

## CHANGES IN THE LOWER DRAVA RIVER WATER QUALITY PARAMETERS OVER 24 YEARS

Vlatka GVOZDIĆ<sup>1</sup>, Josip BRANA<sup>2</sup>, Dinko PUNTARIĆ<sup>3</sup>, Domagoj VIDOSAVLJEVIĆ<sup>4</sup>,  
and Danijela ROLAND<sup>1</sup>

*Department of Chemistry<sup>1</sup>, Department of Physics<sup>2</sup>, University of J. J. Strossmayer, Osijek, Zagreb Public Health Institute, Department of Health Ecology, Zagreb<sup>3</sup>, Vukovar General Hospital, Vukovar<sup>4</sup>, Croatia*

Received in July 2011

CrossChecked in November 2011

Accepted in November 2011

The goal of this study was to analyse 13 physico-chemical and microbiological parameters of the Drava River water at three sampling sites in the lower Drava region (eastern Croatia) over two distinct periods: the pre-war period between 1985 and 1992 and the post-war period between 1993 and 2008. Over both periods, most parameters kept within the tolerable water quality limits, while  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$  and  $\text{BOD}_5$  were higher. The lower Drava showed slight organic pollution with high concentrations of dissolved oxygen. High levels of total coliforms and heterotrophic bacteria in the post-war period were only found downstream of the town of Osijek. Upstream of Osijek, the river showed a tendency for improvement.

**KEY WORDS:** *cluster analysis, Drava River, microbiological parameters, organic pollution, physico-chemical parameters*

The Drava River is an international river, part of which runs through Croatia. The section that runs from Legrad and drains into the Danube is called the Lower Drava. This section has long been a border between Hungary and Croatia and was spared from man-made pollution (1). In fact, it has become a unique oasis of numerous plant and animal species, Kopački Rit Nature Park in particular. However, recent groundwater findings in eastern Croatia point to extremely high concentrations of arsenic of up to  $610 \mu\text{g L}^{-1}$  (2, 3). Since the late eighties, groundwater has been the main source of drinking water for the population of nearly 200,000 people in this part of Croatia.

Current regulations in Croatia (4, 5) divide ground and surface waters in five quality classes. Class I are ground and surface waters that can be used for drinking and in food industry in its natural state or after disinfection, as well for breeding trout. Class II is water that can be used in its natural state for swimming and recreation or can be treated for drinking

and other industrial purposes. Class III is water that can be used by industries with no specific water quality requirements and in agriculture. Class IV waters must be treated before any kind of use, where other water supply is not available. Class V are waters that cannot be used for any purpose.

The goal of the national water protection strategy (4, 5) is to keep the Drava River within the Class II limits. Following a purification procedure, it can be used for drinking and in industry.

Water quality of the Drava River is highly influenced by its tributary the Mura River (6), which is classified as Class IV stream by Croatian standards (5). A number of studies have reported improvements in the water quality of the Danube drainage basin over the last two decades (7-11). Vitale et al. (12) claim that the improving trend started in the late 1980s and again in 1995. Since 1991, industrial pollution dropped significantly throughout Croatia, that was hit by war operations, Osijek in particular.

However, the Drava River is a wastewater recipient for many towns and villages. As these grow, so do the volumes of domestic sewage that are usually rich in biodegradable organic matter and surface runoff. Pathogens from these discharges may pose a risk to downstream water users. Additionally, micro-organisms often accumulate in river sediments.

Temporal distribution of pollutant concentrations can be determined either by sampling water at low frequency over a long period of time or at high frequency over one hydrologic cycle (one year) (1, 12). The data analysed in this study were obtained from Hrvatske vode, the national water management agency that is responsible for surface and ground water quality monitoring. Most of the data are from samples collected at weekly intervals. Microbiological parameters were analysed from samples collected at monthly intervals.

The aim of the study was to provide a more comprehensive view of the Drava water pollution over 24 years and see whether war and ensuing economic recession affected it in any way. We also wanted to see if there were differences between measurement sites.

