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TECHNICAL ARTICLE

Whitefish (*Coregonus lavaretus*) Response to Varying Potassium and Sodium Concentrations: A Model of Mining Water Toxic Response

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Abstract Boreal waters are typically low in minerals and oligotrophic, and therefore particularly sensitive to changes in mineral composition. We investigated the effects of potassium and the potassium: sodium (K^+: Na^+) ratio in freshwater on growth performance and oxidative stress in a typical northern species of whitefish, *Coregonus lavaretus*. Fish were subjected to 0.8 mM Na and 4.4 mM K, which corresponds to the K^+:Na^+ ratio in a lake contaminated by mining wastes from the Kostomuksha iron mine and ore dressing mill in northwestern Russia. The control group was subjected to water with similar mineralization levels and equal amounts of Na and K (approximately 0.3 mM of each). Potassium excess caused a decrease in fish growth rate and oxidative stress, as indicated by the level of lipid peroxidation product malondialdehyde (MDA). Glutathione-S-transferase (GST) activity and the level of reduced glutathione (GSH) were not affected by cation composition.

Keywords Freshwater · Growth · Kostomuksha iron mine · Mining wastes · Oxidative stress

Introduction

Freshwater organisms can adapt to changes in the ionic composition of water (Ern et al. 2014; Kwong et al. 2009; Nguyen et al. 2014) and the specific mechanisms of fish osmoregulation at the genetic, molecular, morphological, and behavioral levels have been previously described (Evans 2008; Hiroi et al. 2012; Seale et al. 2012). However, there is insufficient research on the excess of specific ions in water bodies. While this problem is not widespread in nature, it is relevant to isolated bodies of freshwater where the chemistry is largely determined by the composition of the underlying rock or where the water is exposed to industrial effluents.

Since 1982, a natural lake has been used to dispose of tailings from the Kostomuksha iron mine and ore dressing mill (64°61′N, 30°47′E, northwestern Russia). In the 30 years after mining, the hydrochemistry of this lake, now a tailings pond (TP), has drastically changed when compared to the natural background (Table 1). Dissolution of minerals from the tailings has resulted in a 20-fold increase in the concentration of major ions (from 30 to 600 mg/L) as well as a change in the water type, from a regional Ca-HCO_3 type to K-SO_4-HCO_3 (Lozovik et al. 2007). Industrial activity has caused a dramatic decline in biodiversity, as indicated by diminishing plankton, fish, and higher plant communities (Ilmast et al. 2013; Kalinkina et al. 2003; Vlasova 1998). Altered fish growth and reproduction parameters, as well as marked biochemical and histological disorders, were described in fish from the TP and downstream lakes (Borvinskaya et al. 2011, 2012; Churova et al.

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2014; Ilmast et al. 2013; Murzina et al. 2011; Nemova et al. 2012; Tkatcheva et al. 2004).

Based on the literature, the high levels of K^+ (4 mM) could be extremely challenging for aquatic organisms and a major cause of the TP water toxicity (Lozovik et al. 2007; Tkatcheva et al. 2007). Experimental studies have shown that of the common ions found in freshwater, potassium is arguably the most dangerous. In aquaria experiments, the K > Mg > Ca > Na order of relative toxicity of cations has been established for most water organisms (Fischer et al. 1991; Mount et al. 1997; Trama 1954). Mount et al. (1997) found that the median lethal doses of potassium chloride, potassium sulfate, and potassium bicarbonate for fish and crustaceans were significantly lower than for sodium, magnesium, and calcium salts. Similarly, potassium nitrate is more toxic to aquatic organisms than sodium nitrate (Dowden and Bennett 1965) indicating that potassium ions contribute to toxicity more than the accompanying anions.

Potassium is an essential constituent of the body for intracellular osmotic pressure and buffering, cell permeability, acid-base balance, muscle contraction, and nerve function. Shifting the chemical gradient of K^+ between cell cytoplasm and blood plasma disrupts these processes. Its regulation is critical in all vertebrates because a constant K+ concentration is essential for protein and glycogen synthesis, enzyme activities, and cell division and growth (Weiner and Wingo 1998; Opoku-Okrah et al. 2015).

