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LONG TERM SEASONAL CHANGES OF THE DANUBE RIVER ECO-CHEMICAL STATUS IN THE REGION OF SERBIA

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Abstract

Seasonal spatial and temporal changes of selected eco-chemical parameters in section of the Danube River flowing through Serbia were analyzed. Data for electrical conductivity (EC), dry and suspended matter (SM), residue on ignition, chemical oxygen demand (COD), biochemical oxygen demand (BOD-5), ultra-violet (UV) extinction, dissolved oxygen (DO), oxygen saturation, pH, nitrates, total phosphorus (P) and nitrogen (N) was collected between 1992 and 2006. The use of monthly medians combined with linear regression and two sided t-test has been proven to be the best approach for resolving trends from natural variability of investigated parameters and for determining trend significance. Patterns of temporal changes between different months were examined. It was also determined that spatial trends of some parameters oscillate in predictable manner, increasing in one part of the year and declining in other. Regression slope coefficients, an excellent indicator for determining when the water quality is changing the most along the course of the Danube, reach their maximum during summer for temperature (t), electric conductivity, nitrates and total N, while in the same season suspended matter, COD, BOD-5, DO and oxygen saturation coefficients reach their minimum. Correlations for used data sets of selected parameters were analyzed for better understanding of their behavior and mutual relations. It was observed that as Danube flows through Serbia, its general eco-chemical status either stagnates or improves, but the rate of river self purification often depends on the season of the year.

Keywords: Danube; Temporal and spatial trends; Seasonality; Median; Water quality parameters.

1. Introduction

The Danube River runs through Serbia at a length of 587.4 km entering Serbia at 1433rd km and leaving it at 845th km from its mouth. The whole Danube River is 2783 km long and has a basin of 817,000 km^2, out of which around 10% belongs to Serbia. Serbian part of the Danube belongs to the middle section of the river which extends from the Devin Gate (at the border of Slovakia and Austria) to the Iron Gate (at the border of Serbia and Romania). The riverbed widens here and the average bottom gradient is 0.00006% (ICPDR 2005). The average Danube flow on entering Serbia is 2400 m^3/s, while on leaving the country it reaches 5500 m^3/s (ICPDR 2005).

The Iron Gate I (943 km) and II (863.4 km) dam complex located at the border area of Romania and Serbia strongly influence the Danube dividing it into upper and lower section (Figure 1). The upper section, covering the stretch from the Hungarian border to Belgrade, belongs to the Pannonian basin. The lower section, from Belgrade to the Bulgarian border runs along the southern border of Pannonian basin and through the Iron Gate gorge. Dams cause the slowdown of the flow velocity, the rise of the water level and the increase in sedimentation (Vukov et al. 2008). Under conditions of mean water level, a slowdown of flow velocity is observed from 1155th km (which is at the mouth of river Tamiš), while under conditions of a high water level, a reduction of flow velocity is observed on its tributaries (Sava, Tisza, Tamiš, etc.).

The biggest Danube tributaries with estuaries in the Serbian part of the Danube are: Tisza (794), Tamiš (47) on the left side, and Drava (577), Sava (1564) and Velika Morava (232) on the right side (numbers in brackets show their average discharge in m^3/s). The Danube-Tisza-Danube (DTD) canal system is connected to the Danube River and has a total length of 929 km. It is divided into two practically independent parts, in the Bačka and in the Banat region. In Bačka, the main canals receive water from the Danube River both gravitationally (up to 72 m^3/s) and by pumping (33 m^3/s). In the Banat region, the main canals are fed from the Tisza River (120 m^3/s) and from the smaller intercepting rivers (ICPDR 2005).

Two big cities, Belgrade (1.7 million inhabitants), and Novi Sad (300,000 inhabitants) lie on the Danube River, as well as many smaller towns (Apatin, Bačka Palanka, Pančevo, Smederevo, Donji Milanovac, Kladovo) and villages (small settlements with less than 10,000 inhabitants make 48% Serbian population). None of them has any kind of system for treating municipal waste waters (Veljković 2005).

For the purpose of ensuring a sustainable and equitable use of waters and freshwater resources in the Danube River basin, eco-chemical status of the Danube River was monitored both on the local level, in each country through which it flows, and on the international level through organizations like The International Commission for the Protection of the Danube River (ICPDR 2005). The data on the Danube's eco-chemical status in Serbia have been collected over many years. After validating the available records we have decided to process the data sets for the period from 1992 until 2006 (a period of 15 years).

There is a range of factors that can influence the eco-chemical dynamics of a river but a full investigation may be performed only when the long-term time-series data are available. The goal of this paper was to investigate the long-term changes of the eco-chemical status of the Danube River in relation to the pollution changes during previous years and to identify the seasonal fluctuations, averaged during the investigation period, which could reveal some regularity in the Danube behavior over time and especially during different seasons of the year. Special attention was paid to determining the trends of the averaged monthly data with the aim to forecast the behavior of the pollutants under different conditions or in the near future.

The Danube River is constantly being in the focus of various environmental studies. The most exploited topics were pollution with: metals in water (Madarasz and Horvath 2001; Dumbrava et al. 2008; Guieu and Martin 2002; Dumbrava and Birghila 2009) and sediments (Milenković et al 2005; Enache 2008; Crnković et al. 2008; Orescanin 2005, Relic et al. 2009), nutrients (van Gils et al. 2005; Teodoru and Wehrli 2005; Schreiber et al. 2005; Behrendt et al. 2005; Kalchev et al. 2008; Lair et al. 2009), radioisotopes (Vuković et al. 2006; Miljević et al. 2008; Krmar et al. 2009), oil (Literathy 2006) etc. There are many studies dealing with the general pollution status of the river, covering more than one group of pollutants (Vogel 2003; Galatchi and Vladimir 2006; Pawellek et al. 2002; Kundev et al. 2001) as well as from the regulatory point of view (Avis and Weller 2000). Nevertheless, the number of studies involving the long-term changes is limited due to the necessity of performing long, coherent monitoring programs and the abundance of data produced by them that needs to be processed.

2. Materials and Methods

The main sampling material for measurement was the river water, sampled and analyzed according to APHA (1976-1992) and US EPA standard methods (1983) (APHA 1992; US EPA 1983). The measured parameters (corresponding methods are given in the brackets) important for determining the eco-chemical status of the Danube River were:

- Suspended matter **(SRPS EN 872: 2008)**
- Nitrates (NO_3 - N) **(APHA AWWA WEF 4500-NO3: 1992)**
- Total nitrogen (N) **(SRPS ISO 5663: 2000)**

- Total phosphorus (P) **(APHA AWWA WEF 4500-P: 1992)**
- BOD-5 **(EPA 360.2: 1971)**
- COD (with permanganate) – **(SRPS EN ISO 8467: 2007)**

The analysis of the blanks and duplicates were the main instruments of QA/QC during measurement throughout the years.

The regular monthly measurements were performed every year in the period of 15 years (1992-2006). Sampling and the analysis have been performed by the Republic Hydrometeorological Service, which is the only institution in Serbia appointed by the law to perform systematic monitoring of surface and ground waters.

The surface water samples were taken according to ISO standard (ISO 5667-6:1990) at distance from the river bank equal or greater than 15 meters. This precaution was necessary to eliminate potential influence of the sediments to surface water quality. All sampling sites were at considerable distance from mouths of the Danube's tributaries (Figure 1), so it was safe to assume that their water has always been well mixed with water of the Danube prior to the sampling (Miljevic et al. 2008). Water column was also well mixed (Winter et al. 2008), therefore collected samples have been considered to be representative for the entire water stream. The sampling was performed 40 cm below the water surface in the water-front area, in order to prevent contamination of the sample by mud from the bottom or floating particles from the water surface. Samples were collected into 5 liter plastic canisters.

Temperature of the water samples and pH parameters were determined on site. The samples for the determination of the dissolved oxygen concentrations were collected and treated separately. All samples were stored at $4^{o}C$ and normally analyzed within a day. The maximum storage time was less than 2 days after the sampling.

2.1. Sampling locations

There were seventeen sampling stations at the Serbian part of The Danube River (Figure 1), but four of them were excluded because the data they provided has been insufficient for our research due to too short operational time of just a few years. The data from the remaining stations were analyzed for the selected period, although some parameters were not monitored for all the years and during every month. In other cases, the sampling was performed one to two times per month.

Fig. 1 Sampling stations located at the Serbian part of The Danube River

The list of the sampling stations in order as they appear going down the river with the description of the exact location:

1. **Bezdan** – Hungarian border (inflow of Danube River into Serbia)
2. **Apatin** – downstream from town
3. *Bogojevo (excluded from considerations)*
4. *Bačka Palanka (excluded from considerations)*
5. **Novi Sad** – before confluence of DTD canal
6. **Slankamen** – upstream from Tisza confluence
7. *Čenta (excluded from considerations)*
8. **Zemun** – before Sava confluence
9. **Pančevo** – downstream from Višnjica, at confluence of Tamiš
10. *Vinča (excluded from considerations)*
11. **Smederevo** – above steel factory, before Velika Morava confluence
12. **Banatska Palanka** – at confluence of Vršac canal, upstream from Nera confluence
13. **Veliko Gradište** – at water meter
14. **Dobra** – in town
15. **Tekija** – in town, before Iron Gate I dam
16. **Brza Palanka** – at water meter, between Iron Gate I and II dams
17. **Radujevac** – after Iron Gate II dam (outflow of Danube River from Serbia)

3. Results and Discussion

In the first part of the project "Long term changes of the Danube river eco-chemical status in the region of Serbia" (Živadinović et al. 2010) the overall trends in time and space were identified, using linear regression analysis of the selected eco-chemical parameter yearly median values, with the defined significance level and resolving them from natural variability. It was also identified that the seasonal changes deserve additional investigations. For the investigation of seasonal changes and trends of the selected eco-chemical parameters of the Danube River, the same investigation model has been used, but on different sets of the parameter values. While our previous work dealt with the yearly medians, in this one we calculated the monthly medians which represent the average values for all the measurements made in the particular month (e.g. January, February etc.) during the 1992-2006 period.

