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Selected Quality Indicators of Surface Waters of the Czestochowa City and Neighbouring Municipalities

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ABSTRACT
The surface water quality significantly affects the purity level of groundwater drawn for the municipal purposes. The pollution presence in surface waters is fundamentally the effect of the anthropogenic activity in a particular area while the type and volume of pollution depend closely on the intensity of any such activity. The paper presents the results of types of selected quality indicators of surface waters, *i.e.* pH, electrical conductivity and heavy metal concentration: Fe, Mn, Zn, Cu, Cd, Ni, Pb and Cr in the surface waters collected from the city of Czestochowa and neighbouring municipalities – the locations of water intakes and deep wells operated by the Water Supply and Sewerage Joint Stock Company of the Czestochowa District in order to provide the citizens with potable water. The findings of analyses of water collected every month in the period from January to September 2020 in 9 points were the basis for an observation of a time and space variability of the values of the quality parameters studied, which is evident of a diversified impact of the surroundings on water environment in consecutive research months. The potential water pollution sources were also indicated.

Keywords: surface waters, water quality indicators, heavy metals, pH, conductivity, pollutions

INTRODUCTION

Global economic development over the centuries has caused significant changes reflected in the improved quality of human life; nevertheless, it entails negative effects within the environmental as well as health aspects. The literature indicates that 95% of the known chemical substances are artefacts – artificial products which do not exist in nature [Afeltowicz 2012], which, however, may reach the natural environment with solid industrial, agricultural or communal waste and affect living organisms to a greater or lesser extent. In order to prevent further deterioration of water condition, in the year 2000 the European Union passed a Water Framework Directive [Directive 2000] aimed at protection and improvement of the condition of European (surface and ground) inland waters as well as terrestrial ecosystems dependant on those waters. The intent of the document (with later amendments) creators was to achieve a good ecological condition of waters through such measures as elimination or reduction of emissions of the most hazardous pollutions, in particular the so called "priority substances" and heavy metals. Although many heavy metals, such as iron, zinc, copper or manganese, are crucial to the proper functioning of a living organism, higher amounts in the body may be harmful. Other of those elements, cadmium, mercury, lead, arsenic or barium are toxic even in small amounts and cause acute or chronic intoxication, many serious diseases and even death [Jaishankar et al. 2014, Briffa et al. 2020]. Polish legal acts, based on the EU acts, specify the maximum allowable concentrations of a range of heavy metals in potable waters (Regulation of the Minister of Health [Regulation 2017]), surface waters used to provide people with water intended for consumption (Regulation of the Minister of Maritime Economy and Inland Navigation [Regulation 2019]) or in treated industrial waste water entering the waters and soil, with a list of waste generating industry sectors (Regulation of the Minister of Maritime Economy and Inland Navigation [Regulation 2019a]). The scientific research on surface water conducted in various areas of Poland indicates a significant time variability and sometimes exceedance of the permissible values of quality indicators in those waters [Grzywna 2014, Wojtkowska 2014, Durkowski and Jarnuszewski 2015, Piekutin 2016, Michalski et al. 2018, Michalski et al. 2019, Michalski et al. 2020].

The Water Supply and Sewerage Joint Stock Company of the Czestochowa District (*pl. Przedsiębiorstwo Wodociągów i Kanalizacji Okręgu Częstochowskiego*, CzPWiK), providing over 300 thousand residents and many production plants with water, covers the area of the city of Czestochowa and 9 neighbouring municipalities territorially belonging to the district of Czestochowa and Kłobuck, where 19 water intakes and over 200 monitoring network facilities, such as water treatment stations, water pumping stations, water tanks or lifting plants for wastewater are located [Environmental statement 2019]. Residents of the city and the neighbouring municipalities are provided with water for municipal purposes, which is in 100% drawn from ground waters, mainly from the Upper Jurassic level (Main Reservoir of Ground Waters no. 326) and – to a lesser extent – from the Triassic, the Middle Jurassic and the Quaternary. Although the surface waters in Czestochowa area are used for industrial purposes only, the ground waters abstracted by CzPWiK for municipal purposes, mainly from the tertiary and Upper Jurassic beds, feature a very weak level of natural isolation of an aquifer and at the same time they are exposed to a potentially quick surface pollutant infiltration [Pacholewski et al. 2016].

