Water quality of medium size watercourse under baseflow conditions: the case study of river Sutla in Croatia

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Abstract

The study on medium size river Sutla in Croatia indicated considerable water contamination at specific sites during the baseflow period, probably associated to low flow-rate (0.73-68.8 $m^3 s^{-1}$), and consequently low dilution capacity of this river. Various aspects of contamination were observed: increased conductivity to 1000 $\mu S\ cm^{-1}$, decreased dissolved oxygen level to 50%, 4-5°C increased water temperature, increased concentrations of several dissolved trace elements (e.g. maximal values of Li: 45.4 $\mu g\ L^{-1}$; Rb: 10.4 $\mu g\ L^{-1}$; Mo: 20.1 $\mu g\ L^{-1}$; Cd: 0.31 $\mu g\ L^{-1}$; Sn: 30.2 $\mu g\ L^{-1}$; Sb: 11.8 $\mu g\ L^{-1}$; Pb: 1.18 $\mu g\ L^{-1}$; Ti: 1.03 $\mu g\ L^{-1}$; Mn: 261.1 $\mu g\ L^{-1}$; and Fe: 80.5 $\mu g\ L^{-1}$) and macro elements (e.g. maximal values of Na: 107.5 mg L^{-1}; and K: 17.3 mg L^{-1}), as well as moderate or even critical fecal (*E. coli*: 4888 MPN/100 mL; total coliforms: 45307 MPN/100 mL; enterococci: 1303 MPN/100 mL) and organic pollution (heterotrophic bacteria: 94000 *cfu*/mL). Although metal concentrations still have not exceeded the limits considered as hazardous for aquatic life or eventually for human health, the observed prominent increases of both metal concentrations and bacterial counts in the river water should be considered as a warning and incentive to protect the small and medium size rivers from the future deterioration, as recommended by EU Water Framework Directive.

Key words: baseflow; dissolved trace metals; macro elements; microbiological water quality; river Sutla

1. Introduction

European Water Framework Directive (WFD; EPCEU, 2000) defines water as a heritage which must be protected, defended and treated as such. Good water quality will contribute to securing the drinking water supply, as well as provide economic benefits by contributing towards the protection of fish populations and preservation of biodiversity. Therefore, specific measures should be adopted against water pollution by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment (EPCEU, 2000 and 2008). Among the elements needed for the classification of the water ecological status are chemical and physico-chemical elements, such as thermal, nutrient and oxygenation conditions, acidification status, as well as the levels of priority pollutants in the river water, such as Cd, Pb, Hg, Ni and their compounds (EPCEU, 2000).

Although determination of microbiological parameters is no more mandatory for establishing the river water quality status, these parameters were repeatedly proven as very important in monitoring programs (Baumann and Popp, 1991; Kavka et al., 2006). Even when biological and chemical water quality is acceptable, microbiological parameters can indicate serious anthropogenic impact characterized by high bacterial counts. The examination of microbiological river water quality is obligatory for use-related aspects, such as for drinking water production, irrigation or recreation (Kavka et al., 2006). The parameters that are usually tested are heterotrophic bacteria, which commonly correspond to contamination by organic matter (Kohl, 1975) and fecal indicators. Fecal indicators comprise total coliforms, fecal coliforms - predominantly *Escherichia coli*, and intestinal enterococci, which are excreted by humans and warm-blooded animals. They could be introduced into the river water both through untreated and treated wastewaters, because these bacteria pass sewage treatment plants to a great amount and survive for a certain time in the aquatic environment (Kavka and

Poetsch, 2002). Information on fecal pollution in aquatic environments is therefore crucial for watershed management activities in order to maintain safe waters for recreational and economic purposes (Farnleitner et. al., 2001).

