Hydrochemical transformations of river waters during the flow in the reception basin on the basis of Olechówka River in Łódź

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Abstract. This work presents the results of the research experiment of conducting hydrochemical observation of the Olechówka River in Łódź and its flow from the river source until its estuary. The main aim of the research was to set tendencies of changes in waters flowing down from municipal reception basin with developed rain drain system and in waters flowing into bathing areas at the same time. Along with the flow of the river, 12 measuring-research points were established. In each of those points, measurements of the discharge rate and mean flow velocity of water in the channel were performed, which enabled to set average time of the flow of water between individual measuring-research points. The time of storing water in reservoirs was taken into consideration. The total time of the flow of water in the Olechówka River amounted to 856 h and 15 min. The analyses included in situ measurements (T, pH, SEC), analytical determinations Cl^-, NH_4^+, NO_3^-, TN, PO_4^{3-}, TP and Oxidability. The interchangeability of values of tested indicators and discharge point out to their decrease along with the increase of water flowing in the riverbed. There were self-cleaning processes identified in the Olechówka River: dilution and denitrification, along with the accumulation of total phosphorus in the river flow.

1 Introduction

Changes in the water regime caused by urbanization make the functioning of rivers gain additional local economic importance. Three basic sections can be distinguished on rivers flowing through the city: above the city – flow approximate to natural; within water intakes for the city – flow reduced by consumption; below the city – flow increased by sewage discharge [1]. Small rivers have the additional function of feeding water reservoirs established on their courses, including those with recreational function. In the area of the

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Łódź urban agglomeration, the Ner River serves as an example of a river with a complex economic function. In its upper course, by infiltration, it supplies urban underground water intakes in the vicinity of Rzgów. Further along its course, it feeds the recreational reservoirs in Ruda Pabianicka – so called Stefański ponds. Finally, from Chocianowice, it becomes the receiver of first stormwater, and then sanitary sewage. The Olechówka River belongs to the fluvial system of the Ner River. It is connected to it through the Jasień River. Its entire course is within the boundaries of the city of Łódź, running through its southern districts. The two primary functions of the river are recreational and as a receiver of sewage. The intensity of management of the Olechówka River catchment makes it impossible to designate its sections with specific functions – both of the aforementioned functions overlap.

The far-reaching transformation of water relations in the urban catchment and in the urban river channel itself provided the basis for the distinguishing [2] of a new type of river regime, namely anthropogenic-nival-rain regime. In the case of such a regime, outflow culminations can occur in any month of the hydrological year. Research conducted in the Jasień River catchment [3] showed that in the conditions of 2–5 times lower infiltration, 0.5–2 times lower groundwater retention, 2–3 times higher seasonal variability of precipitation amount, and 2–3 times lower density of the fluvial network, the rate of surface discharge decreased 50-100 times with a simultaneous significant increase in its amplitude. In such circumstances, the urban river starts resembling a mountain stream. It becomes a very dynamic object, not only in terms of hydrological, but also hydrochemical, and qualitative characteristics.

Considering the above, in 2015 and 2016, students of major Geomonitoring at the Faculty of Geographical Sciences of the University of Łódź, under the scientific supervision of the Laboratory of Geology of the University of Łódź, conducted research experiments involving the application of two recognised methods of research on the quality of river waters. The first of the experiments, implemented in 2015, involved the preparation of the hydrochemical image, i.e. performance of simultaneous measurements of physico-chemical parameters, and water sampling for analyses along the entire course of the river. The results were presented in a scientific conference “Hydrology of urbanised areas”, Warsaw University of Life Sciences, Warsaw, September 2016 [4]. The second experiment, conducted in 2016, involved hydrochemical research with consideration of the time of water flow in the channel of the Olechówka River from its “sources” to the place where it flows into the Jasień River. Both of the experiments were conducted in selected measurement and control sites (mcs). The objective of the works was to verify which of the research methods is more relevant for small urban rivers[1]. It seems that the rules of monitoring of surface waters flowing with imprecise flow reflect the specificity of development of the quality of waters of such hydrographic objects.

