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Geochemical State of Wilga River Environment in Kraków (Poland)—Historical Aspects and Existing Issues

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Abstract: Aquatic systems are a very important part of the environment, which requires special attention due to the constant deterioration of the quality and quantity of water globally. Aquatic environments in Poland are mostly affected by the mining and smelting industry, which is especially visible in the south of the country, and one of such anthropogenically affected rivers is the Wilga—a small tributary of the Vistula River (the biggest river in Poland). For many years, the catchment area of the Wilga River accommodated a functioning industry that was based on the use of metals (fur, leather processing, foundry and galvanizing plants), as well as the "Solvay" Kraków Soda Works, which have left behind soda waste piles, and currently, along the course of the river, there are ongoing works connected with the construction of the "Łagiewnicka Route", which required the relocation of a section of the Wilga river bed, among other things. To determine the general condition of the river, selected physico-chemical parameters were analysed in the water (pH, conductivity, anions: Cl^{-}, N-NO_3, P-PO_4 and SO_4 and cations: Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn), suspended particulate matter and sediment (Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn). Samples were taken before the relocation of the river bed (2019) and after its relocation (2021). The obtained data were compared with recorded historical data and this revealed that over the years, the condition of the Wilga environment has improved significantly, especially in terms of the contamination of sediments with metals, the concentrations of which fell several ten-fold. This is attributed to the closure of most industrial plants located within the river's catchment area and to the modernization and legal regulation of the functioning of the remaining plants. An effect of leachates from the soda waste piles on the waters of Wilga has been observed (in the form of higher pH, mineralization and concentration of chlorides), which has however gradually decreased over time. However, no visible impact of road transport on the river's environment has been observed, or any impact of the construction works or the related relocation of the river bed for that matter. The river should still be classified as polluted, but the level of this pollution has decreased significantly and the qualitative composition of the pollution has also changed.

Keywords: metals; chlorides; metallurgical industry; chemical industry; water–suspended particular matter–sediment; Wilga River; Vistula River

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1. Introduction

Aquatic systems are a very important element of the environment, as they provide the habitat for biological life, represent a water source for humans, but also function as a collector of various contaminants and pollutants, derived e.g., from wastewater discharge, fossil fuel combustion or atmospheric deposition, generally connected with growing urbanization and industrialization [1,2]. The deterioration of water quality and quantity is a worldwide problem that concerns not only the developing but also the developed areas of the Earth [3], including European countries [4–6], e.g., Spain [7], Portugal [8], Malta [9] and Poland [10–12]. Both the quality and quantity of water resources in Poland are relatively poor when compared to other countries in Europe and the European Union. Surface waters in Poland are anthropogenically affected mainly due to wastewater discharge, agriculture, urbanization and industry, especially mining, concentrated mostly in the southern areas of the country [13]. Poland is also struggling with droughts (the most extensive in recent years occurred in 1992–1993, 2006, 2008, 2012 and 2015 [14]) and floods (the biggest ones in recent years took place in 1997 [15–17], 2001 [18] and 2010 [19,20]), resulted from gradual climate changes, but also poor water resource management [21] and human economic activity, like regulation of river channels and changes in land use [22,23].

One of the most important roles in water environments is performed by sediments, as they are usually the main collector of contaminants and pollutants introduced into water systems—substances dissolved in water are bonded on the solid particles over time and finally trapped in bottom deposits [24]. Aquatic sediments are also a very dynamic component, in which physico-chemical processes such as transport, diagenesis, bioturbation, remobilization or bioaccumulation, constantly take place [25]. The physico-chemical composition of river sediments in non-industrialised areas depends mainly on the geological structure of the catchment, the dynamics of weathering processes, the morphological structure of the river bed and on the surrounding vegetation [26,27], while in the case of densely populated, urbanised or industrialised catchments, the chemical composition of river sediments reflects the local anthropopressure [28], which may lead to the contamination or pollution of sediments with various substances. Contamination is understood as the increased concentration level of a given chemical in relation to the geochemical background, while pollution means that this concentration poses a threat to biota [24,29]. A distinct, and quite complicated issue, is the appropriate determination of the geochemical background used in environmental risk assessment [30], which may significantly affect the data analysis results [31].

One of the interesting contaminants/pollutants found in water environments are metals due to their non-biodegradability, environmental persistence and a tendency for bioaccumulation [32,33]. Those that are the most frequently examined are: Cd, Cr, Cu, Hg, Ni, Pb, Sn and Zn, as they are potentially toxic, known to be affected by human activity and well documented [34]. The geological structure of Poland and the ensuing location of the main industrial centres (especially in such sectors as mining, metallurgy or power engineering) in the south of the country, has resulted in the contamination or pollution with metals of two biggest Polish rivers (mainly their upper sections)—Vistula and Oder [35–40], as well as many smaller rivers and streams located in southern Poland [41–54]. Economic and social changes in Poland have resulted in the termination or reduction of mining activity in many areas, and although a significant improvement in the condition of the affected aquatic environment could be observed quite rapidly (within a few years), it must be noted that the rate and the level of positive changes depend on many variables [55].

One of the rivers strongly affected by human activity is Wilga [56–58], which mostly runs through the territory of Kraków (the second biggest city in Poland, after the capital city of Warsaw). This river flows through the construction site of the biggest road construction project in recent years in Kraków—the “Łagiewnicka Route” (pol. Trasa Łagiewnicka S.A. [59]) and through the eastern part of the post-industrial area of the former “Solvay” Kraków Soda Works [60]. This factory began its operations in 1906 and was closed in 1989–1996 due to its strong negative impact on the environment. The Solvay technology of soda ash production requires large amounts of raw materials: sodium chloride (NaCl), limestone ($CaCO_3$), ammonia (NH_3) and large quantities of energy [61]. The soda industry also generates large amounts of solid and liquid waste. In the investigated area it was found that post-soda waste, mainly sludge, was deposited in sludge ponds in the amount of a total of 5 million tons across an area of 100 ha [62]. Post-production slurries contain large amounts of inorganic chlorides, carbonates, sulphates, alkali, ammonia, suspended solids and metals [61,63]. Additionally, fur, tanning, foundry and electroplating plants have been operating for many years near the Wilga River, the technologies of which are based on metals. Most of them have already closed down due to their harmful effect on the environment and/or due to social and economical changes, and those that are still operational have been restructured. However, a large amount of contaminants and pollutants from heaps, wild dumps and sewage discharge still find their way into the river [57].

