



## Heavy Metal Accumulation in Fishes of Different Ecological Groups from Kairiai Landfill Regional Aquatic Ecosystem

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### Abstract

The main purpose of this study was to determine heavy metal (HM) accumulation in body tissues (gills, liver and muscle) of different ecological group fishes [benthophagous (gibel carp and roach) and predatory (pike and perch)] from Kairiai landfill regional aquatic ecosystem. Test fish were collected during experimental fishing. Heavy metal analysis was performed in accordance with ISO 11047:2004, and Hg analysis – according to ISO 16772:2004 standard procedures. The following HMs were found in fish body tissues: Cr, Cu, Ni, Zn and Hg, while Pb and Cd content was below the instrument detection limit. The highest amounts were found of Zn, while the lowest of Ni. Nickel and Cr concentration in benthophagous and liver and muscle as well as Zn and Cu concentration in the gills and liver of predatory fish (in mg/kg of raw mass) exceeded Lithuanian hygiene standard [maximum-allowable-amount (MAA)] for human consumption. Correlation (Pearson  $r$ ) between HM content and their concentration in water and bottom sediments as well as various physico-chemical parameters have been also investigated. Very strong and averagely strong relationship has been established between Ni content in benthophagous fish liver and HM concentration in the water and bottom sediments as well as  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ; between Zn content in predatory fish gills and  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ; between Cr content in benthophagous fish liver and HM concentration in the water as well as  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{CO}_2$ ; between Cu content in benthophagous gills and HM concentration in the bottom sediments, and weak relationship between Hg content in both benthophagous and predatory fish tissues and HM concentration in the water, bottom sediments as well as other physico-chemical parameters. Summarizing the obtained results it could be concluded that Kairiai landfill still remains a serious source of permanent environmental pollution, although it is already closed.

**Keywords:** Fish; heavy metal pollution; accumulation; landfill leachate.

### Nomenclature

HM	heavy metal
S/S	sampling station
RM	raw mass
MAA	maximum-allowable-amount

### 1. Introduction

Urban waste landfills still remain ones of the most dangerous pollution sources because their leachates are often referred to highly toxic wastewaters of constant composition containing persistent (stable) organic and inorganic (heavy metals) pollutants which are non-biodegradable. These persistent pollutants are the most dangerous as they migrate from one biological system to another and accumulate in aquatic organisms [1].

Heavy metals are widely used in various antropogenic activities, and when entering natural waters becomes persistent pollutants of aquatic ecosystems. Copper, zinc, nickel, chromium, cadmium lead and mercury are listed as priority hazardous substances (pollutants) in many countries because of their toxicity, persistence, and affinity for bioaccumulation [2, 3]. Heavy metals entering the body of a living organism accumulate in the tissues and join ongoing important protein synthesis reactions, and thus migrate across the entire ecosystem [4]. Fish are unique vertebrate organisms capable to uptake heavy metals by two routes: through water and food (gills and intestinal epithelium absorption processes are taking place here) [5]. Bioaccumulation in different fish species is closely related to the HM uptake rates in the tissues and metabolic

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activity. Many field and laboratory studies showed that HM accumulation in fish tissues depends on a series of abiotic and biotic factors and their complexity, for example: fish species, its trophic level, feeding habits, age and size, interspecific differences in sensitivity to various metals, concentrations of pollutants in water and sediment, the type of food, physical and chemical properties of water, the chemical element speciation and metal bioavailability [6–16]. Fish is an important source of animal protein for human body, and HM bioaccumulation in the human food chain must be constantly monitored in order to assess the risk to health. Due to the ability to accumulate a variety of contaminants, fish are excellent indicators of ecosystem assessment of water pollution [11, 17–19]. Most studies of the effects of metals on fish are addressed to a particular metal. Meanwhile, in the natural environment, fish are exposed to different HM mixtures, which are usually more toxic than individual metal as their action is additive or more-than-additive (synergistic). Therefore, the results obtained from exposure to a single metal in laboratory studies are hardly comparable with those from natural conditions. It seems that interaction between different metals are related to their competitive uptake from the environment and to different distribution in fish tissues, which results from that certain metals affect the accumulation of other metals in fish [20].

At present in Lithuania are currently approved and forced maximum allowable amounts (MAA) of heavy metals in fish and fish products recommended for human consumption presented in Lithuanian hygiene standard HN 54:2001: Zn – 40, Cu – 10, Ni – 0.5, Hg – 0.5, Cr – 0.3, Pb – 0.2 and Cd – 0.05 mg/kg of raw mass, respectively [21].

