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ORIGINAL PAPER

ESTIMATION OF HEAVY METAL CONCENTRATIONS IN ORGANISMS OF THE BAIKALIAN AMPHIPOD *GMELINOIDES FASCIATUS* STEBBING (CRUSTACEA: AMPHIPODA) IN PETROZAVODSK BAY, LAKE ONEGO

Zakhar Slukovskii[1], Anastasiya Sidorova[2], Nataliia Kalinkina[2]

[1] Institute of Geology
[2] Northern Water Problems Institute
Karelian Research Centre, RAS, Russia

Abstract

Data on heavy metal and other chemical element concentrations in organisms of the amphipod *Gmelinoides fasciatus* (Stebbing 1899) from the littoral zone of Petrozavodsk Bay, Lake Onego, are reported. The Baikal sub-endemic species *G. fasciatus* is the only representative of the genus of the Baikal origin. This invader migrated from the Karelian Isthmus lakes to Lake Ladoga, Europe's largest lake, where it was reported in 1988-1990 to be inhabiting the northern and western littoral zones of the lake. Samples of crustaceans, collected in 2016, were dried and analyzed by inductively coupled mass-spectrometry (ICP MS). Mn, Sr, Zn, Cu, Pb, Cd, Tl, As, V, Cr, Ni, Co, Mo and W accumulation levels in living tissues were assessed. Macro- and trace element accumulation patterns, related to the age and sex of amphipods and the time of sampling from Lake Onego, were revealed. A general sequence of all the elements analyzed is: Sr > Mn > Zn > Cu > Ni > Cr > As > V > Pb > Co > Cd > Mo > W > Tl. It shows that the macroelements Sr, Mn, Zn and Cu are essential for small crustaceans and that the sequence results from the harmful influence of anthropogenic factors on the littoral zone of Lake Onego. Pb, Cd, Mn, V, Cr and Co concentrations in juvenile Baikal amphipods, regardless of a sampling season, markedly exceed those in adults. This is associated with the feeding ration of juvenile crustaceans dominated by detritus, which can accumulate metals. Accumulation of heavy metals in organisms of the amphipod may be associated with the presence of various industries in Petrozavodsk, automobile, railway and river transport and domestic waste, including storm sewage, discharged directly into Lake Onego.

Keywords: Lake Onego, Petrozavodsk, *Gmelinoides fasciatus*, heavy metals, biomarkers.

Zakhar Slukovskii, Ph.D., Institute of Geology, Karelian Research Centre, Pushkinskaya Str. 11, Petrozavodsk, Russia, 185910, e-mail: slukovskii_z@igkrc.ru
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INTRODUCTION

Lake Onego is Europe's second largest freshwater body, which is of economic, recreational, social and cultural significance (*Ladoga and Onego*… 2010, Filatov et al. 2016). About 80% of Lake Onego is in the Republic of Karelia. Petrozavodsk, Karelia's largest city with a population of about 270 000, is located on the west shore of Lake Onego, near Petrozavodsk Bay, one of the most heavily polluted lake areas adversely affected by urbanization. The main constituent anthropogenic factors in this case are various industries, automobile, railway and river transport and domestic waste, including storm sewage, discharged directly into Lake Onego (Kalinkina et al. 2013). Many of these sources of pollution deliver petroleum products and heavy metals (HM) to the aquatic environment (Belkina 2006, Sabylina et al. 2010). This deleterious impact on Lake Onego's ecosystem is a matter of concern among specialists, governmental bodies and the public.

