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# Mine Wastewater Effect on the Aquatic Diversity and the Ecological Status of the Watercourses in Southern Poland

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**Abstract:** Coal mining activity contributes to energy security and employment occupation, but is associated with environmental deterioration. Coal combustion leads to GHG emissions, while coal mining results in the generation of saline effluents. These effluents are discharged in inland surface waters, applying significant pressure on their quality, with a negative impact on aquatic life and the economy of a region. This study includes water samples that were analyzed in order to investigate the organic compounds, heavy metals, and other physicochemical parameters. Biological monitoring was done according to the Water Framework Directive methodology. The results from an aquatic area in Southern Poland, which indirectly receives coal mine effluents, indicate elevated salinity with excessive chlorides, sulfates, and sodium ions. The water quality of another non-polluted aquatic area was also assessed to examine the impact of indirect coal mine wastewater discharge on this area. The high salinity levels hinder the use of river water for drinking, agricultural, or industrial purposes. The results obtained show high pressure on the ecological status of streams and rivers that receive mine effluents, and on the density and diversity of aquatic invertebrates. This pressure is clearly visible in the structure of benthic communities and in invertebrate diversity. It also contributes to the appearance of invasive species and increasing water salinity. Limiting discharges of mine water transporting large loads of saline substances would reduce the negative impact on the quality of river waters and biological life.

**Keywords:** benthos; invertebrates; mining; saline effluents; water quality

## 1. Introduction

The EU economy is seeking to decouple from resource depletion and environmental degradation. By 2050, climate neutrality is expected to be achieved. Therefore, all coal mines are facing closure. However, the diffusion of ions from mine effluents will still be hindering the implementation of the Water Framework Directive. The economy of a region strongly depends on its natural resources. Poland is the dominant coal mine producer in

EU, encompassing massive areas of coal mines. Most of the country's mines are located in the Upper Silesian Coal Basin (USCB).

Depending on the site's geology, coal can be excavated by surface mining (accounting for about 40% of worldwide coal production) or underground mining. Coal excavation generates various types of emissions into the environment: solid waste (coal refuse), air emissions (e.g., methane), and wastewater. Underground mining, in particular, generates a lot of wastewater (about 3 $m^3$ per 1 t of coal) [1]. Depending on how deep the coal seam is, the salinity can vary from low-salinity brackish water to brine, with a salinity 2 to 3 times higher than that of seawater. USCB mine effluents affect surface water both quantitatively and qualitatively, especially in small streams where significant changes in the hydrological regime are caused by large loads of contaminants in a high quantity of mine discharges [2]. According to the European Pollutant Release and Transfer Register [3], the total amount of chloride released (as total $Cl^-$) in the Vistula and Oder rivers is estimated to be 2.4 million tons for 2019. The elevated salinity hinders the direct use of river water as drinking water and agricultural or industrial water, thus increasing water stress.

For many years, excessive salt concentrations have been found in the Vistula River, with 94% of the chlorides originating from hard coal mining activity. Salinity is one of the main drivers responsible for changes in aquatic biocoenosis [4,5]. The high ion concentrations in the water and their different ratios compared to freshwater provide unfavorable conditions for biota. It is critical for the survival of aquatic organisms to maintain osmotic equilibrium between internal fluids and the external environment [6]. The ability to osmoregulate has limits and an energy cost; if exceeded, it can compromise organisms, causing stress or death [7]. The increase in water salinity may disturb the life processes of aquatic species; for example, it may limit macrophyte reproduction, diapause egg-laying by zooplankton [8], and fish development and growth [9]. Increasing water salinity provides habitats for saltwater biota and leads to the replacement of sensitive species by eurytopic species and species resistant to high salt concentrations, including non-native species [10–12]. This may result in species disappearance and changes in the composition of biocenoses [7,13]. This leads to further harmful effects on native fauna and ecosystems of special importance due to the possibility of an appearance of invasive and alien species, such as, e.g., gammarids or snails because of their high tolerance to salinity [14,15].

The Polish monitoring program is carried out through different types of monitoring—diagnostic, operational, and research—and it is managed by the Regulation of the Minister of the Infrastructure of 13 July 2021, dictating forms and methods of the monitoring of surface and groundwater bodies [16]. The aim of diagnostic and operational monitoring is to provide information regarding the ecological and chemical condition of streams and rivers in recent years. Monitoring studies are carried out at measurement and control points representative of the assessed water body.

This paper presents a comparison of the results of the national monitoring program with the results of laboratory analysis of the samples from the area's monitoring points, which provide valuable clues to the current situation in the study's area. A sampling process was conducted on the aquatic area of the Goławiecki Stream and the Small Vistula River. Potok Goławiecki is a small stream receiving coal mine effluents, which end up in the Small Vistula River. The parameters analyzed in the water samples were set in accordance with the Water Framework Directive (WFD) for good quality water and coal mine wastewater composition. Both biological elements and physicochemical characteristics were analyzed. The water quality of a nearby, non-polluted stream, called Korzeniec stream, was also evaluated to assess the ecological condition of the stream and the river.

*WFD Objectives on a Surface Water Body Quality*

The WFD (2000/60/EC) requires all EU member states to protect and improve water quality in all water bodies so as to achieve good ecological status, at the latest by 2027. A water body of good status is a water body of good ecological and good chemical status.

The ecological status refers to the quality of the structure and functioning of the aquatic ecosystems in the surface water bodies, while the chemical status refers to the concentration of pollutants that can harm the aquatic life as well as human health. Table 1 demonstrates the ecological and chemical-structural parameters of a surface water body, according to the WFD.