The method used for determining trends in space was linear regression analysis. Based upon these results it is possible to describe the direction of the trend (a negative or positive slope), while the quality of the linear regression trend lines could be described with coefficient of determination (r^2) which is useful because it gives the proportion of the variance of one variable being predictable from the others (Miller and Miller 2005; Meier and Zund 2000; Laurencelle and Dupuis 2002; Kanji 2006).

The selected parameters for our investigations are, in general, sum/collective parameters which cover several inorganic or organic species and these sum/collective parameters are divided in four groups:

1. Suspended matter and dissolved species (dry matter, residue on ignition and electrical conductivity). These parameters describe the burden of the river water with inorganic and organic matter together, while conductivity describes the amount of ionic species in the water.
2. UV extinction on 254nm, COD and BOD-5. These parameters generally cover dissolved organic matter and biological activity in the river water.
3. Oxygen concentration and oxygen saturation. Oxygen parameters are essential to all aquatic life which maintains healthy river water environment.
4. pH, total P, total N and NO_3^-. Nutrients, like nitrogen and phosphorus, occur naturally in the water, but they are very often the main cause of the river pollution due to their elevated concentration levels.

Besides these group parameters, there are numerous single parameters that were not the subject of our work since each of them could be a separate topic of investigation.

Similar investigations were performed on The Danube River tributaries whose confluences lie in Serbian territory. Some of the collected data were used to explain the behavior of the examined eco-chemical parameters.

In this paper, the eco-chemical status of The Danube River as an international river was described through discussing the available results from two particular aspects:

- Seasonal temporal changes among monthly medians at a single monitoring location on The Danube River for the period from 1992 to 2006.
- The analysis of the seasonal spatial trends describing the changes of medians from one sampling location to another in a single/selected month, or in other words, changes of the monthly median concentrations for a particular month in the 1992-2006 period along the Danube stream.

3.1. Seasonal changes of the measured parameters for the period 1992-2006.

The source data sets contain hundreds of measurements and some of them have non normal distributions, therefore median, minimum and maximum values are the only remaining statistical parameters that give meaningful averaged data, appropriate for our investigation. Medians are assumed to be sufficient and very useful for the purposes of our work since their values don't reflect individual outliers sometimes present in our large data sets. Therefore any influence of the extreme values arisen from the misrepresentative sampling, experimental errors and data transcription errors is minimized. Same can be said for the extreme values measured due to the incidents occurring on the sampling sites that led to the temporary, non-characteristic elevation of the parameter values.

The estimated quality of the regression/fitness of the curves were obtained according to the procedure based on a linear regression and two-sided t-test, described elsewhere (Živadinović et al, 2010).

The seasonal spatial and temporal trends are presented by plotting the data to the surface charts (3D charts) whose horizontal axes show months (January to December) and places (Bezdan to Radujevac), while vertical axis shows median concentration of the analyte values for the particular place and month in the 1992-2006 period.

For the purpose of trend detection these 3D charts were divided in series of 2D charts which could be statistically processed and where linear regression (for analysis of spatial trends) could be applied. These 2D charts present the seasonal temporal and spatial (one being perpendicular to the other) trends mentioned above and thoroughly described in the text that follows.

3.1.1 Seasonal temporal trends

Seasonal temporal trends are observed by comparing values of monthly medians gained by calculating median value for all measurements taken in a particular month on specific location from 1992 to 2006 period. Since these changes vary by season, we have expected that the trend could not be properly described by using linear function, but with polynomial function of second (which was used) or higher order. Quadratic function is adequate for describing any eco-chemical parameters which have minimal values in winter months, maximal values in summer months and vice versa. The only difference is that in the first case function is opened downward and in the second it is opened upward. In either case, if investigated parameters do have pronounced seasonality, coefficients of determination (r^2) will be closer to 1.

3.1.2 Seasonal spatial trends

To analyze the seasonal spatial trends which follow the changes of monthly medians (representing the average value of all measurements taken in a specified month at particular sampling locations during the 1992-2006 period) between different sampling locations during one season (month of the year) along the Danube River, a useful simplification was applied. Parameter changes were monitored for every other month (February, April, June, August, October, December). This approach is more convenient for assessing seasonal changes of the observed parameters from Bezdan to Radujevac, in contrast to the method described by Živadinović et al., which follows spatial changes of yearly averages.

3.2 Investigated eco-chemical and hydrological parameters

Eco-chemical parameters which are topic of our investigation were divided into four groups. Prior to them, a two hydrological parameters, river discharge and temperature were analyzed.

3.2.1 Temperature and discharge

Seasonal changes are strongly influenced by the temperature of the water. The temperature reaches its maximum in July and August, and its minimum is in January and February (Figure 2). Analyzing spatial trends it was determined that the temperature rises from Bezdan to Radujevac and that temperature growth is statistically significant for all months, except for February and October. Slope coefficients of spatial trend lines are quite informative. The temperature at the inflow point (Bezdan) is constantly lower in relation to the outflow point (Radujevac) (Figure 3), but the temperature increase is most outstanding in summer months since the slope coefficients are the greatest in those months. There are several ways to explain this pattern. For the purpose of these explanations, average annual climatology data collected by Republic Hydrological Service of Serbia for years 1992, 1998 and 2006 (first, middle and last year of the monitoring period) were used. Flowing through Serbia, the Danube River passes through regions with similar average: yearly temperatures, maximal temperatures, minimal temperatures, insolation, precipitation, the number of rainy days, the number of days with snow cover, and the number of days with frost (RHMZ 2009).

The Danube flows into Serbia from the north, and then runs toward south. When it reaches Belgrade, a capital of Serbia, it turns east (Figure 1) toward Serbian eastern border. All the time the river flows through the regions with similar climatic properties. Flowing through this southern part of Pannonian basin increases the temperature of Danube. To explain why the warming of the river is much smaller in the October-February period, one must bear in mind that during those months, insolation is significantly lesser, and the air temperature often drops below 0^{o}C, although measured water temperatures always remain positive. Since the difference between air and water temperature is smaller in winter period, the effect of river warming is less significant.

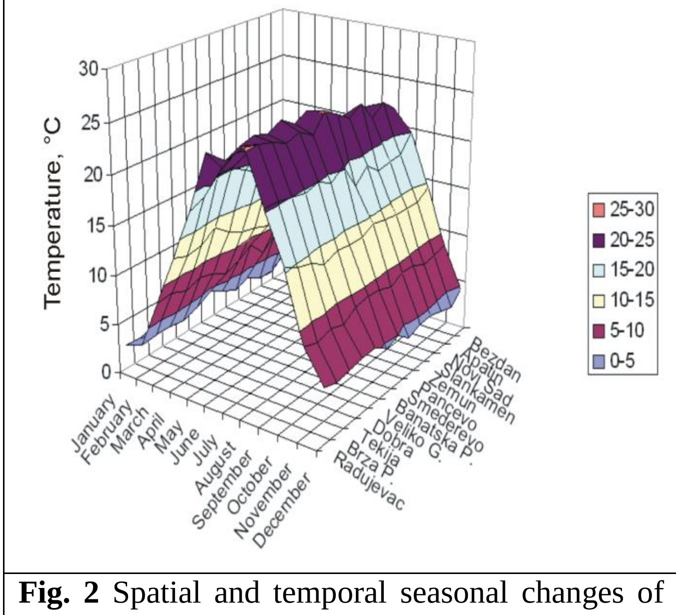

Fig. 2 Spatial and temporal seasonal changes of water temperature presented on the 3D chart

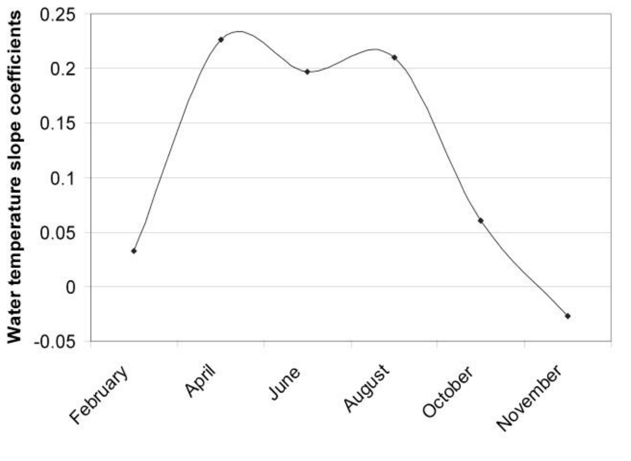

Fig. 3 Seasonal changes of spatial trend line slope coefficients for water temperature

Average discharge gradually increase from January till April due to snowmelt and increased precipitation in the upper Danube and its tributaries (Figure 4). In summer months, discharge decreases significantly - from 2770 m^3/s in July to 1610 m^3/s in October (which is also the yearly minimum). These considerable variations in river discharge affect seasonal changes of some parameter values. Also, mostly because of its tributaries (Drava, Tisza, Sava and Velika Morava), the discharge of the Danube is more than doubled at its leaving point in Serbia, compared to its entering point.

