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Elemental Composition and Freezing Tolerance in High Arctic Fishes and Invertebrates

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Abstract: The elemental composition in different Arctic fishes and invertebrates was investigated using Inductively Coupled Plasma Mass Spectrophotometer (ICPMS). Nineteen elements such as Arsenic (As), Barium (Ba), Bismuth (Bi), Cadmium (Cd), Cesium (Cs), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), Nickel (Ni), Rubidium (Rb), Selinium (Se), Silver (Ag), Strontium (Sr), Uranium (U), Vanadium (V), and Zinc (Zn) were analyzed in six species of fishes (*Anarhichas lupus*, *Gadus ogac*, *Gadus morhu*, *Gymnocanthus tricuspis*, *Liparis* sp., *Myoxocephalus scorpius*) and four benthic invertebrates (*Ophiura albida*, *O. Sarsii*, *Strongylocentrotus droebachiensis*, Polychaete). Elemental data revealed that the invertebrates accumulate higher concentrations of elements than the fishes. The high concentration of elements including Sr, As, and Zn indicated anthropogenic contribution and may affect the fish community in the fragile ecosystem of the High Arctic. The movement of tourists and logistics must be regulated to prevent serious change in Svalbard. Most of the fishes have shown strong antifreeze protein (AFP) activity, and this potential helps fishes to survive in the cold Arctic environment. This is the first study of elemental concentrations and AFPs in fishes and benthic invertebrates filling the knowledge gap from the High Arctic.

Keywords: Arctic; environment; fish; invertebrates; element; AFPs

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1. Introduction

Elements are present at various levels in the geo-spheres (lithosphere, hydrosphere, atmosphere, and biosphere) and are generally classified as lithophiles, chalcophiles, and siderophiles [1]. Among these, some elements are essential components of hormones, enzymes, and enzyme activators [2] and play important roles in physiological and metabolic processes of different life forms [3]. The deficiency and excess intake of elements in different life forms can be detrimental to the health of an ecosystem. Due to the impact of climate change, tourism, and industrialization, the natural habitats have been affected immensely in many parts of the earth's surface [4]. The contamination of the hydrosphere is one of the most serious concerns that affect the ecological balance in aquatic habitats [5]. Fish act as top predators in the food chain of the aquatic ecosystem and also accumulate higher concentrations of trace elements, causing them to be dangerous to eat [6–9]. Fish organs (muscles, livers, and gills) are known for their bioaccumulation process [10]. Recently, analyses of essential (copper (Cu), cobalt (Co), selenium (Se), and zinc (Zn)) and nonessential elements (mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As)) in seven fish species consumed by the indigenous people of the European Russian Arctic were conducted [11].

The Arctic is one of the most pristine regions on earth. The natural processes such as erosion, transportation, and deposition has increased with time since the last glaciation [12]. In order to recognize the effect of such natural processes and/or anthropogenic disturbances, if any, the elemental concentration in different life forms of Kongsfzorden needs to be determined at regular intervals. An unprecedented increase in these elemental values needs to be monitored against the various factors affecting the Kongsfzorden. Environmental monitoring of major, minor, as well as trace elements in the Arctic has been done for aerosols [13–16], lake sediments [17,18], snow, and cryoconite [1,19]. Biomonitoring of lichens and seabirds has also been conducted [20–22] reviewed air pollution in the Arctic through long-range pollutants, while [23] analyzed the element stratigraphy in quaternary sediments of the Arctic Ocean. Hicks and Isaksson [24] assessed the source areas of pollutants in Svalbard snow and ice. Recently, studies on the elemental chemistry of Kongsfjord sediments [25,26], ice cores [27], permafrost [28], lichens [29], and radionuclides [30] have been carried out.

Recently, baseline studies on shallow water fish community determined the abundance and species composition in Kongsfjorden, Svalbard. Among these *Myoxocephalus scorpius* (shorthorn sculpin) (74.9%), *Gadus morhua* (Atlantic cod) (17.2%), and *Gymnocanthus tricuspis* (Arctic staghornsculpin) (3.8%) were identified as the most abundant species across all sampling sites [31]. The diversity and abundance of hard-bottom fauna was recorded at a depth range of 5–10 m [32]. The macro-algal-rich seafloors provide a potential food source and an important habitat for fishes [33]. The resident fish community acts as a secondary producer in the local food web. It prefers shallow water habitats as spawning and nursery grounds [34,35].

Antifreeze proteins (AFPs) are a structurally diverse group of ice-binding proteins that inhibit the growth of ice either by depressing the freezing point (TH activity) or by inhibiting the recrystallization of ice grains [36–38]. By this mechanism of control of ice growth, the membranes of the organisms remain protected from damage caused due to freezing, thereby increasing the survival in cold environments. DeVries et al. [39] were the first to isolate AFPs from Antarctic teleost fishes. Since then, a number of AFPs have been discovered in fishes [40,41].