**Table 1.** Ecological and chemical status of surface water according to the Water Framework Directive (WDF).

| **Status of Surface Water Bodies** | | | | | |
|---|---|---|---|---|---|
| 1. Ecological Status | | | | | |
| Biological Elements | Hydromorphological Elements | | | Chemical/Physico-chemical Elements | |
| Aquatic Flora<br>Benthic invertebrates<br>Fish Fauna | Hydrological Regime<br>• Quantity and dynamics of water flow<br>• Connection to groundwater bodies | River Continuity<br>• Migration of aquatic organisms and sediment transport | Morphological Conditions<br>• River depth and width variation<br>• Structure and substrate of the riverbed<br>• Structure of the riparian zone | General<br>• Thermal conditions<br>• Oxygenation conditions<br>• Salinity<br>• Acidification Status<br>• Nutrient conditions | Specific Pollutants<br>• Priority substances (Annex X)<br>• Other substances |
| 2. Chemical Status | | | | | |
| WFD (200) | | Directive 2008/105/EC | | Directive 2013/39/EU | |
| Article 16(7)<br>EQS for the priority substances in surface waters<br>Annex V<br>Classification of chemical status. | Annex IX<br>Emission limit values and environmental quality standards.<br>Annex X<br>List of priority substances. | Annex II<br>Replaces Annex X of the WFD | Sets EQS for the substances in surface waters | Annex I<br>Replaces Annex X of the WFD (2000) and Annex II of the Priority Substances Directive (2008) | Adds 12 additional priority substances (45 in total) |

## 2. Mine Wastewater Composition and Effect on a Surface Water Body

Coal mine wastewater is a combination of mine water and sewage water generated from mining activities. Mine water or pit water is the water accumulated in a mine, through atmospheric precipitation or through the already existing groundwater. In the case of Polish hard coal mines, none of them are open-pit mines, and all of them are deep coal mines with underground galleries. Such structures require the constant dewatering of galleries by pumping naturally saline groundwater from a depth of a few hundred meters to the surface. Sewage water is generated from coal mining activities, mainly from coal preparation, such as the washing and cutting of coal. Mine waters are rich in metals like nickel (Ni), iron (Fe), copper (Cu) and manganese (Mn). The drainage water from mines in Poland contributes 6500 t chlorides and 0.5 t sulfates daily to the rivers Wisła (Vistula) and Odra (Oder). Even if the mining activities cease for decades, the water pollution in surface waters remains, and this is another factor that makes coal mine wastewater drainage an important environmental challenge.

Coal mine effluents contain acid, alkaline, and metal mine drainage from abandoned mines or produced during mine operations [17]. Their anthropogenic discharge, extension, and accumulation can cause the large-scale destruction of surface waters and aquatic ecosystems [18,19]. They are one of the more important factors causing a significant loss of biodiversity in the biota. The macroinvertebrate communities downstream of wastewater discharges are characterized by low taxonomic richness, a loss of pollution-sensitive taxa, and an increase in pollution-tolerant taxa [20,21]. Metals present in coal mine wastewater can be accumulated in the aquatic macrophytes that are exposed to them [22,23]. The potential of aquatic plants to accumulate heavy metals is beneficial to their use in phytoremediation [24].

## 3. Materials and Methods

### 3.1. The Studied Area

Poland has 10 river basin districts, and they are all international, which means that they extend beyond the country's boundaries. The longest Polish rivers are the Vistula and Odra, and their river basin districts cover almost 97% of the country. The Vistula is 1047 km long. It comes from the slopes of Barania Góra, and it flows into the Bay of Gdańsk. Its length is divided into two parts: The first part is called the Small Vistula River, which is 106 km long and expands from the source to the tributary Przemsza River. The second part, which starts at the conjunction of the Small Vistula River with the Przemsza River, is called Vistula (Navigable Vistula), and it flows for a further 941 km until it falls into the sea [25]. The study area comprises a small stream, called Potok Goławiecki or Goławiecki Stream, and the Small Vistula River zone, into which the stream is discharged (Figure 1. In the 2nd map, the Korzeniec stream is shown (Figure 1).

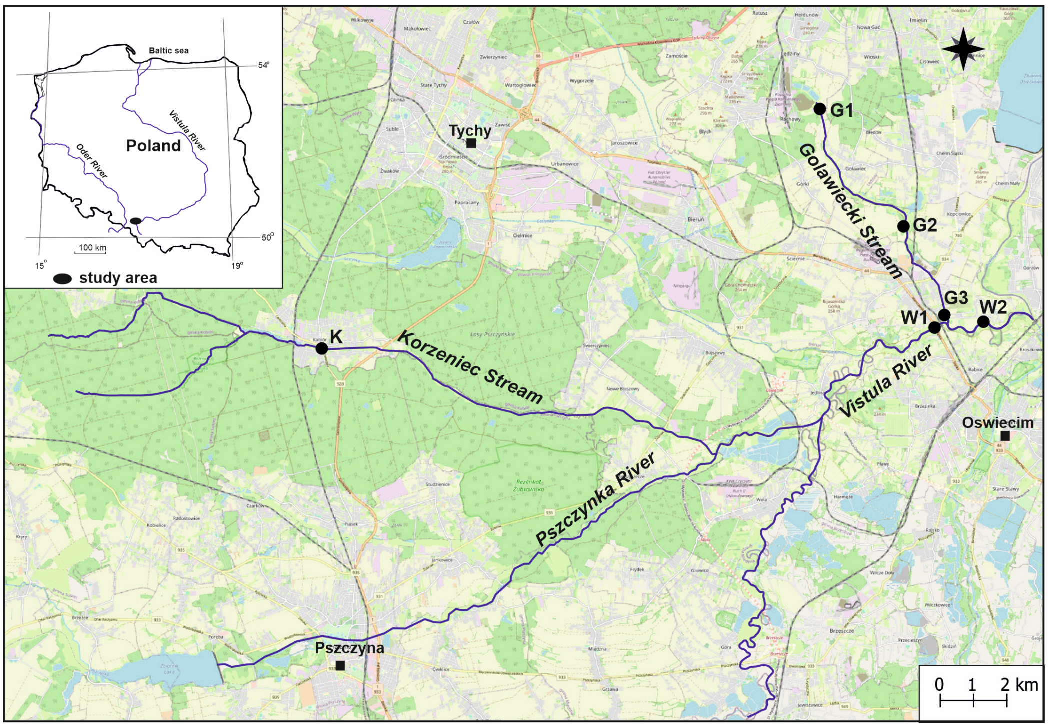


**Figure 1.** Map of the Golawiecki Stream and the Small Vistula River zone, receiving the saline effluents with marked monitoring points G1, G2, G3, W1 and W2. Map of the Korzeniec stream with marked monitoring point K—Korzeniec stream monitoring point.

