

DIURNAL VARIATIONS OF THE BASIC PHYSICO-CHEMICAL CHARACTERISTICS OF A SMALL URBAN RIVER – THE SOKOŁÓWKA IN ŁÓDŹ – A CASE STUDY

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ABSTRACT

The main purpose of the paper was to identify diurnal variations of the selected physico-chemical water characteristics (discharge, specific electrical conductance, temperature, pH and dissolved oxygen) of a small urban river that had been heavily transformed by human activity (Sokołówka river catchment with the area of 7.71 km²). The data came from measurements conducted in the period between 4 October 2011 and 3 October 2012, using the YSI 6920 V2 (multi-parameter sensor) and ISCO 2150 (automatic current meter), in 15- and 10-minute intervals, respectively. The research has proven the existence of rhythms of diurnal and seasonal variability to the selected water characteristics. The variability of the hourly values of the tested characteristics in particular days depends to a large extent on the value of the analysed parameter itself. The variability coefficients of discharge and conductivity increase with the increase in the values thereof. For dissolved oxygen, pH, and water temperature, the variability coefficients decrease with the increase in the values thereof. In the case of water pH, its specific electrical conductance, and temperature, the correlations between the given parameter and its variability observed at different times of day are not linear, but they run along loops of varying curvature. The average diurnal variability of SEC and pH parameters in the Sokołówka river was significantly changed as a result of human impact. The maximum readings of the conductivity and the pH shifted to the morning hours, with no change to the minimum readings.

Keywords: water quality, physico-chemical characteristics of waters, diurnal variations, anthropogenic pressure, urban hydrology, Poland

INTRODUCTION

Surface waters are among those links in the water circulation system, which are the most vulnerable to anthropogenic pressure. This impact is felt particularly strongly in the case of small urban streams, in which the pressure of human activity is significant, whereas the buffer properties of the river are negligible. Often the physico-chemical characteristics of the waters in these watercourses are distinguished by the existence of non-natural diurnal rhythms (for instance,

the so-called social cycle) and seasonal rhythms (related to, *inter alia*, winter road maintenance) (Halliday et al. 2012).

Until now, series of short-term measurements of physico-chemical characteristics of water in small watercourses have rarely been the focus of researchers' interest, mainly due to the difficulty in obtaining them (the technical aspect) and in their interpretation (internal correlation between the sequence elements). The most frequently analysed sequences of this type were registered only during the passing of flood waves

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(Poor, McDonnell 2007; Ciupa, Suligowski 2014) or for very short periods of time (Ziułkiewicz et al. 2016). The majority of researchers who have studied this issue note that as the discharge increases, the water mineralization in the watercourse decreases due to the dilution of groundwater with less mineralized surface and groundwater runoff (Edwards 1973; Froehlich 1975; Walling, Foster 1975; Foster 1978; Bhangu, Whitfield 1997; Kostrzewski et al. 1992; Siwek 2001; Chmiel et al. 2009; Siwek 2012). Other factors affecting the changes in physico-chemical parameters of water in these periods include: the nature of the drainage area (urban, karst, mountain, etc.) (Ciupa 2009), the period (season of the year) when the freshets are formed (Suzuki 1984 and 2003), the length of the period in-between the freshets (Piñol et al. 1992), intensity of precipitation (Kostrzewski et al. 1992), snow cover chemistry (Suzuki 1995), the topographic and geological features of the catchment together with its cover (Ciupa 2002; Ciupa 2009), as well as the mechanism of water circulation (Bonell 1993). Especially noteworthy are the changes and variability of the physico-chemical characteristics of river waters under particularly strong anthropogenic pressure, notably in urbanized areas (Ciupa 2014; Bartnik, Moniewski 2016). We consider urban areas to be so strongly transformed that we usually do not pay attention to certain regularities in the diurnal and seasonal course of their physico-chemical properties (Hessen 1997; Bartnik, Moniewski 2015), focusing only on long-term tendencies associated with the changes in their quality (Gutry-Korycka 1993; Czaja 1999; Gutry-Korycka 2003; Bartnik 2017).

For a long time, it was thought that during the periods in-between the freshets, physico-chemical parameters of river waters undergo only slight changes, therefore studies on capturing their dynamics were carried out relatively seldom (Siwek 2012). This was compounded by difficulties in obtaining high-resolution data over longer periods of time that would allow for drawing general conclusions. The use of multi-parameter probes with recorders and the so-called auto-samplers made it possible to deal with this particular problem. Therefore, it became possible to capture short-term changes in physico-chemical characteristics of water that occur during the day, as well as their course in different seasons of the year, even in a small

river within the city that is particularly variable in this respect. Among reports regarding the diurnal rhythm of water temperature in the catchments of the lowland part of Poland, the study by Łaszewski deserves attention (2018). Soja (1973) conducted similar research in mountainous areas, whereas Wiejaczka (2007a) investigated the changes in this parameter under the impact of the Klimkówka reservoir construction. The latter author also described cases of changes in the daily course of temperature during various interesting hydro-meteorological phenomena (Wiejaczka 2007b). Relatively, the researchers devoted the most attention to daily changes of oxygen dissolved in water. Known to the authors of the present paper are a dozen or so works describing this phenomenon in both clean and heavily polluted waters. Suffice it to list some of them: Allan (1998), Wilcock et al. (1998), Young, Huryn (1999), Kayombo et al. (2002), Wang et al. (2003), Tadesse et al. (2004), Garcia et al. (2006), Baulch et al. (2012). Studies into the diurnal fluctuations in water pH and their relationship with photosynthesis and breathing of aquatic organisms have been conducted by Bourg, Bertin (1996), Guash et al. (1998), and Neal et al. (2002), among others. Relatively, the least number of researchers describe the diurnal variation in specific electrical conductance (Bourg, Bertin 1996, Barringer et al. 2008, Halliday et al. 2014).

Nevertheless, most of the above-mentioned studies concern relatively short measurement periods, sometimes only 48 hours, rarely up to several months. Therefore, the purpose of the present study was to identify the diurnal variability of selected physico-chemical characteristics of water in the watercourse that had been transformed as a result of human activity. The one-year-long measurement period also made it possible to present seasonal variation of their course. This issue seems important to the authors, due to the possibility of answering the question whether the diurnal variability of the analysed characteristics is the same in each season, or perhaps it changes with the seasons.

