http://dx.doi.org/10.1016/j.ecolind.2017.03.002 The role of annual periodic behavior of water quality parameters in primary production 1 - chlorophyll-a estimation -2 3 József Kovács^a, Péter Tanos^{b,c}, Gábor Várbíró^{d,e}, Angéla Anda^b, Sándor Molnár^c, István Gábor 4 Hatvanif* 5 6 ^aEötvös Loránd University, Department of Physical and Applied Geology, H-1117 Budapest, 7 Pázmány Péter stny. 1/C, Hungary; kevesolt@gmail.com 8 ^bUniversity of Pannonia Georgikon Faculty, Department of Meteorology and Water 9 Management, H-8360 Keszthely, Festetics u. 7, Hungary; tanospeter@gmail.com, 10 11 anda-a@georgikon.hu ^cSzent István University, Department of Mathematics and Informatics, H-2100 Gödöllő, Páter 12 Károly utca 1, Hungary; molnar.sandor@gek.szie.hu 13 ^dMTA Centre for Ecological Research, Danube Research Institute Department of Tisza River 14 Research, H-4026 Debrecen, Bem tér 18/C, Hungary varbiro.gabor@okologia.mta.hu 15 ^eMTA Centre for Ecological Research, GINOP Sustainable Ecosystems Group, H-8237 Tihany, 16 Klebensberg Kuno u. 3, Hungary; 17 ^f Institute for Geological and Geochemical Research, Research Center for Astronomy and Earth 18 Sciences, MTA, H-1112 Budapest, Budaörsi út 45, Hungary; hatvaniig@gmail.com 19 20

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 - **Abstract**: Since phytoplankton is an autochthonous primary producer, it plays a vital role in driving the water quality of rivers and lakes. Therefore, in cases where measurements are lacking, its estimation is of the essence. In the present study, Morlet wavelet spectrum (periodicity) and multiple regression analyses were conducted on 15 chemical, biological and physical water quality variables sampled at 14 sites along the Hungarian section of the River Tisza and 4 sites from artificial tributary channels for 1993 2005. Results show that annual periodicity was not always to be found in the water quality parameters, at least at certain sampling sites. Periodicity was found to vary over space and time, but in general, an increase was observed in the company of higher trophic states of the river heading downstream. Based on the spatial distribution of the periodic behavior of the water quality parameters (runoff, ions, and nutrients given in so-called periodicity indices), an improved model was constructed which was capable of explaining about half (adjusted $R^2 = 0.5$) of the phytoplankton variance in the study area.

Keywords: annual periodicity water quality, chlorophyll-a estimation, Morlet wavelet spectrum

analysis, multiple regression analysis, River Tisza

1. Introduction

River networks present dynamically changing physical gradients to all biota, including phytoplankton (Kingsford, 2000). From the headwater, the characteristics of streams may vary,

from the heavily shaded streams of forested catchments to the deep channels of large autotrophic lowland rivers, where inorganic turbidity often restricts light availability (Dokulil, 2006; Istvánovics and Honti, 2012). The highest autotrophic productivity is to be expected in medium to large rivers, and in large floodplain rivers (Istvánovics et al., 2014).

With urbanization and rapid population growth, water bodies are being more and more threatened by over exploitation and pollution, rivers being one of the most endangered among them (Hering et al., 2006). Therefore, their monitoring is an absolute necessity if we are to be able to follow and predict negative changes/scenarios. The Water Framework Directive of the European Union (EC, 2000) stipulated the achievement of "good ecological status" in natural water bodies by 2015; this, in turn, requires the continuous development and cross-border intercalibration of monitoring networks in order to achieve a better understanding of rivers processes (Chapman et al., 2016).

One focal issue in this is eutrophication (Neal et al., 2008), which highlights the use of phytoplankton in the assessment of large rivers as a new and emerging task of the EU (Hering et al., 2010; Reyjol et al., 2014). Offering increasing development time, the lower stretches of a river may more easily become dominated by the planktonic element (Moss and Balls, 1989; Várbíró et al., 2007). This is manifested in a progressive increase in planktonic chlorophyll as one moves from the upper reaches to the middle- and lower sections of the river. Although, chlorophyll-a determination is neither a difficult nor expensive measurement, long term data is generally only available from the 1990s in Eastern Europe, as only then was it first included as an important parameter in national water quality monitoring programs.

Phytoplankton play a vital role in fluvial ecosystems, especially in cases of changing climatic and environmental conditions (Villegas and de Giner, 1973). Also, due to their short life cycle,

they serve as important indicator of water quality (Wu et al., 2014; 2012). Taken together, these points show why forecasting algal content is fundamental to the management of river systems (Jeong et al., 2008; Read et al., 2014). The need for the creation of a model of phytoplankton dynamics which is capable of approximating real life phenomena as closely as possible has already been formulated (Elliott et al., 2010), and successful models have been derived in the case of rivers (Jeong et al., 2001; Wu et al., 2014) and a lake, Lake Taihu (China; Huang et al., 2014, 2012). However, none of these models has taken the periodic behavior of various water quality parameters into account as a possible driving factor. despite the fact that, as emphasized much earlier (Reynolds, 1984), the role of periodic cycles of phytoplankton has a crucial impact on population dynamics and shaping community structure.