In view of all of the above, the main purpose of the article was to investigate the current condition of the Wilga River environment, with the consideration of the historical pollution, the existing dangers, connected mainly with the construction of the "Łagiewnicka Route" and the related relocation of the river bed, as well as the impact of the nearby soda waste piles and other sources of contaminants and pollutants. Wilga is a tributary of Vistula River, which flows directly into the Baltic Sea, and it has been demonstrated that Wilga is a significant source of contamination found in this biggest river in Poland [56–58]. This makes it a global issue, due to the relatively poor chemoecological state of the Baltic Sea environment [64–66].

2. Materials and Methods

2.1. Study Area and Sampling

The Wilga River is a small, right-bank tributary of Vistula (the biggest river in Poland) and its source is located in the village of Raciborsko-Pawlikowice (several kilometres from Kraków). The total length of the river is 26.7 km, of which approximately one half runs within the administrative boundaries of Kraków, while its entrance into the Vistula River is situated close to the city centre (Figure 1). In its upper course, the river has a "wild" and meandering character, whereas within the boundaries of Kraków it is regulated and strengthened with backwater embankments [57,60]. Wilga is a submountain river with an average discharge of 0.93–1.35 m^3/s and the presence of two discharge peaks: Spring and Summer peaks and one Autumn/Winter low [23,67]. The river catchment of the area of about 100 km^2 is mostly used for agriculture, except for the part located within Kraków. The area of the river basin is made of Tertiary claystone and Quaternary sands, and the river banks are quite densely populated with trees and bushes. Wilga does not pose a serious flooding risk for Kraków [10,68].

The area which the Wilga runs through is currently affected by works connected with the construction of a section of the third ringway of Kraków, the "Łagiewnicka Route", which required the relocation of a section of the river bed of the length of approx. 550 m (Figures 1 and 2), which was done on 29 February 2020. The new river bed was also designed to provide more protection against flooding [59]. The Wilga also runs across the area of the former "Solvay" Kraków Soda Works, which contains soda waste piles that have been partially recultivated and redeveloped [69] (Figures 1 and 3). Moreover, the Wilga basin was heavily affected for several decades by the chemical industry, being a source of toxic elements, among others. The most significant object in the Wilga River catchment area was the Kraków Tannery (pol. Krakowskie Zakłady Garbarskie). Its history started in 1885, when the Dłużyński brothers began production at a facility named (pol.) "Bracia Dłużyńscy, Garbarnia Ludwinów przy Krakowie", and ended in 1990 when the old departments located in the city centre (Ludwinów) were closed down in view of environmental protection. That year saw the completion of the construction of the plant in Bieżanów, where the production of all departments of the Kraków Tannery were relocated. Modern production halls, a sewage treatment plant and an office building were built on an area of approx. 16 ha [70]. The remaining industrial facilities located in the Wilga catchment area are: Kraków Fur Processing Plant (pol. Krakowskie Zakłady Futrzarskie), active in the years 1951–1974; Kraków Metal Hardware Plant "Metaloplast" (pol. Wytwórnia Galanterii Metalowej "Metaloplast"), active in years 1951–1976 and the previously-mentioned "Solvay" Kraków Soda Works (pol. Krakowskie Zakłady Sodowe), active in years 1906–1996 (Figure 1). Waste generated during the process of obtaining sodium carbonate using the Solvay method (Figure 3), consists of $CaCO_3$ (approx. 70% of dry mass), NaCl, $CaCl_2$, $CaSO_4$, $MgSO_4$, $BaSO_4$, P_2O_5 and SiO_2 [67].