STUDY AREA AND RESEARCH METHODS APPLIED

The research was conducted in the catchment of Sokołówka river, which is a small watercourse located almost entirely within the administrative boundaries

of Łódź, in the northern part of that city (see: Fig. 1A). It is a watercourse of the third grade, which is the second left-bank tributary of the Bzura river, with a catchment area not exceeding 46 km² (Projekt generalny..., 2003). The Department of Hydrology and Water Management at the University of Łódź has been conducting research in this area since 2006. The present article uses data recorded by automatic measuring devices, installed in the gauge section at Lewa street in Łódź (see: Fig. 1B). The sub-catchment enclosed within this point ($A = 7.71 \text{ km}^2$) drains the area made up mainly of boulder clay (till) separated by fluvio-glacial sands (Różycki, Kluczyński 1966) with large slope inclinations of the valley, especially in the lower part of the analysed area (Bartnik 2017). Land coverage of the area consists mostly of farming and residential development, while in the northern part, there is a compact forest complex of Łagiewniki (see: Fig. 1C). The Sokołówka catchment up to the Lewa cross-section remains almost entirely within the rainwater sewage system that discharges rainwater with numerous collectors directly to the riverbed (except for its upper part and the aforementioned forest complex). The length of the main channel of the watercourse, within the section with a constant water flow, is 3.15 km, whereas its average drop is 4.43 ‰.

The data used in the present work were recorded for the period of one year, starting from 4 October 2011, using a multi-parameter YSI 6920 V2 measurement probe and an ISCO 2150 flowmeter. The following water parameters were taken into account: discharge (Q), electrolytic conductivity (SEC), pH index (pH), water temperature (T), and dissolved oxygen (O₂). The probe was calibrated every month (for a few hours in one day), and the observation gaps thus created were supplemented with a “trend”. This is a commonly used procedure to supplement short-term data gaps in time series (Kondrashov, Ghil 2006). The use of the analogue method was not possible, because there do not yet exist time series of the analysed variables that would be suitable for use in this procedure. The measuring probe recorded the results in 15-minute intervals, and the flowmeter, in 10-minute intervals. In the next step, raw measurement data were averaged to hourly values (arithmetic mean values of the measurements were calculated, which were recorded within the hour following the date to which the result was assigned –

i.e. for example 1:00 p.m. was assigned the mean value from the measurements of a given value registered by the devices during the period between 1:00 p.m. and 1:50 p.m.). Based on such series, for each variable and each given hour in the year, half-year, and month, the following values were calculated: mean, minimum, maximum, and coefficient of variation. In the case of pH reading, all source data were converted first to hydrogen ion concentrations, and after calculating their characteristics, they were converted into values expressed in the pH scale.

RESULTS AND DISCUSSION

Discharge

The mean annual discharge of Sokołówka river in the period from 4 October 2011 to 3 October 2012 was $0.021 \text{ m}^3 \cdot \text{s}^{-1}$ ($Sq = 2.72 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$). The mean amount of water flowing throughout the day varied cyclically (see: Fig. 2A). The highest volume was recorded in the afternoon (between 4:00 p.m. and 7:00 p.m.), when torrential rains were the most frequent. The lowest discharges were recorded in the morning (at 9:00 a.m.), with average daily fluctuations not exceeding 8% per year. With the increase of the mean discharge during 24 hours, its variability increased significantly (see: Fig. 2B). This was an obvious consequence of the more frequent emergence of quickflow, and a much greater variability of discharge at that time.

Extremes of low, medium and high discharges occurred at different hours during the year (see: Fig. 2A), whereas the differences between them ranged from about three hours in the case of maxima up to five, in the case of minima. Note that the hourly flow minima are characterized by a slightly different course of diurnal variation, whereas their extremes occur earlier than those of the other characteristics. This is due to the fact that their value is shaped only by the underground runoff. At the same time, within the urbanized catchment, it is largely transformed (due to drainage water, sewerage, the cone of depression, isolated river-bed, etc.). Studies conducted in the rainfall-free period in farming areas have shown that daily flow minima occur there in the morning hours (Wondzell et al. 2007), and in the case of Sokołówka river, they occurred at night. The course of the hourly

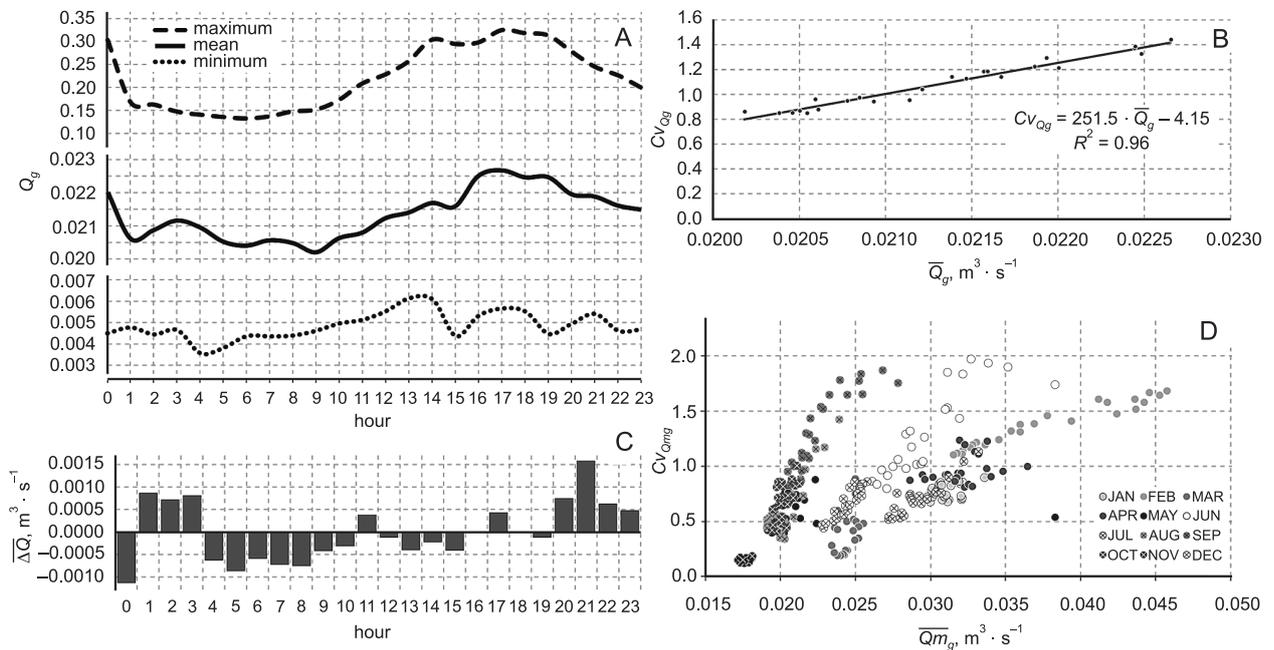


Fig. 2. Hourly variation characteristics of Sokołówka river discharge in Lewa cross-section in the period between October 2011 and October 2012

