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Long-term changes in the eco-chemical status of the Danube River in the region of Serbia

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Abstract: The Danube River is an international river, one part of which flows through Serbia. The eco-chemical status of the Danube River is a constant topic of interest both at the local level, in each country through which the Danube flows, and at the international level. General interest to ensure the sustainable and equitable use of waters and freshwater resources in the Danube River Basin led to the development of a system for monitoring the river, which has produced data sets of its eco-chemical status. These have been collected over many years in Serbia; however, the present interest was focused only on the period from 1992 until 2006, *i.e.*, a 15-year period. The process of defining trends of selected eco-chemical parameters, using linear regression analysis with a defined level of significance, and their separation from natural variability is of the highest importance for defining the changes in the water parameters. Through them, the fate and behavior of the eco-chemical parameters of the Danube in Serbia can be recognized and the prediction of their trends in the near future can be attempted. The obtained results revealed a constant improvement and acceptable trends of the eco-chemical status of the Danube River, as well as, substantial differences in the quality of the inflowing and out flowing water.

Keywords: Danube River; long-term spatial and temporal trends; self-purification; linear regression.

INTRODUCTION

The Danube River is 2783 km long and has a basin of 817000 km^2. Around 10 % of its length belongs to the territory of Serbia, through which the Danube runs 587.4 km. It enters into Serbia from the north, from Hungary (1425.5 km away from the sea), and outflows to the east, right on the border between Serbia,

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Romania and Bulgaria (825 km away from the sea). The Serbian part of Danube belongs to the middle section of the river, from the Devín Gate (at the border of Slovakia and Austria) to the Iron Gate (at the border of Serbia and Romania), where the riverbed widens and the average bottom gradient is 0.6×10^{-4} %.[1] The average water volume of the Danube on entering Serbia is 2400 $m^3 s^{-1}$ and 5500 $m^3 s^{-1}$ on leaving the country.[1]

The Serbian Danube can be divided into an upper and a lower section (Fig. 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, is strongly influenced by the Iron Gates I and II dam complex (943 km and 863.4 km, respectively), which are located in the border area of Romania and Serbia. The dams cause slowdown of the flow velocity which can be observed at the confluence of the Nera River (Romania) or at the end of Danube–Tisza–Danube (DTD) canal near Banatska Palanka (Serbia) during high water level. During low water level, the slowdown of flow velocity becomes observable at the village Surduk (Serbia) 37 km upstream of Belgrade, but the confluences of the big Danube tributaries (Tisza, Tamis, Sava and Velika Morava) can also be affected.[2]

The biggest Danube tributaries with confluences in the territory of Serbia are the Tisza, the Tamiš and the DTD canal on the left side, and Drava, Sava and Velika Morava on the right side.

Two large 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 and Kladovo) and villages (small settlements with less than 10,000 inhabitants contribute 48 % to the Serbian population). None of them have a system for treating municipal waste waters.[3]

The eco-chemical status of the Danube River is a topic of constant interest both on the local level, in each country thought which the Danube flows, and on the international level through organizations such as the International Commission for the Protection of the Danube River (ICPDR).[1] Their main interest is to ensure sustainable and equitable use of the waters and freshwater resources in the Danube River Basin. Protection of the River is strongly supported by data of its eco-chemical status that have been collected over many years in Serbia. After validation of the available records, it was decided to process 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. They are useful only over a range of time scales; therefore eco-chemical dynamics may only be fully investigated when long-term time-series data are available.

The goal of this work was to investigate long-term changes of the eco-chemical status of the Danube River in relation to pollution changes during previous years and to identify seasonal fluctuations, averaged during the investigation period, which could reveal some regularities of the Danube pollution over time. Particular attention was paid to determine the average trends over time with the aim to forecast the behavior of pollutants under different conditions or in the near future.

The Danube River is constantly the focus of various environmental studies. The most considered topics were pollution with: metals in the water[4–7] and sediments, [8–11] nutrients,[12–17] radioisotopes,[18–20] oil,[21] *etc*. There are many studies dealing with the general pollution status of the river, hence covering more than one group of pollutants[22–25] and also from a regulatory point of view.[26]

EXPERIMENTAL

Materials and methods

The main sampling material for the measurement was the river water sampled and analyzed according to APHA (1976–1992)[27] and US EPA standard methods (1983).[28] The measured parameters (the corresponding methods are given in brackets) important for the determination of the eco-chemical status of the Danube River were:

– suspended matter (13.060.30 JUS H.Z1. 160);[29]
– nitrates (NO_3-N) (APHA AWWA WEF 4500-NO3);[30]
– total nitrogen (N) (JUS ISO 5663);[31]
– total phosphorus (P) (APHA AWWA WEF 4500-P);[32]
– Biological oxygen demand for 5 days (BOD-5) (EPA 360.2);[33]
– Chemical oxygen demand (COD) (JUS ISO 8467, ISO 8467).[34]

Analysis of blanks and duplicates were the main instruments of quality assurance/quality control (QA/QC) during measurement throughout the years.

Regular monthly measurements were performed every year for a period of 15 years (1992–2006).

Surface water samples were taken as they were assumed representative for the entire water stream, while the water was always well mixed. Sampling was performed 40 cm below the water surface from the water-front area, in order to prevent contamination of the sample with mud from the bottom or floating particles from the water surface. The samples were collected in 5-L plastic jerry cans.

The temperatures and pH of the water samples were determined on site. Samples for the determination of dissolved oxygen concentrations were collected and treated separately. All samples were stored at 4 °C and normally analyzed within one day. The maximum storage time was less than 2 days after sampling.

Sampling locations

Seventeen sampling stations are located on the Serbian part of the Danube River (Fig. 1), of which four were excluded from consideration because the data they provided was insufficient for the present investigations, due to a too short an operation time (just a few years). Data from 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, sampling was performed one to two times per month.

List of the sampling stations:

1. Bezdan – Hungarian border (inflow of the Danube River into Serbia),

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

Fig. 1. Location of the sampling stations on the Serbian part of the Danube River.

RESULTS

The process of defining trends and their extrication from natural variability is of highest importance for defining how environmental parameters change and thereby recognizing the fate and behavior of the environment in the near future.