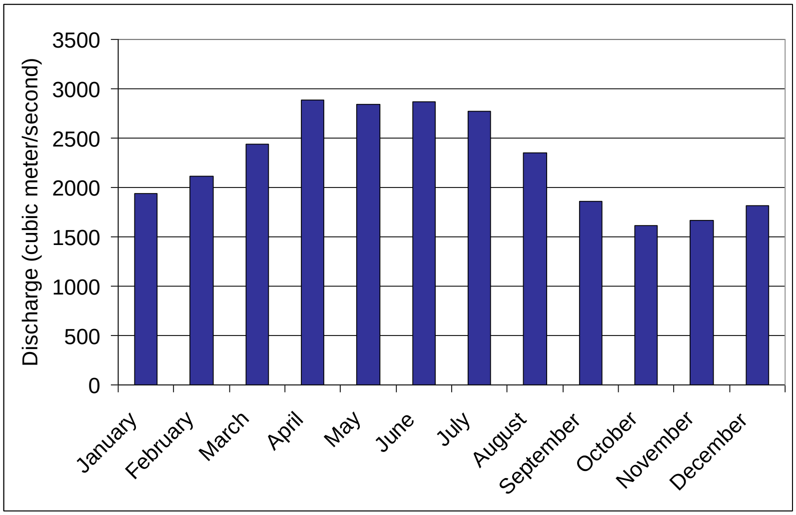

Fig. 4 Average discharge (Q) for Bezdan during 1949-2006 period

3.2.2 First group parameters

Suspended matter: Monthly median concentrations of suspended matter vary by month considerably, having maximum values between March and June (at 10 of 13 locations) while minimal concentrations appear during the winter and summer period (Figure 5). The discharge shows good correlation with suspended matter concentrations (average correlation coefficient, $r = 0.48$) and the suspended matter peak period overlaps with the period of larger discharge in spring (April-May), and smaller discharge in autumn (November) (Prathumratana et al. 2008). In the lower section of the Danube River, after Smederevo, quadratic regression line opens upwards, due to the emerging of higher concentrations of suspended matter in winter (though not as high as in spring). This may be attributed to the influence of tributaries, and to different river regime caused by the Đerdap lake accumulation whose water level and water outflow is mainly controlled by the human factor.

Seasonal spatial trends show decrease for every month (statistically significant in February, June, August and October) which is attributed to slowdown of the river flow due to the dam complex (Pajević et al. 2008).

If regression slope coefficients are mutually compared, monotonic drop of values from December to June and monotonic growth from June to December is observed (Figure 6). This indicates that self-remediation of the Danube from Bezdan to Radujevac is greater in summer than in winter. This is caused by lower levels of suspended matter in the winter period, which, in turn, is caused by the smaller quantity of rain precipitation and, consequently, much smaller run-off contribution from river banks. More importantly, during higher discharge (Figure 4), the river becomes more turbulent, so its ability to suspend matter is increased. On the other side, when concentrations of suspended matter approach to its natural minimum, the rate of decrease of suspended matter becomes smaller. Analysis of correlations between monthly median concentrations, measured at Bezdan and Brza Palanka (first and the last sampling sites before Iron Gate II Dam, respectively) and spatial trend slope coefficients for suspended matter, lead to conclusion that self-purification potential of the river is mainly controlled by variations of suspended matter concentrations at Bezdan. The correlation coefficient for correlations between spatial trend slope coefficients and suspended matter monthly median concentrations measured at Bezdan is negative (r = - 0.92), since the decrease was the greatest during suspended matter peaks. The same calculations done for Brza Palanka (r = - 0.04) show that variations of suspended matter concentrations at Brza Palanka had little influence on spatial trends.

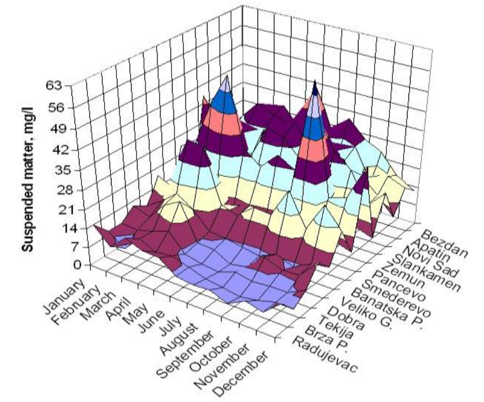

Fig. 5 Spatial and temporal seasonal changes of suspended matter presented on the 3D chart

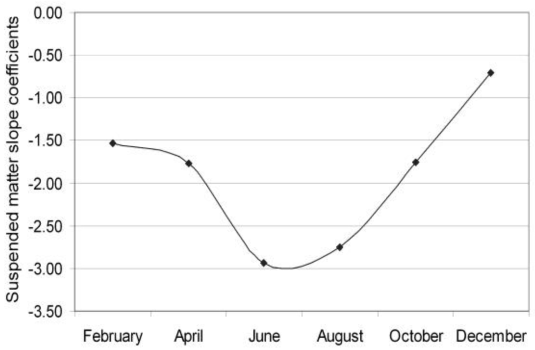

Fig. 6 Seasonal changes of spatial trend line slope coefficients for suspended matter

Dry matter monthly medians were reaching maximums in January or February at every location, while minimums appeared between May and September (Figure 7). Changes can be relatively well described with quadratic function opened upwards with correlation coefficient squares varying between 0.55 and 0.90 (the sole exception being 0.11 for Radujevac); the average of 0.67 indicates a pattern in seasonal changes.

Seasonal spatial trends show a decrease for every month (statistically significant in October, $r^2 = 0.68$ and December, $r^2 = 0.66$).

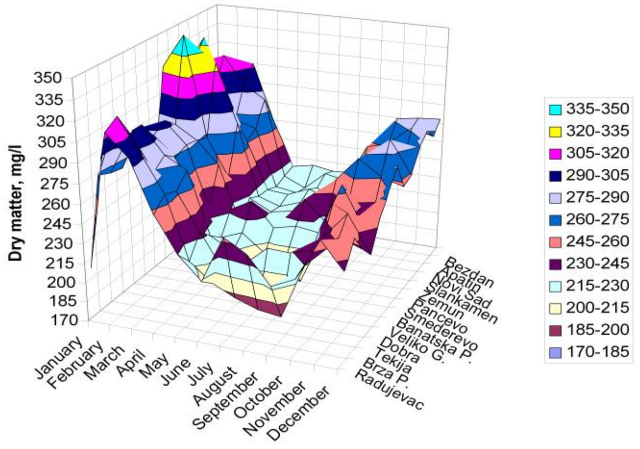

Fig. 7 Spatial and temporal seasonal changes of dry matter presented on the 3D chart

Residue on ignition: Seasonal temporal trends described by changes of monthly median values of residue on ignitions have maximal values in January, February and March (at 4, 5 and 2 locations, respectively) while minimal values most often occurred in May, June and August (at

3, 4 and 3 locations, respectively) (Figure 8). The trends of changes between months can be described with quadratic functions opened upward with correlation coefficient squares varying between 0.17 and 0.83, average 0.51. These findings are consistent with trends for electrical conductivity, dry and suspended matter.

Seasonal spatial trends do not show statistically significant trend, and vary between positive and negative values.

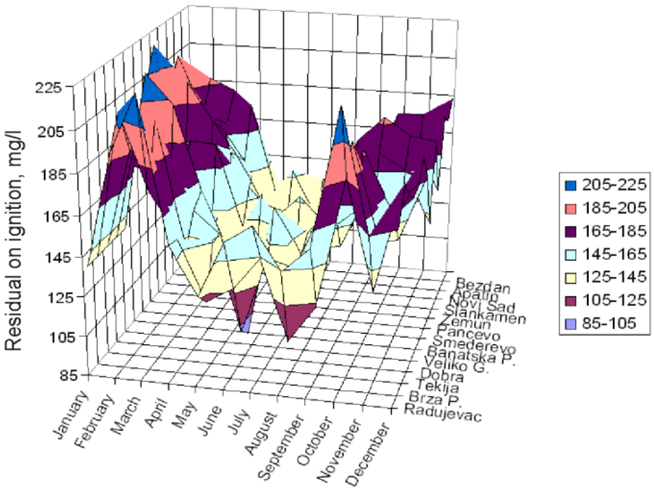

Fig. 8 Spatial and temporal seasonal changes of residue on ignition presented on the 3D chart

Electrical conductivity: Median monthly values of electrical conductivity were the highest in January, February and March (at 4, 7 and 2 out of 13 locations, respectively), while minimal values were observed between May and August, most frequently in June (at 5 out of 13 locations) and July (4 out of 13) (Figure 9). Change between months was quite regular and seasonal temporal trends were well described with quadratic regression line opened upwards with correlation coefficient squares varying between 0.35 and 0.95, average 0.66.

Seasonal spatial trends varied significantly among summer and winter months. In June and August, increasing spatial trends were statistically significant and in December and February, the trends were statistically significantly decreasing. Trends for April and October are slightly negative but show no statistical significance and the reason for that is not large deviation of graph points, but the fact that slope coefficients of trend lines are close to zero. When presented graphically, trend slopes show regular pattern (Figure 10). These results are consistent with findings of Živadinović et al. that spatial trends of median yearly value changes from Bezdan to Radujevac did not show statistical significance (Živadinović et al. 2010). Seasonal analysis is more subtle, and able to show different tendencies during year which can be lost when measurements are averaged by calculating yearly medians.

It is obvious that the behavior of this parameter is very specific. One of the key factors influencing temporal trends of electrical conductivity was river discharge. This is supported by calculating correlations at the Bezdan sampling site between data for average river discharge (in 1946-2006 period) and electrical conductivity monthly medians for Bezdan. The correlation coefficient was negative ($r = -0.44$). The same procedure was applied to major tributaries (Tisza, Sava, Velika Morava) at their sampling sites closest to their mouths, and all turned with negative correlation coefficients ($r = -0.58$, $r = -0.41$, and $r = -0.51$ respectively).