The gap in knowledge of different elements and AFPs in High Arctic fishes and other organisms is an area requiring investigation; therefore, the present study was undertaken on the fishes and benthic invertebrates of the Kongsfzorden, Arctic.

2. Materials and Methods

2.1. Study Area and Sampling

Samples were collected from different locations of Kongsfzorden, Svalbard, Arctic (Figure 1). There are many melting glaciers around, but two are the main sources of water to the Bayelva river finally discharged in Kongsfzorden. In the present study, six different fish species (*Anarhichas lupus*, *Gadus ogac*, *Gadus morhu*, *Gymnocanthus tricuspis*, *Liparis* spp., *Myoxocephalus scorpius*,) were collected using one fyke net (diameter 40 cm, length 90 cm, mesh size 12 mm (bar mesh), deployed in about 3 m water depth with its mouth set perpendicular to the shoreline and one trammel net (inner/outer mesh size 1/15 cm, length 20 m, height 2 m) deployed from about 5 to 12 m water depth [31].

The most common species of Kongsfizorden are shown in Figure 2a–d. Invertebrate's organisms (*Ophiura arctica*, *Ophioceten sericeum*, *Strongylocentrotus droebachiensis* and Polychaetes) were collected using a grab sampler (Figure 2e–h).

The ten collected samples were kept in polystyrene boxes and transported to Kings Bay Marine laboratory at Ny Ålesund to sustain freshness. The fishes were identified on the basis of morphological characteristics [42–45]. The fishes belonging to family Liparidae showed morphological plasticity and were therefore indented up to genus level. The upper water temperature during the summer was ~5.7 °C to 6.7 °C, while it was ~0 °C during the month of February [31]. Fish samples were measured for length and weight (Table 1).

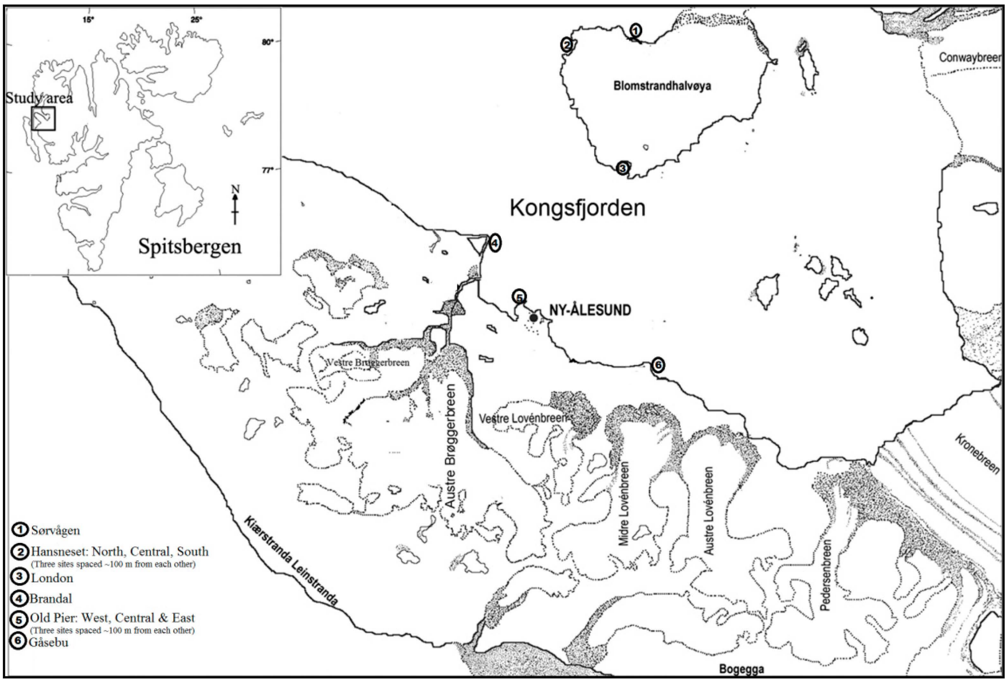

Figure 1. Sampling sites into Kongsfzorden, Svalbard, High Arctic. Map modified from the Norwegian Polar Institute's map resource (www.toposvalbard.npolar.no, accessed on 18 May 2022).

Figure 2. High Arctic fish and invertebrates. (**a**) *Myoxocephalus scorpius*; (**b**) *Gadus ogac*; (**c**) *Anarhichas lupus*; (**d**) *Liparis* sp.; (**e**) *Ophioceten sericeum*; (**f**) *Ophiura arctica*; (**g**) *Strongylocentrotus droebachiensis*; (**h**) Worm: Polychaetes.