### 3.2. Sampling Process

For the baseline monitoring of the study area, five (5) points were selected, due to their specific local conditions. Three of them are placed in the stream (G1, G2, G3—Figure 1)—one near its source (G1), one in the middle of it (G2) where the water from the Kurdowiec reservoir falls in, and one near the stream's estuary leading to the Small Vistula River (G3). The other two points are located in the Small Vistula River, before and after the stream's runoff into the river (W1, W2).

Sampling was carried out in January, 2021 (1st sampling campaign, sampling points: G1, G2, G3, W1, W2) and in June, 2022 (2nd sampling campaign, sampling points: G1, G2, G3, W1, W2, K). An additional monitoring point (K) was added in the 2nd sampling campaign, to compare the water quality of the study area with the water quality of a nearby surface water body, which is non-polluted. This point is located in the Korzeniec stream, in the Pszczyna forest area. The Korzeniec stream is not exposed to anthropogenic pressures, and therefore, its biological status serves as a reference point for studies on the biological status of polluted water bodies (Figure 1). The valley of the Korzeniec stream in the Pszczyna Forest is characterized by a high vegetation diversity and the existence of rare forest communities [26].

### 3.3. Water Samples Analysis

Organic compounds in water samples, such as dichlorodifenylotrichloroethane (DDT-o,p′ and DDT-p,p′) heptachlor, hexachlorocyclohexane ($\alpha$-, $\beta$, and $\gamma$ isomers), phenol, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c, d)pyrene, dibenzo(a, h)anthracene, and benzo(g, h, i)perylene, were determined based on ISO17025 using the Gas Chromatography–Mass Spectrometry method (GC-MS) in which the injector temperature started at 50 °C for 1 min, increased at 35 °C/min to 85 °C for 2 min, then increased at 250 °C/min to 300 °C and held at 300 °C for 27 min. Helium (carrier gas) was used under constant linear velocity conditions of 37.5 cm/s. The MS detector was operated at 70 eV. Kjeldahl Nitrogen, in general, was determined by the ISO 1871:2009 standard method.

Polycyclic aromatic hydrocarbons (PA) were analyzed by HPLC and FL detection using the Waters Acquity FL detector, Merck Purospher Star RP-18e column (250 × 2.5 mm, 5 µm) and gradient elution (0.25 mL/min at room temperature), with 70% acetonitrile and 30% water for 30 min and a linear increase in acetonitrile content up to 100% (40 min), and after 5 min, the initial content was restored and held to 55 min [27]. The samples (500 mL) were preconcentrated with SPE (CHROMABOND C18 15 ML, 2000 MG, acetonitrile elution 5 mL).

The concentrations of $Br^-$, $Ca^{2+}$, $Cl^-$, $F^-$, $K^+$, $Mg^{2+}$, $Na^+$, $NO^{3-}$, $PO_4{}^{3-}$, and $SO_4{}^{2-}$ were determined using a Thermo Scientific Dionex ICS-5000 ion chromatograph equipped with a CS-16 column for cations or an AS-19 column for anions. The contents of B, Ba, Cd, Cu, Hg, Mn, Mo, Ni, Pb, Si, P, Sr, Ti, and Zn were measured using the ICP-OES method (Varian 710 ES). The $HCO_3$ concentration was determined using volumetric titration with HCl and phenolphthalein/methyl orange indicators. TSS was determined using the standard method EN 872:2005. Dissolved oxygen was measured using the Elmetron CO-404 oxygen optical sensor. BOD was determined by measuring the change in $O_2$ content after 5 days of sample incubation in the dark at 25 °C (no dilution was used). Conductivity was measured using an Elmetron CX-505 multi-function meter with an ECF-1t electrode.

### 3.4. Analysis of Biological Elements

The ecological status of the stream and the river was assessed according to the methodology of sampling benthic macroinvertebrates for the purposes of ecological monitoring, based on the Water Framework Directive (2000/60/EC) [28]. This method is widely used to assess the quality of surface waters. Benthic macroinvertebrates were collected in June 2021. The sampling method was chosen according to the river's size and nature (hard-to-reach river or easy-to-reach river). All sampling points had a distance of 50 m from each other. Due to the small depth of the Goławiecki Stream, it was possible to cross its entire width to assess the heterogeneity of the bottom substrate. The percentages of mineral and organic substrates in the sampling points of the river were also estimated. Habitats that comprised less than 5% of the bottom cover were not selected for macroinvertebrate sampling. In the Goławiecki Stream, macroinvertebrate samples were collected using a 500 µm mesh hydrobiological net for kick sampling. In the Vistula River, samples were taken in four transects, with 5 points at each of them, using a benthic dredge sampler. According to the methodology, due to the impossibility of the visual assessment of the bottom habitats, it was assumed that the variability in the habitats of the bottoms of large rivers is determined by the differentiation of the flow velocity in the cross-section of the riverbed, and therefore, the changes in the habitats take the form of gradients directed from the shores towards the current axis.

According to the methodology of the representative sampling of benthos communities, 20 partial samples were collected from each measuring point from the main habitats, with a total area of 1.25 $m^2$. In the laboratory, the material collected was washed using sieves with a mesh diameter of 0.40 mm. Then it was placed on a monitoring cuvette, and 5 subsamples were randomly selected. According to the rules for selecting macrobenthos subsamples, the minimum number of organisms from 5 subsamples should be 350 individuals. When such a number was not achieved, a larger number of fields (subsamples) was selected to obtain the required number of benthic invertebrates.