## MATERIALS AND METHODS

### *Measurement sites*

Monitoring that took place between 1985 and 2008 included three sites: 1) Bistrinci (rural area) at 45° 41' 30" North, 18° 23' 55" East; 2) Višnjevac (suburbia upstream of Osijek) at 45° 41' 30" North, 18° 23' 55" East; and 3) Nemetin (suburbia downstream of Osijek) at 45° 32' 24" North, 18° 46' 25" East.

The major economic activity in Bistrinci area includes intensive crop and vegetable production, wood processing, and paper industry. The town of Osijek is the biggest urban center in eastern Croatia with a population of 120,000. The wastewater coming from the city of Osijek and surrounding urban areas is being discharged into the river Drava without being previously treated.

### *Sampling*

Weekly sample analysis (totalling 940 water samples per site) included temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), oxygen saturation (OS), chemical oxygen demand (COD),

total suspended solids (TSS), nitrate nitrogen ( $\text{NO}_3\text{-N}$ ), nitrite nitrogen ( $\text{NO}_2\text{-N}$ ), ammonia-nitrogen ( $\text{NH}_4\text{-N}$ ), and five-day biochemical oxygen demand ( $\text{BOD}_5$ ).

Monthly samples were taken for microbiological analysis that included total coliforms (TC) and heterotrophic (HE) bacteria (303 samples per site).

Samples were analysed right after collection using ion chromatography to determine the concentrations of  $\text{NO}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$ , and  $\text{NH}_4\text{-N}$ , (13, 14) and titration to measure biochemical and chemical oxygen demand (15, 16). Total suspended solids were determined gravimetrically (17), while dissolved oxygen, oxygen saturation, electrical conductivity and pH electrochemically (18-21). Coliform bacteria were isolated on lactose TTC agar and scored using membrane filtration and HE were inoculated on yeast extract agar and determined by colony count (22, 23). All the water quality parameters are expressed in  $\text{mg L}^{-1}$ , except pH, EC ( $\mu\text{S cm}^{-1}$ ), T ( $^{\circ}\text{C}$ ), total coliforms (the most probable number, MPN per 100 mL) and heterotrophic bacteria (MPN  $\text{mL}^{-1}$ ).

### *Statistics*

Statistical analysis of the water quality parameters was performed using the statistical software Statistica, version 7.0. In addition to standard descriptive statistics, we also used cluster analysis (24-26), which was based on recalculated average monthly values of chemical parameters to adjust for microbiological data based on monthly samples. To normalise data using Euclidean distance and to quantify the (dis)similarity between sampling sites, we applied an agglomerative single-linkage algorithm ("nearest neighbours"). The results obtained by hierarchical clustering are presented in the form of dendrograms.

## RESULTS AND DISCUSSION

Here we report the results of a spatial and temporal analysis of 13 chemical, microbiological, and ecological parameters assessed at three sampling sites over 24 years.

Table 1 shows the measured parameters that met Class I or II requirements set by the current national regulation (4). Figures 2 to 6 use box and whiskers plots to show the parameters that did not meet Class I or Class II water quality requirements ( $\text{BOD}_5$ ,  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ , total coliforms, and heterotrophic bacteria, respectively).