It has been noticed that after Veliko Gradište, when the Danube flows into the Iron Gate Gorge, lacking any larger tributary, it displays lesser variability of electrical conductivity parameter values than in the upper stream regarded both spatially and temporally. One of the causes for opposite seasonal spatial trends (positive in summer and negative in winter) is a different (to some extent) regime of electrical conductivity in tributaries, which is supported by the fact that the greatest changes among electrical conductivity values, during spatial tend analysis, were determined in the middle section of the Danube, where tributary confluences are placed. Another possible cause might be a greater spatial decrease of suspended matter concentrations in summer months (described above), which can contribute to spatial increase of el. conductivity in the same period due to smaller concentrations of colloidal particles able to adsorb ions in the water. Nevertheless, electrical conductivity is a collective eco-chemical parameter dependent on concentrations of various cations and anions, both organic (Küchler 2000) and inorganic, it is undoubted that numerous other factors affect electrical conductivity trends.

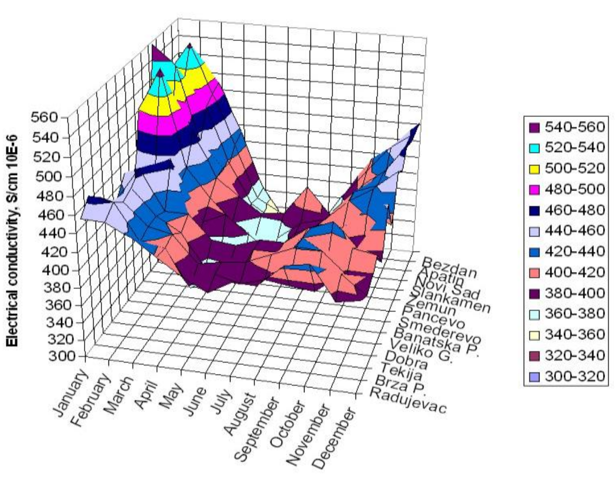

Fig. 9 Spatial and temporal seasonal changes of electrical conductivity presented on the 3D chart

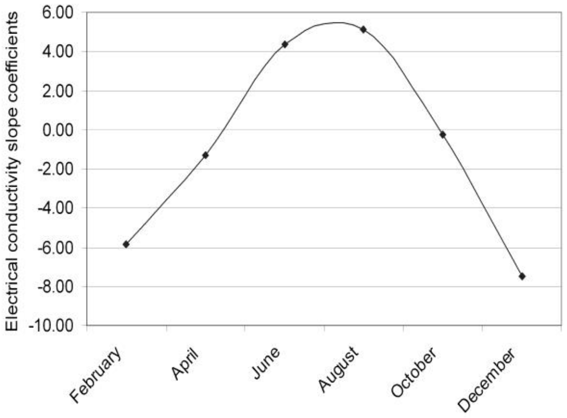

Fig. 10 Seasonal changes of spatial trend line slope coefficients for electrical Conductivity

3.2.3 Second group parameters

COD: Seasonal temporal trends described by the changes of monthly medians show change of pattern depending on the sampling location (Figure 11). From Bezdan to Slankamen changes between months are well described with quadratic function opened downwards having correlation coefficient squares between 0.60 and 0.77, from Zemun toward Veliko Gradište, the functions keep the same shape but the correlation coefficient squares do not exceed 0.55. Maximum values appear between March and June (most often in April and June) while minimum values appear between December and February (most often in December, 5 times). From Duboka to Radujevac the regression line changes from: close to linear to quadratic opened upward (best fitted for Tekija and Radujevac having correlation coefficient squares 0.74 and 0.72 respectively). Minimum values most often appear in April, while the maximum ones appear in January.

The seasonal spatial trends show a decrease from Bezdan to Radujevac in every month (statistically significant in April, June, August and October with correlation coefficient squares between 0.49 and 0.62). The regression line slope is most negative in April and then gradually becomes less negative till December (Figure 12).

COD at the inflow point (Bezdan) is constantly high in relation to the outflow point (Radujevac) (Figure 11), but its decrease is most outstanding during summer months since that is when the slope coefficients are the lowest. These changes result from the fact that more polluted Danube, coming from North, is gradually purified during its flow through Serbia and the purification process is more intensive in summer than in winter months. That is understandable because the higher temperature in summer makes the purification process faster (Kenarova 2005).

To get a better perspective on this, the correlation between monthly medians at the sampling sites and seasonal spatial trend line coefficients were calculated. At the observed locations (Bezdan, Slankamen, Zemun and Pančevo) in the upper stream, the r-values were extremely negative: -0.98, -0.83, -0.89 and -0.91 respectively, meaning that when monthly medians were elevated, declining spatial trends were most distinguished (as well as river self-purification). On the contrary, the variation of monthly medians at the locations in the lower stream of the river (Smederevo, Banatska Palanka, Veliko Gradiste and Radujevac) showed less or no influence on temporal trends (correlation coefficients were: -0.23, -0.58, -0.035 and 0.125, respectively). The variability of the monthly medians in the upper stream was also greater (difference between maximal and minimal value was 34.1%) than downstream (18.8% difference). These findings might be explained by the fact that in the upper stream the Danube has less discharge, enters Serbia with a big COD load and still runs through landscape with highly productive soil, significantly exposed to fertilizers. It is logical to assume that these sampling sites have greater influence than those located downstream where the pollution runoff is expected to be smaller, the discharge (related to dilution) is bigger as well as sedimentation process (connected to hydrology characteristics of that region) (Pajević et al. 2008).

The trend lines for every month showed local maximum at Slankamen, Pančevo and Banatska Palanka and local minimums at Zemun and Smederevo. This can be attributed (among other sources) to the pollution coming from Belgrade, since Belgrade does not have a system for communal water treatment. The same pattern is recognized for suspended matter.

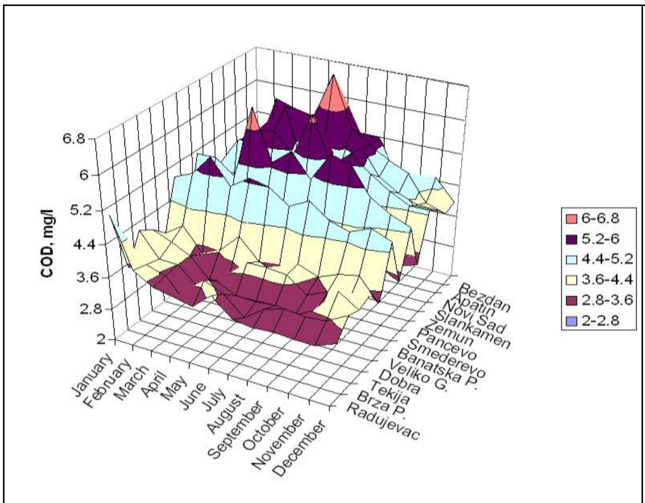

Fig. 11 Spatial and temporal seasonal changes of COD presented on the 3D chart

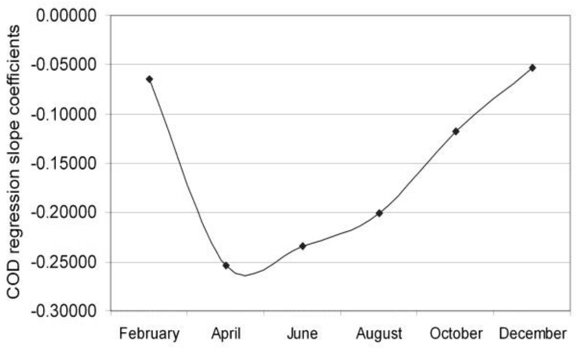

Fig. 12 Seasonal changes of spatial trend line slope coefficients for COD

BOD-5: Seasonal changes described by median monthly values (1992-2006 period) of BOD-5 show recognizable trend (Figure 13) described by quadratic function opened downwards at first 4 locations (Bezdan to Slankamen) with correlation coefficient squares 0.85 , 0.61 , 0.60, 0.59 , respectively. Maximal values occur between April and July, minimal in November and December. After Slankamen, the correlation coefficient square of regression lines becomes less than 0.43 (average 0.29) and close to correlation coefficient squares of linear regression.

Seasonal spatial trends show a decrease in each month except December (statistically significant in April, June, August and October whose correlation coefficient squares vary between 0.41 and 0.58). When mutually compared, the regression slope coefficients display monotonic drop of values from December to June and monotonic growth from June to December (Figure 14). This indicates that self-remediation of the Danube from Bezdan to Radujevac is larger in summer than in winter. The argumentation for this phenomenon is exactly the same as for COD: the elevated values in spring and summer in the upper stream, dictate the rate of the river self purification (Kenarova, 2005). Also, in summer time temperature is higher, the water purification is faster, going through Serbia water quality is better and better and therefore the slope coefficient for BOD-5 is more negative.