Although at present a huge amount of the data on HM bioaccumulation in fish from natural water bodies has been compiled interspecific differences still remains investigated insufficiently. Obviously, it depends on the chemical nature of HM, the presence of other HM in the water, fish species-specific ecological, behavioral, biochemical and physiological fish body properties. Moreover, evident differences in HM bioaccumulation patterns in different fish species have been observed.

The main objectives of the present study was (1) to investigate priority heavy metal (Zn, Cu, Ni, Cr, Pb, Cd and Hg) accumulation process in body tissues (gills, liver and muscle) of different ecological group fishes [benthophagous (gibel carp and roach) and predatory (pike and perch)] from Kairiai landfill regional aquatic ecosystem, (2) to establish the factors which could influence or affect metal accumulation in different fish tissues using correlation analysis (Pearson  $r$ ) between different heavy metals, their concentrations in tissues and various external and internal biotic and abiotic factors and (3) to determine Zn and Hg accumulation patterns and compare the amounts of these metals in predatory and benthophagous fish body tissues.

## 2. Materials and Methods

### 2.1. Test aquatic ecosystem

Kairiai landfill is located 5 km east of the Šiauliai City (55°55'42.7", 23°23'42.81", WGS). The landfill began operation in 1960 and was closed in 2007. Large-scale household, municipal and industrial waste from various anthropogenic activities containing toxic substances has been deposited in it. The landfill is still continued to seep leachate, which is channeled into two isolated holding reservoirs, and maintained under open-air conditions. It is evident that landfill leachate is penetrating through permeable soils from holding reservoirs and pollute neighboring water bodies. The hydroecosystem incorporated in the landfill area consists of the nameless drainage channel surrounding the landfill which for the 1.5-km falls into the Ginkūnai Pond (of 1.1 km<sup>2</sup> area), and in turn the Švedė Creek flows out of the pond.

### 2.2. Sampling and water chemistry analysis

Test fish, water and bottom sediment samples were collected in six sampling stations (S/S) (No. 0, 1, 2, 3, 4, 5) moving away from the leachate holding reservoirs were set at the distance of about 10, 800, 1300, 2200, 2900 and 3200 meters, respectively in the drainage channel, the pond and the creek along the water flow direction (Fig. 1).

All water samples underwent complete hydrochemical analysis. The following physico-chemical characteristics of water samples were established: dissolved O<sub>2</sub>, pH, salinity (‰), conductivity (μS/cm), permanganate number (mg O/l), equilibrium CO<sub>2</sub> (mg/l), total hardness as CaCO<sub>3</sub> (mg/l), alkalinity as CaCO<sub>3</sub> (mg/l), cations: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, anions: Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, as well as total priority heavy metal (Cu, Zn, Ni, Cr, Pb, Cd, Hg) concentrations in the water and bottom sediments were determined according to standardized procedures (ISO: 10304; 9963-1; 14911; 10523; 8467; 27888; 15586:2003; 1483:2000).

### 2.3. Fish, fish tissue and metal analysis

After the experimental fishing was completed, individuals of the same length group and approximately of the same age have been selected. Predatory fish (pike and perch) and benthophagous fish (gibel carp and roach) has been merged into two main ecologically different groups (benthophagous and predators). The following body tissues have been taken for the analysis:

- Gills (whole organ);
- Liver (whole organ);
- Muscle without skin (~ 3 g).

In total from 6 to 9 individuals of mentioned-above groups have been used for every sample station. It should be mentioned that every fish selected for accumulation testing underwent the complete ichthyological analysis procedure (total

length, standard length, total weight, weight without internal organs, gill and liver somatic indexes, and condition factors according to Fulton and Clark [22, 23]).

The samples were dried in a hot air oven at 85°C for 24 hours and heavy metal analysis was performed by atomic absorption spectrophotometry using graphite furnace technique (ISO 11047:2004). Mercury analysis was performed according to ISO 16772:2004 the final concentration being expressed as mg/kg of raw mass (RM).



Fig. 1. The scheme of the study area and sampling stations (S/S): landfill leachate reservoir (F), drainage channel (station No. 0 and 1), Ginkūnai pond (station No. 2, 3, and 4) and Švedė creek flowing out of the pond (station No. 5)

## 2.4. Statistics

It is also very important to determine the factors which could influence or affect metal accumulation in different fish tissues. Therefore, correlation analysis (Pearson  $r$ ) between different heavy metals, their concentrations in tissues and various external and internal biotic and abiotic factors has been performed using STATISTICA 6.0 (StatSoft Inc., Tulsa, Oklahoma, USA) software.