**Table 1** Median, range, and the percentile values of the quality parameters for the Drava water

Variable	Class <sup>#</sup>	Values	Pre-war (1985-1992)			Post-war (1993-2008)		
			Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
T / °C	*	median	13	14	14	12	12.6	13
		range	-15 to 32	-13 to 32	-10 to 32	-10 to 29	-9 to 29	-9 to 31
		90 <sup>th</sup> percentile	22.0	23.0	23.0	22.7	22.7	24.1
pH	I	median	7.7	7.7	7.7	7.9	7.9	7.9
		range	6.9 to 8.1	6.9 to 8.1	7.1 to 8.1	6.9 to 9.5	6.9 to 9.6	6.9 to 9.2
		90 <sup>th</sup> percentile	7.8	7.8	7.8	8.3	8.3	8.3
EC/ $\mu\text{S cm}^{-1}$	I	median	319	320	322	323	326	330
		range	200 to 453	206 to 468	200 to 565	190 to 580	147 to 681	164 to 577
		90 <sup>th</sup> percentile	351	351	351	422	434	435
TSS/ $\text{mg L}^{-1}$	*	median	60	60	60	30	37	40
		range	20 to 210	20 to 200	20 to 160	2 to 220	2 to 250	2 to 182
		90 <sup>th</sup> percentile	70.0	80.0	70.0	66.5	80.0	90.0
$\text{NO}_2\text{-N/ mg L}^{-1}$	II	median	0.010	0.010	0.010	0.017	0.017	0.017
		range	0.001 to 0.025	0.001 to 0.033	0.001 to 0.030	0.001 to 0.05	0.001 to 0.066	0.001 to 0.066
		90 <sup>th</sup> percentile	0.020	0.020	0.020	0.020	0.020	0.020
$\text{DO/ mg L}^{-1} \text{ O}_2$	I	median	9.8	9.8	9.8	9.7	9.48	9.5
		range	4.7 to 8.3	4.4 to 18.6	4.1 to 18.0	5.9 to 24.4	5.9 to 23.1	5.23 to 24.2
		10 <sup>th</sup> percentile	7.5	7.5	7.4	7.6	7.5	7.4
OS / %	II	median	92	92	91.3	92.7	89.7	89.7
		range	45 to 178	41 to 176	38 to 172	56 to 254	57 to 261	36.8 to 249
		10 <sup>th</sup> percentile	70.1	70.0	70.0	71.8	70.1	70.1
$\text{COD/ mg L}^{-1} \text{ O}_2$	II	median	4.8	5	5.1	3	3.2	3.4
		range	1 to 10	1 to 11	1.5 to 10.1	1.0 to 9.4	0.9 to 11.0	1.3 to 18.2
		90 <sup>th</sup> percentile	7.0	7.3	7.6	4.3	4.8	5.3

\* not included in classification

Site 1 Bistrinci, Site 2 Višnjevac, Site 3 Nemetin

# - classes are defined according to the current Croatian regulation (see reference 4)

T – temperature

EC – electrical conductivity

TSS – total suspended solids

$\text{NO}_2\text{-N}$  – nitrite nitrogen

DO – dissolved oxygen

OS – oxygen saturation

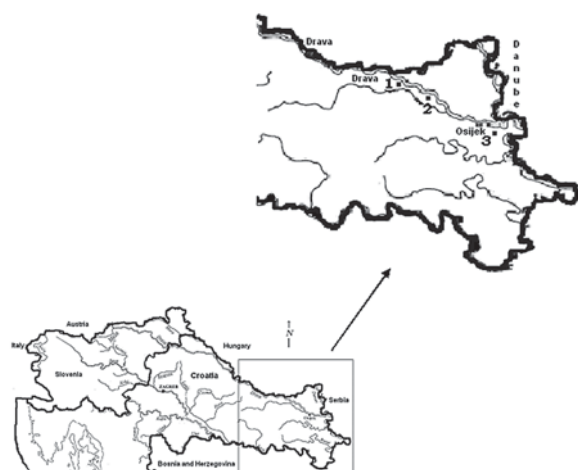
COD – chemical oxygen demand

To group variables by similarity, we applied the hierarchical cluster analysis. Its results are presented in the form of dendrograms in Figures 7 and 8. Pre- and post-war data cluster analyses show that the relations between parameters changed over time.

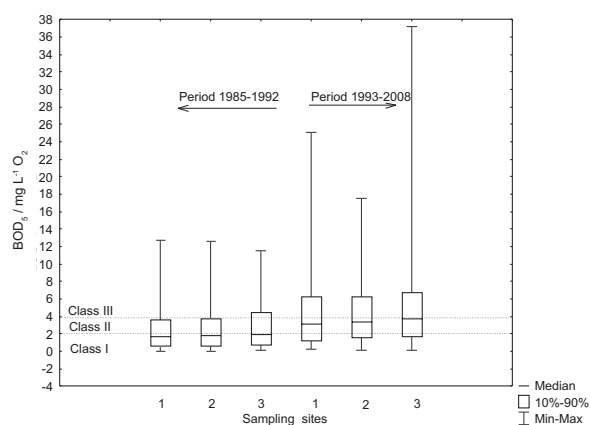
We obtained interesting results for parameters measured during the post-war period (Figure 8). Hierarchical cluster analysis shows two clusters at higher distances; a single-member cluster corresponding to  $\text{TC}_3$ , and a two-member cluster containing  $\text{HE}_3$  and  $\text{HE}_2$ . The third multi-member cluster splits at a lower distance into clusters that comprise the remaining variables. The single-member cluster 1 corresponds

to total coliform bacteria at sampling site 3. The sub-cluster 2a corresponds to the spatial variation of only heterotrophic bacteria. The clustering of  $\text{HE}_2$  and  $\text{HE}_3$  in the separate cluster points to significant differences in HE measurements from sampling site 1. Sub-cluster 2b was characterised by closer distances between members.