According to guidance of WFD (EPCEU, 2000), the significant point and diffuse sources of pollution from urban, industrial, agricultural and other activities should be estimated and identified. Although the assessment of the water quality of small and medium rural watercourses seems to be of local importance, precisely those streams have a vital importance and a critical influence on the life and economy of the regions they flow through. The sources of pollution are usually more scarce and of smaller quantity than for the major urban rivers. However, due to lower flow rate and consequently smaller dilution capacity, especially during the periods of low water discharge, water contamination in such streams could be more pronounced than in the major rivers with high flow rate, despite the fact that major rivers are usually influenced by various pollution sources of larger quantity, such as industry, municipal sewage outlets of big cities, traffic, etc.

As emphasized by Kavka et al. (2006), knowledge on pollution status of the aquatic environments appears essential for decision makers in order to take appropriate measures which result in acceptable river water quality and compliance with national and international quality standards and directives. For this study we have selected a typical rural stream in Croatia, the river Sutla, with the general aim to broaden the existing knowledge on the water contamination of the medium size watercourses. The specific aim was to define the water quality of this river with the reference to European regulations and available literature, as well as to distinguish between the specific point and diffuse sources of pollution, both of anthropogenic and natural origin, such as medium-scale industrial facilities, agricultural activities, municipal sewages, and thermal waters. To achieve this, sampling locations covering the entire course of the Sutla River from its source to the mouth have been examined for a wide range of water quality determinands including physico-chemical parameters, dissolved macro and trace elements, as well as the bacterial counts. Taking in consideration the fact that the problem of low dilution is the most prominent during the baseflow periods, the study was conducted during prolonged period of low water discharge in autumn of 2009.

2. Materials and methods

2.1. Study area and period

Sutla is a 91 km long river flowing through Croatia and Slovenia, mostly forming their state border, with water discharge in the range from 0.73 to 68.8 m^3 s^{-1}. It has the catchment area of 581 km^2, and falls into the category of medium rivers (EPCEU, 2000). It is a left tributary to the Sava River - a major river in Croatia, with water discharge in the range from 78.6 to 2219 m^3 s^{-1}. Furthermore, the river Sutla is situated in the north-western section of Croatia, called Hrvatsko Zagorje, which is rich on thermal springs and baths (Teskeredžić et al., 2009). Eight sampling sites (Fig. 1, Table 1) were selected to enable the assessment of the influence of different anthropogenic pressures on the river water quality. Due to a presence of a known point source of pollution - glass production facility - in a small town Hum na Sutli, the first three sampling sites were chosen on a short stretch of the river flow within this town (upstream, next to and downstream of the plant). The river water was sampled in the period of prolonged low water discharge, from September 14th to October 21st, 2009.

2.2. Physico-chemical and hydrological parameters

Samplings and *in situ* measurements of physico-chemical parameters were conducted simultaneously with samplings for dissolved metal and microbiological analyses (September-October, 2009; Tables 1-3). The river water was sampled in the plastic bottles for the determination of pH (pH-meter MP120, Mettler Toledo) and conductivity (conductivity meter S30 Seven Easy, Mettler Toledo). Measurements of dissolved oxygen (DO) level in the river water and the water temperature were carried out *in situ*, using the portable digital probe (Central Kagaku, Japan). The concentrations of nutrients (ammonium, nitrate, nitrite, total nitrogen and total phosphorus) were determined in the same samples of the river water as bacterial counts. The concentrations of free ammonium (NH_4^+) were determined using SevenGo pro/Ion probe (Mettler Toledo) and electrode DC218-NH4. The concentrations of nitrates (NO_3^-), nitrites (NO_2^-), total nitrogen (N) and total phosphorus (P) were determined using Hach Colorimeter DR/870 according to standard ISO 9001:2000. Nitrates were determined by cadmium reduction method and nitrites by diazotization method (Hach-DR/870, 2004a-b). For the determination of total N and P, the samples were digested using Hach reactor DRB/2000. Total N was determined by oxidative digestion with peroxodisulphate and total P by molybdate method (Hach-DR/870, 2004c-d). The hydrological information (water discharges) for the station Zelenjak (Sutla River) and the station Zagreb (Sava River) were obtained from the Meteorological and Hydrological Service of the Republic of Croatia (Fig. 2; Table 3).