The presence or absence of annual periodicity, as demonstrated in our research, is not as evident as it may seem at first. The complex nature of the interactions and the superimposed presence of (i) anthropogenic, as well as (ii) other natural processes may disturb the natural periodic behavior of different water systems (Kovács et al., 2010; Fehér et al., 2016). Therefore, the periodic behavior of the main characteristics of water quality and the status of a river section (both) play a determining role in whether the growth of riverine phytoplankton – a main characteristic of any given river section - occurs or not. In the upper section the natural riverine phytoplankton consist of mainly tichoplatonic elements (Ruyter van Steveninck et al., 1990; Descy, 1987) while in the lower-, true euplactonic centrales diatoms tend to dominate the primary production pillar of riverine food webs (Descy et al., 2017). As primary producers, planktonic algae in aquatic environments have a determining role in shaping the composition of aquatic ecosystems through their production of organic carbon, oxygen, as well as providing a source of food for herbivorous grazers (Wehr and Descy, 1998). In addition, the disturbance in periodic behavior of phytoplankton in riverine

systems triggers a chain reaction through the food web, as periodic behavior makes its effects felt through all sections of the riverine ecosystem and the ecosystem services provided (Daily, 1997). There is therefore, an obvious need to understand the driving constraints of phytoplankton dynamics in rivers.

Annual periodicity is a natural behavior of riverine systems in the moderate climate zone and has been shown (Tanos et al., 2015) to play a major role in driving the periodic behavior of water quality parameters and in the shaping of natural phytoplankton dynamics. These in turn, can be traced by its main proxy, the chlorophyll-a content of the water (Borics et al., 2007; Tanos et al., 2015). Although a number of empirical models have been developed to describe the relationship between macronutrients - mainly total phosphorus and total nitrogen - and phytoplankton chlorophyll-a, these models mostly focus on lakes (Phillips et al., 2008; Poikane et al., 2011). Therefore, if the periodic behavior of the general water quality parameters (runoff, ions, nutrients etc.) can be shown to play a significant role in driving the variance of chlorophyll-a content and quantify that effect, it could serve as a direct link in creating a new way of estimating phytoplankton chlorophyll-a presence.

Therefore, the aims of the study are (i) to determine the change in annual periodic behavior of the water quality parameters of the riverine system of the Tisza and (ii) with the information gained to derive a model for the estimation of chlorophyll-a values from it in cases where direct measurements of these were lacking.

2. Materials and methods

2.1. Hungarian section of the River Tisza

The River Tisza collects the waters of the Carpathian Basin's Eastern region. It is therefore a highly important ecological corridor (Zsuga et al., 2004). It stretches from its source in the Eastern Carpathians in the Ukraine to its confluence with the Danube at Titel in Serbia. The area of its watershed is 157,186 km² (Lászlóffy, 1982), almost one third of which is located in Hungary (approx. 47,000 km²). The average amount of water brought by the Tisza into the Danube is 25.4×10⁶ m³ y¹ (Pécsi, 1969). The main branch (river 966 km; Sakan et al., 2007) passes through five countries (the Ukraine, Romania, Hungary, Slovakia, and Serbia). 594.5 km of this main branch are to be found in Hungary. Its water quality, solely in Hungary, directly affects the lives of approx. 1.5M inhabitants. Heading downstream on the river's Hungarian section, its tributaries are the following: the Szamos, Bodrog, Sajó, Zagyva, Kőrös, and Maros (Fig. 1). It becomes clear from the runoff values that the affluent having the strongest effect on the main flow is the Szamos (at its mouth its average runoff exceeds half of the average runoff of the Tisza) and a considerable "changing effect" is expected from the Bodrog, Sajó, Zagyva, Kőrös, and Maros Rivers regarding the periodic behavior of the river (Table A1).

It has been documented that, besides the tributaries, other, mostly anthropogenic factors, such as e.g. the Tiszalök water barrage systems (WBS; Fig. 1), or lakes (e.g. Lake Tisza; Fig. 1) affect the water quality of the analyzed river section (Kentel and Alp, 2013; Moreira and Poole, 1993). Even the current river ice regime may have changed due to the installation of WBSs (Takács et al., 2013; Takács and Kern, 2015). An artificial lake exists on the river, Lake Tisza, constructed in 1973. It was planned to function as a part of a future WBS. Nowadays, it is a much-frequented recreation zone and nature reserve. The lake's length is 27 km, its mean depth is 1.3 m, and it has a total area of 127 km². Moreover, non-point source nutrient loads arriving from agricultural areas have to be accounted for as well (Mander and Forsberg, 2000). Regarding large cities, there are

several along the river (e.g. Szolnok at sampling site T10 and Szeged at sampling site T13), which

also have an environmental impact on the river's water quality (Fig.1).