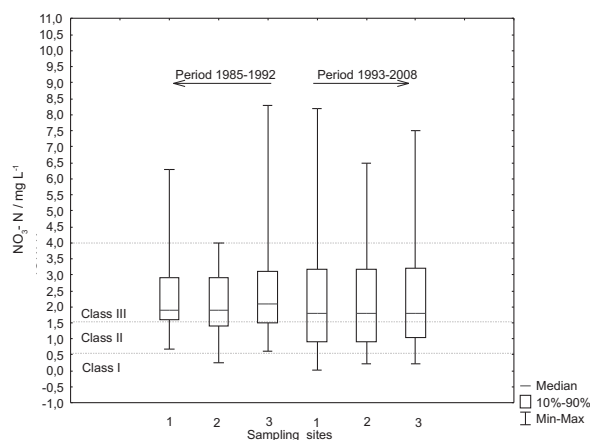
The clustering of  $\text{BOD}_{(1,2,3)}$ ,  $\text{NH}_4\text{-N}_{(1,2,3)}$ ,  $\text{NO}_2\text{-N}_{(1,2,3)}$ ,  $\text{NO}_3\text{-N}_{(1,2,3)}$  in the same cluster (Figure 8) reflects stronger correlations between these parameters. In addition, there are no relevant deviations in the levels between the sampling sites. This suggests that Osijek and its wastewaters do not contribute significantly to



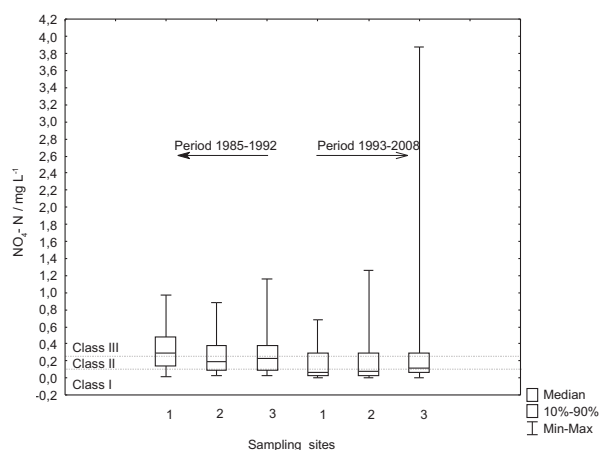
**Figure 1** Location of the measuring sites



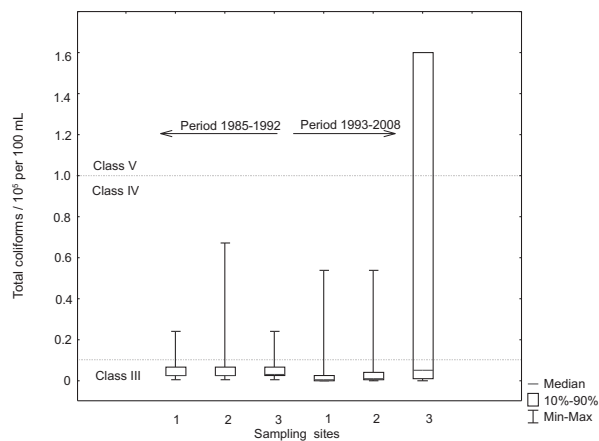
**Figure 2** Box and whiskers plots of five-day biochemical oxygen demand ( $BOD_5$ )  
1 - Bistrinci, 2 - Višnjevac, 3 - Nemetin  
Classes I, II, and III - see definition in the text