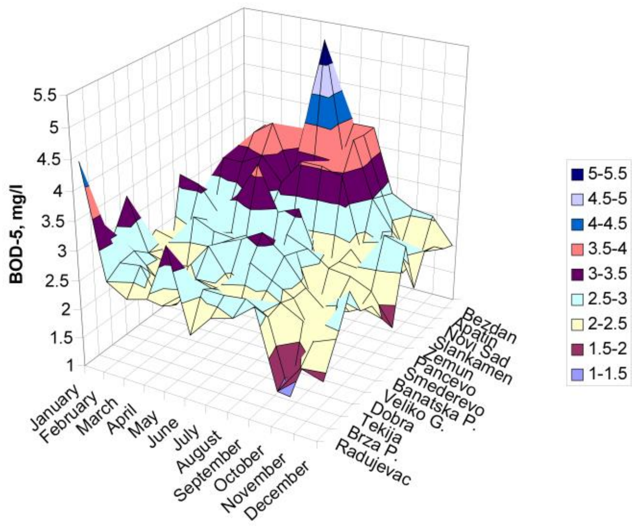

Fig. 13 Spatial and temporal seasonal changes of BOD-5 presented on the 3D chart

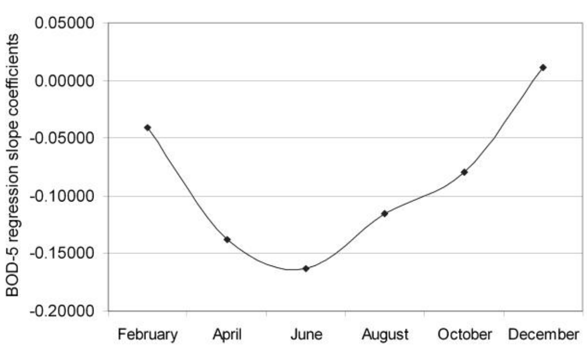

Fig. 14 Seasonal changes of spatial trend line slope coefficients for BOD-5

UV extinction on 254nm: Seasonal temporal trends of UV extinction on 254nm moderately fit into quadratic regression line opened upward in the first 6 locations (Bezdan to Pančevo) with average correlation coefficient square 0.47 (Figure 15). After Pančevo, the regression is much worse (average correlation coefficient square is 0.09) and more similar to the linear line. The minimum most often occurs between May and July, maximum between October and April.

Seasonal spatial trends show a decrease from Bezdan to Radujevac in February and April and an increase in other months (statistically significant in June and October).

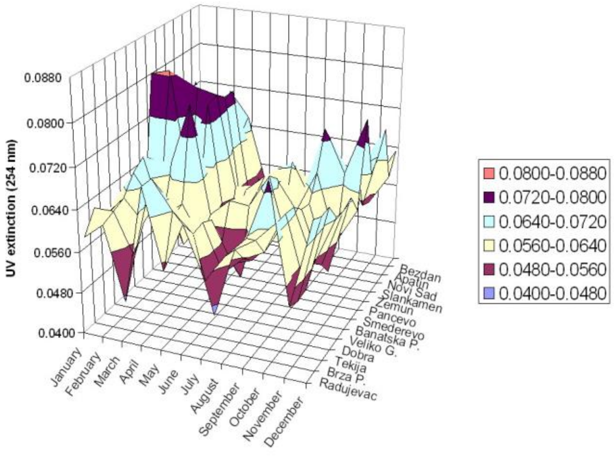

Fig. 15 Spatial and temporal seasonal changes of UV extinction on 254nm presented on the 3D chart

3.2.4 Third group parameters

Dissolved oxygen (DO): Dissolved oxygen seasonal temporal trends are very well described by the quadratic regression line (correlation coefficient square varying between 0.61 and 0.90, with 0.80 average). The maximal values occur between January and March (most often in February at 9 out of 13 locations), the minimal between June and October (most often in July and August in 4 and 6 locations out of 13, respectively). These results are strongly correlated: with temperature due to temperature differences between spring and summer since oxygen is more readily dissolved in colder water, and with algal growth responsible for the oxygen production and its elevated concentrations (Kraus-Miljević 1985).

Seasonal spatial trends were decreasing in April, June and August (statistically significant in April and August), and were slightly increasing in other months, but without statistical significance. When mutually compared, the regression slope coefficients display drop of values from December to August and monotonic growth from August to December (Figure 17). This indicates that DO decrease along the Danube River, from Bezdan to Radujevac is larger in summer than in winter (Figure 16). The biggest increase in temperature along the river stream described above, overlaps with the biggest spatial decrease of DO in spring and summer. However, a more thorough analysis of the organic matter decaying processes and air-water temperature relations is needed for a complete explanation of these results.

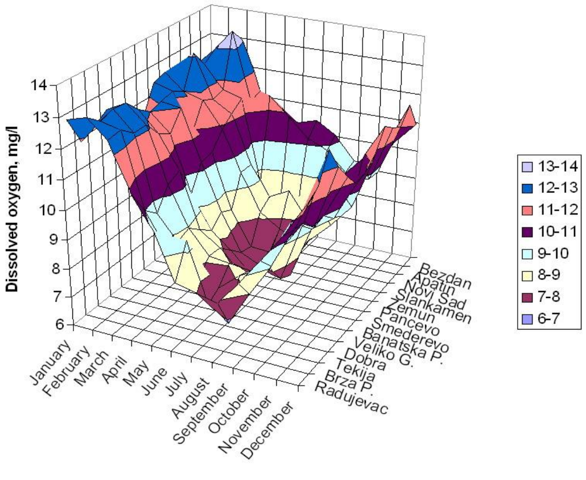

Fig. 16 Spatial and temporal seasonal changes of dissolved oxygen presented on the 3D chart

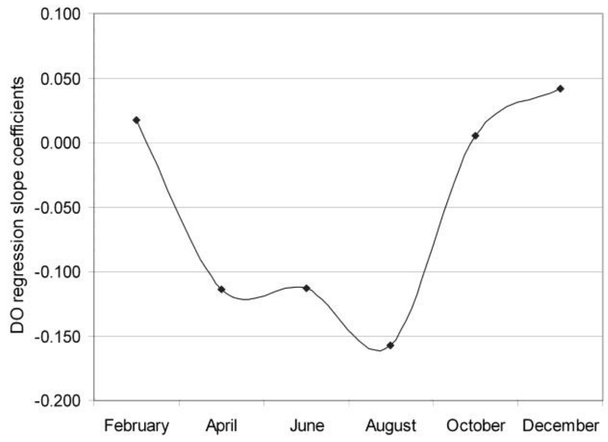

Fig. 17 Seasonal changes of spatial trend line slope coefficients for dissolved oxygen

Oxygen saturation: Seasonal temporal trends of oxygen saturation are well described by the quadratic regression line opened downwards on the first few locations: Bezdan, Apatin, Slankamen (correlation coefficient squares 0.77, 0.79 and 0.56 respectively) but the downstream correlation is diminishing and the regression line becomes close to linear (Figure 18). Maximal values most often occur between March and June, minimal between July and December. This lack of trend compared to dissolved oxygen comes from the fact that temperature and salinity do not affect the measured values of oxygen saturation directly since their influence is already calculated into maximal saturation constants. Therefore, the processes of oxygen production and consumption, whose influence compared to temperature is much harder to predict, dictate the trends of oxygen saturation (Kraus-Miljević 1985; Polic et al. 1994).

Seasonal spatial trends were decreasing in April, June and August (statistically significant in August), and increasing in other months, but without the statistical significance. These trends are the same as those of the dissolved oxygen. The regression slope coefficients display a drop of values from December to August and monotonic growth from August to December similar to the slopes for dissolved oxygen (Figure 19).

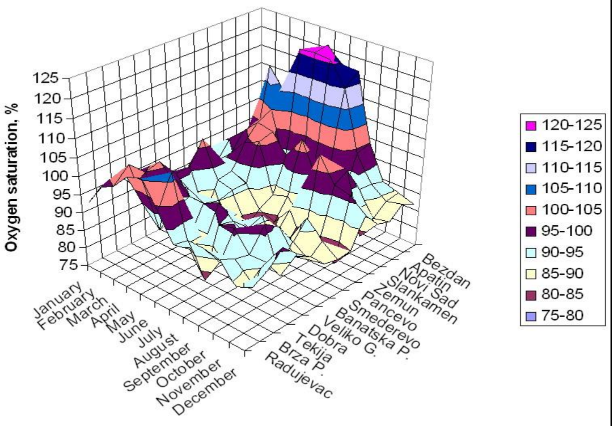

Fig. 18 Spatial and temporal seasonal changes of oxygen saturation presented on the 3D chart

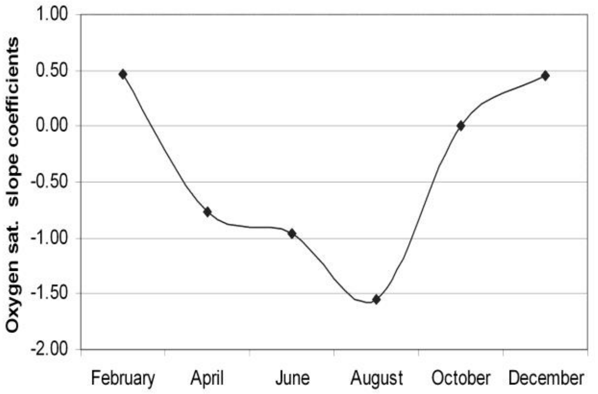

Fig. 19 Seasonal changes of spatial trend line slope coefficients for oxygen saturation

3.2.5 Fourth group parameters

pH: Seasonal temporal trends are well described by quadratic regression line opened downwards on the first few locations Bezdan, Apatin, Slankamen (with correlation coefficient squares 0.90, 0.58 and 0.52 respectively), but the downstream correlation is diminishing and regression line becomes close to linear (Figure 20). The occurrence of the maximal and minimal values is equally distributed through year, because pH values do not vary considerably (just a few tenths of pH units).

pH is affected by numerous factors, but based on available data we can suppose that the increase in summer at the upper stream sampling locations is influenced by photosynthesis, where phosphates and CO_2 are consumed (which causes pH elevation) in order to produce organic matter and oxygen (connected to BOD, COD and oxygen demand) (Liu et al. 2008; Kraus-Miljević, 1985). Positive correlation between pH and suspended matter might be related to the influence of the humic substances, whose wash off to the river might decrease its pH (Park et al. 2005) , but further investigations must be performed.

Seasonal spatial trends show statistically significant decrease from Bezdan to Radujevac in every analyzed month except in December. The regression slope coefficients display a drop of values from December to August and a monotonic growth from August to December.