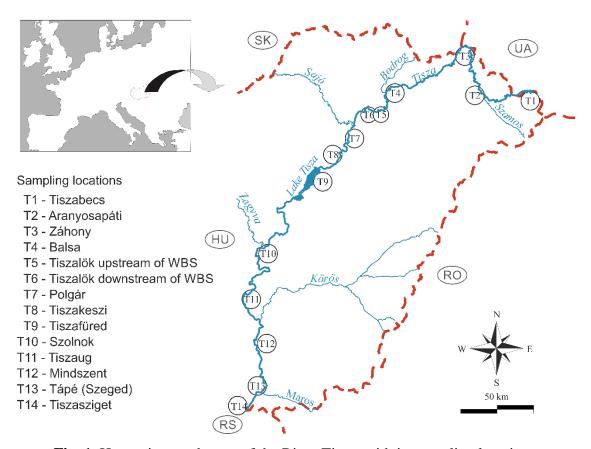


Fig. 1. Hungarian catchment of the River Tisza, with its sampling locations.

In the course of the analyses, the time series of 14 water quality variables (Table 1) for the years 1993-2005 were examined from 14 sampling sites (Fig. 1). The parameters were sampled by the various water inspectorates weekly and biweekly. Due to the large area monitored, these samples were not taken on the same day. Thus, after 2005, the sampling frequency was rarefied and the set of parameters changed. The number of data analyzed was ~50,000 in total.

Table 1. Groups of water quality/quantity variables assessed in the study

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Variables	Variable Groups
Runoff (m ³ s ⁻¹)	
Dissolved oxygen (DO; mg L ⁻¹)	
Biological oxygen demand (BOD-5; mg L ⁻¹)	
Ca ²⁺ (mg L ⁻¹)	
Mg^{2+} (mg L ⁻¹)	
$Na^+ (mg L^{-1})$	
$K^+ (mg L^{-1})$	Ions
Cl^{-} (mg L^{-1})	
SO_4^{2-} (mg L ⁻¹)	
HCO_3^- (mg L ⁻¹)	
NH ₄ -N (mg L ⁻¹)	
NO_2 -N (mg L ⁻¹)	North
NO_3 -N (mg L ⁻¹)	Nutrients
PO ₄ -P (μg L ⁻¹)	

Data preparation was performed so that the dataset would meet the basic requirements of the applied method. Possible typos and incorrectly recorded extreme values were sought manually, because there were occasions when an "act of God" (e.g. the anomalies caused by the cyanide pollution that occurred in 2000 in the river (Koenig, 2000) caused the water quality parameters to behave differently (produce an extreme record) from the general tendencies, although its measurements were probably accurate. The equidistant characteristic of the dataset was achieved by the fitting a cubic spline function to it (for details see Table A1). Thus, the time intervals between the resampled data were adjusted to the longest temporal interval of the original dataset, 30 days.

2.2. Methodology

Based on the presumption that a fair amount of the variance of chlorophyll-a is driven by other water quality parameters, the following procedure was developed. First, the annual periodic behavior of the water quality parameters is determined as periodicity indices using wavelet spectrum analysis and averaged for each sampling site for the investigated time interval (1993-2005) (see Section 2.2.2). Then various combinations (averages for sites and/or parameter groups e.g. nutrients) of these periodicity indices are incorporated into multiple regression models (Draper and Smith, 1998) to find the one which best explains chlorophyll-a variance based on multiple criteria (O'Brien, 2007).

2.2.1. Periodicity analysis in practice

The most basic way to assess annual periodicity is to calculate the monthly averages of all monthly values and visually inspect whether those are periodic or not. Clearly, there are more sophisticated approaches to dealing with periodicity, such as the Lomb-Scargle method (Lomb, 1976; Scargle, 1982; Fig. 2A). However, this is only capable of indicating the presence of the annual period, but not its location in time or even if the periodic characteristic is present over the whole time period.

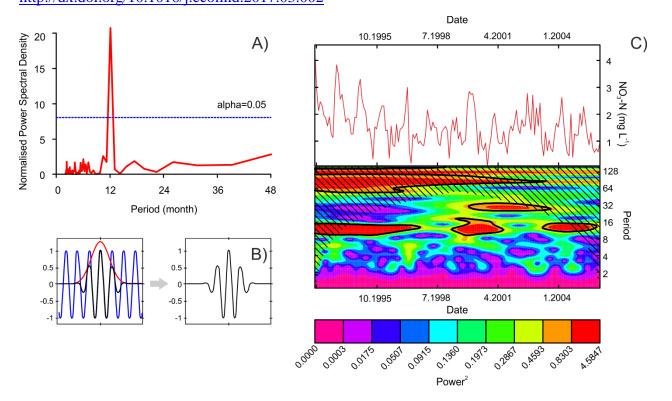


Fig. 2. Lomb-Scargle periodogram for NO₃-N, indicating a 12 month period A). The Morlet mother wavelet (Morlet, et al., 1982) B). The wavelet spectrum analysis C). The upper figure in panel C represents the resampled datasets of the parameter, while the lower represents its PSD graph, on which the 5% significance level against red noise is shown as a thick black contour (for details see Torrence and Compo, 1998). The black shaded areas mark the COI and the black horizontal dashed line indicates the annual period.

In numerous cases, it is not the type of the period which is important, but its location in time. To deal with such questions, the Short-Time Fourier Transformation is at hand (Allen, 1977). This uses a fixed width windowed approach, which is not, however, capable of arriving at a balance between an optimal resolution in time and frequency.