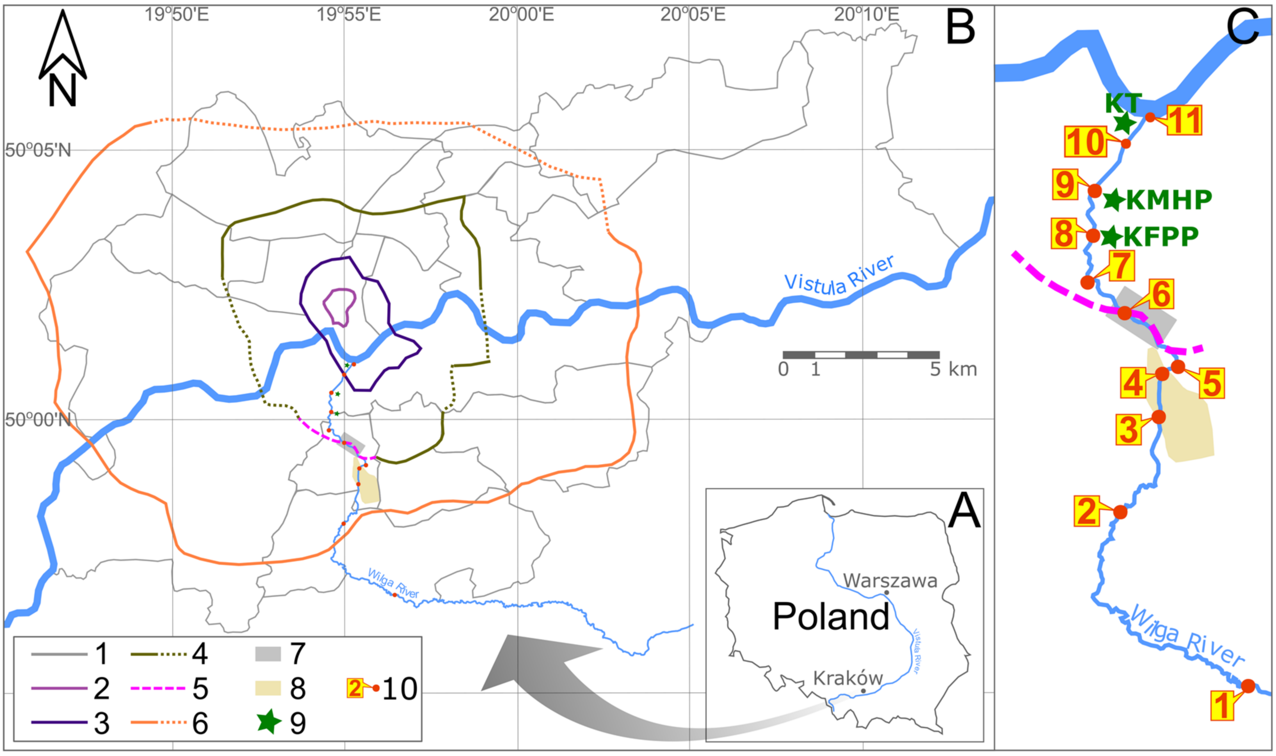

Figure 1. Study area: (**A**)—location of the study area (Kraków city) on the map of Poland; (**B**)—sampling cites at the Wilga River (in general); (**C**)—sampling cites at the Wilga River (in details); 1—boundaries of the Kraków city and its districts; 2—first ringway of Kraków; 3—second ringway of Kraków; 4—third ringway of Kraków (existing sections are marked with a continuous line, while planned sections are marked with a dashed line); 5—"Łagiewnicka Route", a section of the third ringway of Kraków under construction; 6—fourth ringway of Kraków (existing sections are marked with a continuous line, while planned sections are marked with a dashed line); 7—relocated section of the Wilga River (Figure 2); 8—waste piles of former "Solvay" Kraków Soda Works (Figure 3); 9—locations of chemical industry objects (KFPP—Kraków Fur Processing Plant, KMHP—Kraków Metal Hardware Plant "Metaloplast", KT—Kraków Tannery); 10—sampling points.

Figure 2. Relocated section of the Wilga River: (**A**)—photomap with the indication of the old river bed (light blue) and new river bed (dark blue) (obtained courtesy of Trasa Łagiewnicka S.A. [59]), as well as the location of sampling point No. 6 (red dot); (**B**)—section of old river bed seen from the vicinity of sampling point No. 6; (**C**)—section of new river bed seen from the vicinity of sampling point No. 6 (Figure 1).

Figure 3. Wastes of former "Solvay" Kraków Soda Works, so-called "White Seas" (pol. Białe Morza): (**A**)—vicinity of sampling point No. 6 (Figure 1) during construction works and relocation of the Wilga River bed (obtained courtesy of Trasa Łagiewnicka S.A. [59]), with waste piles visible in the background (red arrow); (**B**)—soda waste up close; (**C**)—non-processed soda waste piles in the vicinity of the Wilga River, next to the recultivated and redeveloped area.

To capture the potential impact of the relocation of the Wilga bed on its geochemical state, the river was sampled twice: before (2019) and after (2021) relocation. 11 sampling points for the extraction of bottom sediment, suspended particulate matter (SPM) and river water, have been established between the border of the city of Krakow (No. 1) and the entrance to the Vistula (No. 11, Figure 1), in characteristic locations along the route of the river bed. Samples of water, from which suspended particulate matter was extracted, were taken in 2019 in four different locations: No. 1—in the vicinity of the city border, No. 5—upstream the construction of the "Łagiewnicka Route", No. 7—downstream the construction of the "Łagiewnicka Route" and No. 11—in the vicinity of the entrance of Wilga into the Vistula.

2.2. Water Samples Analysis

The physical parameters of Wilga water such as pH and conductivity were determined in the river in situ, using a portable multiparameter meter (model Orion Star A329 by Thermo Scientific, Waltham, MA, USA), in accordance with the ISO 10523 [71] and ISO 7888 [72] protocols, respectively. Water samples were collected into 250 mL glass vessels, for the purpose of cation (with acidification with 10 µL of concentrated HNO_3) and anion (without acidification) content definition. The samples were transported to the laboratory, filtered using 0.45 µm membrane filters and stored at 4 °C for further analysis. The concentrations of nitrate-nitrogen ($N\text{-}NO_3$) and phosphate-phosphorus ($P\text{-}PO_4$) were determined via the spectrometric method, using spectrophotometer UV-Vis (model M501 by CamSpec, Leeds, UK), in accordance with the ISO 13395 [73] and ISO 6878 [74] protocols, respectively. The contents of chlorides were determined via titration—Mohr's method in accordance with the ISO 9297 protocol [75]. The concentrations of the analysed cations were determined using the ICP-OES emission spectrometer, with inductively coupled plasma (model Plasma 40 by Perkin-Elmer, Wellesley, MA, USA), in accordance with the ISO 11885 protocol [76] or using the ICP-MS mass spectrometer (model iCAP RQ (C2) by Thermo Scientific, Waltham, MA, USA), in accordance with the ISO 17294-2 protocol [77].

2.3. Suspended Particulate Matter (SPM) Samples Analysis

Water samples were collected into 2000 mL glass containers and filtered under vacuum through a 0.45-µm porosity membrane filter. The suspended matter was dried at 105 °C and then digested in aqua regia with the use of a digestion system (model DigiPREP HT by SCP SCIENCE, Baie D'Urfé, QC, Canada), in accordance with the ISO 11466 protocol [78]. The concentration of cations was defined using an ICP-OES spectrometer (model Optima 7300 DV by Perkin Elmer, Wellesley, MA, USA), in accordance with the ISO 11885 protocol [76].

2.4. Sediment Samples Analysis

Bottom sediment samples were homogenised, mixed and part of the sample was sieved through <63 µm and some through <20 µm. About 1 g of both separated grain fractions were dried at 105 °C and digested in aqua regia with the use of a digestion system (model DigiPREP HT by SCP SCIENCE, Baie D'Urfé, QC, Canada). The concentration of cations in fraction <20 µm was established using the ICP-OES spectrometer (model Optima 7300 DV by Perkin Elmer, Wellesley, MA, USA), in accordance with the ISO 11885 protocol [76] and in fraction <63 µm using flame atomic absorption spectroscopy F-AAS (model iCE 3500 by Thermo Scientific, Waltham, MA, USA) in accordance with the ISO 11047 protocol [79].