2.3. Determination of dissolved macro and trace elements in the river water

The river water samples were collected in duplicate in the polyethylene plastic bottles (0.25-0.50 L) which were, prior to sampling, rinsed with nitric acid (v/v 10%, *p.a.,* Kemika, Croatia) and Milli-Q water. River water samples were filtered through a cellulose nitrate filter (0.45 μm pore diameter, Sartorius, Germany). The filtrates were acidified with nitric acid

(S*uprapur*, Merck, Germany), and stored at 4°C. Dissolved trace elements (Li, Rb, Cs, Sr, Ba, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Cd, Al, Tl, Sn, Pb, Sb, U, As) were measured directly in filtered river water samples, whereas macro elements (Na, K, Ca, Mg) were measured in 10 times diluted filtered samples, due to their higher concentrations. The measurements of both trace and macro elements were performed on high resolution inductively coupled plasma-mass spectrometer (HR ICP-MS, Element 2, Thermo Finnigan, Germany), equipped with an autosampler ASX 510 (CETAC Technologies, USA). Indium (1 $\mu g\ L^{-1}$; Indium Atomic Spectroscopy Standard Solution, Fluka, Germany) was added to samples as an internal standard (Dautović, 2006). Measurements of ^{7}Li, ^{85}Rb, ^{95}Mo, ^{111}Cd, ^{120}Sn, ^{121}Sb, ^{133}Cs, ^{205}Tl, ^{208}Pb and ^{238}U were operated in low resolution mode, ^{23}Na, ^{24}Mg, ^{27}Al, ^{42}Ca, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{86}Sr and ^{138}Ba in medium resolution mode, whereas ^{39}K and ^{75}As were measured in high resolution mode. The external calibration was performed using standard solutions prepared from multielement stock standard solution for trace elements (100 mg L^{-1}, Analitika, Czech Republic) and for macro elements (Ca 2.0 g L^{-1}; Mg 0.4 g L^{-1}; Na 1.0 g L^{-1}; K 2.0 g L^{-1}; Fluka, Germany) adequately diluted in 5% HNO_3 (S*uprapur*, Merck, Germany). Measurements were also performed in filtration blanks (Milli-Q water filtered and acidified in the same way as the samples of river water). If necessary, the blank corrections of measured trace element concentrations in the river water were made. The limits of quantification (LOQs), based on 10 standard deviations of 10 consecutive measurements of trace elements in the blank sample, are presented in Table 4 (Dautović, 2006). If metal concentrations were below LOQs, half of the LOQ values were used to enable the statistical analyses. The accuracy of metal determination was controlled with 10 times diluted quality control sample for macro elements (QC Minerals, Catalog number 8052, Lot Number 41751-41752, UNEP GEMS, Burlington, Canada) and with the certified river water reference material for trace metals (SLRS-4 - river water from Ottawa River, Ontario, Canada, certified by the National Research Council Canada). The results of quality control are presented in Table 4. A generally good agreement was observed between our data and the certified values.

2.4. Determination of bacterial counts in the river water

Water samples for microbiological analyses were collected in the sterilized plastic bottles (0.5 L) from the subsurface layer of river water (0.5 m). Samples were immediately transported to the laboratory in the refrigerated containers and all bacterial counts (heterotrophic bacteria, total coliform bacteria, *E. coli* and enterococci) were performed in duplicate. Prior to determination of heterotrophic bacterial counts (HPC), water samples were serially diluted using sterile PBS (Phosphate Buffered Saline, Merck, Germany) and inoculated by spread plate method on the Yeast extract agar. Incubation was performed at 22°C for 3-5 days. Thereafter, the colonies were isolated and enumerated, and expressed as CFU mL^{-1} (colony forming units per milliliter; Kapetanović et al., 2009). Total coliform bacteria and *E. coli* were identified using Colilert (IDEXX Laboratories, Inc., Westbrook, USA), a defined substrate technology (Edberg et al., 1990). Enterococci were identified similarly, using Enterolert-E (IDEXX Laboratories, Inc., Westbrook, USA). These methods were shown to correlate well with traditional membrane filtration techniques for the analysis of freshwater samples (Clark et al., 1991; Eckner et al., 1998). Total coliforms, *E. coli* and enterococci were enumerated using the Quantitray2000 (IDEXX Laboratories, Inc., Westbrook, USA), which utilizes a 97-test-well system and provides the most probable number of bacteria per 100 milliliters (MPN / 100 mL).