Regression analysis was employed for determining whether a trend over time was, on average, linear. Based upon these results, it was possible to describe the direction of a trend (a negative or positive slope), while the quality of linear regression lines of the trend could be described by the Pearson's coefficient of determination (R^2). This is useful because it gives the proportion of the variance of one variable that is predictable from the others.[35,36]

Selected parameters for the present investigations were, in principle, sum/ /collective parameters which covered several inorganic or organic species. These sum/collective parameters were divided into four groups:

1. Suspended matter and dissolved species (dry matter, residue after ignition and conductivity). These parameters describe, in general, how much the river water is burdened with inorganic and organic matter together, while the conductivity describes the amount of ionic species present in the water;
2. UV Absorption at 254 nm, COD and BOD. These parameters generally cover dissolved organic matter and the biological activity in the river water;
3. Oxygen concentration and oxygen saturation. The oxygen parameters are essential to all aquatic life, which maintains a healthy river water environment;
4. The pH, total P, total N, NO_3, and N/P ratio. Nutrients, such as nitrogen and phosphorus, occur naturally in water but very often they are the main causes of pollution of rivers when their concentration levels are elevated.

In addition to these group parameters, there are numerous single parameters that were, however, not the subject of this work since each of them could be a separate topic of investigation.

The eco-chemical status of the Danube River, as an international river, is best described through discussions of the available results from two different aspects:

– trends of the measured parameters during time – investigation of long term changes for the 1992–2006 period and

– trends of the measured parameters in space – investigation of long term changes from place to place from the inflow to outflow points in Serbia.

Trends of the measured parameters in time and in space

Numerous studies in which the spatial and temporal trends of the water quality parameters of the Danube River were analyzed, have been performed in recent years,[13,37] many of them with the goal of predicting their values in future,[38,39] or improving the theoretical models for their understanding.[40–42]

However, the present study is specific as it deals with the largest quantity of data covering the broadest range of water quality parameters for the Danube that has ever been accumulated. It applies median values for data reduction instead of arithmetic or geometric means, which enables the use well-known parametric tests for trend detection. Therefore, one more aspect of investigations of the Danube River is herewith revealed.

The source data sets each 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 the present investigation. Hence, each number used in this work corresponds to a yearly median value. Medians were assumed to be sufficient and very useful for the purposes of this study as they are values that do not reflect individual outliers which are sometimes present in large data sets.[35,36]

To estimate the quality of the regression/fitness of the curves, the square of the Pearson's correlation coefficient, R^2, was used. However, the value of R^2 gives no information as to whether a correlation is significant or not. Thus, for this purpose, a parametric method for calculating *t* values was used. The *t* value was calculated using the formula:

$$t = \frac{R\sqrt{n-2}}{\sqrt{1-R^2}} \tag{1}$$

where *R* is the correlation coefficient and *n* is number of observations.

The *t* value was calculated using a two-sided *t*-test and then compared with the tabulated value[43] at the desired level of significance and (*n*–2) degrees of freedom. The null hypothesis that there is no significant correlation between the *x* and *y* coordinates in the charts (and therefore no significant trend) was rejected if the calculated *t* value was greater than the tabulated value at the desired significance level. A 95 % significance level ($\alpha = 0.05$) was used. The coefficients *R*, and therefore *t*, are influenced by the slope of the regression line and by the size of the residuals, because the more the points are scattered from the regression line, the worse the correlation coefficient is.[35,37,44]

Long term changes in the Danube River parameters were recognized in time and space. These changes can be well-presented in 3D (3 dimensions) surface charts with continuous curves, which are very convenient for quick visual estimation of trends, in addition to statistical analysis. The horizontal *x* and *y* axes present time (years from 1992 until 2006) and space (sampling locations from Bezdan to Radujevac). The vertical *z* axis shows the yearly median values.

To determine whether there was a temporal trend, the change between median yearly values at each single location was observed for the period from 1992 until 2006.

To determine whether there was a spatial trend, the change of median yearly values between sampling locations was observed for every year from 1992 until 2006.

First group of parameters (Fig. 2)

Suspended matter (Fig. 2a). Temporal trends for change of median yearly values between 1992 and 2006 observed for each sampling station (from Bezdan to Radujevac) had positive slope for 8 locations and negative ones for 5; the average slope was positive but significant trends were observed only at Slankamen, Radujevac (negative trends) and Smederevo (positive trend). Therefore, no clear tendency for changes in the amount of suspended matter over the years could be estimated.

Spatial trends for the change of median yearly values between sampling locations observed for each year from 1992 until 2006 had negative slope for every year and all of them were statistically significant, except for years 1993 and 2005 (which also had negative slope but their *t*-value vas less than the critical value). A decreasing tendency of the amount of suspended matter from Bezdan toward Radujevac was evident.

Dry matter (Fig. 2b). The temporal trends for the change of the median yearly values for the period from year 1992 until 2004 observed for each sampling station (from Bezdan to Radujevac) had positive slopes for only 2 locations (but not statistically significant) and negative for 11. The average slope was negative, but statistically significant negative trends were observed only for 2 locations (Smederevo and Dobra), and 2 more had *t*-values close to the critical value. On the other hand, 11 of 13 locations showed negative trends which statistically had a very low probability ($P < 0.05$); therefore, a negative trend for dry matter over the years was observed.

The dry matter concentrations are well correlated with conductivity and ignition residual. The correlation coefficients for dry matter/ conductivity correlation were positive for all 13 sampling locations and statistically significant for 5 of them (average $R = 0.42$) and for dry matter/ignited residual correlation, the coefficients were positive at 11 and statistically significant at 6 sampling locations (average $R = 0.37$). It is interesting that the dry matter and ignition residual were much better correlated at the first 5 sampling locations (from Bezdan to Zemun with the average R being 0.76) than at other sampling locations downstream from Zemun.

The spatial trends for the change of median yearly values from place to place observed for each year from 1992 until 2004 (without 1993) had negative values in 10 years out of 12; the average slope was also negative. The slope was significant for 4 negative trends (years 1994, 2002, 2003 and 2004) while two positive slopes (for years 1992 and 2000) had *t*-values less then critical. It can be concluded that the dry matter content decreases from Bezdan toward Radujevac.

