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DIFFERENCES IN THE SYNERGIC ACCUMULATION OF TOXIC ELEMENTS IN PELAGIC AND BENTHIC FISH FROM GLACIER-FED RIVERS OF THE DZUNGARIAN ALATAU

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Abstract

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The determination of potentially toxic element concentrations in fish is an important topic from the point of view of both nature conservation and human consumption. The aim of this study was to assess the concentrations of S, K, Ca, Cr, Mn, Fe, Zn, Rb, Sr, Mo, and P in benthic and pelagic fish species in the Karatal river, which is fed by melting glaciers from the Dzungarian Alatau in Kazakhstan. In September 2022, 48 fish samples were collected. It has been demonstrated that the accumulation of chemical elements in fish species can be explained by both the physiological parameters of the fish species and the influence of glaciers that feed river habitats. The data presented in this study provide a synergistic view of pollutants affecting fish populations. Benthic fish contained more manganese and strontium than pelagic species, while the mutual accumulation of potassium, chromium, rubidium, and molybdenum was higher in pelagic fish. The synergistic concentration of calcium and phosphorus in pelagic fish was higher than that in benthic species, while the amount of zinc and sulfur was higher in benthic animals. Relatively elevated levels of mercury in fish were found. The study contributes to the discussion about the role of glacial environments in loading pollutants to aquatic systems.

Key words: potentially toxic elements, pelagic and benthic fish, Karatal river, Dzungarian Alatau.

Introduction

Mountainous areas of the world include some of the most glaciated landscapes. Recently, studies have shown that organic, metal, and other pollutants originating from outside a large mountain system can be transported long range through atmospheric circulation and deposited onto surrounding glaciers, endangering downstream regions of glacier-fed river basins (Huang et al., 2014; Zhang et al., 2014). Glaciers are currently subject to a rapid rate of melt and thus release large quantities of these historical contaminants into their meltwater (Zhang et al., 2015). Glacial melt as a significant source of pollutants has been expressed in many studies (Villa et al., 2006; Schmid et al., 2007; Thies et al., 2007; Bizzotto et al., 2009), particularly as glaciers undergo a downward flow of ice from their higher to lower elevation extremes. Therefore, a small amount of ice can represent a significant reservoir of contaminants (Blais et al., 2001; Bettinetti et al., 2008).

In the hydrological cycles of alpine glaciers, pollutants are characterized by two important properties. The first phenomenon is their historical accumulation in ice, which plays a vital role in the contamination of surrounding alpine water environments. In addition, snowfall also acts as a transitional medium between the atmosphere and aquatic ecosystems, playing a significant role in the cycling of contaminants in the high mountains, particularly during spring melt (Janiga, 2001, 2002; Janiga, Haas, 2019). The second phenomenon is the effect of glacier melt on stream and river hydrodynamics, influencing the release of contaminants into downstream watercourses. Therefore, metals and other pollutants released from water and sediments from melting glaciers may accumulate in the biomass of downstream ecosystems (Zhang et al., 2012; Huang et al., 2014). Accelerated ablation of glaciers can result in significant release of chemicals from high mountain ranges into valley catchments (Sun et al., 2017). This becomes more significant for the downstream ecosystems in the light of ongoing global warming (Zhang et al., 2015).

The Dzungarian Alatau is an isolated mountainous country lying at the junction of two biogeographic regions: the northern boreal and the southern Mediterranean area. Biota has a transitional character from the Altai to the Tian Shan. The Dzhungar mountain region consists of a series of latitudinally oriented