2 Study object

The Olechówka River is an order V watercourse belonging to the Odra River catchment. It is connected to the Odra River through Warta, Ner, and Jasień. The river has a length of 12.5 km, and catchment with an area of 35.2 km^2. The drainage area in its upper course covers areas of multi-family residential building development (residential districts of Widzew Wschód and Olechów), industrial development, as well as post-industrial and recreational areas (Dąbrowa). In its lower course, it covers single-family and service

[1]Understood as a watercourse that begins and ends in the city and whose catchment substantially coincides with the urban area.

building development (Ruda Pabianicka). Due to this, the sewage system of the catchment covers 32.6 km^2 (approximately 93%), and surface seal is reaching 13.4 km^2 (38%). Between strongly urbanised areas, in its middle course, the river flows through areas of agricultural fallow land in Stare Chojny. At the end of this section, it flows into Stawy Jana – the largest retention reservoir on its course with a volume of 44.5 thousand m^3. Smaller reservoirs include: Górna (Upper) Olechówka (7.7 thousand m^3), Tomaszowska (17.5 thousand m^3), and Młynek (31 thousand m^3). The two largest ones have the recreational function, and are dried in the autumn-winter period. The remaining ones regulate discharges, and water is retained in them all year round. Apart from the establishment of the reservoirs, the valley and channel itself were subject to strong transformations aimed at the adjustment of the river to fulfilling the role of precipitation sewage collector. The course of the river was corrected. Sedimentation tanks were constructed at the outlets of larger stormwater collectors. The banks and bottom of the channel were reinforced with concrete. The natural spring niches were subject to building development, and the course of the river currently has its beginning at the outlet from the stormwater collector from the residential district Łódź-Olechów. The Olechówka River has become an integral part of the storm sewage system of the city, and the main collector of stormwaters from 70 sewage outlets [4] – Fig. 1.

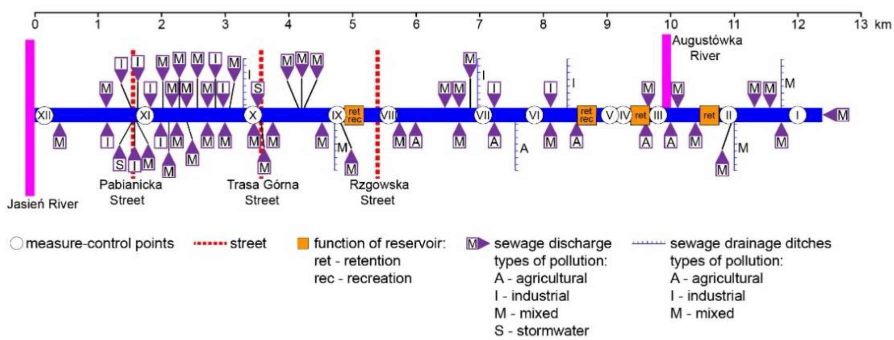

Fig. 1. Scheme of the Olechówka River.

3 Material and methods

The implementation of the adopted research objective required the performance of hydrometric measurements for the determination of the discharge rate (Q) and mean flow velocity of water in the channel ($\bar{\upsilon}$) at selected study sites. This involves the application of a method proposed by Mańczak, which is based on a statistical analysis of the relationship Q with water quality indicators [5]. The location of measurement-control sites is presented in Fig. 1. Their location was determined based on the criteria binding for the monitoring of flowing surface waters [6].

The time of water flow over the distance between subsequent mcs was calculated taking into account the distance determined by the mileage of the river [7] and $\bar{\upsilon}$. The calculations also considered time of water retention in the reservoirs, determined based on their volume, and Q at sites locates directly below the reservoirs.