In the past few years, heavy metals and their accumulation in living organisms as biomarkers of the state of the natural environment, including water bodies, have been attracting increasing attention (Szarek-Gwiazda, Amirowicz 2006, Komulainen, Morozov 2007, Golovanova 2008, Moiseenko, Gashev 2012, Rainbow et al. 2012, Tao et al. 2012, Amoozadeh et al. 2014, Jenyo-Oni, Oladele 2016, Zhang et al. 2016). Therefore, assessment of the biogeochemical aspects of the human-induced pollution of Lake Onego should be part of its environmental monitoring. The littoral zone is the most vulnerable part of any water body, let alone of a large lake like Lake Onego. Hence, it is communities of living organisms in the littoral zone that respond most distinctly to changes in the water environment evoked by external factors. Earlier studies (Sidorova et al. 2012, Kalinkina et al. 2013) showed that the alien species *Gmelinoides fasciatus* (Stebbing 1899) (Crustacea: Amphipoda), occurring in the near-shore zone of Lake Onego, is a good target of ecological and toxicological studies conducted to assess the effect of various pollutants discharged from the watershed area into the lake. Furthermore, it is noted that amphipods contribute greatly to the accumulation of HMs, particularly essential (Fe, Zn, Cu) and non-essential (Pb, Cd, Hg) elements recognized as the most hazardous environmental pollutants (Nassiri et al. 2000, Ugoni et al. 2004).

Thus, the goal of the present paper is to assess heavy metal accumulation levels in organisms of the Baikalian amphipod *G. fasciatus* from Petrozavodsk Bay of Lake Onego.

The Baikal sub-endemic species *G. fasciatus* is the only representative of the genus of the Baikal origin. Until the early 1960s, its distribution area had been restricted to the basins of several Siberian rivers such as the Angara, Barguzin, Irtysh, Lena, Pyasina, Tunguska, Selenga and Yenisey (Berezina 2007, Berezina, Petryashev 2012). In the 1960-1970s, aquatic invertebrates were introduced to increase food supplies for the fish (Panov, Berezina 2002). This invader migrated from the Karelian Isthmus lakes to Lake Ladoga, Europe's largest lake, where it was reported in 1988-1990 to be inhabiting the northern and western littoral zones of the lake (Panov 1996). It did not take long for the Baikal amphipod to spread to the west over hundreds of kilometers along the River Neva (the Neva River estuary, Gulf of Finland, Baltic Sea) and to the east along the River Svir (Lake Onego).

The study of benthic fauna in Lake Onego was launched in the late 18th century. The alien species *G. fasciatus* had not been registered until the 2000s (Ryabinkin, Poljakova 2008). In 2001, the small crustacean was reported to have been found in western Lake Onego (Berezina, Panov 2002). Monitoring, conducted in the past few years, has shown that *G. fasciatus* has actually invaded the entire littoral zone of the lake. The amphipod *G. fasciatus* is a medium-sized benthic crustacean. Sexually mature females in Lake Onego vary in body length from 3.4 to 11 mm, while males show a maximum body length of 15 mm (Sidorova, Belicheva 2017). Being an omnivorous species, the small crustacean *G. fasciatus can survive and reproduce even under impoverished trophic conditions*. The amphipod *G. fasciatus* belongs to the opportunistic ecological category or r-strategist: it has a short time for reproduction of one generation, fast growth and maturation, high resistance to environmental factors (including eutrophication and some pollutants), high genetic variability, and a wide food spectrum (Berezina 2007), increasing food supplies for the fish (Berezina, Strelnikov 2010, Lobanova et al. 2017).

MATERIALS AND METHODS

Material for the study was provided by macrozoobenthos samples collected in 2016 in the sandy, open-type, slime bottom littoral zone with *Phragmítes austrális* reedbed at one station in Petrozavodsk Bay during two surveys (29 June and 19 July) – Figure 1. It is a monitoring station, where observations of the life cycle characteristics (number, biomass, size and weight characteristics and sex composition of the population) of *G. fasciatus* have been carried out since 2005 (Kalinkina et al. 2013, Sidorova, Belicheva 2017). Macrozoobenthos sampling and identification were conducted according to the standard methods (ISO 10870:2012). Benthos samples were taken with a plastic tube over the working area 0.07 m^2 at a depth of 0.4 m, where the abundance of amphipods was the highest (Sidorova, Belicheva 2017). The organisms were weighed in the wet form at an accuracy of 0.0001 g, using analytical laboratory scales. The organisms were identified taxonomically using an identification guide (Barnard, Barnard 1983). In the laboratory, each specimen *G. fasciatus* was measured under a binocular microscope using an eyepiece micrometer with 0.1 mm precision, weighed, and its sex was determined by the presence or absence of oostegites. The total body length was measured as the distance from the rostrum to the base of the