Conductivity (Fig. 2c). The temporal trends for the change of median yearly values for the period 1992 until 2006 were observed for each sampling station (from Bezdan to Radujevac). The slope was negative for 12 locations

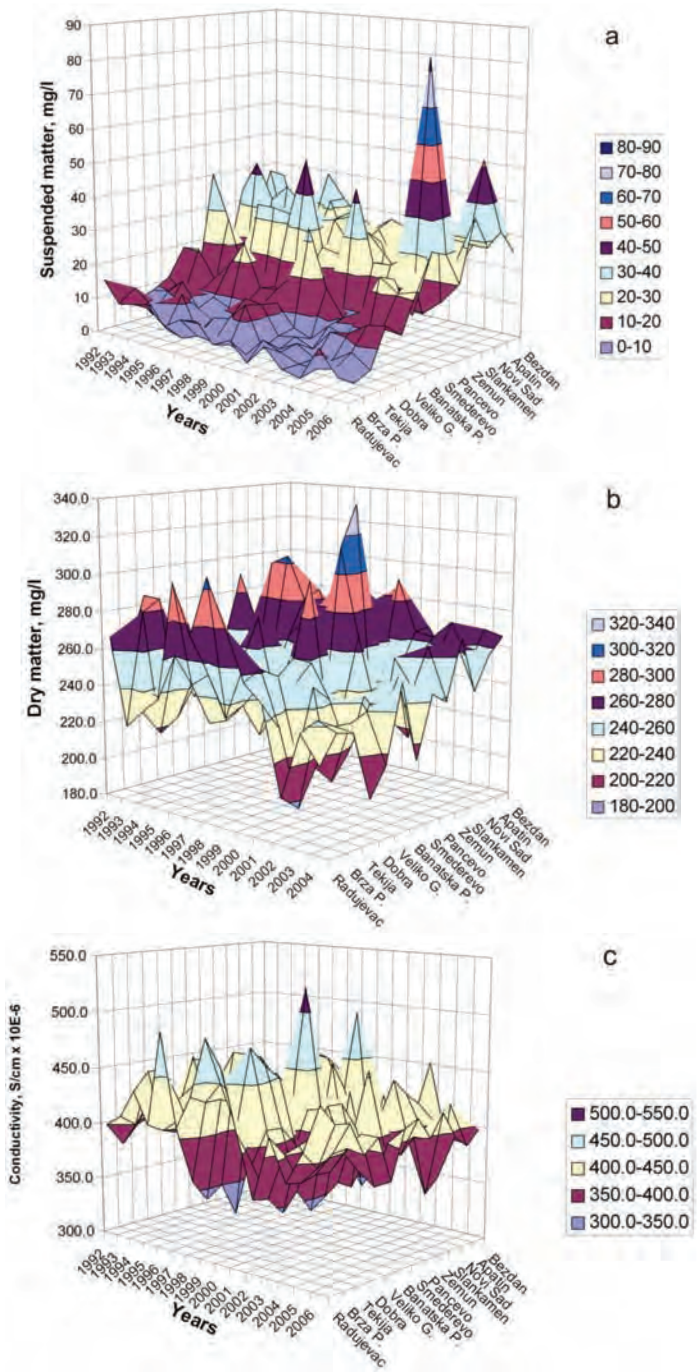

Fig. 2. Temporal and spatial trends of the amount of a) suspended matter, b) dry matter and c) conductivity.

and positive just for one; the average slope was negative but a significant trend was observed only at Zemun. Although a statistically significant negative trend was observed at only one place, a decreasing trend through the years was evident, based on the fact that the slope was negative at 12 out of 13 locations, which is statistically highly unexpected.

The spatial trends for the change of the median yearly values from place to place observed for each year from 1992 until 2006 had negative slopes for 6 years (3 of them statistically significant, 1997, 2002, 2003) and positive slopes for 9 years (4 of them statistically significant 1994, 1998, 2000, 2006). The average slope was slightly positive, but based on an even distribution of statistically significant trends, an unambiguous conclusion about increasing or decreasing of conductivity from Bezdan to Radujevac cannot be drawn.

Generally speaking, suspended mater, dry mater and conductivity are very much dependant on hydrological conditions, such as flow rate and water level, or current seasonal conditions, such as rainy or dry periods.[45] The decrease in the flow rate that is present in the Danube River in Serbia, particularly in the region of the artificial lake before Iron Gate,[8,46] favors a tendency of decreasing suspended matter in the river water from Bezdan toward Radujevac.

Second group of parameters

The surrogate parameters characteristic for organic matter, COD, BOD and UV absorption at 254 nm, are very well correlated. COD and BOD showed negative trends with time (from 1992 until 2006) and in space (from Bezdan to Radujevac) (Fig. 3). The absorbance at 254 nm has long been an acknowledged parameter for the description of organic carbon compounds (aromatics, phenolics, hydrocarbons, and most chromophores) in water analysis (DIN38404). However, the choice of this wavelength was made, above all, for historical rather than analytical reasons. In most cases, organic matter generates the strongest signal at other wavelengths.

As for the first group, the second group of parameters was also investigated through time and space. The same principles for trend analysis were applied.

COD. The temporal trends for the change of median yearly values for the period from 1992 until 2006 observed for all sampling stations (from Bezdan to Radujevac) had negative slope for 12 out of 13 locations; the average slope was also negative and statistically significant trends were observed at Bezdan, Slankamen and Banatska Palanka. Only one positive (and simultaneously statistically significant) trend was observed at the Zemun sampling location. Therefore, it can be concluded that the summary trend for COD decreased over the years.

The COD values were well correlated with the BOD-5 values. The correlation coefficients for the COD/BOD-5 correlation were positive for 12 of the 13 sampling locations and statistically significant for 4 of them (average R = 0.39).