Due to the specificity of urban pollutants, the hydrochemical research on the Olechówka River was conducted in the scope of salinity indices – standardized electrolytic conductivity (SEC) and chloride ion (Cl^-); eutrophication indices – mineral forms of nitrogen (NH_4^+, NO_2^- and NO_3^-), phosphates (PO_4^{3-}), and total nitrogen and phosphorus (TN and

TP). Total suspension (TS) was considered as an indicator of mechanical pollution and Oxidability (COD-Mn) was also considered as an indicator of organic pollution. Samples collected for the determinations of TN, TP, and TS were subject to analyses at the laboratory of the Collective Sewage Treatment Plant in Łódź. The remaining determinations were performed at the laboratory of Laboratory of Geology. Measurements of water temperature and SEC were performed by means of Elmetron CP315 and CX742 devices with an Eg-60 electrode. Chemical analyses were performed in accordance with the guidelines of [8], and according to the method PN-EW 872:2007+Ap.1:2007 in the case of TS.

The statistical processing of results, like a data clustering with Ward method of agglomeration, involved the application of STATISTICA 7.1. software.

4 Results and discussion

4.1 Hydrometeorological conditions

Calculations of the time of water flow in the channel of the Olechówka River from the "sources" to its mouth show that in total it amounts 856 hours (13.04.2016, 7.00 a.m. – 19.05.2016, 11.23 p.m.) partial results of the time of water flow are presented in Fig. 2.

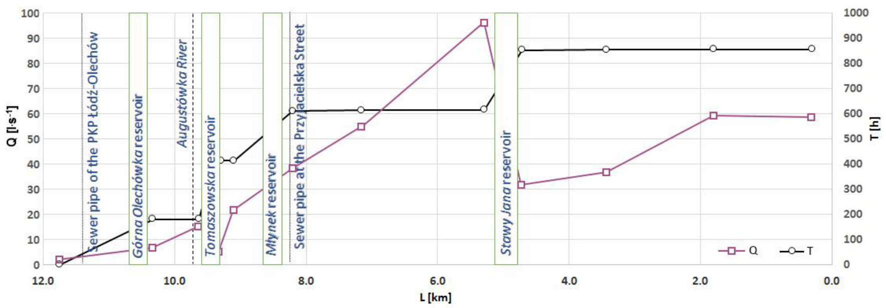

Fig. 2. Accumulated time of water flow in the channel of the Olechówka River and changes in the discharge rate in the Olechówka River in the period of the hydrochemical research.

Measurements of Q performed during sampling document a gradual increase in the amount of water flowing in the Olechówka River (Fig. 2). A reduction of discharges in reservoir Tomaszowska and Stawy Jana was recorded. According to materials obtained from the Department of Meteorology and Climatology of the University of Łódź, in the first week of the research period, low precipitation was recorded (<10 mm), resulting in a slight wetting of the Olechówka catchment area. During the conducted research, small and relatively short rainfalls occurred, in the majority of cases very short or in the form of a drizzle. They were observed more frequently and in higher amounts in the middle and lower course of the river than along its upper course. This suggests that the recorded increase in discharges in the Olechówka River was primarily caused by drainage of groundwaters in the catchment, either directly by the channel, or by the stormwater system.

4.2 Hydrochemical conditions

The hypothesis adopted in the methodological assumption, regarding the implemented scope of research, stating the possibility of occurrence of characteristic types of pollutants in the Olechówka River, can be subject to preliminary verification through the calculation of values of coefficients of correlation between the determined hydrochemical elements. This was performed for standardised data, with use the mean value and standard deviation of each data set. The results of the calculations are presented in Table 1.

Table 1. Matrix of correlation of hydrochemical elements and discharge rate and time of water flow in the channel of the Olechówka River; value of Pearson correlation coefficient (r), significant cases (p<0,05) were bolded.

	Time	Temp.	SEC	Cl^-	PO_4^{3-}	NO_3^-	TS
Q	**0.662/ p = 0.019**	**0.696/ p = 0.012**	–0.528/ p = 0.078	–0.453/ p = 0.14	–0.451/ p = 0.141	**–0.586/ p = 0.045**	–0.255/ p = 0.425
Time	–	0.43/ p = 0.163	**–0.61/ p = 0.035**	**–0.592/ p = 0.043**	**–0.677/ p = 0.016**	**–0.857/ p = 0.000**	–0.082/ p = 0.8
SEC			–	**0.978/ p = 0.000**	**0.828/ p = 0.001**	**0.79/ p = 0.002**	–0.095/ p = 0.769
Cl^-				–	**0.827/ p = 0.001**	**0.761/ p = 0.004**	–0.132/ p = 0.682
TP					–0.232/ p = 0.468	–0.233/ p = 0.466	**0.657/ p = 0.02**
PO_4^{3-}					–	**0.89/ p = 0.000**	–0.068/ p = 0.834
COD-Mn							**0.918/ p = 0.000**