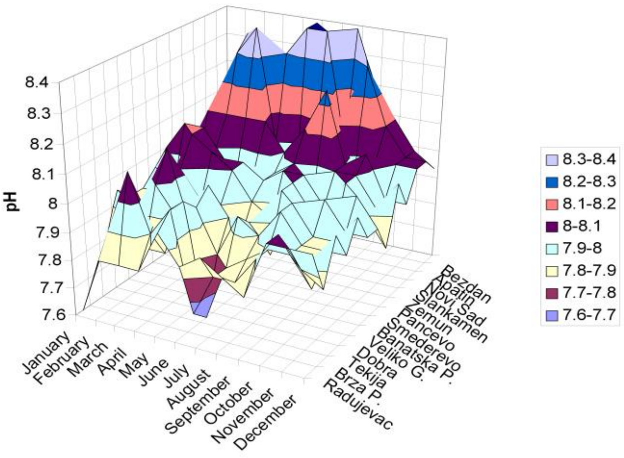

Fig. 20 Spatial and temporal seasonal changes of pH presented on the 3D chart

Nitrates: Monthly medians of nitrate concentrations were the largest in February and March (at 7 and 5 out of 13 locations, respectively), and minimal values were observed between June and August, most frequently in July (at 5 out of 13 locations) and August (also 5 out of 13 locations) (Figure 21). The trends followed quadratic functions opened upwards relatively well, with correlation coefficient squares varying between 0.47 and 0.87, average 0.74. The maximums in spring are the consequence of the fertilizer washout, and summer minimums appear due to the increased consumption of nutrients by the river algae. In autumn, a new cycle of field fertilizing begins and nitrate concentrations show steady growth until they reach their maximal values in spring.

Seasonal spatial trends decreased between October and April, and increased in June and August (trend was statistically significant in August, October and December). When mutually compared, the regression slope coefficients display monotonic drop of values from August to December and growth from December to August (Figure 22) showing pattern of trend changes.

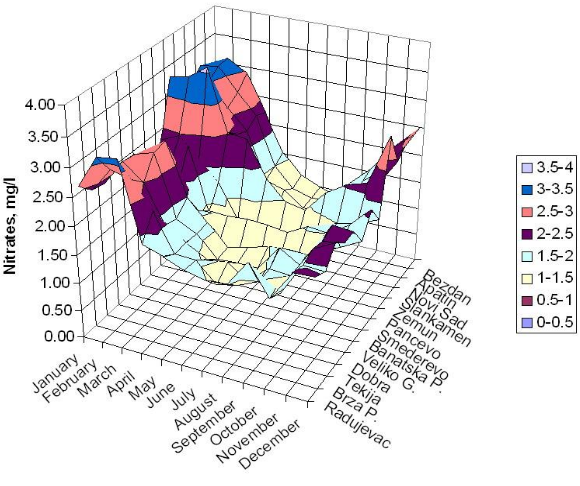

Fig. 21 Spatial and temporal seasonal changes of nitrates presented on the 3D chart

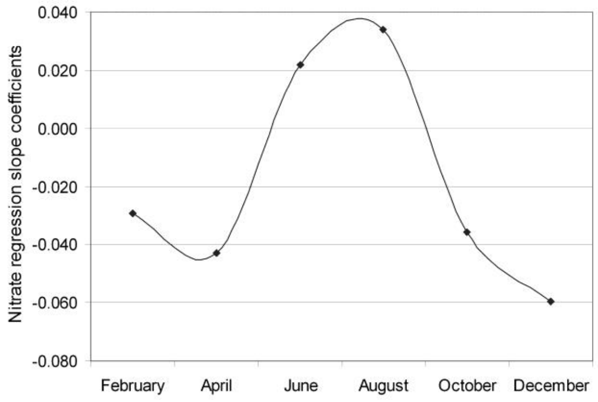

Fig. 22 Seasonal changes of spatial trend line slope coefficients for nitrates

Total N: The data for total N is lacking for some locations and years but the existing measurements show similar trends with changes of nitrate concentrations (Figure 23). Quadratic functions used to describe seasonal temporal trends among monthly medians are opened upwards with average correlation coefficient square of 0.60.

Seasonal temporal trends decrease for each month except June (trend is statistically significant in February and December). When mutually compared, the regression slope coefficients display a monotonic drop of values from June to December and growth from December to June (Figure 24) showing clear pattern of trend changes.

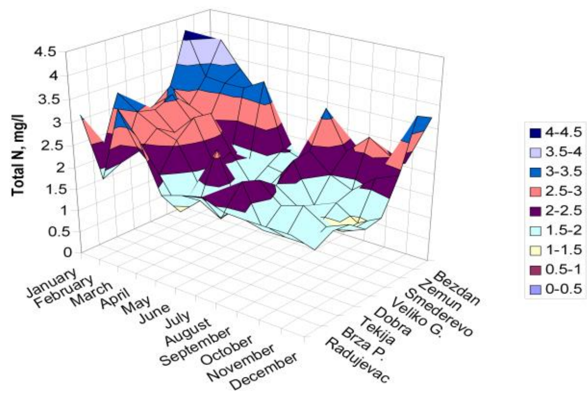

Fig. 23 Spatial and temporal seasonal changes of Total N presented on the 3D chart

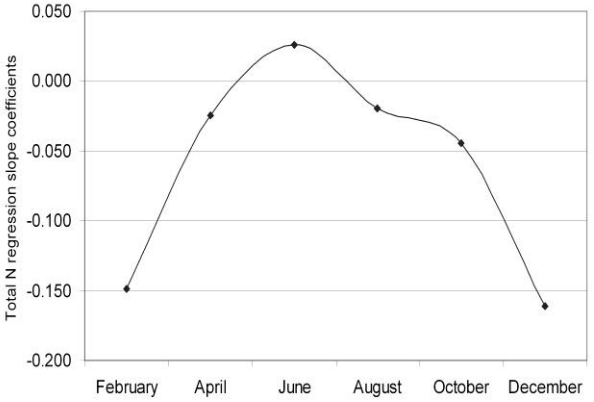

Fig. 24 Seasonal changes of spatial trend line slope coefficients for Total N

Total P: Seasonal temporal trends (for period 1992-2006) of total P monthly median values can not be well described with either linear or quadratic functions (whose correlation coefficient squares with one exception do not exceed 0.55, average 0.34). Minimal values most often come in April and May (in 5 and 4 out of 13 locations, respectively), maximal between January and March (Figure 25).

Seasonal spatial trends decreased from Bezdan to Radujevac in every month (statistically significant in February, June and December). There is no pattern of slope changes.

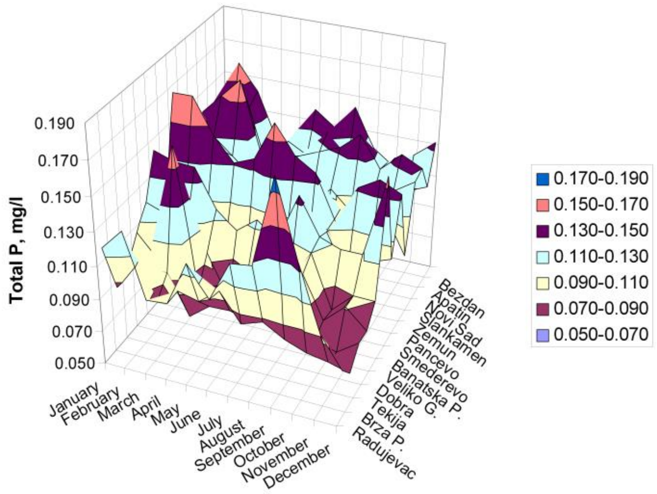

Fig 25 Spatial and temporal seasonal changes of Total P presented on the 3D chart

In this fourth, nutrient group, the behavior of some parameters like nitrates and total N shows seasonality (for pH this can be applied only in the upper stream), while seasonal temporal changes of total P cannot be described well with function used for other parameters.

Spatial trend slope coefficient for nitrates, total N and P are rather complex. The most negative values appear during colder periods of the year, but they increase and become more positive in summer months. Very good and acceptable explanation for that are the agricultural melioration campaigns (application of manure and fertilizers) in the autumn. The nutrients are partially washed to the river during winter, and at the same time their consumption by river vegetation is suppressed because of the low temperatures. This process is more intense in the upper stream regions with the intense agricultural activity, and results in decreasing spatial trends. Nevertheless, chemodynamics of these eco-chemical parameters is very complex since it involves processes of discharge into the river (equally important both from point and diffuse sources), uptake by river flora and fauna, dilution, volatilization, immobilization, mineralization and various transformations (like nitrification and denitrification etc).

3.3 Temporal trend correlations

We calculated correlations between temporal trends at every sampling site. Average correlation coefficients (for all sampling sites) are presented in Table 1. Eco-chemical parameters whose values change in similar fashion from January till December will be highly correlated. This does not necessarily mean that they are directly connected, because it is possible that they are both affected by the same factor (like temperature or water discharge) which governs their behavior.

Table 1 Average correlations of the temporal tends of analyzed eco-chemical parameters. Values given in bold are statistically significant at P = 0.05 level.