2.2.2 Wavelet spectrum (periodicity) analysis

To achieve a balance between the optimal resolution in time and frequency, wavelet spectrum analysis (WSA) was chosen, as has often been the case in related studies for different water bodies (Kovács et al., 2010, 2004; Lafreniére and Sharp, 2003; Tauber et al., 2011; Yanyou et al., 2006; Zhang et al., 2008), since WSA is localized in time (space) and scale (frequency), enabling it to grasp the signals' temporarily changing characteristics. The wavelet transformation (WT; Eq. 1) may be defined as the convolution of the data and the wavelet function (Kovács et al., 2010) of a time series (X_n , $n=1,\ldots,N$) with uniform time steps δt , (Eq. 1), it is a function with a mean of zero and is localized in both frequency and time (Grinsted et al., 2004).

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$$W_n^X(s) = \sqrt{\frac{\delta t}{s}} \sum_{n'=1}^N X_{n'} \Psi_0 \left[(n'-n) \frac{\delta t}{s} \right]$$
 (1)

Where 's' represents the scale, ' ψ_0 ' the wavelet function, and ' δ ' the degree of the resolution. Its adaptability lies in the scaling method. In the present study, a Morlet mother wavelet (Morlet, et al., 1982; Fig.2B) provided the source function to generate daughter wavelets. This was achieved by scaling and transforming the mother wavelet. Thanks to its adaptability, WSA is even able to handle the problem of non-stationarity (Daubechies, 1990). The purpose of the wavelet transformation is multiple dissociation, by decomposing the data in the scaling space. In this way, it is possible to reveal its self-similarity structure (Farge, 1992; Hatvani, 2014; Kern et al., 2016). Because wavelet spectrum is composed of two independent variables (time and frequency), it can be visualized in 3D through the plotting of power spectrum density (PSD) graphs (Fig. 2C). Note here that WTC produces edge artifacts, since the wavelet is not completely localized in time. Thus, the introduction of a cone of influence (COI), in which edge effects cannot be ignored (Torrence and Compo, 1998; Fig. 2C), is suggested.

Since the more thorough discussion of the WSA is not the main aim of the study, readers are referred to the following publications for further details: Benedetto and Frazier (1994) and Vidakovic (2009).

For easier interpretation, the presence of the significant annual periods of the PSD graphs (Fig. 2C) was transformed into percentages (periodicity indices, PI), where the full time interval was taken as 100%. These PIs can be explored in terms of parameter-, parameter group and sampling site (Table 2).

Table 2. Definitions of the periodicity indices

Abbreviation	Definition
PI_{v}	The ratio of time where the annual period is present
	to the full assessed time period in percentages for a
	particular variable.
$\mathrm{PI}_{\mathrm{gv}}$	Average PI _v of a particular variable group at a
	certain sampling site.
PI_{sl}	The ratio of the sum of the length of time where the
	annual period is present to the sum of the time
	periods assessed at a particular sampling site
	considering all variable together.
	$ ext{PI}_{ ext{v}}$

All mathematical and statistical computations were performed using R 3.2.3 (R Core Team 2015) and MS Excel 2016. The WSA was conducted using the dplR package (Bunn, 2010; Bunn et al, 2016). For the visualizations of the results, CorelDRAW Graphics Suite X7 and MS Office 2013 were used.

3. Results

3.1. Possibilities for the application of WSA

Most periodicity analysis methods require equidistant sampling. Environmental data often fail to meet this criterion. On the Hungarian section of the River Tisza, due to the fact that it is about 600 km long, and the various sampling sites of the river are managed by different authorities, this criterion is very incompletely met. In the early years of the assessed time period, sampling was bi-weekly then monthly, in some cases with gaps even in this frequency. In the latter case, interpolation was necessary e.g. using a spline function (Fig. S1). A 30 day resampling was commenced complying with the requirements of the planned Wavelet spectrum analysis (WSA; see Section 2.2.2 for details). If, however, there was a gap in the data, spline interpolation has to be used with caution, because it supposes a certain smoothness of the data.

In the course of WSA, special attention should be paid to those parameters which indicate shifts (changes in order of magnitude), because such anomalies will corrupt the periodic behavior detectable by WSA and mask any underlying periodicity. According to WSA, at the Szolnok sampling site annual periodicity was present in the time series (1974-2005) of the NH₄-N parameter 53% of the time (Fig. 3A). It should be noted that, after 1993, the concentration of NH₄-N greatly decreases (Fig. 3A upper figure), causing the periodic behavior seemingly to diminish. Therefore,

if the period between 1993 and 2005 is assessed separately from the whole dataset (Fig. 3B), it becomes clear that NH₄-N did indeed display periodic behavior between 1993-2005. Thus, based on the two spectra, over 93% of the investigated time period, annual periodicity was present in the data, which is far more than the 53% indicated in Fig. 3A for 1974-2005.