For fish, the physiological level of K^+ in cells is 140 to 150 mM in cells and 3.5–5 mM in plasma (Furukawa et al. 2015, 2014; Gardaire et al. 1991). Gills are the main organ of K^+ regulation; freshwater fish absorb potassium through the gills and release it through branchial K^+ canals (ROMKa) (Furukawa et al. 2014, 2015). Potassium transport is strongly coordinated with Na^+, H^+, and Cl^- transport through specific membrane channels and typically takes place when there are higher concentrations of sodium in both natural waters (Na:K molar = 20–50:1) and blood plasma (Na:K molar = 30–40:1). An imbalance can make normal osmotic regulation problematic. For freshwater catfish *Ictalurus punctatus*, the LC_{50} dose is 10 mM of potassium chloride; potassium sulfate and potassium bicarbonate are even more toxic (LC_{50} doses are 4mM and 5 mM for 96 h, respectively) (Mount et al. 1997). However, potassium tolerance varies between fish species; Furukawa et al. (2014) report that euryhaline tilapia *Oreochromis mossambicus* placed into freshwater containing 10 mM potassium chloride showed no mortality or changes of physiological levels of plasma potassium, thus demonstrating effective mechanisms to rapidly eliminate excess K^+.

In this study, the effects of various K^+:Na^+ ratios on the whitefish *Coregonus lavaretus*, a species known to live and reproduce successfully in the Kostomuksha tailings pond, were studied as a simplified model of toxicity associated with mine waste. Levels of tissue oxidation, antioxidant system response, and growth performance were evaluated as stress markers. Other potentially threatening compounds found in the TP were not the focus of this study and will be addressed in later research.

Table 1 Chemistry of the Kostomuksha tailings pond water and the unpolluted Kamennoe Lake (64°27′N, 30°15′E, northwestern Russia) (Lozovik et al. 2007; our data) and EC water quality standards

Parameters	Kostomuksha tailings pond (TP)	Kamennoe lake	EC regulation
Dissolved O_2 (mg/L)	7.0–10.8	7.0–9.0	–
pH	7.6–8.0	6.3–7.0	–
Major ions (mg/L)			
Na^+	21 ± 6	1.30 ± 0.03	–
K^+	134–178	0.61 ± 0.07	–
Mg^{2+}	19 ± 5	0.62 ± 0.01	–
Ca^{2+}	37 ± 9	3.92 ± 0.03	–
Cl^-	7	0.8	250**
SO_4^{2-}	172–298	2.2	200**
HCO_3^-	128–147	4.4	–
Major and trace elements (µg/L)			
P	42 ± 3	43 ± 2	–
Fe	103 ± 31	189 ± 5	200**
Li	82.84 ± 23.76	0.58 ± 0.02	–
Zn	1.57 ± 0.31	10.78 ± 0.72	30*
Pb	0.042 ± 0.001	0.303 ± 0.021	50**
Ni	2.65 ± 0.69	0.65 ± 0.02	20***
Cu	2.18 ± 0.05	1.85 ± 0.10	<5*
Mn	13.36 ± 0.88	12.02 ± 0.25	50**
Cr	0.83 ± 0.10	19.16 ± 0.41	50**
Cd	0.063 ± 0.015	0.020 ± 0.001	5**

n.d. not determined

*European Communities (Quality of Salmonid Waters) Regulations, 1988 (S.I. No 293 of 1988); **European Communities (Quality of Surface Water Intended for the Abstraction of Drinking Water) Regulations, 1989 (S.I. No 294 of 1989. 5); ***European Union (Drinking Water) Regulations, 2014 (S.I. No. 122 of 2014)

Materials and Methods

Experiment Design

Experimental fish were obtained in April from a local fish farm (The Republic of Karelia, Russia). Juvenile *C. lavaretus* of uniform length were transferred to 300 L tanks (21 fish per tank) filled with tap water (supplemental Table 1) and maintained at 13 °C by a Hailea HC-250A water chiller. Oxygen saturation was maintained

through ceramic oxygen diffusers. A 12L: 12D light regime was provided by 58 W light bulbs (Philips TL-D 58 W/54–765) with a photoperiod controller. The fish were automatically fed once every 24 h using commercial feed (BioMar, 0.5 mm).

