

Article



# Manganese Pollution in Mining-Influenced Rivers and Lakes: Current State and Forecast under Climate Change in the Russian Arctic

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Abstract: Mining regions in different parts of the world have been associated with the significant pollution of water, sediments, and soils by manganese and other chemical elements. This study assessed the degree of geochemical transformation caused by open-pit extraction and processing of mineral resources in the Kovdorsky District of Murmansk Oblast, 20 km from the Russia-Finland border. A second objective was to predict further changes co-driven by industrial pressure and high climatic instability in the polar region. The field study involved sampling water and sediments from virgin background streams and from the tailings storage facility, settling ponds, rivers, and lakes affected by ore mining and disintegration. Laboratory analyses included the study of elemental composition, redox potential, alkalinity and acidity, organic matter content, and other geochemical characteristics for a better understanding of pollutant migration patterns. We revealed elevated levels of potentially toxic elements in surface waters and bottom sediments which pose a risk to the human health via the household and drinking water supply. Pollution with manganese (Mn) was found to be the major environmental issue. Its natural presence in the river water was overridden a hundredfold by anthropogenic enrichment. This is problematic as Mn is easily bioaccumulated, which can lead to unwanted ecotoxicological effects, and—in the case of prolonged exposure to high doses of Mn and its compounds—to detrimental human health impacts. We believe that the changing climate may raise the water flow and thus expand the area of the hydrochemical anomaly. On the other hand, the activation of self-purification and dilution processes could lead to decreasing environmental Mn concentrations.

Keywords: ore mining; water quality; bottom sediments; urban water

# 1. Introduction

Water resources play a major role in social and economic development, and clean water is a fundamental environmental and societal necessity specified among the UN Sustainable Development Goals [1,2]. The chemical composition of water is the result of complex multi-stage processes occurring both in catchment areas and in streams or reservoirs [3,4]. The lithological conditions of the catchment area, i.e., the chemical composition of rocks, the ratio of their types, and resistance to chemical weathering are the key factors that determine the natural elemental composition of water [5–8]. Climate factors (temperature, precipitation, evaporation, etc.) indirectly affect the content of trace elements through the intensity of chemical weathering, bio-production processes, decomposition of organic residues, the speed of chemical and biological processes, and dilution within a water



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). body [8–13]. Anthropogenic activity raises the content of elements in natural waters due to both global dispersion and input from the catchment area and wastewater [14–18]. The progressive technogenic impact has led to increasing pollution of water resources in many parts of the world. In regions with mining or heavy industries, metallic pollutants play a major role, threatening both aquatic ecosystems and municipal water supply systems in industrial regions [19–24].

In recent years, data from monitoring studies have been indicating an increase in the frequency of environmental pollution incidents related to mining and raw material processing in almost all regions of Russia [25–29], which makes the tasks of hydrological research aimed at elucidating the mechanisms of formation, assessment, and forecasting of these phenomena relevant both from a research and practical point of view. This study addresses the situation in the Russian Arctic, where the beginning of the 21st century was marked by a rapid decline in the resource potential of the surface waters under the changing regional environment and global climate [30]. The combined effects of reduced flows and a growing number of pollution incidents led to an unprecedented degradation of the aquatic environment, including radical changes in the structural and functional characteristics of aquatic organisms and communities, the transformation of the trophic status of many lakes, and the decreasing stability of freshwater ecosystems [31]. Today, some of the largest Russian mining and processing plants operate on the Kola Peninsula, near or beyond the Polar Circle: the Apatit phosphorus plant, the Severonikel copper and nickel plant, the Kandalaksha aluminum plant, the Olenegorsk iron plant, the Pechenganikel nickel plant (under closure), the Lovozersky rare-earth element plant, and the Kovdorsky iron plant. Despite a relatively abundant water availability, most of the regional water bodies suffer from technogenic impacts, which besides negative environmental effects in some regions leads to a shortage of high-quality drinking water. According to the Russian classification system for surface water quality, the Kola Peninsula has the largest number of aquatic ecosystems in which the water quality in the long-term period is officially characterized by class 4 ("dirty") and class 5 ("extremely dirty"). During more than 30 years of observations, nickel, copper, manganese, iron, molybdenum compounds, sulfate ions, ammonium, nitrite nitrogen, and cresyl dithiophosphate remain the typical pollutants of the water bodies of the Kola Peninsula, amidst the high levels of COD and BOD<sub>5</sub> [32].

Huge masses of mined rock, the lack of their sustainable and integrated use, a low recovery rate of target substances, outdated processing technologies that use large volumes of water, pyrometallurgical processes for extracting metals, tremendous volumes of watered fine waste, their placement in the waters or the direct vicinity of lakes or riverbeds, wastewater discharge into reservoirs, and atmospheric-deposition pollution at the catchment-scale make mining and processing enterprises the main sources of environmental pollution of the Kola Peninsula. The inefficient management of water resources with a lacking strategy for their use and effective control completes this picture [33]. Deficits include the absence of environmental registers that consider the quantitative and qualitative characteristics of water resources and their use, but also a modern regulatory framework and control system that considers the natural features of the region. The consequence is a sharp deterioration in the quality of surface waters and the continued degradation of their biological resources.

In recent years, repeated cases of high and extremely high pollution levels in water and bottom sediments have been recorded during routine observations of the hydrochemical network of the Russian Hydrometeorological Service. At the same time, the continued accumulation of contaminants in sensitive polar and subpolar hydroecosystems has shifted them close to tipping points beyond which recovery is unlikely. It is worth noting that despite the significant contribution of the rapidly developing mining industry of the Kola Peninsula, due to the peculiarities of the distribution of air masses in the Northern Hemisphere, most of the pollutants released into the atmosphere in the industrialized regions are transferred to the Arctic, where they are deposited and accumulated in the natural environment, in particular in water bodies [31,34,35].

Consequently, the combined impact of local sources, the migration of pollutants via several media, as well as climate change, have led to the disruption of biological, geochemical, and physical processes in the freshwater ecosystems of the North. Although the general direction of climate change is ambiguous, and in some areas may have a multidirectional character, there is no doubt that the climate system is unbalanced, contributing to the weakening of aquatic ecosystems [36].

The level of technogenic transformation of the lake-river systems of the Kola Peninsula was studied in the framework of the conducted research. To date, water bodies in the catchment areas of the largest mining enterprises Apatit JSC and Kovdorsky GOK JSC are affected most intensively. Pollution of the aquatic environment via organized wastewater discharge, the infiltration of atmospheric precipitation at waste storage sites, leaks from wastewater storage facilities, as well as aeolian transfer, result in hydrogeochemical plumes and pollution fluxes with abnormally high concentrations of pollutants.

Our research aimed at (i) assessing the hydrochemical situation in the impact zone of the large ore mining and processing enterprise in the Russian Arctic, (ii) determining the major pollutants in the watercourse that lead to degradation changes and the formation of hydrochemical anomalies, (iii) revealing the danger of secondary pollution from bottom sediments, and (iv) forecasting the fate of geochemical anomalies under climate change.

