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Analysis of the Salinity of the Vistula River Based on Patrol Monitoring and State Environmental Monitoring

Andrzej Woźnica [1,*], Damian Absalon [1], Magdalena Matysik [1], Małgorzata Bąk [2], Anna Cieplok [3], Dariusz Halabowski [3,4], Adrianna Koczorowska [3], Mariola Krodkiewska [3], Marcin Libera [5], Edyta Sierka [3], Aneta Spyra [3], Robert Czerniawski [6], Łukasz Sługocki [6] and Bartosz Łozowski [1,*]

1 Silesian Water Centre, Faculty of Natural Sciences, University of Silesia in Katowice, 40-007 Katowice, Poland
2 Institute of Marine and Environmental Sciences, University of Szczecin, 70-383 Szczecin, Poland
3 Institute of Biology, Biotechnology and Environmental Protection, Faculty of Natural Sciences, University of Silesia in Katowice, 40-007 Katowice, Poland
4 Department of Ecology and Vertebrate Zoology, Faculty of Biology and Environmental Protection, University of Lodz, 90-237 Łódź, Poland
5 Faculty of Science and Technology, University of Silesia in Katowice, 40-007 Katowice, Poland
6 Institute of Biology, University of Szczecin, 71-415 Szczecin, Poland
* Correspondence: andrzej.woznica@us.edu.pl (A.W.); bartosz.lozowski@us.edu.pl (B.Ł.)

Abstract: Background: Secondary salinity of river water reduces the value of ecosystem services, negatively impacting the entire aquatic ecosystem and reducing the possibility of water use. In Poland, significant anthropogenic salinity of rivers and water reservoirs is usually associated with mining activity consisting of pumping salty mine water into settling ponds or often directly into rivers. However, to assess the reasons for the salinity of the Vistula waters, it is necessary to identify all sources of salt in surface waters, enabling the assessment of the salt load in the waters. Methods: The paper presents four sources of data which have been compiled to propose a valuable method for analyzing the threat of the river. Patrol monitoring was one method of data acquisition, and State Environmental Monitoring data ware also used. Clustering and correlation statistical techniques were used for analysis. Results: Of the 20 physical and chemical parameters analyzed, chloride, calcium sulphate and magnesium ions are important for salinity. Measurements with multi-parameter probes allowed for the identification of increased salinity pressure sites, while flow analyses were required to calculate the load. Conclusions: The Vistula River had the highest concentrations of the analyzed ions in the Silesia Region. The use of patrol monitoring can be highly useful in determining the causes of emerging problems with water quality and supporting State Environmental Monitoring.

Keywords: patrol monitoring; Vistula River; secondary salinization; water quality; pollution; anthropopressure; mining's water; water ions

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1. Introduction

Water salinity is related to the appearance of inorganic ions in surface waters, such as chlorides, sulphates, nitrates, sodium, calcium and potassium. The increase in the concentration of these ions in surface waters may be the result of natural runoff from the catchment area from the erosion of rocks and minerals (primary salinization) or could be a consequence of human activity, namely through the discharge of sewage into rivers, runoff of surface waters containing ions from artificial fertilizers or from the discharge of saline groundwater to surface water (secondary salinization) [1]. Among the causative sources of salinity may be human activities such as mining, using salt as a road de-icing agent or irrigation of fields, as a result of which salt is leached from the soil [2]. The source of substances dissolved in a saline aquatic environment may be the mixing of precipitation water with saline water (seawater, hydrothermal waters, mine waters); dissolution of evaporites left after the last withdrawal of seawater or brine; weathering of aquifer minerals;

accumulation of salts from long-term deposition of precipitation; pollution with sewage (domestic or industrial); and salinization as a result of the discharge of agricultural water (farm sewage, surface runoff from agricultural fields) [3]. It may also result from the concentration of surface waters used in agriculture. The removal of native vegetation and inefficient large-scale irrigation systems also contributes to the increase in salinity. Both increase evaporation, causing condensation of the salt concentration. Agricultural chemicals, animal excrements and municipal wastewater also contribute to the increase in ion concentrations in surface waters. In addition, increased evapotranspiration as a result of irrigation of agricultural fields causes an increase in salt concentration in surface runoff water, which in turn leads to an increase in salinity. Irrigation practices, plant water use and groundwater processes are critical to understanding salt accumulation, mobilization and agricultural movement [4,5].

Secondary salinity of water significantly reduces the value of ecosystem services provided by water-related ecosystems by affecting organisms living in water [2,6] and the possibility of recreational use of surface waters. The consequence of the increased salt content in the waters may be the limitation of the possibility of using surface waters for irrigation. On the other hand, due to changes in the living conditions of aquatic plants and animals living in watercourses (saline waters) and wetlands (salted land), increased salinity may cause ecosystem changes leading to a decrease in biodiversity [7]. Secondary salinization of rivers is a growing global problem that may be exacerbated by anthropogenic changes in the hydrological cycle with ongoing climate change [8]. The influence of climatic factors on salinity is quite obvious: high temperatures increase evaporation from the water surface, which, for the same load, results in an increase in salt concentration in the river. On the other hand, precipitation influences an increase in river flows, which, for the same load of salt supplied with mine water, results in a decrease in the salt concentration in the rivers. Moreover, an increase in the salt content of water can lead to the distribution and overgrowth of eurytopic organisms (including alien and alien invasives species) such as *Prymnesium parvum* N.Carter, which can lead to the so-called "Mass Fish Kills" phenomenon. In the summer of 2022, such an event was observed in Poland in the Oder River, which is one of the largest rivers in Central Europe. Literature analyses indicate the prevalence of such phenomena in the world. The largest fish kills associated with *P. parvum* have occurred in the United States [9–12] and Norway [13]. Another unfavorable consequence of the increased salinity of inland waters may be increased costs of treating water from surface sources used for consumption. It is, therefore, necessary to assess the economic and environmental impact of using such brackish water for irrigation, which is needed for some regions due to ongoing climate change. Therefore, the problem of secondary salinity requires raising community awareness, better understanding and developing better management systems, in particular, nature-based solutions [5,14,15].

In Poland, significant anthropogenic salinity of rivers and water reservoirs is usually associated with mining activity, consisting of pumping salty mine water into settling ponds or often directly into rivers. This is particularly intensive in the Upper Silesian Coal Basin (USCB), one of the world's largest hard coal mining areas. Currently, about 35 hard coal mines are still operating in this area, which directly or indirectly pump salt mine water into rivers, including one of the largest rivers in Central Europe (the Oder and the Vistula) [16]. So far, no comprehensive research has been undertaken, including the analysis of environmental variables along the entire course of these rivers, in order to locate at least the main sources of anthropogenic salinity. With this in mind, in July 2021, a research expedition was carried out along the Vistula River, during which the water's physical and chemical parameters were analyzed at distances of approximately 1.4 km.

In the Vistula river basin, the causative factors of increased ion content in the water should be taken into account, such as discharges of underground waters from Upper Silesian mines, runoff of domestic sewage, surface runoff from agricultural areas (fertilizers, irrigation), the inflow of cooling water from power plants (Połaniec and Kozienice), discharges of saline waters in other areas (regions of Toruń and Kujawy) and other unidentified sources of ions in the catchment, which have not yet been identified but were located during the research expedition. Therefore, to assess the reasons for the salinity of the Vistula waters, it is necessary to identify all sources of salt in surface waters, enabling the assessment of the salt load in the waters. This applies not only to large brine emitters such as mines, power plants and heating plants based on heat exchangers using highly mineralized water but also to small dispersed brine emitters, where the introduced salt load can be significant in the overall balance of salt load in surface waters. So far, there has been no comprehensive study that has analyzed the state of the water in the Vistula from Goczałkowice to Gdańsk in a uniform manner simultaneously.

This study aimed to assess the impact of discharges of saline waters on the condition of the Vistula waters, together with the assessment of salinity changes resulting from the water supply by tributaries and the immobilization of ions in organic matter on the section from the 41.5 km mark of the Little Vistula (Goczałkowice sluice) to the 941.5 km mark of the Vistula (the mouth of the Vistula at the Baltic Sea) as well as develop new methods for quantitative and qualitative assessment of the concentration of substances dissolved in water. For this purpose, the measurement results collected during the research expedition on the Vistula River on 18–31 July 2021, on the section of the Vistula River from Goczałkowice to Gdańsk, were used. At an average interval of about 1.4 km, analyses of the physical and chemical parameters of the Vistula River water were carried out in the field. This resulted in 693 online water measurements using multi-parameter probes. At the previously selected points, most important from the point of view of the salinity of the Vistula River, additional water samples were collected for chemical analysis in an accredited laboratory, and water flow measurements were made in the Vistula. This allowed the determination of the speciation of the analyzed ions in the water and to balance the salinity in the studied section of the Vistula (determination of loads of substances dissolved in water). The obtained results were compared with the results of monitoring carried out at some points by the General Inspectorate of Environmental Protection (GIOŚ) of the Surface Water Bodies (JCWP) of the Vistula for the period 2016–2019 [17].