To avoid metal contamination of the samples, the laboratory wares were soaked in 2 M HNO3 for hours and rinsed with distilled water and deionized water prior to use. The head and gut of the fish samples were removed. The muscles were detached on plastic sheets with a steel knife, packed into plastic bags, and frozen in a −86 °C freezer. Samples were transported to a laboratory via air cargo in insulated boxes with dry ice. Further, muscles tissue was taken for analysis of trace metals and blood samples for AFPs.

Table 1. Sampling locations and length and weight of Kongsfzorden fishes.

Fish Code Number	Fjord Side	Location	Catch Device	Depth (m)	Species	Length_Std (cm)	Weight Total	Sex
F (1738)	North	Hansneset Central	Double Fyke Net	5	*Anarhichas lupus*	49	1321.07	F
E (1643)	North	London	Double Fyke Net	5	*Gadus ozak*	30	352.88	F
A2 (1644)	South	Old Pier Central	Double Fyke Net	5	*Gadus morhua*	37.5	634.7	F
A1 (1707)	North	Hansneset South	Double Fyke Net	5	*Gadus morhua*	16.5	49.23	U
B2 (1737)	South	Gasebu	Double Fyke Net	5	*Gymnocanthus tricuspis*	14.5	65.63	F
C1 (1770)	North	Hansneset South	Double Fyke Net	5	*Liparis* sp.	12.5	36.6	M
C2 (1703)	North	Hansneset South	Fyke Net with Bait	3	*Liparis* sp.	14.5	71.58	M
D1 (1700)	South	Old Pier Central	Double Fyke Net	5	*Myoxocephalus Scorpius*	13.5	53.6	F
D2 (1702)	South	Old Pier Central	Fyke Net with Bait	3	*Myoxocephalus Scorpius*	11.5	28.76	M
D3 (1704)	North	Hansneset South	Fyke Net with Bait	12	*Myoxocephalus Scorpius*	17	108.9	F

2.2. Analytical Procedure

The freeze-dried, powdered, and weighed (0.25 g) samples (fish, Brittle star, Sea Urchin, and Worm sample) were kept in PTFE TFM vessels for microwave digestion following the standard method [1,26,27]. With the completion of the digestion program, the vessels were cooled, and the digested solution transferred into a 25 mL volumetric flask with deionized water. Blank samples were also prepared using the same procedure of samples, and the values obtained were subtracted from the samples. The individual samples were subjected to analysis of elements following the standard method using ICPM [1,26,27]. Elemental concentrations were measured in triplicates and were recorded in mg/kg.

Blood samples from 11 fishes belonging to 6 species (*Anashichas lupus* F (1738), *Gadus morhva* A2 (1644), *Gadus morhva* A1 (1707), *Gadus oguc* E (1643), *Gymnocanthus tricuspis* B1 (1763), *Gymnocanthus tricuspis* B2 (1737), *Liparis* spp. C2 (1703), *Liparis* spp. C1 (1770), *Myoxocephalus scorpius* D1 (1700), *Myoxocephalus scorpius* D2 (1702), *Myoxocephalus scorpius* D3 (1704)) were collected through sterile syringe and kept in sterile blood sampling tubes and preserved in a −80 °C deep freezer. A Leica DMLB 100 photomicroscope (Leica Microsystems AG, Wetzlar, Germany) equipped with a Linkam LK600 temperature controller (Linkam, Surrey, UK) was used to examine the antifreeze activity. A total of 5 µL of supernatant of blood sample was taken and observed under a 50× magnifying lens. The blood supernatant was briefly frozen (at about −25 °C) and warmed to 0 °C on the sample stage of the photomicroscope to create several ice crystal seeds in solution. This solution was then cooled to approximately −1 to −5 °C, and the growth of ice crystal seeds was monitored. According to the shape of the ice crystals, the positive and negative activity of the strains were noted. Hexagonal crystals indicated positive activity, while rounded type indicated negative activity.

3. Results and Discussion

The length and weight of Kongsfzorden fishes showed variation (Table 1). Among the fishes studied, *Liparis* sp. had the least length and weight (12.5–14.5 cm and 36.6 g–71.58 kg, respectively) followed by *Myoxocephalus scorpius* (11.5–17 cm and 28.76 g–108.9 kg), *Gymnocanthus tricuspis* (14.5 cm and 65.63 g), *Gadus morhua* (16.5–37.5 cm and 49.23, 634.7 g), *Gadus ozac* (30.0 cm and 352.88 g), and *Anarhichas lupus* (49.0 cm and 1321.07 g) with a higher length and weight. The length of the fishes gradually increased depending on the weight of the fish. Similar findings were also observed in the fish assemblage of a tidal creek in the Niger Delta, Nigeria [46].

