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Hydrobionts of a freshwater oil-polluted northern lake: bioaccumulation of heavy metals in fish and the rate of ecosystem recovery

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The response of phytoplankton, zooplankton, benthic and fish community structure to one of the biggest oil spill in history of Komi Republic (north-west part of Russia) was investigated using data from a long-term survey off the polluted lake. The characteristics of aquatic freshwater communities observed in the study area 10, 11 and 22 years after the spill (1994) were compared to find out the rate of natural recovery of the ecosystem after oil decontamination of bottom sediments. The concentrations of fifteen trace metals (Al, Cr, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Pb, U, Bi, Th) were analyzed in the tissues (muscle) of three fish species. The concentrations of Al (3-309 mg/kg), Cr (0,1-3,71 mg/kg), Fe (8,6-317 mg/kg), and Cu (0,09-99 mg/kg) in fishes from polluted lake resulted in most cases higher than reference thresholds. Quantitative and qualitative indicators of aquatic invertebrates from polluted lake reach those one of unpolluted lake but do not fully recover 22 years after the spill, despite that oil concentration in water column and in bottom sediments was lower than reference tresholds. We conclude that natural recovery rate of aquatic freshwater ecosystems in northern regions after oil pollution is extremely low. The purification of water and bottom sediments of oil-polluted northern water bodies is necessary for stimulation of ecosystem restoration.
Key words: Pollution; oil spill; recovery of freshwater ecosystem; heavy metals; bioaccumulation; aquatic invertebrates; arctic lake

Introduction

Petroleum hydrocarbons are one of the most dangerous and widespread pollutants at present (Abdurakhmanov et al., 2006; Carls et al., 2002). Natural petroleum seeps, extraction, transportation, and consumption are the main sources of crude oil to the water (Cushing, 1989). Oil has a negative impact on all groups of organisms that live both in the water column and in the bottom sediments. Phytoplankton, zooplankton, zoobenthos, fish, birds and mammals are adversely affected through trophic chains. Many investigations have been devoted to the acute and subacute toxic effects of oil pollution. Most of them focus on the sensitivity of individuals or populations (Jiang et al., 2012; Almeda et al., 2014; Cohen et al., 2014; Agersted et al., 2018). There is a lack of knowledge on the toxic effects at the community and ecosystem levels, as well as on the recovery of freshwater aquatic ecosystems after purifying from oil.

In case of large oil spills, crude oil can completely cover bottom sediments and complete degradation of benthic organisms is observed. Under oxygen deficiency, low photo-oxidation rates and low temperatures, the rate of destruction of petroleum hydrocarbons in bottom sediments is significantly reduced. Instead of oxidation, sulfate reduction and methane formation occur, with the accumulation of toxic substances in the water column (Kondratyeva, 2000).

In addition to the direct negative impact of petroleum hydrocarbons on ecosystem components, oil pollution is accompanied by an increase in the concentration of heavy metals in the environment (Makarenkova, 2007; Korchina et al., 2010). This leads to an increase of their content in the organs and tissues of hydrobionts, especially fish (Malik et al., 2010). Trace metals play an important role in the organisms, since many of them are part of enzymes, vitamins, hormones. Many vital processes such as breathing, blood formation, protein, carbohydrate and fat metabolism are impossible without these elements. The danger of a change in the background metal content of the organism is explained by the fact that the individual need of hydrobionts in these elements is very small. The release from the environment of their excess amounts leads to various toxic effects (Vetrov, 1997; Popov, 2002). Heavy metals have been found associated with fish (Sfakianakis et al. 2015) and invertebrate (Chironomus) deformities (Bertrand, Hare, 2017) in both natural and laboratory populations. In Usinsk region, after several years of the spill, pikes with deformities of the upper jaw (Monitoring..., 2003), perch and roach fins (Noskov et al., unpublished) were registered. Generally, such deformities have negative effects on populations of hydrobionts because deformities affect their survival, growth rates, welfare and external image.

In 1994 one of the largest oil spills in the history of Komi republic (north-western part of Russia) occurred in the Usinsk region. More than 250 thousand tons of oil leaked and covered dozens of square kilometers of land and polluted many water bodies. Among them were such important fishery rivers as Kolva, Usa and Pechora.

In 2004–2005 bottom sediments of one of the oil-polluted lakes - Shchuchye No.1 (Fig. 1), were purified using the flotation technology (Lushnikov, Vorobiev, 2006) for the first time. As a result of a two-year refining cycle, the concentration of oil in bottom sediments significantly decreased (from 50 to 4 g/kg), benthic organisms began to recolonise the sediments, the growth rates and linear indicators of fish increased (Vorobiev et al., 2008).