After a 2-week acclimation period, fish were randomly assigned into two groups (each of sample size 21); each group was subjected to a specific mineralization regime. Target mineralization values were produced by addition of concentrated solutions of NaCl and KCl and maintained by replacing approximately one-third of the water volume with freshwater with dissolved salts (Table 2) every 24 h.

The experimental fish group was exposed to water with 4.4 mM potassium, 0.8 mM sodium, and a K^+:Na^+ molar ratio of 5:1; these conditions mimic those recorded in the TP (K5Na1 group). The control fish group was subjected to a solution with K^+ and Na^+ concentrations equal to that of natural potassium-rich waters (K1Na1 group). The total concentration of major ions in the water for both groups was approximately 400 mg/L, which corresponds to the mineralization in the TP. Experiments were performed in duplicate.

The work was carried out in accordance with the EU Directive 2010/63/EU for animal experiments. Seven individuals from each group were sampled before initiating the experiment (day 0) and on the 5th and 20th day following the exposure onset. At each time point tested, whole fish individuals were weighed and liver and white muscle were then excised and frozen in liquid nitrogen for further analysis.

Hydrochemistry

Measurements of pH, oxygen saturation, and temperature were performed on the fish tank water using a CCO-505 oxygen meter and CPI-505 pH/ion meter (Elmetron). Phosphorus and metal concentrations were determined by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS, Thermo Scientific). The certified reference material (CRM) ICP-MS Calibration Standard 21 - IV-STOCK-21-125ML (Inorganic Ventures) was analyzed simultaneously. Chloride and sulfate anion concentrations were determined spectrophotometrically (Utsumi et al. 1978; Kirsten and Lindholm-Franzén 1980). Hydrochemistry analyses were performed daily throughout the experiment period. No significant variations in temperatures, pH, or oxygen saturation were observed between the two tanks (one-way ANOVA) during experimentation. The coefficient of variation in registered ion concentration in each tank did not exceed 25 % during the experiment.

Table 2 Physicochemical characteristics of water for control (K1Na1) and experimental (K5Na1) fish tanks

Parameters	K1Na1	K5Na1
Water temperature (°C)	13.6 ± 0.3	13.4 ± 0.2
Dissolved oxygen (mg/L)	7.0 ± 0.5	6.9 ± 0.4
pH	7.5 ± 0.0	7.5 ± 0.1
K^+:Na^+molar ratio	1:1	5:1
Major ions (mM)		
Na^+	3.34 ± 0.04	0.81 ± 0.02
K^+	3.01 ± 0.04	4.39 ± 0.06
Mg^{2+}	0.09 ± 0.01	0.08 ± 0.001
Ca^{2+}	0.17 ± 0.01	0.16 ± 0.006
Cl^-	5.51 ± 0.03	4.99 ± 0.03
SO_4^-	0.04 ± 0.002	0.04 ± 0.001

Growth Performance

The specific growth rate (SGR) was calculated according to the following equation:

$$SGR = 100 \times (\ln W_1 - W_0) \times (\text{days})^{-1} \quad (1)$$

In this equation, W refers to the mass of the sampled fish in grams, and W_0 and W_1 are the initial and the final mean mass values in grams, respectively.

Biochemical Assay

All chemicals and reagents for biochemical assay were purchased from Sigma–Aldrich. For glutathione S-transferase activity (GST) measurements, fish tissues were individually homogenized in 50 mM Tris–HCl buffer (pH 7.5) containing 5 mM EDTA, followed by 1 h centrifugation at 100,000 g, 4 °C. Supernatant obtained was added to the reaction mixture, which was a 0.125 M phosphate buffer (pH 6.5) with 1 mM 1-chloro-2,4-dinitrobenzene and 1mM GSH (Habig et al. 1974). Enzyme activity was measured by recording any increase in the optical density at 340 nm ($\varepsilon = 9.6\ mM^{-1}cm^{-1}$). Specific enzymatic activity was defined as the amount of substrate metabolized by the enzyme (in mM/min/mg).