## 2. Materials and Methods

## 2.1. Study Area

In the field seasons of 2016–2018, we carried out environmental research to assess the transformation of surface waters and bottom sediments of the Kovdorsky district (Figure 1). This was based on two pre-conditions: (1) The apparently stressed geoecological situation, and (2) the lack of recent systematic studies in the operation area of Kovdorsky Mining and Processing Plant (hereinafter, Kovdorsky GOK) [37].



**Figure 1.** Study area: (a) the Kovdor deposit in Murmansk Oblast (based on the free blank map, d-maps.com); (b) mineral processing waste after the production of iron ore, apatite, and baddeleyite concentrates, southwards of the open pit mine and Lake Kovdor (based on a Google Earth image).

The environmental impact of a mining enterprise is assessed mainly by standard indicators of atmospheric, water and soil pollution, the volume of extracted rock mass and stored production waste (overburden, tailings, etc.), and landcover changes due to mining and their secondary effects (e.g., biodiversity losses, soil erosion). Water pollution

is not only a very common feature of mining regions, but often affects large regions due to pollutant transport. The composition of surface waters may be transformed directly via discharging insufficiently treated wastewater into natural water bodies, but also indirectly via leaching from contaminated sites such as mine tailings. In the study area, a common phenomenon is an increase in mineralization, and previously very soft water turning moderately hard. Furthermore, acidic water has become alkaline [37,38]. The observed changes underline the need for regular study, analysis, assessment, and prediction of environmental transformation.

Kovdorsky GOK started developing the deposit of magnetite-apatite-baddeleyite ores in 1955 [39]. For more than 60 years, operations at the Kovdorsky GOK have been accompanied by large volumes of discharged wastewater and released atmospheric pollutants. Transformed natural geochemical cycles of elements led to the formation of hydrochemical anomalies in the immediate vicinity of the industrialized area [40]. Moreover, such large man-made facilities as quarries, tailings dumps, waste rock dumps, and processing plants disturbed the hydrological regime. The study of levels and redistribution patterns of elements in the wastewater flux is a prerequisite for a reasonable prediction of the quality of affected natural waters [41–43]. Due to their geographical location and economic significance, the study of surface waters is an urgent and policy-relevant research task.

The studied Upper Kovdora, Lower Kovdora, and Mozhel rivers (Table 1) belong to the drainage basin of the Niva (Njavejohka) River that flows into the Kandalaksha Gulf of the White Sea. The Upper Kovdora River passes through Lake Kovdor. This lake was drained to free up space for the mine water discharge. The wastewater intake transforms the lake and raises mineralization and pH values caused by increasing concentrations of alkaline earth metals; however, pH tends to decrease as discharged sulfur and nitrogen oxides acidify the catchment area in other reservoirs of the study area [44]. Acidification processes can lead to the leaching of potentially toxic elements from the catchment area [45].

Parameters	Upper Kovdora	Lower Kovdora	Mozhel
Length, km	13.0	21.0	11.7
Catchment area, km <sup>2</sup>	84.7	110.0	47.2
Depth, m	0.5-1.0	0.5-1.0	0.2-1.0
Width, m	5–25	20–50	2–8
Average stream velocity, m/s	0.50	0.05	0.91
Average multi-year flow, m <sup>3</sup> /s	0.49	0.90	0.18

Table 1. Hydrological characteristics of the Upper Kovdora, Lower Kovdora, and Mozhel rivers.

In the study area the climate is continental. Winters are cold and long, the average air temperature is below 0 °C from November until May, and the average atmospheric precipitation is ca. 30–50 mm per month. Summers are short and cool. July is the hottest month of the year, with an average air temperature of about +15 °C. The year's maximum precipitation of 70–80 mm per month falls during the 3 summer months. The total average annual rainfall is 609 mm. The predominance of lotic systems is a feature of the Kovdorsky District. This circumstance determines the spatiotemporal patterns of the distribution of pollutants. For lotic systems, the rapid and significant dilution of wastewater is characteristic both at the discharge point and throughout the flow due to tributaries. Other typical pollution patterns include the dependence of the distribution of pollutants on hydrological conditions and catchment processes, a pronounced longitudinal gradient of concentrations, substance accumulation in lake or stream pool areas, and a high probability of the mobilization of buried pollutants from bottom sediments [46].

## 2.2. Sampling and Analysis of the Background and Polluted Water

For the sampling campaign, the study area was divided into 3 zones: (i) background areas located outside the direct and indirect impact of the industrial site; (ii) water bodies receiving wastewater of the plant, e.g., Lake Kovdor, the Mozhel River, the Kovdora River (upper course); and (iii) water bodies indirectly influenced by the mining enterprise, e.g., the Kovdora River (lower course, the Ena River). To choose the sampling points, we considered hydrological conditions, natural factors affecting water quality, specifics of man-made impact, and the typical self-purification capacity of aquatic systems. Quarry water and wastewater from the tailings were sampled as the major suppliers of pollutants to the studied water bodies. As of now, wastewater enters the Upper Kovdora River—Lake Kovdor system through 3 pathways.

- Discharge No. 1 annually releases 3.5 million m<sup>3</sup> of the quarry waters from the western water-reducing wells into the Upper Kovdora River;
- Discharge No. 2 annually releases 4.0 million m<sup>3</sup> of the quarry waters from the northern water-reducing wells into the drainage channel of the Upper Kovdora River;
- Discharge No. 3 annually releases 25.1 million m<sup>3</sup> of the quarry waters, treated industrial water from the power plant and storm sewer of the industrial site, from the pit water sump into Lake Kovdor.

The tailings storage facility (TSF) occupies the valley of the Mozhel River and disturbs its natural flow. The TSF construction dates to 1961, when Dam No. 1 blocked the middle part of the river (3.1 km from the mouth), and the filling with enrichment waste began. Discharge No. 6 releases pond water after gravitational desilting into the Mozhel River and subsequently into the Lower Kovdora River. The total volume of annually discharged wastewater from the mining and processing plant accounts for 21.8 million m<sup>3</sup>.

A comprehensive survey at more than 30 points allowed the accurate assessment of the water pollution patterns. The studied rivers, streams, and ponds are listed in the Section 3.1 *Pollution of Aquatic Ecosystems*, and the basemap is shown in Figure 1b. The dots indicating the locations of sampling points are not shown on the map due to the scale and relatively short distances (tens of meters) between the wastewater discharge pipes and the interconnected settling ponds on the one hand, and longer distances (hundreds of meters) to the river confluence and outlet points on the other hand. The volume of a representative sample of surface waters was 1 dm<sup>3</sup>. At each point, 2 duplicate water samples were taken for analysis. We filtered water through a 0.45  $\mu$ m pore size membrane immediately after sampling, and preserved it to prevent the redistribution of elements between the phases, reduce the bacterial activity, and avoid the loss of trace elements due to biochemical processes and sorption on the walls of the vessel. The samples were preserved for the study of metal content by adding 2–3 cm<sup>3</sup> of nitric or hydrochloric acid per 1 dm<sup>3</sup> of a sample, to bring pH to the level < 2 [47]. To assess the total content and the ratio of the phases, the filters were also prepared for transportation to the laboratory and analysis.

