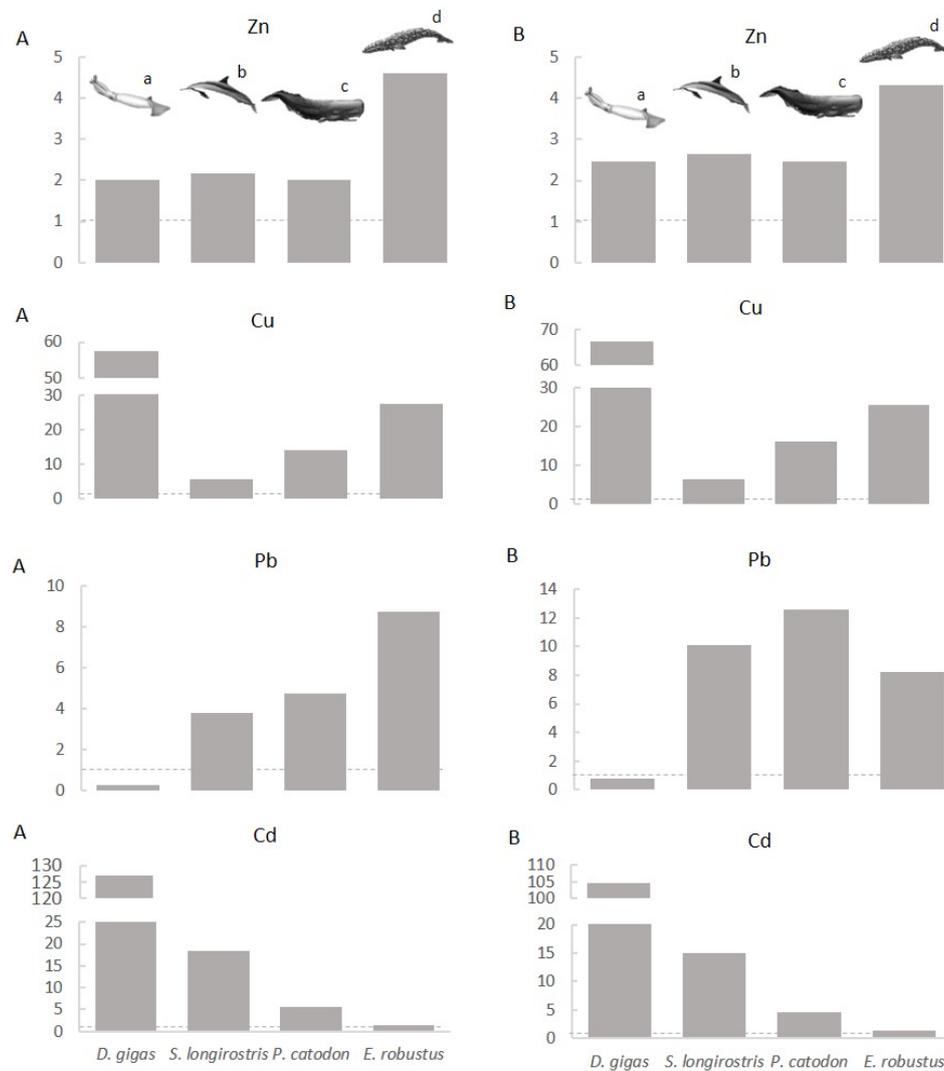


Figure 3. Biomagnification Factor (for the elements Cu, Zn, Pb and Cd) of *T. mexicanus* (A) and *B. panamense* (B) top predators from the Gulf of California. References: a—*Dosidicus gigas*, Raimundo et al. [21]; b—*Stenella longirostris*, Ruelas and Páez-Osuna [44]; c—*Physeter catodon*, Ruelas-Inzunza and Páez-Osuna [45]; d—*Eschrichtius robustus*, Méndez et al. [46].

The top predators' BMF's, for each element, were greater than 1, except for Pb in *D. gigas* in regard to both *T. mexicanus* and *B. panamense*.

4. Discussion

4.1. Geographical Differences in Elemental Composition

The available information on the trace element bioaccumulation of myctophids is scarce e.g., [47–49]. In general, the data presented herein are comparable to those obtained for other myctophid species, with the exception of As (Table 2), whose concentrations varied greatly among distinct sites of collection.