2. Materials and Methods

2.1. Subject of Research

The Vistula is the longest river in Poland according to its mileage; it is 1046.7 km (105.5 + 941.2) long. From the point of view of the morphology of the river, four sections are distinguished: Little Vistula (LV) from the 105.5 to 0.0 km points of the river (from the source to the mouth of the Przemsza River); Upper Vistula (UV) up to the 279.7 km point of the river (to the mouth of the San); the middle Vistula (MV) up to the 674.5 km point (Włocławek sluice); and the Lower Vistula (LoV) up to the 941.2 km point (the mouth to the Baltic Sea). A total of 23 surface water bodies (JCWP) have been identified in the Vistula area. The total area of the Vistula River basin is 182.6 km^2, of which 3.932 thousand km^2 cover the catchment area of the Little Vistula, 42.98 thousand km^2 cover the catchment area of the Upper Vistula, 100.6 thousand km^2 cover the catchment area of the Middle Vistula and 34.97 thousand km^2 cover the catchment area of the Lower Vistula. The river is divided across 12 thresholds: Wisła Czarne (96.5 km of the MV), Goczałkowice (41.3 km of the MV), Dwory (4.35 km of the river), Smolice (19.5 km of the river), Łączany (57.8 km of the river), Kościuszko (66.4 km of the river), Dąbie (80.8 km of the river), Przewóz (92.6 km of the river); Włocławek (674.5 km of the river) and thresholds on the river near the Połaniec power plant (223.65 km of the river) and Kozienice (425.95 km of the river). The Vistula River is considered to be the last river in Europe whose landscape (in large part) is that of a natural, unregulated, large European river. In fact, on the section of the upper Vistula River, there is a 92.3 km canalized section (from the mouth of the Przemsza River to the Przewóz sluice below Kraków). On the Central and Lower Vistula sections, numerous unrepaired groynes constitute the hydrotechnical constructions of the existing E40 and E70 waterways. In addition, the Vistula River has ramparts almost along its entire course.

The distribution of the Vistula river basin area is asymmetric, with about 73% of the basin area falling on the right-bank tributaries, where the course of geological structures plays a significant role [18]. The Vistula starts in the Silesian Beskid Mts, belonging to the Outer Western Carpathians, which are made up of several overlapping flysch series—the mantle—consisting of alternating layers of shale and sandstone, with local marls and limestone. After leaving the Carpathian Mountains, the Vistula flows into the area of the Northern Subcarpathians area. From the Silesian Upland, rivers carrying saline mine waters, resulting from the drainage of underground coal mines, flow into the Vistula. The inflow cones of the Carpathian rivers drive the Vistula to the northern margins of the Northern Subcarpathians. In the Sandomierz area, the river reaches a watershed section in the bedrock of outcrops of old Palaeozoic rocks belonging to structures known from the Świętokrzyskie Mountains. It then flows north and northwest along the edge of the Precambrian East European Plate. However, the riverbed's bedrock is a thick series of Palaeozoic and Mesozoic sediments. The Vistula valley to Puławy was eroded in the bedrock of the Mesozoic Cretaceous and Palaeocene series of lithic rocks, while, in the Masovia basin, there are local Neogene or Palaeogene layers under the Vistula's channel sediments. In the vicinity of Fordon, the river touches the Western European Palaeozoic platform. It turns towards the north, flowing over old rocks of the Eastern European platform, in which a smaller unit—the Peribaltic Syneclise, covered by Palaeozoic and Mesozoic sediments—is distinguished.

2.2. Patrol Monitoring

The data were collected during the research expedition, the form of patrol monitoring consisting of many measurements made in a short time on sections of the river or lake surface. Based on this type of monitoring, it is possible to analyze the spatial distribution of selected parameters. Patrol monitoring was proposed in [19] and enables the location of pollutant discharges, showing the area of river waters mixing with tributary waters.

In this study, patrol monitoring was realized by the use of online measurements of the physical and chemical parameters of the Vistula River water using multi-parameter Xylem YSI ProDSS (Yellow Springs, OH, USA) and YSI EXO2 (Yellow Springs, OH, USA) probes equipped with detectors for measuring dissolved oxygen, pH, RedOx potential, conductivity, turbidity, chlorophyll a, phycocyanin, Cl^- ion-selective electrodes and fluorescent dissolved organic matter (fDOM). In total, 693 measurements were performed at average intervals of about 1.4 km (Figure 1A). The mass of salt was determined based on the PSU (probe) value, assuming that 1 PSU corresponds to 1 mg of salt, according to UNESCO [20] and Millero [21]. The probes were equipped with the Global Positioning System (GPS) World Geodetic System 84 (WGS 84) for determining the measurement position and measuring the depth of immersion of the probe during the measurement. Data pre-processed by YSI KorDSS 1.7.4.0 and exported to Microsoft Excel 2018 were statistically analyzed using TIBCO Software Inc. Statistica 13.3 (data analysis software system) and for spatial analysis using QGIS 3.26 and Golden Software Surfer 23.

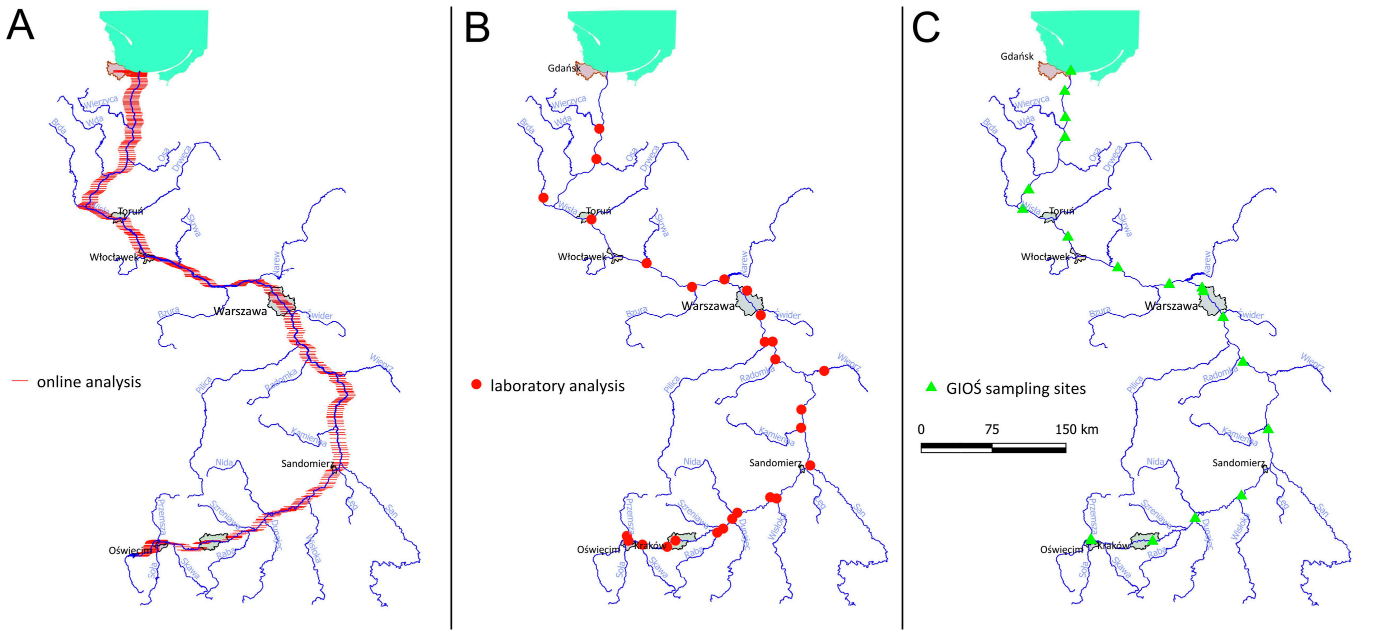

Figure 1. Maps of the location of sampling sites on the Vistula River used in this paper: (**A**) Measurement points for the Vistula River scientific expedition with the use of multi-parameter probes on 18–31 July 2022; (**B**) Sampling sites for analysis performed in accredited laboratories; (**C**) Sampling sites of the General Inspectorate of Environmental Protection (GIOŚ) on the Vistula in the 2016–2019 period which were used in the analysis.