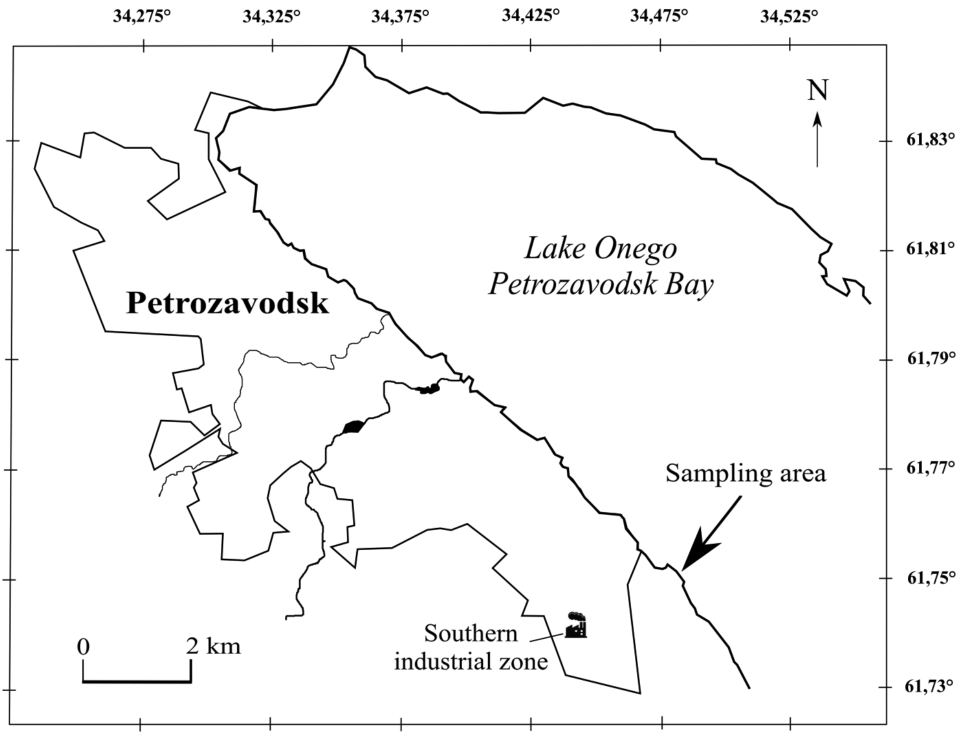

Fig. 1. Sketch map of the study area

telson. Females, males and juveniles with a body length of up to 3 mm were selected and dried separately. A total of six samples were examined. Each contained about several hundred specimens of *G. fasciatus*, confirming that the samples are highly representative and the element concentration values are not accidental.

Dried samples of hydrobiological material were decomposed by acid autopsy with an acid mixture in an open system. The method for preparing the samples for chemical analysis was described in Slukovskii, Polyakova (2017). Mn, Sr, Zn, Cu, Pb, Cd, Tl, As, V, Cr, Ni, Co, Mo and W concentrations in the amphipod organism were estimated using the mass-spectral method on a XSeries-2 ICP-MS («ThermoScientific») instrument at the Analytical Centre of the Institute of Geology, KarRC, RAS, Petrozavodsk. The results were processed statistically by calculating the median, standard deviation of the median, minimum and maximum values and variation coefficients of sample values. MS Excel 2016 and Inkscape 0.48.4 software were used to illustrate the results in diagrams.