A multi-parametric index (Polish Multimetric Index MMI PL) was used to assess the ecological status of rivers using benthic invertebrates (in Excel). The index includes six-component metrics: ASPT_PL (Average Score Per Taxon PL), Log10 (sel_EPTD + 1) (selected families from Ephemeroptera, Plecoptera, Trichoptera, and Diptera), 1—GOLD (abundance of Gastropoda, Oligochaeta, and Diptera), S (the total number of families), EPT (the number of families of Ephemeroptera, Plecoptera, Trichoptera), and the Shannon–Wiener Diversity Index. It enables the determination of the degree of river degradation due to salinization, eutrophication, and saprobization.

Samples of benthic invertebrates were also collected in June and July 2021 to assess their density and diversity. At all study sites, quantitative samples were taken using hydrobiological methods for sampling benthic invertebrates from an area of 1 $m^2$ of bottom sediments, stones, and plants. Biological material was placed in plastic containers and transported to the laboratory, where the samples were washed in the sieves (0.04 mm mesh size), and the material was carefully examined under a stereomicroscope. Benthic invertebrates were preserved in 75% ethanol and identified to a family or species rank. Density, species diversity, and community structure may reflect the stresses caused by different pollutants. The following diversity indices, the Shannon–Wiener index (H′) and the Pielou index, were used to compare diversity between sampling sites (MVSP software, 3.13.p, Kovach Computing Services, UK).

## 4. Results and Discussion

### *4.1. Evaluation of the Salinity Effect in the Goławiecki Stream*

In the water quality analysis of the Goławiecki Stream, a clear impact of the different conditions prevailing in each monitoring point can be detected. In point G1, which was set right after the river source, the conductivity—equal to 36.4 mS/cm—reaches that of seawater, while the values of the sodium ions and the chlorides are 11,000 mg/L and 20,000 mg/L, respectively. To compare, mid-range conductivity (200 to 1000 µS/cm) is the normal background for most major rivers. In point G2, where the Goławiecki Stream's water is diluted by the Kurdowiec reservoir's water, a noticeable decrease in the values of all parameters is observed. However, the pollution of the area is still at a high level, since the conductivity is equal to 31.2 mS/cm, the sodium ions equal 10,100 mg/L, and the chlorides equal 18,300 mg/L. The distance between point G2, in which the two different water bodies are mixed, and point G3, which is near the estuary of these waters to the Small Vistula River, is around 4 km. There is no significant change in the water quality between these monitoring points. Overall, the Goławiecki Stream is highly affected by ion diffusion caused by the indirect flow of coal mine wastewater from the artificial lagoons. So, the parameters associated with salinity, such as conductivity, chlorides, sodium, calcium, and magnesium ions concentrations, are high (Table 2).

**Table 2.** Analysis of samples in the monitoring points of the study area during the 1st sampling campaign.

| Parameter | G1 | G2 | G3 | W1 | W2 |
|---|---|---|---|---|---|
| B, mg/L | 6.90 | 5.97 | 5.46 | 0.24 | 0.38 |
| Ba, mg/L | 0.08 | 0.06 | 0.06 | 0.35 | 0.33 |
| $Br^-$, mg/L | 72.9 | 61.6 | 55.5 | 3.5 | 5 |

**Table 2.** *Cont.*

| Parameter | G1 | G2 | G3 | W1 | W2 |
|---|---|---|---|---|---|
| $Ca^{2+}$, mg/L | 916 | 784 | 716 | 95.9 | 113 |
| Cd, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 |
| $Cl^{-}$, mg/L | 24,000 | 20,800 | 18,600 | 1190 | 1690 |
| Conductivity, mS/cm | 40.1 | 36.6 | 31.9 | 3.03 | 3.96 |
| Cu, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 |
| $F^{-}$, mg/L | <10 | <10 | <10 | <1 | <1 |
| $HCO_3^{-}$, mg/L | 741 | 644 | 660 | 338.1 | 354.2 |
| Hg, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 |
| $K^{+}$, mg/L | 229 | 196 | 178 | 13.8 | 18.2 |
| $Mg^{2+}$, mg/L | 1020 | 867 | 783 | 47.1 | 67.7 |
| $Mn^{2+}$, mg/L | 1.26 | 1.12 | 0.89 | <0.01 | <0.01 |
| Mo, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 |
| $Na^{+}$, mg/L | 13,400 | 11,500 | 10,300 | 633 | 909 |
| Ni, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 |
| $NO_3^{-}$, mg/L | <10 | 10.6 | 13.9 | 11.4 | 10.2 |
| P, mg/L | 0.06 | <0.05 | <0.05 | 0.05 | 0.03 |
| Pb, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 |
| pH | 6.58 | 6.58 | 6.65 | 7.53 | 7.67 |
| $PO_4^{3-}$, mg/L | <10 | <10 | <10 | <1 | <1 |
| Si, mg/L | 4.14 | 3.91 | 4.17 | 4.56 | 4.47 |
| $SO_4^{2-}$, mg/L | 1440 | 1220 | 1100 | 86.5 | 111 |
| Sr, mg/L | 21.34 | 18.39 | 17.06 | 1.98 | 2.40 |
| Ti, mg/L | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| TSS, mg/L | 159 | 127 | 135 | 74.2 | 66.0 |
| Zn, mg/L | <0.05 | <0.05 | <0.05 | 0.01 | 0.02 |
| $O_2$, mg/L | 8.76 | 9.13 | 9.21 | 9.48 | 9.65 |
| BOD, mg/L | 0.23 | 0.85 | 1.00 | 2.61 | 1.63 |
| Kjeldahl Nitrogen, mg/L | 0.33 | 0.35 | 0.3 | <0.1 | <0.1 |
| PAHs, ng/L | <0.36 | <0.36 | <0.36 | <0.36 | <0.36 |
| DDT-o,p′, µg/L | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| DDT-p,p′, µg/L | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| Heptachlor, µg/L | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| Phenol index, µg/L | <0.01 | <0.01 | <0.01 | 0.11 | 0.09 |
| PAHs—Sum (EPA16), µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Naphthalene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Acenaphthylene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Acenaphthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Fluorene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Phenanthrene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Anthracene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Fluoranthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Pyrene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(a)anthracene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Chrysene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(b)fluoranthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(k)fluoranthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(a)pyrene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Indeno(1,2,3-cd)pyrene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Di-benzo(a,h)anthracene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(ghi)perylene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Hexachlorocyclohexane (sum α-,β-, γ-), µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |