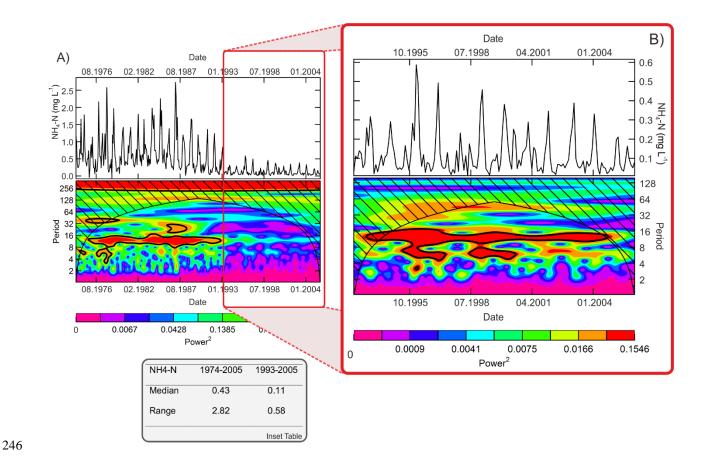


Fig. 3. PSD graphs of the WSA of NH₄-N from the Szolnok sampling site between 1975-2005 A) and 1993-2005 - the time interval assessed in the study B). The statistics for two different time periods demonstrate the shift in its measured values (inset table).

From 1990, about 75% and 40% of the decrease in P and N emissions, respectively, was due to improved sewage treatment and a significant drop in fertilizer application rates, down to 5

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kg P ha⁻¹ (Csathó et al., 2007; Schreiber et al., 2005). The concentration of ammonium-nitrogen decreased greatly starting in the beginning of the 1990s (Mander and Forsberg (2000), especially in the Eastern European region, more specifically the River Tisza in Hungary (Tanos et al., 2015). The reason behind this phenomenon lies in the fact that WSA was unable to follow the signal if there are explicit discontinuities in it as stated before. One solution to this problem is to split the

dataset into separate segments at the discontinuities and assess these separately.

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A similar problem may arise in the case of a large number of missing values (Fig. 4), when WSA gives false results for the interpolated segment, as in Fig. 4B, because it substituted the missing values with extreme values (Fig. 4B). Thus, the dataset should be split and assessed in two parts, leaving out the problematic section (Fig. 4C; Part I & II). Although, this increases the proportion of edge artifacts, in contrast to the original case, it nonetheless gives a meaningful result.

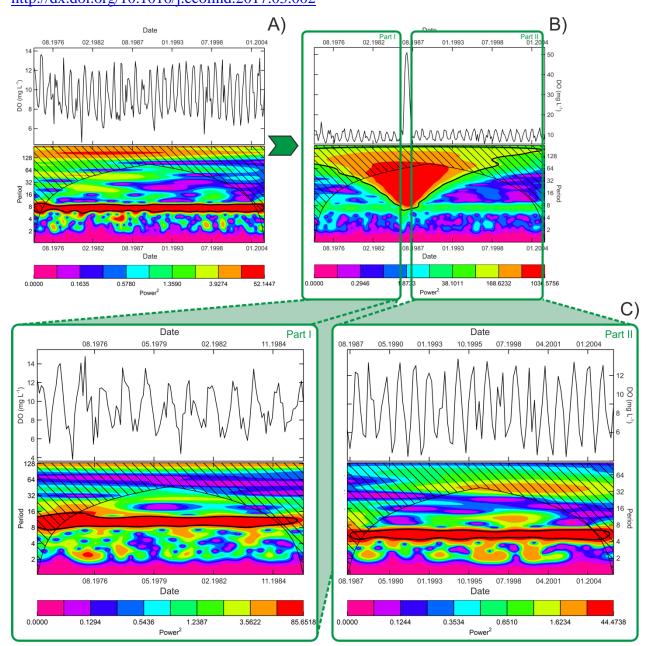


Fig. 4. Example of the PDS graph of dissolved oxygen from the Szolnok sampling site A). An artificial 1 year gap was introduced to the time series B) to show its negative effect on the wavelet spectra. Than by splitting the time series at the gap and exploring its wavelet spectrum in two section (Part I & Part II) its PSD graphs become meaningful and evaluable.

3.2. General trends observed

The assessed river section is characterized by widely varying runoff (min 26 m³s⁻¹ max 3220 m³s⁻¹; Table A1) with the average runoff increasing 4-fold in Hungary as we proceed downstream. The water quality parameters increased in concentration downstream as well, by a factor of between 1.02-2.45. The only exception is DO, the concentration of which decreased about 25% over the Hungarian section. The two most variable parameters were ammonium and runoff, while the other parameters' coefficient of variation (CV) remained between 20-60%, which may be considered as quite conservative. The CVs showed a decrease downstream (Table S1; Fig. S2).

3.3. Periodicity analysis

The annual periodicity of the water quality parameters differed at the sampling sites, with an average 36% increase in its value downstream (Fig. 5). The smallest PI_{sl} was seen at T1 (22%), while the largest PI_{sl} at the penultimate site in Hungary, T13 (58%). The increase was not even because of the anomaly seen at the water barrage system of Tiszalök. Before the obstacle at sampling site T5, the water is slowed down and PI_{sl} drops to 40%, while right after the dam (at T6), a remarkable increase is seen in annual periodicity (PI_{sl}=49%), however, at one site downstream (T7), a less mature annual periodic behavior is once again to be (PI_{sl}=46%, for details see Table A2).