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mountain ranges with glaciers separated by intermountain basins. The area of glaciation is about 1,000 km^2. These glaciers are mostly in decline. Snow cover at altitudes of 2000 m and higher begins to occur between October and November and melts between March and April. During uncharacteristically warm winters, this melt can begin as early as February (Zhavoronko, 2018; TOO, 2021). In central Asia, long-range transboundary air pollution plays a key role in the contamination of glaciers with metals and other pollutants. As westerly air masses prevail in the Dzhungar mountains through winter and into late springtime (Dong et al., 2015; TOO, 2021), large amounts of anthropogenic pollutants from urban areas are transported and deposited. Some countries in central Asia are significant sources of this contamination, with sizable anthropogenic emissions into the atmosphere (Kakareka et al., 2004). Within Kazakhstan, emissions largely originate from industrial centers, including Almaty, Nur-Sultan, Ust-Kamenogorsk, Temirtau, Atyrau, Aktau, Zhezkazgan, Aktobe, Balkhash, Pavlodar, and Taldykorgan (Kazgidromet, 2021). In this region, approximately 3–4 million tonnes of polluting chemicals are released into the air annually (Saparov, 2014). Today, 73% of electricity in Kazakhstan is generated by coal-fired thermal power plants, which are sources of many metal emissions. In 1999, emissions of mercury, cadmium, and lead were half of levels recorded in the early 1990s, but by 2011, emissions had returned to previous levels (Yeserkepova, 2014). Owing to increased economic development, these emissions have continued to increase throughout mountainous regions of central Asia (Ohara et al., 2007), and this process coupled with the gradual warming and retreating of glaciers (Sun et al., 2018) will increase the accumulation of pollutants in Kazakh glacier-fed rivers (Zhanykhan, Kozykeeva, 2017; Zhavoronko, 2018).

The Karatal river is the second-largest river in the Kazakh Semirechye region in terms of volume and water content (F=19,100 km^2, L=390 km). It originates on the north-western slopes of the central Dzungarian Alatau ridge. Its waters originate from the Tronova glacial complex, and its main tributaries are the Kora and Motanive (Zhavoronko, 2018). Prevailing ions detected the water of this river are bicarbonate and calcium ions. The water quality level above the town of Taldykorgan is characterized as polluted (TOO, 2021). Excessive levels of metals such as manganese, copper, and iron have been measured in the river (Kazgidromet, 2018). Concentrations of other metals, such as lead and arsenic, also increased significantly between 2010 and 2014 (Zhanykhan, Kozykeeva, 2017). Today, concern over glacial melt-induced release of heavy metals and its potential impact on glacier-fed ecosystems has been escalated. Recent contamination (Lin et al., 2017; Neupane et al., 2019) and historical contamination (Huang et al., 2012) of melting glaciers in central Asia as well as increased erosion of an area rich in lead, copper, arsenic, radionuclides, and other elements (Andasbayev et al., 2013; Zhavoronko, 2018; Cherednichenko et al., 2021) have a significant impact on the contamination of river biota, particularly fish (Biyasheva, 2010).

Determining metal concentration in fish is an important subject, with respect to both nature management and human consumption of fish. Pollutants enter fish via their food, through their gills, through oral consumption of water, and water contact with skin. Pollutants are carried through the blood stream, stored in the liver, excreted by gills or kidneys, or stored in muscles and fat tissues. Some metal pollutants are highly toxic to fish (Danabas, Ural, 2012). Understanding the metal distribution in fish tissues is important as different fish species living in different habitats have developed variable thresholds for adaptation to ambient waterborne chemicals during their long evolutionary history. Because benthic fish often inhabit the bottom layers of watercourses, they tend to have a higher capacity for absorption of some metal ions through their gills and body surface compared to pelagic fish species, thereby reducing their demand for metal element absorption from food. For example, when it comes to mercury, numerous studies have found that food segregation – benthic versus pelagic – has significant effects on fish mercury concentrations. Fish with benthic diets tend to have higher mercury concentrations (France, 1995; Power et al., 2002; Andreji et al., 2006; Noël et al., 2013; Andreji, Dvořák, 2018; Chiapella et al., 2021). Conversely, zinc accumulates mainly in omnivorous fish, especially in common carp, a species that has been shown to accumulate this element to a greater extent than other fish (Lowe et al., 1985; Andreji et al., 2006; Andreji, Stráňai, 2007). Small fish species may be also sensitive to elevated levels of zinc in waters (Koca et al., 2005; Danabas, Ural, 2012; Pastorino et al., 2020). The dietary Zn requirement of typical benthic fish species is always lower than that of freshwater pelagic species (Satoh et al., 1992; Paripatananont, Lovell, 1995; Luo et al., 2011; Welker et al., 2016). In addition, due to their chemical properties and ability to bind ions, elements can accumulate in fish bodies independently, competitively, or mutually, often with a negative synergistic effect on the organism. For example, the concentrations of rubidium and molybdenum in some benthic lacustrine fish remain in their body longer than sulfur and potassium. As a result, the ratio of metals to these macro-minerals is higher in lacustrine fish than in fluvial fish. Rubidium can compete with potassium (Peters et al., 1999), suggesting that rubidium concentration in lacustrine fish is dependent on the quantity of other alkali chemical elements in the surrounding water environment.