The discharge rate shows a significant positive correlation with water temperature, and negative with the concentration of nitrates. The time of water flow is positively correlated with Q and negatively with SEC and Cl^- as well as PO_4^{3-} and NO_3^-. Based on statistically significant values of coefficients of correlation between hydrochemical elements, their two groups with the strongest correlations can be distinguished: SEC, Cl^-, PO_4^{3-}, and NO_3^-, as well as COD-Mn, TS and TP. The first group represents mineral substances in ion forms, and the second one – suspended substances and total phosphorus. Only the elements of the first group show a significant correlation with the time of water flow in the channel of the Olechówka River – Table 1. Changes in the values of representatives of both of the groups are presented in Fig. 3. The association of the analyzed elements into such groups corresponds with the results of observations of Olechówka from 2015. Based on the observations it was documented that pollutants supplied to the catchment show a certain sequentiality. The obtained hydrochemical image of a precipitation flood showed runoff from the catchment of first dissolved substances, then suspension, and derivatives of organic substances [4].

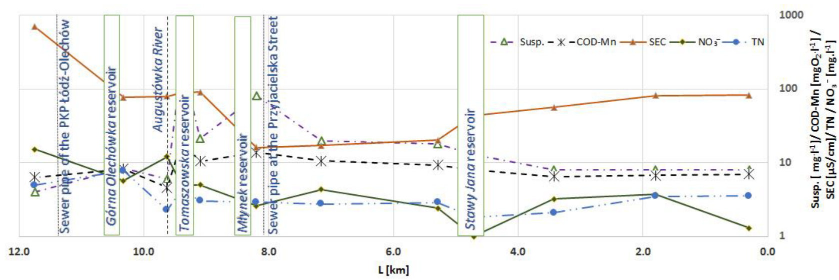

Fig. 3. Changes of selected hydrochemical elements.

The hydrochemical element showing an evident correlation with hydrological characteristics (Q and T) in the Olechówka River is nitrate ion. Negative values of the coefficient of correlation suggest that concentrations of NO_3^- decrease with an increase in the volume of flowing water and increase in the duration of such movement – Fig. 4.

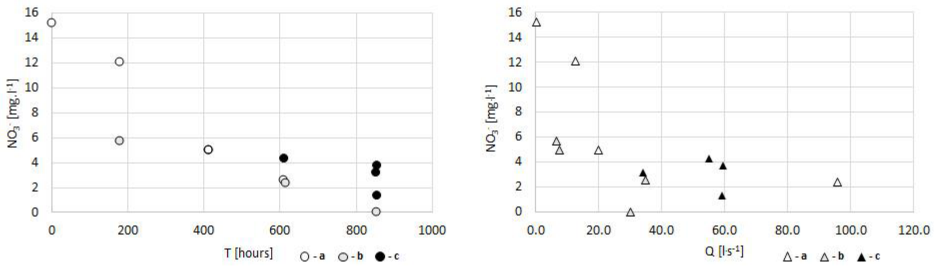

Fig. 4. Changes of concentrations of nitrates in relation to the time of water flow in the channel of the Olechówka River (a.) and discharge rate value at particular mcs (b.); explanation of the symbols a – mcs above the retention reservoirs, b – mcs directly below the reservoirs, c – mcs on the river.

The consideration in the reduction of nitrate concentrations of the presence of retention reservoir on the course of the Olechówka River and the resulting changes in discharge conditions suggests that the basic role of elimination of this form of mineral nitrogen results from water retention and therefore assimilation by phytoplankton or denitrification, depending on the conditions occurring in the reservoir [9]. The graphic image of co-variability of NO_3^- and Q suggests that the Olechówka River is a strongly polluted river according to the classification of rivers by Mańczak [5]. At low discharges, concentrations of pollutants are high, and decrease as a result of dissolution with waters successively supplied to the river channel along its course.