*4.2. Effect of the Goławiecki Stream Flow in the Small Vistula River*

It is quite clear that the Small Vistula River's water is affected by the inflow of the Goławiecki Stream. All the parameters indicating salinity are elevated in point W2, which is set after the estuary connecting the stream to the river, compared with those in point W1, which is placed before the estuary. The conductivity in point W1 is equal to 6.78 mS/cm, while in point W2, it is equal to 7.86 mS/cm. Finally, the chloride concentration is equal to 3780 mg/L in point W1, while in point W2, it is equal to 4070 mg/L. The sodium concentration, though, remains the same between the two points, and is equal to 2110 mg/L in point W1 and 2230 mg/L in point W2 (Table 2).

### 4.3. Effect of Other Saline Effluents in the Small Vistula River

It must be noted that the level of the Small Vistula River's pollution is high even in the area before the discharge of the Goławiecki Stream into it. In greater detail, a comparison of the most important parameters indicating water pollution among points W1 and K demonstrates the extent of pollution in the Small Vistula River originating from other polluted effluents. Point W1 is located upstream of the Goławiecki's estuary to the river, while point K is located in the Korzeniec stream, a nearby, non-polluted stream with good water quality.

Mid-range conductivity (0.200 to 1 mS/cm) is the normal background for most major rivers. In the Korzeniec stream, the conductivity is equal to 0.440 mS/cm, while in point W1, it is equal to 6.780 mS/cm, indicating an elevated level of salinity in the river and an unsuitable environment for aquatic life (Table 3). The maximum chloride concentration in an inland surface water body should not be higher than 600 mg/L [29]. The chloride content in point W1 is equal to 3780 mg/L, which is far higher than that in the non-polluted Korzeniec stream, in which the chloride concentration is 16 mg/L. In point W1, the sodium ion concentration is equal to 2110 mg/L, which is ten times higher than the top limit of sodium ion content for good quality water (200 mg/L) (Table 3). The concentration of calcium in freshwater is in the range of 0 to 100 mg/L. Calcium and magnesium ions contribute to water's total hardness. At point W1, the calcium ions concentration is equal to 191 mg/L, while in the Korzeniec stream, it is five times less than that, equal to 48 mg/L. This variation is one more clue that the Small Vistula River receives saline wastewater inflow before the Goławiecki stream falls into it. The concentration of the potassium ions in the Korzeniec stream is less than 10 mg/L, which is an expected value for a non-polluted water body. In point W1, it is equal to 37 mg/L. Barium (Ba) can be found in naturally occurring mineral deposits. The World Health Organization limit is equal to 0.7 mg/L [30]. Thus, the barium concentration in the Small Vistula River is not considered alarming, as in point W1 it is equal to 0.64 mg/L, but this is still six times higher than in point K, which is equal to 0.12 mg/L (Table 3).

**Table 3.** Analysis of samples from the polluted area (G1, G2, G3, W1, W2) and the non-polluted stream (K)—2nd sampling campaign.

| Parameter | G1 | G2 | G3 | W1 | W2 | K |
|---|---|---|---|---|---|---|
| ASPT | 4.00 | 2.67 | 4.50 | 4.20 | 4.50 | 4.80 |
| Log10(sel_EPTD+1) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.99 |
| 1-GOLD | 0.01 | 0.00 | 0.04 | 0.35 | 0.93 | 0.35 |
| S | 6 | 3 | 2 | 5 | 5 | 17 |
| EPT | 1 | 0 | 0 | 1 | 1 | 4 |
| H' | 0.88 | 0.12 | 0.02 | 0.74 | 0.30 | 1.75 |
| ICMI | 0.073 | −0.162 | 0.064 | 0.040 | 0.118 | 0.498 |
| MMI_PL | 0.073 | 0.000 | 0.064 | 0.040 | 0.118 | 0.498 |
| MMI—Quality class | V | V | V | V | V | III |
| B, mg/L | 6.67 | 6.25 | 5.73 | 0.83 | 1.01 | 0.07 |
| Ba, mg/L | 0.08 | 0.09 | 0.07 | 0.64 | 0.45 | 0.12 |
| $Br^-$, mg/L | <10 | 14 | <10 | <10 | <10 | <10 |
| $Ca^{2+}$, mg/L | 717 | 680 | 627 | 191 | 202 | 48 |
| Cd, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 | <0.01 |
| $Cl^-$, mg/L | 20,000 | 18,300 | 16,800 | 3870 | 4070 | 16 |
| Conductivity, μS/cm | 36.4 | 31.2 | 29.5 | 6.78 | 7.86 | 0.44 |