The fish element concentration ranged from 0.134 to 0.757 mg/kg for Chromium in *Liparis* sp. and *Myoxocephalus scorpius*; 0.165 to 1.311 mg/kg for Manganese in *Anarhichas lupus* and *Myoxocephalus scorpius*; 0.000 to 0.051 mg/kg for Cobalt in *Gadus ogac* and *Liparis* spp.; 0.255 to 1.74 mg/kg for Copper in *Gadus morhu* and *Gymnocanthus tricuspis*; 8.569 to 37.358 mg/kg for Zinc in *Gadus morhu* and *Myoxocephalus scorpius*; 2.781 to 35.84 mg/kg for Arsenic in *Myoxocephalus scorpius* and *Gymnocanthus tricuspis*; 0.000 to 0.161 mg/kg for Mercury in *Liparis* sp. and *Gymnocanthus tricuspis*; and 0.000 to 0.117 mg/kg for Lead and 0.501 to 1.206 mg/kg for Selenium in *Gymnocanthus tricuspis* and *Gadus morhu*, respectively. However, these elements in invertebrates ranged from 0.392 to 0.916 mg/kg for Chromium in *Ophiura albida* (Brittle star) and *O. sarsii* (Brittle star); 14.13 to 64.834 mg/kg for Manganese in *Polychaete* (Worm) and *O. sarsii* (Brittle star); 0.541 to 1.336 mg/kg for Cobalt in *O. albida* and *Polychaete*; 0.775 to 10.045 mg/kg for Copper in *O. albida* and *O. Sarsii*; 20.178 to 77.622 mg/kg for Zinc in *O. albida* and *Polychaete*; 1.221 to 13.458 mg/kg for Arsenic in *O. albida* and *Polychaete*; 0.000 to 0.018 mg/kg for Mercury in *Strongylocentrotus droebachiensis* (Sea Urchin); 0.261 to 5.258 mg/kg for Lead in *O. albida* and *O. sarsii*; and 0.395 to 3.978 mg/kg for Selenium in *O. albida* and *Polychaete* (Worm), respectively.

Elemental analyses of fish muscles and invertebrates showed the presence of three groups of elements such as lithophiles, chalcophiles, and siderophiles. The lithophiles include Barium (Ba), Chromium (Cr), Cesium (Cs), Rubidium (Rb), Strontium (Sr), Uranium (U), and Vanadium (V); chalcophiles include Arsenic (As), Bismuth (Bi), Cadmium (Cd), Copper (Cu), Lead (Pb), and Zinc (Zn); while siderophiles include Cobalt (Co), Iron (Fe), Manganese (Mn), and Nickel (Ni). The concentration of lithophiles, chalcophiles, siderophiles, and a few others in fish muscles and invertebrates are presented in Tables 2–5.

Table 2. Lithophilic elemental composition (in mg/kg) in the Arctic fish and invertebrates.

Study Site	Organism	Sample	Ba	Cr	Cs	Rb	Sr	U	V
		LOQ (mg/kg)	**0.01**	**0.01**	**0.01**	**0.01**	**0.05**	**0.01**	**0.01**
Kongsfzorden	Fish	F (1738)	BLQ	0.149 ± 0.00	0.028 ± 0.00	1.509 ± 0.01	0.692 ± 0.01	BLQ	BLQ
		E (1643)	0.129 ± 0.01	0.144 ± 0.01	0.100 ± 0.00	2.16 ± 0.03	2.927 ± 0.01	BLQ	BLQ
		A2 (1644)	0.026 ± 0.00	0.197 ± 0.00	0.052 ± 0.00	2.171 ± 0.02	0.708 ± 0.01	BLQ	BLQ
		A1 (1707)	0.056 ± 0.01	0.363 ± 0.01	0.069 ± 0.00	4.046 ± 0.02	8.651 ± 0.01	BLQ	BLQ
		B2 (1737)	0.032 ± 0.01	0.319 ± 0.00	0.035 ± 0.00	1.665 ± 0.01	8.276 ± 0.04	BLQ	0.017 ± 0.00
		B1 (1763)	0.024 ± 0.01	0.442 ± 0.01	0.087 ± 0.00	2.894 ± 0.02	4.094 ± 0.05	BLQ	BLQ
		C1 (1770)	0.013 ± 0.00	0.235 ± 0.01	0.022 ± 0.00	1.866 ± 0.01	2.989 ± 0.04	BLQ	0.020 ± 0.00
		C2 (1703)	0.042 ± 0.00	0.134 ± 0.01	0.031 ± 0.00	1.682 ± 0.01	5.798 ± 0.05	BLQ	0.031 ± 0.00
		D1 (1700)	0.073 ± 0.01	0.378 ± 0.01	0.027 ± 0.00	1.619 ± 0.01	4.277 ± 0.07	BLQ	0.021 ± 0.00
		D2 (1702)	0.143 ± 0.01	0.757 ± 0.01	0.034 ± 0.00	1.669 ± 0.02	21.903 ± 0.14	BLQ	0.051 ± 0.00