2.5. Quality Assurance and Quality Control

To ensure adequate analytical quality, all reagents were of the highest analytical purity and a blank sample was performed for each analysis. For the purpose of the definition of the method's precision, six samples of sediment (fraction <20 µm) were prepared as prescribed above. The analysis of the method's precision relies on the coefficient of variation (CV), i.e., standard deviation (SD) between 6 replicate samples, as an indicator of concordance described by the following formula: RSD (relative standard deviation) = (SD/mean)·100. The calculated values of RSD, in the case of all analysed elements, were $\leq$5%, except for arsenic.

A sample of the reference material Loam Soil ERM-CC141 was analysed, to ensure that the analytical method is accurate and provides good quality of the obtained measurement results. Precisely about 1 g of ERM material was dried at 105 °C and then digested in aqua regia under the same conditions and analysed in the same way, as in the case of samples of the Wilga River bottom sediments. The obtained results are consistent with the results of the certificate, except for arsenic. The unsatisfactory results obtained for arsenic are most likely due to a not entirely adequate method being chosen for its extraction, as it has been demonstrated that microwave aqua regia digestion gives better results for this element [80]. The system precision of ICP-MS, ICP-OES and AAS apparatus was verified by six injections of a selected solution. The performed tests demonstrated that the systems are precise enough to generate reliable results. The limits of quantification (LOQ) values for the investigated elements, discussed further are as follows (in mg/L): ICP-OES (0.005 for Cu, Li and Mn; 0.01 for Al, Ba, Cd, Co, Cr, Fe, Pb and Zn; 0.05 for Ni; 0.1 for Mg and Na; 0.2 for K and Sr; 10 for Ca); ICP-MS (0.0001 for Pb; 0.0002 for Co; 0.0003 for Cd and Sr; 0.0005 for Ba; 0.001 for Cu, Li, Mg, Ni and Zn; 0.003 for Mn; 0.005 for Al and Cr; 0.01 for Na; 0.02 for Fe; 0.05 for Ca and K); AAS (0.0029 for Mg; 0.0039 for Na; 0.0076 for Li; 0.0083 for K; 0.0092 for Ca; 0.01 for Zn; 0.013 for Cd; 0.02 for Mn; 0.033 for Cu; 0.05 for Cr and Ni; 0.052 for Fe; 0.058 for Co; 0.073 for Pb; 0.13 for Ba; 0.29 for Al).

The duplicate method was used to estimate the combined uncertainty, including sampling. According to the Eurachem Guide [81], this is the simplest and probably most cost-effective of the four methods described in it: duplicates, protocols, CTS (collaborative trial in sampling) and SPT (sampling proficiency test). The total variability of the determined parameters is the sum of the geochemical variance (spatial and/or temporal variability), sampling variance (errors generated during sampling, transport and storage of samples) and analytical variance (analytical errors) [82]. The population variances have been replaced by their estimates (s^2): $s^2_{total} = s^2_{between\text{-}target} + s^2_{sampling} + s^2_{analytical}$ [81]. The empirical method with the use of the ROBAN computer program was used to estimate the uncertainty of the results of the determination of selected elements in the Wilga sediment (fraction <20 μm). The analyses revealed that the geochemical variance related to the variability of the river parameters is predominant. However, a high contribution of sampling variance related to the sampling location was found.

3. Results and Discussion

The concentration of a wide spectrum of elements has been defined in the water, suspended particulate matter (SPM) as well as in sediments, and additionally, for the water samples, physico-chemical parameters (pH and conductivity) and anions (chlorides, nitrates, phosphates and sulphates) have been established. Some of the analysed elements will not be considered for further data analysis and discussion, due to unsatisfactory method's precision result (arsenic), or a considerable amount of results below the limit of quantification (<LOQ) or low and irrelevant in the context of the analysis of the geochemical condition of the Wilga. The remaining results have been compiled in Table 1 (water) and in Table 2 (SPM and sediment), along with reference values such as data of the Geochemical Atlas of Europe [83] (water and sediment), the results of the Voivodeship Inspectorate of Environmental Protection in Poland [84] (water), permissible levels provided by the Regulation of the Minister of Maritime Economy and Inland Water Navigation [85] (water), the results of the Chief Inspectorate of Environmental Protection in Poland [86] (sediment), and with geochemical background values for aquatic sediments in Poland [87] (sediment).

3.1. The Impact of Waste Piles of Former "Solvay" Kraków Soda Works on the Wilga River Water and Associated Groundwater

As a result of the analysis of the waters of the Wilga River, high values of electrical conductivity (between 830 and 3600, 2264 μS/cm on average in 2019 and between 970 and 2910, 2024 μS/cm on average in 2021), as well as high concentrations of chlorides (between 61.8 and 896.4, 557.8 mg/L on average in 2019 and between 49.9 and 422.5, 261.2 mg/L on average in 2021) were obtained (Table 1). The highest values of both parameters were observed at point No. 7, located below the industrial soda waste piles (Figure 1). This is consistent with data obtained during previous research [62], according to which water flowing out of the waste ponds is strongly mineralised (contains large amounts of chlorides, sulphates, calcium ions and magnesium ions) and generates leachates from the bottom of the slopes and the banks of the Wilga River. This has been also confirmed by other research [60], where high concentrations of chloride ions (between 312 and 854 mg/L) and electrical conductivity (between 795 and 3175 μS/cm) were recorded and represented above-average values. The highest values of the concentration of chloride ions, pH and conductivity during that research [60] were observed at the measurement point located below the area of soda waste piles. Additionally, the concentrations of chlorides were the most varied in the individual points along the route of the river bed (with a general growing trend in the direction of the river mouth) and seasonally variable (during dry seasons, their concentrations were much lower than during periods of intensive rainfall). These observations suggest that chloride ions are leached from the pile area by the infiltrating rainwater. Tests carried out at a similar time as presented in this paper [67] also revealed that the highest concentrations of Cl^-, Na^+, Ca^{2+} ions and EC were present in the Wilga River below the waste ponds. Seasonal variability was also observed, i.e., the highest concentrations of the above ions were detected in autumn, which was attributed to the intensification of precipitation and the leaching of sediments into the water of the Wilga River. The large load of sodium, calcium and chloride that is discharged into the river system, is connected with the absence of effective insulation [67]. In the case of a similar post-industrial area (Soda Production Plant in Inowrocław, Poland), which featured a drainage system installed around the spoil piles, a significant reduction of the concentration of chloride ions in the analysed waters was observed [88].