A – the mean, minimum and maximum annual diurnal discharge within twenty-four hours (Q_g); B – the mean annual discharge in particular hours (\bar{Q}_g) and its corresponding variation coefficient (CV_{Q_g}); C – the differences between mean discharge in particular hours ($\Delta\bar{Q}$) in the cool and warm half-years; D – the mean monthly discharge in particular hours (\bar{Q}_{m_g}) and its corresponding variation coefficient ($CV_{Q_{m_g}}$).

maximum annual discharge during the day is the effect of the overlap of the discharge coming from the underground drainage and direct runoff. In the summer season, the highest rainfall occurs in the afternoon. In winter and spring seasons (during the thaw), the largest amount of water reaches the riverbed also during these hours. In turn, reducing the discharge in the night hours is mainly the result of lowered intensity of both processes.

Interesting conclusions can be drawn from the analysis of the course of diurnal differences between deviations from the mean discharge recorded at a specific hour in the cool (XI-IV) and warm (X-X) half-years – see: Figure 2C. They were calculated, for all tested characteristics here designated as X, according to the following formula:

$$\overline{\Delta X} = (\overline{X_{Z_g}} - \overline{X_Z}) - (\overline{X_{I_g}} - \overline{X_I}) \quad (1)$$

where:

- $\overline{\Delta X}$ – difference of the mean value of the X parameter recorded at the given hour, in the cool and warm half-years;
- $\overline{X_{Z_g}}$ – the mean value of the X parameter recorded at the given hour, in the cool half-year (XI-IV);
- $\overline{X_Z}$ – the mean diurnal value of the X parameter in the cool half-year;
- $\overline{X_{I_g}}$ – the mean value of the X parameter recorded at the given hour, in the warm half-year (V-X);
- $\overline{X_I}$ – the mean diurnal value of the X parameter in the warm half-year.

Positive differences indicate that in the cool half-year, at a given hour, greater deviations were recorded than during the whole day (the difference between the deviations recorded at a specified time and the mean

values of these deviations within 24 hours). If the result of formula 1 is negative, this means that deviations (differentiation) of a given characteristic at a specific hour of the day exceeded the average deviations in the warm period.

Between the hours of 4:00 and 10:00 a.m., the discharge of Sokołówka river in the warm half-year is higher than the mean value for this period. This is probably due to the occurrence of minimum daily temperatures just after sunrise (unless there is no advection of air masses) and therefore the smallest water losses from evaporation. This, in turn, translates into minor losses of water from the channel and water-through ponds, as well as into higher discharges. In the cool half of the year, there may be periods in which only at this time of the day temperatures are negative, which does not allow for the melting of snow and feeding the channel with quickflow. As a result, discharges in the morning hours may be lower than average. Siwek (2012) arrived at similar conclusions by examining the daily cycle of changes in various parameters of water quality in agricultural and forest catchments located in the Carpathian Foothills. Based on her research, she postulated that it is evapotranspiration that is the main process shaping the daily variability of their course. At this point, one should also pay closer attention to the Sokołówka catchment area presented herein. It is not exactly a “typical urban river” (Bartnik 2017). Throughout the year, the flow is maintained in its channel. Above the measurement point, there is a cascade of water-through ponds, while in the valley of the watercourse itself, green areas dominate, such as parks, meadows, and wasteland. Thus, its valley resembles a suburban (rural) setting, while the daily course of the discharge variability is similar to the one recorded in quasi-natural areas.

The discharge of Sokołówka in the cool half-year at night is relatively higher than the mean values calculated for the warm half-year (except for the period between midnight and 1:00 am). During the rest of the day (between 11:00 a.m. and 7:00 p.m.) one cannot speak of a clear advantage of discharges in any one half of the year.

For each month, the mean water discharge at a specific time was also calculated (in subsequent steps, also the mean values of the other analysed characteristics). For particular hours, the coefficient of variation of the

discharge (or other parameters) was also estimated according to the formula:

$$Cv_{X_g} = \frac{\sigma_{X_g}}{\overline{X_g}} \quad (2)$$

- Cv_{X_g} – coefficient of variation of the X parameter value at a specific hour;
- σ_{X_g} – standard deviation of the X parameter value recorded at a specific hour throughout the year;
- $\overline{X_g}$ – arithmetic mean of the X parameter value recorded at a specific hour throughout the year.

The covariance of the above-described variables in particular months are presented in Figure 2D.

The biggest differences in the flow between particular hours during the day occurred in February (resulting from winter maintenance of streets) and in June (due to torrential rains). The different genesis of the discharge formation in these months leads to the situation where similar amounts of discharge at a given time are accompanied by a different level of their variability. For the month of February, it is always smaller than for the month of June, which can be explained by the lower probability of torrential rain. On the other hand, the autumn discharges (X–XII) were not very variable, with particular reference to November. The hydrological situation in that month was very stable, whereas the mean hourly discharges were always low and hardly changeable. In the presented graph, this resulted in an exceptional concentration of points representing mean hourly discharges in this particular month. This is another proof of the repeatedly formed belief that the dynamics of river runoff in November tends to be low.

WATER TEMPERATURE

The mean annual temperature of water in the Sokołówka in the analysed period was 10.7°C. On average, the maximum daily water temperatures occurred at 4:00 p.m., whereas the minimum temperatures were recorded in the morning (between 6:00 and 7:00 a.m.), which obviously refers to the daily variability of air temperature (see: Fig. 3A). Similar differences were also noted for other Polish lowland rivers (Łaszewski

ki 2018). Unlike in the case of discharges, the diurnal variability of the lowest, medium and maximum temperatures differs significantly. We should bear in mind that the data analysed was obtained during the period of one year. Due to the fact that the water temperature strongly depends on air temperature, the course of the lowest and highest water temperatures corresponds to the coldest and the hottest weather incidents during that period. Therefore, it is possible to experience the highest maximum temperature and the lowest minimum water temperature at the same hour (see: Fig. 3A). Only the record of extreme hourly temperatures from a period of at least several years would allow us to draw general conclusions about the diurnal variability of these characteristics.