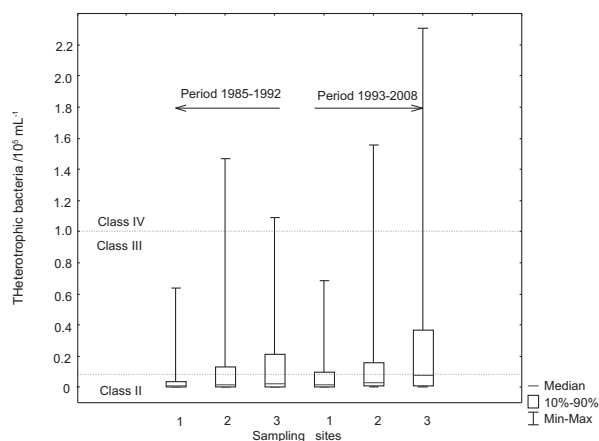
**Figure 3** Box and whiskers plots of nitrate nitrogen ( $NO_3-N$ )  
1 - Bistrinci, 2 - Višnjevac, 3 - Nemetin.  
Classes I, II, and III - see definition in the text



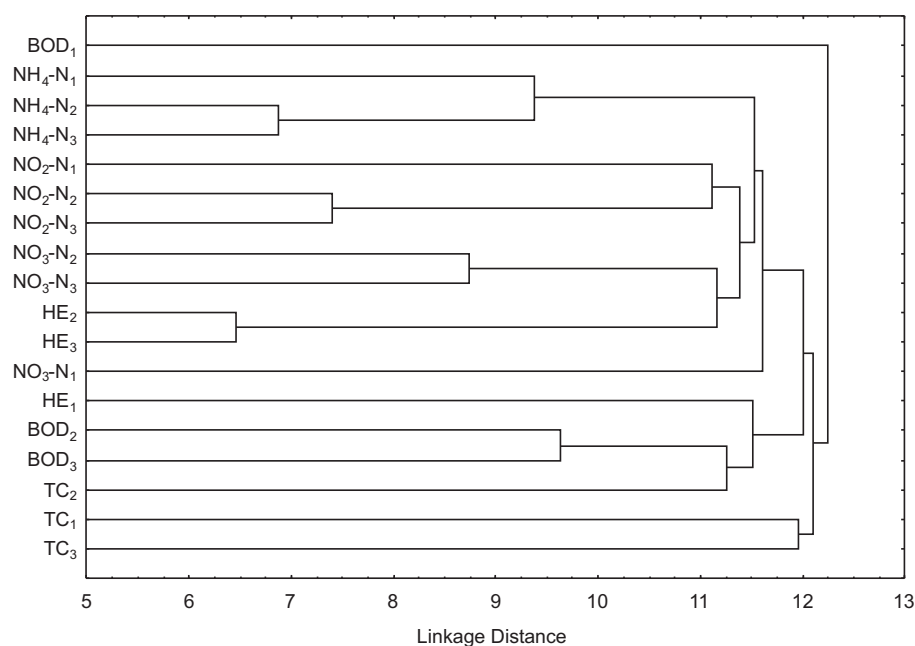
**Figure 4** Box and whiskers plots of ammonia-nitrogen ( $NH_4-N$ )  
1 - Bistrinci, 2 - Višnjevac, 3 - Nemetin  
Classes I, II, and III - see definition in the text



**Figure 5** Box and whiskers plots of total coliform bacteria  
1 - Bistrinci, 2 - Višnjevac, 3 - Nemetin  
Classes III, IV, and V - see definition in the text



**Figure 6** Box and whiskers plots of heterotrophic bacteria  
1 - Bistrinci, 2 - Višnjevac, 3 - Nemetin  
Classes II, III, and IV - see definition in the text