RESULTS AND DISCUSSION

All the above chemical elements, except for As in a June 2016 sample, were found in amphipod samples from Petrozavodsk Bay of Lake Onego. Maximum median values were obtained for four essential elements (Sr, Mn, Zn, Cu) and minimum values were achieved for trace elements (Mo, W, Tl), as seen in Table 1 and in Figures 2, 3 and 4. The total geochemical sequence of all the elements analyzed is: Sr > Mn > Zn > Cu > Ni > Cr > As > V > Pb > Co > Cd > Mo > W > Tl. However, the sequence is conditional, because it has been found that the concentrations of the above elements, mostly heavy and other metals, vary from volume 6% (Ni and Co) to 80% (V) – Table 1, last column. These variations depend directly on such parameters as the age and sex of the amphipods and sampling season (June or July).

In accordance with the ecological classification, all the above elements belong to hazard classes 1, 2 and 3. The accumulation of these heavy metals and metalloids is associated with the human impact on Petrozavodsk Bay of Lake Onego (Sabylina et al. 2010). It has been noted, in particular, that the bay is considerably affected by the discharge of wastewater and storm sewage, containing various pollutants, which are later accumulated in the bottom sediments inhabited by amphipods (Sidorova et al. 2012). Furthermore, the water environment of Petrozavodsk may be enriched with heavy

Table 1

Chemical element concentrations in organisms of amphipods from Petrozavodsk Bay of Lake Onego (mg kg^{-1})

Element	Me	S_{Me}	x_{max}	x_{min}	V (%)
Sr	284.0	50.00	339.0	243.0	17.60
Mn	109.0	36.00	281.0	65.00	33.10
Zn	96.20	14.30	129.3	85.40	14.90
Cu	27.60	7.800	44.80	22.10	28.30
Ni	10.60	0.700	16.00	9.900	6.100
Cr	2.580	0.280	11.60	2.240	11.00
As	1.690	0.340	1.960	1.380	20.40
V	0.970	0.780	3.970	0.890	80.60
Pb	0.820	0.100	3.700	0.730	12.20
Co	0.390	0.020	1.140	0.370	6.000
Cd	0.340	0.100	0.980	0.260	31.10
Mo	0.280	0.050	0.390	0.200	17.20
W	0.130	0.020	0.250	0.110	15.40
Tl	0.080	0.010	0.130	0.050	16.20

Me – median, S_{Me} – standard deviation of the sampling median, x_{max} and x_{min} – maximum and minimum values, V – variation coefficient