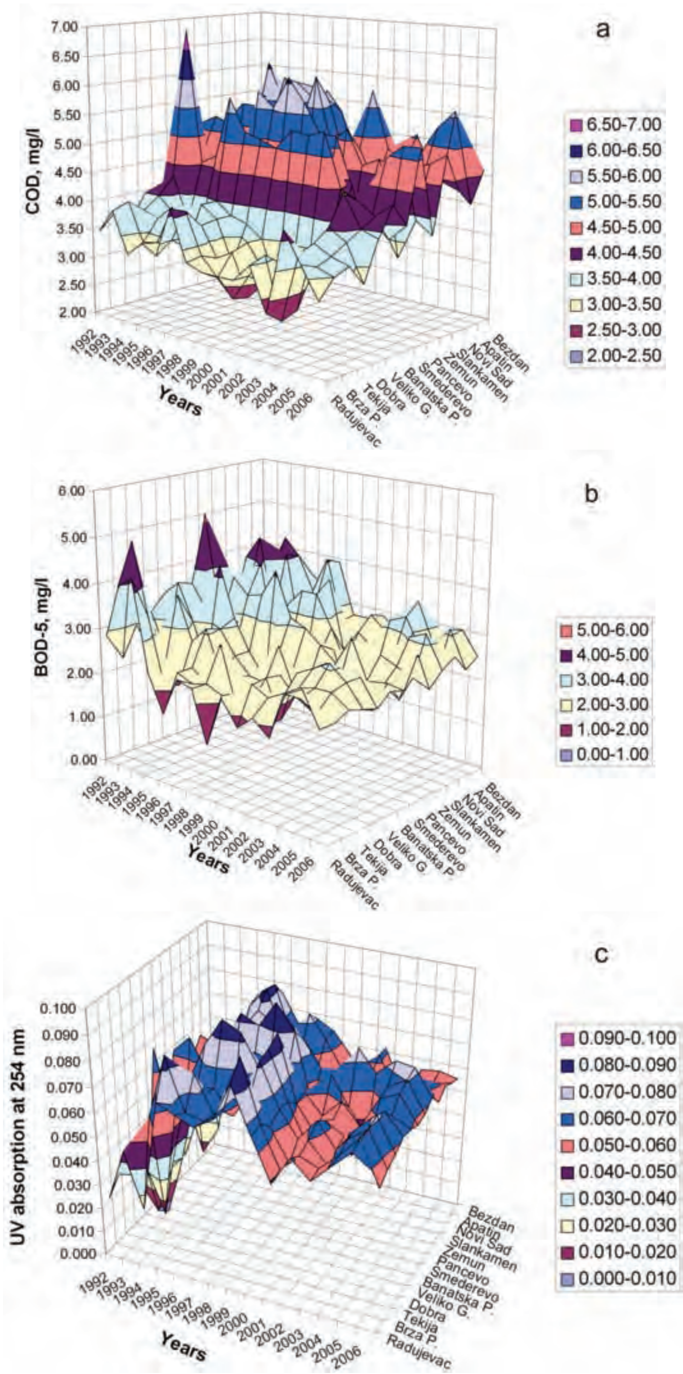

Fig. 3. Temporal and spatial trends of the a) COD values, b) BOD-5 values and c) UV absorption.

The spatial trends for the change of the median yearly values from location to location observed for each year from 1992 until 2006 had negative slopes for every year and all of them were significant, except for the years 1993 and 2004 (which also had a negative slope but their *t* value vas smaller than the critical value). A decreasing tendency of COD from Bezdan toward Radujevac was evident.

BOD-5. The temporal trends for the change of the median yearly values for the period from 1992 until 2006 observed for each sampling station (from Bezdan to Radujevac) had negative slopes for 12 out of 13 locations; the average slope was also negative and statistically significant trends were observed at Bezdan, Apatin, Slankamen Pancevo, Banatska Palanka and Veliko Gradište. The only positive (but not statistically significant) trend was observed at Tekija sampling location. Therefore, it can be concluded that the BOD-5 value decreased through the investigated years.

The spatial trends for the change of the median yearly values from location to location observed for every year from 1992 until 2006 had negative slopes for all year (except in 1993 which was not statistically significant). Four years (1995, 1997, 1999 and 2000) were statistically significant while for another four years (1992, 1996, 2001 and 2003), the *t* values were close to the critical level. A decreasing tendency of BOD-5 from Bezdan toward Radujevac was evident, but a change of the rate of decrease was observed and it became less negative from 1995 to 2006. If the slope coefficients are plotted against time, a regression line with a positive slope was obtained, with an R^2 value of 0.706, a *t* value of 4.897 and a *P* value of 0.000625, indicating that soon after 2006 there will be no further decrease of the BOD-5 value in the Serbian part of the Danube.

UV Absorption at 254 nm. The temporal trends for the change of the median yearly values for the period 1992 until 2006 observed for every sampling station (from Bezdan to Radujevac) were evenly distributed (6 negative and 7 positive). The negative slopes possessed no statistical significance and among the positive slopes, 4 were statistically significant (Zemun, Smederevo, Veliko Gradište, Dobra). The average slope was also positive but, nevertheless, it cannot be unambiguously stated that the UV absorption increased over the years. However, it is interesting that at first 4 (of the 13 in total) sampling locations (Bezdan to Slankamen), the regression slopes were all negative and at last five sampling locations (Veliko Gradište. to Radujevac), the regression slopes were all positive. After closer data inspection, it was noticed that the UV absorption rapidly increased until 1995 or 1996, after which it slowly decreased or stagnated. The rate of decrease after 1996 was larger in upper than in lower section of the River, resulting in negative overall temporal trends in the upper and positive overall temporal trends in the lower section.

The UV absorbance values are well correlated with the pH values. The correlation coefficients for the UV absorption/pH correlation were positive for 10 out of the 13 sampling locations and statistically significant for 5 of them (average $R = 0.32$).

Spatial trends for change of median yearly values from place to place observed for each year from 1992 until 2006 had negative slope for first 7 years (1992–1998) and 3 of them were statistically significant (1992, 1994 and 1996). In 1999 and afterwards, the regression slope became positive (except in 2001 and 2002) but it was statistically significant only for the years 1999, 2000 and 2005. Therefore, an increasing or decreasing tendency of UV absorption from Bezdan toward Radujevac cannot be declared.