Table 2. *Cont.*

Study Site Organism		Sample	Ba	Cr	Cs	Rb	Sr	U	V
		LOQ (mg/kg)	**0.01**	**0.01**	**0.01**	**0.01**	**0.05**	**0.01**	**0.01**
		D3 (1704)	0.048 ± 0.01	0.182 ± 0.01	0.044 ± 0.00	1.581 ± 0.03	7.212 ± 0.06	BLQ	0.018 ± 0.00
Kongsfzorden	Invertebrates	G (SFS)	6.823 ± 0.03	0.392 ± 0.00	0.032 ± 0.00	1.048 ± 0.02	1116.6 ± 10.69	0.169 ± 0.00	0.453 ± 0.01
		H (SFB)	27.559 ± 0.28	0.916 ± 0.01	0.029 ± 0.00	1.404 ± 0.01	1080.1 ± 3.97	0.519 ± 0.01	4.849 ± 0.02
		I (SU)	16.123 ± 0.08	0.914 ± 0.01	0.095 ± 0.00	1.943 ± 0.01	971.53 ± 10.20	0.098 ± 0.00	1.56 ± 0.01
		J (WOEM)	0.880 ± 0.02	0.394 ± 0.00	0.017 ± 0.00	1.171 ± 0.02	48.578 ± 0.66	0.161 ± 0.00	1.418 ± 0.01

F (1738) = *Anarhichas lupus*; E (1643) = *Gadus ogac*; A2 (1644) = *Gadus morhu*; A1 (1707) = *Gadus morhu*; B2 (1737) = *Gymnocanthus tricuspis*; B1 (1763) = *Gymnocanthus tricuspis*; C1 (1770) = *Liparis* spp.; C2 (1703) = *Liparis* spp.; D1 (1700) = *Myoxocephalus scorpius*; D2 (1702) = *Myoxocephalus scorpius*; D3 (1704) = *Myoxocephalus scorpius*; G (SFS) = Brittle star: *Ophiura albida*; H (SFB) = Brittle star: *Ophiura sarsii*; I (SU) = Sea Urchin: *Strongylocentrotus droebachiensis*; J (WOEM) = Worm: Polychaetes. BLQ = Below limit of quantification; LOQ = Limit of quantification.

Table 3. Chalcophilic elemental composition (in mg/kg) in the Arctic fish and invertebrates.

Study Site Organism		Sample	As	Bi	Cd	Cu	Pb	Zn
		LOQ (mg/kg)	**0.01**	**0.05**	**0.02**	**0.05**	**0.01**	**0.1**
Kongsfzorden	Fish	F (1738)	14.541 ± 0.11	BLQ	BLQ	0.262 ± 0.01	BLQ	11.616 ± 0.05
		E (1643)	26.181 ± 0.02	BLQ	BLQ	0.594 ± 0.01	0.037 ± 0.00	13.006 ± 0.13
		A2 (1644)	13.212 ± 0.06	BLQ	BLQ	0.255 ± 0.01	0.117 ± 0.01	8.569 ± 0.02
		A1 (1707)	6.982 ± 0.12	BLQ	BLQ	0.880 ± 0.01	BLQ	22.264 ± 0.22
		B2 (1737)	9.828 ± 0.07	BLQ	BLQ	0.609 ± 0.01	0.015 ± 0.00	12.811 ± 0.02
		B1 (1763)	35.84 ± 0.15	BLQ	BLQ	1.740 ± 0.04	0.028 ± 0.00	27.245 ± 0.54
		C1 (1770)	8.694 ± 0.04	BLQ	BLQ	0.901 ± 0.01	0.029 ± 0.00	15.084 ± 0.1
		C2 (1703)	16.253 ± 0.10	BLQ	BLQ	0.840 ± 0.02	0.011 ± 0.00	16.326 ± 0.05
		D1 (1700)	3.291 ± 0.01	BLQ	BLQ	0.946 ± 0.01	0.020 ± 0.00	16.578 ± 0.1
		D2 (1702)	2.781 ± 0.03	BLQ	BLQ	0.857 ± 0.02	0.029 ± 0.00	37.358 ± 0.30
		D3 (1704)	4.537 ± 0.09	BLQ	BLQ	0.814 ± 0.01	0.030 ± 0.00	14.544 ± 0.16
Kongsfzorden	Invertebrates	G (SFS)	1.221 ± 0.02	BLQ	0.214 ± 0.01	0.775 ± 0.02	0.261 ± 0.01	20.178 ± 0.19
		H (SFB)	4.139 ± 0.04	0.652 ± 0.02	BLQ	10.045 ± 0.05	5.258 ± 0.05	40.695 ± 0.20
		I (SU)	4.506 ± 0.04	BLQ	BLQ	0.918 ± 0.02	0.473 ± 0.01	23.731 ± 0.02
		J (WOEM)	13.458 ± 0.14	0.904 ± 0.01	BLQ	2.113 ± 0.01	0.884 ± 0.01	77.622 ± 0.34

All data are mean of triplicate readings.

