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Small Lakes Ecosystems under the Impact of Non-Ferrous Metallurgy (Russia, Murmansk Region)

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Abstract: This paper presents integrated research on ecosystems of small lakes experiencing the direct impact of a copper-nickel ore processing plant, the "Kolskaya GMK" (MS KGMK), near the town of Monchegorsk Kola Peninsula, Russia. An integrated research method with the analysis of both abiotic and biotic components of aquatic ecosystems was used. It was found that the water ecosystems developed under the conditions of extreme pollution depleted the species composition of the hydrobionts and the number indices. Much of the pollution resulted in a transformation in the phytoplankton community structure: the share of mixotrophic algae and Cyanobacteria increased. Anthropogenic eutrophication resulted in a decrease in toxic impact. Despite high anthropogenic load, Salmonid and Coregonid species were found in a number of water bodies. The size and weight indices and the heavy metal accumulation intensity had a distinct gradient nature. The macrozoobenthos in the water bodies studied was characterized by depleted taxonomic composition and extremely low numbers. The basis of the zoobenthos was formed by chironomids Psectrocladius, Procladius, Cricotopus, and Orthocladius, spread widely in water bodies polluted with heavy metals.

Keywords: small lakes; copper-nickel production; hydrochemistry; plankton; benthos; ichthyofauna

1. Introduction

Non-ferrous metallurgy is one of the industries with the greatest impact on areas in which smelters are located. Due to their high toxicity and ability to accumulate in hydrobionts, heavy metals (HMs) are basic pollutants of water ecosystems [1–6]. The industrial impact on aquatic ecosystems in the arctic regions is the subject of much research [7–10]. Changes in geochemical and hydrobiological indicators as a result of the long-term anthropogenic impact have been shown [11,12]. Small freshwater bodies located in industrial areas of the Arctic region are the most vulnerable components of the environment, which makes them good indicators of anthropogenic pollution. A number of small lakes located in the area affected by the Monchegorsk site of the Norilsk Nickel Kol'skaya Gorno-metalurgicheskaya Kompanya (MS KGMK) are directly polluted by copper-nickel production waste and are exposed to intensive aero-technogenic pollution. The water bodies' ecosystems develop under conditions of long-term, extreme anthropogenic load combined with high concentrations of pollutants in water and bottom sediments [7,8], significant degradation of the soil cover and vegetation in the water catchment area, and acid rain. Smelter discharge and pollutants eventually travel from the water catchment area to Monche Bay of Lake Imandra with the sewage from the town of Monchegorsk, resulting in a dramatic transformation of the water quality conditions [9,10]. The aim of the study is to assess the current state of the basic abiotic (water chemical composition) and biotic (phytoplankton, zoobenthos, ichthyofauna) components of water ecosystems affected by copper-nickel production and to reveal the relationships and impact of pollution on the lakes ecosystems.

2. Materials and Methods

The study area is located in the west of the Kola Peninsula in the Monchegorsk area of the Murmansk region. Five lakes located in the vicinity of buildings and structures that belong to MS KGMK and Monche Bay of Lake Imandra were studied (Figure 1). In addition, one sample of groundwater was obtained from a self-flowing well near of Kumuzhye Lake (number 7 in Figure 1).

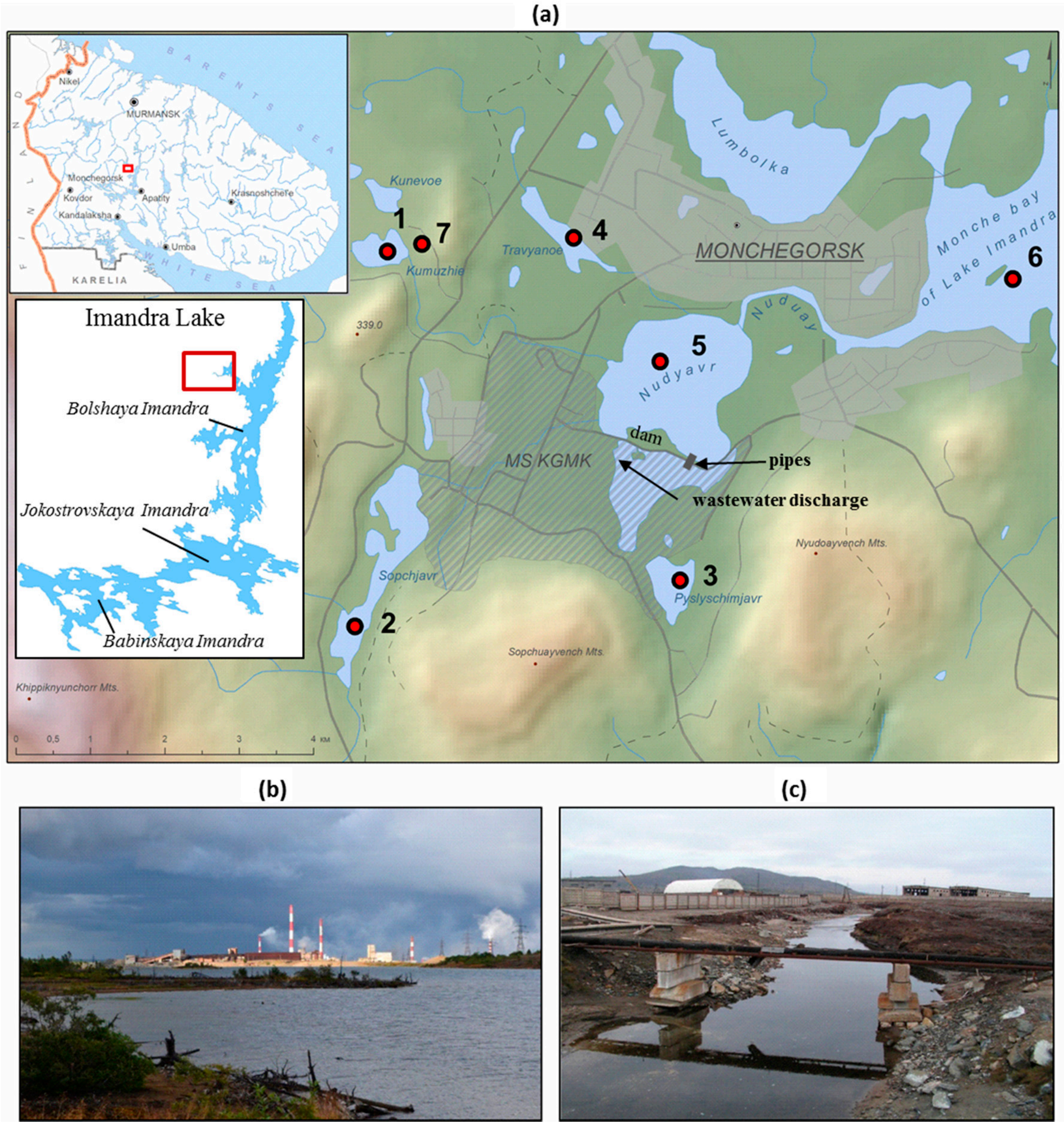

Figure 1. (**a**) The water bodies studied and sampling points; (**b**) a view of MS KGMK from Lake Sopchjavr and remains of dead trees; (**c**) a typically disturbed landscape near MS KGMK.