The recent accelerated mass loss of alpine glaciers leads to an increased release of chemicals from surficial ice layers, which under stable climate conditions would have been retained much longer within the glacier (Nawab et al., 2022). The coupling of glacier dynamics and pollutant cycling is a complex topic, and synergic effects of chemicals on different ecological groups of fish in glacial rivers represent a poorly studied research field. This study aims to assess the effects of mutual accumulation of twelve chemical elements in pelagic and benthic fish species living in a river whose waters come from melting glaciers. The analysis was conducted during autumn, and the accumulation of elements was measured in juvenile fish, which are thought to absorb pollution from glaciers more intensively than adult individuals.

Material and methods

Sampling was conducted in the Karatal river, which is part of the Zhetysu region (eastern Kazakhstan, city of Taldykorgan (Fig. 1) in September 2022 (45°1´51.267´´N 78°23 ´55.400´´E). A total of 35 benthic Tibetan Stone Loaches, *Triplophysa stoichkai* (Steindachner, 1866), and 13 samples of two pelagic species [nine of Aral Basin Snowtrout *Schizothorax intermedius* (McClelland, 1842) and four of Naked Osman *Gymnodiptychus dybowskii* (Kessler, 1874)] were collected. All individuals were found deceased and were all juveniles, with a length ranging between 6 and 11 cm. The samples were stored in marked plastic bags and then dried.



Fig. 1. Location of fish sample collection from the Karatal river, Taldykorgan city, Kazakhstan (Author: S. Feješ, 2022).

A DELTA ED-XRF spectrometer was used to analyze the elements in the fish skulls. Analysis was performed in a closed portable Delta XRF workstation where each sample was handled and examined in the same manner. Results were reported in ppm units, and detection limits were determined continuously for each measurement. The CONOSTAN calibration standard and Compton's normalization algorithm were used to obtain the lowest limit of detection (LOD). The limits of detection were determined for each element, and the minimum value for a particular element represented the spectrometer's actual limit of detection for the material being measured. The accuracy of this method was determined by analysis of certified standard reference material. The following elements were detected: S, K, Ca, Cr, Mn, Fe, Zn, Rb, Sr, Mo, and P.

For mercury analysis, dried fins were used. From each sample, the right or left pectoral fin was used. The fins were cut off with a scalpel, and the scalpel was washed after each measurement with 96% ethyl alcohol. Then, the samples were inserted into a DMA-80 Direct Mercury Analyzer (Milestone, Italy). Total mercury (dry weight) was measured for each sample. The accuracy of the measurement was verified through analysis of standard reference material, including NCS ZC 7001 bovine liver (CHNACIS, China) and bone meal standard (SRM 1486, Maryland).

Principal component analysis (PCA, correlation matrix) was used to determine synergistic accumulation of chemical elements in the tissues of benthic and pelagic fish in a glacial river. PAST software, version 4.12 (Hammer et al., 2001), was used to compare the scores of multivariate vectors (expressed by coordinates of variables) of the original data in relation to element concentrations in fish from different habitats. The scores were compared using one-way ANOVA. In the case that scores of groups had unequal variances, we used the unequal-variance Welch version of ANOVA. Principal component analysis finds hypothetical variables (components) to account for as much of the variance as possible in multivariate data. These new variables are linear combinations of the original variables. The correlation matrix was used. Percentages of variance accounted for by the components are also given. Researchers differ in opinion regarding how many PCs should be interpreted from a given data set. In our sets of chemical element concentrations in the tissues of fish, the procedure does not depend on a file of limiting assumptions (cf. Jolicoeur, 1984). An implicit assumption in the use of ordination methods is that the experienced ecologist can separate meaningful patterns from random noise. An ability to distinguish "signal" from "noise" is essential. The synergistic accumulation of chemical elements are usually expressed by different principal components. Differing groups of elements accumulate depending on distinct factors, including fish physiology, season, substrate, and flooding. Therefore, focusing on the percentage of variance, and potentially on a limited number of components, may not be a decisive methodology by which to determine how chemicals accumulate in fish. The failure to distinguish valuable categories can lead to the rejection of useful information (Jackson, 1991). The most promising models (broken-stick or boot-strapped eigenvalue-eigenvector) suggest that one-quarter

Table 1. Coordinates of variables (vectors) of the first six principal components (PC1 - PC6) with the percentages of variance accounted for by the components. The highest numbers in a column (highlighted) denote the main effects of element accumulation in the bodies of fish.