The lithophiles were found in lower concentrations in different fishes than the benthic organisms studied in the present study (Table 2). The concentration of Sr was significantly higher than the values recorded in most of the fishes and invertebrates. Uranium values were below the quantification in all the fishes, while the lowest concentration was detected in invertebrates. The values of lithophiles were much lower than the values reported from the sediments of Kongsfzorden [25–27], lichens, and glacier cryoconites [1,29] of Svalbard.

Table 4. Siderophilic elemental composition (in mg/kg) in Arctic fish and invertebrates.

Study Site	Organism	Sample	Co	Fe	Mn	Ni
		LOQ (mg/kg)	**0.01**	**0.5**	**0.05**	**0.1**
Kongsfzorden	Fish	F (1738)	BLQ	0.799 ± 0.01	0.165 ± 0.00	0.124 ± 0.02
		E (1643)	BLQ	2.91 ± 0.02	0.344 ± 0.00	0.165 ± 0.03
		A2 (1644)	BLQ	0.907 ± 0.01	0.262 ± 0.01	0.249 ± 0.04
		A1 (1707)	0.024 ± 0.00	5.479 ± 0.06	1.094 ± 0.01	0.225 ± 0.07
		B2 (1737)	0.021 ± 0.00	3.179 ± 0.01	0.626 ± 0.01	0.273 ± 0.05
		B1 (1763)	0.029 ± 0.00	8.141 ± 0.12	1.168 ± 0.01	0.177 ± 0.05
		C1 (1770)	0.038 ± 0.00	3.395 ± 0.04	0.407 ± 0.00	0.257 ± 0.04
		C2 (1703)	0.051 ± 0.00	4.573 ± 0.04	0.554 ± 0.01	0.24 ± 0.03
		D1 (1700)	0.028 ± 0.00	4.401 ± 0.05	0.517 ± 0.01	0.246 ± 0.03
		D2 (1702)	0.041 ± 0.00	7.248 ± 0.06	1.311 ± 0.01	0.439 ± 0.04
		D3 (1704)	0.015 ± 0.00	3.533 ± 0.06	0.656 ± 0.01	0.364 ± 0.06
Kongsfzorden	Invertebrates	G (SFS)	0.541 ± 0.01	83.72 ± 0.14	19.848 ± 0.21	2.668 ± 0.05
		H (SFB)	0.774 ± 0.01	438.34 ± 1.95	64.834 ± 0.20	3.778 ± 0.08
		I (SU)	0.733 ± 0.01	240.95 ± 2.08	19.491 ± 0.21	2.616 ± 0.07
		J (WOEM)	1.336 ± 0.01	129.50 ± 1.09	14.13 ± 0.06	1.686 ± 0.02

All data are mean of triplicate readings.

Table 5. Other elemental composition (in mg/kg) in the Arctic fish and invertebrates.

Study Site	Organism	Sample	Se	Ag
		LOQ (mg/kg)	**0.05**	**0.05**
Kongsfzorden	Fish	F (1738)	0.816 ± 0.04	BLQ
		E (1643)	0.663 ± 0.03	BLQ
		A2 (1644)	0.501 ± 0.02	BLQ
		A1 (1707)	0.829 ± 0.08	BLQ
		B2 (1737)	0.654 ± 0.03	BLQ
		B1 (1763)	1.206 ± 0.05	BLQ
		C1 (1770)	0.643 ± 0.01	BLQ
		C2 (1703)	1.034 ± 0.01	BLQ
		D1 (1700)	0.804 ± 0.02	BLQ
		D2 (1702)	0.663 ± 0.05	BLQ
		D3 (1704)	0.697 ± 0.02	BLQ
Kongsfzorden	Invertebrates	G (SFS)	0.395 ± 0.03	1.143 ± 0.01
		H (SFB)	1.171 ± 0.05	1.189 ± 0.02
		I (SU)	1.063 ± 0.10	0.367 ± 0.01
		J (WOEM)	3.978 ± 0.02	0.330 ± 0.01

All data are mean of triplicate readings.