All the industrial and transport infrastructures in the area have been intensively developed since 1938, and the great amounts of sulfur dioxide and HMs emitted into the atmosphere have resulted in degradation of the soil and vegetation cover (from lichen depression to the complete depletion of soils to technogenic barren formation in the lakes' landscape). The transformation of the Lake Kumuzhie lowlands as a result of anthropogenic impact was insignificant, and mainly the north-taiga vegetation—typical for the area—was preserved there. The investigated lakes represent a single system and have a water catchment area of 90.54 km^2. Connected to its northern part through pipes, the southern part of the Lake Nyudjavr basin, which is separated from the main water basin by a dam, serves as a technological basin to settle saline wastewater transported from the smelter and domestic waste transported from MS KGMK (Figure 1). The wastewaters belong to the chloride-sulfate class, and to the sodium group. In 2017, suspended solids in the sewages amounted up to 503 mg/dm^3 and contained extremely high concentrations of sulfate ions (up to 2720 mg/dm^3), sodium ions (up to 2085 mg/dm^3), chloride ions (up to 1246 mg/dm^3) and borate ions (up to 63 mg/dm^3). Concentrations of acid-soluble forms of HMs in wastewaters are also high: Cu up to 20.5 mg/g, Ni up to 156 mg/g, and Co up to 0.96 mg/g.

A channel connects Lake Pyslyschimjavr to the northern part of Lake Nyudjavr, through which waste is transported around the southern part of Lake Nyudjavr. The Nyuduai river basin discharges into Monche Bay of Lake Imandra. Municipal sewage from the Monchegorsk town pours into the northern part of Monche Bay.

We carried out water sampling in 2016 and 2017. There were two water samples taken from the surface and the bottom water layers from each lake and Monche Bay annually. Water samples were taken in polyethylene bottles from Nalgen®, the material of which does not have sorbing properties. Previously, the bottles were thoroughly washed in the laboratory. When sampling water, the bottles were rinsed twice with lake water, then placed in dark containers and refrigerated (~+4 °C) in a short time transported to the laboratory. Filtration of water samples was carried out in the laboratory during discharge at the Millipore phase separation unit from high-density polypropylene through glass and polycarbonate membrane filters of Millipore HVLPO 4700, Schleicher and Schuell ME 25/21 ST, Whatman GF/A with a pore size of 0.45 µm. The following parameters were determined in unfiltered samples: pH, conductivity, alkalinity, NH^{4+}, NO^{3-}, PO_4^{3+}, metals (after acidification with concentrated nitric acid). In the filtered samples, Si, P, color, Cl^-, SO_4^{2+} were determined. Water chemistry was determined at the resource sharing center of the Institute of North Industrial Ecology Problems (INEP) Kola SC RAS using the same methods described in *Guidelines for Methods* ... [13] and *Standard Method* ... [14]. For the quality control of the measurements of pH, alkalinity, concentrations of chlorides, sulfates, alkali, and alkaline-earth metals, the specialized ALPEFORM software suite was used, including an assessment of ion balance, measured and calculated electrical conductivity. The quality of the laboratory analytical measurements was evidenced by annual international verification [15].

A hydro-chemical analysis was carried out by Analytical Laboratory INIEP KSC following the techniques described in *Guidelines for Methods* ... [13] and *Standard Method* ... [14]. We compared the results of the analysis to the averaged hydro-chemical indices of the lakes in the north-taiga zone of the Murmansk region, taking these indices conditionally as the background ones [16–19]. We analysed the chemical composition of groundwater from a self-discharged well located near Lake Kumuzhie (Figure 1). We sampled and analysed phytoplankton in the summer periods of 2016 and 2017 following the Russian state's standards [20] and the standard techniques recommended in *Guidance on Methods* ... [21] and *Guidance on Hydrobiological Monitoring* ... [22], according to the scheme defined in the INEP [23]. We sampled phytoplankton with a typical Ruttner water sampler with a 2.2-litre capacity. Plankton was concentrated with a plankton net (29 µm) and the final sample was placed into a 50 ml plastic flask and fixed with a Lugol solution layer. The phytoplankton samples were concentrated in the laboratory through sedimentation (settling). We calculated the phytoplankton biomass using the counting-volume technique, using the counting-volume technique by calculating the volume of an individual cell (or dense colonies) of each species [24–26]. We calculated the abundance and determined the taxonomic identification of the algae in a 0.1 mL Nageotte chamber through a light microscope, Motic BA300, with an immersion lens. We merged the taxa names with the international algae database [27]. The algae communities' floristic similarity was assessed using the Sörensen–Czekanowski coefficient [28,29] and the analysis was carried out by the program module Graphs [30]. We assessed the species diversity using the Shannon–Weaver index and the Simpson's reverse (polydominance) index [31,32]. To assess water quality, we calculated the saprobic index (S) using the Pantle–Buck method modified by Sladechek [33,34], in accordance with the Russian state's standards [20]. The ecological characteristics of the discovered taxa were taken from Barinova et al. [35].

To determine the concentration of chlorophyll "a" in the plankton, we put the water samples (600 mL) through a membrane filter with a pore diameter of 0.47 µm with the help of a Millipore injector and a filtering nozzle. To avoid photosynthetic pigments changing in the water samples in transport, we filtered the water near the water body. We extracted chlorophyll with pure acetone solution (90%, PA) and measured the optical density of the extracts using the Hitachi UV-VIS 181 spectrophotometer. We calculated the photosynthetic pigment concentrations using standard methods, generally accepted in international and domestic practice, following the scheme employed at INIEP KSC RAS [23,36,37].

We sampled and analysed the zoobenthos according to the Russian state's standards, using standard techniques [17,19]. The bottom sediment samples were taken from deep zones with an Ekman–Birge grab, the catchment area being 290 cm^2. For the littoral zone, we took quality samples with a hydrobiological netscraper. Quality and quantity zoobenthos sampling was carried out in the late summer in lakes Kumuzhie, Sopchjavr, Pyslyschimjavr, Travyanoe, Nyudjavr (August 2016 and 2017) and Monche Bay of Lake Imandra (August 2013). Invertebrates were identified by the key to zooplankton and zoobenthos of the fresh waters of European Russia [38] and the key to freshwater invertebrates in Russia and adjacent territories [39].

