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CHANGES OF WATER POLLUTION DYNAMICS IN VISTULA RIVER ON WARSAW CITY AREA

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Abstract

The paper presents change of water quality within Vistula River in the city of Warsaw. Water samples for analysis were taken from four different measurement points in the period from February to June 2016. Based on the results of laboratory studies it was demonstrated that the Vistula River in Warsaw is exposed to the input of pollutants contributing to increase the salinity, especially in winter and early spring. The concentration of both chlorides and sulphates were highest in February and was decreasing in subsequent months of the year. At the same time it has been shown that during the entire study period the concentration of Cl^- ion exceeded the limit values for water quality II class in Poland. While the SO_4^{2-} concentrations in water samples taken in the winter months (February-March) exceeded the limit values for the second quality class, in April, it was within the acceptable range for II class water quality, and in May and June does not exceed the value referred to as standard for I class of water quality. Based on the analysis of indicators of nutrients ($N\text{-}NH_4$, $N\text{-}NO_3$, Ptot.) it was found that the Vistula is not exposed to eutrophication due to their low concentration, which indicates a very good water quality. At the same time permanganate index (COD_{Mn}) indicates a low organic load of Vistula.

Key words: water quality, Vistula river, Warsaw, salinity, biogenic elements, permanganate index

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INTRODUCTION

The adverse effect of waters pollution are changes in physical, chemical and bacteriological properties of water, which are caused by the introduction into the waters of excessive amounts of inorganic and organic substances. The consequence of these changes is the limitation and exclusion or prevention of the possibility of use of water intended for human consumption and economic purposes (Pytka et al., 2013). The main source of water pollution is a human activity, since most pollutants is discharged to the water together with sewage. Wastewater treatment plants are point sources of pollution, municipal wastewater are a source of sulfur compounds, while household sewage contain mainly nitrogen and phosphorus compounds (Mosiej et al., 2007; Policht-Latawiec et al., 2013). Diffuse pollution come from, among others, agricultural lands. Surface runoff from these areas contain mainly nitrogen and phosphorus, which are the remains of mineral fertilizers. (Kornaś and Grześkowiak, 2011). Another source of pollution is runoff water flowing from the hardened, impervious surface from urban areas, e.g. parking lots, commercial and industrial areas. Pollution of water reservoirs may also come from industry. Increased salinity of waters near the coal mines is caused by the discharge of mining water to the rivers, and the sewage from the zinc-lead mines ores may include, among others, heavy metals (Nocoń and Nocoń, 2011).

The purpose of the paper was to analyze the variability of quality physico-chemical parameters of water in the Vistula River in the city of Warsaw and impact of industrial facilities located in Warsaw (thermal power plant Siekierki and Żerań) on river purity.

DESCRIPTION OF THE OBJECT OF RESEARCH

The study was conducted in the middle section of the Vistula River in the city of Warsaw. Vistula is the longest river in Poland, it has its source in Barania Góra and flows into the Gulf of Gdańsk (Baltic Sea). Vistula has a length of about 1047 km and basins with an area of 194 424 km^2 (Czarnecka, 2005). Vistula belongs to large rivers, because its length is in the range from 500 to 2500 km. Flowing through Warsaw, Vistula is a lowland river, it means that it has a meandering riverbed, with a significant width covered with debris, and a small decrease (less than 5 per mille). The water level here changes slowly and then remains unchanged for a long time (Bajkiewicz–Grabowska and Mikulski, 2013). Macro-region the Middle Vistula is mostly agricultural. Main sources of Vistula pollution are: spatial sources like run-off from agricultural areas and woodlands, spot sources – pollutant from sewage systems (municipal and industry waste), linear sources – source of those pollution are transport lines. Vistula's ballast of sewage is 24,2 m^3/day/km^2 and just 50% of them are biologically purified. Over the last few years the quantity of sewage flowing into the Vistula has dropped (Buszewski et al., 2005).

MATERIAL AND METHODS

Water samples for chemical analysis were taken 100 meters to the north and south of the thermal power plant Siekierki and Żerań. Samples were collected once a month (from February to June 2016) from the following four measurement points: 1 – south of Siekierki thermal power plant, 2 – north of Siekierki thermal power plant, 3 – south of Żerań thermal power plant, 4 – north of Żerań. A total of 20 water samples were taken.