	PC1	PC2	PC3	PC4	PC5	PC6
S	0.022858	0.208748	-0.498588	**0.669327**	-0.212956	-0.382026
K	-0.345373	**0.615634**	-0.136950	-0.256128	-0.493329	-0.288828
Ca	0.362722	-0.253735	**-0.787555**	-0.345866	0.134601	-0.015077
Cr	0.424635	**0.732732**	0.175437	0.066441	0.291668	-0.082348
Mn	**0.815511**	0.025820	0.111890	-0.338439	-0.115752	-0.012620
Fe	0.558255	0.386204	0.505387	-0.384615	-0.226318	-0.028634
Zn	0.465937	0.332729	-0.127646	**0.681284**	-0.120253	0.187234
Rb	-0.446335	**0.659737**	-0.125990	-0.292454	-0.372232	0.166761
Sr	**0.879619**	-0.125867	-0.261859	-0.023882	-0.181144	-0.119435
Mo	0.082224	**0.739994**	-0.372463	0.111192	0.200653	**0.416916**
P	-0.087372	0.028780	**-0.885100**	-0.390867	0.113798	0.009518
Hg	-0.106473	0.526866	0.105655	-0.130930	**0.702316**	-0.323956
Var.	21.9%	21.4%	18.5%	13.6%	9.9%	4.9%

to one-half of the components should be interpreted (Jackson, 1993; Hammer et al., 2001). Six components were retained in our analyses, and then, PC scores were compared between pelagic and benthic groups of fish.

Results and discussion

Differential accumulation of strontium and manganese versus rubidium in pelagic and benthic fish

Benthic fish contained significantly more manganese and strontium in their bodies than pelagic species (Fig. 2, *x*-axis). The accumulation of these elements was partially accompanied by the accumulation of zinc, iron, and calcium. The second significant factor (Table 1, PC2) is characterized by the mutual accumulation of potassium, chromium, rubidium, and molybdenum. Significantly higher levels were found in pelagic fish than in benthic fish (Fig. 2, *y*-axis).

According to the percentage of variance in the principal component analysis, we can conclude that the differential accumulation of strontium and manganese versus rubidium is one of the most significant phenomena (PC1) currently affecting fish in the icy waters of the Karatal river. This reflects the intense chemical weathering process in the high mountains of Dzungarian Alatau. While benthic fish contain more manganese and strontium accompanied by calcium or iron, they have less rubidium and potassium in their bones. Pelagic species, however, have significantly more rubidium but less strontium and manganese. Strontium and rubidium are components of geochemical processes in high-elevation mountain regions. If the strontium/rubidium ratio becomes higher, it indicates a higher prevalence of chemical weathering in a water ecosystem (Jin et al., 2015; Zhu et al., 2020). This weathering can be very intense in warm and humid climates (Jiang et al., 2018), and under these conditions, strontium content in the water increases rapidly. Strontium and rubidium often occur in dissolved form, but strontium is less mobile because of rapid precipitation with calcium as strontium carbonate (Neal et al., 1996). Manganese also occurs naturally at higher concentrations in running water during spring runoff or snowmelt (Reimer, 1999) and was found in higher concentrations in fish during summer and fall (Salem et al., 2014). Strontium concentrations in fish also increase with altitude (Perinajová et al., 2020). In the mountains of Central Asia, strontium, manganese, and zinc levels in stream and river waters are highest at altitudes of 3000–4000 m (Solár, Janiga, 2023), while levels of rubidium and potassium peak in water about 1000 m lower (Janigová, Janiga, 2023). This means that sedimentation of manganese and strontium starts earlier in the mountains than rubidium, and subsequently, at lower elevations, the concentrations of manganese and strontium in sediments may already be exceedingly high. In the case of the Karatal river, the concentration of manganese in sediments is at 700–900 ppm (Zhanykhan, Kozykeeva, 2017). Therefore, it is likely that the phenomenon of chemical weathering causes the ratio of strontium, manganese, zinc, and calcium to rubidium and potassium to be higher in benthic fish than in pelagic fish (Linnik et al., 2002; Du et al., 2020). Benthic fish live on the river bottom for most of their lives and absorb higher quantities of metals through their gills from their environment than pelagic fish species (Welker et al., 2016;