The areas, where the CzPWiK water intakes are located, are subjected to a continuous impact of a variety of anthropogenic factors which may be the cause of the groundwater quality degradation. The main sources of groundwater pollutions in the Czestochowa region are: infiltration of water and precipitation from industry polluted areas (e.g. steelworks, glassworks operation), transport (e.g. the DK1 national road, the A1 motorway), washing out of toxic agents from post-industrial and municipal waste (e.g. sewage sludge from the Central Wastewater Treatment Plant), illegal landfills or flooded closed iron ore mines. Furthermore, leaky sewage tanks (or lack thereof) constitute a serious hazard, which causes untreated municipal wastewater and that generated by small production plants (such as plating plants, furniture plants, butchers and animal farms) as well as arable, fruit and horticultural farms (in 2018 only 47.2% citizens of Czestochowa district used a wastewater treatment plant disposal into the environment [Report 2020]). In response to the need of groundwater resources quality protection in the water intake utilisation, the direct and indirect protection zones, with a range of restrictions, were introduced. Nevertheless, a regular and long-term monitoring of surface water quality is essential to maintain a good physical, chemical and microbiological condition; furthermore, it is an excellent source of information for proper water resources management in the region.

The objective of the research conducted was to define the basic water quality indicators, *i.e.* pH, electrical conductivity and selected heavy metals (Pb, Cd, Zn, Cu, Ni, Cr, Fe and Mn) concentration in the surface waters from the areas of potable water intake for the citizens of the city of Czestochowa and the neighbouring municipalities.

MATERIAL AND METHODOLOGY

The water samples were collected once a month from January until September 2020 at nine points marked on the map with letters A–I (Fig. 1) and depicted in Table 1.

In total, 81 water samples were collected, with pH and electrical conductivity determined in compliance with the procedures detailed in the PN-EN ISO 10523:2012 and PN-EN 27888:1999 standards, respectively. A portion taken from each sample was acidified with ultra pure nitric acid (V) to pH of about 2.0, filtered through a membrane filter with a pore diameter 0.45 μm and the metal concentration was established with the use of microwave induced plasma-atomic emission spectrometry (spectrometer MP-AES Agilent 4200).

RESULTS AND DISCUSSION

The findings of the studied surface water analyses, with their reference to the requirements of the Regulation of the Minister of Maritime Economy and Inland Navigation regarding surface water quality used to provide residents with water suitable for human use [Regulation 2019] are presented in Table 2.