Table 2. Ranges, median and standard deviation concentrations of Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd and Pb ($\mu\text{g}\cdot\text{g}^{-1}$, dry weight) in *Triphoturus mexicanus* and *Benthoosema panamense* and elemental concentrations ($\mu\text{g}\cdot\text{g}^{-1}$, dw) in other myctophids from the literature. ND stands for Not-Detected. References: a—present study; b—Fernandez et al. [47]; c—Bocher et al. [50]; d—Cutshall et al. [51]; e—Schulz-Baldes [52]; f—Windom et al. [53]; g—Fowler [54]; h—Asante et al. [48]; i—Bustamante et al. [49]; j—Cipro et al. [55].

id	Region	n	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Cd	Pb	Ref.
<i>Triphoturus mexicanus</i>	Guaymas Basin	45	1.3 (1–2.5)	1.5 (1.2–2.6)	0.039 (0.0085–0.055)	0.33 (0.2–1.5)	2.6 (2.3–3.3)	40 (31–98)	6.8 (5.8–9.3)	4.1 (3.2–4.4)	1.02 (0.55–1.7)	0.66 (0.12–4.5)	a
<i>Benthoosema panamense</i>		45	0.97 (0.70–1.2)	1.6 (1.2–2.3)	0.034 (0.017–0.049)	0.32 (0.17–0.40)	2.1 (1.7–2.6)	31 (26–37)	7.1 (5.3–8.3)	3.7 (3.0–4.6)	1.2 (0.57–1.9)	0.27 (0.07–0.47)	
<i>Diaphus effulgens</i>	India	-	-	ND	-	-	ND	ND	-	-	ND	-	b
<i>Diaphus hudsoni</i>		-	-	1 ± 0.2	-	-	ND	ND	-	-	ND	-	
<i>Myctophidae</i>	Kerguelen archipelago	45	-	-	-	-	1.0 ± 0.3	9 ± 2	-	-	0.011 ± 0.007	-	c
<i>Myctophidae</i>	Western United States	9	-	-	-	-	-	10	-	-	0.060	-	d
<i>Myctophidae</i>	Atlantic Ocean 48N and 40S	76	-	-	-	-	6.2	-	-	-	1.5	-	e
<i>Hygophum hygomi</i>	Sargasso Sea	2	-	-	-	-	3.4	15	<1.0	-	<1.0	-	
<i>Ceratoscopelus warmingii</i>		2	-	-	-	-	2.2	35	<1.0	-	0.7	-	
<i>Notoscopelus caudispinus</i>		2	-	-	-	-	3.2	81	<1.0	-	0.4	-	
<i>Lobianchia dofleini</i>		1	-	-	-	-	23.0	49	<1.0	-	1.6	-	f
<i>Lepidophanes indicas</i>		1	-	-	-	-	13.0	56	<1.0	-	0.9	-	
<i>Diaphus mollis</i>		1	-	-	-	-	7.0	34	<1.0	-	0.8	-	
<i>Lampanyctus pusillus</i>		1	-	-	-	-	23.0	48	<1.0	-	1.6	-	
<i>Lampanyctus pusillus</i>		1	-	-	-	-	2.7	27	<1.0	-	0.4	-	
<i>Myctophum glaciale</i>	Mediterranean			4.1–11	0.03–0.24	-	2–6.4		1.3–44.8		0.10–0.28		g
<i>Ceratoscopelus warmingii</i>	Sulu Sea	3	3–8.4	5.6–6.5	0.13	-	3.8–5.2	39–47	28–46	2.2–3.1	0.75–0.99	0.19–0.21	
<i>Diaphus problematicus</i>		1	0.23	3.4	0.081	-	3.8	39.9	25.1	2.5	0.78	0.091	h
<i>Diaphus regani</i>		1	1.2	6.9	0.11	-	5.6	36.1	15.9	1.9	0.76	0.099	
<i>Gymnoscopelus nicholsi</i>	Kerguelen Islands	4	-	-	-	-	1.9–3.4	6.6–15.0	-	-	0.004–0.021	-	i
<i>Gymnoscopelus piabilis</i>		5	-	-	-	-	0.8–1.7	8.4–11.3	-	-	0.004–0.021	-	
<i>Electrona antarctica</i>	Kerguelen Islands	15	-	-	-	-	2.1 ± 0.5 (1.6 - 3.5)	22 ± 3 (17–28)	-	-	0.270 ± 0.101 (0.132–0.506)	-	
<i>Gymnoscopelus fraseri</i>		15	-	-	-	-	3.2 ± 0.6 (2.4–4.8)	27 ± 2 (24–31)	-	-	0.496 ± 0.233 (0.256–0.929)	-	j
<i>Gymnoscopelus nicholsi</i>		4	-	-	-	-	2.2 ± 0.7 (1.4–2.9)	19 ± 1 (17–20)	-	-	0.251 ± 0.098 (0.180–0.392)	-	
<i>Gymnoscopelus piabilis</i>		14	-	-	-	-	2.3 ± 0.3 (1.6–2.9)	28 ± 4 (20–35)	-	-	0.887 ± 0.454 (0.453–1.826)	-	