The chalcophile elements were in a higher concentration in the fishes than the lithophiles (Table 3). In the fishes, elements such as As and Zn were present in concentrations higher than the values of Cu and Pb. The concentrations of Bi and Cd values were below the quantification in all the fishes, while in a few invertebrates the lowest concentration was detected. The high concentrations of As in fishes E(1643) and B1(1763), and Zn in B1(1763) and D2(1702) were recorded. The concentration of Zn was comparatively much higher in invertebrates (Brittle star: *Ophioceten sericeum* and Worm: Polychaetes) than the fishes. The high concentrations of As in fishes E(1643) and B1(1763) is evidence that proves that there is a process of bioaccumulation in fishes which may lead to Arsenic poisoning in the fish population, which is sourced from the Svalbard terrestrial habitats. High concentrations of As have also been reported in sediments from Kongsfzorden [26] and glacier cryoconites [1]. These observations provide a clue that the Svalbard probably holds enriched sources of elements such as As and Zn. A bio-monitoring study by Borgå et al. [20] found elevated levels of Zn and Cu in Arctic seabirds as a consequence of bioaccumulation. In the fish muscles, elements such as Cd and Pb were present in lower concentrations, while for Zn, the concentrations exceeded the values reported from the Red Sea [47–49]. In the case of Cu, the concentrations were higher in the present study than the two estimates at the Red Sea [47,49]. Since no previous information is available on the concentration of these elements from Arctic fjords, no comparison could be made.

The siderophiles (Co, Fe, Mn, and Ni) were lower in the Arctic fishes than the invertebrates (Table 4). However, the Fe and Mn values of Arctic fishes were very similar to estimates at the Red Sea and lay in between the reported values [49]. In the case of Ni and Cu, concentrations were lower in the present study than the estimates for the fish muscles at Chascomus lake [50]. Siderophiles from sediments from Kongsfzorden [26] and glacier cryoconite [1] habitats of Svalbard close by corroborate with the present results. A comparison of siderophilic elements from the present study with other habitats of Svalbard showed comparatively lower concentrations of siderophiles [1,26]. Elements such as Ag and Se were also analyzed from Kongsfzorden fishes and invertebrates of the Arctic region (Table 5). The concentration of Ag and Se was higher in invertebrates than fishes.

Determining the exact source of the elements is often difficult as it may arise from multiple sources [51]. We can, however, segregate the sources into two groups: local deposition and long-distance (transboundary) transmission [52]. Pollutants from various sources (natural or anthropogenic) are released into the atmosphere and through wind movement travel long distances [51]. Moreover, the erosive action of glacial ice also deposits sediments with different elements into Kongsfzorden, which is another important contributor. High concentrations of anthropogenic (^{137}Cs, ^{90}Sr) and natural (^{210}Pb) radionuclides and heavy metal (Pb, Cd, Cu, Zn, Fe, and Mn) deposition were reported from glacial cryoconite of Spitsbergen [30]. The glacial cryoconite elements with melt water finally enter into the Kongsfzorden and accumulate in aquatic organisms including fishes and invertebrates.

In the fishes and invertebrates studied, the concentration of most of the elements in the invertebrates were much higher than the fishes present in Kongsfzorden, probably because the invertebrates are benthic and stay on the seafloor where all the sediments are accumulated, brought down by wind and the surrounding glaciers. The high velocity winds, after hitting the mountainous terrain, subside into the valley depositing the dust it carries. The difference in depths of collection sites may also affect the deposition patterns of elements. In the Arctic fishes and invertebrates, the values of elements such as Cd, Cr, Cu, Pb and Zn were different than the values reported in lichens and cryoconites [29], Kongsfjorden sediments [25,26], and ice cores [27] (Table 3).

The observed elemental concentrations in the present study were below the EU maximum concentrations of 0.050 mg/kg for Cd and 0.3 mg/kg for Pb for fish species [53]. The amount of As (2.78–35.84 mg/kg) in the present study exceeds the Russian regulation limit of 5.0 mg/kg (wet-weight) in seawater fish [54]. Recently, Sobolev et al. [11] also recorded higher concentrations of As in the Russian Arctic which were not recommended for human consumption. Further, the comparison of the current study on essential elements such as copper (Cu: 0.255–1.740 mg/kg), cobalt (Co: 0.015–0.051 mg/kg), selenium (Se: 0.501–1.206 mg/kg), and zinc (Zn: 8.569–37.358 mg/kg) showed considerably higher concentrations in fish species of Svalbard, High Arctic, than the fish species of the Russian Arctic [11]. Benthic organisms analyzed during the present study showed significantly higher concentrations than the fish species of Svalbard. Arctic fishes feed primarily on zooplankton, salmon eggs, insects, and benthos [55], which may possibly result in a bioaccumulation process through the food chain in the High Arctic.

Out of eleven blood samples of different fishes screened for AFPs, two species (*Gadus morhva* and *Anashichas lupus*) have shown weak activity, while four species (*Gadus oguc*, *Gymnocanthus tricuspis*, *Liparis* spp., *Myoxocephalus scorpius*) have shown strong AFP activity (Figure 3a–f). AFPs help fishes to survive in the cold Arctic water.