2.5. Statistical analyses

Statistical analyses were performed using SAS for Windows, SAS 9.1.3 Service Pack 4. One-way ANOVAs were applied to compare the levels of measured parameters at eight different sampling sites, with levels of significance indicated in the figures. If necessary, data were transformed to obtain normal distribution which was confirmed by Shapiro-Wilk or Kolmogorov-Smirnov test:

- original data for pH, DO, NH_4^+, NO_2^-, NO_3^-, total N, total P, Ba, Ca and Sr;
- $\log_{10}$ for conductivity, As, Cr, Cs, Fe, Li, Mg, Mn, Na, Ni, Rb, Sn, U, V, *E. coli*, total coliforms, HPC-22 and enterococci;
- square root for Al;
- inverse of square root for Cd, Cu, Mo and Sb;
- inverse for Co, K, Pb, Ti and Tl.

Post-hoc pair-wise comparisons were made by Tukey's method, with level of significance set at $p<0.05$. The correlation analysis was performed by use of Pearson correlation coefficient.

3. Results and discussion

3.1. Physico-chemical characterization of Sutla River water during the baseflow conditions

During the entire study period water discharges of the Sutla River were rather low (0.83-1.21 $m^3\ s^{-1}$), just slightly above the annual minimum (0.73 $m^3\ s^{-1}$; Table 3). Since approximately 40% of the days in the year 2009 the water discharges were lower than 1.5 $m^3\ s^{-1}$, and as much as 60% of the year they were below 3.0 $m^3\ s^{-1}$ (Fig. 2), the selected study period can be regarded as representative for this watercourse. Based on the pH values in the range from 7.70 to 8.31 (Table 1), Sutla River water during the baseflow period can be classified as 1st category water (GRC, 1998 and 2008). Two distinct sets of sampling sites could be distinguished: upstream sites (1-4) with average pH of 7.85, and downstream sites (5-8) with average pH of 8.21. Although the differences were rather small, they were statistically significant (ANOVA: $p<0.0001$). Similar spatial distribution was obtained for DO (Table 1), and confirmed by positive correlation between DO and pH ($r=0.900$; $p<0.0001$). Rather low DO levels were observed at upstream sites (sites 1-4: average 55%) corresponding to 3rd category water, which was also confirmed by total P level (sites 1-3: >0.25 mg L^{-1}; Table 2). The water quality at downstream sites was much better (1st category based on average DO level of 92%, and 2nd category based on total P level <0.25 mg L^{-1}). The conductivity (Table 1) and the concentrations of NH_4^+, NO_2^-, NO_3^- and total N (Table 2) mainly indicated 1st and 2nd category water. The exceptions were slightly increased conductivity at the site 3, and pronouncedly increased conductivity only at the site 4, amounting to 1010 μS cm^{-1} and corresponding to 4th category water. Similarly, the increased values of NH_4^+, NO_2^-, NO_3^- were obtained at the sites 2-4, and total N at the site 3. Water temperatures (Table 1) were mostly comparable at all sampling sites, ranging from 7-18°C, depending on the sampling date. An exception of 4-5°C higher water temperatures was always observed at the sampling site 3.