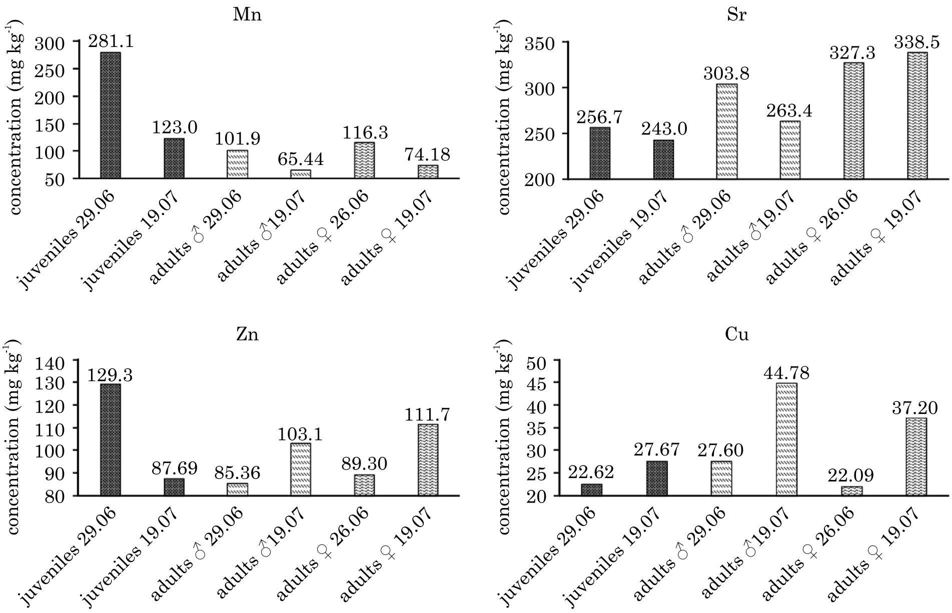

Fig. 2. Mn, Sr, Zn and Cu accumulation levels in organisms of the amphipod *Gmelinoides fasciatus* from Lake Onego in 2016

metals from the city, because the soil cover and bottom sediments in the small lakes in Petrozavodsk are known to contain elevated concentrations of these pollutants (Novikov 2014, Slukovskii 2015, Krutskikh et al. 2016, Slukovskii et al. 2017). Anomalous Pb, Ni, Cu and As concentrations were revealed in the soil in the southern part of the city near the study area in the littoral zone of Lake Onego (*Climatic…* 2013, Novikov 2014). The anomalies are associated with the southern industrial zone of the city (Figure 1), where several companies are situated. Also, these anomalies are associated with the automobile and railway transport and with natural factors (mainly responsible for As) (*Climatic…* 2013, Slukovskii, Medvedev 2015). It should be noted that the highest median Ni value, in comparison with the other heavy metals, in the organism of *G. fasciatus* is presumably due to the elevated Ni concentration in the soil of the sampling area located near a railway used for transportation of cargo from the Petrozavodsk Oil Storage (Novikov 2014). Elevated Pb and Cu concentrations in the upper layers of the bottom sediments from Lake Chetyrekhverstnoye, located 2 km from the littoral area of Lake Onego submitted to this study, also indicate poor ecological and geochemical conditions in the southern part of Petrozavodsk (Slukovskii, Medvedev 2015).

Another factor to be taken into account is the effect exerted on Petrozavodsk Bay of Lake Onego by the runoff from the Shuya River watershed, where Pb, Mn, As, Sn concentrations in bottom sediments exceed background values (Shelekhova, Krutskikh 2013). These two authors have also revealed