In the water samples were determined selected indicators of physico-chemical elements, such as pH – potentiometric method according to PN-EN ISO 10523, chloride concentration – by titration according to ISO 9297, the concentration of sulfate by ion chromatography (IC) according to PN-EN ISO 10304, the concentration of calcium by atomic absorption spectrometry (ASA) according to PN-EN ISO 7980, the concentration of magnesium by atomic absorption spectrometry (AAS) according to PN-EN ISO 7980, COD_{Mn} (index permanganate) according to PN-EN ISO 8467, the concentration of ammonium ion by method of flow analysis according to EN ISO 11732, nitrate concentration using flow analysis according to ISO 13395, the concentration of total phosphorus – by ascorbate.

(https://pl.wikipedia.org/wiki/Warszawa)

Figure 1. Location of measuring-control points

Table 1. Weather characteristics during measurement period

Date of sampling	Average air temperature	Total fallout for the month
28.02.2016	2 °C	60-70 mm
26.03.2016	4 °C	30-40 mm
26.04.2016	10 °C	30-40 mm
22.05.2016	16 °C	20-30 mm
30.06.2016	20 °C	50-60 mm

The obtained results of chemical analysis were statistically analyzed using the method of multivariate analysis of variance. To assess the significance of differences between the means, Tuckey's test was used at the significance level of p = 0.05. For statistical calculations was used the Statistica 10 PL.

The results of physico-chemical measurements were compared with the limit values of indicators of water quality set provided by the Regulation of the Minister of the Environment of 5 August 2016 (Journal of Law s of 2016 no. 0, item 1187).

RESULTS AND DISCUSSION

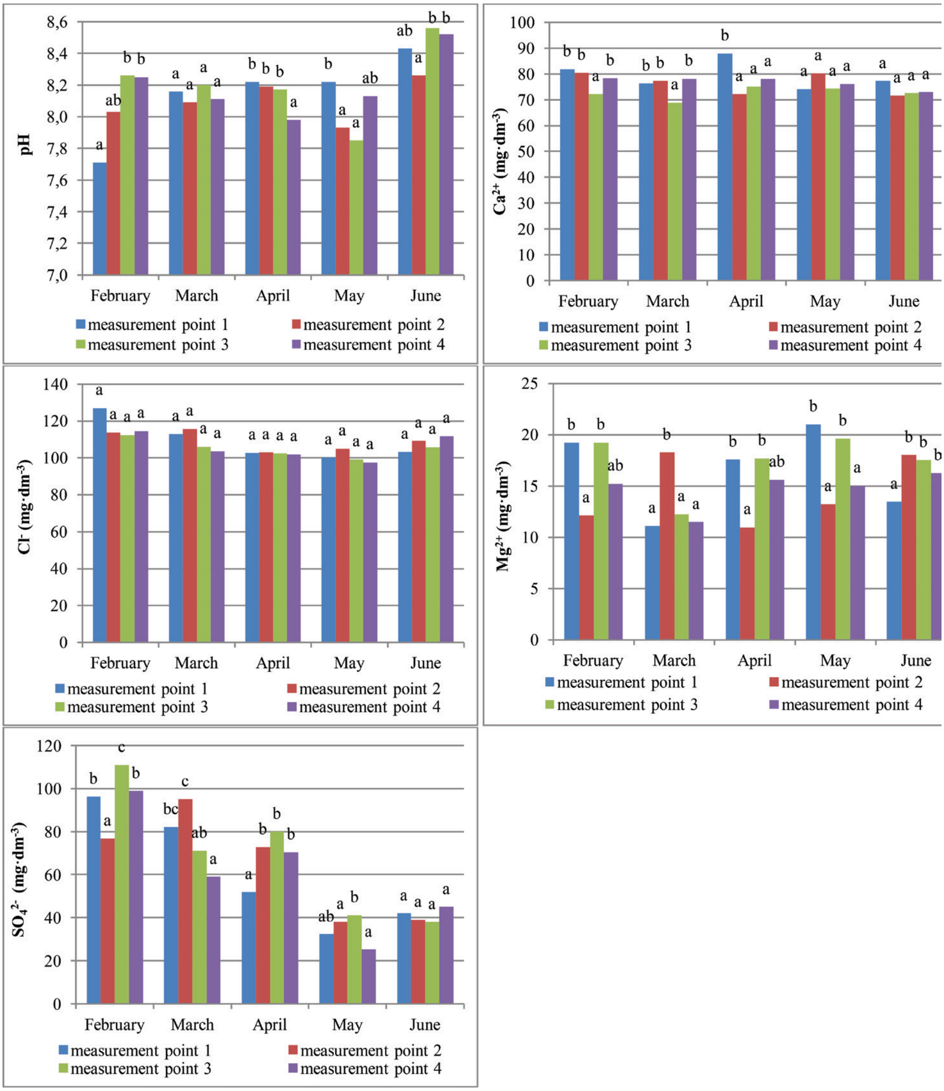
The quality and class of river waters is influenced by many factors, one of the most important is the pH value of water. The source of low pH in rivers are among others precipitations comprising nitric acid and sulfuric acid. On the direct effects of acidification of waters primarily fish roe, eggs, insects and fish are exposed (most species cannot survive at pH below 5). Another effect of lowering the pH is the increased solubility of heavy metals such as lead, aluminum, iron and nickel in contaminated water (Sommer, 1996). The increase in the pH of water can be affected by anthropogenic factors e.g. intensive fish farming, or be the result of alkalizing ability of vadose zones (Moniewski and Stolarska, 2007).