Reduced glutathione (GSH) concentration was determined using a procedure modified from that of Cohn and Lyle (1966) and Hissin and Hilf (1976). Soluble proteins were precipitated from the homogenate by 5 % trichloroacetic acid and removed by centrifugation at 2500 g for 15 min. The supernatant was adjusted to pH 8.5 by 6 M NaOH and diluted by 0.4 M Tris–HCl buffer (pH 8.5) with 5 mM EDTA. Fluorescence of the reaction product was measured after 15 min of incubation with 0.01 % orthophthalaldehyde in methanol at room temperature (Em at 420 nm; Ex at 350 nm). Final GSH concentrations were

determined in accordance with the standard calibration curve of reduced glutathione in 0.01 % ortho-phthalaldehyde; relative GSH concentration is expressed in micrograms of GSH per milligrams of soluble protein (μg/mg).

Lipid peroxidation product malondialdehyde (MDA) was measured by the TBARS method (Bird and Draper 1984; Okhawa et al. 1979) by adding of 0.2 mL of tissue homogenate to 1.5 mL 20 % orthophosphoric acid (pH 3.5) and 1.5 mL of 0.8 % thiobarbituric acid. Samples were then heated in a 95 °C water bath for 1 h. After cooling, 1.0 mL of chilled water and 5.0 mL butanol-pyridine mixture (15:1, v/v) were added and samples were vortexed for 15 s; the flocculent precipitate was then removed by centrifugation at 3000 g for 10 min. Homogenate absorbance was measured at 532 nm using1,1,3,3-tetra-ethoxy-propane as a reference. The MDA level was expressed in nM/g of wet tissue. Protein content in the supernatant was measured spectrophotometrically by recording absorption at 205 nm, using bovine serum albumin as a standard (Noble and Bailey 2009; Sukhovskaya et al. 2010).

Data Analyses

Statistical analyses were performed with Past 3.10 Software. A two-way ANOVA was performed to examine effects of time and treatment; a post-hoc pairwise Tukey HSD test was used to determine significant differences between the datasets. Parameters relations were analyzed using Spearman's correlation coefficients. Data are presented as the mean ± standard deviation with $p \leq 0.05$ in all analyses.

Results

Growth Performance

Growth rates of fish exposed to different modes of mineralization are significantly different. In the K1Na1 group, a linear increase of the body mass was observed during the entire experimental period. However, in the K5Na1 group, the fish did not grow; by the 5th and 20th days, their final weight was similar to the starting condition and significantly lower than in the control group (Table 3).

Biochemical Parameters

Studied biochemical parameters demonstrated different responses to the exposure conditions. The MDA level variations appear to be tissue-specific (Fig. 1). The effect of potassium on the liver appears to depend on concentration and duration. MDA levels in liver from the K5Na1 group significantly increased by the end of the experiment. Liver MDA in the K1Na1 group also increased over 20 days; however, this elevation was not statistically significant. ANOVA results show that treatment and duration had no effect on the MDA response in muscle tissue; however, interaction between these factors was significant ($F_{2.78}$=5.0). MDA levels in fish muscles from the K5Na1 group declined over the course of the experiment.

The GSH level in both liver and muscle tissue was not affected by different K^+:Na^+ ratios (Fig. 1). However, GSH concentration in muscle tissue was found to be dependent on the duration of the experiment ($F_{2.78}$ = 4.3). It decreased in both groups after 20 days compared to the beginning of experiment, and in the K5Na1 group, it was significantly lower from that at day 5.

No significant difference in glutathione S-transferase activity in liver and muscle tissue was detected between the two sample groups and time points through two-way ANOVA and post-hoc testing (Fig. 1).