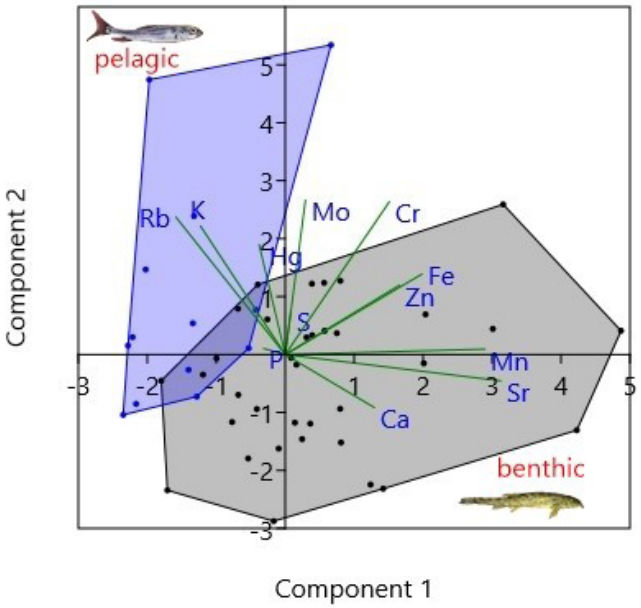


Fig. 2. Differences in mutual accumulation of manganese and strontium (x-axis) and potassium, chromium, rubidium, and molybdenum (y-axis) in benthic (grey convex hull) and pelagic (blue convex hull) fish from the river Karatal, Kazakhstan. Benthic fish contained significantly more manganese and strontium than pelagic species (One-way ANOVA: F = 19.5, p = 0.000), while the mutual accumulation of potassium, chromium, rubidium, and molybdenum was higher in the head bones of pelagic fish than benthic fish (F = 7.9, p = 0.001). The first two principal component scores from PCA were compared.

Du et al., 2020). Manganese and strontium are elements that fish absorb from the aquatic environment (Shotyk et al., 2019) primarily through their gills (Milošković et al., 2022). Evidence suggests that strontium enters the body using calcium transport (Chowdhury, Blust, 2011). Strontium and manganese in fish can vary significantly both within and between years (Templeton, Brown, 1964; Janiga et al., 2021) and their amount in bone tissue correlates with age; younger individuals exhibit higher levels than older ones (Speckman, Norris, 1964; Janiga, Janiga, 2023). Increased glacial melt exacerbated by climate change must be considered a significant source of inorganic compounds impacting ecosystems in the lower catchment (Thies et al., 2007).

Potassium, chromium, rubidium, and molybdenum in pelagic versus benthic fish

Elevated levels of these elements in the aquatic environment can be very toxic to fish, especially if they act synergistically within the organism. Rubidium and molybdenum can inhibit spermatogenesis and cause necrosis of spermatogonia (Yamaguchi et al., 2007). Higher concentrations of rubidium are typically found in muscle than in liver, bone, or skin (Plessl et al., 2017; Alti et al., 2022). Molybdenum accumulates in the bones, stomach, kidneys, and liver (Ward, 1973), and elevated levels can be toxic to young fish (Davies et al., 2005).

Potassium is a common macronutrient in nature, but potassium salts are highly toxic to freshwater fish. For example, hy-