As follows from the conducted study (Table 2, Figure 2) the pH value of water of water in the Vistula over the study period remained relatively stable. The pH values determined in water samples collected from February to May 2016 ranged between in the range of 7.71 to 8.26 and did not exceed the range defined as standard for water quality I class (Regulation of Ministry of Environment, 2016). Only in the summer (June) it was observed a significant increase in pH compared to the other periods of sampling. At the same time, within this period pH of the water samples exceeded the values considered acceptable for first and second class.

Table 2. The values of selected indicators of water quality of the river Vistula in 2016

term	parameter	pH	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	COD_{Mn}	$N\text{-}NH_4$	$N\text{-}NO_3$	Ptot.
			$mg \cdot dm^{-3}$				$mg\ O_2 \cdot dm^{-3}$	$mg \cdot dm^{-3}$		
February	min.	7.71	112.41	76.83	72.19	12.13	1.74	0.14	1.39	0.031
	max.	8.26	127.04	110.94	81.83	19.24	2.60	0.24	1.74	0.072
	$\bar{x}$	8.06^{a}	116.98^{b}	95.72^{c}	78.21^{a}	16.46^{a}	2.08^{a}	0.20^{c}	1.58^{d}	0.045^{c}
	σ	0.26	6.77	14.12	4.26	3.45	0.40	0.04	0.17	0.019
	V (%)	3.2	5.8	14.8	5.4	20.9	19.3	21.6	10.6	41.4
March	min.	8.09	103.63	59.04	68.94	11.12	7.75	0.09	0.88	0.026
	max.	8.20	115.71	95.11	78.18	18.26	8.91	0.19	1.34	0.054
	$\bar{x}$	8.14^{a}	109.58^{ab}	76.84^{b}	75.18^{a}	13.28^{a}	8.51^{c}	0.14^{b}	1.12^{bc}	0.039^{bc}
	σ	0.05	5.64	15.39	4.23	3.35	0.52	0.04	0.24	0.012
	V (%)	0.6	5.1	20.0	5.6	25.2	6.1	29.7	21.5	30.6
April	min.	7.98	102.02	51.94	72.24	10.98	1.79	0.04	0.21	0.007
	max.	8.22	103.03	79.94	87.90	17.69	2.36	0.09	0.84	0.089
	$\bar{x}$	8.14^{a}	102.58^{a}	68.78^{b}	78.34^{a}	15.47^{a}	2.04^{a}	0.06^{a}	0.54^{a}	0.039^{bc}
	σ	0.11	0.45	11.93	6.80	3.14	0.24	0.02	0.26	0.035
	V (%)	1.3	0.4	17.3	8.7	20.3	11.7	36.0	48.2	91.8
May	min.	7.85	97.59	25.25	74.16	13.23	2.23	0.06	0.78	0.029
	max.	8.22	105.03	41.19	80.28	21.01	3.38	0.13	1.15	0.041
	$\bar{x}$	8.03^{a}	100.51^{a}	34.23^{a}	76.23^{a}	17.22^{a}	2.93^{b}	0.09^{ab}	0.97^{b}	0.033^{b}
	σ	0.17	3.20	7.03	2.85	3.69	0.50	0.03	0.19	0.005
	V (%)	2.1	3.2	20.5	3.7	21.4	16.9	32.7	19.9	16.5
June	min.	8.26	103.22	38.07	71.65	13.47	1.95	0.09	1.13	0.000
	max.	8.56	111.87	45.03	77.28	18.01	2.66	0.17	1.55	0.037
	$\bar{x}$	8.44^{b}	107.55^{ab}	41.07^{a}	73.63^{a}	16.31^{a}	2.33^{ab}	0.13^{b}	1.37^{c}	0.016^{a}
	σ	0.13	3.80	3.13	2.50	2.03	0.33	0.04	0.21	0.016
	V (%)	1.6	3.5	7.6	3.4	12.5	14.0	28.1	15.1	98.3
Quality class	The limit indicator of water quality according to Regulation of Ministry of Environment (Journal of Law s of 2016 no. 0, item 1187)									
I		7.7-8.4	≤33.6	≤64.3	≤100.0	≤11.2	≤10	≤0.76	≤2.0	≤0.20
II		7.5-8.4	≤75.6	≤71.5	≤114.6	≤13.4	≤12	≤0.84	≤2.2	≤0.30