	Dry matter	SM	EC	Resid. on ign.	COD	BOD-5	UV ext. (254nm)	DO	Oxygen sat.	pH	Nitrates	Tot. P	t
Dry matter	1												
SM	0.04	1											
EC	**0.80**	0.02	1										
Residue on ignition	**0.70**	-0.08	**0.68**	1									
COD	-0.16	0.28	-0.08	-0.20	1								
BOD-5	-0.15	0.23	-0.06	-0.27	0.42	1							
UV ext. (254nm)	0.44	-0.01	0.42	0.38	-0.01	-0.06	1						
DO	**0.81**	0.19	**0.75**	**0.63**	0.05	0.06	0.44	1					
Oxygen sat.	0.11	0.39	0.02	0.01	0.31	0.41	0.05	0.26	1				
pH	0.00	0.27	-0.11	0.06	0.11	0.20	-0.08	0.06	0.45	1			
Nitrates	**0.86**	0.15	**0.81**	**0.64**	-0.06	-0.05	0.40	**0.89**	0.10	0.00	1		
Tot. P	0.37	-0.03	0.47	0.21	-0.06	0.09	0.15	0.37	0.11	0.06	0.41	1	
t	**-0.83**	-0.06	**-0.79**	**-0.69**	0.14	0.10	-0.44	**-0.92**	0.02	0.09	**-0.90**	-0.30	1

Seasonal temporal trends of dry matter, electrical conductivity and residue on ignition are highly positively correlated, which was expected because they all represent the river's load with dissolved inorganic substances. Negative correlation with temperature is related to the smaller amount of precipitation in colder winter months and more abundant precipitation in the summer, which cause dilution of inorganic species during summer time. High temperatures in summer also cause decline of dissolved oxygen, which is a reason why dry matter, electrical conductivity and residue on ignition positively correlate with dissolved oxygen. None of these parameters show any correlations with suspended matter which might indicate that they have different way of introduction into the river system. On the other side good correlation with nitrates, which also peak in the autumn and winter (probably as the consequence of increased fertilizer usage in autumn combined with decreased consumption and fixation by the vegetation in winter), suggests that seasonality of dry matter, electrical conductivity and residue on ignition might be under severe anthropogenic influence.

Average temporal trend correlations of suspended matter (SM), COD and BOD-5 with other eco-chemical parameters don't appear to be statistically significant (Table 1) but more detailed inspection showed that correlation coefficients at upstream locations can be substantial, than diminish in midsection of the river and at downstream locations totally change their sign (from - to + and vice versa) even becoming statistically significant again. Nevertheless, when average correlation coefficient for these positive and negative values is calculated, result is statistically insignificant value close to zero. Such behavior is expected because some parameters (like temperature, DO, EC, nitrates etc.) have pronounced temporal trends with similar shape at all sampling locations (regardless of location position along the river), while other parameters (like SM, COD, BOD-5 etc.) behave differently in upper section of the river compared to the lower section.

Ambivalent tendencies of these correlations can be illustrated with the examples of COD and BOD-5. Correlations of COD with: electrical conductivity (min r = -0.54, max r = 0.55), residue on ignition (min r = -0.64, max r = 0.43), dry matter (min r = -0.55, max r = 0.50), phosphates (min r = -0.90, max r = 0.30), nitrates (min r = -0.53, max r = 0.66) and dissolved oxygen (min r = -0.38, max r = 0.72) are negative in the upstream part of the river and become positive at the sampling sites located downstream (values in brackets stand for correlation coefficients observed at the sampling sites with maximal and minimal correlations). The opposite tendencies are observed for correlations of COD with: discharge (max r = 0.53, min r = -0.47), pH (max r = 0.85, min r = -0.85), oxygen saturation (max r = 0.89, min r = -0.20) and BOD-5 (max r = 0.90, min r = -0.06). In both groups the reversal of r values happens at the locations in the middle stream of the Danube between Zemun and Veliko Gradište. This is the part of the river where the biggest tributaries (Tisza, Sava, Velika Morava) flow into the Danube, Belgrade discharges its untreated communal waters, where influence of the Iron Gate Dame becomes observable and after which the Danube River leaves the Pannonian Plain (with intense agricultural and food industry activity, also densely populated) and flows into the Iron Gate Gorge.

When correlations of BOD-5 and other eco-chemical parameters are investigated, the results obtained are similar to those of the COD. Correlations with el. conductivity (min r = -0.72, max r = 0.50), residue on ignition (min r = -0.76, max r = 0.25), dry matter (min r = -0.75, max r = 0.46), phosphates (min r = -0.88, max r = 0.36) and nitrates (min r = -0.62, max r = 0.38) are negative in the upstream part of the river and become positive at sampling sites located downstream (values in brackets stand for correlation coefficients observed at sampling sites with maximal and minimal correlations). The opposite tendencies are observed for discharge (max r = 0.74, min r = -0.56), suspended matter (max r = 0.73, min r = -0.73), pH (max r = 0.95, min r = -0.77), oxygen saturation (max r = 0.93, min r = -0.30) and COD (max r = 0.90, min r = -0.07). The same as for COD, reversal of r values happens at locations in the middle stream of the Danube, but little bit more upstream, between Slankamen and Smederevo. In the lower part of the river, the parameters tend to be less correlated which is attributed to the various influences of tributaries, point pollution sources (cities, industry etc.), different input of diffuse sources etc.

Based on the very strong (positive or negative) correlations of BOD-5 with COD, nutrient and oxygen parameters, in the upper stream, it can be suspected that algal blooms and runoff of organic matter and nutrients from agricultural land has the strongest influence on the obtained results. A decrease of nitrates and phosphates in water overlaps with increase of COD, BOD-5 and oxygen saturation, which means that the nutrients were consumed in order to produce organic matter which saturated water with oxygen due to photosynthesis. The side effect of this process - the increase of pH due to CO_2 consumption (Liu et al. 2008; Kraus-Miljević 1985), was also confirmed by very high positive correlation of BOD-5 with pH.

In the upper stream very good statistically significant correlation (correlation coefficients range between locations with min. and max. value is specified in brackets) exists between temporal trends of pH and oxygen saturation (from 0.67 to 0.93), COD (from 0.55 to 0.85), BOD (from 0.61 to 0.95) and phosphates (from -0.33 to -0.91). None of these correlations extends to downstream sampling sites, and that suggests that pH variations are connected with pollution related to agriculture and organic waste.

It is interesting to notice that average correlation coefficient for all 13 locations for BOD-5 and oxygen saturation is 0.41 while for BOD-5 and dissolved oxygen amounts only to 0.06. The dissolved oxygen is much more influenced by temperature and salinity, while oxygen saturation does not rely on these variables because they are already calculated in maximal oxygen dissolubility in water. Oxygen saturation depends just on the sources which produce and consume oxygen in the water, therefore it is expected that it is going to be positively correlated with abundance of organic matter and elevation of BOD-5 values.

Poor correlation of DO with oxygen saturation (av. $r = 0.26$) is not surprising, because temperature has a major negative influence on DO (av. $r = -0.92$), but not on oxygen saturation (av. $r = 0.02$) because high temperatures also contribute to algal growth, one of the key factors for oxygen saturation (Kraus-Miljević 1985).

The temporal changes of the UV extinction monthly medians are not well correlated with the changes of other eco-chemical parameters when average correlation coefficients are observed, but in the upstream section of the river electrical conductivity, residue on ignition, dry matter, nitrates and dissolved oxygen are positively and statistically significantly correlated with UV extinction.

3.4 Characteristic patterns of spatial trends

A characteristic spatial pattern was recognized in the case of certain eco-chemical parameters. Each month the values were below average in Zemun and Smederevo and above average in Pančevo and Banatska Palanka (the pattern could be summarized as sequence Slankamen-Zemun-Pančevo-Smederevo-Banatska Palanka = local max - min - max - min - max). These phenomena were observed for suspended matter, COD, BOD-5 and total P.

Usually, the most distinguished were the peaks which appear at Pančevo, the first sampling station after Belgrade. Sand and gravel depot, located at the river banks of Belgrade, might increase suspended matter concentrations measured at Pančevo. The largest Danube tributaries probably contribute more to this pattern by causing turbulences of Danube water at their confluences, then by their suspended matter load, since average concentrations of tributary suspended matter are lower (except for Tisza) than those measured at Danube sampling sites situated before and after tributary confluences.

Elevation of COD and total P values could also be attributed (among other sources) to the pollution coming from Belgrade, since Belgrade does not have a system for municipal water treatment. In the case of BOD-5 this pattern is not so apparent, although it is recognized during some months. Nevertheless, the elevation of BOD-5 between Zemun and Pančevo occurs in each analyzed month.

4. Conclusion

The chosen procedure, which was based on usage of monthly medians, is clearly capable of detecting the spatial and temporal trends of the selected eco-chemical parameters. Considerable seasonal variations of some parameters were determined as well as variations of spatial trends. Slopes of spatial trend lines can seriously vary in different parts of the year or even change from negative to positive and vice versa. The trend lines were derived from data sets of monthly medians and correlations among these medians for different eco-chemical parameters were calculated. These correlations help to reveal mutual influences of investigated parameters to their behavior and trends. Quadratic function was able to describe temporal trends, while linear regression analysis, with the defined significance level of 95%, was used for seasonal spatial trends.

The quadratic function proved to be capable to describe trends of parameters that show maximal values in summer and minimal in winter, or vice versa. Logarithmic, power, and exponential functions were excluded from consideration for the same reasons as linear function, being inappropriate to describe parameters which regularly increase in one part of the year and decrease in other.

Shape of the quadratic function (whether it has a maximum or minimum), the square of the Pearson correlation coefficient (r^2) and the occurrence of extremes during a particular period of the year were analyzed. It has been noticed that, as one moves from one sampling station to the next, the value of squared Pearson correlation coefficients might change considerably, even shape of fitted function might reverse, so that it opens upwards instead of downwards and vice versa. Consequently, it can be assumed that the natural process of seasonal changes might be disturbed by the influence of new pollution sources (with different seasonal patterns, if any) appearing downstream, the dilution (or increase) of pollution by tributaries and other sources of less (or more) polluted water, or by changes of the river characteristics, affecting its potential for self-purification.