The presence of chlorides may also result from the winter maintenance of roads, which in Poland is mainly based on the use of sodium chloride in various forms and mixtures. It has been demonstrated, however [89], that the risk to the water/soil environment in Kraków related to the winter maintenance of roads is not significant.

Table 1. Statistical parameters in the Wilga River water (2017, 2019 and 2021), European rivers and permissible levels of the selected parameters.

Parameter	Unit	Wilga 2019 (This Study) Min–Max (Mean)	Wilga 2021 (This Study) Min–Max (Mean)	Wilga 2017 [84] Mean *	Water of European Rivers [83] Min–Max (Mean)	Class I [85] **	Class II [85] **
pH	–	7.0–7.5 (7.3)	7.6–8.2 (8.1)	7.8	2.2–9.8 (7.5)	7.4–8.0	6.5–8.0
EC	µS/cm	830–3600 (2264)	970–2910 (2024)	2834	<500–1,710,000 (44,600)	≤542	≤677
Cl^-	mg/L	61.8–896.4 (557.8)	49.9–422.5 (261.2)	922.5	0.14–4560 (33.3)	≤29.9	≤44.8
N-NO_3	mg/L	0.20–2.43 (1.48)	nd	1.5	<0.009–24.2 (2.05)	≤2.0	≤5.0
P-PO_4	mg/L	0.031–0.525 (0.165)	nd	0.016	nd	≤0.065	≤0.101
SO_4	mg/L	nd	61.6–119.6 (96.9)	120.8	0.3–2420 (52.1)	≤49.5	≤79.8
Al	mg/L	<LOQ–0.020 (0.013)	0.082–0.510 (0.198)	nd	0.0007–3.37 (0.0755)	≤0.4	≤0.4
Ba	mg/L	0.018–0.092 (0.064)	0.029–0.048 (0.040)	0.062	0.0002–0.436 (0.0354)	≤0.5	≤0.5
Ca	mg/L	66.0–318.3 (221.2)	93.2–210.0 (157.9)	nd	0.226–592 (55.2)	≤80.1	≤89.5
Cd	mg/L	<LOQ–<LOQ (<LOQ)	<LOQ–<LOQ (<LOQ)	0.03	<0.000002–0.00125 (0.000026)	0.00045 ***	0.00045 ***
Co	mg/L	<LOQ–<LOQ (<LOQ)	0.00021–0.00034 (0.00026)	nd	0.00001–0.0157 (0.000333)	≤0.05	≤0.05
Cr	mg/L	<LOQ–<LOQ (<LOQ)	<LOQ–<LOQ (<LOQ)	nd	<0.00001–0.043 (0.000792)	≤0.05	≤0.05
Cu	mg/L	<LOQ–<LOQ (<LOQ)	<LOQ–<LOQ (<LOQ)	<LOQ	0.00008–0.0146 (0.00123)	≤0.05	≤0.05
Fe	mg/L	0.016–0.074 (0.039)	0.179–0.787 (0.538)	nd	<0.001–4.82 (0.268)	–	–
K	mg/L	1.32–7.91 (4.42)	3.64–5.53 (4.78)	nd	<0.01–182 (3.07)	–	–
Li	mg/L	<LOQ–0.010 (0.009)	0.005–0.010 (0.008)	nd	<0.000005–0.356 (0.00667)	–	–
Mg	mg/L	11.25–19.17 (14.88)	9.48–13.76 (12.35)	nd	0.048–230 (11.5)	≤6.6	≤12.0
Mn	mg/L	<LOQ–<LOQ (<LOQ)	0.092–0.219 (0.170)	nd	<0.00005–3.01 (0.0567)	–	–
Na	mg/L	32.6–304.5 (191.0)	31.19–167.06 (101.43)	nd	0.231–4030 (23.1)	–	–
Ni	mg/L	<LOQ–<LOQ (<LOQ)	0.0014–0.0020 (0.0016)	2.0	0.00003–0.0246 (0.00243)	0.034 ***	0.034 ***
Pb	mg/L	<LOQ–<LOQ (<LOQ)	<LOQ–0.00053 (0.00027)	nd	<0.000005–0.0106 (0.000224)	0.014 ***	0.014 ***
Sr	mg/L	0.36–1.35 (0.92)	0.40–1.08 (0.71)	nd	0.001-13.6 (0.327)	–	–
Zn	mg/L	<LOQ–0.059 (0.036)	<LOQ–<LOQ (<LOQ)	0.050	0.00009–0.31 (0.00601)	≤1	≤1

nd—not determined; <LOQ—below the limit of quantification (<LOQ were substituted with LOQ/2 in the calculations of mean values [85,90]); * data based on the results of the Voivodeship Inspectorate of Environmental Protection [84]; ** permissible levels of parameters for class I and II, respectively, of water quality, provided by the Ministry of Maritime Economy and Inland Water Navigation [85]; *** maximum allowable concentration according to environmental quality standards—MAC-EQS [85].

The main ecological problem related to the presence of waste piles of former "Solvay" Kraków Soda Works in the drainage basin of the Wilga River is the leaching of salts into the surface water and presumably also groundwater in the area of Kraków. Such waters are present in this area in several aquifers, in Devonian, Jurassic, Cretaceous, Tertiary and Quaternary formations, of which the most important for the economy are Quaternary waters, then Tertiary and Jurassic waters. The chemical composition of groundwater is highly variable and related to the geological structure of respective aquifers. The chemical composition of the uppermost Quaternary waters is not natural, due to contamination infiltrating these waters from the air (via precipitation), from surface waters (via infiltration from the Vistula River and its distributaries) and the soil. However, the direct influence of the waste piles is not evident in the chemical composition of groundwaters and other factors also play a significant role here. These waters are somewhat variable in different areas of Kraków, but generally demonstrate a neutral pH and a relatively high level of hardness and mineralization. The most prevalent anions are sulphates and carbonates, whereas the most prevalent cations are calcium, magnesium and iron, and sometimes also manganese. Only the high concentration of iron is of partially natural origin and is related to the saturation of Pleistocene aquifers with iron [22,23].