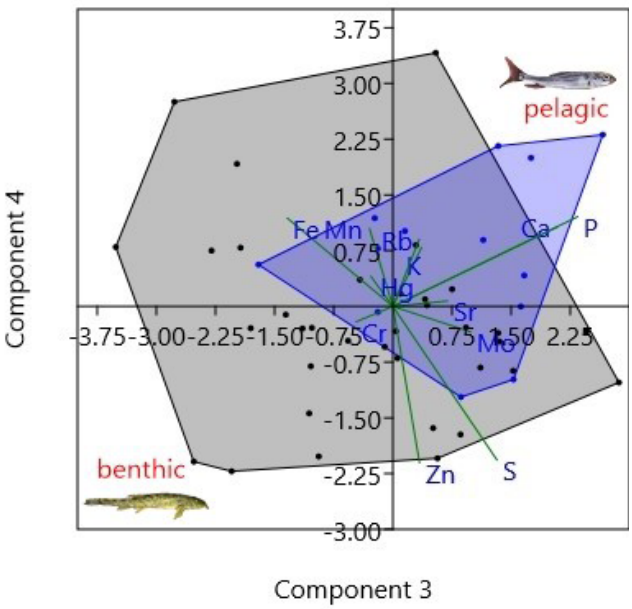


Fig. 3. Mutual accumulation of calcium and phosphorus (x-axis) in the skulls of pelagic fish (blue convex hull) was higher than in benthic specimens (grey convex hull) species (F = 5.7, p = 0.02). The samples significantly differed in zinc and sulphur accumulation. In benthic fish, the amount of these elements was higher (y-axis down) than in pelagic species. Component 4: One way ANOVA F = 5.8, p = 0.02. The scores from principal component analysis were compared.

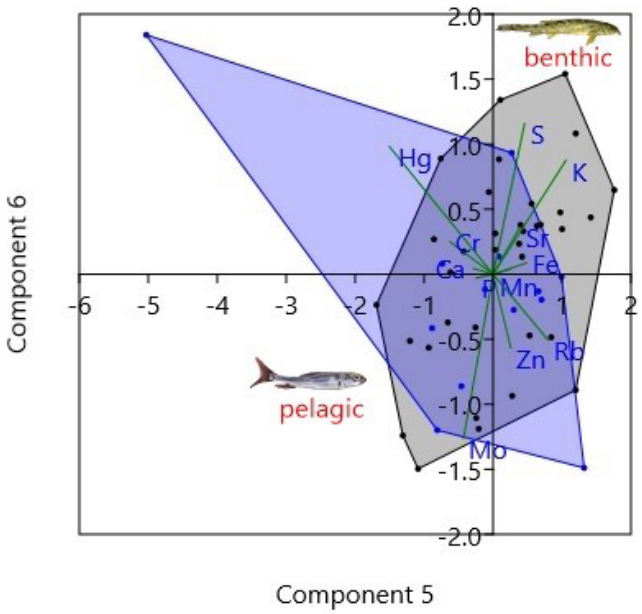


Fig. 4. Component 5 is a unipolar vector that describes mercury accumulation in fish. Mercury was measured in the pectoral fins. Concentrations did not differ between pelagic (blue) and benthic (grey) fish. (F = 1.2, p = 0.27). Component 6 primarily describes the accumulation of molybdenum. Again, pelagic and benthic species did not differ (F = 0.51, p = 0.47). The scores from principal component analysis were compared.

perkalemia is known to be lethal through disruption of cardiac function and depolarization of cell membranes in many aquatic organisms (Cruz, Tamse, 1989; Cripps et al., 2013). Potassium is a rubidium analogue, and the two substances can compete in fish (Peters et al., 1999). Higher concentrations of chromium can also be toxic to fish, causing hypertrophy, paraplegia at the gill epithelium, or anemia (Aslam, Yousafzai, 2017). In general, pelagic, primarily carnivorous or omnivorous, fish species typically contain more rubidium (Guevara et al., 2006), chromium (Andreji, Stráňai, 2007), molybdenum (Saiki et al., 1993; Ikemoto et al., 2008), and potassium (Espinoza-Quiñones et al., 2011) than similar benthic fishes. The different life strategies of pelagic and benthic fishes are undoubtedly influenced by distinct levels of water pollution and the accumulation of different contaminants in their diet. Many pelagic species feed on zooplankton during juvenile development, and it has been shown that higher concentrations of the above elements are often present in this food source (Guevara et al., 2006). In glacial rivers, water contamination depends on the solubility rate of compounds containing toxic elements. The impact of glaciers on rivers is particularly evident in early autumn. In Central Asia, molybdenum and chromium are deposited on glacial surfaces largely due to anthropogenic processes, while rubidium originates in the Earth's crust (Dong et al., 2015). High levels of rubidium occur in granitic soils, as it is a lithophilic element and its concentrations in glacial waters mainly reflect natural input (Anke et al., 2005). Measurements of element contents in rivers in the Tian Shan Mountains of Kyrgyzstan have shown that potassium, chlorine, and rubidium increase steadily with decreasing elevation until 3,000 to 2,500 m, but at even lower elevations (2,000 to 1,000 m), their concentrations decrease (Janigová, Janiga, 2023). Similarly, chromium abundance also decreases rapidly with decreasing elevation (Solár, Janiga, 2023), while molybdenum concentrations increase (Janigová, Janiga, 2023), indicative of a different lowland pattern of anthropogenic molybdenum emissions.