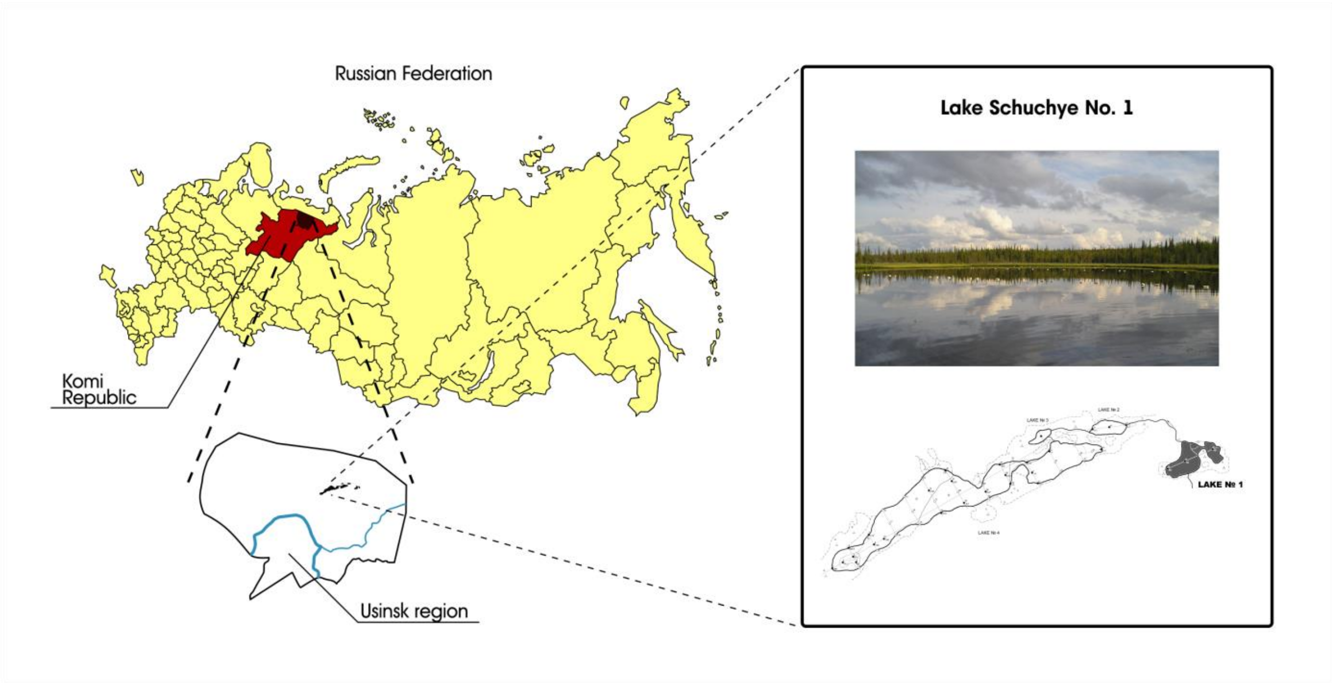

Fig. 1. Map of the Usinsk region (Komi Republic, Russia) and the studied oil polluted lake Schuchye No.1.

To determine the extent and rate of ecosystem recovery 22 years after the spill and 11 years after the purifying of bottom sediments, a comprehensive hydrobiological survey of the lake was carried out in 2016. In terms of the lack of long-term studies on the impact of oil spills on freshwater biota, our data should be useful for estimating response times for recovery of aquatic freshwater communities in comparable environmental conditions.

Methods

Lake Shchuchye (N 66.654316, E 57.149421) located in the Usinsk district of the Komi Republic, on the border of the Arctic Circle. It is a system of four low-flow thermokarst lakes and is the head of the Vorgayel brook. The total area of the lakes is more than 56 hectares. The area of lake No.1, on which the experimental purifying work was carried out is 6.26 ha. The maximum depth of the lake reaches 7 m. The purification technology and the results of the two-year purification cycle are elicidated in previous works (Lushnikov, Vorobyev, 2006; Lushnikov et al., 2006)

In July 2016 comprehensive hydrobiological studies were carried out on Lake Shchuchye No. 1. To compare the obtained data with the native ecosystem, a lake of a similar type not subjected to oil pollution was investigated.

Phytoplankton samples were collected from surface layer and immediately fixed with formaldehyde to its final concentration of 2-4 %. The samples were subsequently filtered through Vladipor no. 6 membrane filters with pore diameter of 0.55–0.65 mkm. The phytoplankton abundance was obtained from direct independent counts of cells and individuals (i.e. solitary cells, colonies, coenobia, filaments, temporary cell aggregates etc.) with light microscopy in Fuchs-Rosenthal counting chamber. To calculate the biomass (biovolume), cell volumes were approximated as simple or combined geometric figures. The species or aggregated components which reliable identification was impossible with relative abundance above 5 % were recognized as the most abundant ones.

Zooplankton samples were taken by filtering 50 liters of water through the Apstein plankton net, with a mesh size of 82 microns. Rotifers and planktonic crustaceans were classified by species (except for juvenile copepods) using as references (Fefilova, Dobrynina, 2010; Smirnov, 1971; Ermolaeva, 2007, Kutikova, 1970). The calculation of the number (N, ind./m^3) was carried out by recalculating the number of individuals in a sample per 1 m^3 of water. The calculation of biomass (B, mg/m^3) was carried out by multiplying the individual weight on the number of a species in 1 m^3 of water. The individual mass of crustaceans and rotifers was determined by body length using the equation of the relationship between these indicators (Balushkina, Vinberg, 1979).