We sampled and analysed the ichthyology material according to Russian state standards applied by the research institutions during ichthyologic researches [40–44]. The trout organs were analysed for HM accumulation, and the samples were frozen to be further analysed. To achieve the constatnt weight, the organ samples were dried in a laboratory drying oven at 90 °C. Then, the organic matrix was removed in a concentrated nitric acid solution in a microwave decomposition system (Multiwave 3000, Anton Paar, Austria), followed by further filtration. We determined HM concentration in the fish using atomic adsorption spectroscopy with atomisation in flame or in graphite pipes using a PerkinElmer 5000 in graphite oven. The HM concentration was calculated in µg/g of dry tissue weight. We compared the solution samples used to identify the metals with the certified standard sample of Fluka Chemie GmbH, Switzerland, and controlled quality using DORM-2 standard samples.

3. Results and Discussion

3.1. Hydro-Chemical Indices

All five lakes exceeded the regional background level for all the basic pollutants—HMs Cu, Ni, Pb, and Cd—and for nutrients—nitrogen and phosphorus compounds (Table 1). The highest pollutant concentrations were recorded in Lake Nyudjavr, which received wastewater in which the chloride, sulfate, copper, and nickel concentrations were two orders of magnitude higher than that of the conditional background [7]. The hydro-chemical parameters of the other water bodies were mainly the result of aero-technogenic pollution. It was suggested [9,16] that the lake ecosystems develop under the influence of two main factors: biogenic and toxic loads. It seemed that the presence of available biogenic elements could increase water organisms' resistance to the impact of toxicants. Groundwater was characterized by the hydro-chemical parameters that were most like the background ones. The nickel and sulfate concentrations exceeded the background ones (Table 1).

The inflow of comparatively less polluted groundwater to Lake Kumuzhie was likely to have a positive effect on the water body's ecosystem. The water chemical composition in Monche Bay of Lake Imandra was affected by the polluted discharge from the Nyuduai River and by sewage works located near the town of Monchegorsk. The nutrients and HM concentrations in Monche Bay were found to be lower than those in the lakes being studied, which can be explained by the high water exchange, the connection with the main water basin of Lake Imandra, and the greater water volumes than those of the five lakes in question.

Table 1. Selected average chemical parameters (2016–2017) of the water bodies under non-ferrous metallurgy impact (1—Kumuzhie; 2—Sopchjavr; 3—Pyslyschimjavr; 4—Travyanoe; 5—Nyudjavr; 6—Monche bay of Lake Imandra; 7—ground water) in comparison to the background (b). TOC—total organic carbon.

	pH	NH_4 µg N/L	SO_4 mg/L	NO_3 µg N/L	Cl mg/L	N(tot) µg N/L	PO_4 µg P/L	P(tot) µg/L	TOC Mg C/L	Cu µg/L	Ni µg/L	Pb µg/L	Cd µg/L
1	6.89	31.0	14.0	13.4	0.8	174.0	6.0	10.7	3.6	16.4	77.8	0.3	0.02
2	7.06	17.0	20.3	139.1	4.3	288.6	4.3	12.1	2.5	41.0	270.3	1.4	0.04
3	6.70	16.0	26.5	15.7	1.2	252.4	2.4	9.3	4.4	98.6	275.6	0.4	0.12
4	6.97	38.7	13.2	46.3	4.5	350.9	6.7	20.3	6.5	177.3	186.1	0.9	0.08
5	8.62	74.0	550.0	95.9	241.9	518.1	19.0	41.4	4.8	199.5	335.3	0.5	0.10
6	7.10	60.5	24.9	5.0	11.0	328.0	6.0	26.0	4.3	10.5	0.7	-	0.01
7	7.50	0	67.5	2.0	1.5	28.0	2.5	2.8	1.9	0.06	0.7	0	0
b	6.80	15.0	2.0	3.5	1.6	130.0	0.8	6.0	5.0	<1.0	<1.0	0	0

3.2. Phytoplankton

In total, there were 89 algae and Cyanobacteria taxa found in all the water bodies studied. They were below the rank of the following systematic groups: Cyanobacteria (8), Dinophyceae (5), Cryptophyta (1), Bacillariophyta (43), Chlorophyta (15), Charophyta (12), Chrysophyceae (3), and Euglenophyta (1). All the lakes differed greatly in taxonomic composition, dominating taxa, and species richness (Figure 2).

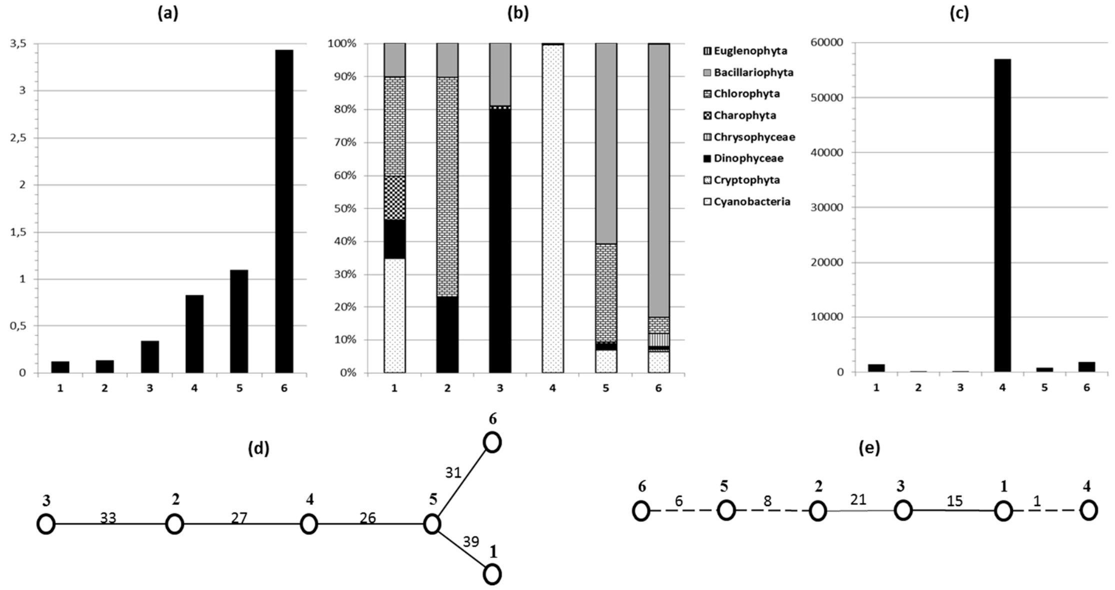

Figure 2. Phytoplankton communities under non-ferrous metallurgy impact. (**a**) Biomass, g/m^3; (**b**) abundance proportion of the large taxa categories, by percent (**c**) abundance, ind./l; dendrogram of the algae communities' similarity using the Sörensen–Czekanowski coefficient: (**d**) based on taxa presence; (**e**) based on taxa abundance (1: Kumuzhie, 2: Sopchjavr, 3: Pyslyschimjavr, 4: Travyanoe, 5: Nyudjavr, 6: Monche Bay of Lake Imandra).