Since the River Tisza can be considered a linear system (Kovács et al., 2015), the PI_{sl}s of the sites can be evaluated against the distance between the sites, giving significant (p<0.01) linear models (adjusted R² (R⁻²) = 0.5-0.8; Fig. 5). The PI of the nutrients increases most rapidly downstream (steepest slope), while the model with the PI of the ions included has the shallowest slope.

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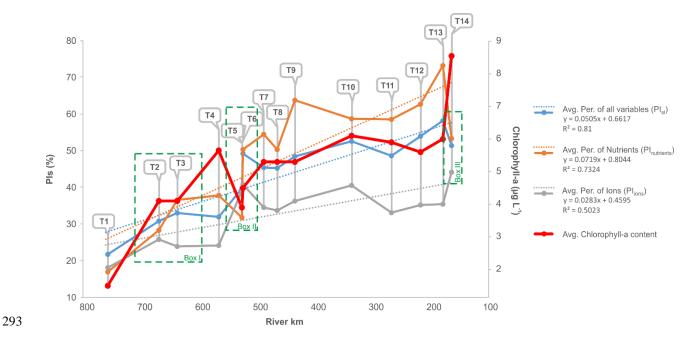


Fig. 5. Summary figure of the linear regression models of periodicity indices (PIs – defined in Table 2) with different combinations of water quality variables incorporated into them vs. river km.

3.4. Chlorophyll-a estimation

In the study, seven multiple regression models were derived to estimate the chlorophyll-a content of the water using the PIs of the water quality parameters at the different sites (Table 3). The obtained models were evaluated by taking into account multiple factors - R^{-2} , root mean square error (RMSE), model p-value, and variance inflation factor (VIF) - as suggested by O'Brien (2007), in order to find the best combination of driving PIs.

The estimated and measured chlorophyll-a values correlated at r>0.6, all the models were proven to be significant according to the chi square test (p<0.05), and a VIF of <2.48 indicated that

there is no multicollinearity in either model. The average RMSE was 1.048 μg L⁻¹, the average R⁻²=0.446. Based on the preceding, it was possible to make a clear distinction between the models, with, two out of the seven proving to be better, lm6 & lm7. Regarding R⁻², lm6 performed better than lm7 (difference in R⁻² =0.041), while lm7 had a smaller RMSE than lm6 (difference 0.01 μg L⁻¹).

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Table 3. Parameters of the linear regression models used to estimate chlorophyll-a, the best two models are in bold (for equations of the linear regression models see Table A3)

Code	Dependent variable	Independent variable(s)	R~2	p-value	RMSE
lm1		PI_{runoff}	0.357	0.014	1.16
lm2		PI _{nutrients}	0.460	0.005	1.06
lm3	<i>e</i> -	PIions	0.411	0.008	1.11
lm4	clorophyll-a	PI runoff, nutrients	0.447	0.015	1.03
lm5	clore	PI runoff, ions	0.433	0.018	1.04
lm6		PI nutrients, ions	0.504	0.008	0.98
lm7		PI runoff, nutrients, ions	0.463	0.026	0.97

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4. Discussion

The presence of an annual period was to be expected in the analyzed section of the river, since the main meteorological processes driving the water quality of the river have annual periodicity (Tanos et al., 2015). This annual periodic behavior increases downstream, and so does chlorophyll-a content, as the river turns into more of a lower section stream having "lake-like"

characteristics. Its waters' residence time increases, flow velocity decreases, better light conditions are achieved, with more available nutrients etc. downstream. This was similar to the phenomenon observed on the Loire (Abonyi et al., 2012), or as an "extreme" example, that section of the River Zala beyond the point where its waters reach a constructed wetland. The River Zala's flow velocity decreased, chlorophyll-a content increased and so did the annual periodicity of its water quality parameters (Kovács et al., 2010). A similar phenomenon was expected and observed in the case of the River Tisza as well, and will be discussed in the following section. Consequently, for the first time, the periodic behavior of water quality parameters was used to model the phytoplankton biomass in rivers.

4.1. General trends

Starting from the upper section of the river Tisza in Hungary, a higher variability was observed for runoff, dissolved oxygen and nutrients than for other parameters, and this then decreased downstream. In parallel with this decrease in their variability, their periodic behavior increased, indicating a fundamental change in the most important characteristics of the river (Reynolds, 1984). As the water slows down, the residence time increases, furnishing the conditions for a close-to-equilibrium state to form (Kovács et al., 2010). Thus, heading downstream, the river becomes ever more similar to a turbid lake than to a fast flowing upper section river (Reynolds, 1984; Stanković, et al., 2012).

4.2 Changes in the periodic behavior of the River Tisza

If the above information is combined not only in the case of the focus parameters, but for all the measured parameters and each sapling site, then the same pattern as discussed above may be seen, that is, increasingly periodic behavior downstream (Fig. 5). This was observed to be interrupted by (i) anthropogenic influences and/or (ii) natural ones (Fig. 5 boxes).

As for the former (i), site T06 can be mentioned as an example, where the increasing trend of PI_{sl} is interrupted by the Tiszalök Water Barrage System. Here, the river temporarily slows down, the PI_{sl} peaks (Fig. 5: box2), then decreases once again. This concurs with the more general observation that with an increased residence time, periodic behavior should increase as well (Tanos et al., 2015).