Unlike the case of discharge, the variability of mean hourly temperatures decreases with their increase (see: Fig. 3B). However, this correlation is not

linear (running along the “loop” marked on the graph) because the water heating and cooling conditions are different (for instance, mean water temperatures measured throughout the year at 1:00 p.m. and 8:00 p.m. are almost identical, however their series differ in the coefficient of variation). The heating of river water as a result of absorbing both shortwave radiation (embedding the exposed riverbeds with concrete is of great importance for urban rivers, usually carrying small amounts of water; so is the presence of water-through ponds) and long-term radiation (in the case of cities, the effect of a larger surface albedo may be more pronounced than in quasi-natural areas) proceeds in a more stable manner than the process of its radiation-based cooling. These differences may be additionally intensified by the strong convective rainfall, often occurring during the summer in the afternoons (the temperature of water after summer rains is often

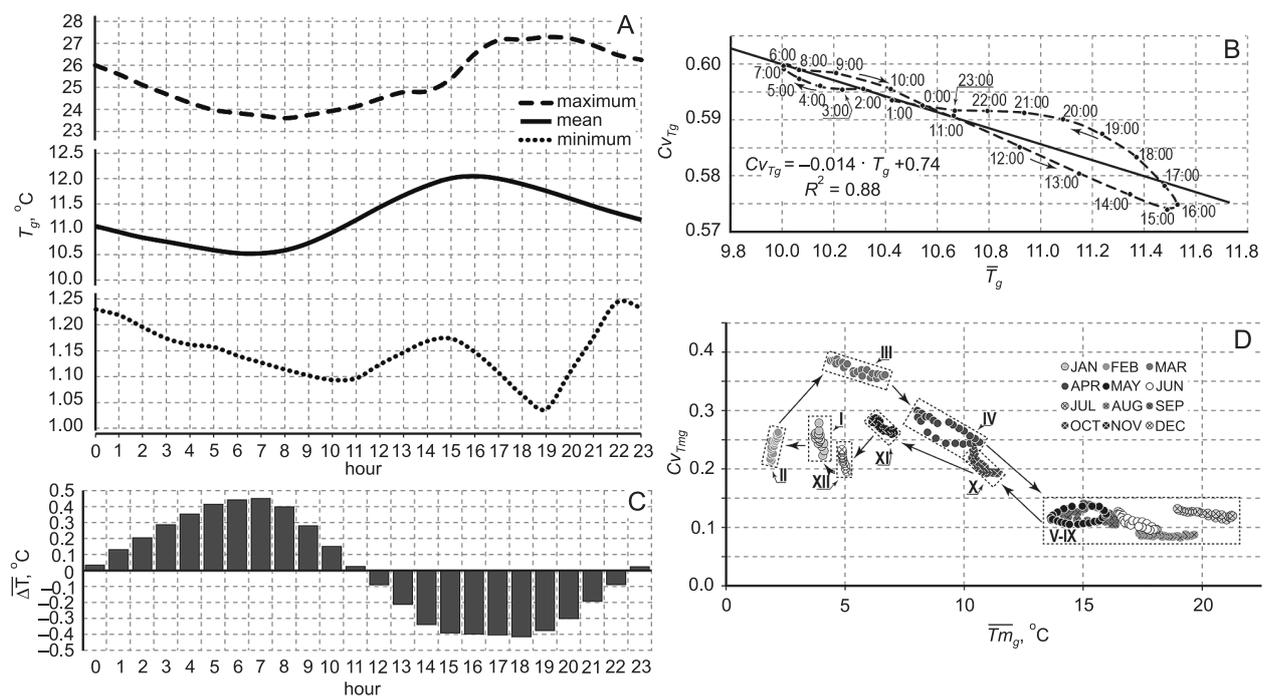


Fig. 3. Hourly variation characteristics of water temperature in Sokołówka river, in the Lewa cross-section in the period between October 2011 and October 2012

A – the mean, minimum and maximum annual water temperature within twenty four hours (T_g); B – the mean annual water temperature in particular hours (\bar{T}_g) and the corresponding variation coefficient (Cv_{T_g}); C – the differences between mean water temperature in particular hours ($\Delta \bar{T}$) in warm and cool half-years; D – the mean monthly water temperature in particular hours (\bar{T}_{m_g}) and its corresponding variation coefficient ($Cv_{T_{m_g}}$).

diversified; in the first phase, it is marked by a significant increase resulting from ‘washing away the heat’ from heated streets, roofs and pavements, while in the later phase, it is much lower than that of the river’s water). The greatest variability of water temperature was observed in late-night and early-morning hours, in the period when there is lack of direct solar irradiance to the surface of the earth and the maximum radiating of the heat away from it.

The curve of daily water temperature in the warm and cool half-years differs significantly (see: Fig. 3C). This is influenced by the significant factors shaping air temperature (and hence also the water temperature) in different seasons. In the warm season, the supply of solar energy, affecting the significantly above-average daily water temperature in the afternoon hours (from noon to 10:00 p.m.), is of dominant importance to the formation of the daily water temperature regime. During this time, the water heats up from the air and from direct solar irradiance. The shift of higher temperatures up to 10:00 p.m. is the result of a longer duration of insolation, and the accumulation of thermal energy in the water-through ponds above the control cross-section (the impact of water reservoirs on the temperature of river waters was described, *inter alia*, by Wiejaczka, 2007a). During the night hours, the opposite happens. In winter season, it is at this time that water temperatures are higher than the annual mean values recorded at the particular hours. Again, the biggest role in this process is played by water reservoirs that maintain a relatively constant water temperature throughout the day, reducing the amplitude of temperatures recorded in the measurement cross-section.

Average monthly water temperatures recorded at the same time were the least differentiated in the winter (from December to February). Small variations in the mean hourly temperature of water were accompanied by high variability (demonstrated in Figure 3D in the vertical spread of the points cloud). During this period, temperature changes from hour to hour can be more strongly influenced by the advection of air masses than by the solar radiation reaching the Earth’s surface. The advection of air masses is not conditioned by the time of day, which affects the large variation in the changeability of water temperatures in particular hours. It is not so in the summer, when temperature

changes during the day are most affected by solar radiation, with lesser participation of air mass advection. In this case, the variation in the mean hourly water temperature is high (as demonstrated by the horizontal spread of the points cloud, seen in Figure 3D), however, the variability in their range is very similar. We can also observe that in the spring months (March and April) there was definitely more variation recorded in the mean hourly water temperatures than in the autumn months (October and November). This is undoubtedly connected with the autumn stability (or lack thereof in the spring months) of the air circulation conditions over Poland.