## 3. Results and Discussion

### 3.1. Heavy metal accumulation

The following heavy metals have been detected in test fish body tissues: Cr, Cu, Ni, Zn and Hg. Lead and Cd content in the samples were below instrument detection limit. Quantitatively, maximum levels in fish body tissues found were of Zn while the minimum of Ni (Table 1).



Table 1. Heavy metal accumulation [raw mass (RM) in mg/kg, respectively] in body tissues of bentophagous (gibel carp and roach) and predatory (pike and perch) fishes from Kairiai landfill regional aquatic ecosystem (Mean  $\pm$  SD)

Sampling Station (S/S)	Fish ecological type	Body tissue	Heavy metal				
			Cr	Cu	Ni	Zn	Hg
0	Bentophagous	G	1.0 $\pm$ 0.0*	1.6 $\pm$ 0.0	0.0 $\pm$ 0.0	49.2 $\pm$ 0.0*	0.02 $\pm$ 0.00
		L	2.0 $\pm$ 0.0*	17.8 $\pm$ 0.0*	1.6 $\pm$ 0.0*	32.1 $\pm$ 0.0	0.04 $\pm$ 0.00
		M	1.5 $\pm$ 0.0*	0.0 $\pm$ 0.0	1.2 $\pm$ 0.0*	8.5 $\pm$ 0.0	0.07 $\pm$ 0.00
	Predatory	G	1.8 $\pm$ 0.0*	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	78.4 $\pm$ 0.0*	0.06 $\pm$ 0.00
		L	0.0 $\pm$ 0.0	7.7 $\pm$ 0.0	0.0 $\pm$ 0.0	29.9 $\pm$ 0.0	0.05 $\pm$ 0.00
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	5.1 $\pm$ 0.0	0.13 $\pm$ 0.00
1	Bentophagous	G	0.0 $\pm$ 0.0	1.2 $\pm$ 0.0	0.0 $\pm$ 0.0	90.5 $\pm$ 0.0*	0.06 $\pm$ 0.00
		L	0.0 $\pm$ 0.0	4.4 $\pm$ 0.0	0.0 $\pm$ 0.0	50.0 $\pm$ 0.0*	0.04 $\pm$ 0.00
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	10.9 $\pm$ 0.0	0.14 $\pm$ 0.00
	Predatory	G	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	14.8 $\pm$ 0.0	0.05 $\pm$ 0.00
		L	0.0 $\pm$ 0.0	1.9 $\pm$ 0.0	0.0 $\pm$ 0.0	20.7 $\pm$ 0.0	0.03 $\pm$ 0.00
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	7.6 $\pm$ 0.0	0.09 $\pm$ 0.00
2	Bentophagous	G	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	79.0 $\pm$ 7.7*	0.04 $\pm$ 0.00
		L	0.0 $\pm$ 0.0	10.8 $\pm$ 3.2*	0.0 $\pm$ 0.0	20.4 $\pm$ 13.6	0.04 $\pm$ 0.01
		M	0.9 $\pm$ 1.5	0.0 $\pm$ 0.0	0.6 $\pm$ 1.0*	7.1 $\pm$ 2.2	0.15 $\pm$ 0.03
	Predatory	G	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	15.5 $\pm$ 4.5	0.06 $\pm$ 0.00
		L	0.0 $\pm$ 0.0	3.0 $\pm$ 2.0	0.0 $\pm$ 0.0	18.4 $\pm$ 0.8	0.09 $\pm$ 0.08
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	4.6 $\pm$ 4.7	0.23 $\pm$ 0.16
3	Bentophagous	G	0.5 $\pm$ 0.8*	0.4 $\pm$ 0.6	0.0 $\pm$ 0.0	62.5 $\pm$ 18.5*	0.03 $\pm$ 0.01
		L	0.2 $\pm$ 0.3	10.9 $\pm$ 3.2*	0.0 $\pm$ 0.0	19.3 $\pm$ 2.5	0.03 $\pm$ 0.01
		M	0.3 $\pm$ 0.4	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	3.8 $\pm$ 3.5	0.16 $\pm$ 0.01
	Predatory	G	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	13.1 $\pm$ 1.9	0.10 $\pm$ 0.04
		L	0.0 $\pm$ 0.0	3.9 $\pm$ 0.5	0.0 $\pm$ 0.0	18.6 $\pm$ 4.5	0.27 $\pm$ 0.08
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	4.7 $\pm$ 0.6	0.44 $\pm$ 0.19
4	Bentophagous	G	0.0 $\pm$ 0.0	0.9 $\pm$ 0.8	0.0 $\pm$ 0.0	84.0 $\pm$ 20.0*	0.03 $\pm$ 0.01
		L	0.0 $\pm$ 0.0	10.7 $\pm$ 5.2*	0.0 $\pm$ 0.0	16.3 $\pm$ 1.3	0.02 $\pm$ 0.01
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.10 $\pm$ 0.04
	Predatory	G	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	13.2 $\pm$ 1.3	0.08 $\pm$ 0.02
		L	0.0 $\pm$ 0.0	3.3 $\pm$ 0.5	0.0 $\pm$ 0.0	17.5 $\pm$ 2.7	0.30 $\pm$ 0.17
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	2.5 $\pm$ 2.2	0.50 $\pm$ 0.16
5	Bentophagous	G	0.0 $\pm$ 0.0	1.0 $\pm$ 0.0	0.0 $\pm$ 0.0	65.7 $\pm$ 0.0*	0.04 $\pm$ 0.00
		L	3.0 $\pm$ 0.0*	4.4 $\pm$ 0.0	2.0 $\pm$ 0.0*	46.0 $\pm$ 0.0*	0.07 $\pm$ 0.00
		M	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	7.9 $\pm$ 0.0	0.09 $\pm$ 0.00
	Predatory	G	0.4 $\pm$ 0.6*	0.7 $\pm$ 0.9	0.0 $\pm$ 0.0	44.2 $\pm$ 44*	0.05 $\pm$ 0.02
		L	0.0 $\pm$ 0.0	11.3 $\pm$ 12.5*	0.0 $\pm$ 0.0	26.5 $\pm$ 22.2	0.04 $\pm$ 0.01
		M	0.4 $\pm$ 0.6*	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.09 $\pm$ 0.03