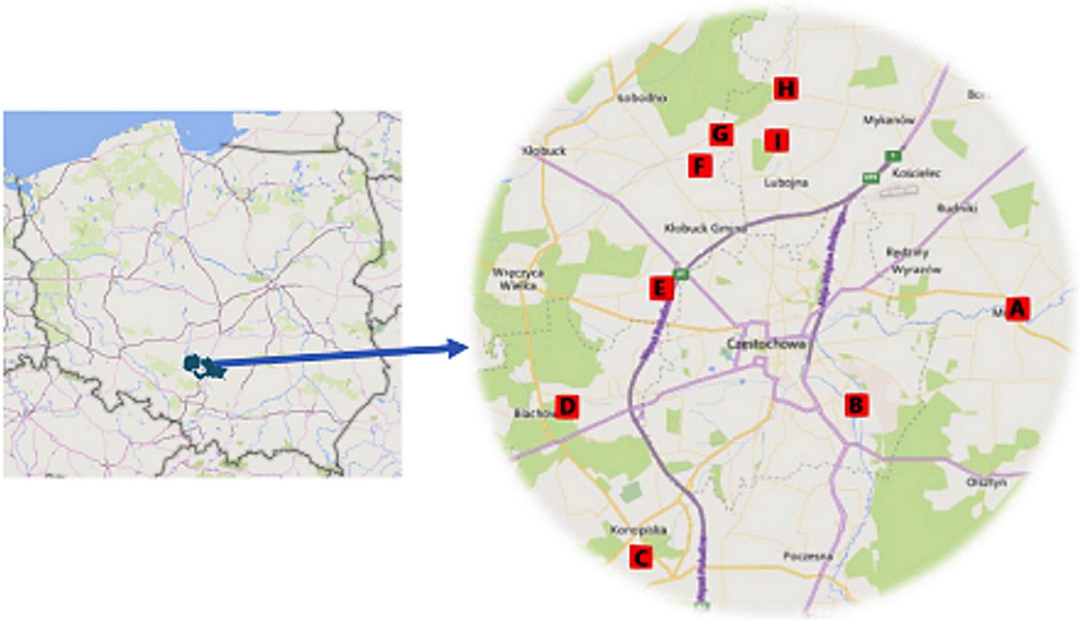

Fig. 1. Location of water sample collection points

Table 1. Water collection point characteristics ([1] TSR – treated sewage receiver)

Point	GPS coordinates	Location	Source	Water (W) and terrain (T) characteristics
A	50° 49' 50.498" N 19° 17' 24.858" E	Mstów	Warta River	W: past its course through Częstochowa, past the water entry points of the rivers: Stradomka[1], Konopka and Kucelinka[1], running through Częstochowa district area and the city industrial quarters T: industrial and agricultural, municipal (city of Częstochowa) and rural (municipality of Mstów), near the river, e.g. steelworks, glassworks, no. 1 national road, Central Sewage Treatment Plant, Mirów water intake)
B	50° 47' 10.534" N 19° 10' 19.204" E	Częstochowa	Huta Reservoir	W: storage reservoir located within the city, fishery T: industrial, direct neighbourhood of a rolling mill and still mill of steel-works as well as Warta and Kucelinka rivers
C	50° 42' 57.655" N 19° 0' 51.938" E	Konopiska	Pająk Reservoir	W: reservoir on Konopka river, of a recreational nature, fishery T: agricultural and forest, in direct neighbourhood of the Municipal Culture and Recreation Centre and CzPWiK premises
D	50° 47' 6.593" N 18° 57' 36.096" E	Blachownia	Blachownia Reservoir	W: storage reservoir on Stradomka river, with a tributary of Trzepizurka stream waters, running through the rural and forest areas of the Konopiska and Blachownia municipalities, of a recreational nature, fishery T: urban-rural, in the vicinity of the city centre
E	50° 50' 24.917" N 19° 1' 45.257" E	Szarlejka	Białka River	W: waters running through the centre of the location, catchment of rainwater canal-driven from the surrounding areas T: rural, the A1 motorway and farmlands in the vicinity
F	50° 53' 49.593" N 19° 3' 24.929" E	Kopiec	Fishing pond	W: fishing pond T: rural, in direct neighbourhood of farmlands and Białka river
G	50° 54' 40.76" N 19° 4' 21.297" E	Kuźnica Kiedrzyńska	Kocinka River	W: past the water entry points of Czarna Oksza river, which runs through the rural areas of the municipality of Wręczyca Wielka and Kłobuck and Białka river, cutting the A1 motorway twice on the Szarlejka – Kuźnica section T: rural, specialising in horticulture, petrol station and CzPWiK premises in direct neighbourhood
H	50° 55' 57.588" N 19° 7' 11.474" E	Rybna	Sękawica River	W: past its course through the rural area past the Tylinka river mouth[1] T: Mykanów municipality rural areas (small industrial plants, agriculture, horticulture), in a direct neighbourhood of the CzPWiK well
I	50° 54' 31.444" N 19° 6' 48.202" E	Tylin	Tylinka River	W: past its course through the rural areas of Mykanów municipality, next to the Wierzchowisko water intake, spring near the A1 motorway T: rural, specialising in horticulture, CzPWiK premises in direct neighbourhood

Table 2. The results of water analyses with regards to the Polish legal regulations

Indicator	Water category			Measured values	
	A1	A2	A3	Minimum ± σ*	Maksimum ± σ
Group I					
pH	6.5–8.5	5.5–9.0	5.5–9.0	6.20 ± 0.01	9.48 ± 0.02
conductivity (20⁰C) (μS/cm)	1000	1000	1000	259.1	1396.4
Group II					
Fe (μg/L)	300	2000	2000	< 2.0	1978.7 ± 7.8
Mn (μg/L)	50	100	1000	< 0.3	275.9 ± 2.9
Cu (μg/L)	50	50	500	< 0.9	29.7 ± 2.3
Zn (μg/L)	3000	5000	5000	3.6 ± 1.1	96.0 ± 8.5
Group III					
Cd (μg/L)	5	5	5	< 1.5	15.3 ± 1.2
Ni (μg/L)	50	50	200	< 1.1	28.7 ± 0.6
Cr total (μg/L)	50	50	50	< 1.0	51.4 ± 0.4
Pb (μg/L)	50	50	50	< 1.7	36.0 ± 2.0

*σ – standard deviation for three independent measurements.