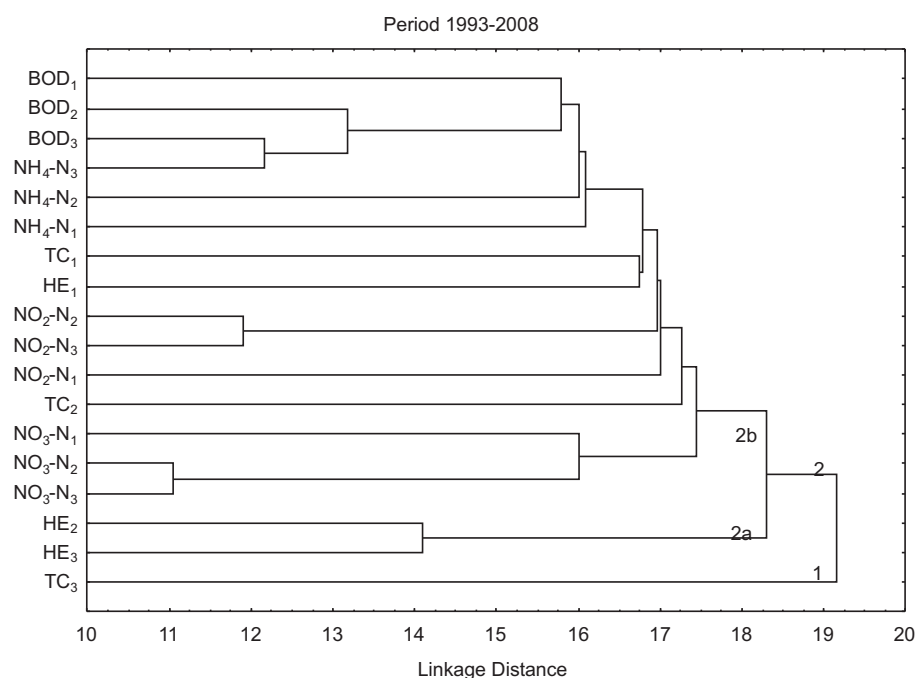


**Figure 7** Single linkage clustering (nearest neighbours) of the pre-war water samples using Euclidean distance metrics

Legend:

1 - Bistrinci, 2 - Višnjevac, 3 - Nemetin  
 TC – total coliforms  
 HE – heterotrophic bacteria

$BOD_5$  – five-day biochemical oxygen demand  
 $NO_3-N$  – nitrate nitrogen  
 $NO_2-N$  – nitrite nitrogen  
 $NH_4-N$  – ammonia-nitrogen



**Figure 8** Single linkage clustering (nearest neighbours) of the post-war water samples using Euclidean distance metrics

Legend:

1 - Bistrinci, 2 - Višnjevac, 3 - Nemetin  
 TC – total coliforms  
 HE – heterotrophic bacteria

$BOD_5$  – five-day biochemical oxygen demand  
 $NO_3-N$  – nitrate nitrogen  
 $NO_2-N$  – nitrite nitrogen  
 $NH_4-N$  – ammonia-nitrogen

the levels of nutrients and organic matter, but the significant sources are to be found upstream or across the border.

The clustering procedure obtained on the variables measured during pre-war period (Figure 7) highlighted a quite different situation because the measuring stations have more uniform characteristics with respect to all the variables. Here we also briefly discuss the significance of particular physico-chemical parameters of interest. The temperature of running waters of the most of mid, east, and south European rivers varies between 0 °C and 30 °C. Abnormally high temperatures in river water can arise from thermal discharges, usually from power plants or sewage treatment plants (27). In our study, the temperature of the Drava showed minor temporal and spatial variations.

Another important parameter is pH, as most aquatic organisms are adapted to pH from 7.2 to 8.7. We found that alkalinity in the Drava river water rose in the post-war period, but remained within the Class I limits.

According to the current regulation (4), the assessment of spatio-temporal variations should take into account 90<sup>th</sup> percentiles of a particular parameter, as they may point to outstanding events that occurred at a particular moment.

We found that the 90<sup>th</sup> percentile of EC also increased in the post-war period, but the medians do not indicate any significant variation between the three sites over the monitored 24 years.

To get a better insight in the water quality, we also analysed total suspended solids (TSS). We found that TSS median values dropped in the post-war period and show a higher variability between the three sampling sites. TSS often points to intense anthropogenic activity along the river. It may involve sanitary and industrial wastewater, runoff from streets that can bring solids, debris, human waste, and other solid material into the river. Our results are supported by earlier findings (28), which have shown that the Drava River bed and floodplain sediments consist of sand, mud, and gravelly sand. In addition, sand and gravel are exploited from the river bed of the Drava in a number of places (29), which can result in sudden variations of total suspended solids at any time of the year.