Third group parameters

Oxygen parameters are quite significant. They are very well correlated, they show practically negative trends in time (from 1992 until 2006) and in space (from Bezdan to Radujevac) but they are statistically insignificant (Fig. 4).

Dissolved oxygen. The temporal trends for the change of the median yearly values for 1992 until 2006 was observed for every sampling station (from Bezdan to Radujevac) and they had negative slopes for 11 out of the 13 locations; the average slope was also negative but a statistically significant trend was observed only at Banatska Palanka. Positive, but statistically insignificant, trends, were observed only at the Pancevo and Smederevo sampling locations. A decreasing trend through the years can be postulated based on the fact that the slope was negative at 11 out of 13 locations, which statistically would have a very low probability.

A negative correlation was observed between the amount of dissolved oxygen and temperature at 11 out of 13 locations (3 out of the 11 were statistically significant) with an average R value of –0.32. Oxygen saturation was positively correlated with dissolved oxygen at all 13 locations (7 of them with statistical significance). The average R value was 0.59.

The spatial trends for the change of the median yearly values from location to location observed for each year from 1992 until 2006 had a negative slope for every year (except in 1998 which was not statistically significant). Three of them (2002, 2003 and 2006) were statistically significant. The average slope was also negative. Therefore it can be inferred that dissolved oxygen decreased from Bezdan toward Radujevac.

Oxygen saturation. The temporal trends for the change of the median yearly values for the period from 1992 until 2006 observed for all sampling stations (from Bezdan to Radujevac) varied between 6 negative and 7 positive values none of them statistically significant. The average slope was slightly negative. No trend through the years could be identified.

The spatial trends for the change of the median yearly values from location to location observed for all years from 1992 until 2006 were equally distributed among positive and negative values. The average slope was only slightly negative and there was only one statistically significant trend (negative in 2005). No decrease in the oxygen saturation from Bezdan toward Radujevac could be proven.

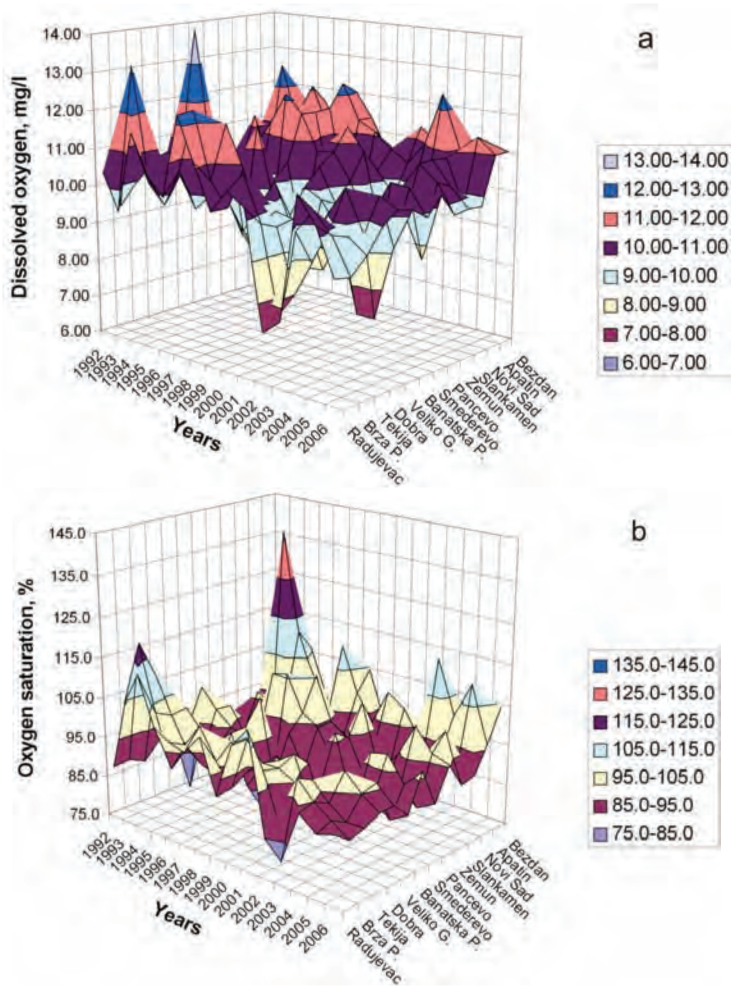

Fig. 4. Temporal and spatial trends of a) the amount of dissolved oxygen and b) the oxygen saturation values.

Fourth group of parameters

Among these parameters (Fig. 5), the pH value is a special parameter. Levels of pH greater than 8.5 usually indicate the presence of algal blooms because intense photosynthesis by algae removes CO_2 from the water, which increases the pH value. Increased algal activities are closely related to the nutrient content (N and P) and oxygen saturation. The greater is the content of nutrients, the greater is the algal activity and, consequently, the production of oxygen increases resulting in increased oxygen saturation.