Discussion

Natural freshwater contains ionic constituents, which are vital for aquatic life. However, many natural and anthropogenic sources can increase ion concentrations to levels toxic to hydrobionts (Mount et al. 1997; Talling et al. 2010). Although potassium is abundant in nature and its common salts are highly soluble, it is seldom found in freshwater at high concentrations (Hem 1985). In relatively fresh water (up to 15 g/L of dissolved salts), potassium has been recorded to range between 0.001 and 2.0 mM; sodium is commonly found at much higher concentrations, approximately 0.1–50 mM (Hem 1985; Meybeck 2003; Talling 1992, 2010). Salt water K^+ concentrations can be as high as 10 mM, but K^+: Na^+ molar ratios are generally less than 0.02 (Hem 1985). In K-rich waters associated with volcanic areas and alkaline lakes, up to 20 % of total cations can be potassium, and sodium concentrations can be equivalent (Mccarraher 1971; Talling 1992). In 1982, Kilham (according to Talling 1992) reported that specific hippo pools accumulated very high concentrations of potassium (2.6 mM K^+, with a K^+: Na^+ ratio of 4.0) as a result of megafaunal activity.

Table 3 Fish weight and specific growth rate alteration

Sample	Weight, g			SGR, %/20 days
	0 day	5 days	20 days	
K1Na1	6.5 ± 1.6	7.1 ± 1.0	8.1 ± 1.1	1.1
K5Na1	6.4 ± 1.0	6.2 ± 0.6[a]	6.2 ± 0.8[a]	−0.2