During the expedition, samples were collected for the laboratory analysis of water quality from 20 points of the Vistula River, which are crucial from the hydrological point of view (Figure 1B). The samples were delivered to the laboratory immediately after sampling. Analyses of the quality of water samples taken during the trip included 30 physical and chemical parameters. The following analyses were performed in an accredited laboratory: organochlorine pesticides (PN-EN ISO 6468:2002); sulfates, PB-128 ed. and of 15.06.2011, dissolved substances (PN-EN 15216:2010); general alkalinity (PN-EN ISO 9963–1:2001) + Ap1:2004; chromium (VI) (PN-EN ISO 18412:2007); cation content (PN-EN ISO 17294-2:2016); phosphorus (PN-EN ISO 11885:2009); ammonium nitrogen (PN-ISO 5664:2002); Kjeldahl nitrogen (PN-EN 25663:2001); chlorides (PN-ISO 9297:1994), phosphates (PB-127 ed. and of 15 June 2011); volatile organic compounds (PB-147/GC ed. II of 20 October 2014); petroleum hydrocarbons as an index of mineral oil (PN-EN ISO 9377-2:2003); and free and bound cyanides (PB-129 ed. and of 15 June 2011) [22].

2.3. Flow Measurements of the Vistula River

During the research expedition, apart from observing water gauge stations in 20 sections of the Vistula riverbed, water flow velocity measurements were performed using the Acoustic Doppler Current Profiler (ADCP) SonTek RiverSurveyor M9 (San Diego, CA, USA), acoustic current meter, which works on the principle of ultrasonic wave reflection. The flow measurement was carried out continuously. Using a compass and a GPS receiver causes each measure (automatically selected by the device depending on the channel characteristics) to be vertically oriented in space, giving complete information about the location and direction of individual velocity vectors in the entire measurement cross-section [23]. Measurements of water flow velocity were used to determine salt loads in the Vistula waters. A load of salt in water presented in the paper resulted from the concentration of ions determined in water samples carried out in laboratory tests and the flow rate specified in the tested profiles.

2.4. Data Compilation

In this paper, four sources of data were compiled and analyzed: data obtained during a scientific expedition on the Vistula River in the period from 18 to 31 July 2021, laboratory physical and chemical analyses of water from the same expedition, flow of water from measurement points and state monitoring data obtained from the General Inspectorate of Environmental Protection (GIOŚ) for the period 2016–2019 (Figure 1C). These analyses included 20 water quality parameters from samples taken in 22 JCWP of the Vistula River. To determine the average value of the analyzed parameters in the JCWP of the Vistula River, online measurements were assigned to the areas of the JCWP of the Vistula River based on GPS spatial location. The number of measurement points per each JCWP of the Vistula River is shown in the table (Appendix A Table A1).

2.5. GIS Data Analysis and Statistical Analysis

Databases, processing and construction of result matrices were carried out and analyzed using Microsoft Excel 2018, TIBCO Software Inc. Statistica 13.3 (data analysis software system) and OriginLab Origin 9.0. The maps of the variability of the Vistula's physicochemical parameters were created on the basis of physicochemical measurements using multi-parameter probes with a GPS locator using the kriging method using Golden Software Surfer 23. QGIS 3.26 was used for spatial analysis and the spatial location of points. To assess the relationship between the analyzed physical and chemical parameters of the Vistula River water, hierarchical clustering analysis [24] and Spearman's rank correlation analysis were used [25]. Statistical analyses of water quality for the JCWP of the Vistula River were carried out based on data obtained from the GIOŚ and grouped according to the JCWP code. Then, the 1st, 2nd, 3rd quartile, minimum and maximum for non-outliers and extreme values were determined for each JCWP.

3. Results

3.1. Salinization of the Vistula River

Online analyses using multi-parameter probes allowed for the preparation of longitudinal profiles of the Vistula River in terms of the analyzed parameters on the section from the Goczałkowice Reservoir (42 km LV) to the mouth of the Vistula River (941.2 km). Specific conductivity analyses showed a significant variation along the river's entire length (Figure 2A). Noteworthy is the high value of Total Dissolved Solids (TDS) in the upper course of the river in the area from the first discharge of mine water, which amounted to an average of 1124 mgL^{-1}, up to the mouth of the Dunajec River, and its maximum value reached 1 km of the Little Vistula and amounted to 8300 µS. Noteworthy also is the high conductivity maintained along the entire length of the Vistula up to its mouth. (Figure 2B,C). It also indicates the range of impact of the discharge of waters with a high content of mineral compounds, which had an effect up to the mouth of the Dunajec River (160.6 km of the Vistula River) (Figure 2B). The highest electrolytic conductivity of the Vistula water was observed in the water bodies covering the river's upper reaches. This was mainly due to the inflow of saline mine waters. Increased TDS values were observed up to the mouth of the Dunajec River, where it reached the value of 375 mgL^{-1} and remained at an average level of 458.6 ± 75.07 mgL^{-1} until the mouth of the Vistula into the Baltic Sea in Mikoszewo. In further analysis of the Vistula River waters, measurements made on the section from Goczałkowice to the mouth of the Vistula in Mikoszewo were used. It should be added that the measurements in the Przegalin lock (936)—Gdańsk (Martwa Wisła) section were rejected due to high water salinity associated with the strong influence of the Baltic Sea waters in this section (Figure 2A).

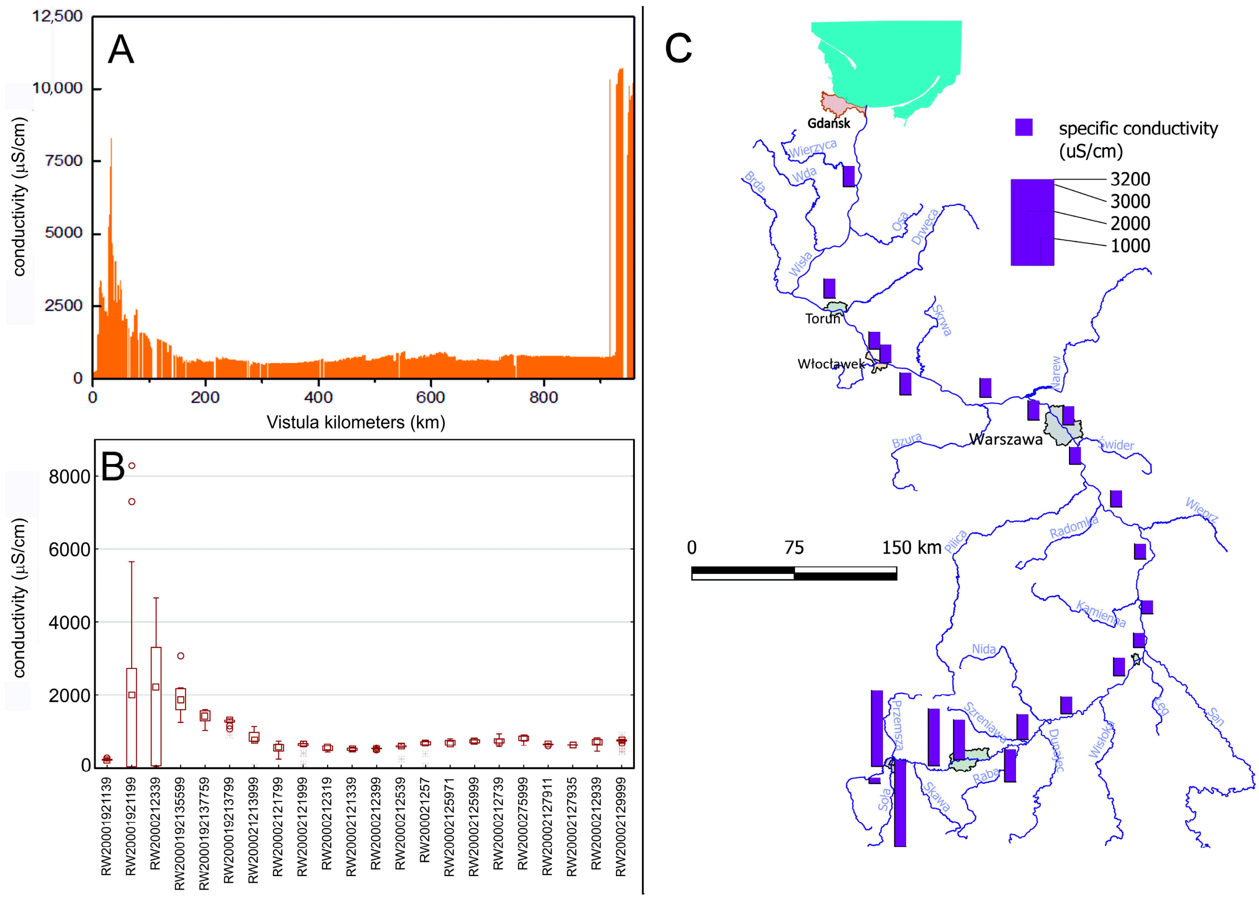

Figure 2. Analyses of specific conductivity measured with the multi-parameter probes Xylem YSI ProDSS and YSI EXO2: (**A**) Variability of the conductivity along subsequent kilometers of the Vistula (high conductivity in section 940–980 was recorded in the Martwa Wisła River and resulted from the large inflow of Baltic waters, hence, these measurements were not included in the analyses); (**B**) Variability of specific conductivity in the JCWP (squares—median, boxes—first and third quartile, whiskers—minimum and maximum values, circles—outstanding values; (**C**) Map of specific conductivity variability in the JCWP.