Biogens – calcium, phosphorus, zinc, sulfur

The third factor (PC3, Table 1) describes the synergic concentration of calcium and phosphorus (Fig. 3, x-axis) and reflects the difference between the amount of these biogens in benthic species compared to pelagic fish species. Pelagic fish species tend to contain more calcium and phosphorus than benthic fish species. (Fig. 3). The fourth factor (13.6% of data variance, Table 1) is also a unipolar vector and mainly describes the positive relationship between zinc and sulfur accumulation in fish. In this case, benthic fish contained significantly more S and Zn than pelagic individuals (Fig. 3, y-axis).

Zinc concentrations in Karatal fish are further reflected by the variability of data in component 4 (PC4; Table 1, Fig. 3). In this case, zinc and sulfur have higher levels of synergistic concentration in benthic fish than in pelagic fish. This phenomena appears to be unrelated to the chemical weathering impacting the first component and is more likely related to the presence of sulfates and other zinc salts in the water. Their concentration in fish may be due to rainfall and flooding events in which sulfur and heavy metals are washed out of the mountains (Hrivnáková et al., 2020) and accumulated at lower elevations. Previous re-

search has shown a similar pattern to the accumulation of zinc and sulfur in fish after floods events (Janiga et al., 2021). Zinc can be also transported long distances through the atmosphere and deposited in alpine regions (Kyllönen et al., 2009; Dong et al., 2015). Anthropogenic activities, such as agriculture, urbanization, and mining, have resulted in elevated levels of zinc in natural waters. It accumulates in moderately reducible sediments (Espinoza-Quiñones et al., 2011), alpine lakes (Dočkalová et al., 2015), and phytoplankton and zooplankton (Parsons et al., 2001). In the Karatal river, the zinc content in fish flesh was recorded to be twice as high compared to the maximum permissible concentration in food (Biyasheva, 2010). This metal is one of the most accumulated chemical elements in omnivorous fish (Andreji et al., 2006). Generally, benthic fish have a lower requirement for zinc than freshwater pelagic fish species (Paripatananont, Lovell, 1995; Luo et al., 2011; Welker et al., 2016). Therefore, due to its high concentrations in the river Karatal, benthic fish may indeed be significantly threatened (Du et al., 2020). Fish can absorb zinc through the epithelial or mucosal surface of their skin (Xu et al., 2014), gills, and gastrointestinal tract (Hogstrand et al., 1994; McRae et al., 2016). Zinc toxicity occurs at the site of absorption, as a divalent cation of zinc disrupts the absorption of calcium by competing with this important ion for uptake (Bury et al., 2003; McRae et al., 2016). The toxicity of zinc sulfate and resultant fish mortality are usually caused by damage to the gill epithelium (Lloyd, 2008).

Mercury

It is highly likely that the phenomena that characterize each factor arise independently in nature. This is also true for the accumulation of mercury (PC5, Fig. 4) or the individual accumulation of zinc (PC6). In both cases, benthic and pelagic fish in the Karatal river did not differ significantly.