Table 2. Statistical parameters of selected elements in suspended particulate matter (SPM) and sediment of the Wilga River (2019, 2021), in Vistula River sediment (2018), European rivers and geochemical background for aquatic sediments in Poland.

Parameter [mg/kg]	2019 (This Study) Wilga Suspended Particulate Matter Min–Max (Mean)	2019 (This Study) Wilga Sediment (Fraction <20 µm) Min–Max (Mean)	2021 (This Study) Wilga Sediment (Fraction <20 µm) Min–Max (Mean)	2018 Vistula Sediment below Kraków (Fraction <2 mm) [86] *	Stream Sediments of European Rivers [83] Min–Max (Mean)	Geochemical Background for Aquatic Sediments in Poland [87]
Al	8665–15,607 (11,827)	13,717–21,085 (17,622)	16,064–21,201 (17,750)	1500	nd	–
Ba	126–545 (277)	109–328 (168)	95–193 (146)	19.0	4.0–3120 (117)	<52
Ca	22,474–79,621 (50,869)	15,452–38,280 (24,795)	16,241–50,871 (31,076)	1400	nd	–
Cd	<LOQ–<LOQ (<LOQ)	0.522–1.041 (0.701)	<LOQ–1.068 (0.498)	0.226	<0.02–43.1 (0.527)	<0.5
Co	<LOQ–<LOQ (<LOQ)	8.81–13.06 (10.58)	8.53–11.54 (9.89)	<0.20	<1.0–245 (10.3)	<3
Cr	<LOQ–<LOQ (<LOQ)	34.2–47.2 (40.5)	29.9–40.9 (36.5)	3.05	2..0–1750 (31.0)	<6
Cu	59.7–576.5 (275.2)	36.3–98.9 (58.6)	40.8–88.6 (63.5)	3.94	1.0–998 (19.0)	<7
Fe	30,850–148,422 (82,648)	22,935–31,875 (27,243)	23,090–29,668 (25,772)	7100	600–200,000 (22,500)	–
K	<LOQ–<LOQ (<LOQ)	2980–4224 (3688)	2847–4763 (3317)	240	nd	–
Li	<LOQ–<LOQ (<LOQ)	15.6–23.4 (18.8)	21.4–60.4 (28.5)	nd	0.28–271 (29.7)	–
Mg	4602–10,298 (7716)	4649–8401 (5837)	3839–12,860 (6716)	600	nd	–
Mn	3583–21,884 (11,336)	375–1009 (640)	491–1079 (660)	330	24–18,900 (716)	–
Na	<LOQ–<LOQ (<LOQ)	274–3159 (1000)	315–3693 (1257)	nd	nd	–
Ni	<LOQ–<LOQ (<LOQ)	26.2–40.2 (32.0)	27.4–39.0 (31.3)	3.76	2.0–1200 (28.6)	<6
Pb	<LOQ–<LOQ (<LOQ)	31.8–71.8 (45.7)	26.2–57.1 (41.6)	<1.00	<3.0–4880 (29.8)	<15
Sr	<LOQ–<LOQ (<LOQ)	56.6–110.6 (77.9)	44.5–1603.3 (239.7)	11.0	31–1352 (171)	–
Zn	87–1017 (455)	154–383 (250)	130–358 (249)	13.7	7.0–11,400 (98)	<73

nd—not determined; <LOQ—below the limit of quantification (<LOQ were substituted with LOQ/2 in calculations of mean values [85,90]); * data based on the results of the Chief Inspectorate of Environmental Protection in 2018 [86].

When comparing the results obtained during the presented research and the monitoring results of the Voivodeship Inspectorate of Environmental Protection [84], with standard values provided by the Ministry of Maritime Economy and Inland Water Navigation [85], the waters of the Wilga River should be considered as unclassified waters (ones that exceed the maximum limits for the II water quality class) in terms of parameters such as conductivity, chlorides, calcium and magnesium, and to a lesser extent also in terms of pH and phosphates (Table 1). A slightly higher pH value is related to leachates coming from the soda waste piles, which have a pH of 11–12 [62], although it seems that over the years this impact is subsiding because the previous tests have recorded higher pH values of the Wilga waters and these values also demonstrated higher variability [57]. The average concentrations of metals in the water of the Wilga River are approximately equal to or lower than the average concentrations of metals in European rivers provided by the Geochemical Atlas of Europe [83] (Table 1). However, significantly higher concentrations of chlorides, calcium and sodium were observed in the water of the Wilga River, which yet again would suggest the leaching of these elements from soda waste piles.

3.2. The Impact of Traffic and Construction Works of "Łagiewnicka Route" on the Wilga River Environment

Wilga flows through an area with a highly developed road network with heavy traffic. Therefore its waters may become infiltrated, via surface runoff, by pollutants such as petroleum-based compounds or abrasive products generated during the use of road vehicles, e.g., metals, dust, soot [91–93]. However, the average content of metals dissolved in water is generally low and similar in samples taken in 2019 as well as in 2021 (Table 1). No significant differences were also observed in the case of particular element concentrations obtained for sediment samples taken before (2019) and after (2021) the relocation of the Wilga bed, and the results of some of the parameters obtained for point No. 6 located in the area of the new river bed are even slightly lower than those obtained at the remaining sampling points (Table 2, Figure 4). These data show a minor impact of road transport on the geochemical condition of the river, and an insignificant impact of works connected with the construction of the "Łagiewnicka Route".