The hierarchical clustering analysis revealed two primary clusters: the first one contains mineral substances and elements dissolved in the water that significantly affect the content of TDS and electrolytic conductivity, and the second contains indicators related to the presence of nutrients in the water (Figure 3). Spearman's rank correlation analysis revealed high coefficients for the physical and chemical parameters of the Vistula River waters, indicating that the concentrations of Cl^- ions present in the water (0.93), Mg^{2+} (0.81) and sulfate ions (0.87) strongly, with positive correlation (statistically significant), impacted the observed TDS of the Vistula River waters. Additionally, TDS was affected to a lesser extent (lower correlation coefficients) by NO_2^- (0.64), Ca^{2+} (0.40), N-NH_4^+ (0.30) and P-PO_4^{3-} (0.22) ions. On the other hand, the increase in the content of P-PO_4^{3-} ions significantly reduced the TDS value (−0.35). Therefore, these parameters were used for analyses related to high water conductivity. The second cluster revealed high values of the correlation coefficient between Chlorophyll and Biological Oxygen Demand (BOD) (0.70), Chemical Oxygen Demand COD (0.58), pH (0.44) and water temperature (0.68). Negative correlations of Chlorophyll a with Ca^{2+}, N-NO_3^- and TOC ions may indicate the incorporation of these substances into the biomass of planktonic organisms. These parameters can be related to the growth of planktonic organisms in the water. It should be emphasized that the negative correlations existed between cluster II parameters and the concentrations of Mg and Ca ions, as well as TOC. The negative value of the correlation coefficient indicates the influence of these factors on the decrease in the concentration of the analyzed ions in the Vistula River waters. In addition, there is a significant effect of temperature on both TDS and conductivity as an effect of the concentration of ions dissolved in water ($N\text{-}NO_3^-$, $N\text{-}NO_2^-$, $N\text{-}NH_4^+$, Ca^{2+}, Mg^{2+}, SO_4^{2-}).

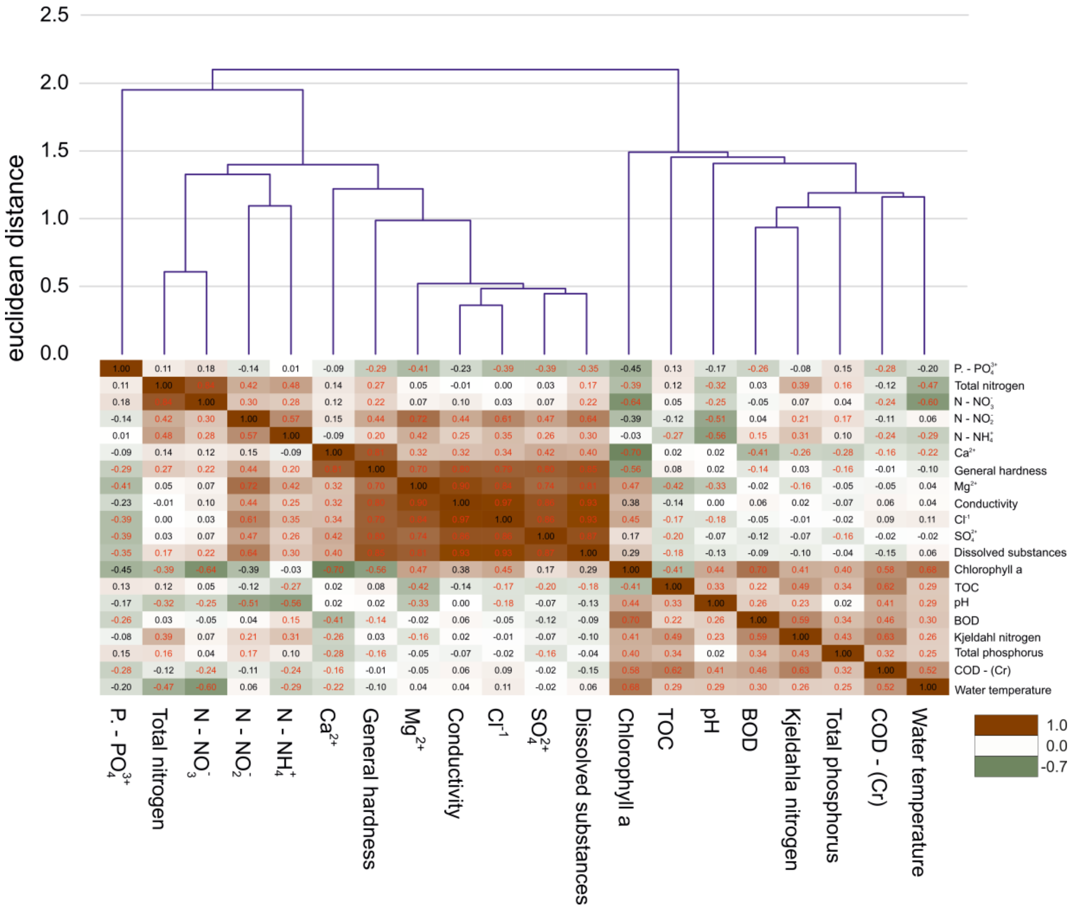

Figure 3. Analysis of the similarity of 20 parameters of the Vistula River water quality based on the value of the correlation of the Spearman's rank order determined on the basis of General Inspectorate of Environmental Protection (GIOŚ) data from the 2016–2020 period. Values of correlations are expressed as the color scale, where dark brown is the highest positive correlation (a decrease in the intensity of the brown color indicates a decrease in the correlation coefficient, up to the white color indicating no correlation), white is the lack of correlation, and dark green is highest negative correlations (a decrease in the intensity of the green color indicates a decrease in the correlation coefficient). Red correlation values indicate statistically significant correlations, $p < 0.05$.

The key section of the Vistula River (JCWP) in terms of salinity was located between the mouths of the Biała and Przemsza rivers. Therefore, Figure 4 shows the specific conductivity values in the water on 18 July 2021. In the analyzed section, a significant value increase was observed directly after the mine water's first discharge in the Silesia mine area in Czechowice (Figure 4A,D). The conducted analyses showed that the subsequent left tributaries of the Vistula River, namely the Gostynia and Potok Goławiecki rivers, significantly increased the specific conductivity values in the Vistula River waters. In contrast, right tributaries (e.g., the Soła River) caused a decrease in the specific conductivity values. The low specific conductivity value of the Przemsza River in the analyzed period was not expected, but it was observed and caused a decrease in the specific conductivity value of the Vistula River in the mouth of the Przemsza River (and in the lower section of the river).