In Lake Kumuzhie, the typical representatives were Cyanobacteria *Pseudanabaena limnetica* (Lemm.) Kom.; dinoflagellates *Peridinium bipes* Stein; diatoms *Aulacoseira alpigena* (Grun.) Kramm., *Tabellaria flocculosa*; green algae *Chlorella mucosa* Korsh.; Charophyta *Spondylosium secedens* (De Bary) Arch.; and *Spirogyra* sp. Green filamentous algae *Ulothrix* sp. were found in the phytoplankton of Lake Sopchjavr, representatives of Chlamydomonas and dinoflagellates *Peridinium bipes*. Dominating in Lake Pyslyschimjavr were diniflagellate *Peridinium bipes*. Diatoms *Aulacoseira alpigena* (Grun.) Kramm. were also found.

Highly dominating in Lake Travyanoe was *Pseudanabaena limnetica* (Lemm.) Kom. Great taxonomic richness was characteristic of Lake Nyudjavr, where diatoms dominated. They included *Fragilaria capucina* subsp. *rumpens* (Kütz.) Lange-Bert., *F. capucina var. gracilis* (Oestr.) Huste., *Surirellabre bissonii* Kramm., and Lange-Bert., green algae *Stigeoclonium longipilum* Kütz., and Cyanobacteria *Anabaena* sp. The composition of phytoplankton from Monche Bay of Lake Imandra corresponded to that typical of the eutrophicated zones of Lake Imandra [45]—*Asterionella formosa* Hass., *A. islandica* (Müll.) Simons., *Fragilaria crotonensis* Kitt.—and differed greatly in taxonomic richness.

According to floristic analysis, there was slight similarity in the quality characteristics (the taxonomic composition) and community structure (taking each species' richness into account) of the phytoplankton flora sampled from the lakes studied. The phytoplankton communities of Lake Nyudjavr and Monche Bay, where diatom algae dominated, as well as those of Lakes Sopchjavr and Pyslyschimjavr, in which dinoflagellates dominated, were found to be the closest in taxonomic composition. The most significant difference in the taxonomic composition was in the algal flora of Lake Travyanoe, where Cyanobacteria dominated (Figure 2d,e).

As a whole, the phytoplankton species' composition and the community structure in all the water bodies differed from those in the lakes located in the background areas of Murmansk region: the Cyanobacteria and dinoflagellate levels, indicators of toxic load, were relatively high. The phytoplankton in small lakes included filamentous algae characteristic of fouling. Some features of natural water bodies were provided by algal flora in Monche Bay of Lake Imandra: the diatom level was high, and one could find the Chrysophyceae *Dinobryon divergens* Imh. and *Synura* sp. due to the large size of the water body and intensive water-exchange processes.

The state of the phytoplankton algae communities in Monche Bay and of the sensitive-to-pollution Charophyta algae of Lake Kumuzhie was found to be the closest to the natural state. The algal flora in Lake Travyanoe was found to be the most transformed, with utter domination of Cyanobacteria in both amount and biomass. In the slightly saline, alkaline Lake Nyudjavr, under both toxic load and anthropogenic eutrophication, we observed the formation of specific alkaliphilic algal flora in the relatively stable-to-pollution diatom species *Surirella brebissonii* Kramm. and Lange-Bert, *Fragilaria capucina var. gracilis* (Oestr.) Hust., and *F. capucina* subsp. *rumpens* (Kütz.) Lange-Bert. The presence of toxic substances (primarily HMs) suppressing photosynthetic activity seemed to prevent abundant phytoplankton mass development. The presence of nutrients was likely to increase algae resistivity to toxic load.

The average amount of phytoplankton biomass was small, ranging from 0.13 to 3.43 g/m^3; its abundance, however, varied greatly—from 88 to 56979 ind./L (Figure 2). The greatest amount of biomass was recorded in Monche Bay. In other water bodies, the quantitative indices of phytoplankton corresponded to those of oligotrophic water. The highest amount of phytoplankton was recorded in Lake Travyanoe, in which one could observe mass development of the Cyanobacteria *Pseudanabaena limnetica*. The amount of chlorophyll "a" in the phytoplankton ranged from 0.51 to 6.98 mg/m^3. The highest photosynthesis activity was observed in the algocoenoses in Monche Bay of Lake Imandra, and the lowest activity was observed in Lake Kumuzhie (Table 2).

We calculated the degree of saprobity (S) using the phytoplankton indices, and all the water bodies were classified from xenosaprobic (x) to beta-oligosaprobic (β-o). We also classified the water quality, which ranged from I (very clear) to III (moderately polluted) within the limnosaprobic category. The lowest S-index (0.36) was characteristic of Lake Sopchjavr, and the highest index S (1.60) was characteristic of Lake Travyanoe. It was clear that the intensive impact produced by non-ferrous plants limited the supplication of the S-index to determine water quality in water bodies for two reasons: firstly, the amount of saprobionts was not enough to be calculated due to the extremely small number of taxa; secondly, the presence of an intensive toxic load suppressed algae development, even with sufficient nutrients (nitrogen and phosphorus compounds). In the present study, the objectively lowered values of the S-index under the biogenic load could be taken as indicators of toxic water pollution.

Table 2. Some phytoplankton parameters and water trophic state. $N_{sp.}$—subgenera taxa number, Chl «*a*»—chlorophyll «*a*» content, mg/m^3; H′—Shannon-Weaver index, bit/ind; 1/D—Simpson's reverse index, S—sabrobity index; QC—water quality class according to Russian state standard; T—water trophic state (1—Kumuzhie, 2—Sopchjavr, 3—Pyslyschimjavr, 4—Travyanoe, 5—Nyudjavr, 6—Monche bay of Lake Imandra).

	$N_{sp.}$	Chl «*a*»	H′	1/D	S	QC	T
1	29	0.88	1.30	2.26	0.90	I	α-oligitrophic
2	8	0.87	2.76	10.55	0.36	I	α-oligitrophic
3	10	1.16	1.74	5.41	1.10	II	α-oligitrophic
4	21	2.99	0.03	1.01	1.60	III	β-oligitrophic
5	32	2.71	2.22	5.92	0.91	I	β-oligitrophic
6	44	6.98	2.55	8.81	1.22	II	α-mesotrophic

The presence of enough biogenic elements could be one of the factors affecting plankton organism resistivity to toxic load. Barinova S.S. [46] showed that nitrate nitrogen is depleted by photoautotrophes in all cases when any impact—for instance, toxic pollution—does not prevent photosynthesis. In most water bodies studied, the NO_3 concentration exceeded the background indices (Table 1), which indicates that the degree of photosynthesis activity suppression was affected by the toxic impact of HMs. At the same time, the critical concentrations of toxicants hindered the eutrophication processes, supporting the phytoplankton indices' indication that the trophic status of the lakes was low [8].