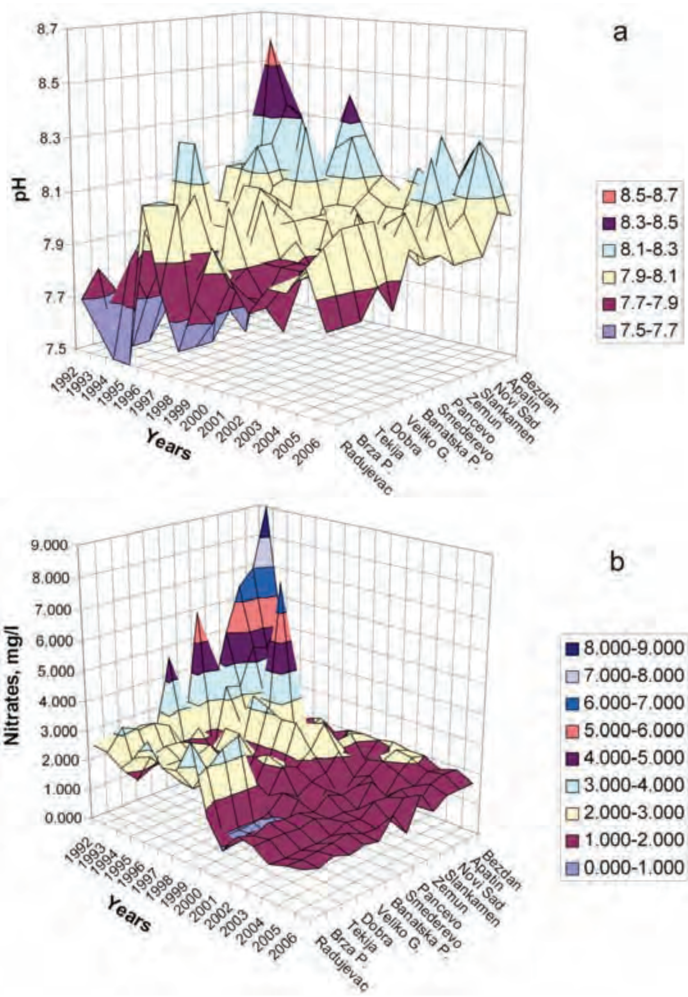

Fig. 5. Temporal and spatial trends of a) the pH values and b) concentration of nitrates.

pH Value. The temporal trends for the change of the median yearly values for the period from 1992 until 2006, observed for all sampling station (from Bezdan to Radujevac) had a negative slope for 6 out of 13 locations, while the other 7 were positive. Among the 4 statistically significant slopes, one was negative and other 3 were positive. The average slope was slightly positive. Interesting, before Smederevo, almost all the slopes were negative and thereafter positive.

The spatial trends for the change of the median yearly values from location to location observed from 1992 until 2006 had negative slope for every year and 9 of the 15 were statistically significant. A tendency of decreasing pH value from Bezdan toward Radujevac is evident.

Concentration of nitrates. The temporal trends for the change of the median yearly values for the period 1992 until 2006 observed at all sampling station (from Bezdan to Radujevac) had negative slopes, and 8 of them were statistically significant. Therefore, it can be concluded that the concentration of nitrates decreased over the years.

A slight negative correlation was established between the nitrate concentrations and the pH values at 10 of 13 locations, with an average R value of –0.17. The nitrate concentrations were positively correlated with the total P concentrations at all 13 locations (8 of them with statistical significance). The average R value was 0.65.

The spatial trends for the change of the median yearly values from location to location observed for every year from 1992 until 2006 had negative slopes for 9 years (6 had statistically significant slopes) while for the other 5, the trends were positive but only one was statistically significant. The average slope was negative; hence, a decreasing tendency of the nitrate concentration from Bezdan toward Radujevac was evident.

In general, the total P and total N showed negative trends in time (from 1992 until 2006) and in space (from Bezdan to Radujevac) (Fig. 6). Nutrients are usually the limiting factors in algal growth.

Concentration of total P. The temporal trends for the change of the median yearly values for period 1992 until 2006 observed for every sampling station (from Bezdan to Radujevac) had negative slopes for all locations, 2 of them (Bezdan, Slankamen) were statistically significant, but another four had t values close to critical value. Therefore, it can be concluded that the total P decreased over the years.

The spatial trends for the change of the median yearly values from location to location observed every year from 1992 until 2006 had negative slopes for 14 out of the 15 years (8 were statistically significant), and just one was positive but not statistically significant. The average slope was negative. Hence, total P concentration showed a decreasing tendency from Bezdan toward Radujevac.

Concentration of total N. Unfortunately, the data for the assessment of trend in the total N concentration was insufficient due to a lack of measurements prior to 2002 (with exception of the year 1995 for some sampling locations). For this reason, it is very hard to detect statistically significant trends within the small data sets because they have very high critical t values for comparison with test statistics. These limited data, however, indicated that the concentration of total N decreased over the years, which is consistent with the negative trend of nitrate concentrations (nitrates participate to a significant extent to the total N load).

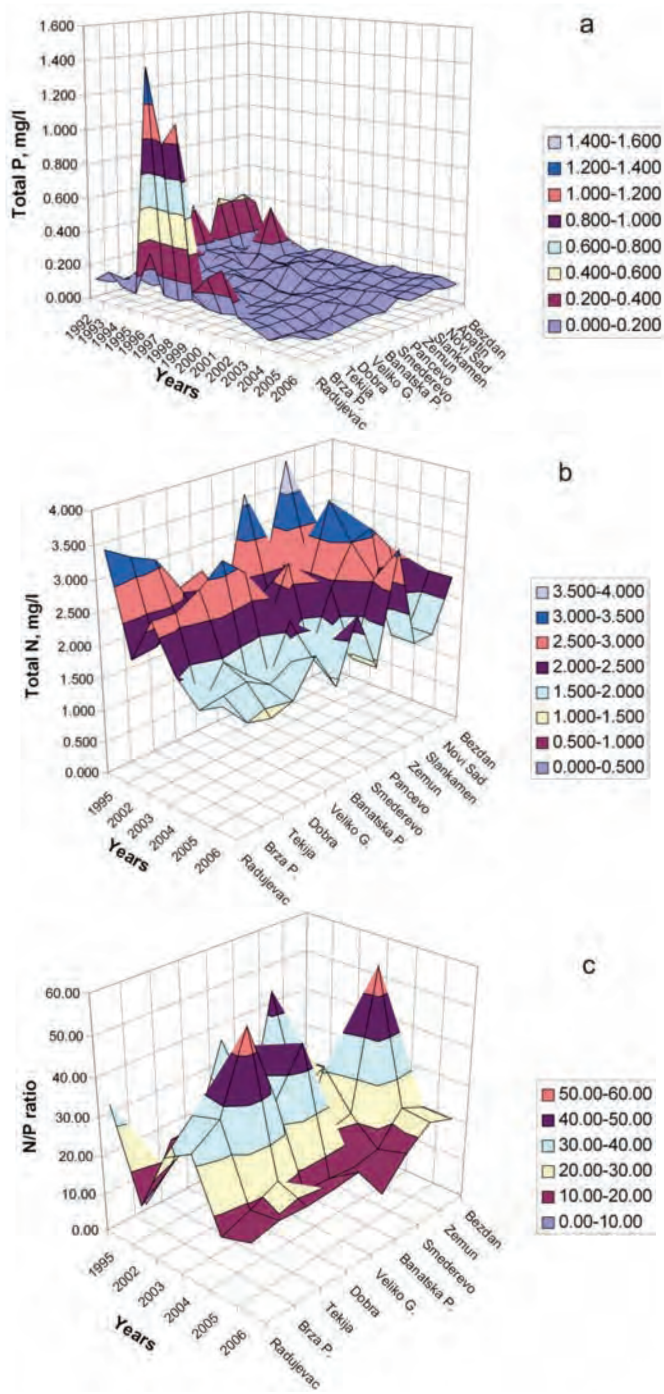

Fig. 6. Temporal and spatial trends of the amount of a) total P, b) total N and c) the N/P ratio.