Samples of *T. mexicanus* and *B. panamense* exhibited much lower As values than those found in myctophids from the Mediterranean and Sulu Seas [48,54], but higher than those from the Sargasso Sea [53]. We argue that the myctophids' diet composition in GC plays a key role in the low accumulation of As, since it has a nutrient-like behavior and food intake is the main source of As in marine organisms [56]. Concentrations of Cd and Pb (particularly in *T. mexicanus*) were generally higher than those found in myctophids from other regions. Delgadillo-Hinojosa et al. [57] reported that the midriff island region (North West of the GC) showed an intense vertical mixing of Cd, reporting this as a source of Cd and nutrients. García-Rico et al. [26] have studied the dissolved and particulate metals in water from a pristine zone of the Gulf of California and found that dissolved metal concentrations were lower than the Environmental Protection Agency criteria, with the exception of Pb, suggesting that Pb levels are linked to anthropogenic inputs. The greater availability in this location may result in a greater bioaccumulation of Cd and Pb in the studied species.

Not surprisingly, the concentrations found in the present study for elements like Zn are much higher than those in the Kerguelen Islands by Bocher et al. [50], Bustamante et al. [49] and Cipro et al. [55] (Table 2), as the Guaymas Bay receives untreated municipal sewage, and effluents from industrial activities such as a thermoelectric plant, a cement factory and various fish processing plants and shipyards [58], which may explain the higher observed values of such elements.

4.2. Interspecific Differences

T. mexicanus showed a tendency to accumulate greater amounts of the studied trace elements, when compared with *B. panamense*, accumulating significantly greater amounts of Cr, Cu, Zn and Pb. Although these myctophids display different depth range distributions during daytime (*T. mexicanus* is mainly distributed between 300–400 m depth, while *B. panamense* occupies a more superficial layer, around 200–300 m depth; 3), both inhabit the same water mass, the Subtropical Subsurface Water, found approximately between 150 and 500 m depth in the Guaymas Basin [59]. Thus, it is unlikely that distinct depth distributions may result in differential exposure to trace elements throughout their life, causing interspecific differences. We argue that these trace element differences may most likely be related with intrinsic species-specific features. In fact, Barham [60] has described the existence of two myctophid types with regard to their behavior, vertical orientation and swimbladder morphology. Barham [60] described *B. panamense* as the “active” type, with a firm bodied that dwells within the DSL at mesopelagic depths diurnally, migrating to the warm oxygenated photic zone at night. While *T. mexicanus* was described as the “inactive” type, soft-bodied, that concentrates diurnally below DSL depths, in deeper suboxic waters, migrating upward at night. A study by Raimundo et al. [61] showed that other fish species with sedentary behaviour, slow metabolic rate and longer life history, tend to accumulate greater amounts of trace elements in the muscle, a long-term indicator tissue of metal exposure. As such, the obtained interspecific differences should occur due to a greater role of inherent physiological and ecological traits in accumulation mechanisms rather than environmental elemental availability.

4.3. Myctophids as Potential Vectors of Trace Elements

Myctophids have been described as one of the most abundant vertical migratory mesopelagic fish in the North Pacific [62], playing a crucial role in the transfer of energy from epipelagic to mesopelagic environments [63]. These fishes also act as a pivotal link within pelagic food webs as they are greatly consumed by a diverse range of oceanic top predators, accounting for almost 100% of the food items included in the diet of the penguin *Aptenodytes patagonicus* (Figure 4).