SPECIFIC ELECTRICAL CONDUCTANCE (SEC)

The mean electrical conductance of water in the Sokołówka river in the control cross section at Lewa street was $1158 \mu\text{S} \cdot \text{cm}^{-1}$ during the period under consideration. The highest mean hourly electrical conductance of water was recorded in the morning (almost $1200 \mu\text{S} \cdot \text{cm}^{-1}$ at approximately 8:00 a.m.), however between 6:00 a.m. and 8:00 a.m. there was an abrupt increase in SEC value (see: Fig. 4A). This was the effect of the impact of winter road maintenance (the largest number of sand trucks in the city is usually in operation before the morning traffic peak). In the absence of chloride supply to the watercourse, the maximum electrical conductance occurs a few hours later. It should be noted that low values of specific electrical conductance characteristically occur during the night, which is also confirmed by studies conducted in other watercourses (Bourg, Bertin 1996, Barringer et al. 2008). On the other hand, the research conducted by Siwek (2012) in the rainfall-free period, in the winter, within the forest catchment, indicates a completely opposite distribution of conductivity during the day – increase during the night, and decrease during the day. The author explains this phenomenon with melting occurring during the day, and the inflow of poorly mineralized waters from snow and ice into river channels. These differences in opinions lead to the conclusion about the special significance of anthropogenic pressure for the diurnal SEC variability. It can be assumed that in the Sokołówka river catchment, the human impact on the diurnal variability of water conductivity is manifested by shift-

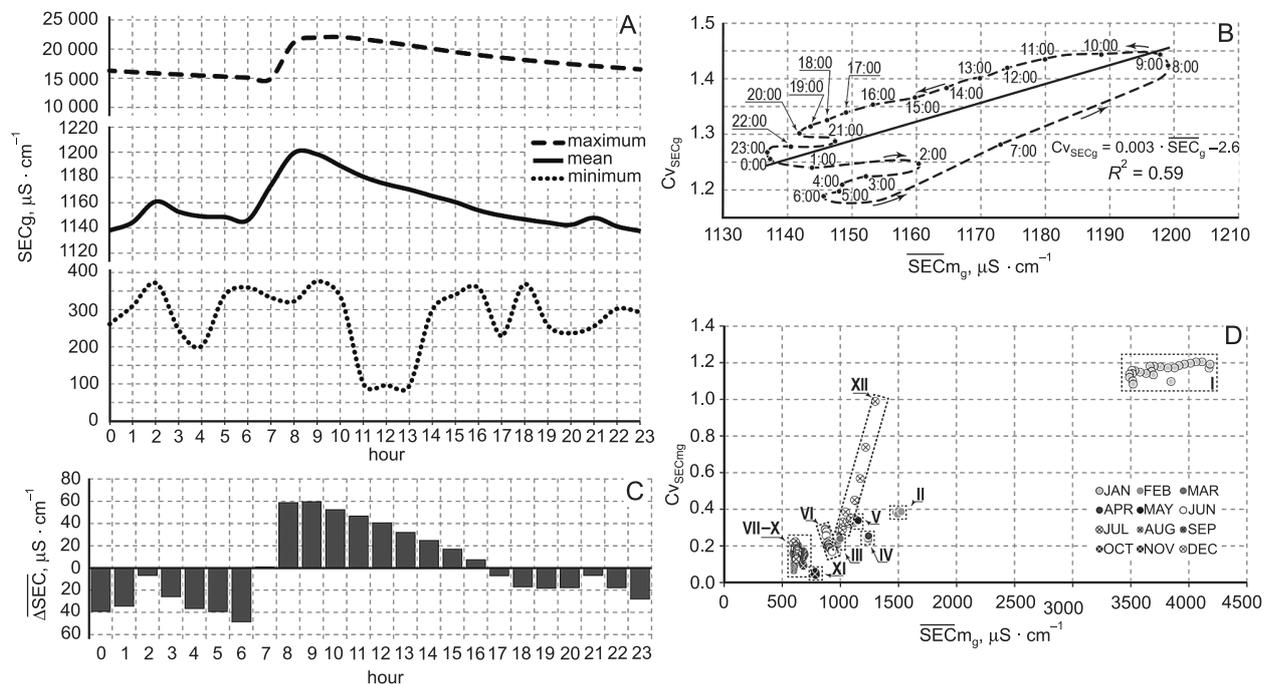


Fig. 4. Hourly variation characteristics of Sokółówka river water conductivity in the Lewa cross-section during the period from October 2011 to October 2012

A – the mean, minimum and maximum annual water conductivity in particular hours (SEC_g); B – the mean annual water conductivity in particular hours (\overline{SEC}_g) and its corresponding variation coefficient (CV_{SEC_g}); C – the differences between mean water conductivity in particular hours (ΔSEC) in warm and cool half-years; D – the mean monthly water conductivity in particular hours (\overline{SEC}_{m_g}) and its corresponding variation coefficient ($CV_{SEC_{m_g}}$).

ing its maxima to the morning hours, with no changes to the times when the minima occur.

The curve of the diurnal variability of the mean and maximum electrolytic conductivity is very similar, since extremely high water conductivities (up to almost $22000 \mu\text{S} \cdot \text{cm}^{-1}$) that are recorded in winter strongly affect the mean value. The course of daily variability of the minimum hourly SEC of water differs significantly from the above. It is impossible to distinguish one specific time of day with increased conductivity, as it occurs at different times of the day. The period of minimum conductivity (less than $100 \mu\text{S} \cdot \text{cm}^{-1}$, between the hours of 11:00 a.m. and 11:00 p.m.) is strongly marked, most likely due to the overlap effect of an intense supply of water from melting ice and snow with low conductivity that is typical at this time (water with a high chloride content discharges most intensively in the early hours of the

thaw), and the strong convective precipitation that occurs during these hours in the summer period.