3.2. The possible sources of water contamination

The Sutla River, as a tributary of the upper flow of the Sava River, is included in the regular monitoring of the water quality in the Republic of Croatia, with monthly samplings performed at four selected locations (Hrvatske vode, 2009). In accordance with Croatian Directive on Water Classification from 1998 (GRC, 1998), metal analyses referred to total metal levels in the river water, and included Cu, Zn, Pb, Hg, Cr and Ni, whereas the measurements of the dissolved metal concentrations, as suggested by EU WFD (EPCEU, 2000), were performed less frequently. Total concentrations of six selected metals in the river Sutla during 2008 mainly corresponded to 1st and 2nd category water, with exceptions of two locations (Prišlin – located between our sampling sites 3 and 4; Harmica – upstream of our sampling site 7), where Cr and Hg concentrations corresponded to 3rd category water, and Pb to 4th category water (Hrvatske vode, 2009). These results were first warning signs and an indication that systematic investigation is necessary to obtain complete information on water quality of this river. Therefore, following the recommendations of the WFD (EPCEU, 2000), we have collected the data on larger number of dissolved trace metals for the entire course of the Sutla River. Generally, the most pronounced water contamination with metals was observed at the sampling site 4, Donje Brezno, whereas the sampling site 1, Hum na Sutli, was the least contaminated site (Figs. 3-4). Taking in consideration the metal concentrations presented in Figs. 3-4, as well as the results of microbiological (Fig. 5) and physico-chemical analyses (Tables 1-2) of the river water, we have tried to distinguish between different point and diffuse sources of pollution.

3.2.1. Point source water contamination

3.2.1.1. Possible influence of mixed wastewater outlet at the site 4

At the site 4 (Donje Brezno), the increase of conductivity (Table 1), macro elements (Fig. 3), and majority of trace elements (Fig. 4) was observed as a possible sign of the impact of a mixed wastewater and sewage outlet. In addition, comparable concentration increases observed in all four samplings were an indication of constant inflow of contaminants into this medium size stream. This finding was unexpected because during the samplings there was no available information about any point source of pollution at this specific site. Ratios between the average metal concentrations obtained at the site 4 and generally the lowest concentrations obtained at the site 1 (Table 5) pointed to the most prominent increase of Na and K among macro elements, and Sn, Sb, Mo, Cd, Li and Pb among trace elements. The contribution of the sewage outlets to occasional concentration increases of several trace elements in the river water was previously reported by Dautović (2006) (Li, Mo, Cd, Cu and Zn in the river water and Pb, Co and Ni in the sewage itself), by Dragun et al. (2009) (Fe, Mn and Co) and by Alzieu and Michel (1998) (Sn). In the case of macro elements, Dautović et al. (2006) have reported more pronounced increase of Na and K compared to Mg and Ca in the Sava River downstream from the main sewage outlet of the city of Zagreb. The same finding in the Sutla River at the site 4 (Fig. 3) could also point to the household sewage as the source of water contamination. However, there were several counteracting facts. It could be noticed that several parameters were much higher in the Sutla River water at the site 4 than previously reported for the sewage of the city of Zagreb (e.g. Li, Mo, Tl and Sr) and for the river Sava downstream from the sewage outlets (Na and the conductivity) (Dautović, 2006; Dragun et al., 2009). Furthermore, Sutla does not flow nearby any major city which could be capable of producing comparable quantity of wastewater as, for example, the city of Zagreb. As already mentioned, Sutla flows through the geographic area rich on thermal springs (Teskeredžić et al., 2009), and therefore the influence of mineral spring and thermal bath water on the composition of the river water should also be considered. Higher contents of Li, Ba, Mn, Ni, Sr and Tl were recently reported for the mineral waters produced in this area compared to spring and tap water (Fiket et al., 2007). Furthermore, trace levels of Cs accumulate in certain potassium-containing minerals or mineral waters (Hecht, 2004), whereas Rb is also commonly found with Li, K and Cs (Anke and Angelov, 2004). According to Fiket et al. (2007), Li concentration was highly correlated with the concentrations of Na, Ca, K and Mg, and therefore is a good indicator of the overall mineral content of water. All these facts support the possibility of the contribution of mineral water spring or thermal bath discharge to metal concentration increases observed at the site 4. In addition, although bacterial counts showed high variability both between sites and within each site, the common pattern could be recognized for *E. coli*, total coliforms and enterococci. Generally higher counts were found at three sampling sites (2-4), including Donje Brezno (Fig. 5). At these same sites, increased concentrations of NH_4^+, NO_2^- and NO_3^- were also found (Table 2). Nutrients have been shown to play an important role in fecal indicator survival in natural systems (Korhonen and