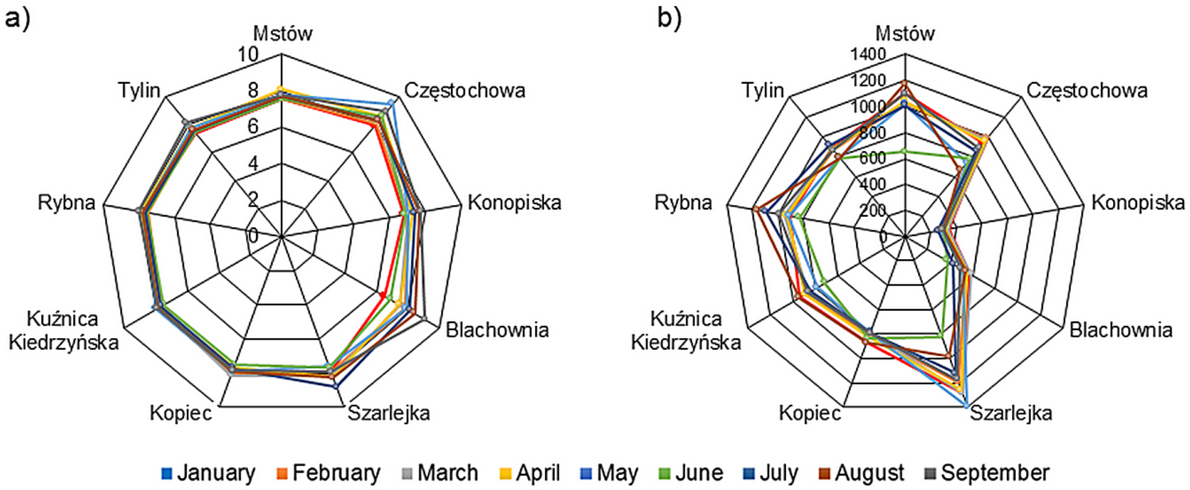

Fig. 2. Time and space variability of the pH (a) and electrical conductivity (b) of surface waters studied

Group I water quality indicators

The time variability of physicochemical parameters, under the Regulation [Regulation 2019] classified as group I water quality indicators *i.e.* pH and electrical conductivity, specified for the surface waters studied in individual months is presented in Figure 2.

The pH of the studied water samples ranged from 6.20 for the Blachownia reservoir water collected in January to 9.48 for the pond in Czestochowa water, collected in May. In most points, the pH values in the period studied remained at a steady level, within the 6.5–8.5 range required for the A1 category of surface waters. An exception was the water from the reservoir in Czestochowa, where a gradual pH increase was observed from January until May and its stabilisation in the following months, as well as the water from the reservoir in Blachownia, with a significant pH increase observed in the period June – September. In the instance of Blachownia, high pH values may stem from an intense recreational use of the reservoir in the summer by large numbers of visitors (bathing beach, water sports). The pH values over 9 (Czestochowa – May; Blachownia – September) prevent them from being used to provide the population with potable water. On the other hand, the water from the Blachownia reservoir, aside the water collected from the Pająk reservoir in Konopiska, demonstrated the highest electrical conductivity, which is evident of a lower mineralisation level in comparison to other water samples. The acceptable conductivity value limit – 1000 µS/cm was exceeded twice (July and August) in the instance of the Sękawica river (Rybna) and eight times (exception is June, when the samples were collected following intense rainfalls) in the Warta (Mstów) and Białka (Szarlejka) river waters.

Group II water quality indicators

Group II indicators include e.g. heavy metals such as iron, manganese, zinc and copper. The results of the analyses related to the concentration of those metals in surface waters are presented in a graphic form in Figure 3.