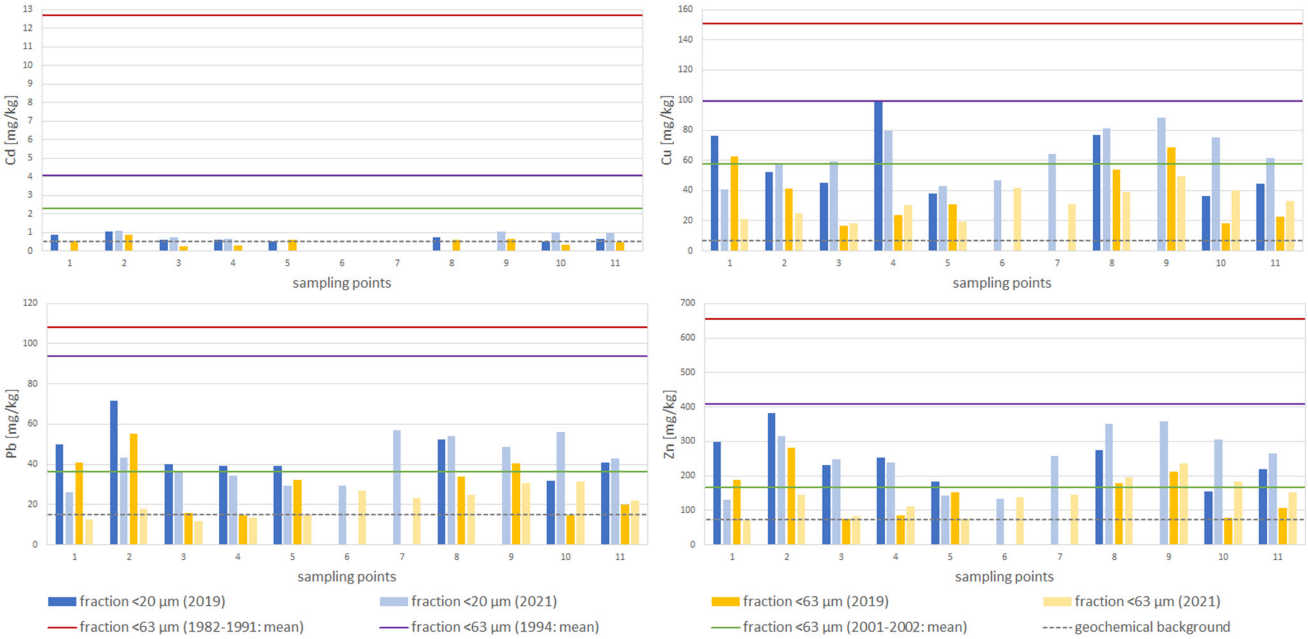

Figure 4. Comparison of selected metal concentrations (Cd, Cu, Pb and Zn) in Wilga River bottom sediments (fraction <20 µm and <63 µm; 2019 and 2021) with geochemical background [87] and with data from previous studies: mean concentrations in fraction <63 µm from two sampling campaigns (1982–1991 and 1994), according to [56] and mean concentrations in fraction <63 µm from sampling campaign 2001–2002, according to [57].

3.3. The Long-Term Impact of Chemical Industry on the Wilga River Sediments

Wilga basin was heavily affected by the chemical industry (Kraków Fur Processing Plant, Kraków Metal Hardware Plant "Metaloplast", Kraków Tannery—Figure 1) for several decades, which was a source of toxic elements, among others. Recent Wilga bottom sediments are enriched with elements whose concentrations exceed several times the geochemical background (GB) values established for aquatic sediments in Poland [87] (Table 2, Figures 4 and 5). Deposits are most heavily contaminated with Cu (9 times higher than GB), Cr (6 times), Ni (5 times) and Ba, Co, Pb and Zn (3 times). However, it should be borne in mind that the data compared were established for different sediment fractions, so they are not completely comparable. In turn, a comparison of concentrations of the analysed elements in the sediments of the Wilga River with average values observed in the sediments of other European rivers [83] (Table 2) reveals that they are similar.

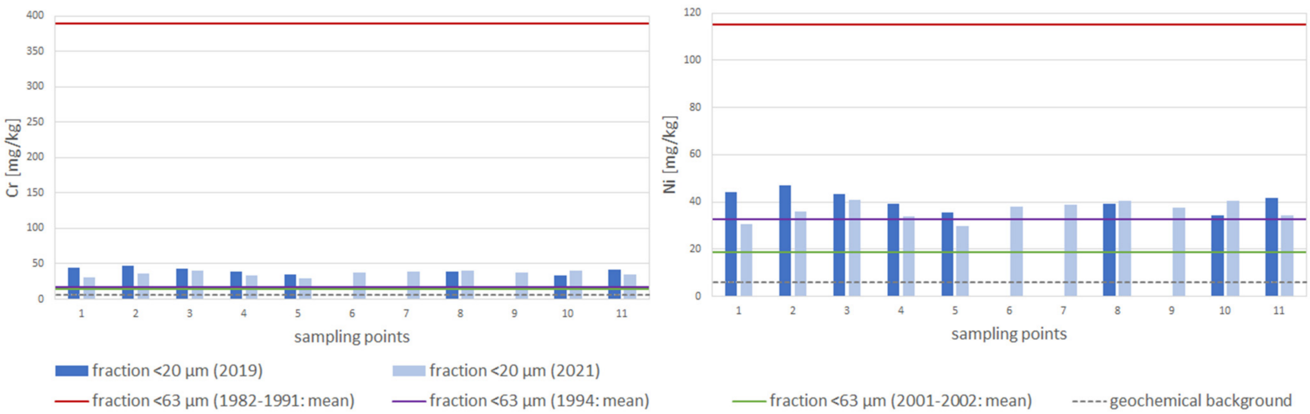

Figure 5. Comparison of selected metal concentrations (Cr and Ni) in Wilga River bottom sediments (fraction <20 µm; 2019 and 2021) with geochemical background [87] and with data from previous studies: mean concentrations in fraction <63 µm from two sampling campaigns (1982–1991 and 1994), according to [56] and mean concentrations in fraction <63 µm from sampling campaign 2001–2002, according to [57].

No significant differences were observed between the different sampling points or between different sampling periods—the average content of most elements in sediments extracted in 2019 and 2021 is very similar (Table 2, Figures 4 and 5). However, the concentration of As and Cd was approximately halved, while the concentration of Sr increased four times. Strontium present in the sediment alongside elements such as beryllium and barium is an alkaline earth metal and is widely used in industry [94]. An analysis of a sample of soda waste carried out for the purposes of this article revealed high concentrations of elements such as barium (426 mg/kg) and strontium (205 mg/kg). Strontium salts are also present in the sulphurous mineral springs in Swoszowice [95], a settlement situated above sampling point No. 1.