Zoobenthos sampling was carried out using a Petersen bottom grab with a capture area of 1/80 m^2. To eliminate the possible error associated with the non-uniform distribution of hydrobionts, each zoobenthos sample at one point included three bottom samplers. The abundance and biomass of the main ecological groups of zoobenthos were determined. To assess the quality of bottom sediments and water, the abundance, biomass (in terms of 1 m^2) and the number of taxons (ecological groups) of benthic organisms were counted.

Fishes were caught using fixed nets with 18-24 mm meshes. The following parameters were investigated under field conditions: absolute body length (L, mm), body length (l) —from the top of the snout to the end of the scale cover, body weight with viscera (Q), body weight without viscera (q), sex and the stage of maturity of the gonads in each specimen were determined.

Muscle tissue was used to determine the metal content in fish. Muscles were selected under the dorsal fin above the lateral line, crushed and dried. After drying, the samples were dried in a muffle furnace at a controlled temperature (max t = 400 ° C). The ash residue was homogenized by wiping thoroughly in an agate mortar. Acid decomposition of fish samples using 150 mg of the tissue was performed in a Speedwave microwave oven (Berghof, Germany) with a 12-autotor DAP-60 rotor with a HNO_3 + H_2O_2 mixture in a 4: 1 ratio. The three-step decomposition program included: step 1 – 8 minutes at 170 ° C; step 2 – 20 minutes at 220 ° C; step 3 – 10 minutes at 50 ° C. At the end of decomposition, the contents of the autoclaves were transferred to glass-carbon crucibles.

The destruction of the chloride complexes was performed by double evaporation of the dry residue of the sample in 4 ml of concentrated HNO_3 at a temperature of 110 °C. After adding 2 ml of 5N HNO_3, the solution was again evaporated and deionized by water (MilliQ, Millipore, USA), then reduced to a 50 ml aliquot with a final concentration of the nitric acid matrix of 0.5n. All the acids were additionally purified on the BSB-939-IR distillation unit (Berghof, Germany).

Analysis of the prepared solutions was performed by mass spectrometry with inductively coupled plasma using an Agilent 7700x (Japan). The modes of operation of the mass spectrometer are shown in Table 1. The analysis scheme included: “blank” analysis (included in a batch of 20 samples, one sample with all the reagents mentioned, which passed all successively specified procedures); analysis of calibration solutions and the construction of calibration lines with three points for concentrations of 10, 100 and 1000 μg/l; analysis of 15 samples with re-calibration in the middle of the measured sample lot. The content of 15 elements was analyzed: Al, Cr, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Pb, U, Bi, Th. The detection limits were, in terms of the primary sample, from 20 to 100 μg/kg.

Table 1. Operating parameters of an Agilent 7700x mass spectrometer with inductively coupled plasma

Parameters	Values
Perilstatic pump rotation speed (rev/s)	0.1
Plasma power (W)	1550
Oscillator Frequency (MHz)	27.1
The distance from the burner to the selection cone (mm)	9
Plasma-forming gas flow (l/min)	15
The flow rate of the carrier gas (argon) (l/min)	1.0
Collision cell gas flow rate (He) (ml/min)	4.0
Scan counts to calculate concentrations	Peak hight
Resolution (atomic units / cell)	0.7
The number of reads in replicas	3
Number of replicas	3
Isotopes of elements for assessing concentrations	^{63}Cu,^{65}Zn,^{75}As,^{111}Cd,^{208}Pb,^{205}Tl

Results

We compared densities of hydrobionts from different trophic level collected both 11 years after the 1994 oil spill (in 2005) and 22 years after the spill (in 2016) to determine if they had changed in the intervening decades.

The concentration of petroleum hydrocarbons in water column in 2005, after the first stage of purifying process, ranged from 0.3 to 0.6 mg/l, which is significantly exceeded the maximum permissible concentration (MPC) for fishery waters (0.05 mg/l). In 2016, the oil content in the water column of Lake Shchuchye (polluted lake – PL) varied from 0.02 to 0.05 mg/l, which corresponds to the MPC for fishery waters. The concentration of oil in the bottom sediments of lake Shchuchye did not exceed 0.9 g/kg, in the Lake Bezymyannoye (unpolluted lake – UL) – 0.6 g/kg, which corresponds to background values for this type of bottom sediments.

Phytoplankton. Taken into account direct connectivity of the lakes studied with a stream and upper location of UL with low level of human impact, the restoration of hydrobionts of PL can be expected as a consequence of appropriate remediation of the lake.

In July 2005 phytoplankton cell number in surface layer of UL was 1.1-2.4 10^6 cells dm-3 and 0.3-5.5 10^6 cells dm^{-3} in near bottom layer. In August 2005 phytoplankton cell number in surface layer varied within 0.56-8.4 10^6 cells dm^{-3} with dominance of diatom *Tabellaria fenestrata* (Lyngbye) Kützing and chlorophyte *Dictyosphaerium pulchellum* H.C. Wood.

In July 2005 cell number in surface layers of PL varied between 3.1-4.4 10^6 cells dm^{-3} with *D. pulchellum* being most abundant, and – 1.7-5.2 10^6 cells dm^{-3} in near bottom layer with dominance of chrysophyte *Dinobryon suecicum* Lemm. In August 2005 cell number was 1.3-11.4 10^6 cells dm^{-3} in surface layer of PL with dominance of *D. pulchellum* in a single case only.