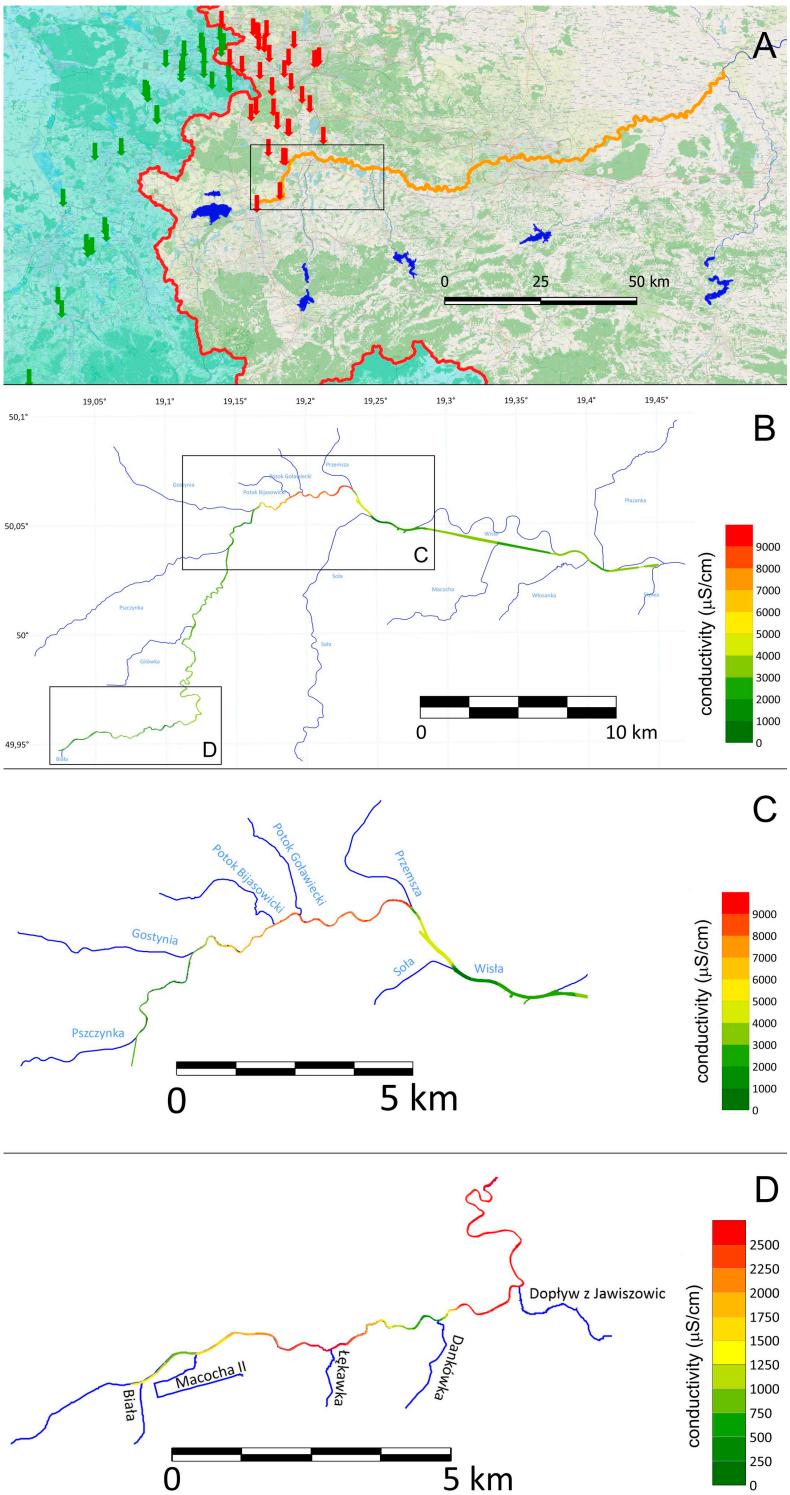

Figure 4. Map of the variability of specific conductivity in the waters of the Little Vistula. Values determined on multi-parameter probes Xylem YSI ProDSS and YSI EXO2, taken during an expedition on the Vistula River on 18 July 2021: (**A**) Map of the Little Vistula. (**B**) The specific conductivity variability in the area of the Little Vistula. (**C**,**D**) Areas with greatest salt water load. Red and green arrows show the locations of mine water dumps on Oder River catchment area (green area) and Vistula River catchment area (rest of map area). Map background licensed by the OpenStreetMap Foundation.

3.2. Ion Speciation in the Water

The speciation of anions, significant from the view of salinity in the waters of the Vistula River, was analyzed. Analyses were carried out based on measurement data obtained from the analysis of samples taken during the scientific expedition. The results of analyses of the state monitoring of GIOŚ for the period 2016–2019 were used for comparison. In this analysis, sodium and potassium cations were not included due to the lack of determination of these ions in the analyses of the state GIOŚ monitoring. The share of these ions can be estimated, assuming that they are dominant among the undetermined ions, and it can therefore be considered that the concentration of these ions is the difference between the TDS value and the sum of the concentrations of the other ions present in the water at the analyzed point. In the Vistula River waters, the water salinity level is determined by chloride and sulphate anions as well as sodium, potassium, calcium and magnesium cations. The differentiation of the share of these ions in the waters of the Vistula in the analyzed section indicates many sources of these ions in the waters of the Vistula River. The share of chlorides in the Vistula River waters changes, which dominated in the section of contamination of the Vistula River waters with mine waters in Silesia, accounted for up to 75% of the mass of ions in the tested waters and decreased to about 50% at the confluence of the Dunajec River with the Vistula River. At this level, it oscillated up to the mouth of the Vistula River into the Baltic Sea. The decrease in the share of chlorides was correlated with the increase in the share of sulphates.

The analysis of the speciation of ions in the Vistula River water samples taken during the expedition in the summer of 2021 indicates the dominance of Cl^- ions. The water also contained sulphates, calcium and magnesium cations, and the share of these ions increased from about 25% in the upper course of the Vistula River to over 50% in the lower course of the river. The share of nitrogen ions was small. The significant increase in the share of calcium ions should be emphasized, which in the lower section exceeded even 25% of the share of all ions. In the case of long-term monitoring analyses carried out by GIOŚ (for the JCWP of the Vistula River), chlorides dominated, as in our research, but despite higher total concentrations of the analyzed ions, their diversity was smaller. Apart from Cl^- ions, sulphates dominated in the water. A small amount of magnesium was also observed. Analyses of sulphate concentrations in the water of the Vistula River from the sources to the mouth, based on measurements of the GIOŚ (averages for the period 2016–2020), indicate a difference in the ionic composition of water in the case of the GIOŚ analyses and analyses carried out during the scientific expedition along the Vistula River. In both cases, chlorides dominated in the water. However, in monitoring studies, a small representation of sulphate anions and calcium and magnesium cations was observed, which accounted for less than 25% of the composition of all analyzed ions. In the studies carried out in July 2021, a 25% share of these ions was observed in the area of the Little Vistula. In subsequent sections of the Vistula River, this share systematically increased to about 50% (Figure 5).

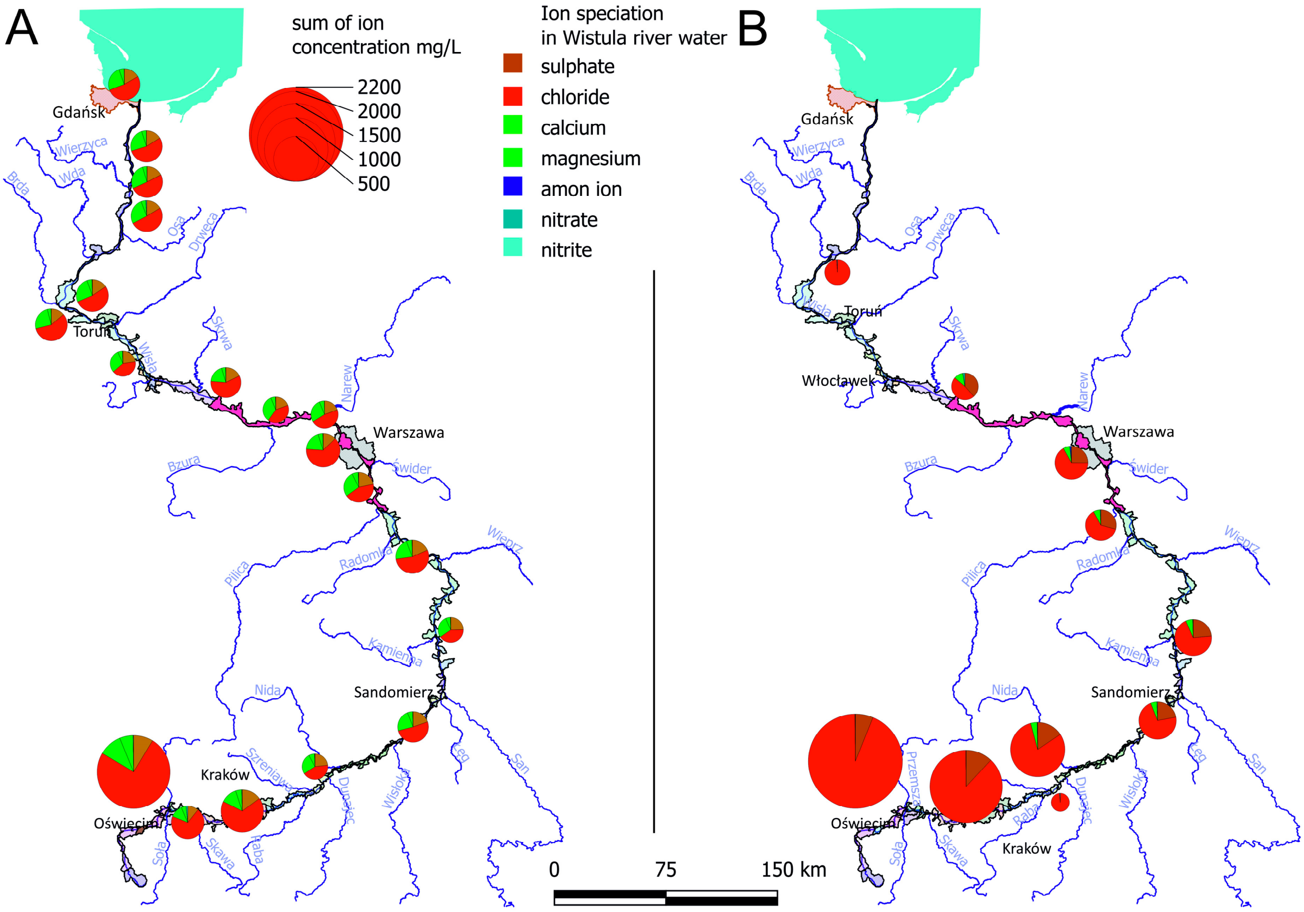

Figure 5. The share of the main ions accountable for the salinity of the Vistula River waters in TDS in the water collected from the Vistula River: (**A**) During the scientific expedition, analyzed in the accredited laboratory; (**B**) Based on the General Inspectorate of Environmental Protection (GIOŚ) data from the period 2016–2020.