Consumption of aquatic products, including fish, is a significant pathway for mercury exposure in both humans and wildlife. Mercury contamination of aquatic ecosystems has become a prevalent topic of arctic and alpine research (Zhang et al., 2014; Sun et al., 2016; 2017, St Pierre et al., 2019). So much so that mercury contamination of high mountain streams is an area of research distinct from contamination by other harmful chemical elements (Šoltés, 2023). In some mountain and Arctic countries, there has been some success in reducing heavy metal pollution, but mercury inputs to downstream glaciers have increased (Blais et al., 2006). Stored mercury in mountain glaciers is trapped in glacial ice, released with meltwater, and enters lowland aquatic habitats with ongoing global warming (Zhang et al., 2012; Huang et al., 2014; Sun et al., 2017). One of the main tributaries of the Karatal river is the Kora river during peak summer runoff reaches 50–70 m^3/s. The salinity of the Karatal near Taldykorgan is around 160 mg/dm^3 with hardness of 1.96 mg-eq/dm^3 and a pH of 7,97 (TOO, 2021). This likely explains why pelagic fish tended to contain more total mercury in their fins than benthic species (benthic: x = 0.06 ppm, SD = 0.04, min. = 0.0034, max. = 0.21, n = 35, pelagic x = 0.16 ppm, SD = 0.02, min. = 0.02, max. = 0.78, n = 13). Although benthic fish are often reported to be more contaminated with total mercury than pelagic fish (Chiapella et al., 2021) in more oligotrophic and less acidic systems, pelagic pathways tend to accumulate mercury more efficiently than benthic habitats (Power et al., 2002; Karimi et al., 2016). This is the reason that the two groups of fish did not differ in the synergistic expression of mercury with other elements (Fig. 3, component 5). Seventy to hundred percent of mercury are present in the fish in methylated (MeHg) form (Bloom, 1992). Lange et al. (1993) reported that the uptake of MeHg in fish was shown to be negatively correlated with alkalinity, calcium, magnesium, pH, and total hardness. Sulfur also significantly inhibits methylation (Gabriel et al., 2014, see Fig. 3). In contrast, enhanced mercury methylation by sulfate-reducing bacteria at low pH is considered a major factor in elevated fish mercury levels in acidified aquatic environments (Grieb et al., 1990). In fish species, mercury accumulates primarily in muscle tissue (Milošković et al., 2014, 2022; Milošković, Simić, 2023), although significant amounts of mercury may also accumulate in the hepatopancreas and kidneys (Andreji et al., 2018), with less significant accumulation found in the liver, gills, skin, and gonads (Milošković et al., 2014; Andreji et al., 2018). In a given fish specimen, the fins and skin usually contain about five times less mercury than muscle tissue (Tóth et al., 2012). Total Hg concentrations in fish are useful indicators of relative methylmercury levels among different ecosystems, and this information may be relevant to the public and policy community. To obtain relevant results, it is useful to compare mercury levels within the same species or genus of fish. Information on Hg concentrations in fish from Central Asian rivers has been reported in several Chinese studies from the Tibetan Plateau (Yang et al., 2013; Zhang et al., 2014; Shao et al., 2016). The authors measured total Hg concentrations in local snowtrout (*Schizothorax)* and found large variances in muscles (0.2 to 1.4 ppm, dry weight) (Shao et al., 2016). Results of these studies have shown that the consumption of some species of snowtrout may pose a risk to human health. The level of water pollution in the river Karatal above the town of Taldykorgan is usually classified as "polluted" (Zhanyhkan, Kozykeeva, 2017; Zhavoronko, 2018). Although the amount of mercury measured in our study is in the pectoral fins and not in the muscles, we confirm that the aquatic habitats of the Karatal river near Taldykorgan provide a polluted environment for the life of many fish species.

The pattern of molybdenum accumulation contrasted with lower mercury values is described by Component 6 (Fig. 4). This component represents river pollution at lower elevations. In this case, the impact to pelagic and benthic fish does not differ. Overall, it can be concluded that rapidly accumulating compounds in the Karatal river, including potassium, chromium, molybdenum, calcium, and phosphorus, accumulate differently in pelagic and benthic fish species. Pelagic species contain higher concentrations of these elements, and this can be exacerbated through their synergic effect.

Conclusion

The coupling of glacier dynamics and pollutant cycling is a complex topic, and the synergistic effects of chemicals on different ecological groups of fish in glacial rivers are an understudied area of research. Potentially toxic elements usually do not affect fish life alone, but synergistically, in compounds, inhibiting or accelerating each other in the fish organism. The aim of this study was to assess the effects of mutual accumulation of 12 chemical elements in pelagic and benthic fish species living in a glacial river. The use of multivariate statistics advances knowledge of how the chemical weathering process affects the interrelationship of strontium and

rubidium concentrations in fish or under what conditions potassium, chromium, rubidium, or molybdenum are mutually deposited in fish. As far as mercury is concerned, its contamination of high mountain streams and rivers is now largely distinct from that of some other harmful metals. Mercury stored in ancient layers of mountain glaciers is making its own way into lowland landscapes as global warming continues. Results from Central Asia have shown that the accumulation of metals in some fish species could have serious implications for the food chain, in which fish are a key component of the aquatic ecosystem.

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