A large part of our study deals with the parameters that refer to water oxygenation. Although dissolved oxygen (DO) is essential for aquatic organisms, both deficiency and extremely high levels indicate an

unhealthy river. We used the 10<sup>th</sup> percentile of DO and OS, as it points to outstanding events in water oxygen deficiency (4). Our results show that DO and OS do not indicate any spatial or temporal pattern.

BOD<sub>5</sub> and COD are other important parameters that point to the oxygen regime in the river water. Both refer to biochemical reactions in natural waterways, which contain bacteria and nutrients. While COD test measures the oxygen demand of oxidizable pollutants, the BOD<sub>5</sub> test measures the oxygen demand of biochemically degradable organic matter present in water. In our study COD values generally dropped compared to the pre-war period.

A drop in organic pollution during the two observed periods is probably associated with lower post-war industrial and agricultural activity.

The DO, OS, and COD values suggest that the oxygen regime in the Drava River water is relatively favourable, and its water belongs to Class II.

In contrast, BOD<sub>5</sub> was noticeably higher in the post-war period (Figure 2). BOD is used to establish self-purification of surface waters, and indicates water load with dissolved organic matter. Contributors to this load with oxygen-depleting substances include food, pulp and paper production, sugar beet processing, discharge of poorly treated industrial waste, landfill leachate, agricultural effluents, wetlands and riparian vegetation (30). The Drava comes to Croatia highly polluted with organic matter (12) (Class IV by Croatian standards). The Lower Drava receives poorly treated wastewaters from a number of Croatian and Hungarian towns (31) and even though it does not follow the BOD<sub>5</sub> lowering trends observed in other European rivers (7, 10), it seems to reaerate pretty well.

In this study, we also evaluated the concentrations of nitrite nitrogen (NO<sub>2</sub>-N) that were in the range of Class II, according to the current regulations (4). Nitrite nitrogen concentrations in freshwaters are usually low, 0.01 mg L<sup>-1</sup>, and higher values are indicative of industrial effluents. Nitrites appear as intermediaries in the nitrogen cycle; they are unstable and can transform into nitrates or ammonia (32).

Nitrate concentrations in water seldom exceed 0.1 mg L<sup>-1</sup> of NO<sub>3</sub>-N. Increased levels of nitrates usually point to contamination by the inappropriate disposal of human and industrial waste, or the use of nitrogenated fertilisers in agriculture (27). Our results (Figure 3) show a decreasing post-war trend, which may suggest lower agricultural activity. The level of nitrate nitrogen in this study was lower than in other



European rivers (10), about the same as in the Danube (8), and higher than in the Sava River (7).

Unpolluted waters usually contain small concentrations of ammonia ( $<0.1 \text{ mg L}^{-1}$  of  $\text{NH}_4\text{-N}$ ) (32). Increased ammonium often indicates discharge of untreated domestic wastewaters (32-34). In our study, the levels of ammonia-nitrogen ( $\text{NH}_4\text{-N}$ ) showed a clear decreasing trend (from  $0.3 \text{ mg L}^{-1}$  to  $0.1 \text{ mg L}^{-1}$ ) between the pre- and post-war periods and are lower than in other European rivers (10). However, site Nemetin showed much higher values in the post-war period (Figure 4), which may point to pollution from Osijek wastewaters.

Nitrogen in river waters may provide information about pollution. Since  $\text{NH}_4\text{-N}$  is one of the first steps in organic matter decomposition, higher  $\text{NH}_4\text{-N}$  points to recent pollution, while elevated levels of nitrite and nitrate point to more remote contamination..

Based on the results shown in Figure 4 it seems that wastewater in Osijek greatly affects the quality of water at the sampling site 3 located a few kilometres downstream. The median concentration of  $\text{NH}_4\text{-N}$  between the two observed periods dropped from  $0.3 \text{ mg L}^{-1}$  to  $0.1 \text{ mg L}^{-1}$ , which is still a lower value compared to other European rivers ( $0.8 \text{ mg L}^{-1}$  to  $0.3 \text{ mg L}^{-1}$ ) (10).