As for the latter (ii), after T01, the River Szamos enters the Tisza, and this tributary displays approximately 30% higher periodic behavior. The Szamos-PI $_{sl}$ = 50%, and its runoff was 52% more than the closest site upstream from the mouth in the River Tisza (T01). This boosted the increase in periodicity in the main branch (Fig. 5: box1). As the Kőrös tributary is reached, it might be though that a change should be anticipated in the PI $_{sl}$ of the River Tisza. Interestingly, however, no such phenomenon is observed. The reason is probably because the Kőrös River (Kőrös-PI $_{sl}$ =41%) only brings an additional 23% runoff compared to the nearest site of the main branch upstream (Tanos et al., 2015), which was not enough for the periodic behavior of the River Tisza to change. The River Maros (Maros- PI $_{sl}$ =40%), however, brought an additional 30% runoff, which was enough to interrupt the periodicity of the water quality parameters in the Tisza, decreasing the PI $_{sl}$ from 58 to 52% between sites T13 and T14 respectively (Fig. 5: box III).

4.3 Estimating chlorophyll-a content based on the periodicity indices of the sampling locations (PI_{sl})

As periodicity is a natural behavior of a riverine system, it plays a role in forming natural phytoplankton dynamics. Heading downstream, the River Tisza takes on the characteristics of a lower section type river (Section 4.1), its periodic behavior increases (Section 4.2) and so does its chlorophyll-a content (Table A1). The light conditions get better, due to the decreased amount of sediments supporting phytoplankton growth. In parallel with this, the longer residence time allows true riverine phytoplankton to grow. These natural longitudinal changes are reflected in the transition from benthic Pennales in the upper section to meroplanktic greens via unicellular centric diatoms at the lower sections (Abonyi et al., 2012; Duleba et al., 2014)

However, besides the clear longitudinal changes, there were anomalies in the general picture, as in some sections the chlorophyll-a decreased. Thus, it was a logical step to investigate the strength of the parallel change of chlorophyll-a content and periodic behavior of the different combinations of parameters by means of multiple regression analysis. This formed the backbone of the presented chlorophyll-a estimation approach. The best two estimations for chlorophyll-a were provided by the models consisting of the PIs of the nutrients, ions and, in the case of lm7, the PI of runoff.

To verify the wide applicability of the methodology, using the same set of water quality variables and the same time interval (1993-2005), the possibility of estimating chlorophyll-a with the presented methodology in the Hungarian section of the River Danube was assessed and shown to be successful (Table A4). The results converged with those from the River Tisza (Table 3). In the best two models for estimating chlorophyll-a in the River Danube, one was the same as in the case of the River Tisza (PI_{runoff, nutrients, ions}), while the other one was PI_{runoff, ions}. This observation

provides an additional example of the success of the presented approach in estimating chlorophylla concentrations.

These results support the idea that the periodicity of these parameters has a significant and quantifiable effect on primary production. Both anthropogenic and natural disturbances which reduce periodicity decrease primary production as well. This can then affect the whole riverine ecosystem through the food web (Ou and Winemiller, 2016; Roach and Winemiller, 2015). The increasing number and frequency of extreme events due to climate change in turn makes a decreasing phytoplankton biomass in rivers more likely. Extreme flooding can change the growth and resistance to flow detachment of the algae, as has been found to be the case in Taiwan (Chiu et al., 2016), and could be partly the effect of decreased algal biomass in rivers reported through Europe (Duleba et al., 2014). An additional important result is that in the lower section from the model a baseline chlorophyll-a concentration could be established (~8.5 µg L⁻¹). This can be considered as a natural background chlorophyll-a level of the Tisza, indicating that the river should be in a mesotrophic state. This is accordance with the recommendation of the large river intercalibration group that riverine plankton be accorded high status.

6. Conclusions

Rivers are one of the most endangered ecosystems; besides their environmental value, they produce a wide range of ecosystem services. Therefore, their monitoring is a focal point of action strategies with the aim of conserving/improving environmental conditions. Through the analysis of a river on a broad timescale (1993-2005) it was proven that the periodicity of water quality variables has a significant and quantifiable effect on riverine ecosystems, specifically

phytoplankton biomass. Unfortunately, because there is still insufficient information available on species—habitat interactions, the integration and prognosis of ecosystem properties is not yet fully available (Wu et al., 2014). By modeling such water quality parameters as indicators of phytoplankton biomass we have the opportunity to bypass this step. In this sense, the present study:

- (i) fills a gap by determining the spatial distribution of the periodic behavior of a river's general water quality parameters with Wavelet spectrum analysis,
 - (ii) by the means of multiple regression analysis indicates a clear relationship between the obtained periodicity indices and chlorophyll-a, and
- (iii) presents a significant model explaining about 50% of the phytoplankton variance in the studied river section.

Thus, the present predictions will hopefully now help to make the assessment of future changes in ecosystem services, ecological status and the development of the most efficient water management policy possible (Chapman et al., 2016). Further studies are encouraged, if we are to see how this relationship changes if different rivers, or river sections (e.g. lower section, river delta) are assessed and additional (meteorological, physical, etc.) parameters are incorporated into the model.