Note: G (gills), L (liver), M (muscle). Asterisks (\*) denote exceeded metal content (MAA) recommended for human consumption in fish and fish products indicated in Lithuanian hygiene standard HN 54: 2001: Zn – 40, Cu – 10, Ni – 0.5, Hg – 0.5, Cr – 0.3, Pb – 0.2 and Cd – 0.05 mg/kg of RM, respectively [21].

Data obtained showed that HM accumulation in fish was metal and tissue specific, i.e. a different tissue showed different capacity for accumulating HMs. In general, all tissues contained high concentrations of Zn and Cu, but a much lower concentrations of Cr, Ni, and Hg. Such great differences in HM accumulation could be explained, apparently, by their reliance to different categories of HM as described by Roy [24]: essential (Zn, Cu), non-essential (Ni, Cr), toxic (Cd, Hg) heavy metals.

Chromium has been accumulated in the tissues tendentiously and fragmentally. The highest amount of Cr has been found in all tissues of bentophagous fish (gills, liver and muscle) from S/S No 0 and ranged from 1.0 to 2.0 mg/kg of RM. Moderate amounts of Cr (0.5 and 0.9 mg/kg of RM) were also found in the gills and muscle of bentophagous fish from S/S No 2 and 3. The highest amount of Cr (3.0 mg/kg of RM) has been established in the liver of bentophagous fish from S/S No 5. Whereas, also the highest content of Cr (1.8 mg/kg of RM) has been detected in the gills of predatory fish from S/S No 0, and much smaller (0.4 mg/kg of RM) in the gills and muscle of predatory fish from S/S No 5. In all cases Cr concentration exceeded MAA (0.3 mg Cr/kg of RM) in fish and fish products.

Nickel has been found only in the liver and muscle of bentophagous fish (1.2 and 1.6 mg/kg of RM) from S/S No 1 as well as in the muscle (0.6 mg/kg of RM) of fish from S/S No 2 and in the liver (0.5 mg/kg of RM) of the fish from S/S No 5. In all cases Ni concentration exceeded MAA (0.5 mg Ni/kg of RM) in fish and fish products.