Table 2 Seasonal temporal trends of investigated eco-chemical parameters. The shape of quadratic function and average Pearson correlation square for all 13 sampling sites are presented, as well as locations with the best and worst fitted trend lines, correlation coefficient square of mentioned trend line and ordinal number of location.

Parameter	Shape of quadratic function	Location with best and worst correlation coef. square						Av. correl. coef. square
		No.	Name	r^2	No.	Name	r^2	
Dry matter	Opened upward	13	Radujevac	0.106	3	Novi Sad	0.899	0.667
Suspended matter	Op. down. to up. [a]	8	Banatska Palanka	0.002	1	Bezdan	0.747	0.364
Electrical conductivity	Opened upward	5	Zemun	0.353	4	Slankamen	0.951	0.659
Residue on ignition	Opened upward	9	Veliko Gradiste	0.167	3	Novi Sad	0.832	0.511
COD	Op. down. to upward [a]	9	Veliko Gradiste	0.033	2	Apatin	0.777	0.445
BOD-5	Op. down. to linear [c]	5	Zemun	0.157	1	Bezdan	0.847	0.405
UV extinction (254nm)	Op. up to linear [b]	8	Banatska Palanka	0.049	2	Apatin	0.612	0.268
Dissolved oxygen	Opened upward	2	Apatin	0.607	6	Pančevo	0.905	0.795
Oxygen saturation	Op. down to linear [c]	8	Banatska Palanka	0.110	2	Apatin	0.782	0.358
pH	Op. down to linear [c]	12	Brza Palanka	0.003	1	Bezdan	0.896	0.299
Nitrates	Opened upward	9	Veliko Gradiste	0.466	2	Apatin	0.866	0.738
Total P	-	1	Radujevac	0.100	4	Slankamen	0.550	0.346

[a] At sampling sites located upstream, trend line is quadratic function opened downward while in downstream it becomes opened upward

[b] At sampling sites located upstream, trend line is quadratic function opened upward while downstream it becomes more similar to linear function

[c] At sampling sites located upstream, trend line is quadratic function opened downward while downstream it becomes more similar to linear function

Investigation of the eco-chemical parameters based on yearly medians for the period from 1992 to 2006, gave a very clear picture of the improvement in the river water quality from Bezdan to Radujevac (Živadinović et al. 2010). The fact that improvement of the Danube River water is strongly influenced by seasonal changes needed additional investigations that are summarized tables 2 and 3.

Table 3 Seasonal spatial trends of investigated eco-chemical parameters. Number of all positive, statistically significant positive, all negative, statistically significant negative with their average Pearson correlation coefficient squares is presented

Parameter [a]	No. of positive trends	Average Pearson correlation coefficient square.	No. of stat. signif. positive trends	Average Pearson correlation coefficient square.	No. of negative trends	Average Parsons correlation coefficient square.	No. of stat. signif. negative trends	Average Parsons correlation coefficient square.	Overall trend estimation [b]
Temperature	6	0.447	4	0.614	0	0.000	0	0.000	Positive trend
Dry matter	0	0.000	0	0.000	6	0.265	2	0.668	Negative trend
Suspended matter	0	0.000	0	0.000	6	0.503	4	0.660	Negative trend
Electrical conductivity	2	0.618	2	0.618	4	0.304	2	0.563	Ambivalent
Residue on ignition	4	0.082	0	0.000	2	0.039	0	0.000	No trend
COD	0	0.000	0	0.000	6	0.447	4	0.581	Negative trend
BOD-5	1	0.014	0	0.000	5	0.449	4	0.496	Negative trend
UV extinction (254nm)	4	0.239	2	0.462	2	0.032	0	0.000	Inconclusive
Dissolved oxygen	3	0.044	0	0.000	3	0.320	2	0.408	Ambivalent
Oxygen saturation	3	0.199	0	0.000	3	0.195	1	0.310	Ambivalent
pH	0	0.000	0	0.000	6	0.480	5	0.574	Negative trend
Nitrates	2	0.247	1	0.370	4	0.286	2	0.418	Ambivalent
Total P	0	0.000	0	0.000	6	0.327	3	0.421	Negative trend
Total N	1	0.079	0	0.000	5	0.344	2	0.740	Negative trend

[a] trends were calculated for every second month in the year so maximal number of positive or negative seasonal trends for one parameter is 6

[b] overall trend was described as “ambivalent” when different tendencies are observed in opposite seasons of the year, “inconclusive” was used when there was no obvious pattern in slope coefficient changes between opposite seasonal trends (among which some were statistically significant).

In the conclusion we would like to sum up all the particular conclusions drawn on the basis of temporal and spatial trend analysis:

Hydrological parameters: Discharge is the largest in April and least in October. It is more than 2 times greater at the outflow than at the inflow location. The spatial increase of water temperature is most significant in spring and summer, between April and August.

First group parameters: Data analysis of the first group parameters gives a very clear picture that the river water quality improves from Bezdan to Radujevac. Dry matter and suspended matter have clear negative spatial trends. Residue on ignition has no spatial trend and the electrical conductivity trends are ambivalent. Temporal changes of the river discharge during year affect suspended matter and electrical conductivity spatial trends. Rate of suspended matter decrease along the stream is mainly controlled by concentrations at the inflow point. Spatial trends of electrical conductivity are influenced by the Danube’s tributaries.

All parameters are influenced by different seasons; they show differences between winter months, among which the maximum is achieved, and summer months when they always reach their minimum. The exception is suspended matter whose temporal changes do not follow the same pattern in the upper part of the river as in the lower part, but characteristic maximums in spring are observed along the whole river. Higher values of dry matter, residue on ignition and electric conductivity in winter months are related to lower water flow (Figure 4) and smaller precipitation. As soon as melting of snow and ice begins and precipitation increases, dilution process starts, the relative amount of water increases while the content of dissolved species decreases which is very well described by parameters like dry mater and residue on ignition.

Second group parameters in general show the improvement of the eco-chemical status of The Danube from Bezdan to Radujevac, observed in the period of 1992 to 2006. Data for COD and BOD-5 parameters are influenced by different seasons; they show differences between winter months, among which the minimum is achieved, and summer months when they reach the maximum values. It is interesting that in the middle section of the river, the shape of the temporal trend line changes completely (as for COD when quadratic function becomes opened upward instead downward) or becomes close to linear. This phenomenon is followed by reversal of correlations between COD and BOD-5 temporal trends with electrical conductivity, residue on ignition, dry matter, phosphates, nitrates, dissolved oxygen, discharge, pH and oxygen saturation. Also, COD and BOD-5 correlations change from very good and positive in the upper stream to close to zero at the locations in the lower stream.

Positive correlations of BOD-5 with oxygen saturation and pH, and negative with nitrates and phosphates suggest that photosynthetic processes are of great importance for describing relations between these parameters.

Although COD and BOD-5 appear to have negative spatial trends in all seasons, rate of the river self-purification is the biggest in April and June. Rate of self-purification (observed as spatial trend slope coefficient) is more dependent on COD values measured in the upper stream locations which also show greater variability of COD values.

Pollution coming from Belgrade appears to be responsible for COD and BOD-5 increase at Pančevo sampling site.

Third group parameters are very informative and they are influenced by different seasons. Data for dissolved oxygen behave as expected: lower temperatures in winter months induce a higher oxygen content, and in summer oxygen content becomes lower. But oxygen saturation in the upper stream shows just the opposite; during cold months when algal activity is low, oxygen saturation is low, whereas in summer when algae bloom, the saturation is high.

Behavior of oxygen parameters along the river course is ambivalent, because in both spring and summer, DO and oxygen saturation, show decreasing spatial trend (often statistically significant) while in colder months their values stagnate or increase along the river course.

Temporal trends of DO and oxygen saturation are very weakly correlated because the increase of water temperature has negative influence to DO concentrations due to less solubility of oxygen during considerably higher temperatures in summer, while temperature increase might also affect positively oxygen saturation, because of increased oxygen production by river plants. On the other side when DO and oxygen saturation seasonal spatial trends were analyzed, excellent correlation (av. $r = 0.91$) between them was observed, meaning that when temperature does not oscillate a lot (as it is the case when it is measured during the same month along the river course), oxygen production and consumption processes dictate spatial distribution of oxygen parameters values (although, some weak negative correlation was observed in summer between slight spatial temperature increase and DO decrease).

Fourth group parameters show that seasonal changes of pH are not significant on the entire water stream, but the decrease of pH from Bezdan to Radujevac is obvious. Total P and total N also show very clear fall of concentrations from Bezdan to Radujevac, but spatial trend of nitrates oscillate between positive values in summer and negative in winter.

Concentration of nitrates and total N show minimum in summer months, which corresponds to the pH, COD and BOD-5 maximum in the upper stream. These temporal variations of nutrients are related to increased runoff from agricultural fields along with increased precipitation in winter and spring, and increased consumption by living organisms from spring to summer. Excellent temporal trend correlation of nitrates and DO does not have to mean that there is direct link between them because of negligible correlation with oxygen saturation and good negative correlation with temperature.

As a final remark we can conclude that when analyzed spatially, parameters that affect the Danube River water quality, either improve or stagnate with the exception of el. conductivity, nitrates, DO and oxygen saturation in summer months. Temporal trends of the most of investigated parameters show pronounced seasonality, especially in the upper stream.

When analyzed spatially, the status of eco-chemical parameters either improved or stagnated, but for none of them deteriorated. Spatial trends were detected notwithstanding complexity of Danube's eco-chemical dynamics, which comes from various influence of: tributaries, dams, various pollution sources, substance transformations, deposition, dilution, changes of river hydrology etc. It was noticed that in the case of some parameters, self-purification potential of the river, varied significantly depending on the season.

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