3.3. Zoobenthos

The HM concentration in the water and bottom sediments was the limiting factor for benthos invertebrates. For instance, in the toxic environment of the small lakes of the Pechenga area, the species diversity and amount and biomass of zoobenthos sharply decreased. Of all the systematic groups, only nematods, chironomids, hemiptera, caddisflies, and alderflies (Sialidae) were found in water in which Ni and Cu concentrations were high [47]. The typical trends were also found in small lakes near the Monchegorsk KGMK site. The macrozoobenthos sampled in the five water bodies was characterized by depleted taxonomic composition and extremely low quantity indices. No bottom organisms were found in Lake Pyslyschimjavr, located in the vicinity of the Monchegorsk KGMK site. The basis of zoobenthos of the remaining water bodies and streams located in this area was formed by chironomids Psectrocladius, Procladius, Cricotopus, and Orthocladius, usually found in water bodies polluted with HMs.

Larvas Psectrocladius dominated the benthos composition of Lake Sopchjavr (95% of the total zoobenthos amount and biomass), and Polypedilum (Pentapedilum) and Procladius dominated in Lake Travyanoe (97%). The amount of bottom invertebrates in the water bodies did not exceed 40 ind./m^2. The biomass was equal to 0.2 g/m^2. Single chironomids Procladius (Holotanypus) choreus gr, widely found in freshwater bodies of the subarctic zone, were found in the bottom sediments of the deep zone of Lake Nyudjavr.

The benthos fauna diversity was much greater and developed throughout the stony littoral zone of Lake Nyudjavr. Found there were chironomids Psectrocladius, Glyptotendipes, Procladius (Holotanypus) choreus gr., Cricotopus, and Orthocladius. Larvas Psectrocladius dominated in the composition of the communities (66% of the total amount and 54% of the total zoobenthos biomass), and the representatives of Cricotopus sub-dominated (15% and 12%, respectively). Also found there were water bugs: boat bugs (*Sigara* sp.) and water striders (*Gerris* sp.). The average amount of the littoral zoobenthos in Lake Nyudjavr was equal to 812 ind./m^2. That of the biomass was 1.1 g/m^2. The bottom biocenosis in Moncha Bay, Lake Imandra, degraded greatly. In the study periods, no benthos invertebrates were found in the littoral zone of the Nyuduai River's mouth. In the zoobenthos communities in deep zones, we only found chironomids Chironomus—typical of Moncha Bay.

In the profundal zone of Lake Kumuzhie, the basis of zoobenthos was formed by chironomids Procladius (Holotanypus) choreus gr., Chironomus sp., Polypedilum (Pentapedilum) sp., (>80% of the total macrozoobenthos amount and biomass), and amphipoda *Gammarus lacustris* Sars, 1863 (18%). In the littoral zone, the dominating complex was complemented with caddis *Polycentropus flavomaculatus* Pictet, 1834, *Molanna* sp., and the Diptera larvae (Rhagionidae and Dolihopodidae). In the littoral zone, the quantity indices were low: The zoobenthos amount accounted for 90 ind./m^2, and the biomass accounted for 1.8 g/m^2; in the profundal zone, these accounted for 154 ind./m^2 and 1.2 g/m^2, respectively. The macrozoobenthos composition of Lake Kumuzhie was relatively similar to that of the water bodies located in unpolluted areas in the north-taiga zone of the Murmansk region.

Most distinguished zoobenthos systematic groups were rather resistant to HM water pollution and were widely found in both "background" and polluted water bodies and streams in the Murmansk region, excluding amphipod *G. lacustris*, which was found only under very low Ni (7 µg/L) and Cu (<5 µg/L) concentrations in water [47]. This situation was highly likely to occur due to running water in the lake and due to the presence of several permanent wells located in the water basin and on the banks of the water body, whose water, which runs to the lake, helps dilute polluted water and reduce toxic load. The trophic status of the five water bodies was assessed as oligotrophic, which, to a significant extent, was due to the impact exerted on the water bodies by aero-technogenic discharges produced by the smelter. When there was a general slowing down of the bioproduction processes in the toxic environment, these discharges induced water oligotrophication.

3.4. Ichthyofauna

Fish fauna were found only in Lake Nyudjavr (European vendace *Coregonus albula* L., 1758) and in Lake Kumuzhie (trout *Salmo trutta* L., 1758; common minnow *Phoxinus phoxinis* L., 1758; and burbot *Lota lota* L., 1758). The trout found in Lake Kumuzhie was the most valuable representative of the fish community of the five water bodies. The amount of fish caught and the size and weight indices were extremely low. With a mass of 93–207 g (160 g on average) and a length of 19.7–26.7 cm (23.8 cm on average), the fish ages varied from 3+ to 5+ (Table 3).

Table 3. The main biological parameters of fish in the lakes studied.

Weight, g	Length AC, cm	♂:♀	Age
	Kumuzhye Trout		
160 ± 45 93–207	23.8 ± 2.6 19.7–26.7	1:5	3+–5+
	Minnow		
4.1 ± 2.8 1.4–6.9	6.8 ± 2.1 5.3–8.3	- -	- -
	Burbot		
226	37.5	1:0	5+
	Nudyavr		
	Vendace		
4 ± 1.7 1.8–5.9	7.9 ± 1.4 6–9.2	1:6	0+–1+

The trout found in Lake Kumuzhie were likely to represent the local population spread in this lake and in an adventive lake located upstream. It is necessary to point out that in several water bodies located in areas of industrial pollution [42,48], no pathological transformations of inner and outer organs—otherwise typical in the fish in Lake Kumuzhie—were found.

Only isolated vendace were found in Lake Nyudjavr, which could be indicative of unfavourable conditions for their inhabitance. The fish ranged from 1.8 to 5.9 g (4 g on average) in mass and from 6 to 9.2 cm (7.9 cm on average) in length (Table 3). Comparative analysis showed that the growth rate of vendace in Lake Nyudjavr was lower compared to the similar index of fish from the central part of Lake Imandra. The size-and-weight indices of vendace compared to those from various areas of Lake Imandra were also lower (Figure 3).