The graphs above demonstrate that the presence and volume of the studied elements in water significantly depends on the place and time of water collection. In the instance of some collection points, one may observe an upward trend of the Fe, Mn and Cu concentration in the water collected in the winter and spring months (for example Fe, Mn – Blachownia (D), Szarlejka (E), Cu – Rybna (H), Tylin (I)). The identified volume of Fe and Mn in studied waters is categorised in accordance with the categories specified in the Regulation [2019], to the A1, A2 or A3 category. The water collected in Czestochowa, Szarlejka, Kopiec, Kuźnica Kiedrzyńska and Rybna, with the Fe content below 300 µg/L may be included in the A1 category, whereas other water samples, up to 2000 µg Fe/L – in the A2/A3 category. The maximum Fe concentration ranging from 800 to 1947 µg Fe/L was noted in June and July in the Konopiska (C) and Blachownia (D) waters. The results of manganese concentration analyses indicate a slightly different categorisation of studied waters. Considering the above, only the water collected from the reservoir in Czestochowa (B) and a fishing pond in Kopiec (F) (maximum Mn concentration is 24 and 19 µg/L, respectively) meet the A1 category, the water collected from the rivers: Białka in Szarlejka (E), Kucelinka in Kuźnica Kiedrzyńska (G) and Sękawica in Rybna (H), with a maximum content of 54, 93 and 100 µg Mn/L, respectively, may be assigned to the A2 category. Other water samples, due to the manganese content with 105 to 276 µg/L concentration, are the A3 category waters. A definitely higher iron and manganese content, in comparison to other points, was recorded in the Konopiska (C)