The dominance of chlorides in the waters of the Vistula River indicated the need to conduct a detailed analysis of the concentrations of these ions in the waters of the Vistula River. The obtained results indicate a similar character of salinity of the Vistula River, indicating mine water discharges as a source of high concentrations of chlorides in the river. The observed decrease in salinity had a similar course, and the concentration of chlorides reached an equal value in both cases at the mouth of the Dunajec River. However, in the case of the analyses in the summer of 2021, the concentration values were higher than those in the WIOŚ analyses. The results of the conducted analyses indicate that the effects of the discharge of saline mine waters into the Vistula River can be observed up to the mouth of the Dunajec River. This is confirmed by the results of analyses using multi-parameter probes and laboratory analyses carried out during the expedition and measurements of the GIOŚ. In addition, the load of chlorides in the Vistula River in Warsaw or Korzeniewo was over ten times higher than in Oświęcim. Moreover, the observed differences in the concentration of chlorides in the Vistula River waters of the upper and lower reaches of the Vistula River result from the amount of water flowing in the river (Figure 6).

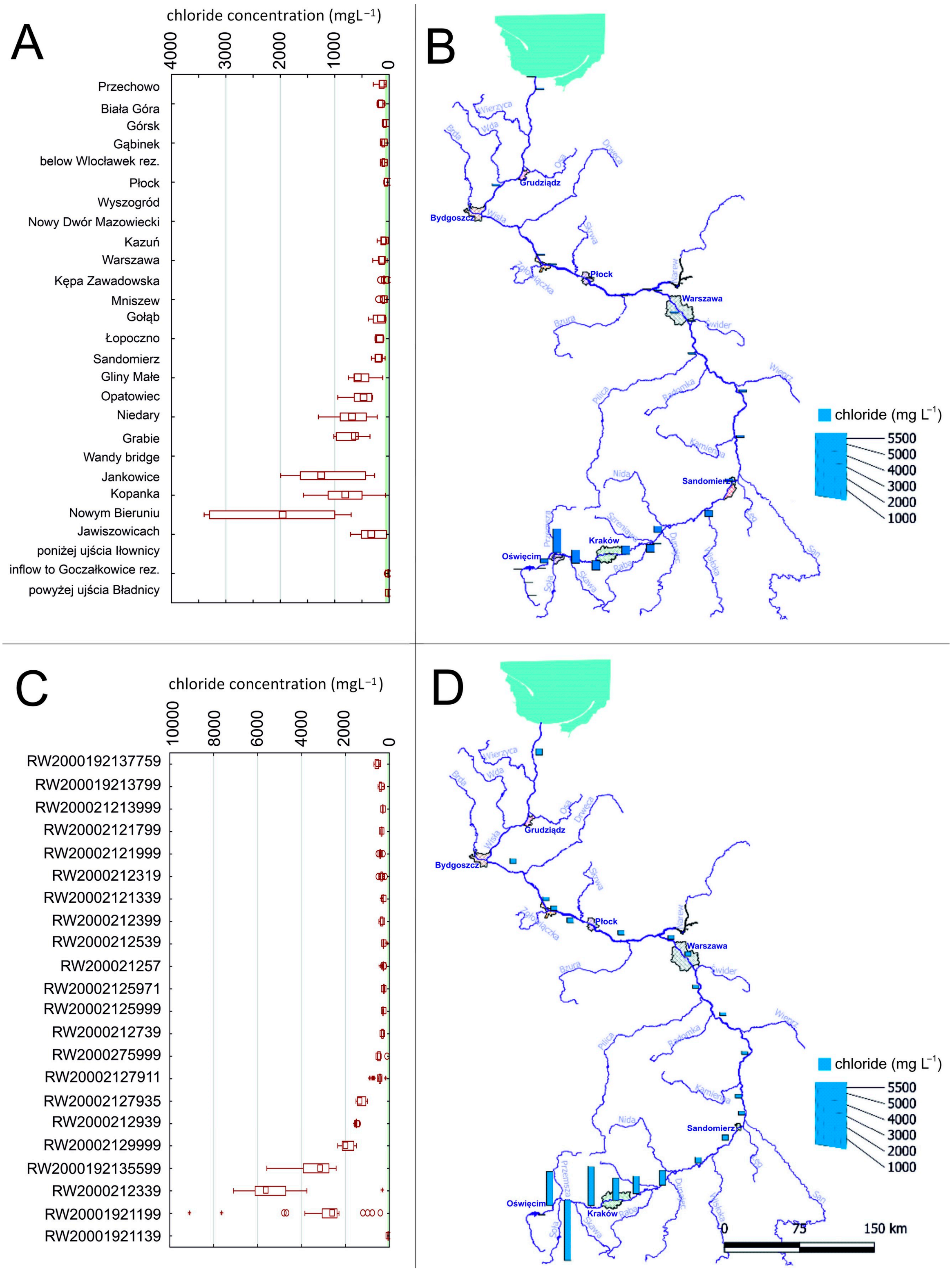

Figure 6. Variability of chloride concentration in the Vistula River: (**A**,**B**) Analysis based on the General Inspectorate of Environmental Protection (GIOŚ) data; (**C**,**D**) Measurements performed during the scientific expedition, values determined on multi-parameter probes Xylem YSI ProDSS and YSI EXO2, on 18 July 2021. For (**A**,**C**): squares—median, boxes—first and third quartile, whiskers—minimum and maximum values, circles—outstanding values and stars—extreme values; green and blue lines indicate the level of water classification as good quality according Polish law.

To balance the salinity in the Vistula River waters, the total salt load in the river waters was included and determined based on the concentration and flow rate of the Vistula River at the intake point. The performed analysis allowed us to estimate the total salt load in the Vistula River waters (Figure 7). It revealed that the load of chlorides in the Vistula River in the analyzed period systematically increased from Goczałkowice to the mouth part of the Vistula River. In addition, in the upper course of the Vistula River, despite high concentrations of chlorides, the salt load was lower and amounted mainly around the mouth part of the Przemsza River (0 km), with a concentration of about 986 mgL^{-1} a load was 735 Mg day^{-1}, and in Gassy (near Warsaw, 487.5 km) at a concentration of 96 mgL^{-1} a load was about 3.376 Mg day^{-1}. In comparison, the Lower Vistula (Korzeniewo 867 km) had a concentration of 121 mgL^{-1} and a load about 8000 Mg day^{-1}, which means that in Gassy and at the mouth of the Vistula to the Baltic, the load of chlorides is higher than at the mouth of the Przemsza at 4.6 and 9.4, respectively.

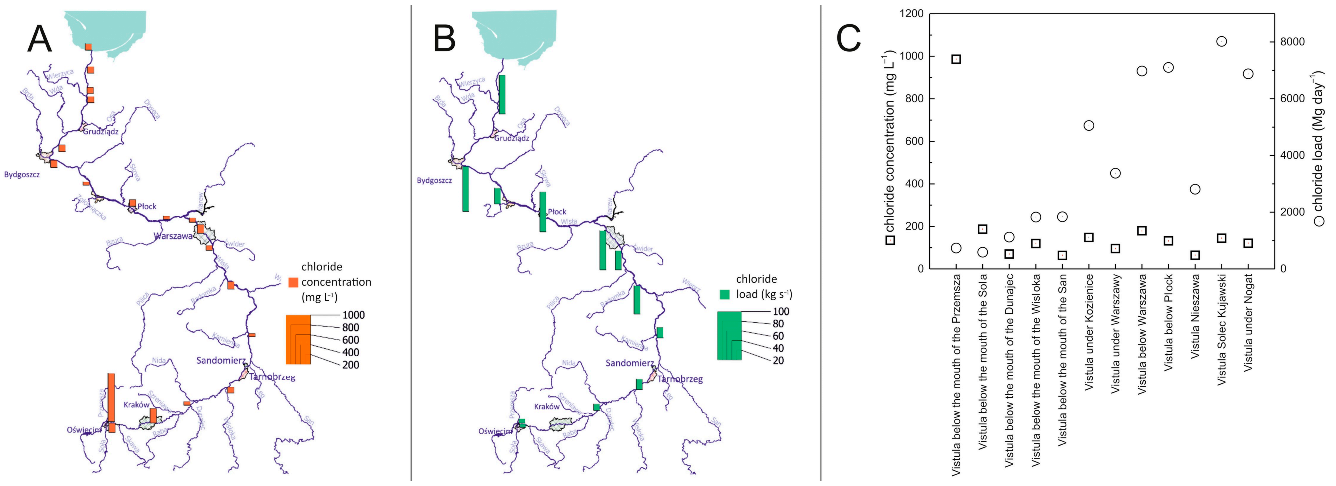

Figure 7. Changes in: (**A**) Chloride concentration in Vistula River; (**B**) Chloride loads in Vistula River; (**C**) Comparison of concentrations (squares) and loads (circles) of chloride in the Vistula River waters from Goczałkowice to the mouth part of the Vistula River, based on measurements with Xylem YSI ProDSS and YSI EXO2 multi-parameter probes. Loads were determined based on flow measurements in Vistula River cross-sections.