The 27 species of algae including diatoms, chrysophytes, chlorophytes, cryptophytes and dinophytes have been found in summer phytoplankton of the lakes studied in 2016. The 25 species have been identified in UL and 16 – in PL. The species composition is similar and therefore it can be concluded that phytoplankton of PL is an impoverished in comparison with UL.
According to the low abundance of phytoplankton not exceeding 0.5 10^6 cells dm^{-3}, 0.206 g m^{-3} the studied lakes can be referred as ultraoligotrophic (Kitaev, 2007). The chlorophytes, cryptophytes, diatoms and chrysophytes have been the main components of phytoplankton. Small-celled centric diatoms *Aulacoseira* cf. *alpigena* (Grun.) Krammer and *Cyclotella* sp., chrysophyte *Dinobryon divergens* Imh., small-celled coccoid green algae as well as large-celled *Cryptomonas* spp. and small-celled cryptophytes have been the most abundant in UL. Therefore phytoplankton of UL can be recognized as quite typical for clear oligotrophic water bodies of high latitudes during open water period. Nearly the same species have dominated in PL, which differed with absence of *Aulacoseira* cf. *alpigena*, lower abundance of diatoms and chrysophytes, higher number and biomass of large-celled *Cryptomonas* spp. and small-celled coccoid chlorophytes.
The uniformity in phytoplankton composition, abundance and dominant species composition at different stations have been noted, e.g. 15-19 species occurring together, 320-420 10^3 cells dm^{-3}, 279-375 10^3 individuals dm^{-3}, 0.169-0.206 g m^{-3} in UL and 12-14 species occurring together, 182-589 10^3 cells dm^{-3}, 176-405 10^3 individuals dm^{-3}, 0.045-0.174 g m^{-3} in PL. It can be recognized as absence of significant environmental heterogeneity in the lakes from plankton perspective. In the whole apparent similarity of phytoplankton in both lakes can indicate quite favorable environment for phytoplankton in PL.
Zooplankton. The species encountered in the studied lakes are mainly represented by pelagic filter feeders *Daphnia longispina* (O.F. Müller, 1776), *Bosmina obtusirostris* G.O. Sars , 1862, *Eudiaptomus gracilis* (Sars G.O., 1863), eurytopic species *Chydorus sphaericus* (O.F. Müller, 1776), and predators *Heterocopa appendiculata* Sars G.O., 1863*, Macrocyclops albidus* (Jurine, 1820), Cyclops. The composition of zooplankton communities included both widespread species (*D. longispina, Ceriodapnia quadrangula* (O.F. Müller, 1776)*, Ch. sphaericus*), and arctic or northern species (*Kellicottia longispina* (Kellicott, 1879)*, B. obtusirostris, H. appendiculata*).
In 2005 the abundance of zooplankton in UL was significantly higher than in PL (Fig. 2). The ratio of zooplankton groups in the lakes was also different. In PL copepods were the dominant in terms of abundance and absolute dominants in biomass. In UL the three main groups of zooplankton (Cladocera, Copepoda and Rotifera) were represented in approximately equal proportions.
In 2005, the surveyed areas of PL were dominated by copepods *E. gracilis*, *H. appendiculata* and their juveniles, the subdominant species were *B. obtusirostris* or *D. longispina*. Diaptomus dominated in UL, as subdominants were *D. longispina, Polyphemus pediculus* (Linnaeus, 1761) and *K. longispina*. The values of the Shannon index in PL at different sampling stations varied from 0.9 to 1.7 (1.4 on average), in UL – from 2.1 to 2.2 (2.1 on average).

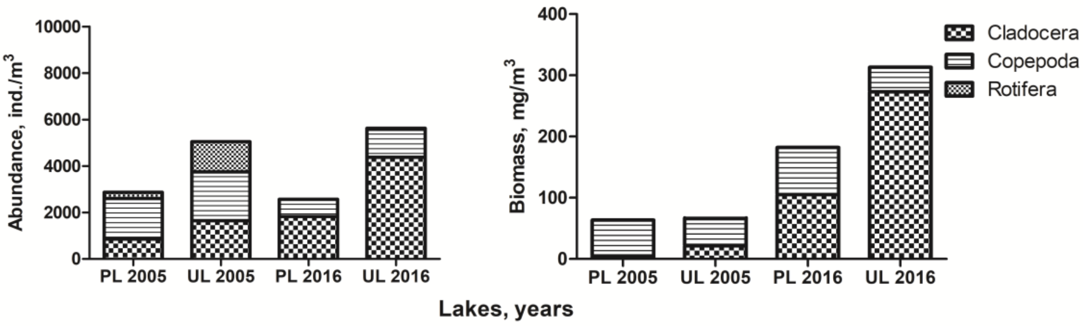

Fig. 2. Abundance (ind./m^3) and biomass (mg/m^3) of zooplankton from polluted (PL) and unpolluted (UL) lakes of different years.