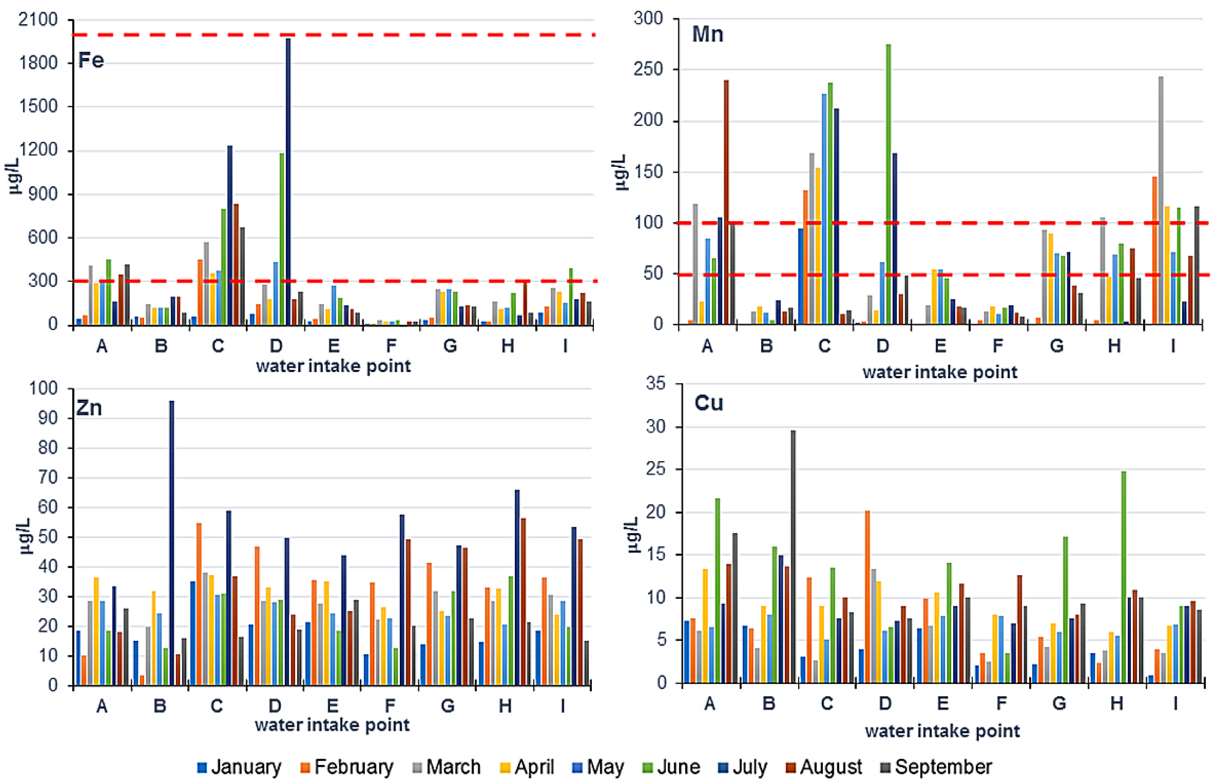

Fig. 3. Changes of concentration of iron, manganese, zinc and copper in waters studied over a time period

and Blachownia (D) reservoirs, which may be related to their location within the Czestochowa Iron Ore Basin, where waste heaps from iron ore mining and processing remained once the mine was closed [Gawor et al. 2015]. Those areas may also affect the Fe concentration level in the Warta river, fed with water from the Stradomka and Konopka river tributaries, running through the iron ore-bearing areas. Significantly higher Zn concentrations were noted in the water samples collected in July, with the 96 μg/L value, in the Czestochowa water reservoir (B), nevertheless this value constitutes a third of the acceptable value for the A1 category waters. In September, in the same place, the highest Cu concentration (30 μg/L) results were recorded, while in June the concentration of this element was noticeably higher in almost all water samples, e.g. Sękawica river (H) the recorded values were 2–3 times higher than in the other months.

Considering the average total values of group II indicators at a particular point of water sample collection for the entire research period (Fig. 4), it can be noted that the surface waters collected at the points located in the rural areas to the north of Czestochowa (points E – I) feature a prominently lower content of the studied metals (with the lowest value for water in the fishing pond in point F (Kopiec)) as compared to the water samples collected from the eastern and western areas of the Czestochowa district, which are under the influence of industry, transport as well as post-mining and iron ore processing waste (points A, C, D).

Group III water quality indicators

Group III of surface water quality indicators includes such heavy metals as cadmium, nickel, lead and chromium. The results of analyses of those elements in individual water samples and months are presented in Figure 5.

Comparing the obtained results to the requirements specified in the Regulation [2019] for individual category waters, it can be noted that not all group III quality indicators of the studied water fit within the range of the indicated standards. The concentration of cadmium, considered one of the priority substances which may occur in surface waters in a concentration not exceeding 5 μg/L, was exceeded in the researched time interval five times, while in four instances, those exceedances were negligible; however, in one instance – in the water collected in Czestochowa in September (B) – as much as 15 μg Cd/L was recorded. Other heavy metals occurred in the studied waters in the concentrations not exceeding the specified norms, with a significantly higher Pb concentrations observed in the Warta river water sample collected in Mstów (A) as well as in the Czestochowa reservoir water (B), where this element concentration was highest among all the water samples studied, in August (36 μg/L). In the same month, the nickel concentration in three points was higher than in the other months with the values ranging from 20 to 26 μg/L for the waters in Mstów (A), Czestochowa (B) and Konopiska (C).

The research regarding chromium demonstrated high concentrations, distinctive in

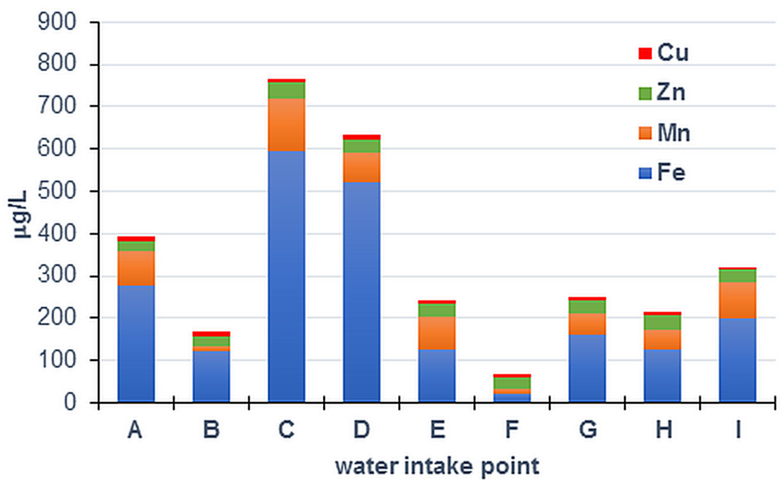

Fig. 4. Total average of the iron, manganese, zinc and copper concentrations in individual water samples collected in the research period