The variability of the mean diurnal water conductivity increases with its value (see: Fig. 4B). With lower conductivity, variability is also low, and the changes between mean hourly values are quite chaotic (this applies to the afternoon and night hours, between 5:00 p.m. and 6:00 a.m.). At times when mean conductivity is strongly influenced by the high SEC values associated with the necessity of winter road maintenance (between 6:00 a.m. and 4:00 p.m., see: Fig. 4C), the mean electrolytic conductivity and its variability increase rapidly, reaching a maximum at about 9:00 a.m. The decrease in this characteristic, which takes place later, is accompanied with a relatively greater variability, which can be explained by the varying lag time of water reaching the control cross-section from different parts of the catchment.

Throughout the year, the differences in water conductivity during the day and night were small. This does not apply only to winter months (December and January) when these differences grew rapidly (see: Fig. 4D). Particularly high conductivity (over $3500 \mu\text{S} \cdot \text{cm}^{-1}$) with very high variability (over 100%) was noted in January. In 2012, this month was characterized by a large number of days with rainfall or snowfall (only seven days without rain or snow) and temperatures close to zero (the mean temperature at the Łódź-Lublinek meteorological station was -0.9°C). This necessitated frequent use of anti-icing agents by municipal services. The situation was completely different in December 2011, when precipitation occurred mainly in the form of rain, and at high air temperatures. There were only two rainy episodes that could trigger the response of municipal services, hence the

very large changeability in the coefficient of variation between particular hours in that month.

WATER PH

The mean hourly pH of the water in Sokołówka river at the Lewa section, in the studied period, was slightly alkaline (pH 7.37) and only slightly changeable (differences were less than 0.03 pH). Diurnal extremes in the mean annual course of water pH occur in the early morning (at 5:00 a.m. the waters were the closest to neutral pH) and in the afternoon (between 3:00 p.m. and 6:00 p.m., see: Fig. 5A). A similar rise in the pH of water during the day had already been observed by Bourg and Bertin (1996) and Neal et al. (2002). They attributed it to a simultaneous decrease in the concentration of carbon dioxide in the water, taken

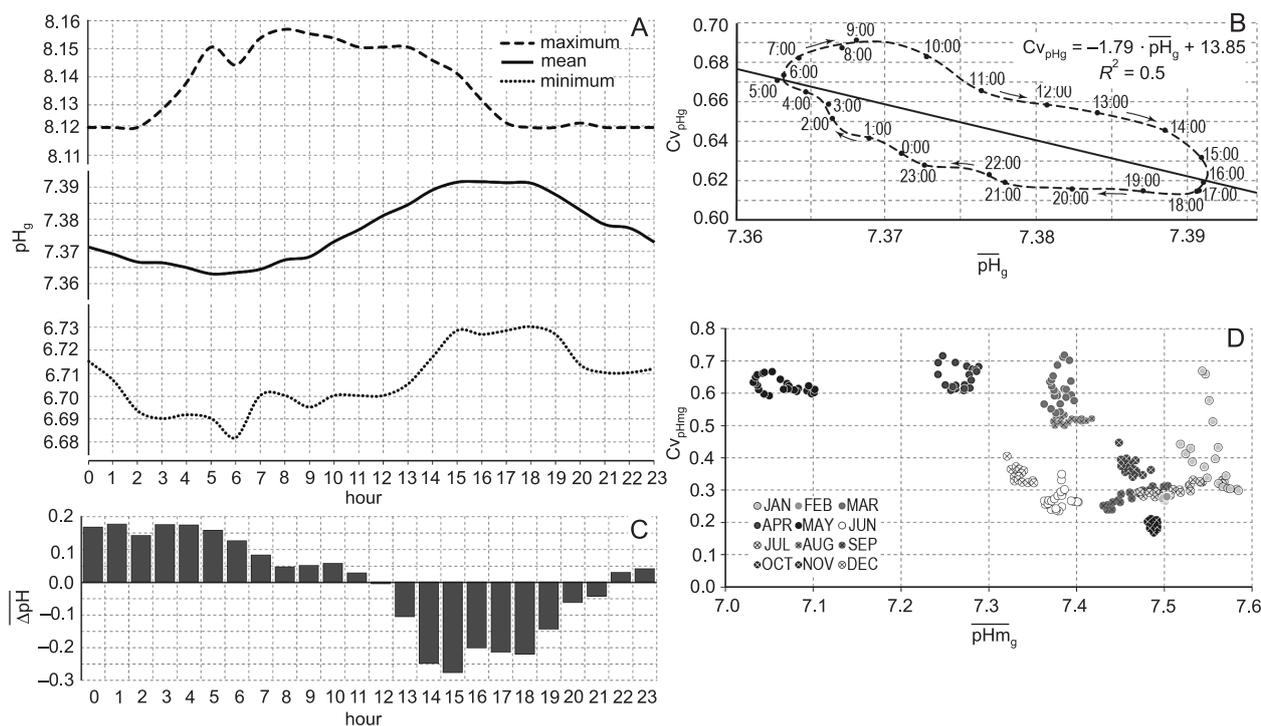


Fig. 5. Diurnal variation characteristics of Sokołówka's water pH in the Lewa cross-section, in the period between October 2011 and Oct.2012

A – the mean, minimum and maximum annual pH in particular hours (pH_g); B – the mean annual pH in particular hours ($\overline{pH_g}$) and its corresponding variation coefficient (Cv_{pH_g}); C – the differences between mean pH index in particular hours (ΔpH) in warm and cool half-years; D – the mean monthly pH in particular hours ($\overline{pHm_g}$) and its corresponding variation coefficient (Cv_{pHm_g}).

by the plants for the photosynthesis process. In their research, Guash et al. (1998) argue that the intensification of photosynthesis during the day and the related increase in the pH of water result in precipitation of carbonates from the waters. Hessen et al. (1997) and Sullivan et al. (1998) argued that it is the changing demand of aquatic organisms for biogenic compounds, changing over the course of the day, that is the main cause for the changes in water pH in watercourses throughout the day and night. Almost identical diurnal variation of water pH was also observed in the case of polluted sedimentation pond (Kayombo et al. 2002) and rivers contaminated with the presence of heavy metals (Bourg, Bertin 1996).

The differences between absolute extremes are larger, and they amount to about 1.5 pH units per year. The most acidic waters were recorded in the morning (at 6:00 a.m.), and the most alkaline waters, only two hours later. The time of their occurrence coincided with the time of rapid increase in water conductivity indicating the identical cause for both maxima. During the night and morning hours, relatively more acidic water in Sokołówka flows in the cool period (see: Fig. 5C); whereas in the warm half of the year, between noon and 9:00 p.m.