In 2016, a larger number of zooplankton species were found in PL (17) than in UL (15). The species composition was similar, but the average values of zooplankton abundance and biomass in UL were twice as high. However, statistically significant differences were observed only in the copepods abundance, while their biomass was higher in the PL due to the presence of a large body species of *S. calanoides*. The composition of the dominant species in the studied lakes differed. *B. obtusirostris, Peracantha truncata* (O.F. Müller, 1785), and *S. calanoides* dominated in PL, and *Ch. sphaericus, P. pediculus, Graptoleberis testudinaria* (Fisher, 1851) dominated in UL. The values of the Shannon index in PL ranged from 0.5 to 2.3 (1.3 on average). In UL - from 1.1 to 1.5 (1.3 on average).
Zoobenthos. In 2003–2004 no benthic organisms were found in PL. In 2005, after two seasons of purifying of the lake from oil, invertebrates started to recolonise bottom sediments (apparently from UL). The abundance of benthic organisms of PL and UL did not differ significantly, but the ratio of groups was different (Fig. 3). Oligochaetes dominated in PL in terms of abundance and biomass (530 ind./m^2), in UL – chironomids (514 ind./m^2). In total, 3 and 4 groups of benthic organisms were found in the bottom sediments of the studied lakes, respectively.
In addition to oligochaetes and chironomids, bivalve and gastropod mollusks were found in the lakes, but their abundance was low. In the macrophytes of PL, 8 groups of benthic organisms were found (gastropods, bivalves, chironomids, mites, oligochaetes, leeches, dragonfly larvae and mayflies), in UL – 9 groups (oligochaetes, chironomids, bivalves, cheleids, caddisflies, leeches, ticks, gastropods and stoneflies).
The greater qualitative diversity of macrozoobenthos of macrophytes, as compared with detritic-silty sediments, was due to the fact that organisms using aquatic plants as a substrate depend more on water quality than on bottom sediments quality. In

terms of the average trophic index, the studied biotopes were classified as very low trophic class (α-oligotrophic) on the Kitaev scale.

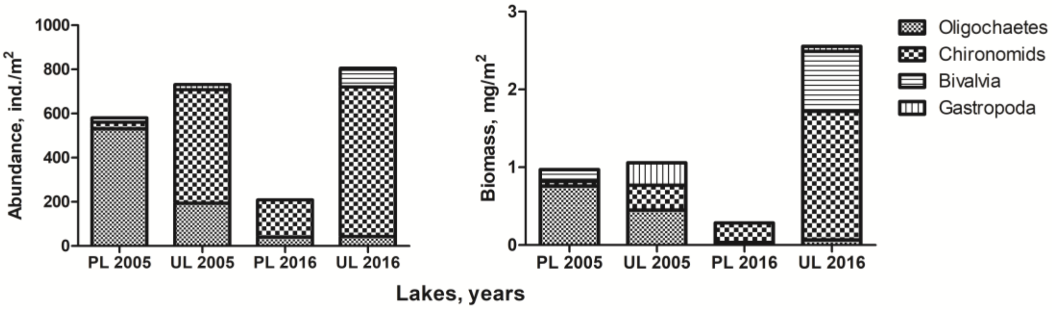

Fig. 3. Abundance (ind./m²) and biomass (ind./m²) of macrozoobenthos from polluted (PL) and unpolluted (UL) lakes of different years.

In 2016, the average abundance and number of species in PL was significantly lower than in UL. However, the same group of invertebrates, the chironomids, dominated in both lakes. In addition to chironomid, oligochaetes, mollusks, mayfly, gammarids, nematodes, and caddis flies were singly registered in samples. In the lake. 22 years after the spill, the dominant complex in PL is represented by the same group of benthic organisms as in UL, but the number of species and the total abundance of zoobenthos do not reach the values of an intact lake. The trophic index of the detrital-silty biotopes of PL corresponded to the α-oligotrophic class (very low trophicity) according to the Kitaev scale, UL – to the β-oligotrophic class.

Table 2. Metal content (mg/kg dry weight ± mean error) in the muscles of three fish species from polluted (PL) and unpolluted (UL) lakes.

Metal	PL			UL		PRC (mgkg)
	roach	perch	pike	perch	pike	
Al	20.3±4.3	24.7±5.2	72.2±29.1*	17.2±3.4	14.5±7.8	30.0
Cr	0.6±0.09*	0.9±0.2*	0.3±0.04	0.5±0.08*	0.2±0.04	0.3
Fe	84.0±13.5*	80.5±15.4*	58.0±19.8*	33.9±6.2	20.4±5.7	30.0
Co	0.2±0.08	0.1±0.02	0.05±0.008	0.2±0.1	0.04±0.01	0.5
Ni	0.3±0.06	0.2±0.06	0.06±0.01	0.1±0.1	0.01±0.004	0.5
Cu	30.7±25.1*	6.9±4.2	3.9±1.9	0.9±0.08	3.5±2.9	5.0
Zn	53.8±3.3	26.2±1.4	43.5±8.8	23.1±1.3	23±1.7	70.0
As	0.3±0.2	0.09±0.08	0.004±0	0.004±0	0.004±0	1.0
Mo	0.02±0.008	0.6±0.5	0.003±0	0.01±0.01	0.07±0.06	-
Cd	0.1±0.08	0.03±0.007	0.007±0.002	0.03±0.01	0.004±0.0004	0.2
Sb	0.02±0.002	0.02±0.004	0.004±0.002	0.004±0.001	0.002±0	-
Pb	0.2±0.09	0.1±0.02	0.1±0.08	0.05±0.05	0.002±0	1.0
U	0.003±0.001	0.01±0.002	0.003±0.001	0.001±0	0.002±0.001	-
Bi	0.003±0.001	0.003±0.001	0.002±0.001	0.001±0	0.001±0	-
Th	0.004±0.002	0.003±0.001	0.004±0.001	0.001±0	0.001±0.0003	-

* – Excess of permissible residual concentration (PRC) in the muscles of fish ($p < 0.05$).