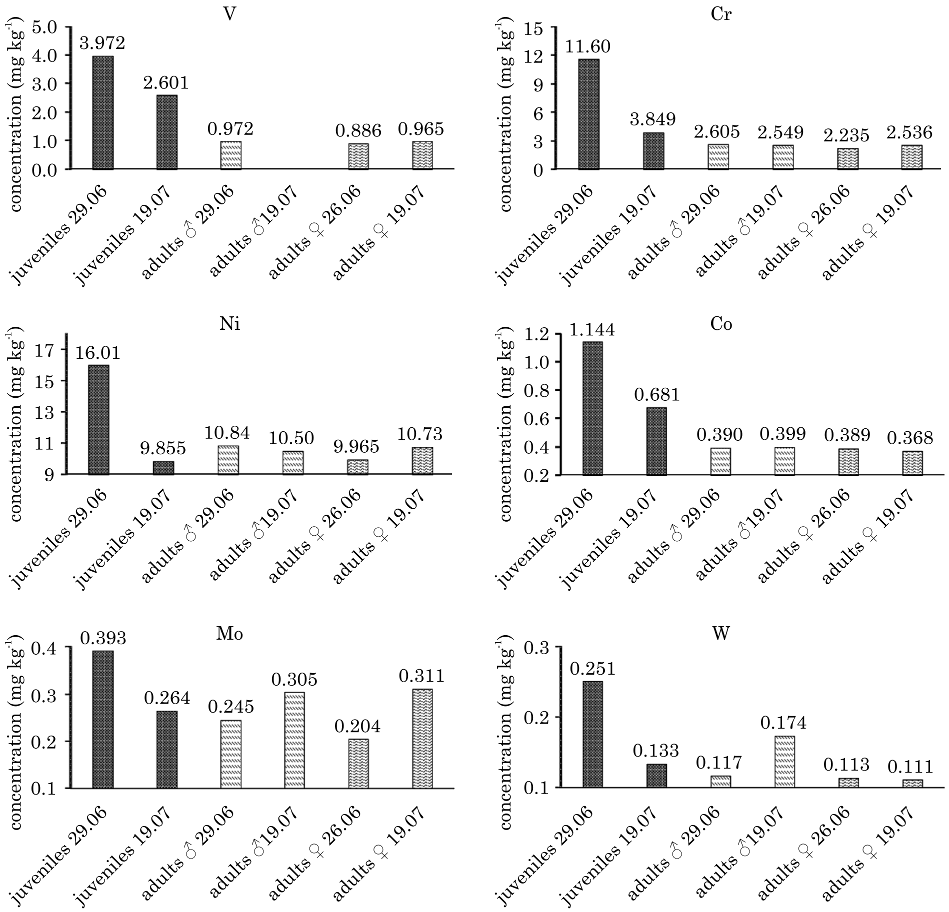

Fig. 3. V, Cr, Ni, Co, Mo and W accumulation levels in organisms of the amphipod *Gmelinoides fasciatus* from Lake Onego in 2016

the negative effect of metals on the diatom flora of bottom sediments in the River Shuya due to the toxic pollutants studied. Elevated Ni, Cu, Cd and Zn concentrations in the surface layers of bottom sediments and organisms in Petrozavodsk Bay of Lake Onego provide evidence for the migration of heavy metals and other pollutants from the watershed area into Petrozavodsk Bay of Lake Onego (Belkina et al. 2016).

With respect to essential elements (Figure 2), Sr accumulates more actively in adult amphipods. The highest Sr concentrations were reported from small female crustaceans. Another metal, Cu, behaves in a similar manner, but its accumulation depends also on a sampling season because the Cu concentration in June samples is lower than in July samples. Zn concentrations in adult crustaceans, like Cu concentrations, are higher in July samples. However, the Zn concentration in juvenile amphipods from Lake Onego is

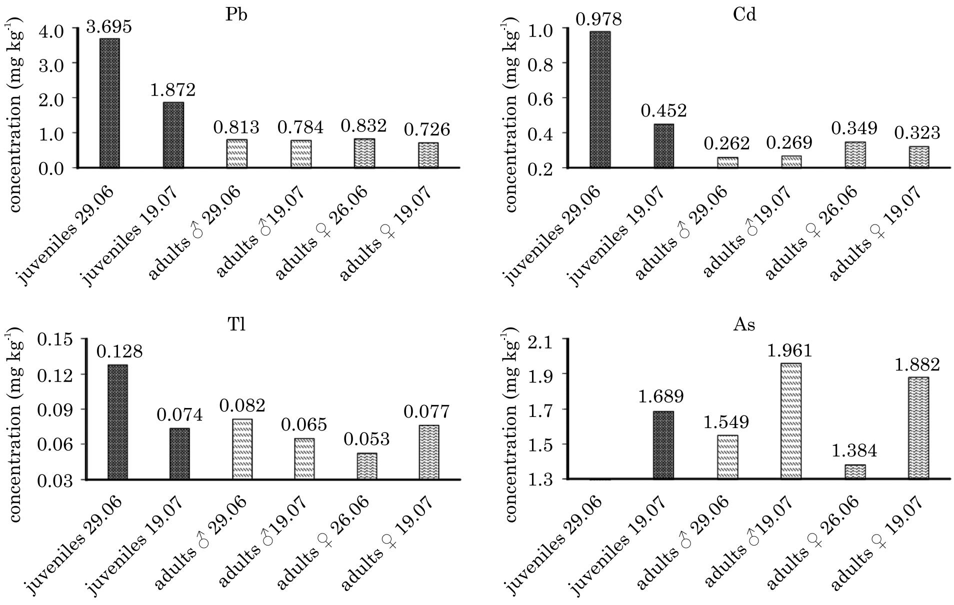

Fig. 4. Pb, Cd, Tl and As accumulation levels in organisms of the amphipod *Gmelinoides fasciatus* from Lake Onego in 2016