Copper has been accumulated tendentiously in bentophagous fish as well as in predatory fish tissues. The highest amount of Cu [averagely  $9.8 \pm 1.9$  in bentophagous fish and  $5.2 \pm 2.3$  mg/kg of RM, respectively in predatory fish (mean  $\pm$  SD)] has been found in fish liver. Copper accumulates statistically significantly more in the liver of predatory fish than in the liver of bentophagous fish ( $p < 0.01$ ). Only moderate amounts of Cu (0.4 to 1.6 mg/kg of RM) have been found in fish gills. In many cases the Cu concentration in the liver exceeded MAA (10 mg Cu/kg of RM) in fish and fish products.

Zinc has been detected absolutely in all fish tissues. The highest amount of Zn (84 mg/kg of RM) has been established in the gills of bentophagous fish from S/S No 4. Average Zn concentration in bentophagous fish gills amounted  $71.8 \pm 7.7$ , in the liver  $30.7 \pm 2.9$  and in the muscle  $6.4 \pm 1.0$  mg Zn/kg of RM, respectively (mean  $\pm$  SD). Average zinc concentration in

predatory fish gills amounted  $30.0 \pm 10.6$ , in the liver  $21.3 \pm 5.0$  and in the muscle  $4.1 \pm 1.3$  mg Zn/kg of RM, respectively (mean  $\pm$  SD). Zinc has been much more intensively accumulated in body tissues of bentophagous fish in comparison with predatory fish ( $p < 0.01$ ) and in many cases exceeded MAA (40 mg Zn/kg of RM) in fish and fish products.

Mercury has been detected absolutely in all fish tissues and ranged from 0.02 to 0.5 mg Hg/kg of RM. Mercury has been accumulated mostly in fish muscle and at least in the gills. Average Hg concentration in bentophagous fish gills amounted  $0.04 \pm 0.003$ , in the liver  $0.04 \pm 0.005$  and in the muscle  $0.12 \pm 0.01$  mg Hg/kg of RM, respectively (mean  $\pm$  SD). In the gills of predatory fish average Hg concentration amounted  $0.07 \pm 0.01$ , in the liver  $0.13 \pm 0.06$  and in the muscle  $0.25 \pm 0.09$  mg Hg/kg of RM, respectively (mean  $\pm$  SD). Mercury has been much more intensively accumulated in body tissues of predatory fish in comparison with bentophagous fish ( $p < 0.01$ ) and did not exceed MAA (0.5 mg Hg/kg of RM) in fish and fish products.

### 3.2. Correlation analysis

Significant positive relationship between Cr concentration in bentophagous fish liver and the gill somatic index as well as Fulton's condition factor has been established ( $r = 0.81$  to  $0.92$ ). Also significant negative relationship between Cr concentration in predatory fish gills and both types of condition factors (Fulton's and Clark's) has been determined ( $r = -0.99$ ). Significant positive relationship between total water toxicity and Cr concentration in bentophagous fish muscle and predatory fish gills as well as Cr and Ni concentration in the water and Cr concentration in predatory fish gills also has been established ( $r = 0.83$  to  $0.87$ ). Chromium concentration in bentophagous fish gills and liver significantly correlated with  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  concentration ( $r = 0.84$  to  $0.97$ ). Significant positive relationship between Cr concentration in predatory fish gills and  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and equilibrium  $\text{CO}_2$  also has been found ( $r = 0.95$  to  $0.98$ ).

Statistically significant and strong positive relationship between Cu concentration in predatory fish liver and the liver somatic index has been found ( $r = 0.92$ ). Also moderate and very strong negative relationship between Cu concentration in bentophagous fish gills and HM concentration in bottom sediments has been established ( $r = -0.84$  to  $-0.91$ ). Copper concentration in bentophagous as well as in predatory fish body tissues significantly weaker correlated with all physico-chemical parameters ( $r = \pm 0.65$  to  $-0.79$ ). Whereas the Cu concentration in the bentophagous fish liver significantly positively correlated with  $\text{HCO}_3^-$  concentration ( $r = 0.82$ ).

Statistically significant moderate and strong positive and negative relationship between Ni concentration in the bentophagous fish liver and HM concentration in bottom sediments has been found ( $r = -0.75$  to  $0.95$ ). The very strong positive relationship between total water toxicity ( $r = 0.92$ ) and average distance from pollution source as well as Cr and Ni concentration in the water also has been established ( $r = 0.71$  to  $-0.75$ ). Nickel concentration in bentophagous fish muscle significantly positively correlated with  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  concentration ( $r = 0.88$  to  $0.92$ ). The correlation between Ni and other physico-chemical parameters has been found to be weak. Whereas, the relationship between Ni concentration in predatory fish body tissues and other abiotic and biotic factors has been found to be non-estimated.