Further, the samples were delivered to the Environmental Modeling Laboratory of the Common Use Center, Saint Petersburg Mining University. The decomposition of the particulate phase on the filter was carried out using a mixture of inorganic acids (nitric, hydrofluoric, hydrochloric, and boric) in a microwave oven. The cation contents in dissolved (filtered samples) and particulate phases (suspended fraction on the filters) were determined using the AA-7000 atomic absorption spectrophotometer (Shimadzu, Tokyo, Japan). The possibility of flame and electrothermal atomization allows the analyzing of samples in a wide range of concentrations. Weight concentrations of  $NO_2^-$ ,  $NO_3^-$ ,  $CI^-$ ,  $SO_4^{2-}$ ,  $F^-$ ,  $PO_4^{3-}$ , and  $Br^-$  were determined in aqueous samples using the LC-20 Prominence high-performance liquid chromatograph (Shimadzu, Japan). When determining the concentrations of Mn, Zn, Ni, Co, Cd, and Cr in analyte, the samples were concentrated by evaporation. In several cases, the complex matrix of samples necessitated that the addition method was used, with the analyzed sample being supplemented with a solution containing the same analyzed ion. The detection limits for analytical methods used to

Table 2. Limits of detection and measurement errors in dissolved and particulate phases.

Element	Fe	Ca	Mg	Mn	Cu	Zn	Sr	Ni	Со	Cd	Cr
I imit of detection in dissolved phase				mg/dm <sup>3</sup>		μg/dm <sup>3</sup>					
Emili of detection in dissolved phase	0.01	2.0	0.1	0.005	0.0005	0.005	0.5	0.002	0.0025	0.0005	0.005
The relative total measurement error in dissolved phase at the confidence level of $p = 0.95$ (%)	11	13	10	15	16	10	15	19	33	17	26

To ensure quality control, the standard analysis procedure was applied [48]. To confirm the measurement results, the stability of the calibration curve was monitored by analyzing 1 of the calibration solutions as each tenth sample. In addition, during the measurements, the correctness of measurements was checked using a standard sample.

### 2.3. Sampling and Analysis of Bottom Sediments

To comprehensively assess the state of water bodies, the composition of bottom sediments was studied as well. Bottom sediments can accumulate chemical elements and compounds from the water column; therefore, they were considered as an informative indicator of water quality and, at the same time, a source of secondary pollution. Technogenic bottom sediments may be dangerous due to the potentially high content of mobile forms of elements. Transforming physicochemical conditions, the activity of organisms, and several other factors will contribute to the transfer of pollutants into the solution. According to the earlier studies, the average regional sedimentation rate ranges from 0.3 to 1 mm/year [49,50].

Bottom sediment sampling was done at the same sampling sites as surface water sampling. To identify the maximum thickness of bottom sediments, the sampling was also carried out in places where the exchange of pollutants between the water mass and bottom sediments could be characterized by extreme values: in areas of reservoirs with depths up to 10 m, with wind movement or on river rifts, and in areas of lateral tributary support.

A rod dredger was used for the sampling of unconsolidated silty and sandy-gravelly bottom sediments. Samples were put in polyethylene bottles with a wide neck, hermetically sealed lids with a volume of  $0.5 \text{ dm}^3$ , and stored at a temperature of  $4 \,^\circ\text{C}$ . In some areas exposed to the maximum anthropogenic impact, additional samples were taken by a stratimeter without rupturing the structure. The preparation and analysis of samples, analogously to the surface waters, was carried out by the authors in the laboratory of the Mining University. The first stage of preparation consisted in drying on pallets at room temperature to obtain an air-dry sample. Small inclusions (pebbles, debris, algae, etc.) were extracted manually from the sample using tweezers. The homogeneous sample was ground in a mortar. To determine the loss on ignition (LOI) as an indirect indicator of the organic matter content, the samples were calcined in a muffle furnace LVT 15/11/B180 (Nabertherm, Germany) at a temperature of 500 °C for 4 h. The obtained results of the LOI allowed the minimizing of error in determining the qualitative and quantitative composition of bottom sediments.

Since the early research by U. Förstner and L. Håkanson it is well known that representative information on the degree of pollution of water bodies is most effectively obtained by analyzing the finest particles that contain the highest concentrations of pollutants [51,52]. In this regard, at the next stage of preparatory work for the analysis, a sieve analysis was carried out mechanically on a vibrating screen. Particle size distribution was studied using the LA-950 laser analyzer (Horiba, Kyoto, Japan). To determine the total content of elements, the decomposition of sediment samples was carried out with a mixture of inorganic acids in a Multiwave 3000 microwave oven (Anton Paar, Graz, Austria). The decomposition was performed in 2 stages: (i) application of concentrated HNO<sub>3</sub>, HF, and HCl with H<sub>2</sub>O under 210 °C, 1200 Wt, and 17,500 kPa during 20 min; and (ii) application of 3% H<sub>3</sub>BO<sub>3</sub> under 170 °C, 1200 Wt, and 10,000 kPa during 5 min. The decomposition of samples for the determination of acid soluble mobile forms of elements was completed by adding nitric acid to the suspension with a molar concentration of 0.5 mol/dm<sup>3</sup> and holding at a temperature of 90 °C on the electric stove for 3 h [53]. To extract the mobile forms of the element from the stored tailings, the samples were kept in an acetate-ammonium buffer (pH = 4.8) at a sample/solution ratio = 1/10 for 24 h. The concentrations of elements in the sediment samples were determined by optical emission spectroscopy with induction-coupled plasma on the Shimadzu ICPE-9000 spectrometer. The detection limits for analytical methods used to analyze metals accounts for 0.005 mg/kg for Cd and 0.5 mg/kg for Mn, Sr, Co, Cr, Cu, Ni, and Zn. The relative total measurement error at the confidence level of *p* = 0.95 is within the limit of 30% for all the analyzed elements.

# 3. Results and Discussion

# 3.1. Pollution of Aquatic Ecosystems

The total concentration of dissolved and suspended fractions determined by the spectral analysis of surface waters (Table 3) showed that manganese and strontium pose the greatest danger to the regional aquatic ecosystems. At the same time, the presence of Mn at specific sampling points allows us to unequivocally state that the main source of its entry into water bodies is tailings wastewater, in which the Mn content is more than 100 times higher than the background values. The dilution of wastewater in the Mozhel River practically does not occur, which leads to complete geochemical transformation of the watercourse.