It is interesting that such dissolution does not result in a response of indices of content of mineral salts. The correlation of SEC and Cl^- ion with hydrochemical elements only concerns time of water flow, and is weaker than biogenic ions – Table 1. Changes in SEC (Fig. 3) suggest the impact of strong sources of release of salts in the upper part of the catchment, and weaker in its lower part. The middle section of the Olechówka River seems to be devoid of such an impact, and the retention reservoirs contribute to changes in SEC both in plus and in minus.

COD-Mn is a representative of the group showing no correlations with the hydrological characteristics of the Olechówka River. The hydrochemical profile (Fig. 3) shows the impact of the largest sewage collector, located at the outlet of the Olechówka River and reservoir. Both of the objects contribute to a significant increase in values of COD-Mn and TS. This evidences a direct effect of the stormwater system on the river, and indirect effect of the retention reservoir. The biological assimilation of NO_3^- mentioned before results in the emission of an increased load of organic matter and total nitrogen (Fig. 3) and (organic?) suspension. An increase in the concentration of TN which occurred in the Olechówka River after its flowing through the reservoir suggests that also a release of certain amounts of nitrogen occurs from bottom sediments. Analogical changes occur in the case of reservoir Górna Olechówka. In reservoirs where waters are seasonally drained out, this type of changes are not recorded. Notice that Stawy Jana contributes to the reduction of both of the forms of nitrogen and suspension.

The complex image of changes in the waters of the Olechówka River in the scope of hydrological and hydrochemical characteristics of particular mcs is provided by the similarity analysis, conducted in the Euclidean space by means of the Ward method. In a river representing the continuum of hydrological and hydrochemical changes, functioning in a space subject to anthropopressure to a weaker degree than an urban catchment, subsequent mcs should show a considerable degree of similarity, and be ordered in accordance with the actual distribution of mcs in the course of the river, reflecting among others the course of the self-cleaning process. The result of the similarity analysis of waters flowing in the channel of the Olechówka River was presented in Fig. 5.

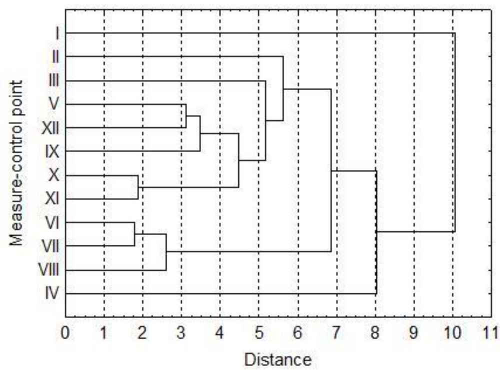

Fig. 5. Dendrogram of similarity of particular mcs in hydrochemical terms.

The greatest similarity occurs in the case of mcs VI and VIII. Together with mcs No. VIII, they constitute the only group of sites ordered in the diagram (Fig. 5) in the same way as in reality (Fig. 1). The sites are distinguished by average values of hydrochemical elements at high discharge progression. On the section between mcs VI and VIII, Olechówka flows through agricultural fallow land, in an unsealed channel, where possible channel drainage is possible, and the number of outlets of the sewage system is lower than on other sections (Fig. 1). Mcs I is distinguished among all the others. It is locates on the initial section of the Olechówka River. High index values are observed here at simultaneous very low discharge. Mcs IV is also characterized by high degree of individualism. It is located below reservoir Tomaszowska. This evidences the importance of the reservoir for the maintenance of the continuity of processes occurring in the channel. The reservoir can be considered as a specific hydrochemical barrier. The remaining reservoirs also contribute to the disturbance of the hydrochemical continuum of the river, as manifested in sifting sites VI and IX in the sequence, far from sites located above the reservoirs (V and VIII).