On average, a statistically weak correlation between pH index and variability at a given time is observed during the 24-hour period (see: Fig. 5B). This points to a decrease in variability, with increasing alkalinity of water. The increase in the alkalinity of water always takes place with greater variability, because in the spring it is associated with the capture of carbon dioxide from the water as a result of the photosynthesis process. Changeable weather conditions of this period, on the other hand, cause a large variation in its intensity between successive days. Interestingly enough, during the averaged diurnal period, the correlation takes the form of an ellipse with points of maximum variability during the morning increase in the reaction associated with the increased CO₂ uptake by the plants, and the minimum in the hours of the lowest variability in the afternoon.

The most highly alkaline waters, characterized by highly changeable variability of pH, were recorded in January (see: Fig. 5D). It should be noted that analogous results (high values and highly differentiated variability thereof) were obtained for conductivity,

which confirms the relationship between changes in the recorded water pH and its conductivity during the increased inflow of water from the streets in winter. The spring months (from March to May) are characterized by a very high variability of water pH. During this period, the changeability between particular hours during the 24-hour period is similar to the relationship obtained for the entire year (see: Fig. 5B and 5D). It can therefore be assumed that the processes taking place in these months are of highest impact on the correlation obtained for the 1-year sample.

DISSOLVED OXYGEN

The dissolved oxygen content in the waters of Sokołówka river is highly varied. The minimum hourly values are always 0 mg · dm⁻³ and therefore they are not included in Figure 6A. On average, during the year, there is 4.15 mg · dm⁻³ of dissolved oxygen in water, with a minimum at night at 10:00 p.m., and the morning maximum at 8:00 a.m. A completely different course is taken by maximum values, reaching their peak in the afternoon (7:00 p.m. and 9:00 p.m.), and their lowest point at 11 a.m. The content of oxygen dissolved in water depends on many factors (Whitney 1942). Therefore, the values of diurnal variability recorded by the authors conducting their research in different watercourses will differ significantly from one another. In the literature, diurnal changeability was noted that was evidently dependent on photosynthesis (Garcia et al. 2006, Baulch et al. 2012) with a maximum at noon, and a minimum around midnight. Other daily variability is also reported, with minima in the morning and afternoon peaks (Bourg, Bertin 1996, Wilcock et al. 1998, Kayombo et al. 2002, Barringer et al. 2008). This variability was also noted for another watercourse in Łódź city – the Jasień river (Bartnik, Moniewski 2016). Such variability is similar to the course of maximum concentrations of oxygen dissolved in the waters of Sokołówka, and is often multimodal in character. It is interesting to note that the studies mentioned above concerned both the watercourses draining agricultural areas, and objects contaminated with heavy metals or sewage. Therefore, one can draw a cautious conclusion that the pollution load on the watercourse changes the level of oxygen concentration in the water, without changing its diurnal

nal fluctuations. Therefore, the interpretation of the daily variability of this parameter is not an easy task. Among the daily trajectories, there are also those in which the impact of strong afternoon freshets in the summer period is clearly visible (see: Fig. 2A). Water flow velocities are then higher, and therefore the oxygen in the atmospheric air dissolves more efficiently. This produces the effect of maximum dissolved oxygen concentrations occurring with a shift of about 2 hours with respect to maximum discharges. In turn, in the daily course of mean values, the increase of dissolved oxygen is indicated as a result of the delivery of storm water from the drainage to the watercourse (convergence of times when maximum hourly mean values are recorded).

The concentration of oxygen in the waters of Sokołówka in the warmer half of the year is higher than the mean value in the morning and early morning hours (from 5:00 a.m. to 2:00 p.m., see: Fig. 6C). This corresponds to the discharge distribution (higher than the mean value recorded in the warm period, oc-

curing between 4:00 a.m. and 3:00 p.m.). Thus, the effect of mechanical oxygenation of the water associated with the speed at which the water is flowing is visible here.

The multitude of factors determining the concentration of oxygen dissolved in water heightens the variability of the obtained results. It decreases with the increasing oxygen content in water, but the correlation is weak (see: Fig. 6B). The observable high variability in October (see: Fig. 6D) results from faulty operation of the oxygen sensor over several days, and should therefore be ignored. The oxygen content in May is very variable, and at the same time, it is the lowest. Water temperature in that month is already high (on average almost 15°C), so the ability to dissolve oxygen is limited. At the same time, the discharges were small; hence the mechanical oxygenation of water outside the freshet episodes has been weak. The most variable, and simultaneously the highest dissolved oxygen content had been recorded in November. Water temperature was then almost 10°C lower, the discharg-

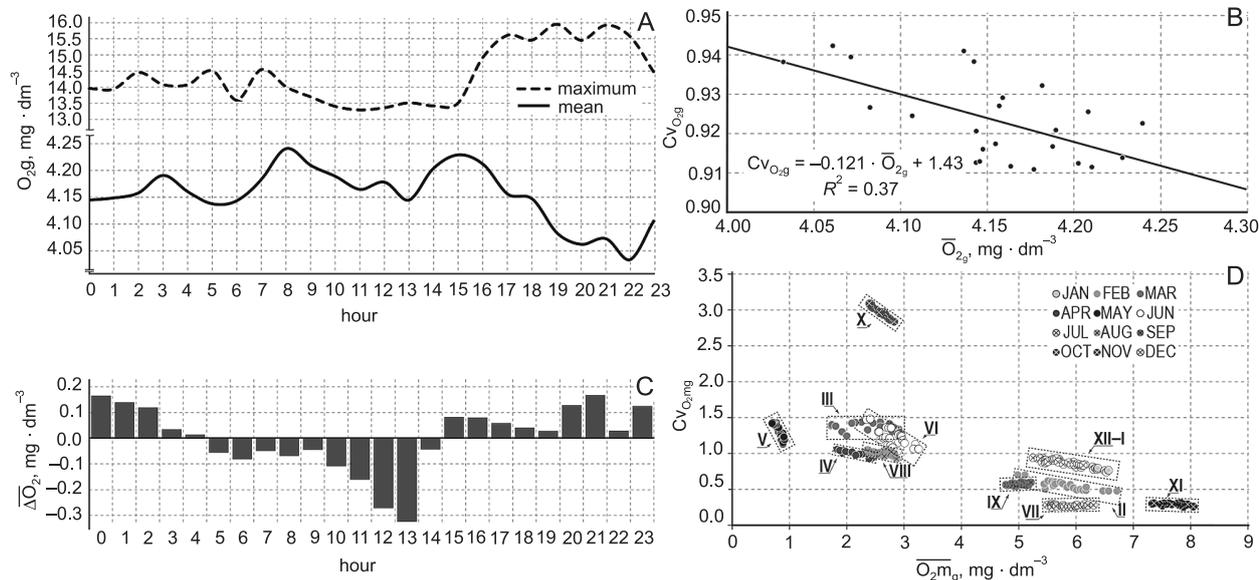


Fig. 6. Diurnal variation characteristics of dissolved oxygen (O_2) in Sokołówka's water in the Lewa cross-section in period between October 2011 and October 2012