Table 3. Total metal content in the natural river water and the discharged wastew	ater.
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Element	Fe	Ca	Mg	Mn	Cu	Zn	Sr	Ni	Со	Cd	Cr
Measurement Units				mg/dm <sup>3</sup>						µg/dm <sup>3</sup>	
Russian surface water standard [54]											
	0.05	180.0	40.0	0.01 for Mn <sup>2+</sup>	0.001	0.01	0.4	10.0	10.0	5.0	20.0 for Cr <sup>6+</sup> , 70.0 for Cr <sup>3+</sup>
				River wate	r						
Upper Kovdora River (UKR), background	0.06	10.0	4.3	0.007	0.002	0.003	0.18	0.1	0.2	0.05	0.6
UKR, 100 m downstream from the confluence with the Bystry Current	0.04	16.0	5.5	0.010	0.002	0.001	0.40	0.6	0.8	0.22	0.8
UKR, 500 m downstream from the Discharge No. 1	0.05	30.1	12.8	0.008	0.002	0.003	0.16	0.2	0.2	0.07	0.8
UKR, 200 m downstream from the Discharge No. 2	0.06	29.0	12.2	0.010	0.002	0.002	0.70	0.5	0.5	0.15	0.6
UKR, 500 m downstream from the Discharge No. 3	0.09	33.1	16.4	0.015	0.002	0.002	1.03	0.5	1.0	0.5	0.2
Mozhel River (MR), background	0.01	15.0	6.1	0.008	0.002	0.002	0.26	0.1	0.2	0.05	0.5
MR, 250 m downstream from the Discharge No. 6	0.09	64.2	46.0	0.910	0.002	0.002	2.57	1.0	1.2	0.56	0.2
Lower Kovdora River (LKR), 200 m upstream from the mouth of MR	0.06	36.1	16.4	0.009	0.002	0.009	1.14	0.1	0.9	0.32	0.2

Element	Fe	Ca	Mg	Mn	Cu	Zn	Sr	Ni	Со	Cd	Cr
Measurement Units				mg/dm <sup>3</sup>						µg/dm <sup>3</sup>	
LKR, 500 m downstream from the mouth of MR	0.09	29.1	7.9	0.080	0.002	0.005	0.80	0.1	0.2	0.11	0.2
Ena River (ER), upstream from LKR	0.08	6.4	2.1	0.002	0.001	0.001	0.04	0.1	0.2	0.05	0.5
ER, downstream from LKR	0.09	6.9	2.4	0.021	0.002	0.001	0.07	0.1	0.5	0.05	0.4
				Wastewate	er						
Discharge No. 1	0.03	165	69	0.005	0.001	-	0.18	0.1	0.2	0.05	0.8
Discharge No. 2	0.02	27	10	0.004	0.001	-	1.00	0.5	0.5	0.21	0.7
Discharge No. 3	0.04	40	32	0.017	0.002	-	2.35	0.3	0.7	0.68	0.2
Discharge No. 6	0.09	64	49	0.930	0.002	0.010	2.62	0.4	1.0	0.98	0.2
Discharge of drainage wastewater into the first settling pond	0.06	57	24	0.070	0.002	-	1.65	0.9	1.0	0.58	0.2
Discharge of filtration wastewater into the second settling pond	0.12	69	52	1.390	0.002	0.019	2.98	0.6	1.8	1.00	0.2
Discharge of mine wastewater into the first settling pond	0.06	60	48	0.030	0.002	-	2.70	1.6	2.8	1.10	0.2

Table 3. Cont.

Sr exceedance is associated with the discharge of wastewater during the extraction and processing of magnetite-apatite-baddeleyite ores; its concentration decreases downstream. Additionally, Sr enters water bodies via fine particle deposition due to the dusting of tailings and because of infiltration of technological effluents through the tailings dam.

The high levels of Mn and Sr in the studied samples allowed focusing on these two metals as key polluting elements in the water system affected by the mining and processing plant. For that reason, the natural and wastewater flows were additionally sampled near the points where elevated concentrations had been found. Table 4 shows the content of Mn and Sr in dissolved and suspended form in these samples of aqueous media experiencing the maximum load from the operation of the tailings storage facility. The filtration of samples listed in Table 3 gave the minor mass of suspended particles that showed the concentrations of metals below the detection limit. On the contrary, the water samples listed in Table 4 had larger shares of particulate phases in which Mn and Sr concentrations were high enough to be revealed by the analysis.

Table 4. Distribution of Mn and Sr between phases in the studied waters, mg/dm<sup>3</sup>.

Analyzed Samples	Recycled Water of the TSF	Wastewater after Filtering through the Tailings Dam	Settling Pond	Discharge from the Settling Pond	Mouth of the Mozhel River, Wastewater- Receiver
		Mn			
Liquid (obtained after filtration)	0.009	1.380	1.100	0.930	0.072
Suspended fraction (filtered residue on 0.45 µm pore size membrane)	0.013	0.073	0.017	0.018	0.017
		Sr			
Liquid (obtained after filtration)	0.820	2.940	2.640	2.610	2.510
Suspended fraction (filtered residue on 0.45 µm pore size membrane)	0.020	0.027	0.006	0.008	0.002

The data presented show that Mn and Sr are mainly dissolved and migrate over considerable distances, forming technogenic hydrochemical anomalies in surface waters.

### 3.2. Pollution of Bottom Sediments

The results of the chemical analysis of sediment samples presented in Table 5 indicate that Mn and Sr predominate in the studied sediments. This is inextricably linked with the high concentrations of these elements in the wastewater discharged from the processing of complex and natural waters in the zone of the plant's impact. It is worth noting that the sedimentation of these wastewater components occurs mainly after the treatment facilities in the Mozhel River. This fact confirms the low efficiency of the implemented water protection measures.

**Table 5.** Total and mobile element concentrations in the bottom sediments of natural and artificial aquatic ecosystems affected by the processing plant; reference concentrations in soils.

Sampling Sites	Total Content (T) or Content of Mobile	Q	/o			mg/kg	g		
Sampring Sites	Fractions (M)	Mn	Sr	Cd	Со	Cr	Cu	Ni	Zn
Settling pond upstream from the	Т	0.29	0.17	3.0	40	23	200	30	90
separation dam	М	0.16	0.07	0.4	2	1	18	4	10
Settling pond downstream from the	Т	0.17	0.10	4.0	23	60	80	28	40
separation dam	М	0.12	0.04	0.3	2	1	5	2	3
Lower Kovdora River upstream from the	Т	0.07	0.04	4.0	29	75	210	130	160
confluence with the Mozhel River	М	0.03	0.01	0.2	3	2	20	4	40
Mozhel River downstream from the	Т	4.40	0.15	7.0	40	80	80	50	80
wastewater discharge	М	3.00	0.05	0.8	7	5	5	9	19
Mozhel River 250 m downstream from the	Т	3.80	0.11	5.0	25	50	50	40	50
wastewater discharge	М	2.50	0.04	0.7	4	3	3	7	11
Mozhel River upstream from the	Т	4.40	0.14	9.0	45	130	100	70	90
confluence with the Lower Kovdora River	М	0.30	0.08	0.6	< 0.5	2	5	4	10
Lower Kovdora River 100 m downstream	Т	0.35	0.07	8.0	51	230	230	210	180
from the confluence with the Mozhel River	М	0.25	0.02	0.5	5	6	6	5	17
Lower Kovdora River 250 m downstream	Т	0.25	0.03	4.0	28	90	90	100	90
from the confluence with the Mozhel River	М	0.18	0.01	0.4	4	5	5	4	16
Lower Kovdora River 1000 m downstream	Т	0.12	0.03	6.0	21	70	70	70	80
from the confluence with the Mozhel River	М	0.10	0.01	0.3	3	4	4	3	14
Russian Maximum Permissible	T (except for Co and	1 50		1.0	5	6 (Cr <sup>3+</sup> ,	66	40	110
Concentration in soils [55]	Cr)	1.50	_	1.0	(M)	M)	00	40	110
Mean concentration in urban soils worldwide [56]	Т	0.73	0.05	0.9	14	80	39	33	158
Threshold Effect Concentration [57]	Т	_	_	0.99	_	43.4	31.6	22.7	12