In the middle and lower Vistula sections, slight water salt concentration changes were observed. However, this translated into a large load of salt in the water in these river sections. Such changes were observed in the Vistula River near Kozienice, near the mouth of Świder to the Vistula River and in the area of Toruń at the ~740–750 km point of the Vistula (Figure 8). Such changes in the area near Kozienice can be explained by the accumulation or stopping of the flow of ions down the Vistula River and thresholds on the river near the Kozienice power plant. The cause of increasing salinity in the area of Toruń may be the discharge of saline industrial waters, including residues from sodium recovery plants in the area of Inowrocław or discharges of geothermal waters. However, it should be noted that the conductivity level in the middle and lower Vistula regions did not exceed 1000 μScm^{-1}. In the Silesia Region, the Vistula River had the highest concentrations of the analyzed ions. Still, due to low water flows, the ion load in the river was low and accounted for approximately 10% of the load at the mouth of the Vistula.

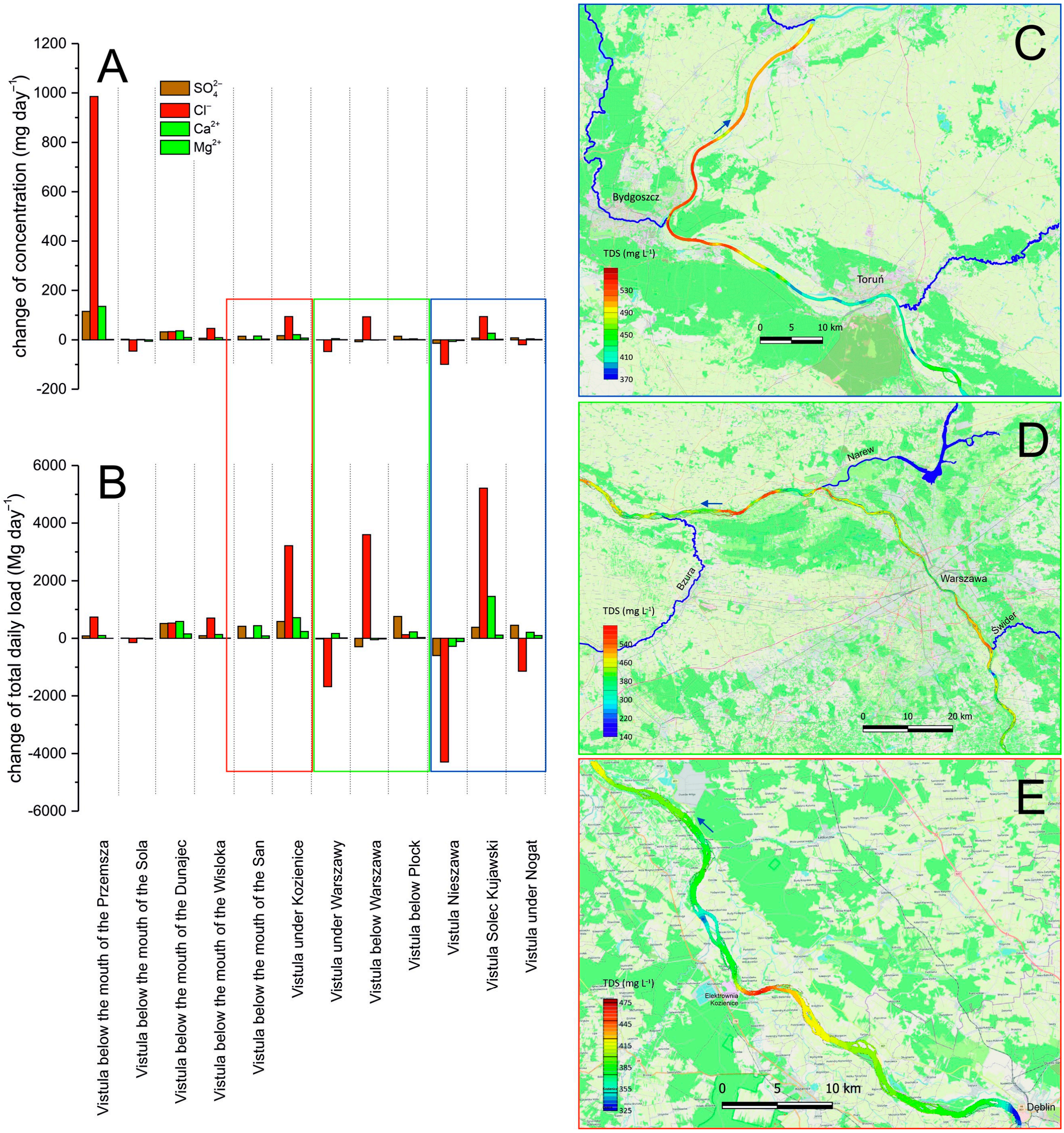

Figure 8. Changes in concentration (**A**) and loads (**B**) as well as speciation of ions accountable for the salinity of the Vistula River water in the section from Goczałkowice to the mouth part of the Vistula River based on the analysis of waters collected during the scientific expedition. The color of the three boxes in charts A and B corresponds to the color of the borders of the maps showing the corresponding sections of the Vistula River (**C**–**E**). Map background licensed by the OpenStreetMap Foundation.

4. Discussion

Salinization of inland waters may vary from 10 mgL^{-1} to 100 gL^{-1} and can be the main factor limiting the distribution of living organisms in these waters [2,26]. The conductivity observed during our scientific expedition reveals that the salinity of the Vistula River ranges from 0.14 PSU to 4.75 PSU with an average of 0.37 PSU. This indicates that, for the research period, the Vistula River waters can be classified as oligohaline, while in the area of mining (where underground salty water discharges into the river), there are mostly mesohaline waters. As much as 98% of the analyzed section of the Vistula River from Czechowice to the mouth part of the river in Mikoszewo can be classified as mesohaline waters in terms of salinity. Only 2% of the analyzed section of the Vistula River can be classified as oligohaline, namely the section of the Little Vistula from Goczałkowice to the first discharge of mine water in Czechowice. Although the section of the Martwa Wisła (from Przegalin to the mouth part of the Śmiała Wisła section into the Baltic Sea and in Gdańsk) was not analyzed due to the slight contact of these waters with the waters of the Vistula (in the analyzed period, an evident influence of the Baltic Sea waters was observed), the salinity values of these sections could be compared to the section of the Vistula River under the strongest pressure from mine's waters. Secondary salinization is a significant ecological and economic problem. For example, in the Colorado catchment, it is estimated that the additional costs resulting from water salinity amount to USD 300 million per year, mainly in agricultural sector (irrigation) costs. An additional USD 80 million per year are costs incurred due to damage to municipal infrastructure (increased corrosion of pipes and other water) [27].

The resulting salt concentration will be higher the lower the river flow for the same amount of salt delivered pointwise to the river. Hence, there are high salt concentrations in the water of the Vistula River in its upper reaches loaded with the inflow of saline water from coal mine drainage. For the same reason, in the lower reaches of the Vistula, despite the inflow of saline waters, the salt concentrations in the river are relatively low (due to the high river flow). However, in return, high salt loads are observed in the lower reaches. The conducted research showed that discharges of saline waters influenced the salinity of the Vistula River along the entire section of the river. It is well known that high salt concentrations in the river's upper course affect the downstream or even the whole catchment area [28,29]. The change in the ionic composition in the lower course of the Vistula River should be emphasized, where chloride ions dominate in the upper course, while the share of sulphates, Ca and Mg ions increases in the lower course.

The high concentrations of chlorides and sulphates in the upper section of the Vistula River are influenced by coal mines. It is necessary to dewater the mine workings constantly in the coal mining process. These waters are a specific type of wastewater, as they do not result from traditionally understood technological processes and are highly differentiated in terms of their chemical composition and mineralization values. There are 34 mine water discharges in the Vistula catchment area, discharged directly into the Vistula and its tributaries, such as the Gostynia with the Mleczna River, the Goławiecki Stream and the Przemsza River and its tributaries. The average amount of mine water discharged into the Vistula between 1967 and 2013 was about 4.6 m^3/s [30]. The average annual load of Cl^- and SO_4^{2-} of 11,513.1 tonnes/year was discharged with mine waters between 2003 and 2013. In the Vistula-Pustynia cross-section, where the mine waters discharged to the Vistula can be balanced, the maximum contribution of mine waters to mean annual flows was 31%, averaging 19% of annual flows between 1971 and 2013 [30]. Mine waters are often discharged into the Vistula River through retention and dosing reservoirs to protect the river from excessive salinity, but direct discharge into watercourses is still in operation.