Ichthyofauna of investigated lakes.

In the study of the ichthyofauna of PL and UL in 2005 and 2016, three species of fish were found – perch (*Perca fluviatilis* Linnaeus, 1758), roach (*Rutilus rutilus lacustris* (Pallas)) and pike (*Esox lucius* Linnaeus, 1758). Due to the lack of significant differences in the size-age and linear indicators of fish between the lakes, we present a comparison of the results of PL between years (2005 and 2016).

In 2005, perch was the dominant species (69%), subdominant – roach (29%). In 2016, roach (51%) began to dominate. Pike as well as in 2005 was represented by the minimum number and in the catches did not exceed 5% of the total.

Perch. Comparison of the age structure of the perch population in 2005 and 2016 revealed a shift towards younger ages. In 2005 individuals aged from 6+ to 11+ years were noted, with a predominance of individuals aged 8+ years, and in 2016 - from 2+ to 7+ years, with a predominance of individuals aged 4+ years. In 2016, perch growth rates were higher than in 2005. Despite the dominance of the older age groups in 2005, the size and weight indicators of perch in 2016 were within similar range and

had similar average values of length and body weight. However, the values of fatness (Fulton) in 2005 (1.85 ± 0.01) slightly exceeded this indicator of 2016 (1.76 ± 0.02), which is probably due to the predominance of young individuals in the population.
Roach. The age structure of roach in 2016 also changed – there was an increase in age from 4 + –7 + to 4 + –9 + years. Despite the appearance of older ages, a shift in the age structure towards juveniles was noted – predominance of individuals aged 6+ years in 2005 was replaced by the prevalence of 5+ year olds in 2016. In addition, in 2016 there was an increase in the size and weight indicators of roach of similar ages. The average value of the fatness ratio in 2016 was also lower than in 2005 (1.96 ± 0.02 and 2.12 ± 0.02, respectively).
Pike. The pike in the catches of 2005 and 2016 was sporadic and was represented by the ages of 5 + -7 + and 4 + -6 + years, respectively. The coefficient of pike nutrition in the catches of 2016 was slightly higher than in 2005 and amounted, respectively, to 0.85 ± 0.03 and 0.75 ± 0.03.
Heavy metals in the tissues of fish. Analysis of the microelement composition of the tissues (muscles) of three species of fish from PL and UL showed that Fe, Zn, Al, Cu, Cr are observed in all fish species in the highest concentrations (Table 2). The minimum content is typical for U, Bi, Th in all fish species in both lakes.
Significant excess of permissible residual concentrations (PRC) of metals is observed in the muscles of fish from PL. The excess of PRC for Al (pike), Cr (roach, perch), Fe (roach, perch, pike) and Cu (roach) was revealed. In the muscles of fish from UL, a slight excess of PRC was noted for Cr (perch) only. The content of the most toxic elements - Pb, Cd and As in the muscles of all investigated fish does not exceed PRC and in most cases is on the border of the determination threshold.

Comparison of metal concentrations in fish from the studied lakes showed that Fe, Bi and Sb concentrations in perch muscles from PL are 2–5 times higher ($p < 0.05$) than in perch from UL (Fig. 4), in pike muscles 2–3 times more Fe and Ni, respectively (Fig. 5). In addition, higher, but statistically insignificant concentrations of Cu and Mo in the muscles of the perch and Al, Zn and Pb in the muscles of pike from PL were revealed (Table 2). Korchina et al. (2010) showed a statistically significant positive correlation between the level of oil pollution of the northern river and the concentration of cadmium and lead. A higher metal content in the muscles of fish from an oil-polluted lake confirms these data and indicates an increase in the concentration of metals in the environment under oil pollution.
In our study it was shown that in different types of fish identical metals accumulate with different intensity. Concentrations of almost all metals were higher in roach muscles than in perch and pike ($p < 0.05$). Significantly higher concentration of Fe, Cr, Ni, Mo, Cd, Sb and Pb accumulate in the perch and roach muscles than in pike ($p < 0.05$). Perch accumulates significantly more Cr, Co, Cd and Bi than pike.