The potential hazard of man-made bottom sediments is due to the fact that in most samples the percentage of mobile forms accounts for up to 80% for Mn and up to 30% for the rest of metals. The concentrations of either total or mobile forms are close to the reference levels in the urban soils, reflecting a high degree of technogenic transformation. In Russia, there are currently no legal provisions for a standardized assessment of bottom sediments' pollution with metals. The often-used ecotoxicological criteria are sediment quality guidelines by MacDonald et al., 2000 [57]. The regional standard "Norms and criteria for assessing the contamination of bottom sediments in water bodies of Saint Petersburg" is applied as well, but only for marine ecosystems. As the national standard for freshwater bottom sediments is not specified in Russia, the soil standards (Maximum Permissible Concentrations) and the mean concentration in urban soils are indicated. By

comparing the data presented, the relatively raised concentration of such potentially toxic elements as Cd, Cr, Cu, and Ni should be noted. However, these metals are accumulated in the bottom layer that is the sign of water self-purification via sedimentation. When compared with the standard values, the content of Mn confirms the necessity for deeper consideration of its hydrochemical behavior, both in the water and bottom sediments of the study area.

Tables 6 and 7 characterize the distribution of metals in the columns of the bottom sediments of Lake Kovdor and the settling pond of the Kovdorsky GOK tailings, respectively. Lake Kovdor is in close proximity to the Kovdorsky GOK, and is affected by both the runoff of the plant and air pollution from industrial enterprises and motor vehicles. The Kovdorsky GOK settling pond for the deposition of suspended solids is located 6 km from the plant.

**Table 6.** Metal concentrations (mg/kg, dry weight) and weight loss on ignition (%) in the column of bottom sediments of Lake Kovdor.

Strata, cm	LOI	Cu	Ni	Zn	Со	Cd	Pb	Mn	Fe	К	Na	Sr	Ca	Mg	Cr	Al
0–1	11.13	149	173	213	92	2.59	61.7	933	43,156	6882	1780	1401	26,542	49,127	100	29,542
1–2	8.67	184	165	210	86	1.84	21.9	331	39,968	6080	1352	1533	30,649	57,359	108	31,804
2–3	9.50	178	156	190	67	2.18	18.0	273	45,028	4438	1091	1103	19,451	46,689	112	30,081
3–4	9.14	175	156	181	48	2.01	14.1	282	48,476	3724	1009	935	13,876	44,068	117	28,763
4–5	8.04	128	158	135	45	1.11	9.4	276	42,447	3220	900	866	12,343	40,852	103	25,494
5–6	14.98	68	79	99	22	0.87	15.1	181	24,212	2121	588	546	7556	19,685	86	17,025
6–7	19.04	45	52	74	17	0.75	10.5	120	16,376	1693	504	486	5888	12,666	82	13,457
7–8	20.34	38	48	64	13	0.74	8.4	95	14,504	1441	452	455	5493	10,969	81	12,273
8–9	20.36	34	38	64	11	0.50	7.7	84	11,600	1234	424	416	5143	16,448	89	10,978
9-10	20.76	27	34	55	11	0.50	7.1	83	10,340	1228	437	405	5117	14,878	83	10,923
10-11	21.14	21	31	56	10	0.42	5.0	58	8143	1115	388	292	5237	7109	81	10,967
11–12	21.76	16	21	58	6	0.40	4.4	46	6912	922	338	248	4763	4256	73	8706

**Table 7.** Metal concentrations (mg/kg, dry weight) and weight loss on ignition (%) in the column of bottom sediments of the Kovdorsky GOK settling pond, upstream from the dam.

Strata, cm	LOI	Cu	Ni	Zn	Со	Cd	Pb	Mn	Fe	К	Na	Sr	Ca	Mg	Cr	Al
0-1	8.75	252	73	146	91	2.75	18.4	3652	16,428	6600	3037	1394	119,221	106,233	28	15,486
1–2	3.20	242	70	120	91	3.40	24.3	2389	7144	7157	2877	1674	159,029	119,450	24	14,863
2–3	2.92	237	65	99	82	3.89	19.5	1465	6430	7645	3000	1526	178,874	122,052	18	13,729
3–4	1.33	259	66	103	80	3.46	24.8	1360	6722	8481	3870	1662	122,113	134,641	16	15,150
4–5	1.30	265	66	100	83	3.46	19.8	1296	6724	9056	4487	1485	112,286	128,931	16	15,953
5–6	1.20	241	58	97	71	3.47	14.9	1232	7665	8241	4242	1709	64,135	130,745	16	15,569
6–7	1.25	253	61	103	71	3.96	19.9	1231	7475	8731	4240	1686	163,456	111,812	13	15,162
7–8	0.95	332	64	94	74	3.48	19.9	1235	6561	8262	3532	1646	174,129	112,120	10	14,409
8–9	1.25	261	63	96	71	3.47	19.9	1167	8795	7990	3697	1663	174,705	113,031	13	13,965

We revealed that the chemical composition of the bottom sediments of Lake Kovdor had been transformed by both the activities of the Kovdorsky GOK and the atmospheric deposition of fine particles from other regional enterprises [58–60]. The upper layers of the bottom sediments were found to have relatively higher concentrations of almost all the metals studied, even though the regional air pollution levels have been steadily declining in recent years [61,62]. The ratio of concentrations in the surface layers to the deepest ones (which are taken as background levels) was in the range from 1.4 to 20.7 for the analyzed metals. For Cu, Ni, Zn, Fe, Sr, Ca, Mg, Cr, and Al, a slight decrease in concentrations in the surface layers was directly related to the physicochemical and biological processes in the sediments. An increase in Al shows that the quantity of fine, clay, sediment particles are increasing, which usually leads to an increase of all other metals which are bound to this fine fraction. According to the accepted sediment quality guidelines, the upper part of the core from the Lake Kovdor (Table 7) is contaminated with Ni, Zn, and Cd; the surface layer is characterized by higher Pb content.

The bottom sediment column of Lake Kovdor was stratified into the lower part (7-13 cm), with relatively low concentrations of metals and high values of LOI, and the upper part (0-5 cm), where the influence of the Kovdorsky GOK led to a significant increase in the concentrations of almost all metals.