Even significantly lower salt concentrations than those observed in the upper course of the Vistula River during the research expedition harm aquatic organisms. Such impacts of anthropogenic salinity on aquatic organisms (especially macroinvertebrates) in rivers have been well-known and described [31–36]. Recently, such studies were conducted on various groups of aquatic organisms, such as benthic macroinvertebrates [37,38], rotifers [39,40], macrophytes [41] and diatoms [42,43] from anthropogenically saline rivers of the Vistula river basin. However, a comprehensive analysis of salinity in the Vistula River, as well as the impact of the salinity of the Vistula River water on aquatic organisms, has not been published so far. For this type of analysis, the patrol monitoring described in this article could be used to analyze the salinity in the Vistula River and the impact of living organisms in this river. Moreover, there are still knowledge gaps on this topic [15].

In addition, the observed significant differences in the salinity of the Vistula River will certainly change regional processes, such as the dispersal of aquatic organisms, and affect regional species pools [44]. It is worth emphasizing that there are no in situ monitoring systems in Poland that would enable the analysis of the effects of pollutant discharge, including primarily saline waters (their mixing with river waters and other natural phenomena affecting the water salinity level). The currently operating state water monitoring system is insufficient to determine the sources of river salinity. In addition, the European Union Water Framework Directive allows each Member State to decide which ions to monitor and how to report their concentrations [5]. This may lead to incorrect conclusions because, according to the presented results, the share of ions in the river can vary significantly depending on the use of the catchment. It is, therefore, necessary to set new monitoring models based on large-area analyses of salinity, taking into account the water flow, changes in the values of the analyzed parameters related to water mixing, inflows causing water dilution and the natural phenomena of removing mineral substances from water, which the presented analyses proved in the case of the Vistula River. In addition, climate change driven by human activities (agriculture, resource exploration and urbanization) contributes and will contribute increasingly to increasing the salinity of freshwater [15]. Due to this, it makes it necessary to assess changes in the salinity of surface waters to recognize all the factors causing them, including a detailed analysis indicating the sources of salt in surface waters. Only that approach can precisely assess the salt load in the water. This concern is not only to large salt emitters such as mines and power plants based on heat exchangers using highly mineralized water but also to small dispersed salt emitters, where the entered salt load can be significant in the overall balance of salt load in surface waters.

As mentioned earlier, an increase in the salinity of inland waters causes a loss of biodiversity and the ecosystem services provided by these ecosystems [2,15]. However, anthropogenically saline habitats can sometimes be substitute habitats (especially in areas where there are no natural water reservoirs) for rare species [45,46], but they are primarily places where salt-sensitive species are replaced by taxa euryhaline, which are often alien and salt-tolerant invasive species [47,48]. Although *Prymnesium parvum* blooms have not been observed in the Vistula River, similar to that recently observed (in August 2022) in the second largest river in Poland—the Oder River—the Vistula River meets many criteria for such an event. Namely, they include potential factors that may cause the development of golden algae, such as periodically occurring low water levels, high temperature of the water, high salinity and local damming. It can be assumed that such phenomena may have already occurred in the Vistula River catchment for several years, as press reports reported on local mass fish kills. Unfortunately, it is impossible to verify the cause of such phenomena, which could be met by adequately implemented patrol monitoring.

Referring to the above arguments, research on both the factors influencing changes in freshwater biodiversity (where patrol monitoring may be applicable) as well as the use of patrol monitoring only to assess the quality of water on a large scale can play an important role for the decision-making processes of the administration and other stakeholders regarding the risk of climate change and the potential impact on human well-being [49]. Patrol monitoring should be a mandatory tool for determining and verifying the locations of primary monitoring points, especially in areas with different anthropopressures, where the tributaries of the main river are very diverse in different terms (anthropogenically and natural). Using such solutions makes it possible to consider the effect of water dilution and mixing, flow dynamics and natural mechanisms of removing mineral substances from water. Certainly, the operational monitoring carried out every few years by state institutions shows a diversity of results suggesting that they may not be reliable, and the presented condition of the monitored rivers may be far from reality. Therefore, the proposed use of patrol monitoring can be highly useful in determining the causes of emerging problems with water quality, both on a local and global scale.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Division of the Vistula River into JCWP with the location of measurements and JCWP centroids (EPSG 2180), typology of sections and the number of online measurements of sections.

JCWP Code	Order	JCWP Name	Centroid		Typo-Logy	Classification	Analysis	Online Meas. Points/JCWP
			Longitude (WGS 84)	Latitude (WGS 84)				
RW20001221113549	−3	to Dobki without Kopydło	197,005.2	493,539.5			SM	-
RW20009211159	−2	from Bładnica to Zb. Goczałkowice	220,480.8	483,878.5			SM	-
RW20009211151	−1	from Dobki to Bładnica	206,638.4	487,036.5			SM	-
RW20000211179	0	Zb. Goczałkowice	228,092.0	488,729.3			SM	-
RW20001921139	1	Wisła from Zb. Goczałkowice to Biała	229,610.4	497,190.4			SM	10
RW20001921199	2	from Biała to Przemsza	237,417.4	509,098.9	19	SZCW	H/SM	30
RW20001921339	3	from Przemsza without Przemsza to Skawa	242,615.5	523,572.1	19	SZCW	H/SM	10
RW2000192135599	4	from Skawa to Skawinka	236,488.5	543,988.5			SM	8
RW2000192137759	5	from Skawinka to Podłężanka	242,503.7	568,683.7	19	SZCW	H/SM	12
RW200019213799	6	from Podłężanka to Raba	248,963.1	594,528,0			SM	16
RW200021213999	7	from Podłężanka to Raba	258,811.4	616,348.4			SM	12
RW20002121799	8	from Dunajec to Wisłoka	275,906.1	646,288.3	21	SZCW	H/SM	30
RW20002121999	9	from Wisłoka to San	304,071.2	685,358.2	21	SZCW	H/SM	27
RW2000212319	10	from San to Sanna	328,995.2	699,931.4			SM	6
RW2000212339	11	from Sanna to Kamienna	346,560.6	700,099.1	21	SZCW	H/SM	8
RW2000212399	13	from Kamienna to Wieprz	383,953,0	698,656.2	21	NAT	H/SM	33
RW2000212539	14	from Wieprz to Pilica	429,460.3	671,429.7			SM	22
RW200021257	15	from Pilica to Jeziorka	455,115.3	655,521.8	21	NAT	H/SM	18
RW20002125971	16	from Jeziorka to Kanał Młociński	486,721.1	639,540.8	21	SZCW	H/SM	14
RW20002125999	17	from Kanał Młociński to Narew	504,707.4	622,761.8	21	NAT	H/SM	51
RW2000212739	18	from Narew to Zb. Włocławek	509,134.6	575,047.6	21	NAT	H/SM	28
RW2000212939	22	from Narew to Zb. Włocławek	578,796.3	461,610.8	21	NAT	H/SM	94
RW2000212939	22	from Narew to Zb. Włocławek	578,796.3	461,610.8	21	NAT	H/SM	
RW2000212939	22	from Narew to Zb. Włocławek	578,796.3	461,610.8	21	NAT	H/SM	
RW20000212339	12	Zb. Włocławek	228,092,0	488,729.3	0	SZCW	H/SM	33

Table A1. *Cont.*

JCWP Code	Order	JCWP Name	Centroid		Typo-Logy	Classification	Analysis	Online Meas. Points/JCWP
			Longitude (WGS 84)	Latitude (WGS 84)				
RW2000275999	19		653,063.1	482,924.6			SM	6
RW20002127911	20	from Zb. Włocławek to border of Region Wodny Środkowej Wisły	530,066.6	505,539.3	21	SZCW	SM	11
RW20002127935	21	border of Region Wodny Środkowej Wisły to tributary from Sierzchów	544,481.3	496,033.0	21	SZCW	SM	74
RW2000212939	22	from tributary from Sierzchów to Wda	578,796.3	461,610.8	21	SZCW	H/SM	94
RW20002129999	23	from Wda to mouth	653,063.1	482,924.6	21	SZCW	H/SM	
RW20002129999	23	from Wda to mouth	653,063.1	482,924.6	21	SZCW	H/SM	
RW20002129999	23	from Wda to mouth	653,063.1	482,924.6	21	SZCW	H/SM	
RW20002129999	23	from Wda to mouth						

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