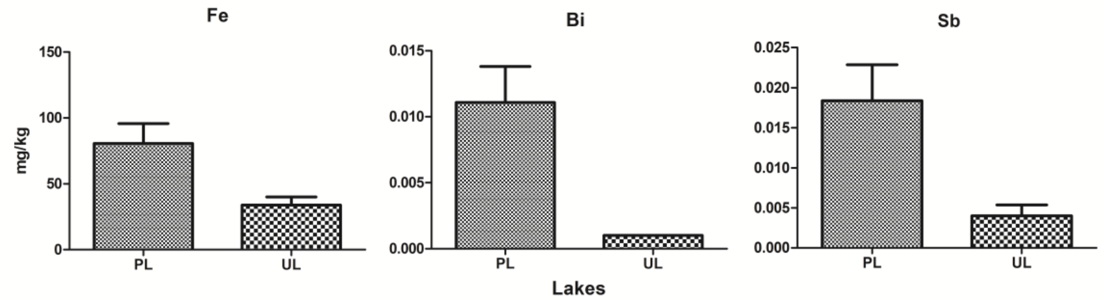

Fig. 4. Concentration of Fe, Bi and Sb in perch (*Perca fluviatilis*) tissues from polluted (PL) and unpolluted (UL) lakes.

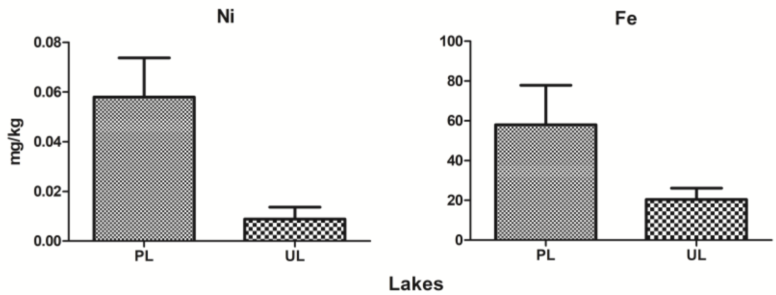

Fig. 5. Concentration of Fe and Ni in pike (*Esox lucius*) tissues from polluted (PL) and unpolluted (UL) lakes.

The relationships between the biological indicators of fish (age, fatness, length) and the content of heavy metals in their tissues were revealed. A positive correlation ($p < 0.05$) between the lead content and the weight of roach ($r = 0.44$) was found. It was noted that the content of nickel ($r = 0.58$) in the perch tissues increases significantly with age, but the content of arsenic ($r = -0.53$), molybdenum ($r = -0.51$) and uranium ($r = -0.4$) decreases. Moreover, it is traced negative correlation ($p < 0.05$) between perch length and zinc content ($r = -0.44$). The decrease in concentrations of these metals in the perch muscles may be due to the change in feeding habits with age.

Discussion

Crude oil is comprised of a complex mixture of petroleum hydro-carbon and non-hydrocarbon compounds. Mixtures vary among different oils and it results in different physical and chemical properties (Board, 2003). The most acute toxic components of fresh crude oil are monocyclic aromatic hydrocarbons and phenols, but their high volatility limits their toxic effects to aquatic organisms (Neff et al., 2000). Weathered oil in aquatic environments poses a significant threat to aquatic organisms, because toxic effects can cascade and accumulate across trophic levels (Gin et al., 2001; Peterson, 2003). When entering into a reservoir, oil enters into a common chain of complex and little studied processes (evaporation, dissolution, emulsification, oxidation, formation of aggregates, sedimentation, biodegradation) (Egorov, Shipulin, 1998). These processes depend both on the composition and amount of oil in the aquatic environment, and on the conditions in water bodies (presence of colloids in the water, suspended particles, plankton, temperature, solar lighting, etc.).

In all forms of oil migration there is an accumulation of components resistant to biodegradation (resins, asphaltenes, paraffins, etc.), and the maximum of petroleum products is concentrated in bottom sediments. After big oil spills, when the reservoir is completely covered with oil and operational measures for its collection are not taken, the bottom sediments are covered with a layer of oil and complete degradation of the bottom communities is observed.

10 years after the 1994 oil spill in the Usinsk district of the Komi Republic, the bottom sediments of the oil-polluted lake Shchuchye were covered with a layer of oil reaching 2 centimeters in some areas. The appearance of zoobenthos in 2005 (mainly oligochaetes), after the first year of purifying, indicates the appearance of fairly clean areas of bottom sediments suitable for some species of zoobenthos.

Comparison of the qualitative composition of the macrozoobenthos of PL and UL in 2005 and 2016 showed that the macrozoobentiic fauna of PL is poorer in both the number of ecological groups and the species diversity of these groups. In 2016, the dominance from oligochaeta turned to chironomids, which corresponds to the structure of benthic communities of UL and thus demonstrates the recovery of benthic fauna. Oligochaeta, along with polychaetes and nematodes, are highly resistant to various pollutants and, under unfavorable conditions, may be the only representatives of zoobenthos in a water body (Peterson et al., 1996). Consequently, an increase of chironomids abundance may indicate an improvement in habitat conditions. However, Kholmogorova (2007) suggested that in mud sediments, with the increasing of oil concentration, domination from oligochaetes change to chironomids. Bertrand et al. (2017) showed that 23 years after the oil spill in Parry Sound Harbor (Canada), density of larvae of *Chironomus cucini* (Webb 1969) was well-established, which suggests that its population density had recovered for 23 years. However, the high incidence of deformities (mentum or mandibules) reported for this species suggests continued contact with polluted sediments. At the same time mean densities of oligochaetes (Tubificidae) were lower in 1973 (23 years after the oil spill) than in 2009 (59 years after the oil spill), which suggests that populations of these species have not recovered by 1973. One of the conclusions of this investigation is that 23 years after the oil spill polluted sediments are covered by new layer of sediments and colonized by benthic organisms. In our study the sediments were covered by oil for 10 years and no colonization of benthic oganisms was noticed. In 2016 (22 years after the oil spill) due to purifying of bottom sediments oil concentration reduced significantly but still was higher than in unpolluted lake. These differences are likely to be due to differences in environmental conditions and types of water bodies (type of bottom sediments, flowage, depth, temperature, etc.). Recovery of benthic communities is reported to be more rapid in shallow, hard substrates subject to strong currents than in deeper regions characterized by soft sediments (Poulton et al., 1997). Thus recovery of the benthic community in the cold, deep water, soft sediments is likely to be relatively slow.