To identify the geochemical input of the Kovdorsky GOK to the river-lake system, a core sample of bottom sediments was taken from the settling pond. The laboratory studies showed that concentrations of Mn, Cu, Cd, Sr, Ca, and Mg are higher in the sediments of the settling pond than in the surface layers of the sediments of Lake Kovdor. On the contrary, Ni, Zn, Pb, Fe, Cr, and Al were accumulated in the sediment of the settling pond in lower concentrations than in the surface sediments of Lake Kovdor. The levels of Co and K were approximately equal. Consequently, the Kovdorsky GOK is a source of Mn, Cu, Cd, Sr, Ca, and Mg; such elements as Ni, Zn, Pb, Fe, Cr, and Al are brought from other sources. It is probable that Ni, Zn, and Cr are carried by air currents from non-ferrous metallurgy enterprises.

The surface waters of the Kovdorsky district have undergone a significant technogenic transformation. Regional studies of water bodies showed that the pollution of surface waters with manganese is one of the urgent issues. The spatial distribution of Mn indicates its technogenic origin in the surface waters of the Kovdorsky district, associated with the peculiarities of the technological process at the plant.

### 3.3. Migration and Accumulation of Mn in Mining-Influenced Aquatic Ecosystems

The maximum concentrations of Mn occur in the waters discharged from the TSF. In quarry and drainage waters from dumps and other technogenic sources, its concentrations slightly exceed the background levels. Further monitoring studies were necessary to identify external and/or internal sources of Mn-containing compounds in the tailings of the processing plant and to assess the behavior of this element in the tailings, wastewater, and natural waters.

Mn is not the main component of ores processed at the plant, and thus it is not among the components to be controlled mandatorily when assessing the quality of raw materials [63]. However, almost all ores of the Kovdorsky massif contain the element as impurities (Table 8).

	Complex	Iron Ores		Low-Iron Ores					
Averaged Complex Iron Ores	Magnetite	Apatite- Forsterite- Magnetite	Forsterite- Magnetite	Apatite- Carbonate- Magnetite	Carbonate- Forsterite- Magnetite	Apatite- Forsterite	Apatite- Carbonatite		
0.37	0.45	0.32	0.47	0.35	0.4	0.2	0.12		

Table 8. MnO content (%) in the ores of the Kovdorsky baddeleyite-apatite-magnetite deposit.

To determine the mode of occurrence of Mn entering the TSF with the pulp, the particle size distribution was studied. This provided data on particles that bear the bulk of insoluble Mn. Figure 2 shows that a major part of the suspended component of the pulp is represented by particles with a diameter of  $2-1000 \mu m$ . After that, we separated the particulate fraction from the pulp by filtering through a membrane with a pore diameter of  $2 \mu m$ .

The mean Mn content in the filtrate was 0.017 mg/dm<sup>3</sup>, which corresponds to the concentration in the recycled water of the TSF, where high pH values are maintained (9.0). The results of the analysis of the filtered sediment showed that the Mn content was 0.1 wt.%. From this, it follows that in the discharged pulp almost all Mn is bound on particles with a diameter of >2.0  $\mu$ m. We believe that Mn remains insoluble in the pulp and the surface layers of the tailings due to the pH > 8.5. The total Mn content in the stored tailings is 0.1 wt.%. The analysis showed that the share of mobile forms of Mn reaches 17% with the pH decreasing to the neutral level.



Figure 2. Particle size distribution in the processing waste of the TSF.

In pulp waters and in circulating waters at pH = 9, the Mn content is 0.017 and 0.023 mg/dm<sup>3</sup>, respectively. Therefore, the major input of Mn into the TSF is in an insoluble state [64]. However, when the pH drops to 8 in the filtration waters of the TSF, the Mn content reaches 1.5 mg/dm<sup>3</sup>. The pH decrease occurs when the pulp waters are mixed with the atmospheric precipitation and filtered through the tailings sediments. At the same time, they are mixed with the natural waters of the Mozhel River and other streams flowing into the tailings pond, which has neutral to acid pH and contains a large volume of fulvic, humic, and other organic acids. As a result, the pH of the water discharged from the TSF drops down by 1.0–1.5 points. In the settling pond, the Mn concentration decreases to 1.1 mg/dm<sup>3</sup> and then to 0.93 mg/dm<sup>3</sup> at the outlet from the settling pond. As the Mozhel River runs into the Lower Kovdora River, the Mn concentration decreases to 0.78 mg/dm<sup>3</sup>; the pH value decreases too.

The redox potential (Eh) also affects the transition of Mn from the insoluble to soluble form [65]. Table 9 presents the data on the vertical distribution of Mn in stale mature tailings provided by the geological survey of Kovdorsky GOK. In the underlying horizons, where an oxygen-free environment is observed, the concentration of Mn increases.

Table 9. Vertical distribution of Mn in the aged tailings of the Kovdorsky GOK, wt.%.

Horizon	LH-1	LH-2	LH-3	LH-4	LH-5
Concentration	0.11	0.11	0.12	0.13	0.15

Ore and its processing tailings are the primary sources of Mn in surface waters. Based on the reviewed studies and our own data, the following scheme of the Mn flow in the tailings wastewater can be drawn. We assume that the difference between the redox conditions in the discharged pulp (Mn in insoluble form) and stale tailings (a significant share of the element passes into the soluble form) explains the increase in the drainage waters. In addition, the TSF was built up in the swampy valley of the Mozhel River. The tailings storage facility is essentially a reservoir filled with enrichment waste, the bed of which had not been cleared of peat and vegetation residues. It divides the Mozhel River into three parts: the practically virgin upper one, the middle one filled by processing waters and tailings, and the lower one, downstream of the TSF. The storage of multi-ton tailings over a relatively small area contributes to land subsidence, and enhances the process of waterlogging of the surrounding landscapes. Numerous small streams—right-hand tributaries of the Mozhel River not diverted during the construction of the TSF—also flow into it. While passing through swamps, they mobilize a large volume of organic substances and become acidic.

The virgin waters of the Mozhel River, with its tributaries and the atmospheric precipitation, de-alkalize the TSF. The pH of the water of the Mozhel River in the upstream flow is close to neutral and averages 7.18. In the settling pond of the circulating waters, the pH is 9.08. The pH of the filtration waters from the TSF is already 7.9 on average. In general, the waters are alkaline in the Mozhel—Lower Kovdora river system. The pH of the polluted stream is 7.90–9.35, regardless of the season of the year. Thus, pulp with a pH of ca. 9.0 enters the TSF. The pulp is hydraulically washed over the upper horizons of the tailings. The waters contained in the pulp are mixed with atmospheric precipitation and surface waters and filtered through the tailings, where the environment is oxygen-free. Upon mixing with the low-pH virgin river waters flowing into the TSF, Mn transforms from the insoluble to soluble state.