The total N concentration correlated very well with the nitrate concentrations. The correlation with the pH values was similar to the correlation with the nitrate concentrations and exhibited a negative average value.

If the change in the total N concentration is followed downstream from Zemun to Radujevac (with exception of Bezdan, there is not sufficient data for the sampling locations before Zemun), a few statistically significant negative trends can be observed (in years 2002 and 2004). The average trend was also negative but the limited monitoring time of the trend prevents a serious conclusion to be derived, although indications of a decrease in the total N concentrations from Bezdan toward Radujevac do exist.

Total nitrogen to total phosphorus ratio (TN/TP). The TN/TP ratio is used to compare the availability of these nutrients. Ratios smaller than 10 indicate that nitrogen is limiting. Ratios greater than 16 indicate that phosphorus is limiting,[47] whereas ratios greater than 10 but smaller than 16 indicate that there are enough of both nutrients for excessive algal growth. Throughout all the years, the TN/TP ratio was over 16, which indicates that phosphorous could be the limiting factor for algal growth in the Danube River, but since data for total N is limited (as mentioned above) serious trend analysis can not be performed.

DISCUSSION

In this discussion, all the particular conclusions drawn on the basis of linear regression analysis with a defined significance level of 95 % concerning time and space trends are summarized (Tables I and II).

First group parameters

Suspended matter. With time (1992–2006) no clear tendency for the suspended matter change could be estimated, but in space (from the inflow to outflow point), a tendency of the suspended matter to decrease from Bezdan toward Radujevac was evident.

Dry matter. With time, a decreasing (improving) trend for the dry matter could be observed and in space, it could be concluded that the dry matter content decreased from Bezdan toward Radujevac.

Conductivity. With time, a decreasing trend was found but in space, no trend of the conductivity from Bezdan to Radujevac could be clearly evidenced.

Second group parameters

COD. With time, a decreasing trend for COD was found and in space, a tendency of the COD to decrease from Bezdan toward Radujevac was evident.

BOD-5. In time, the BOD-5 exhibited a decreasing trend and in space, a tendency of BOD-5 to decrease from Bezdan toward Radujevac was evident. A change in the rates of decrease was observed as they become less negative between 1995 and 2006. This indicates that soon after 2006, the BOD-5 will not be a spatially decreasing parameter in the Serbian part of the Danube.

TABLE I. Temporal trends of the median yearly value changes for the period 1992–2006 observed for all sampling station

Parameter	No. of positive trends	Average Pearson's correlation coefficient square	No. of statistically significant positive trends	Average Pearson's correlation coefficient square	No. of negative trends	Average Pearson's correlation coefficient square	No. of statistically significant positive trends	Average Pearson's correlation coefficient square	Overall trend estimation and comments
Dry matter	2	0.046	0	0.000	11	0.193	2	0.433	Negative trend
Suspended matter	8	0.063	1	0.273	5	0.182	2	0.340	Inconclusive
Conductivity	1	0.000	0	0.000	12	0.072	1	0.323	Negative trend
COD	1	0.495	1	0.495	12	0.168	3	0.368	Negative trend
BOD-5	1	0.001	0	0.000	12	0.275	6	0.398	Negative trend
UV absorption (254 nm)	7	0.306	4	0.388	6	0.051	0	0.000	Negative to positive switch[a]
Dissolved oxygen	2	0.021	0	0.000	11	0.122	1	0.434	Negative trend
Oxygen saturation	7	0.025	0	0.000	6	0.099	0	0.000	Inconclusive
pH	7	0.292	3	0.426	6	0.173	1	0.314	Negative to positive switch[b]
Nitrates	0	0.000	0	0.000	13	0.342	8	0.472	Negative trend
Total P	0	0.000	0	0.000	13	0.171	2	0.273	Negative trend
Total N	1	0.001	0	0.000	7	0.470	0	0.000	Negative trend

[a]The UV absorption at 254 nm increased rapidly until the years 1995 or 1996, after which it slowly decreased or stagnated. The rate of decrease after 1996 was larger in upper than in lower section of the River, resulting in negative overall temporal trends in the upper and positive overall temporal trends in the lower section;
[b]in the upper section of the River, the pH tends to have negative temporal trend while in the lower section, the temporal trend is positive

TABLE II. Spatial trends of the median yearly values changes from location to location observed for every year from 1992 to 2006

Parameter	No. of positive trends	Average Pearson's correlation coefficient square	No. of statistically significant positive trends	Average Pearson's correlation coefficient square	No. of negative trends	Average Pearson's correlation coefficient square	No. of statistically significant positive trends	Average Pearson's correlation coefficient square	Overall trend estimation and comments
Dry matter	2	0.079	0	0.000	10	0.261	4	0.525	Negative trend
Suspended matter	0	0.000	0	0.000	15	0.503	13	0.541	Negative trend
Conductivity	9	0.215	4	0.436	6	0.330	3	0.421	Inconclusive
COD	0	0.000	0	0.000	15	0.468	13	0.505	Negative trend
BOD-5	1	0.008	0	0.000	14	0.227	4	0.416	Negative trend
UV absorption (254 nm)	6	0.343	3	0.603	9	0.167	3	0.385	Negative to positive switch[a]
Dissolved oxygen	1	0.000	0	0.000	14	0.174	3	0.575	Negative trend
Oxygen saturation	7	0.068	0	0.000	8	0.167	1	0.322	Inconclusive
pH	0	0.000	0	0.000	13	0.456	9	0.597	Negative trend
Nitrates	5	0.165	1	0.321	9	0.433	6	0.580	Negative trend
Total P	1	0.005	0	0.000	14	0.330	8	0.484	Negative trend
Total N	1	0.000	0	0.000	6	0.391	2	0.609	Negative trend

[a]UV absorption at 254 nm had a negative spatial trend until the year 1998. In the later years, the spatial trend became positive

UV Absorption at 254 nm. In time, it cannot be unambiguously stated that the UV absorption was increasing and in space, no changing tendency of the UV absorption from Bezdan toward Radujevac was evidenced.