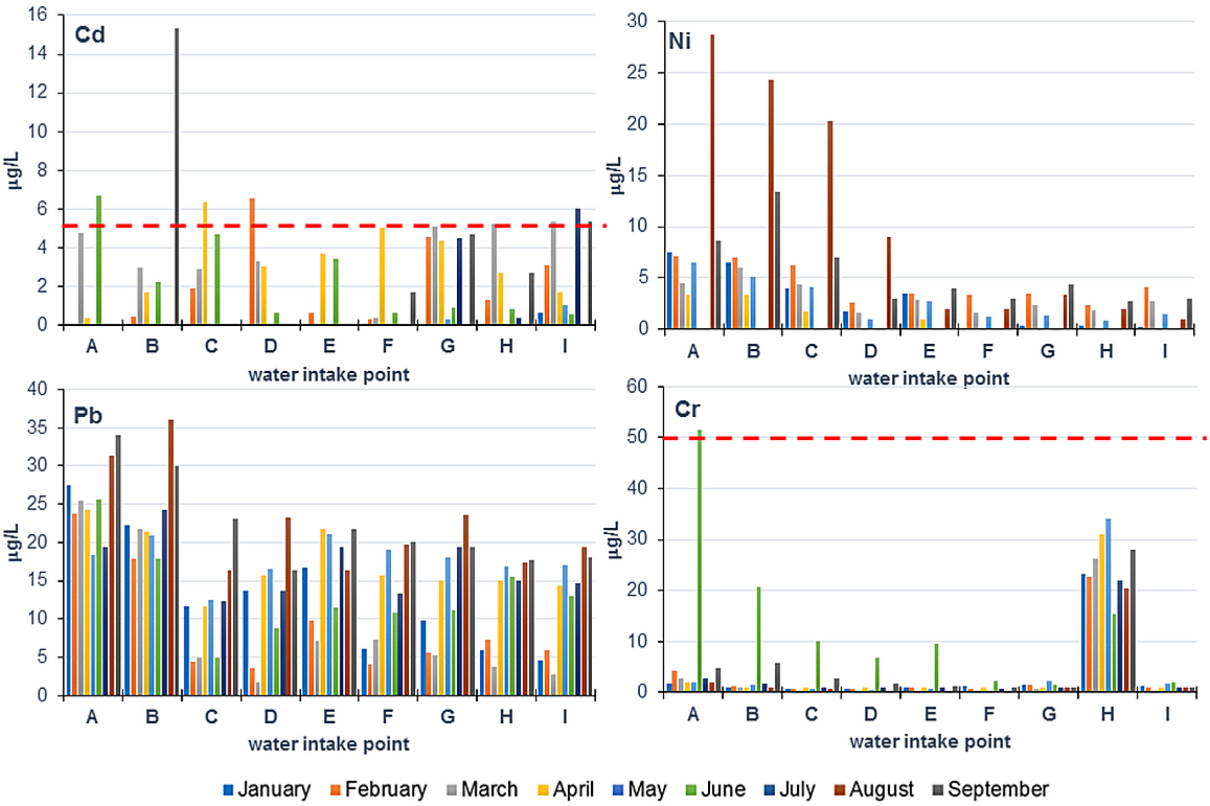

Fig. 5. Changes of cadmium, nickel, lead and total chromium concentration in waters studied over a time period