[a]Differences are significant compared to the K1Na1 group

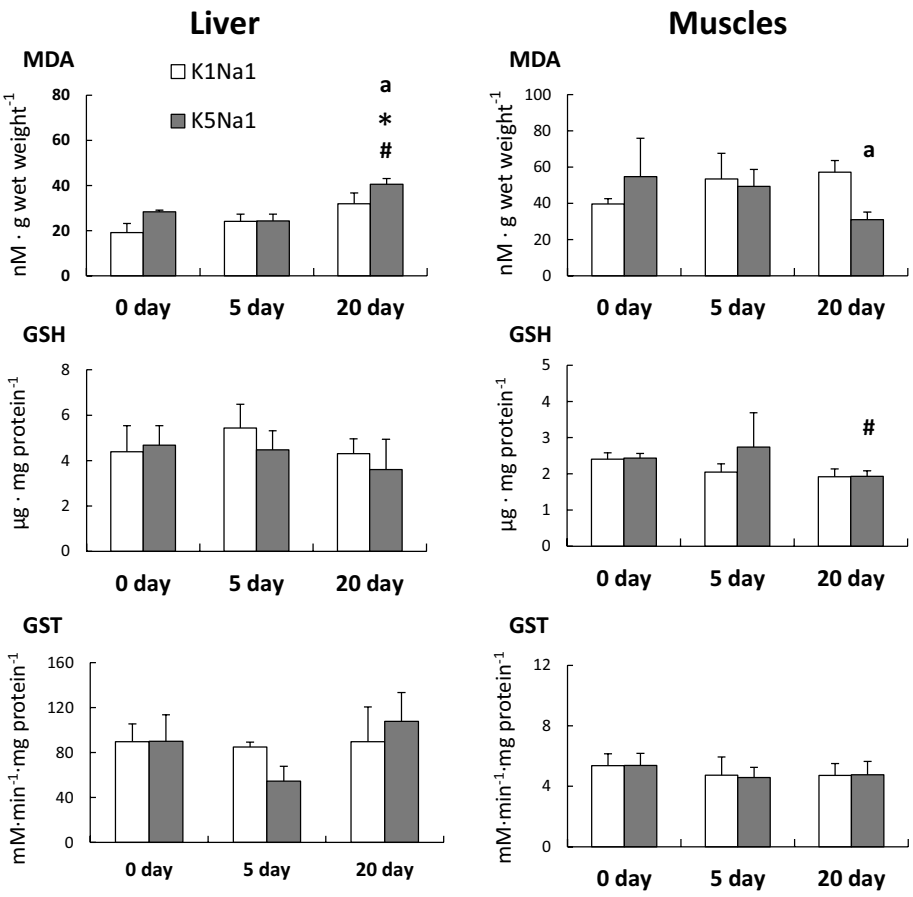

Fig. 1 Malondialdehyde (MDA) content, reduced glutathione (GSH) level, and glutathione S-transferase (GST) activity in liver and muscle tissue of *C. lavaretus* exposed to different mineralization regimes over 20 days. [a]Differences were significant compared to the K1Na1 group; *differences were significant compared to the 0 day; [#]differences are significant compared to the 5th day

Based on these prior reports, the dissolved potassium concentrations, up to 4 mM and equivalent to 40–53 % of all cations, in the tailing pond of the Kostomuksha mine is unusually high for freshwater environments. It has previously been shown that some freshwater bivalves and unionid mussels are sensitive to potassium and can demonstrate adverse effects at potassium concentrations as low as 0.25 mM (Dietz and Byrne 1990; Fischer et al. 1991; Imlay 1973; Wilcox and Dietz 1995). Freshwater fish are reported to be more tolerant to potassium; median lethal doses range from 10 to 27 mM after exposure times of 96 h (Fischer et al. 1991; Mount et al. 1997). It has also been shown that the toxic effects of potassium are reduced in the presence of high concentrations of other cations including sodium, calcium, and magnesium; this suggests a competitive relationship between these cations (Mount et al. 1997).

High potassium levels and disproportionate concentrations of major ions are potential causes of the ecological disturbance observed in the TP (Lozovik et al. 2007; Tkatcheva et al. 2007). Comparison with downstream water bodies shows that TP fish communities show much lower species diversity; there are only three species that can now be found regularly (*C. lavaretus*, roach *Rutilus rutilus*, and pike *Esox lucius*) and two periodically (burbot Lota *lota* and bleak Alburnus alburnus).

Previous studies have demonstrated biochemical and histological disorders in fish from the TP and the river system downstream of the mining waste reservoir; oxidative stress and reduced aerobic metabolism can be indicated by lipid dystrophy (consisting of either infiltration or decomposition in the liver), declined protein synthesis in muscles, energy deficiency, and increased proliferation of the mucus, respiratory, and specific osmoregulatory chloride cells in gills (Churova et al. 2014; Tkatcheva et al. 2004). Specifically, the roach and whitefish from the TP were characterized by a retarded growth rate and earlier maturation (Ilmast et al. 2013; Nemova et al. 2012).

The model experiment herein estimates *C. lavaretus* response to potassium and sodium concentrations relevant to those in the mining waste reservoir TP and natural K^+-rich waters. No fish mortalities occurred in this experiment, confirming exposure tolerance of *C. lavaretus*. However, evidence of altered fish physiological and biochemical parameters was observed in fish exposed to the higher levels of potassium in the water.

Growth Response

Although *C. lavaretus* showed consistent feeding activity (as evidenced by sampling procedure and gastrointestinal dissection, data not shown), there was no observed weight gain within the K5Na1 group (Table 3), while fish in the K1Na1 group demonstrated a linear body mass increase over a period of 20 days. Results indicate that adverse effects on fish physiology can occur at the TP water mineralization level (approximately 400 mg/L of major ions); however, increasing the proportion of sodium ions while maintaining the mineralization level eliminates this inhibitory effect on fish weight gain.

Previous field studies in the Kostomuksha TP indicated low mean values of fish growth parameters compared to that of fish populations in other lakes in this region. Results obtained in the present work suggest that the growth retardation may be to some extent attributed to the prevalence of potassium in the water.

Oxidative Stress

One method for early detection of harm, such as osmotic stress or anoxia, is the identification of oxidative stress by-products. Oxidation agents attack membrane lipids and generate decomposition products of peroxidized polyunsaturated fatty acids (e.g. malondialdehyde), which are known to be reliable indicators of oxidative stress (Abele et al. 2011; Del Rio et al. 2005; Rahman 2007).