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652 Appendices

Table A1. Characteristics of the Hungarian section of the River Tisza

Code	Sampling location	River Km	EOVX	EOVY	Number of data	Chlorophyll-a averages in µg L ⁻¹
T01	Tiszabecs	757	313555	931595	196	1.5
T02	Aranyosapáti	668.6	324874	890067	185	4.1
T03	Záhony	636.8	345788	881408	186	4.1
T04	Balsa	565	317800	836068	176	5.7
T05	Tiszalök upstream of WBS	525.1	300124	819642	313	3.9
T06	Tiszalök downstream of WBS	523.1	300419	815511	164	4.5
T07	Polgár	487.2	287048	801740	181	5.3
T08	Tiszakeszi	464.1	272985	796336	162	5.3
T09	Tiszafüred	433.5	256591	776155	170	5.3
T10	Szolnok	335.4	203891	738554	196	6.1
T11	Tiszaug	266.4	169753	726219	170	5.9
T12	Mindszent	216.2	132631	735619	161	5.6
T13	Tápé	177.5	101759	739083	186	6
T14	Tiszasziget	162.5	93990	731637	191	8.6

Table A2. Average periodicity of water quality variables for each sampling site with the average periodicity indices for the whole Hungarian river section (PI_vs) given in the last row and the PIs giving the average periodic behavior of each sampling location (PI_{sl}) in the last column.

Code	Runoff	DO	BOD-5	Ca ²⁺	Mg^{2+}	Na ⁺	K ⁺	Cl-	SO ₄ ²⁻	HCO ₃ -	NH ₄ -N	NO ₂ -N	NO ₃ -N	PO ₄ -l	P PI _{sl}
T01	41%	70%	0%	43%	10%	13%	8%	12%	14%	29%	0%	0%	68%	0%	22%
T02	52%	54%	32%	21%	0%	46%	28%	29%	28%	32%	17%	13%	59%	26%	31%
T03	79%	40%	31%	36%	9%	38%	12%	32%	42%	0%	18%	31%	63%	36%	33%
T04	53%	31%	44%	28%	0%	51%	15%	34%	31%	12%	20%	39%	58%	36%	32%
T05	57%	100%	0%	17%	45%	55%	49%	41%	0%	57%	39%	0%	35%	48%	40%
T06	87%	99%	16%	46%	16%	48%	75%	54%	0%	50%	59%	3%	100%	39%	49%
T07	77%	100%	0%	19%	26%	26%	75%	37%	30%	30%	62%	17%	99%	39%	46%
T08	75%	100%	22%	20%	32%	15%	85%	29%	24%	32%	60%	12%	98%	30%	45%
T09	65%	100%	4%	23%	13%	42%	88%	40%	17%	32%	88%	19%	98%	50%	49%
T10	79%	100%	38%	14%	35%	44%	81%	43%	19%	46%	72%	22%	97%	43%	53%
T11	79%	100%	36%	28%	14%	28%	75%	30%	13%	45%	83%	12%	99%	40%	49%
T12	83%	100%	76%	55%	24%	20%	20%	58%	20%	50%	37%	32%	95%	86%	54%
T13	72%	100%	100%	29%	22%	37%	53%	51%	14%	46%	88%	22%	97%	82%	58%
T14	83%	100%	15%	50%	30%	59%	47%	72%	28%	24%	66%	33%	95%	19%	52%
PI_{v}	70%	85%	30%	31%	20%	37%	51%	40%	20%	35%	51%	18%	83%	41%	

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Table A3. Equations of the linear regression models

C	ode	Equations of the linear regression models
lı	m1	$chlorophyll$ - $a_i = 6.93 \cdot PI_{runoffi} + 0.27$
lı	m2	$chlorophyll-a_i = 6.99 \cdot PI_{nutrients\ i} + 1.74$
lı	m3	$chlorophyll-a_i = 14.02 \cdot PI_{ions\ i} + 0.45$
lı	m4	chlorophyll- $a_i = 2.79 \cdot PI_{runoff i} + 5.14 \cdot PI_{nutrients i} + 0.68$
lı	m5	$chlorophyll-a_i = 3.68 \cdot PI_{runoff\ i} + 9.35 \cdot PI_{ions\ i} - 0.57$
lı	m6	chlorophyll- $a_i = 4.60 \cdot PI_{nutrients i} + 7.69 \cdot PI_{ions i} + 0.33$
lı	m7	chlorophyll- $a_i = 1.36 \cdot PI_{runoff i} + 3.95 \cdot PI_{nutrients i} + 6.87 \cdot PI_{ions i} - 0.03$

Table A4. Parameters of the linear regression models used to estimate chlorophyll-a on River Danube; the best two models are in bold.

Code	Dependent variable	Independent variable(s)	R~2	p-value	RMSE
lm1_Danube		PI _{runoff}	0.464	0.013	2.224
lm2_Danube		PI _{nutrients}	0.312	0.043	2.250
lm3_Danube	Ġ.	PI _{ions}	0.405	0.021	2.085
lm4_Danube	clorophyll-a	PI runoff, nutrients	0.582	0.012	1.921
lm5_Danube	clore	PI runoff, ions	0.710	0.002	1.736
lm6_Danube		PI nutrients, ions	0.356	0.071	2.109
lm7_Danube		PI runoff, nutrients, ions	0.669	0.013	1.735

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