* – the mean values in the columns marked with the same letters (a, b, c, d, ab, bc) form homogeneous groups



*the mean values marked with the same letters (a, b, c, d, ab, bc) form homogeneous groups

Figure 2. pH and selected indicators of salinity of water in the Vistula

Also Wysocka-Czubaszek and Wojno (2014) when examining the variability chemical composition of the waters of Biała River obtained the highest pH value during the summer. Molenda (2006), studying the water chemistry of small rivers, showed that in the spring there may be lowering of pH under the influence of melt water flow going into the river. The report of the Regional Inspectorate of Environment Protection (www.wios.pl date of access: 22.10.2016) shows that in 2012 in Warsaw, the pH was in the range of 7.7-9.0, indicating that in recent years the pH of water is not subject to significant changes.

Analyzing the chosen indicators of water salinity it was found that in all measurement points the concentration of chlorides and sulfates was the greatest in February and declined in subsequent months of the year (Table 2, Figure 2). At the same time it has been shown that during the entire study period the concentration of chlorides in the water of the Vistula River contained in a range from 97.59 to 127.04 $mg \cdot dm^{-3}$ and exceeded limit values for water quality II class (Regulation of Ministry of Environment, 2016). Also, studies of the Regional Inspectorate of Environment Protection (www.wios.pl date of access: 22.10.2016) of 2012 indicate a high concentration of chloride in the waters of the Vistula River in Warsaw, which was 123.4 mg $Cl^{-} \cdot dm^{-3}$.

Chloride ions are the basic anions present in surface waters. A significant amount of chloride in the water is of natural origin. They come, among others, from oceans of which they evaporate together with water, and then in form of precipitation they get into the land or are released into water in the mineral weathering process and leaching of rock. However, a large amount of chloride ions goes into rivers from municipal, industrial wastewater, and water coming from the mines drainage (Augustyn et al., 2012; Sapek, 2009).

The found in the conducted studies sulphate concentrations showed differences both in terms of the measuring point and the time of year (Table 2, Figure. 2). The concentration of sulfates found in water samples taken in the winter months (February-March) exceeded the limit values for the II class. In April, SO_4^{2-} ion concentration was in the range permitted for II class water quality, and in May and June it did not exceed the value referred to as standard for I water quality class (Table 2). Average concentration of sulphate for the period of the research in the Vistula River in Warsaw was 63.32 $mg \cdot dm^{-3}$ and was close to the annual average concentration of these ions in 2012 (www.wios.pl date of access: 22.10.2016). Sulphate ions (VI) are a common ingredient in surface waters. They come from both natural sources (e.g. weathering of rocks and minerals) as well as anthropogenic. The main source of these ions in surface waters are gas pollution from industry heating. Other sources of this compound contaminating the river may be the use of fertilizers containing sulfur or discharge into rivers of acid mine waters and sewage (Harat and Grmela, 2008; Jakubowski et al., 2013).