The combined effects of the extraction and processing of raw materials significantly transform the hydrochemical conditions of freshwater ecosystems, and reduce their stability [66–68]. We believe that the transition of Mn from tailings to water is significantly influenced by the decreasing pH and Eh [69,70].

### 3.4. Potential Hazard and Fate of Mn in the Aquatic Ecosystems under Climate Change

Mn is an essential chemical element for living organisms [71]. In humans and animals, it acts as a component of several enzymes and participates in physiological processes [72]. Prolonged exposure to lower Mn doses can result in an increased frequency of signs of parkinsonism [73]. Even though Mn is vital, deficiencies are unlikely, as the abundances in the lithosphere, soil, and food products provide enough for human wellbeing [74,75]. On the contrary, elevated levels of Mn can be associated with toxicity [72]. In Russia, Mn is the only chemical element for which guideline values in soils have been established with regard to the stability and shift in the mobility under the changing humus content, acidity, and moisture [76]. The threshold concentrations of other chemical elements are established with fewer environmental parameters considered. Several international authoritative bodies have established health-based values for Mn, including lifetime drinking-water levels [77]. For instance, the World Health Organization (WHO) introduced the guidelines for Mn in drinking water in 1958. In 2011, the 400- $\mu$ g/L drinking-water guideline for Mn was discontinued because "this health-based value is well above concentrations of manganese normally found in drinking water, it is not considered necessary to derive a formal guideline value".

In 2021, WHO released the background document on Mn for the development of guidelines for drinking-water quality [78]. This is not surprising, as, in certain regions, Mn pollution remains an acute issue [79–81]. The main sources of Mn exposure are occupational, including mining, iron/steel making, ferro/silico-Mn alloy and dry alkaline battery production, and welding [82]. Specific industrial emissions include the use of Mn compounds in agriculture and as fuel additives. The rising presence of high Mn content in drinking water and systemic overload can result in toxic effects on the central nervous system, with impairment of motor and cognitive function [83,84].

In the study area, the migration of Mn has clear seasonal differences, with peaks in winter periods due to the changing ratio between surface and underground runoff, increasing anaerobic runoff under the snow and ice cover, and decreasing self-purification (Figure 3).



**Figure 3.** Seasonal dynamics of Mn content in the discharged wastewater of the processing plant. The data for the period from September to May are provided by the Environmental Department of the Kovdorsky GOK, and the measurements during the summer months are conducted by the authors.

We analyzed the behavior of Mn in a changing climate to predict its hydrochemical response. In natural waters, Mn is typically found in the dissolved (oxidation state of +2) and suspended (+4) form. A diagram shows the modes of Mn occurrences depending on pH and Eh (Figure 4) that allow the predicting of the fate of the element in general terms.



**Figure 4.** Modes of occurrence of Mn depending on the values of Eh and pH at +25 °C. Modified after E.P. Nakhshina and N. Takeno [85,86].

The study of Mn<sup>2+</sup> is very important since this form of the element predominates in normal waters, making up 80% of its total content. The kinetics of oxidation of dissolved Mn<sup>2+</sup> in water shows that this is an autocatalytic and heterogeneous reaction. The determining parameters include the concentration of dissolved oxygen, pH, and temperature. At high concentrations of Mn, the reaction rate is affected by the concentration of carbonates. At low concentrations of Mn, which are characteristic of natural waters, the reaction rate is negligible. Increasing the pH dramatically increases the reaction rate. Additionally, the reaction proceeds faster with an increase in surface area, i.e., the process is autocatalytic: a portion of Mn (IV) oxide or hydroxide formed during oxidation sorbs Mn<sup>2+</sup> and catalyzes its oxidation. But the process may well be heterocatalytic. It has been experimentally proved that  $Mn^{2+}$  oxidation is catalyzed by Fe oxide and silicate surfaces [87].  $Mn^{2+}$  complexes with Cl<sup>-</sup> are unstable. To bind 50% Mn<sup>2+</sup> in a complex, the concentration of Cl<sup>-</sup> should be 35 g/L, which is not observed in natural waters. Phosphate ions can also form complexes with Mn<sup>2+</sup>, but the concentrations of phosphates observed in natural waters are also insufficient for the formation of strong compounds. It is also possible to form complexes with polyphosphates, but they are unstable due to the oxidation of  $Mn^{2+}$  and the transition of polyphosphates to orthophosphates. Such complexing reactions can occur only in wastewater with an increased concentration of phosphates. Since the 1960s, it has been reported that the process of  $Mn^{2+}$  oxidation in natural water can hardly take place without the participation of living matter [88], since the atmospheric oxygen cannot oxidize compounds of  $Mn^{2+}$ , even in aqueous solution at ordinary temperatures. Mn-oxidizing bacteria are active agents both in natural and laboratory conditions [89,90].

Mn (IV), represented in nature as an oxide of MnO<sub>2</sub>, pyrolusite [91], is practically the only highly valent Mn phase thermodynamically stable in natural waters. Mn (III) in the dissolved state is stable only in a strongly acidic environment in the presence of significant amounts of such complexing agents as pyrophosphate, sulfate, fluoride, oxalate, and ethylenediaminetetraacetate. In an alkaline medium, Mn (III) is stable in the presence of mannitol. However, the concentrations of these complexing agents in natural waters are insufficient to stabilize Mn (III). Mn (VI) compounds are stable only in a highly alkaline environment, which is not typical for natural waters. Mn (VII) is thermodynamically unstable in aquatic ecosystems since it is reduced to Mn (IV) under the influence of dissolved organic matter in natural waters.

Ions, molecules, and inorganic complexes make up 72% of dissolved Mn in the water of lowland rivers and 52% in mountain ones. The second major type of dissolved Mn is organic: labile complexes with lipids and stable complexes with humic and fulvic acids. The types of suspended Mn vary too, but the main share is taken by sorbed and hydroxide compounds [92,93]. Mn behavior in lakes differs significantly from in river systems. The main sources of Mn intake into lakes and reservoirs include surface and underground flows with plankton and higher aquatic vegetation, as well as terrigenous soil and rock material of the drained basin [94]. Once in a regulated (or closed) reservoir, Mn undergoes numerous physical and chemical transformations. First of all, the oxidation of low-valent dissolved Mn (II) to less or completely insoluble forms, the formation of hydroxides, and the sorption by suspended solids result in Mn precipitation from the water column. The forms of Mn in the sediments of lakes and reservoirs are quite complex. These are mainly oxides  $(MnO_n)$ , sulfides, and carbonates of Mn, Mn<sup>2+</sup> sorbed by iron and manganese oxides, as well as organic Mn compounds. It is believed that the main mineral phases formed at the oxidized/reduced phase section are manganite—Mn<sup>3+</sup>O(OH), birnessite—(Na,Ca)<sub>0.5</sub>(Mn<sup>4+</sup>,Mn<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>·1.5H<sub>2</sub>O, and vernadite—(Mn<sup>4+</sup>,Fe<sup>3+</sup>,Ca,Na)(O,OH)<sub>2</sub>·nH<sub>2</sub>O [95–97]. The Mn content in the bottom sediments of lakes is relevantly high. The key factors determining the accumulation and distribution of Mn in bottom sediments are: (i) the rate and degree of precipitation from the water column; (ii) sampling depth and bottom morphology; (iii) the content of fine fraction and organic matter; and (iv) the redox conditions at the silt-water interface. The desorption of Mn is primarily dependent on the available oxygen and the vital activity of

specific antioxidant bacteria. At the same time, biogenic processes are regulated by changes in the Eh and pH of the medium.