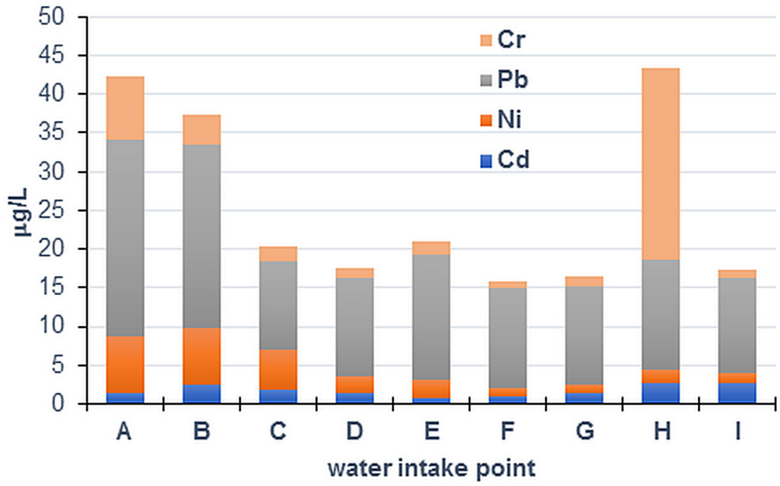

Fig. 6. Total average concentration of cadmium, nickel, lead and total chromium in individual water samples in the research period

comparison to other waters, in the Sękawica river water samples collected in Rybna in every research month, with the highest values (respectively 31 and 34 µg/L) in April and May. The presence of chromium in that water may be caused by the operation of the Wastewater Treatment Plant in Rybna, located close to the point of sample collection for the analyses, with the Sękawica river being the receiver of treated wastewater; nevertheless, the problem of large volumes of chromium in those areas has been known for many years and is related to this element migration from the post-industrial waste landfills of the Chemical Plant in Rudniki [Zdechlik et al. 2013]. In June, an incidental increase of the Cr concentration was noted in five of the studied points (A – E), where this metal concentration in Warta river in Mstów reached the maximum permissible concentration for total chromium (50 µg/L).

The analysis of average monthly values of group III indicators at individual sample collection points in the selected time interval (Fig. 6), indicates higher values of total concentration Cd, Ni, Pb and total Cr for the surface waters collected in the Czestochowa area (point B) and to the east of the city (point A – Mstów), which are directly or indirectly influenced by industrial, transport and municipal wastes, detailed out in Table 1. A comparably high value of a total concentration of group III metals considered as in point A, generated with high values of chromium concentration, noted in the area of Mykanów municipality, in the Sękawica river water (point H).

CONCLUSIONS

On the grounds of the findings obtained during the analyses of surface waters located in the areas of water intakes for the citizens of Czestochowa and neighbouring municipalities, a conclusion may be drawn that the quality of those waters is satisfactory; however, time and space variability of the value of the quality parameters studied is noticeable, which is evident of a diverse impact of the surroundings on the water environment of the area in consecutive months of the year. This prevents an unambiguous categorisation of the studied waters. Considering the location of the test points, the waters from the rural areas located to the north of Czestochowa demonstrate considerably better quality. The water samples collected from a fishing pond in Kopiec meet the A1 water category requirements, while the water from the Kocinka river, collected in Kuźnica Kiedrzyńska as well as from Tylinka river, collected in Tylin, due to an increased manganese concentration values may be categorised as A2 waters. Despite the low values of the other indicators studied, high values of conductivity of the Białka river in the Szarlejka and Sękawica river water place those waters outside the class scope. The focal source of high conductivity values in those waters may be assigned to the agricultural and horticultural activity in those areas and the related presence of high volumes of ionic pollutants resulting from the use of inorganic fertilizers and, in the instance of the Sękawica river, treated municipal wastewater discharge from the neighbouring treatment plant in Rybna. A definitely poorer surface water quality, in comparison to the north of the studied area, was determined in the instance of waters located on the territory of Czestochowa and in the eastern and western part of the Czestochowa district. Considering the maximum values of quality indicators acquired in the research period, although in the instance of most of the measured parameters they fitted within the A1, A2 or A3 water class standards, the cadmium concentrations exceeded in those waters and, additionally, conductivity in the Warta river water in Mstów, place these waters outside the class scope. The industrial plants, which are in a direct neighbourhood of the water reservoirs and the course of Warta river and its tributaries as well as ore-bearing areas, transport routes or a central municipal wastewater treatment plant, constitute significant sources of water pollutions in this area, but their impact fluctuates within the consecutive months of the year. Furthermore, a significant increase of quality indicators was observed in the summer season in the reservoirs of a recreational nature, in spite of the restrictions in economic operation and safety principles introduced with regards to the coronavirus SARS-CoV-2 pandemic.

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