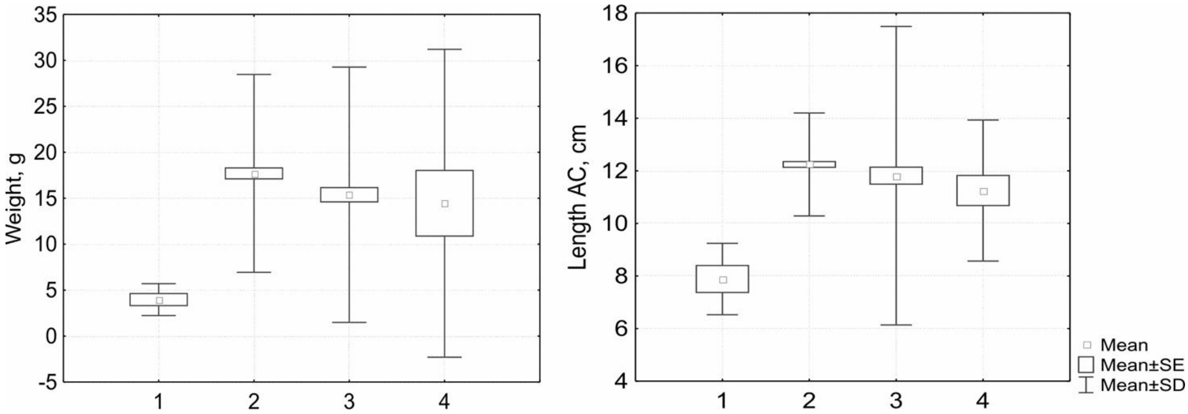

Figure 3. Comparative size-and-weight parameters of vendace in Lake Nyudjavr and different parts of Lake Imandra (1: Nyudjavr; 2: Bolshaya Imandra; 3: Jokostrovskaya Imandra; 4: Babinskaya Imandra).

The absence of other kinds of fish in Lake Nyudjavr was found to be due to intensive water body transformation and the long-term impact caused by MP KGMK.

The levels of HM accumulation in fish organs and tissues can serve as an index of the anthropogenic load placed in the five water bodies. We carried out a comparative analysis to determine the HM concentration in the organs of trout found in Lake Kumuzhie (Table 4).

Table 4. The concentration of heavy metals and Al in trout from Lake Kumuzhie in µg/g of dry weight.

	Cu	**Ni**	**Zn**	**Mn**	**Al**	**Pb**	**Hg**
muscle	1.16 ± 0.19 0.88–1.39	0.42 ± 0.25 0.07–0.77	17.43 ± 2.46 15.40–21.19	0.59 ± 0.38 0.24–1.28	1.48 ± 0.30 1.22–2.04	0.17 ± 0.05 0.12–0.25	0.15 ± 0.03 0.11–0.21
liver	509.44 ± 198.06 326.54–824.34	3.69 ± 1.18 2.24–5.05	128.91 ± 31.39 95.71–184.21	7.20 ± 1.86 4.99–10.12	4.36 ± 1.64 2.92–7.08	0.50 ± 0.41 0.12–1.19	0.21 ± 0.07 0.15–0.35
kidneys	9.25 ± 1.55 7.26–11.37	10.53 ± 3.29 7.37–14.19	165.74 ± 42.02 117.91–225.23	4.79 ± 1.04 3.82–6.75	8.79 ± 3.23 6.34–15.08	0.51 ± 0.24 0.28–0.95	0.31 ± 0.07 0.22–0.42
gills	19.44 ± 16.27 4.62–46.71	6.81 ± 0.77 5.80–8.03	304.56 ± 93.52 207.14–422.44	16.42 ± 3.66 12.56–22.34	7.03 ± 2.89 4.73–12.18	- -	0.10 ± 0.03 0.06–0.14
sceleton	1.07 ± 0.31 0.62–1.46	1.05 ± 0.52 0.47–1.69	168.98 ± 52.65 110.11–256.05	21.26 ± 6.48 12.98–28.56	3.64 ± 0.92 2.53–4.70	- -	0.06 ± 0.001 0.05–0.07

(above—average ± SD; below—concentration range).

It was found that the HM and Al accumulated in muscular tissue to a lesser extent in comparison to other analysed organs. The highest concentrations of copper were found in the liver; those of nickel, cadmium, lead, and mercury in the kidneys; and those of zinc and manganese in the gills and bones (Table 3). The absolute values of copper accumulation, which was a priority pollutant, were high (824.3 µg/g of dry weight). Thus, although Lake Kumuzhie the water body and its catchment area are located rather far from MS KGMK and are protected by the Monchegorskoye tundra massif from the smoke emissions produced by MS KGMK (~3 km), the water body ecosystem was intensively polluted. The comparative analysis of HMs found in the organs and tissues of trout caught in Lake Kumuzhie and different zones of Lake Imandra showed that the concentrations of Cu and Ni, as priority pollutants, were higher in fish near the smelter. The trout from Lake Kumuzhie had the highest copper concentration in their liver (Figure 4). The nickel and lead in their kidneys had similar regularity (Figure 4).

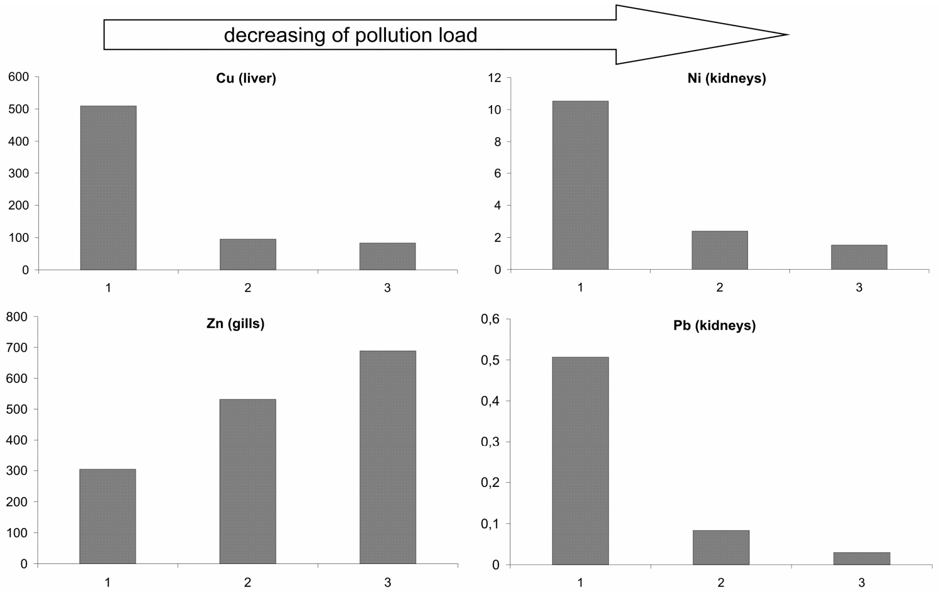

Figure 4. The HM concentration in trout tissues (μg/g of dry weight) (1: Kumuzhie; 2: Jokostrovskaya Imandra; 3: Babinskaya Imandra).