Abundance of phytoplankton was lower during July 2016 in comparison with previous survey with more significant decrease in PL. Obvious differences in cell number and dominant species composition between surveys can indicate more oligotrophic state of UL and especially PL in the last case.

Comparison of quantitative and qualitative indicators of zooplankton of PL from 2004 to 2016 shows a tendency of increasing species diversity, which in 2016 reaches the indicators of the UL. 11 years after the spill the structure of zooplankton community of PL was different from UL. Zooplankton community of PL was represented mainly by copepods while in UL – by cladocerans.It is known that the copepods are more resistant to adverse effects and are able to survive under conditions in which cladocerans die (Kurbatova et al., 2007, Lopez-Mancisidora, 2008). This is due to differences in the feeding habits and the way of nutrient storage. In 2016 (22 years after the spill), the ratio of the main groups of zooplankton – copepods and cladocerans changed towards an increase in the number of cladocerans species to 1: 3, which corresponds to indicators of UL. Nevertheless, the differences in zooplankton characteristics of UL and PL indicate of incomplete ecosystem recovery even 22 years after the spill, despite the low content of oil hydrocarbons in water samples (the concentration of oil in water column was within the limits of MPC values).

Analysis of the trace elements concentration in fish tissues from PL and UL showed that all species contain the highest concentrations of Fe, Zn, Al, Cu, Cr. The content of these metals in the fishes is arranged in the following order: roach> perch> pike. The excess of PRC for Al, Cr, Fe, Cu in the tissues of fish from PL was revealed. In fish tissues from PL, a slight excess of PRC was noted only for Cr (perch). However, it is important to note that PRC in fishery products determine their quality in relation to human health. The effect on the fish themselves remains unknown. Bioaccumulation of metals in fish occurs mainly through water and food, involving dietary and non-dietary routes (skin and gills) (Oost et al., 2003). The degree of metal accumulation in fish depends on a variety of chemical, physical and environmental factors (Farkas et al., 2002; Weber et al., 2013). Strong positive correlation between the metal concentration in fish and feeding habits has been shown in several investigations (Sobolev, 2005). Carnivorous fish are prone to accumulate more metals than omnivorous due to magnification through the trophic chain (Peakall, Burger, 2003; Has-Schön et al., 2006). In contrast, Borisov (2005) and Yousafzai et al. (2010) showed that omnivorous fish accumulate more metals than carnivorous. The habitat of fish may also be the factor involved in metal accumulation in the organism. Some authors suggested that accumulation of metals is higher in benthic fish than in pelagic (Kojadinovic et al., 2007; Monroy et al., 2014). Other authors suggest that metal bioaccumulation is a species-dependent process and more related to detoxification mechanisms and metabolism (Garnero et al., 2018). In our study, concentrations of almost all metals were significantly higher in the tissues of roach (omnivorous species) and perch (facultative predator) compare to pike (obligate predator). Perch can feed on zooplankton and benthos permanently. This fact explains comparatively high concentration of metals in its tissues. Opposite data on Hg concentration in same fish species have been obtained by Pintaeva et al. (2011). They showed that Hg concentration is decreasing in the following order: pike>perch>roach. We did not measure the concentration of Hg in our study and therefore cannot compare these results. Different fish species are significantly heterogeneous: some species prefer contaminated areas (roach), others have a pronounced reaction to avoid contaminated areas (pike) (Davydova, Tagasov, 2002). Apparently, differences in the accumulation of metals are mostly associated with these preferences and with specific environmental conditions (pH of water and bottom sediments, the amount of dissolved organic carbon), ecology (feeding habits, migration, etc.) and physiological and biochemical parameters of fish.

Conclusion

In severe climate conditions recovery rate of the aquatic freshwater ecosystem after oil pollution is low even after purifying processes. Quantitative and qualitative indicators of the aquatic invertebrate communities 22 years after the spill reach those one of unpolluted lake, but do not fully recover, despite the low content of oil hydrocarbons in water and bottom sediments. Oil pollution of the lake is accompanied by an increase in the concentration of trace metals. A significantly higher content of Fe, Ni, Bi and Sb was revealed in fish tissues from polluted lake. In addition, excess of permissible residual concentrations of Al, Fe, Cr, Cu for all fish species were detected. Differences in the accumulation of metals in fish associate with their ecology, physiological and biochemical parameters of fish and with specific environmental conditions. It also depends on metal characteristics.

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