higher in June samples. Mn accumulates in a similar fashion in juvenile *G. fasciatus*; this trend persists for Mn in adult amphipods. Essential element concentrations in all the samples analyzed vary from 15% (Zn) to 33% (Mn). Mn accumulates more actively in small juvenile crustaceans, while Zn behaves so to a lesser extent.

Almost all trace elements, such as the toxic metals Pb and Cd, accumulate most actively in juvenile Onego amphipods (Figures 3 and 4). This trend is less clearly displayed in Mo, Tl and As concentrations in small crustaceans. In the case of Mo, this could be due to the essential contribution of this trace element to the vital activity of aquatic biota. In the case of Tl and As, this probably could be due to the long removal of these carcinogenic elements from the organism of *G. fasciatus*.

The trace element accumulation trend, described for juveniles, is most probably closely associated with the feeding of amphipods, because the feeding spectrum of juvenile amphipods is known to be dominated by plant food and detritus (Panov, Berezina 2002, Panov 1996, Berezina 2007). Detritus in an aquatic environment readily accumulates heavy metals (Ostroumov 2011). Numerous studies of bottom sediments from water bodies also show that organic matter is closely associated with heavy metals, forming strong chemical compounds (Dauvalter 2003). Large-sized crustaceans have a more extensive diet: they often eat animal food such as small crustaceans, rotifers, oligochaetes and insect larvae. In the absence of animal food in experiments, crustaceans can eat their own juveniles, water sowbugs and small mayfly and chironomid larvae (Berezin 2007). The study of heavy metal concentrations in a water environment shows that they also accumulate actively in the above organisms (Woelfl et al. 2006, Arslan et al. 2010). It is obvious, however, that detritus as a sorbent of pollutants contributes more actively to heavy metal accumulation in the organisms of the amphipods studied.

It should be noted that the earlier biogeochemical studies of the Rivers Lososinka and Neglinka, which flow across Petrozavodsk into Petrozavodsk Bay of Lake Onego, revealed considerable heavy metal concentrations in the phytoperiphyton and oligochaetes of the above streams (Komulainen, Morozov 2007, Slukovskii, Polyakova 2017). In both cases, pollutant concentrations markedly exceed those in amphipods from the littoral zone of Petrozavodsk Bay of Lake Onego. This is directly associated with the considerable heavy metal pollution of the city rivers, considering that the chemical composition of their water and bottom sediments is largely formed of the direct runoff from the centre of a large industrial city (Slukovskii 2015). The area chosen for the biogeochemical study of the littoral zone of Lake Onego is located at the outskirts of Petrozavodsk, where the soil cover contains most heavy metals which display near-background values, except for some elements. However, they are potentially hazardous for the aquatic biota of the lake, because even small Cd, Pb and As concentrations may negatively affect the ecosystem.

Maximum concentrations of all trace elements, except As, were revealed in a sample of the small juvenile crustacean *G. fasciatus* collected in June 2016. The ratio of these extrema to the average concentration of one or another element in adult amphipods decreases in the sequence: Pb (4.7) ≈ Cr (4.7) > V (4.2) > Cd (3.3) > Co (3.0) > W (1.9) ≈ Tl (1.9) > Ni (1.5) ≈ Mo (1.5), where numbers in parentheses show the result of the ratio described. Thus, Pb, Cr, V, Cd and Co are major pollutants in the littoral zone of Petrozavodsk Bay of Lake Onego. The former is known to be associated with automobile emissions and global air transfer (the latter factor is responsible for the presence of Cd) (Dauvalter 2006). Such metals as Cr and V seem to be directly related to the presence of oil products in the bay (Belkina 2006), because they are an inseparable part of the above hydrocarbons (Teng et al. 2006). It has been proven earlier that the Petrozavodsk Heat Power Plant, which uses crude oil as a fuel (a major fuel until the 2000s and a reserve fuel nowadays), has a harmful effect on the ecosystem of a small lake at the outskirts of Petrozavodsk, in which anomalous V and Cr concentrations in bottom sediments were revealed (Slukovskii et al. 2017).