Based on the values of  $\text{NO}_2\text{-N}$ , we can conclude that the Drava river waters are still within the guideline values for Class II. However, based on the 90<sup>th</sup> percentiles of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$ , it exceeds recommended limits for Class II (4).

Microbiological parameters evaluated in this study point to a slight deterioration of river water quality in the post-war period. Figure 5 shows that total coliform bacteria slightly decreased in the post-war period. An exception is the sampling site 3 (Nemetin), where the 90<sup>th</sup> percentile value was alarmingly higher than at the other sites. Bacterial contamination at this sampling site is mostly caused by domestic sewage from sanitary and industrial wastewater discharges and urban runoff from city streets and surrounding areas.

Measurements of heterotrophic bacteria (Figure 6) clearly confirm a significant deterioration in bacterial water quality downstream of Osijek. This noticeable deterioration is a consequence of inadequate waste water treatment (31).

The results of descriptive statistics are further confirmed by the cluster analysis, which outlined a lack of correlation between total coliform bacteria obtained at the three sampling sites. Taken together,

these results indicate that microbiological contamination is a local (urban) and not a regional or transboundary problem. Therefore, urban wastewaters have a significant influence on the microbiological composition of the Drava River water.

The overall analysis (see Figures 2-6) suggests that some parameters increased at all locations in the post-war period, which is illustrated by longer upper whiskers. This can be a result of both natural variations and accidents, such as a floods, storm waters, or discharge of manure (10).

The Drava River water quality has improved over the 24 years of measurement. However, biological oxygen demand all along the lower Drava and microbiological contamination downstream of Osijek raise concern about urban and industrial wastewater treatment and discharges.

The task at hand of the national and local authorities is to ensure that the Drava meets all Class II requirements for safe human use and consumption. The results of our study point out the specific parameters that need to be addressed in future preventive activities against pollution.

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## **Sažetak**

### **PROMJENE U KVALITETI VODE RIJEKE DRAVE PRIJE I POSLIJE DOMOVINSKOGA RATA**

Cilj ovoga rada bio je procijeniti kvalitetu vode rijeke Drave, klasificirati je i utvrditi postojanje prostornih i vremenskih promjena tijekom perioda od 24 godine. Analizirali smo 13 fizikalno-kemijskih i mikrobioloških parametara vode rijeke Drave na tri mjerne postaje smještene na području donjeg toka Drave (istočna Hrvatska) tijekom dvaju različitih razdoblja: 1985.-1992. (period prije rata) i 1993.-2008. (period poslije rata). Iako su vrijednosti većine podataka prikupljenih tijekom dvaju promatranih razdoblja oscilirale, vrijednosti su im se još uvijek nalazile u granicama za I. i II. vrstu voda. Vrijednosti nekih fizikalno-kemijskih varijabla, kao što su  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$  i  $\text{BPK}_5$  još su uvijek iznad granice za II. vrstu. Rezultati ovog istraživanja pokazali su blago organsko onečišćenje vode rijeke Drave s visokim koncentracijama otopljenog kisika. Povećanje broja ukupnih koliformnih i heterotrofnih bakterija u poslijeratnom razdoblju veliki je problem u području nizvodno od Osijeka pri čemu njihov broj katkad dostiže i vrijednosti za V. skupinu površinskih voda. Rezultati analize kvalitete vode rijeke Drave u dva različita razdoblja na dva mjerna mjesta uzvodno od Osijeka upućuju na tendenciju poboljšanja, iako neki od promatranih parametara pokazuju vrijednosti više od onih za II. skupinu riječnih voda. Različitosti, odnosno sličnosti među mjernim postajama istražene su metodom klusterske analize.

**KLJUČNE RIJEČI:** *fizikalno-kemijski parametri, klusterska analiza, mikrobiološki parametri, organsko zagađenje, riječna voda*

## **CORRESPONDING AUTHOR:**

Vlatka Gvozdić  
Department of Chemistry  
J.J. Strossmayer University  
F. Kuhača 20, 31000 Osijek, Croatia  
E-mail: [vlatka.gvozdic@kemija.unios.hr](mailto:vlatka.gvozdic@kemija.unios.hr)