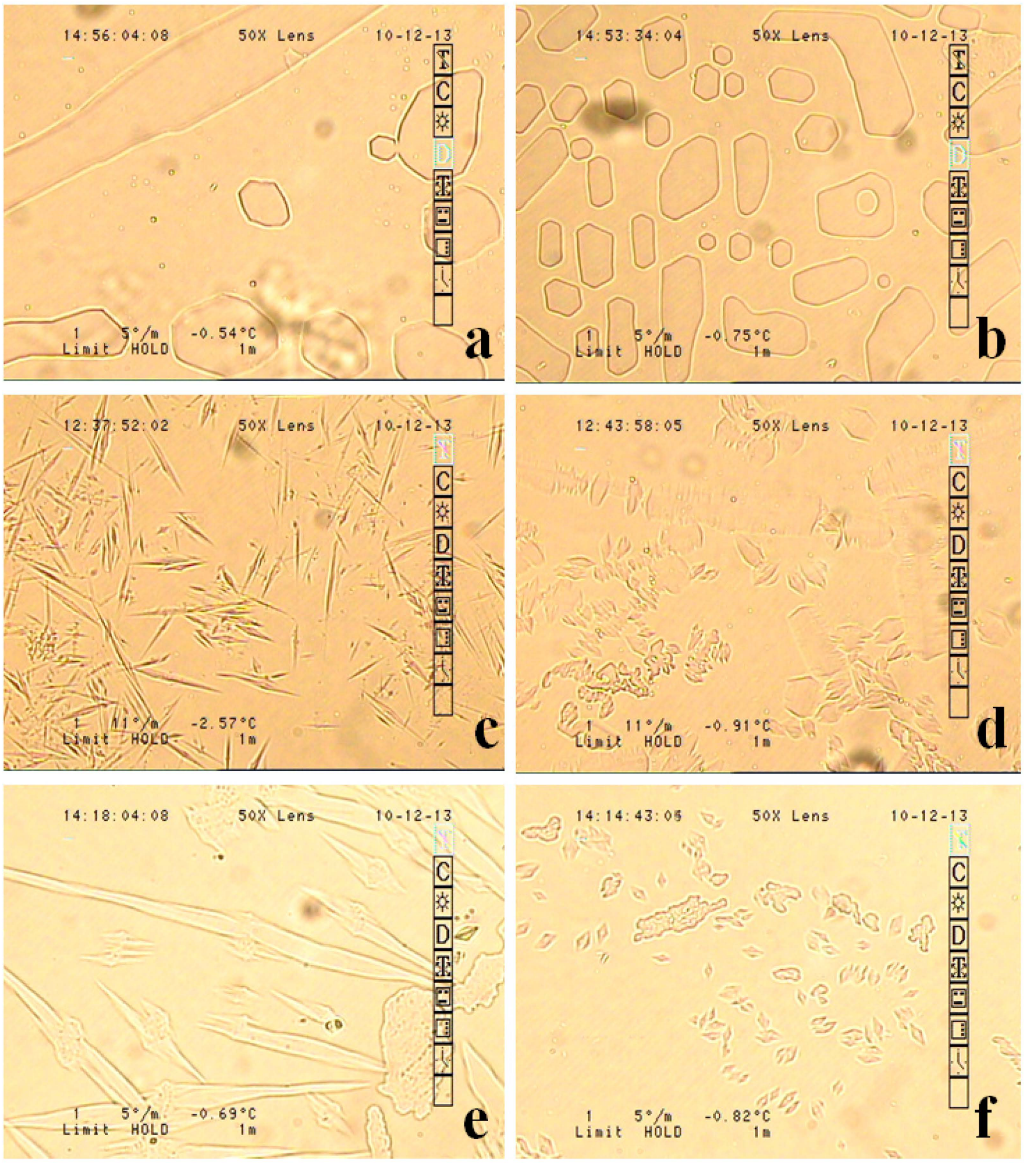

Figure 3. AFP activity of High Arctic fish. (**a**). *Anashichas lupus*; (**b**). *Gadus morhva*; (**c**). *Gadus oguc*; (**d**). *Gymnocanthus tricuspis*; (**e**). *Liparis* sp.; (**f**). *Myoxocephalus scorpius*.

4. Conclusions

An overall comparison between the two sets of data reveals that benthic organisms had a greater concentration of most elements as compared to the fishes. This is the first study on determining the elemental concentration of High Arctic fish and invertebrates. It is assumed that elemental concentrations present in High Arctic organisms are above the normal range. Therefore, it is advised that the human impact must be avoided to protect the fragile ecosystem of the High Arctic. The data of the present study will be useful to the scientific community and public officials involved in the environmental monitoring of Arctic ecosystems.

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