**Table 3.** *Cont.*

| Parameter | G1 | G2 | G3 | W1 | W2 | K |
|---|---|---|---|---|---|---|
| Cu, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 | <0.01 |
| $F^-$, mg/L | <10 | <10 | <10 | <1 | <1 | <1 |
| $HCO_3^-$, mg/L | 347.7 | 317.2 | 225.7 | 158.6 | 170.8 | 195.2 |
| Hg, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 | <0.01 |
| $K^+$, mg/L | 193 | 178 | 160 | 37 | 40 | <10 |
| $Mg^{2+}$, mg/L | 839 | 763 | 736 | 157 | 169 | <10 |
| Mn, mg/L | 0.50 | <0.05 | <0.05 | <0.01 | <0.01 | 0.05 |
| Mo, mg/L | 0.35 | 0.32 | 0.31 | 0.07 | 0.07 | 0.01 |
| $Na^+$, mg/L | 11,000 | 10,100 | 9260 | 2110 | 2230 | 16 |
| Ni, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 | 0.01 |
| $NO_3^-$, mg/L | <10 | 15 | 16 | <10 | <10 | <10 |
| P, mg/L | <0.05 | <0.05 | <0.05 | 0.04 | <0.01 | 0.02 |
| Pb, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 | <0.01 |
| pH | 7.08 | 7.20 | 6.98 | 7.07 | 6.52 | 7.13 |
| $PO_4^{3-}$, mg/L | <10 | <10 | <10 | <1 | <1 | <1 |
| Si, mg/L | 3.79 | 1.99 | 1.47 | 1.70 | 2.48 | 6.59 |
| $SO_4^{2-}$, mg/L | 1290 | 1180 | 1130 | 203 | 238 | 27 |
| Sr, mg/L | 19.70 | 17.94 | 16.39 | 4.74 | 4.55 | 0.42 |
| Ti, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 | <0.01 |
| TSS, mg/L | 432 | 204 | 236 | 12 | 56 | 13.5 |
| Zn, mg/L | <0.05 | <0.05 | <0.05 | <0.01 | <0.01 | <0.01 |
| $O_2$, mg/L | 6.07 | 5.84 | 5.05 | 4.43 | 4.17 | 6.13 |
| BOD, mg/L | 1.09 | 0.20 | 2.31 | 2.39 | 2.92 | 1.02 |
| DDT-o,p′, µg/L | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| DDT-p,p′, µg/L | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| Heptachlor, µg/L | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| Hexachlorocyclohexane (sum α-, β-, γ-), µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Phenol index, mg/L | <0.01 | <0.01 | <0.01 | <0.02 | <0.02 | <0.01 |
| Kjeldahl Nitrogen—general, mg/L | 0.33 | 0.35 | 0.3 | <0.1 | <0.1 | 0.59 |
| WWA—Suma (EPA16), µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Naphthalene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Acenaphthylene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Acenaphthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Fluorene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Phenanthrene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Anthracene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Fluoranthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Pyrene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(a)anthracene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Chrysene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(b)fluoranthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(k)fluoranthene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(a)pyrene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Indeno (1,2,3-cd, µg/L) pyrene | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Di-benzo (a, h) anthracene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzo(ghi)perylene, µg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |

In terms of palatability, a content of more than 1200 mg/L of total suspended solids (TSS) is unacceptable, while if the TSS concentration does not exceed 300 mg/L, then the water quality is considered excellent [30]. Unlike the rest of the parameters, the TSS content in the Small Vistula River is quite good. In point W1, it is equal to 12 mg/L, while in point W2, right after the Goławiecki inflow into the river, the TSS content is equal to 56 mg/L. In point K, it is equal to 13.5 mg/L. The BOD value, which indicates the presence of organic compounds in a water body, is double in the Small Vistula River compared to the Korzeniec stream (Table 3).

### 4.4. Comparison between the Two Water Quality Analyses in the Study Area

There is a notable decrease in the values of the parameters indicating salinity between the two analyses in the Goławiecki stream. The conductivity in point G1, which is near the source of the stream, decreases from 40.1 mS/cm to 36.4 mS/cm, the sodium ions decrease from 13,400 mg/L to 11,000 mg/L, the chlorides content decreases from 24,000 mg/L to 20,000 mg/L, the magnesium ions decrease from 1020 mg/L to 839 mg/L, the potassium ions decrease from 229 mg/L to 193 mg/L and the sulfates decrease from 1440 mg/L to 1290 mg/L. The notable recession is the result of two different factors. The first one relates to the fact that the rainy season intervened between the two sampling campaigns, which may have resulted in lower ion concentrations in mine waters. The second case is the fluctuation in the quantity and/or the composition of the mine water, which is indirectly discharged into the study area, over a time period of six months, which also points to the mine's efforts to reduce water discharge in a controlled manner by taking measures to reduce both the quantity and the composition of the discharged water in artificial lagoons. However, the conductivity and the concentration values still remain at very high levels, characteristics more representative of sea water than fresh surface water streams. The long-term perspective is unsatisfactory. After mines are closed, saline waters are discharged into water surfaces for many years, making them susceptible to degradation. It is possible that climate change exasperates this phenomenon due to the decreased level of surface water. It is likely that in consequence, the effect of salinity will increase.

Bicarbonates are the dominant form of dissolved inorganic carbon in a surface water body. Among the two sampling processes, there is an obvious reduction, since in point G1 their content decreases from 741 mg/L to 347.7 mg/L, while in point W1, in the Small Vistula River, we see a reduction from 338.1 mg/L to 158.6 mg/L. This reduction is partially associated with the rise in temperature in Poland during the spring months, which results in the lower solubility of the atmospheric CO2 in the stream and the river. In Poland, the summer temperature range is from 25 °C to 35 °C, while the corresponding values for January and February, which are the coldest months, are a couple of degrees below zero. However, the pH values, which rely on the bicarbonate content as well, remain at a neutral level in both water analyses results. The dissolved oxygen (DO) content in the study area is quite similar to the bicarbonate content. From 8.76 mg/L, the $O_2$ concentration decreased to 6.07 mg/L in point G1, and in the Small Vistula River it decreased from 9.48 mg/L to 4.43 mg/L, which is less than the DO value in the non-polluted Korzeniec stream (6.13 mg/L). The rise in temperature and the presence of suspended solids in the study area contribute to reductions in the amount of $O_2$ in the stream and the river.