It was found that the concentrations of nickel and lead (in the kidneys) and copper (in the liver) exceeded those in fish of this species in Lake Imandra severalfold. At the same time, zinc accumulation in the fish organisms had an opposite tendency (Figure 4). The highest zinc concentrations were found in fish caught in the southern part of Lake Imandra and the central part of Lake Imandra. We suggested that the zinc was an element resulting from global pollution and its load on the water bodies was not produced by MS KGMK.

4. Conclusions

The ecosystems of the five water bodies developed in conditions with levels of priority pollutants that exceeded those of the conditional background severalfold (HMs and sulphates). Lake Nyudjavr was also exposed to anthropogenic eutrophication. At present, the hydro-chemical conditions are transformed most in Lake Nyudjavr and least in Lake Kumuzhie. The phytoplankton is characterized by depleted species composition and number indices. The taxonomic structure of the phytoplankton differs sharply from that typical of the arctic lakes, with the proportion of the Cyanobacteria and dinoflagellates in the community composition being high. Small lakes located in the vicinity of the sources of pollution differed in their extremely depleted taxonomic composition (less than 10 taxa below the rank of genera). Therefore, in some cases, the abundance could be significant: as a result of the mass development of *Pseudanabaena limnetica* in Lake Travyanoe, the amount of phytoplankton was as high as 60 thousand ind./L. We found that the size of the lake, combined with intensive water exchange and the presence of excessive biogenic elements (phosphorus and nitrogen compounds), increased algae resistance to toxic pollution. Due to low species-saprobiont numbers, the use of the S-index, traditionally used to qualify water, was limited for the lakes being studied. The S-index used to qualify water affected by smelters should take the toxic load into account, which significantly understates the calculated data. The S-index may function as an indirect indicator of the toxic effect on algal cenosis. Nutrient excess seems to be one of the factors affecting phytoplankton resistivity to toxic load. In this case, the extreme toxicant concentrations slow down the process of eutrophication, which demonstrates low trophic status in the lakes.

The macrozoobenthos communities found in the five water bodies were developed under conditions of toxification, resulting in depleted species composition and depleted biomass in the bottom fauna.

The state of the fish found in Lake Nyudjavr was assessed and showed that, despite the significant transformation of the lake ecosystem, European vendace was found. This could be due to their penetration to Lake Nyudjavr from Lake Imandra via the Nyuduai River. The openness of Lake Nyudjavr and its basin system, its connection with Lake Imandra—the greatest water body in the region—and the sufficient amount of plankton organisms make it possible to reduce high anthropogenic load and promote European vendace penetration into Lake Nyudjavr. Being sufficiently mobile, large animals, fish are able, on the one hand, to avoid highly toxic habitats, and, on the other hand, adapt greatly to them.

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References

1. Mousavi, S.K.; Primicerio, P.; Amundsen, P.A. Diversity and structure of Chironomidae (Diptera) communities along a gradient of heavy metal contamination in a subarctic watercourse. *Sci. Total Environ.* **2003**, *307*, 93–110.
2. Dorovskih, G.N.; Mazur, B.B. Metal content in the minnow *Phoxinus phoxinus* (Linnaeus, 1758) (Cypriniformes, Cyprinidae) from the basins of the Pechora and Vychegda rivers. *Bull. Syktyvkar Univ. Biol. Geol. Chem. Ecol.* **2016**, *6*, 36–70.
3. Kolesnik, N.L. Distribution of heavy metals among components of freshwater ecosystems (review). *Ribogospod. Sci. Ukr.* **2014**, *3*, 35–54. [CrossRef]
4. Popov, P.A.; Androsova, N.V. The heavy metal content in the fish muscle from the waters of the Ob River basin. *Bull. Tomsk State Univ. Biol.* **2014**, *4*, 108–122. [CrossRef] [PubMed]
5. Imanpour, N.J.; Mohammadi, M.; Heydari, S. Heavy metals Cu, Zn, Cd and Pb in tissue, liver of *Esox lucius* and sediment from the Anzali international Lagoon-Iran. *Casp. J. Environ. Sci.* **2011**, *9*, 1–8.
6. Łuczyńskaa, J.; Paszczyka, B.; Łuczyńskib, M.J. Fish as a bioindicator of heavy metal pollution in aquatic ecosystem of Pluszne Lake, Poland, and risk assessment for consumers' health. *Ecotoxicol. Environ. Saf.* **2018**, *153*, 60–67. [CrossRef]
7. Dauvalter, V.A.; Kashulin, N.A. Ecological and economic assessment of the need to extract sediments of the Nyudjavr Lake, Monchegorsk district of the Murmansk region. *Vestn. MSTU* **2011**, *4*, 884–891.
8. Denisov, D.B.; Valkova, S.A.; Terentjev, P.M.; Cherepanov, A.A.; Razumovskaya, A.V. Ecological state of small lakes in the impact zone of the Monchegorsk site of JSC "Kolskaya GMK". *Proc. Karel. Sci. Cent. RAS* **2018**, *9*, 65–76. [CrossRef]
9. Moiseenko, T.I.; Dauvalter, V.A.; Lukin, A.A.; Kudryavtzeva, L.P.; Ilyashuk, B.P.; Ilyashuk, L.I.; Sandimirov, S.S.; Kagan, L.Y.; Vandysh, O.I.; Sharova, Y.N.; et al. *Anthropogenic Modifications of the Imandra Lake Ecosystem*; Science: Moscow, Russia, 2002; pp. 1–403.
10. Valkova, S.A.; Kashulin, N.A.; Dauvalter, V.A.; Sandimirov, S.S. The structure and dynamics of zoobenthos of Lake Imandra zoobenthos community in the affected area of the copper-nickel plant. *Proc. Kola Sci. Cent. RAS* **2012**, *3*, 22–39.
11. Moiseenko, T.I. Anthropogenic processes in continental waters of Arctic regions and criteria for their assessment. *Water Res.* **2018**, *45*, 578–588. [CrossRef]
12. Moiseenko, T.I. Bioavailability and ecotoxicity of metals in aquatic systems: Critical levels of pollution. *Geochemistry* **2019**, *64*, 675–688. [CrossRef]