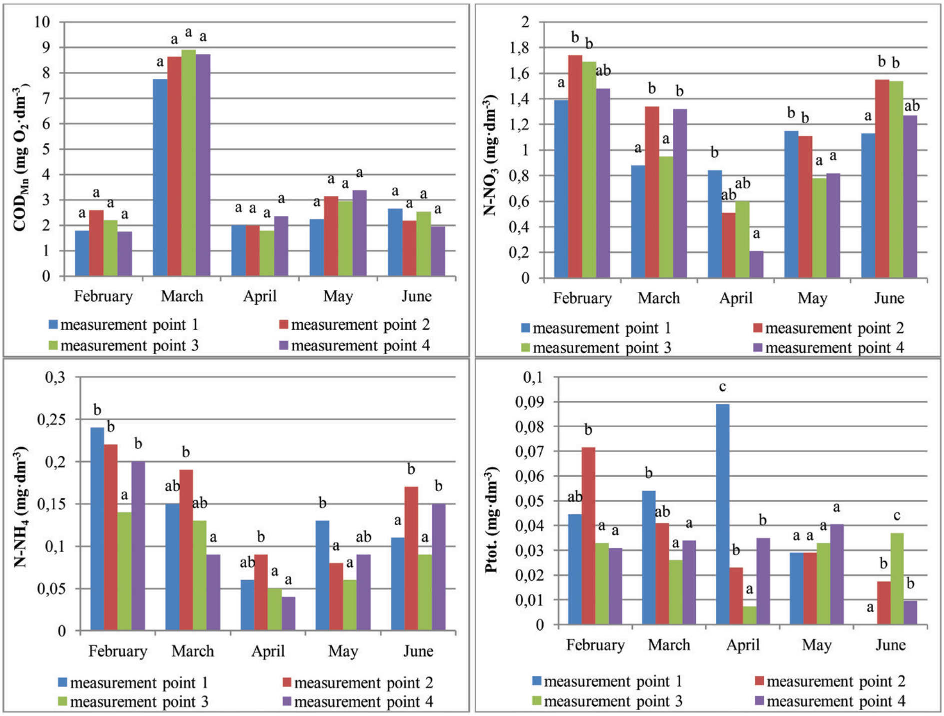
The concentration of calcium in the tested samples of water randeg between of 68.94 to 74.16 mg dm^{-3}, and regardless of the season and the measuring point was lower than that considered standard for I surface water quality class (Table 2, Figure 2). Magnesium levels on the other hand showed greater variation both, depending on the period of sampling and on the place of their collection and contained in the range of 10.98 to 21.01 $mg \cdot dm^{-3}$ (Table 2, Figure 2). Based on the study, it was found that normally the average concentration of Mg^{2+}

ions in the water of the Vistula River exceeds the limit values for II class surface water quality. Only in March, the examined water samples met the criteria specified for II class water quality. Similar concentrations of Ca^{2+} and Mg^{2+} in river waters in urban areas was found by Ciupa (2009), and Wysocka-Czubaszek and Wojno (2014). As indicated by Ciupa (2009), a source of calcium ions in the rivers in urban areas is leaching from materials used in the construction of roads, parking lots, sidewalks and buildings, while the magnesium comes mainly from the leaching of soils. In recent years, there has been an increase in the concentration of magnesium ions in surface waters under the influence of the measures used for de-icing of streets and sidewalks (Bojakowska et al., 2012).