Due to the function of water supply to recreational reservoirs by the Olechówka River, its waters should represent a specific state of quality. The verification was performed in relation to normatives of waters of class II [10][2]. The waters of the Olechówka River are not suitable for bathing over the entire length, as determined by the values of Oxidability and levels of ammonia nitrogen. Moreover, in the upper section, the water is disqualified by excessively high concentrations of nitrate nitrogen and total phosphorus.

5 Summary

In the Olechówka River, during water flow from the "sources" to the river's mouth to the Jasień River, the presence of two types of pollutants was determined. The first one includes mineral salts, including forms of nitrogen and phosphorus, developing its

[2]Existing provisions for water intended for bathing organization do not include hydrochemical elements that were studied. Therefore they resorted to the provisions of the surface water classifications in force until 2004.

concentrations in relation to the hydrological parameters of the studied river, i.e. discharge rate, and particularly time of water flow. Retention reservoirs play an important role in the recorded hydrochemical transformations. The scale of changes determined by reservoirs allows for recognising them as specific hydrochemical barriers, whereas it is of importance whether water in the reservoirs is maintained all year round, or only seasonally.

The second group of hydrochemical elements is total suspension, Oxidability, and TP. The indicators do not refer to hydrological changes in the channel of the Olechówka River, but respond to the presence of retention reservoirs, particularly reservoir Tomaszowska, and water supply from the stormwater system. Both of the hydrotechnical objects should be treated as important sources of pollution of the studied river.

The study shows that the hydrochemical transformations of waters during their flow in the river channel over a length of 12 km for 36 days are subject to changes basically caused by the presence of retention reservoirs. Due to the limited amount of atmospheric precipitation, the influence of the stormwater system was limited, and only manifested itself in the case of the largest sewage collector.

References

1. M.J. Łoś, Wiadomości Melioracyjne i Łąkarskie, **38** (1995)
2. S. Czaja, *Zmiany stosunków wodnych w warunkach silnej antropopresji (na przykładzie konurbacji katowickiej)* (Wydawnictwo Uniwersytetu Śląskiego, Katowice, 1999)
3. R. Dębski, *Komunikat o ukończeniu tematu naukowo-badawczego pt. zakłócenia cykli hydrologicznych w miastach na przykładzie Łodzi jako wynik ich gospodarczego rozwoju i przeciwdziałania ujemnym zjawiskom. Materiały na konferencję na temat: Wpływ aglomeracji przemysłowych na środowisko człowieka na przykładzie makroregionu łódzkiego* (1987)
4. M. Ziułkiewicz, A. Fortuniak, A. Waack-Zając, M. Górecki, S. Grzędzińska, B. Małecka, Monografie Komitetu Gospodarki Wodnej Polskiej Akademii Nauk, **39** (2016)
5. H. Mańczak, *Techniczne podstawy ochrony wód przed zanieczyszczeniem* (Politechnika Wrocławska, Wrocław, 1972)
6. K. Gołębiowska, A. Niespodziewany, T. Reczek, *Wskazówki metodyczne do projektowania regionalnego monitoringu wód powierzchniowych płynących* (Biblioteka Monitoringu Środowiska, Warszawa, 1994)
7. UM Łódź, *Projekt generalny rzeki Olechówki* (Wydział Gospodarki Komunalnej Urzędu Miasta Łodzi, Łódź, 2000, unpublished source)
8. S. Witczak, J. Kania, E. Kmiecik, *Katalog wybranych fizycznych i chemicznych wskaźników zanieczyszczeń wód podziemnych i metod ich oznaczania* (Biblioteka Monitoringu Środowiska, Warszawa, 2013)
9. R. Gołdyn, *Zmiany biologicznych i fizyczno-chemicznych cech jakości wody rzecznej pod wpływem jej piętrzenia we wstępnych, nizinnych zbiornikach zaporowych* (Wydawnictwo Naukowe UAM, Poznań, 2000)
10. Rozporządzenie Ministra Ochrony Środowiska, Zasobów Naturalnych i Leśnictwa z dnia 5 listopada 1991 r. w sprawie klasyfikacji wód oraz warunków, jakim powinny odpowiadać ścieki wprowadzane do wód lub do ziemi (Dz.U. 1991 nr 116 poz. 503)