13. *Guidelines for Methods of Chemical Analysis of Marine Waters*; Hydrometeoizdat: Leningrad, Russia, 1977; pp. 1–208.
14. *Standard Method for Examination of Water and Wastewater*; American Water Works Association: Denver, CO, USA, 1975; pp. 1–119.
15. NIVA. *Intercomparison 1630: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn. ICP*; Waters report 129/2016; Norwegian Institute for Water Research: Oslo, Norway, 2016; pp. 1–72.
16. Moiseenko, T.I.; Yakovlev, V.A. *Anthropogenic Transformation of Aquatic Ecosystems of the Kola North*; Science: Leningrad, Russia, 1990; pp. 1–221.
17. Denisov, D.B. The diatom-infer small subarctic waterbody ecosystem development reconstruction during the last 900 years (Akademicheskoe Lake, Khibiny, Kola Peninsula). *Proc. Kola Sci. Cent. RAS* **2012**, *3*, 127–148.
18. Valkova, S.A.; Denisov, D.B.; Terentjev, P.M.; Vandysh, O.A.; Kashulin, N.A. Hydrobiological characteristics of some small lakes in the northern taiga zone (Kola Peninsula). *Proc. Karel. Res. Cent. RAS* **2015**, *4*, 78–92. [CrossRef]
19. Kashulin, N.A.; Sandimirov, S.S.; Dauvalter, V.A.; Kudryavtseva, L.P.; Terentyev, P.M.; Denisov, D.B.; Vandysh, O.I.; Korolova, I.M.; Valkova, S.A.; Kashulina, T.G. *Annotated Lakes Ecological Catalog of the Murmansk region: The Central and Southwestern Parts (the Basins of the Barents and White Seas and the Gulf of Bothnia of the Baltic Sea)*; Kola Scientific Centre: Apatity, Russia, 2013; pp. 1–253.
20. Rosstandart. *Russian State Standard 17.1.3.07-82*; The Rules for Water Quality Control of Lakes and Streams; Federal Agency on Technical Regulating and Metrology: Moscow, Russia, 1982.
21. Abakumov, V.A. *Guidance on Methods of Hydrobiological Analysis of Surface Water and Sediments*; Hydrometeoizdat: Leningrad, Russia, 1983; pp. 1–240.
22. Abakumov, V.A. *Guidance on Hydrobiological Monitoring of Freshwater Ecosystems*; Hydrometeoizdat: Saint Petersburg, Russia, 1992; pp. 1–320.
23. Denisov, D.B.; Kashulin, N.A. The phytoplankton communities under the Kola nuclear power plant impact (the Imandra Lake). *Proc. Kola Sci. Cent. RAS* **2013**, *3*, 68–94.
24. Guseva, K.A. The phytoplankton accounting methodology. *Proc. Inst. Biol. Reserv.* **1959**, *2*, 44–51.
25. Kuzmin, G.V. *Tables for the Algae Biomass Calculating*; FESC AS USSR: Magadan, Russia, 1984; pp. 1–47.
26. Tikkanen, T. *Kasviplanctonopas. Suomen Luonnonsuojelun*; Tuki Oy: Helsinki, Finland, 1986; pp. 1–279.
27. Guiry, M.D.; Guiry, G.M. *AlgaeBase*; National University of Ireland: Galway, Ireland, 2019; Available online: http://www.algaebase.org (accessed on 20 October 2019).
28. Czekanowski, J. Zur differential Diagnose der Neandertalgruppe. *Korrespbl. Dtsch. Ges. Anthropol.* **1909**, *40*, 44–47.
29. Sörensen, T. A method of establishing groups of equal amplitude in plant sociology based on similarity of species content. *K. Dan. Vidensk. Selskab. Biol. Krifter* **1948**, *4*, 1–34.
30. Novakovsky, A.B. *Abilities and Principles of the "Graphs" Software Module*; Komi Scientific Centre: Syktyvkar, Russia, 2004; pp. 1–27.
31. Shannon, C.E.; Weaver, W. *The Mathematical Theory of Communication*; University of Illinois Press: Urbana, IL, USA, 1949; pp. 1–117.
32. Simpson, E.H. Measurement of species diversity. *Nature* **1949**, *163*, 688. [CrossRef]
33. Pantle, R.; Buck, H. Die biologische Uberwachung der Gewasser und die Darstellung der Ergebnisse. *Gas Wasserbach* **1955**, *96*, 604.
34. Sladechek, V. General Biological Scheme of Water Quality. In *Sanitary and Technical Hydrobiology*; Nauka: Moscow, Russia, 1967; pp. 26–31.
35. Barinova, S.S.; Medvedeva, L.A.; Anisimova, O.V. *Biodiversity of Algae-Environmental Indicators*; Pilies Studio: Tel Aviv, Israel, 2006; pp. 1–498.
36. Mineeva, N.M. *Plant Pigments in the Water of the Volga Reservoirs*; Nauka: Moscow, Russia, 2004; pp. 1–156.
37. UNESCO Scientific Committee on Oceanic Research. *Determination of Photosynthetic Pigments in Sea Water: Monography*; Rep. of SCOP-UNESCO Working Group 17; UNESCO: Paris, France, 1966; pp. 9–18.
38. Alekseev, V.R.; Tsalolihin, S.Y. *The key to Zooplankton and Zoobenthos of the Fresh Waters of European Russia. T.2. Zoobenthos*; KMK Scientific Press Ltd.: Saint-Petersburg, Russia, 2016; pp. 1–457.
39. *The Key to Freshwater Invertebrates in Russia and Adjacent Territories. T.4. Higher Insects. Diptera*; Science: Saint-Petersburg, Russia, 1999; pp. 1–1000.

40. Arshanitsa, N.M.; Lesnikov, L.A. Pathological and Morphological Analysis of the Fish in Field and Experimental Toxicological Studies. In *Book Methods of Ichthyotoxicological Research*; Promrybvod: Saint-Petersburg, Russia, 1987; pp. 7–9.
41. Galkin, G.G. *News of the All-Union Research Institute of Lake and River Fisheries*; T. XLVI; GOSNIORH: Leningrad, Russia, 1956; pp. 1–65.
42. Kashulin, N.A.; Lukin, A.A.; Amundsen, P.A. *Subarctic Freshwater Fish as Bio-Indicators of Industrial Pollution*; Kola Scientific Centre of RAS: Apatity, Russia, 1999; pp. 1–142.
43. Mina, M.V. *Tasks and Methods for the Growth Studying Under Natural Conditions. Modern Problems of Ichthyology*; Nauka: Moscow, Russia, 1981; pp. 177–195.
44. Pravdin, I.F. *Guide to the Study of Fish*; Food Industry: Moscow, Russia, 1966; pp. 1–375.
45. Denisov, D.B.; Kosova, A.L. Diatoms (*Bacillariophyta*) diversity of the Imandra Lake (Kola Peninsula). *Proc. Fersman's Sci. Sess. Geol. Inst. Kola Sci. Cent. RAS* **2017**, *14*, 448–450.
46. Barinova, S.S. The problem of integral toxic effects assessment on photosynthetic organisms in aquatic ecosystems. *Aquat. Bioresour. Habitat* **2018**, *1*, 39–43.
47. Yakovlev, V.A. *Freshwater Zoobenthos of Northern Fennoscandia (Diversity, Structure and Anthropogenic Dynamics)*; Kola Scientific Centre of RAS: Apatity, Russia, 2005; pp. 1–145.
48. Terentjev, P.M.; Kashulin, N.A. The transformation of fish communities of waterbodies of the Murmansk region. *Proc. Kola Sci. Cent. RAS* **2012**, *2*, 61–100.