Unlike the reduction in the parameters of the Goławiecki stream, the exact opposite was observed in the Small Vistula River. In point W1, which is not affected by the Goławiecki stream's discharge but receives effluents from other mines and operations, the values of the parameters that indicate salinity are greater than those measured in the first water analysis. The conductivity in point W1 increased between the two sampling campaigns from 3.03 mS/cm to 6.78 mS/cm. The chlorides concentration increased from 1190 mg/L to 2110 mg/L, the calcium ions from 95.9 mg/L to 191 mg/L, the magnesium ions from 47.1 mg/L to 157 mg/L and the sulfates content from 86.5 mg/L to 203 mg/L. In some cases, the parameters doubled or even tripled. This increase indicates that during the spring months, other mines located in the area upstream of point W1 discharged a greater load of salinity into Small Vistula. However, in point W2, the second water analysis—like the first—has demonstrate the pollution of the Small Vistula River originating from the Goławiecki stream, since all the water parameters are elevated compared to point W1. The TSS content increased from 12 mg/L in point W1 to 56 mg/L, the conductivity increased from 6.78 mS/cm to 7.86 mS/cm, the chlorides concentration increased from 3780 mg/L to 4070 mg/L and the magnesium ions increased from 157 to 169 mg/L. Despite the rise in the water parameters between the two points, it has to be noted that the difference between them is minor. It is clear that the surface water quality in the area is a result of a complicated pattern of mine water discharges upstream of the study area. Still, the impact of indirect mine water discharge in this area is evident on the whole surface water system, not only on the Goławiecki stream. The nutrient condition in the study area (presence of nitrates and phosphates) is quite good, as it is no higher than 16 mg/L, while the phosphate content does not exceed 10 mg/L in the Goławiecki stream and is less than 1 mg/L in the Small Vistula River and the Korzeniec stream.

### 4.5. Biological Water Quality

According to the abiotic classification of the types of surface waters in Poland, which was created for the purposes of monitoring studies, the Goławiecki stream has been recognized within the River code as a carbonate—upland stream with a fine-grained substrate based on loess and loess-like substances (Type 6), and it belongs to the biocenotic type III. According to the MMI_PL index classification, in the sites G1, G2, and G3, the ecological status of water can be defined as bad (class V), which means that the selected habitat for aquatic biocenoses differs significantly from the natural conditions. The value of MMI_PL for G1 was 0.073; for G2 it was 0.0, and for G3 it was 0.064. The biocenotic type III for class V is below 0.233. However, it must be noted that the aquatic area's ecological status cannot be connected only to the mining operations. Both agriculture and other activities take place in the area, affecting its ecological status.

The same abiotic classification recognizes the Vistula within the River code "The Vistula from Biała to Przemsza" as a lowland sandy–clay river (Type 19), and places it in the biocenotic type V (Table 4). In the MMI_PL index, the water quality class of both sites selected in the Vistula River can be defined as bad (class V), which means that the selected habitats for aquatic biocoenoses differ significantly from the natural conditions. The value of the MMI_PL index for W1 was 0.040, and that for W2 was 0.118.

**Table 4.** Density (ind./m$^2$) and diversity (Shannon–Wiener and Pielou diversity indices) of benthic invertebrates from the polluted area (G1, G2, G3, W1, W2) and the non-polluted stream (K); *P. antipodarum*—*Potamopyrgus antipodarum*.

| Taxa | | | G1 | G2 | G3 | W1 | W2 | K |
|---|---|---|---|---|---|---|---|---|
| Crustacea | Isopoda | *Asellus aquaticus* | - | - | - | - | - | 56 |
| | Amphipoda | *Gammarus tigrinus* | - | 1 | 3 | 1059 | 2242 | - |
| Oligochaeta | | | - | - | - | 2 | 58 | 39 |
| Hirudinea | Glossiphonidae | *Helobdella stagnalis* | - | - | - | - | - | 1 |
| Insecta | Plecoptera | Taeniopterygidae | - | - | - | - | - | 1 |
| | Trichoptera | Hydropsychidae | 2 | - | - | 8 | 1 | 28 |
| | | Leptoceridae | - | - | - | - | - | 7 |
| | | Limnephilidae | - | - | - | - | - | 4 |
| | Ephemeroptera | Baetidae | - | - | - | - | - | 12 |
| | Odonata | Calopterygidae | - | - | - | - | - | 4 |
| | | Aeshnidae | - | - | - | - | - | 1 |
| | Megaloptera | *Sialis lutaria* | - | - | - | - | - | 7 |
| | Coleoptera | Dytiscidae | - | - | - | - | - | 3 |
| | | Scirtidae | - | - | - | - | 1 | - |
| | Diptera | Chironomidae | 276 | 680 | 1591 | 1 | - | 173 |
| | | Ceratopogonidae | 1 | 15 | - | - | - | 4 |
| | | Simullidae | - | - | - | - | - | 9 |
| | | Pedicidae | - | - | - | - | - | 3 |
| | | Syrphidae | 270 | 8 | - | - | - | - |
| | | Ephydridae | 1 | - | - | - | - | - |
| | Heteroptera | Corixidae | 0 | - | - | 1 | - | - |
| Gastropoda | Planorbidae | *Segmentina nitida* | - | - | - | - | - | 1 |
| | Hydrobidae | *P. antipodarum* | - | - | - | 343 | 119 | - |
| | Bithynidae | *Bithynia tentaculata* | 18 | - | - | - | - | - |
| | Physidae | *Physella acuta* | - | - | - | 1 | - | - |
| Bivalvia | Sphaeriidae | | 2 | - | - | - | - | 1 |
| | | Total benthos density | 570 | 704 | 1594 | 1415 | 2421 | 354 |
| | | Number of taxa | 7 | 4 | 2 | 7 | 5 | 18 |
| | | Shannon-Wiener index | 0.876 | 0.176 | 0.014 | 0.614 | 0.297 | 1.764 |
| | | Pielou index | 0.45 | 0.127 | 0.02 | 0.316 | 0.184 | 0.61 |

The results of the MMI_PL index indicate that the water quality class of the Korzeniec stream can be defined as moderate (class III), which means that the selected habitats for aquatic biocoenoses differ moderately from the natural conditions. This study shows the highest values of MMI_PL in this system (Table 4) in comparison to other systems studied. In rivers that do not remain under the pressure of indirect saline effluent discharge, the ecological status of the water is higher, as has been shown in the case of the Korzeniec stream.