Marked alterations of MDA levels were detected in the liver and muscle tissue of *C. lavaretus* from the K5Na1 group, indicating the effect of chronic exposure to high potassium concentrations. An intensification of lipid peroxidation in the liver was shown, which is consistent with previous field studies where hepatic MDA levels were much higher in whitefish from the Kostomuksha TP compared to whitefish from an undisturbed lake (Vasilyeva et al. 2012). Thus, enhanced lipid peroxidation in fish liver may indicate a compensatory response to the stress caused by disproportionate cation concentrations. In contrast, muscular MDA levels observed in the present study were much lower in the K5Na1 group; however, field study results showed no significant difference in muscle MDA concentrations of fish from a polluted and a reference site. We can speculate that the observed MDA content decline is likely due to activation of an antioxidant defense system. Induction of antioxidant enzymes, such as catalase and superoxide dismutase, can compensate for lipid peroxidation enhancement, as supported by studies on the influence of polycyclic aromatic hydrocarbons (Ji et al. 2010) and trace metals (Hermenean et al. 2015; Kong et al. 2012). Research performed by Ahmad et al. (2000) also suggests that low lipid peroxidation reflects the protective effects of oxidative enzymes.

Glutathione S-transferase activity and reduced glutathione levels, which can also be used as antioxidant defense system parameters, were shown in the present study to be similar in both K5Na1 and K1Na1 groups. This demonstrates a weak dependence on the proportion of potassium and sodium in the water. In addition, the lack of correlation between studied biomarkers (Spearman rank correlation test, data not shown) was also established, indicating the elimination of peroxidation products not by the glutathione system but by overlapping biochemical pathways. Previous field studies in the Kostomuksha mine area suggest that the GST enzyme is involved in the *C. lavaretus* adaptation to osmotic conditions in the TP. Activity of hepatic GST in tissues of whitefish from the TP was elevated; however, GST activity in muscles was unaffected (Borvinskaya et al. 2011).

Herein, in the present work, we did not get the same GST induction as in field studies, perhaps due to oversimplification of field conditions in the experiment. In the field studies, an unpolluted lake with low mineralization concentrations (≈18 mg/L major ions) was used as a reference, so the contribution of osmotic stress to the biological response could not be considered. Additionally, the TP contains a complex combination of cations and anions, which could be acting as an antagonist or could be having a synergetic effect on the biological response that should be taken into account. An analogous laboratory experiment where rainbow trout was subjected to potassium with significant amounts of lithium, calcium, and manganese confirmed some of the effects obseved in the field studies as gills cholesterol decrease; however, other effects, such as changes in the gill epithelium microstructure, were not repeated (Tkatcheva et al. 2007).

Conclusion

The proposed model for study of the Kostomuksha tailing pond was very simple because it did not account for the complex composition of the TP water. Mount et al. (1997) revealed a two or four fold increase of tolerance by water organisms to potassium chloride after adding equal amounts of magnesium and calcium to the water, while a drastic decrease of tolerance was shown when sulfate and bicarbonate salts of potassium were used. Since the TP is rich in both common cations and anions, the actual effect of mine water should reflect the sum of these opposing effects. Since bicarbonate is the dominant anion in the TP, further study of its effect is planned in evaluating TP water toxicity.

Nevertheless, this study showed that applied concentrations of potassium are potentially dangerous to water organisms. The whitefish under study showed altered levels of lipid oxidation by-products in addition to unexpected

cessation of growth in the K5Na1 group. The last can be regarded as a severe pathological disorder. The mechanism of the observed reactions remains unclear, as these are non-specific biological responses to stress. These effects appear to occur when potassium ions are at greater concentrations than other cations, suggesting that disproportionate ion concentrations may be toxic to water organisms. Results are consistent with previous studies showing that potassium toxicity is determined by the amount relative to other ions present in the medium as opposed to the absolute concentration of potassium.

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