The conducted studies demonstrated that the value of the chemical oxygen demand (permanganate index) for the tested water samples was not dependent on the location of the sampling for analysis and showed little variation over the study period. Only in March, COD_{Mn} value was significantly higher compared to other periods (Table 2, Figure 3). The obtained in conducted studies values of COD_{Mn} ranged from 1.74 to 8.91 mgO_2 dm^{-3} and did not exceed the accepted standard for I water quality class and was lower than annual average value in 2012 in Warsaw – 9,6 mg O_2 dm^{-3} measured by Regional Inspectorate of Environment Protection (www.wios.pl date of access: 22.10.2016).

Analyzing the concentration of nutrients in the water of the Vistula River in Warsaw, was found considerable variation both depending on the sampling site and the time of year (Table 2, Figure 3). The highest concentration of ammonium nitrate and nitrates (V) was found in water samples taken in February, and the lowest in samples taken in April. Regardless of the date and place of sampling, the concentration of ammonium and nitrate ions did not exceed the limit values for I water quality class but concentration of both ammonium nitrate and nitrates (V) ware higher than in 2014 measured in Vistula in Warsaw by the Regional Inspectorate of Environment Protection – 0,100 mg $N\text{-}NH_4 \cdot dm^{-3}$; 1,30 mg $N\text{-}NO_3 \cdot dm^{-3}$ (www.wios.pl date of access: 22.10.2016). The found in the studies total phosphorus concentration was very low and ranged from 0.00 to 0.089 $mg \cdot dm^{-3}$ and independently from the measuring point and the samples for analysis did not exceed the limit values for water quality class (Table 2, Figure 3).

The report of the Regional Inspectorate of Environment Protection (www.wios.pl date of access: 22.10.2016) shows that in 2014 in Warsaw, the concentration of phosphorus was 0,118 mg $P \cdot dm^{-3}$, indicating that in recent years concentration of phosphorus in water was not subject to significant changes. Similar concentrations of phosphorus and ammonium nitrate was found in Seine in France. However concentration of nitrate in Warsaw was significantly lower than in Seine (Romero et al., 2016). The highest concentration of total phosphorus (Ptot.) was determined in samples collected in winter (February) and it decreased in subsequent periods. In June, the concentration of Ptot. in water was nearly three times lower than in February (Table 2). Also, studies of other authors indicate that the highest concentration of nutrients in surface waters occur in winter and early spring, and the lowest in summer (Ostrowska, 2010; Jarosiewicz and Dalszewska, 2008). As indicated by Jarosiewicz and Dalszewska (2008), heavy precipitation and sudden thaw occurring from autumn to early spring may be the cause of the increased concentration of nutrients in surface waters. These ingredients penetrate into surface waters both as a result of leaching and surface runoff. Also, increased emissions of nitrogen compounds into the atmosphere in the winter may increase the concentration of this element in the surface waters. In the summer there is an intense assimilation of biogenic components by phytoplankton, which results in lower concentrations of these elements in surface waters.



*the mean values in the columns marked with the same letters (a, b, c, d, ab, bc) form homogeneous groups

Figure 3. COD and selected indicators characterizing the nutrient conditions in the water of the Vistula

CONCLUSIONS

1. Discharge of wastewater from the power plant Siekierki and Żeran does not affect the quality of water in the Vistula River.
2. The Vistula River in Warsaw is characterized by an alkaine reaction. At the same time, this parameter exhibits little variation in individual months.
3. The concentration of chloride ions and sulfate (VI) points to a significant inflow to the river in the winter and early spring of substances decisive for the increase in water salinity.
4. In terms of the concentration of chlorides and sulfates, water in the Vistula River in Warsaw should be classified into the waters of the state of quality below good.
5. The concentration of calcium ions indicates a very good water quality in the Vistula River and the concentration of magnesium ions to the condition below good.
6. The value of chemical oxygen demand indicates a slight burdening of Vistula River with organic contaminations load. This parameter shows a significant stability over the study period and allows to include the tested water to the water with a very good quality condition.
7. Vistula River in the area of Warsaw is not significantly threatened by the process of eutrophication due to the low concentration of nutrients ($N\text{-}NH_4$, $N\text{-}NO_3$, Ptot.), the concentration of which indicates a very good water quality. The highest concentration of nutrients occurs in the waters of the Vistula River in the winter and early spring, and the lowest in April ($N\text{-}NH_4$, $N\text{-}NO_3$) and June (Ptot.).

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