Especially notable is the fact that over several decades of research documented in scientific literature, we can observe a significant improvement in the geochemical purity of the bottom sediments of the Wilga, and the average concentrations of 6 most frequently examined metals, originating from the industrial plants situated within the catchment area of the Wilga River (Cd, Cr, Cu, Ni, Pb and Zn), have decreased between several times and a dozen times, which is most clearly visible in the case of cadmium and chromium (Figures 4 and 5). The results of sampling in the period 1982–1991 [56] have revealed significant differences in terms of the concentration of elements in the different samples (between several times and several dozen times) and significantly higher concentrations were observed in the area of potential pollution sources such as: leather plant, galvanic plant, tannery and bridges with busy roads. These concentrations also generally increased towards the entrance of the river into the Vistula. Sampling in 1994 [56] also revealed major differences in the concentrations of metals, but their values were generally significantly lower, which was attributed to the economic recession and the introduction of legal regulations which significantly curtailed or regulated the operations of plants especially harmful to the environment. Higher concentrations of metals continued to be observed in the areas of potential sources of pollution, such as pipes draining ponds, grass-covered waste heaps or bridges with heavy traffic. Results obtained from sampling in the period 2001–2002 [57] indicate further reduction of the concentration of metals in the superficial layer of the sediments (Figures 4 and 5), whereas the impact of previously observed sources of metal contamination was already unnoticeable. The same research [57] also reported vertical variability of the concentrations of metals, wherein it was established that it was of major significance, and the most polluted was the profile layer below the depth of 10–20 cm, and that these concentrations were even several dozen times higher than those measured for the surface profile layer, which was especially visible in the case of chromium (originating from the already closed leather processing plant). In some points a reverse effect has been observed (highest concentrations in the top profile layers), which was attributed to the impact of the intensification of vehicle traffic (in the case of Pb) or to the mixing of the Wilga and Vistula sediments during the periods of backwater, in the vicinity of the entrance of Wilga into Vistula.

As mentioned above, improvement of the geochemical condition of the Wilga sediments is mostly associated with the economic recession and the introduction of legal regulations which curtailed or regulated the operations of chemical industry plants. The problem of discharging sewage to the municipal sewage network was regulated in the Act of 27 April 2001—Environmental Protection Law [96], in the Act of 7 June 2001 on the Communal Provision of Water and Communal Discharge of Sewage [97] and in the Regulation of the Minister of Construction of 14 July 2006 on the Methodology of Compliance with the Obligations of Industrial Waste Producers and the Conditions for the Discharge of Waste into Sewage Networks [98]. The existing regulations cover, among others, the conditions for the discharge of waste into sewage networks, including the acceptable values of indexes of pollution in industrial waste discharged into sewage networks, as well as the methodology of controlling the quantity and quality of waste. The present Polish regulations comply with EU law.

Metals introduced into the Wilga environment are not likely to be transported across long distances due to the rather high pH of the river's environment and the related low mobility of metals. Therefore these elements are quickly subject to bonding in the sediments, which is also assisted by their relatively high content of fine fraction, which has the strongest sorption properties in relation to metals [99–102]. This is also confirmed by the results obtained in the course of the current research for fraction <63 μm and <20 μm (Figure 4), where the concentration of all metals (Cd, Cu, Pb and Zn) was higher in the finer fraction. An analysis of the mineral composition of the bottom sediments of the Wilga River [68] revealed that they contain clay minerals (smectite, illite, kaolinite), potassium feldspar, iron oxides, carbonate minerals (siderite) and sulphides. It was revealed that sediments are mainly comprised of the light fraction, which is polluted with cadmium and, to a lesser extent, with lead and zinc, while heavy fraction is polluted with Cu, Zn, Cd and Pb.

It seems that the current contamination of the environment of the Wilga River with elements is low. This is demonstrated not only by the gradually improving geochemical condition of the sediments but also by the low concentrations of elements in the water (Table 1) and in the suspended particulate matter (Table 2). SPM represents a good indicator of processes present in the catchment area of a given river and the anthropogenic pollution of the water environment, including by metals [103], and in polluted aquatic environments, it is indeed suspended matter that is the most polluted. This effect was still observed during previous research [57], where the concentrations of metals in suspended matter were much higher than in the sediments, and amounted to up to (in mg/kg): 60 for Cd, 506 for Cr, 517 for Cu, 250 for Ni, 320 for Pb and 1325 for Zn.

Wilga is considered to be one of the most polluted rivers in Poland, and the critical parameter of this assessment in the past was the concentration of metals, especially chromium [56,57]. The comparison of the concentrations of the analysed elements with those recorded in the Vistula, below Kraków, according to data provided by the Chief Inspectorate of Environmental Protection [86] (Table 2) demonstrates that the sediments of the Wilga are much more contaminated than the sediments of the Vistula. Due to the low discharge of the Wilga river, the load of pollutants introduced into the Vistula River is also relatively low. The average annual discharge of the Wilga River, measured near sampling point No. 9 is 1.07 m^3/s [68] and of the Vistula River, measured in the vicinity of the entrance of Wilga into the Vistula—125 m^3/s [104]. Over the years the general condition of the Wilga has improved significantly, which is reflected in the presented research and in the results of other authors. Currently, the bigger threat to the condition of the Wilga River is the elevated value of parameters such as phytobenthos, BOD_5 (5-day Biochemical Oxygen Demand), general hardness, chlorides, sulphates, ammoniacal nitrogen, nitrite-nitrogen and benzo(a)pyrene (data provided by Voivodeship Inspectorate of Environmental Protection [84]) and its sanitary condition [105].

4. Conclusions

The conducted research allowed us to draw the following conclusions:

1. A significant and gradual improvement of the geochemical condition of the Wilga River has been observed over the last several decades, which is attributed mainly to the termination or the significant reduction of industrial activity within the river's catchment area.
2. The impact of soda waste on the environment of the Wilga River is significant, but a reduction of the leaching of ions from the waste ponds into the river and a gradual improvement of its general condition has been observed, which is also confirmed by the observations of other authors.
3. No noticeable impact of road transport on the river's environment has been observed, even though it flows in the vicinity of major and heavily used roads. No negative impact of the construction of the "Łagiewnicka Route" on its condition has been observed either.

4. The environment of the Wilga is still quite heavily contaminated and it has to be classified as a polluted river, but the level of this pollution has decreased and its character has changed significantly. In the past, the critical parameter was the concentration of metals, especially chromium, currently it is higher mineralization, biogenic substances and sanitary condition.

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