The spatial distribution of Mn in the water of slow-flowing or non-flowing lakes and reservoirs is characterized by the presence of vertical stratification. In most cases, this is due to a downward decrease in dissolved oxygen and the pH of natural water strata, as well as the dissolution and diffusion of Mn ions from the bottom sediments. In wastewater and polluted atmospheric water, the element is found as  $Mn^{2+}$ ,  $MnSO_4$ ,  $MnOH^+$ ,  $MnO_4^-$ ,  $MnCl^+$ ,  $MnCO_3$ ,  $MnHCO_3^+$ , and complexes with organic ligands. In the course of the infiltration of wastewater and atmospheric water through the aeration zone, Mn sorption by minerals and precipitation of  $MnO_2$  occur.

For the Kola Peninsula, climate change and pollution can cause deep restructuring in the freshwater ecosystems and affect fishery or agricultural water use, as well as drinking and domestic supply [98–100]. The speed of such changes has been increasing enormously in recent years. Phenomena that seemed impossible in the 20th century, e.g., algal blooms of blue-green algae in Arctic lakes, now occur regularly [29]. The main consequences of such changes are as follows:

- Pollutant accumulation in water bodies increasingly reaches toxic levels, with negative impacts on aquatic ecosystems;
- Changes in the trophic status of aquatic ecosystems and an increase in the rate of eutrophication, especially in case of relatively warm wastewater discharge;
- Changes in the direction and speed of plant succession;
- The reduction of the ecosystem stability and increasing risks of irreversible degradation.

Such climatic variables as air temperature and amount of precipitation cause changes in runoff, water volume, lake levels, water balance, biological productivity, etc. [101]. Weather observations have been conducted on the Kola Peninsula since the mid-19th century. Since 1976, climatologists have observed a continuous increase the average seasonal air temperature in Russia's northern latitudes. The decadal increase in temperatures has increased from 0.07 degrees (1936 to 1975) to 0.6 degrees for every 10 years since 1976, according to the head of the Murmansk Meteorological Office [102]. An increase in atmospheric air temperature inevitably leads to an increase in surface water temperature. This parameter directly or indirectly affects numerous hydrological and ecological processes [103].

Climatic changes have caused increases in both average annual and maximum annual water temperatures of many rivers of the world [104,105]. An assessment of changes in water temperature in various lakes in the period from June to October showed trends in increasing water temperature in the lakes of the Kola Peninsula. The values of the temperature increase of water for each of the lakes are close enough and range from +0.21 °C per 10 years to +0.29 °C per 10 years [106]. An increase in the water temperature is also associated with an increase in the heat reserves of water bodies, primarily in autumn, which contributes to the shift to later dates of ice formation and the freeze-up date.

Our findings suggest that the key to quantifying the impacts of climate change on Mn mobility is to understand how the interaction between bottom sediments and discharged waters will change in the future under the changing alkalinity and acidity, organic matter content, and other geochemical characteristics. Water heating affects the dynamic and kinematic viscosity of soils and sediments of river beds and banks, thereby changing erosion patterns. The content of dissolved oxygen depends on the temperature of the water, and, consequently, the intensity of the self-purification processes. The higher temperature of the studied waters will primarily intensify diffusion in the bottom sediments, which will facilitate the transition of Mn from the bottom sediments into the water column in dissolved form (Figure 5). In addition, it will entail an increase in aquatic biomass and, as a consequence, the mass of dead remains of higher aquatic vegetation, which will be an additional source of dissolved Mn in water. The redox conditions will be affected too, as the oxygen content in the water decreases with the higher temperature. Under anaerobic

conditions, Mn will be reduced to divalent, followed by the development of events in several scenarios, depending on the forming environment:

- 1. Formation of insoluble compounds from the wastewater of the mining enterprise as a result of interaction with mineral salts;
- 2. Formation of insoluble complexes and sorption of Mn on organic components of suspended solids and bottom sediments. Taking into account the increase in water flow from the catchment area, the mass of organic matter in water bodies will increase significantly;
- 3. Formation of soluble organic and inorganic complex Mn compounds with the subsequent pollutant migration.

![](_page_16_Figure_5.jpeg)

**Figure 5.** Migration of Mn compounds from the processing plant at the baddeleyite-apatite-magnetite deposit as a mixture component in the pulp discharged into the tailings storage facility with the further shift into the soluble state under the changing redox and acidity water parameters.

However, it is necessary to consider the behavior of Mn not only under the redox change, but also under the acid-base transformations. Self-purification from divalent Mn begins only at pH values close to 8.0.

Climate change associated with an increase in temperature is accompanied by a change in the amount of precipitation. Since 1936, an increase in the amount of precipitation has been registered each season and on average each year on the Kola Peninsula [107]. A stable increase in the amount of precipitation may lessen the pH and thereby raise the share of mobile Mn. On the other hand, a higher rainfall may contribute to the input of additional organic matter from the catchment area, which is capable of forming complex compounds with Mn.

Overall, the hydrochemical anomaly of Mn is unlikely to wipe out under regional climate change. Even though lower concentrations of Mn due to the intensified self-purification and dilution are likely to occur, the affected area is predicted to increase. Irrespective of the impacts of a changing climate, the effects of continued mining will lead to a further accumulation of metals in the aquatic environment [107,108].

# 4. Conclusions

The conducted research assessed the hydrochemical situation in the impact zone of the large ore mining and processing enterprise in the Russian Arctic. The elevated levels of metals in surface waters and bottom sediments indicate the occurrence of the potential risk to the health of the local population, for whom the studied water bodies are a source of household and drinking water supply. Monitoring studies have shown that by far the largest contribution to the pollution of water bodies in the district is made by wastewater from the processing plant.

The discharge of untreated wastewater from the tailings storage facility into the Mozhel River led to degradation changes in the watercourse and the formation of a Mn-containing hydrochemical anomaly with a hundredfold excess over the background concentrations. Extremely high concentrations of Mn in wastewater were caused by a combination of factors such as the mobilization of the element after the ore dressing process and its raised accessibility under the redox and acid-base conditions of the tailings. The study of the technogenic sediment formation in water bodies revealed the danger of secondary pollution: 65-80% of the total Mn in the bottom sediments are represented by mobile forms.

The forecast of the hydrological regime of water bodies under climate change suggests that the geochemical anomaly may increase in area, but the contents of Mn will supposedly decrease due to the activation of self-purification and dilution processes. In general, the persisting deterioration of surface water quality will decrease the regional resource potential and require immediate management and control measures, as well as a revision of the water use principles.

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