Third group parameters

Dissolved oxygen. In time, the decreasing trend had a very low probability and in space, it could only be suspected that a decrease in dissolved oxygen content from Bezdan toward Radujevac existed.

Oxygen saturation. In time, no trend through the years could be identified but in space, a decrease in oxygen saturation from Bezdan toward Radujevac could be proven.

Fourth group parameters

pH Value. In time, trends for the change of the median yearly values for period from 1992 until 2006 could not be identified, while in space, a tendency of pH value to decrease from Bezdan toward Radujevac was evident.

Concentration of nitrates. In time, it could be concluded that the concentration of nitrates exhibited a decreasing trend and in space, a tendency of the nitrate concentration to decrease from Bezdan toward Radujevac was evident.

Concentration of total P. In time, it could be concluded that the concentration of total P had a decreasing trend and in space, a tendency of the total P concentration to decrease from Bezdan toward Radujevac was evident.

Concentration of total N. The limited data indicated that the concentration of total N had a decreasing trend in time and in space, the total N concentration decreased from Bezdan toward Radujevac.

TN/TP ratio. Throughout all the years, the TN/TP ratio was over 16, which indicates that phosphorous could be the limiting factor for algal growth in the Danube River, but since the data for total N was limited (as mentioned above), a serious trend analysis could not be realized.

The strong positive correlation of nitrates with total P and total N indicates that these nutrients have same source, probably fertilizers used in agriculture.

The analysis of the trends of the investigated parameters strongly indicates that the eco-chemical status of the Danube River is improving with time. None of the parameters have reached their natural minimum, such as dry matter, conductivity, COD, BOD-5, pH, nitrates, total P and possibly total N, therefore further improvements in the eco-chemical status of the Danube River are to be expected. However, some of the parameters, such as suspended matter, UV absorption at 254 nm, oxygen saturation and pH did not show decreasing trends. For the later group of parameters, there are no indications that they are going to improve in the near future.

The trends related to space, which are particularly important for Serbia, are very indicative; the eco-chemical parameters are improving from the inflow to the outflow point for all parameters except for conductivity, oxygen saturation and UV absorption at 254 nm. Several reasons are responsible for this, such as a decrease in the flow rate, self-purification of the river, contribution of tributaries, but the most important fact is the existence of the Đerdap Dam (Iron Gate I) at the outflow point of Serbia that strongly influences the process of self-purification,[48] which is characteristic for the entire region of Serbia being constantly present for the whole period covered by this article.

Only dissolved oxygen showed undesired but statistically insignificant trends (decreasing) in time and space that are most probably the result of a gradual temperature increase from Bezdan to Radujevac.

CONCLUSIONS

The general concluding remark is that the eco-chemical status of the Danube River is constantly improving. The total river load is much higher at the entrance of the Danube River into Serbia (Bezdan) in comparison to the outflow point (Radujevac). The improvement of the eco-chemical status is twofold: with time (from 1992 until 2006) and in space (from Bezdan to Radujevac).

The results of the present study showed that the slopes of the decreasing trend lines are not significantly affected either by tributaries (Sava, Tisa, Tamiš or Velika Morava) or bigger pollutant sources, such as cities and industrial centers (Novi Sad, Belgrade, Pančevo or Smederevo).

The time improvement is most probably related to several factors:

– the decrease in industrial activities in Serbia during the last decade of the 20th century;

– the coordinated activates of countries located in the Danube Basin – ICPDR;

– the constrained use of fertilizers in the agricultural sector of Serbia.

Space improvements are related to following factors:

– the contribution of tributary rivers, especially the Sava River, to the total discharge (Q) of the Danube River;

– the decrease in the flow rate, particularly in the lower section of the Danube, closely related to the Iron Gate, favors self-purification of some river water quality parameters;

– transition of the river surroundings affected by high agricultural activity and dense population in the upper stream of the River to the Djerdap National Park in the lower part of the River.

It is suspected that a part of the river load is transferred into river sediments due to self-purification and precipitation, but thorough investigations are yet to be performed.

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И З В О Д

ДУГОРОЧНЕ ПРОМЕНЕ ЕКОХЕМИЈСКОГ СТАТУСА ДУНАВА НА ТЕРИТОРИЈИ СРБИЈЕ

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Дунав је међународна река која једним делом пролази и кроз Србију. Екохемијски статус Дунава је тема која је константно у жижи интересовања како на локалном (унутар држава кроз које Дунав протиче), тако и на међународном нивоу. Услед генералног интереса да се обезбеди и одржива равномерна употреба воде и слатководних ресурса у басену реке Дунав, развијен је речни мониторинг систем који је групе података о екохемијском статусу Дунава на простору Србије прикупљао током више година. Овај рад је фокусиран на петнаестогодишњи период, од 1992. до 2006. године. Утврђивање постојања трендова коришћењем линеарне регресије, уз тачно одређен ниво значаја вредности одабраних екохемијских параметара као и утврђивања разлике у односу на природну варијабилност параметара, било је од великог значаја за одређивање промене речних параметара. Помоћу њих, покушано је одређивање судбине и понашања екохемијских параметара Дунава на територији Србије и предвиђање њихове вредности у будућности. Добијени резултати открили су константно поправљање и прихватљиве трендове промена екохемијског статуса Дунава као и приметне разлике квалитета воде између улаза у Србију и излаза Дунава из Србије.

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