It should be noted that the accumulation of the siderophilic elements V, Cr, Ni and Co in adult *G. fasciatus* from Petrozavodsk Bay of Lake Onego is not affected by the sex and sampling season of samples (Figure 2). However, Mo accumulates more actively in July samples and is more abundant in juvenile samples taken in June. W is more abundant in male amphipods then in female amphipods, while Cd is more abundant in females amphipods then in male amphipods (Figures 3 and 4). It is known that Cd in living aquatic organisms can replace the essential element Ca (Golovanova 2008). This probably applies to amphipods, considering the Cd-Sr correlation in adults and the fact that Sr is similar to Ca in living tissues. Females accumulate greater quantities of these metals than males, because some of them are juveniles.

Figure 4 shows that Pb is slightly more abundant in June samples of adult crustaceans. Sex does not affect the accumulation of this toxic element. On the contrary, two other metals, As and Mo, accumulate more actively in July samples.

The results show the considerable impact of an urbanized environment on heavy metal accumulation in the littoral biota of Petrozavodsk Bay of Lake Onego. The amphipod *G. fasciatus* contributes greatly to the feeding of river perch in Lake Onego (Lobanova et al. 2017). Therefore, the pollutants may migrate along trophic chains. Further study is needed, and assessment of the chemical parameters of benthic organisms should be part of a programme of the general monitoring of the ecological state of Europe's second largest lake.

CONCLUSIONS

The biogeochemical study of the Petrozavodsk Bay of Lake Onego, conducted using the small crustaceans *Gmelinoides fasciatus*, has shown that:

1. All the above chemical elements, except for As in June 2016 sample, were found to concentrate in amphipod samples from Petrozavodsk Bay of Lake Onego. A general sequence of all the elements analyzed is: Sr > Mn > Zn > Cu > Ni > Cr > As > V > Pb > Co > Cd > Mo > W > Tl. It shows that the macroelements Sr, Mn, Zn and Cu are essential for small crustaceans and that the sequence results from the harmful influence of anthropogenic factors on the littoral zone of the lake.

2. The highest median Ni value, in comparison with other heavy metals, in organisms of *G. fasciatus* is probably due to the abundance of Ni in the soil of the sampling area located near the railway used for the transportation of cargo from the Petrozavodsk Oil Storage.

3. Pb, Cd, Mn, V, Cr and Co concentrations in juvenile Baikal amphipods, regardless of sampling season, markedly exceed those in adults. This is associated with the feeding ration of juvenile crustaceans dominated by detritus which can accumulate metals.

4. Cd and Sr accumulation levels in the female amphipods *G. fasciatus* exceed those in males. This seems to be associated with the fact that these elements replace Ca, because Sr is analogous to Ca in living systems and Cd can replace it on penetrating into the organism. Females accumulate greater quantities of these metals than males, because some of them are juveniles.

5. Analysis of the ratio of heavy metal extrema to the average concentration of one or another element in adult amphipods shows that Pb, Cr, V, Cd and Co are major pollutants in the littoral zone of Petrozavodsk Bay of Lake Onego near Sainavolok. Their accumulation may be associated with the presence of various industries in Petrozavodsk, automobile, railway and river transport and domestic waste, including storm sewage, discharged directly into Lake Onego.

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