A – the mean, minimum and maximum annual oxygen dissolved in water in particular hours (O_{2g}); B – the mean annual oxygen dissolved in water in particular hours ($\overline{O_{2g}}$) and its corresponding variation coefficient ($Cv_{O_{2g}}$); C – the differences between mean oxygen dissolved in water in particular hours (ΔO_2) in warm and cool half-years; D – the mean monthly oxygen dissolved in water in particular hours ($\overline{O_{2mg}}$) and its corresponding variation coefficient ($Cv_{O_{2mg}}$).

es were stable, and the process of decomposition of dead organic matter delivered to Sokołówka's channel has not yet properly begun. Research conducted over a two-year period in the UK, in an agricultural catchment area, rendered very similar results (Halliday et al. 2014). The largest variability was typical for the spring months, and the smallest variability was observed in the early winter.

CONCLUSIONS

The analyses of short-term variability of physico-chemical properties of water in a period longer than several months are still relatively rare. The main obstacle lies in constraints related to the durability of measuring devices. In particular, this concerns the measurement of pH, and the ion concentration of the substances dissolved in water, including oxygen. These devices require periodic calibration, cleaning and replacement of membranes and electrolytes. This applies especially to heavily polluted watercourses that drain urban areas. It should be assumed that with the development of measurement techniques, similar research will become easier, and it will be undertaken by a wider group of researchers. Currently, all results of such tests are valuable. By comparing the results obtained for quasi-natural and anthropogenic catchments, we are able to determine whether the identified daily variation is natural or anthropogenic.

The research into basic physico-chemical parameters of the Sokołówka catchment area led us to formulate the following conclusions:

- In the hourly series of physico-chemical parameters of the Sokołówka waters, the occurrence of rhythms was found, which confirms the observations of other authors. Naturally recorded daily variability (Siwek 2012) was nevertheless disturbed by anthropogenic factors;
- The most pronounced changes were noted in the case of electrolytic conductivity proper. They manifest themselves by postponing the time of maximum values' occurrence to the morning hours (which is the effect of winter road maintenance) with no changes to the times when the minimum values occur. Similar results have been obtained for other watercourses (Bourg, Bertin 1996, Barringer et al. 2008), it should therefore be assumed that this

is not a change that is specific for Sokołówka but that it is typical of rivers carrying heavily polluted waters;

- Changes to the natural diurnal rhythm (Wilcock et al. 1998) have not been noted for the oxygen dissolved in water. These results were also obtained in other quasi-natural and contaminated streams (Bourg, Bertin 1996, Kayombo et al. 2002, Barringer et al. 2008, Bartnik, Moniewski 2016). It can therefore be assumed that the pollution load on the watercourse modifies the level of oxygen concentration in water, without changing its daily fluctuations;
- Variability of the hourly values of the tested characteristics in particular days depends to a large extent on the value of the analysed parameter. In the case of the discharge and electrolytic conductivity of water, the variability increases with the increase in the value of the parameters, and in the case of the dissolved oxygen, water pH, and temperature – it decreases with the increase in the value of the parameters;
- In the case of water pH, its conductivity and temperature, the correlations observed within the 24-hour period between the value of the analysed parameter and its variability are not linear. For example, water temperatures recorded throughout the year at 1:00 p.m. and at 8:00 p.m. are practically no different from the mean value, but they differ in their variability because the heating and cooling conditions are different.

The changes described in the last two conclusions cannot currently be applied to analogous changes identified in other watercourses, as the authors are not aware of the results of such analyses. Therefore, this is one of the possible directions for further research into time series of basic physico-chemical characteristics of water. With more such data, it will be possible to draw more general conclusions about the nature of these correlations.

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DOBOWY PRZEBIEG WYBRANYCH CECH FIZYKOCHEMICZNYCH WÓD MAŁEGO CIEKU MIEJSKIEGO NA PRZYKŁADZIE SOKOŁÓWKI (ŁÓDŹ)

ABSTRAKT

Celem prezentowanego opracowania była identyfikacja dobowej zmienności wybranych cech fizykochemicznych wody (natężenie przepływu, przewodność, temperatura i odczyn wody oraz stężenie rozpuszczonego w wodzie tlenu) przekształconego przez człowieka cieku miejskiego (zlewnia Sokołówki o powierzchni 7,71 km²). Wykorzystano wyniki pomiarów prowadzonych od 4 X 2011 r. do 3 X 2012 r. przy pomocy wieloparametrycznej sondy pomiarowej YSI 6920 V2 oraz przepływomierza ISCO 2150 zapisujących wyniki z krokiem odpowiednio: 15- i 10-minutowym. Badania udowodniły istnienie rytmów zmienności dobowej i sezonowej. Zmienność godzinowych wartości badanych charakterystyk w poszczególnych dniach w znacznym stopniu zależy od wielkości analizowanej cechy. W przypadku natężenia przepływu i przewodnictwa elektrolitycznego wody zmienność ta (wyrażona współczynnikiem zmienności) rośnie wraz z ich wzrostem, a w przypadku tlenu rozpuszczonego, odczynu wody i temperatury – spada. Dla odczynu wody, jej przewodności i temperatury obserwowane o różnych godzinach zależności pomiędzy daną wielkością a jej zmiennością nie są liniowe lecz tworzą pętle o różnym kształcie. Przeciętna dobowa zmienność przewodnictwa elektrolitycznego właściwego oraz odczynu wód Sokołówki uległa zmianom pod wpływem działalności człowieka. Maksima przewodności i odczynu wody przesunęły się na godziny poranne przy braku zmian terminów występowania minimów.

Słowa kluczowe: cechy fizykochemiczne wód, zmienność wewnątrzdobowa, antropopresja, hydrologia miejska, Polska