The main problems caused by coal mine activities are the salinization and acid mine drainage in the aquatic environment. These result in adverse effects on river functioning and the diversity of biological life. Freshwater salinization is an emerging water quality problem [31–33]. Limiting the salinity of waters will improve their quality, and will also increase biodiversity, provided that other pollutants do not get into the rivers.

Benthic invertebrates are used widely as a biological monitoring tool to detect and assess the extent of human impacts on freshwater systems [34]. There is also a strong need to monitor rivers' ecological status, especially in areas of coal mine activities and after mine closure. As was shown in the study of [35], in the area of gold mine activity, the extreme saline conditions strongly influence the present biota, more than 10 years after the cessation of mining activities at Con Mine. Analyses by Kaushal et al. [36] have shown that freshwater, as one of the most precious resources, is now becoming seriously degraded with multiple ions and chemical mixtures globally, on regional and local scales. Salinization will likely increase in severity and pressure existing freshwater resources tremendously [36]. This will also have an impact on natural stream recovery in areas where salinization is a constant process, such as in the area of our study.

### *4.6. Comparison of Diversity and Density of Aquatic Invertebrates in the Water Systems*

The overall diversity at the monitoring points of the surface waters impacted by saline effluents was lower than in the clean stream, as seen both in the values of diversity and in the number of taxa (from 2 to 7 in the area and 18 in the clean stream) (Table 4). The greatest diversity of benthic invertebrates was found in the Korzeniec stream, despite the lowest density of benthos being found at this site (Table 4). Chironomidae larvae were the most numerous in the Goławiecki stream, while their density increased with the course of the stream. At the G1 site, numerous Syrphidae were found, as this species is extremely resistant to pollution. Only two taxa were recorded at G3, and therefore the diversity of benthic fauna at this site was the lowest (0.014 and 0.02 for Shannon–Wiener and Pielou indices, respectively). The highest density of benthos was found at G3, which was caused by a large number of Chironomidae. In the Vistula River, high densities of two invasive species were found: *Gammarus tigrinus* and *Potamopyrgus antipodarum*.

Coal mine drainage often contains a mixture of acidic waters high in dissolved metals [37] and concentrations of chlorides and sulfates. The diffusion of ions from mine effluents in waterways results in a possible severe threat to stream invertebrate communities. The effects of salinity are notable for different organisms like prokaryote communities in groundwater [38], algal assemblages [35], and benthic invertebrates [39]. Salinization can therefore also modify the ecological status of the water, as was shown in our study, but also be a factor favoring the appearance of alien and invasive species.

Advancing our understanding of how salinity influences benthic invertebrates is urgently needed in order to improve the prediction of invertebrate responses to environmental changes and to protect biological diversity [40]. According to Echols et al. [41] and Kefford et al. [42], at very high conductivity, the concentration at which 50% mortality occurs in bioassays (LC50) for freshwater invertebrates is generally greater than 2000 µS/cm. In our study, we showed different values of salinity and different structures of benthic communities.

According to [36], if the upward trend in freshwater salinization continues, the affected ecosystems will no longer be "fresh" and no longer have the same biological properties. Evolution and natural selection have resulted in species that occupy low-conductivity niches in freshwater ecosystems [39]. Aquatic pollution forces invertebrates to react to unfavorable changes; depending on the extent of the pollution, the structure of invertebrate communities changes, and this has an impact on the ecological status of the water. According to Olson and Hawkins [39], if freshwater taxa have evolved to specialize in or tolerate specific ranges of salinity, relatively small human-caused increases in salinity could adversely affect freshwater invertebrate biodiversity at both local and regional spatial scales.

## 5. Conclusions

The water quality analysis of the stream that indirectly receives the coal mine effluent, and the Small Vistula River zone, including the stream's estuary, has indicated an excessive salinity load. In some of the water samples, the conductivity reached the level of seawater, with the content of chlorides and sodium ions being the most elevated throughout the aquatic area. Observing the two water quality analyses, a notable decrease in the salinity of the Goławiecki Stream has been detected as a result of two different factors: the first one is that the rainy season intervened between the two sampling campaigns, and the second is the change in the quantity or composition of the discharged mine waters between the two sampling campaigns. The second reason is believed to have played a major role since the mine has been conducting a series of measures to reduce the amount of indirectly discharged water. In the Small Vistula River, however, the opposite was observed. The salinity level rose between the two sampling times, indicating that a greater salinity load had been discharged into the river during the spring months upstream of the study area. However, the impact of ion diffusion in the study area via the Goławiecki stream is still evident.

The high pressure of salinity is clearly reflected in the diversity and density of benthos invertebrates. Mine effluents have an impact on biological elements, and establish the ecological status of rivers, as well as influencing the appearance of invasive species in disturbed river ecosystems. In affected watercourses, different structures of invertebrate communities are detected.

In conclusion, the treatment of coal mine wastewater is important in order to reduce its impact on the water quality, the aquatic life, the flora and fauna of the area surrounding surface water, public health, and the economic activities associated with the surface water body. Further research will show how the salinity will impact the biological metrics and water chemistry in the longer term. Further research on the implementation of advanced methods of salt and resource removal from saline mine waters will show whether they enable the elimination and full recovery of resources from saline waters originating from hard coal mining, as well as the purification and direct recovery of end products (salt and water) of high quality and purity.

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