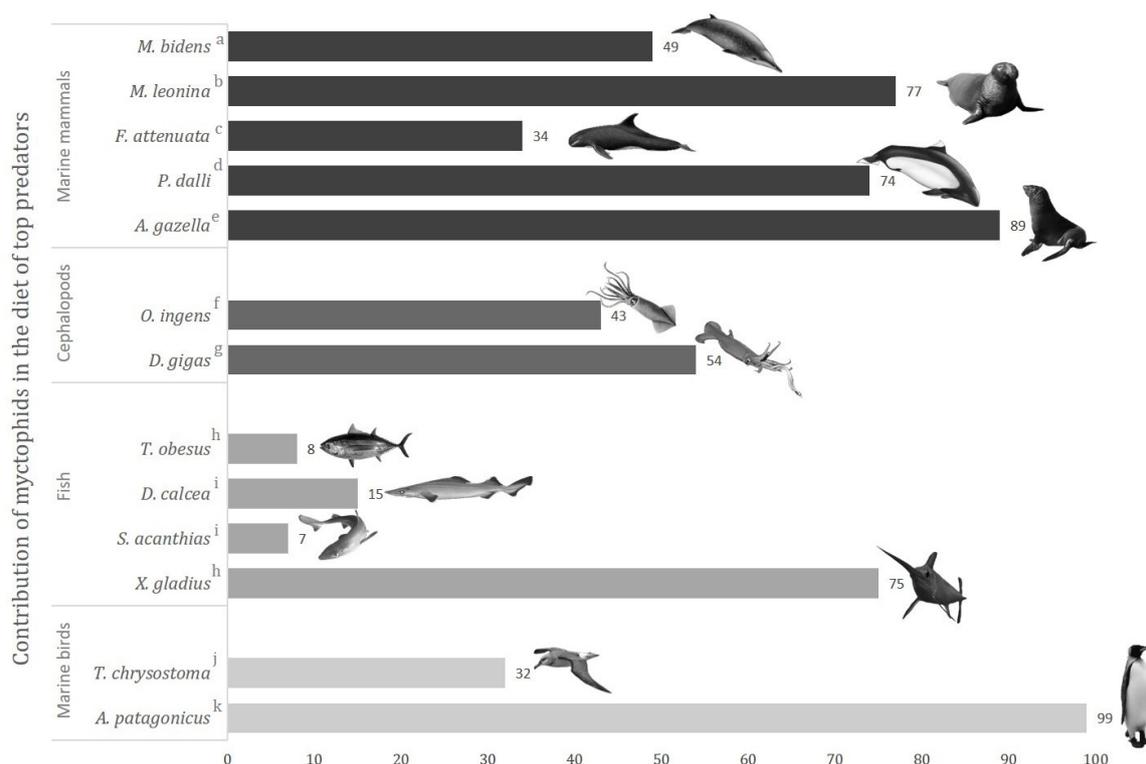


Figure 4. Contribution of myctophids in the diet of top predators from different taxonomic groups. Percentages of frequencies by number (N%) are presented. When different sampling sites or seasons were accessible, the highest documented value was chosen. References: a—*Mesoplo don bidens*, Pereira et al. [64]; b—*Mirounga leonina*, Daneri and Carlini [65]; c—*Feresa attenuata*, O’Dwyer et al. [66]; d—*Phocoenoides dalli*, Ohizumi et al. [67]; e—*Arctocephalus gazelle*, Casaux et al. [68]; f—*Onykia ingens*, Cherel and Duhamel [69]; g—*Dosidicus gigas*, Markaida and Sosa-Nishizaki [70]; h—*Thunnus obesus* and *Xiphias gladius*, Moteki et al. [71]; i—*Deania calcea* and *Squalus acanthias*, Pethybridge et al. [72]; j—*Thalassarche chrysostoma*, Croxall et al. [73]; k—*Aptenodytes patagonicus*, Cherel et al. [74].

Although being a specific case and having into consideration that: i) Cu, Zn, Cd and Pb can be originated from other sources than food; ii) the trace element storage can limit the trophic transfer of elements from prey to predator; and iii) the concentration present in the adult predators greatly depends on their age, when analyzing the BMF’s for Zn, Cu, Pb and Cd of *T. mexicanus* (Figure 3A) and *B. panamense* (Figure 3B) top predators’ (values obtained from the liver of *S. longirostris*, *P. catodon* and *E. robustus* and digestive gland (the detoxification organ in cephalopods) of *D. gigas*), it is clear that these elements could be biomagnified along this food web in the GC (Figure 3; see also Supplemental Table S1). As discussed before, a great amount of myctophids are consumed by top predators (summarized in Figure 4), and the content of these trace elements present in this great biomass could be, hence, transferred to higher trophic levels.

5. Conclusions

As the first study unravelling the trace element composition of two abundant DVM myctophid species and the inherited interspecific differences, this work reinforces the keystone ecological role of *T. mexicanus* and *B. panamense* in the GC pelagic food web. Our data suggest that both species seem to be vectors of trace element transfer to higher trophic levels within the mesopelagic oxygen minimum ecosystem of the GC.

To complement the findings of this research, further studies are needed in other oceanic areas to fully understand the global potential of myctophids as trace element vectors in marine ecosystems.

The analysis of a broader set of trace elements should also be considered, since the previous studies only described a relatively small number of elements e.g., [49–52,55].

Supplementary Materials: The following are available online at <http://www.mdpi.com/2673-1924/1/1/4/s1>, Table S1: Median concentrations of Cu, Zn, Cd and Pb ($\mu\text{g}\cdot\text{g}^{-1}$, dry weight) used to calculate the BMF of the myctophids top predators' present in the Gulf of California. References: a—Raimundo et al. [21]; b—Ruelas and Páez-Osuna [44]; c—Ruelas-Inzunza and Páez-Osuna [45]; d—Méndez et al. [46].

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