Statistically significant negative and strong relationship between Zn concentration in the bentophagous fish liver and a number of exclusive ichthyological analysis characteristics has been established ( $r = -0.94$  to  $-0.98$ ). Also strong negative relationship between Zn concentration in bentophagous fish gills and  $\text{Mg}^{2+}$  concentration ( $r = -0.86$ ) as well as between Zn concentration in predatory fish gills and  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  concentration also has been established ( $r = 0.82$  to  $0.89$ ).

Statistically significant negative and positive average and strong relationship between Hg concentration in bentophagous and predatory fish body tissues as well as in a series of exclusive ichthyological analysis parameters has been established ( $r = -0.79$  to  $0.83$ ). It should be noted that Hg concentration in bentophagous and predatory fish body tissues only weakly correlated with HM concentration in the water and bottom sediments. Strong negative and positive correlation has been found between Hg concentration in bentophagous fish gills and  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{Mg}^{2+}$  ( $r = -0.83$  to  $0.86$ ).

### 3.3. Zinc and mercury accumulation patterns

Since Zn and Hg were detected absolutely in all fish tissue samples we decided to determine their accumulation patterns and compare the amounts of these metals in predatory and bentophagous fish body tissues.

Table 2. Comparison of average content of zinc and mercury (mg/kg of RM) (mean  $\pm$  SD) in body tissues of different ecological type fishes

Fish ecological type	Body tissue	Heavy metal	
		Zn	Hg
Bentophagous	G	$71.8 \pm 7.7^*$	$0.04 \pm 0.003$
	L	$30.7 \pm 2.9^*$	$0.04 \pm 0.05$
	M	$6.4 \pm 1.0^*$	$0.12 \pm 0.01$
Predatory	G	$30.0 \pm 10.6$	$0.07 \pm 0.01^*$
	L	$21.3 \pm 5.0$	$0.13 \pm 0.06^*$
	M	$4.1 \pm 1.3$	$0.25 \pm 0.09^*$

Note: G (gills), L (liver), M (muscle). Asterisks (\*) denote significant differences between means ( $t$ -test,  $p < 0.05$ ).

The data obtained showed that bentophagous fish accumulate more Zn than predatory fish, meanwhile in the case with Hg everything looks quite conversely: bentophagous fish accumulate less Hg than predatory fish. Moreover, Zn is accumulated mostly in the gills while Hg in the muscle. This evidently demonstrates different biochemistry of different HM in biological systems.

#### 4. Conclusion

Heavy metals (HMs) accumulate in both bentophagous (gibel carp and roach) and predatory (pike and perch) fish tissues (gills, liver and muscle) from Kairiai landfill regional aquatic ecosystem. The following HM were found in fish body tissues: Cr, Cu, Ni, Zn and Hg, while Pb and Cd content was below the instrumental detection limit. Heavy metal accumulation in fish was metal and tissue specific, i.e. different tissue showed a different capacity for accumulating HMs. In general, all tissues contained high concentrations of Zn and Cu, but a much lower concentrations of Cr, Ni, and Hg. The highest amounts were found of Zn, while the lowest of Ni. Zinc and Hg were detected in absolutely all fish tissue samples. Other HMs were accumulated quite fragmentary. In most cases (except Hg) HM concentration in fish tissues exceeded Lithuanian hygiene standard [maximum-allowable-amount (MAA) in mg/kg of raw mass in fish and fish products] for human consumption. Correlation analysis (Pearson  $r$ ) between different heavy metals, their concentrations in tissues and various external and internal biotic and abiotic factors showed that no constant rule has existed in patterns of HM accumulation. One metal accumulation is affected more by physico-chemical parameters of the water, and the other by biological parameters (gill and liver somatic indexes, condition factors according to Fulton and Clark, general water toxicity, etc.) Comparative analysis of Zn and Hg accumulation patterns showed that bentophagous fish accumulate more Zn than predatory fish, meanwhile in the case with Hg everything looks quite conversely: bentophagous fish accumulate less Hg than predatory fish. Moreover, Zn is accumulated mostly in the gills while Hg in the muscle. This evidently demonstrates different biochemistry of different HMs in biological systems. Summarizing the obtained results it could be concluded that Kairiai landfill (although it is already closed) still remains a serious source of permanent environmental pollution which causes high-level HM accumulation in fish.

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