Martikainen, 1991), probably because high nutrient concentrations prolong the persistence of fecal indicator bacteria or instigate their growth (Findlay et al., 2002). Based on the previous reports that measurement of nutrients, particularly nitrate, and fecal indicator bacteria can aid in distinguishing human versus non-human sources of surface water contamination (Peeler et al., 2006), observed increases of both fecal bacterial counts and nutrient levels at the site 4 can be perceived as a probable sign of the anthropogenic influence on the river water quality. Which specific source is mainly responsible for the river water contamination, whether it is of natural or anthropogenic origin, or a combination of different sources such as household sewage, thermal spring or thermal bath discharge, it remains to be defined and monitored in the forthcoming studies.

3.2.1.2. Possible influence of glass production at the site 3

At the sampling site 3, border crossing Hum na Sutli-Rogatec, the increase of several specific trace elements was observed (Fig. 4). In comparison with the average concentrations of those elements measured at the site 1, the most prominent concentration increase was again observed for Sn (4000 times compared to LOQ), then Mo and Cd (22 and 20 times, respectively), Cr and Ni (7 and 6 times, respectively), and Cu and Mn (4 and 3 times, respectively). Considering that site 3 is situated downstream from the glass production facility, water contamination with certain metals was anticipated. Among listed metals, Sn, which showed the most pronounced increase, could be directly associated with the assumed source of pollution, because tin (IV) oxide has various uses in the glass industry (Anger, 2004). The remaining metals are also commonly used in the glass production, e.g. Mo and Ni in the parts of the machinery (http1; http2: Jacob, 2010), and Cd, Mn and Cr as pigments (Dararutana and Sirikulrat, 2007; Patrick McCray, 1998; http 3). The slight increase of Cu concentration could be possibly connected to waste effusion from cooling systems in which copper sulfate is commonly applied (Momčilović, 2004). It is in agreement with always 4-5°C higher water temperature measured at the site 3 compared to the remaining sites (Table 1), since emissions of water from industrial cooling systems into the river were previously reported to cause slight increase of water temperature (Dimovski and Kozuxarova, 2002). Microbiological quality of the river water at this site was also degraded. In addition to increased counts of fecal indicators, only at this site a substantial increase of the number of heterotrophic bacteria was also found (Fig. 5), which, in the combination with the highest median value of total N at the site 3 (Table 2), pointed to the organic pollution of the river water. It could be also associated to possible influence of cooling water systems, which are ideal incubators for promoting the growth and proliferation of microorganisms. They provide a continuous source of bacteria from makeup water and ambient air, as well as a continuous supply of nutrients, such as inorganic and organic compounds, either from the makeup or added directly to the cooling water to control corrosion, scale or foam (Choudhary, 1998).

3.2.1.3. Possible influence of waste from nearby husbandries at the sites 7 and 8

At the sites 7 and 8, which otherwise could be considered as rather unpolluted sites, marked temporary increase of seven elements was recorded only during one out of four conducted samplings, in mid of October (Fig. 3-4). The comparison of the metal concentrations obtained at October 14th with the average concentrations obtained in three remaining samplings within the same site revealed 14-17 times increased concentrations of Ti and Cr, and 2-4 times increased concentrations of Co, Cu, Rb, K and V. The presence of corn fields in the immediate vicinity of the last two sampling sites indicated that temporary concentration increases of specific metals could be the consequence of sporadic emissions or leaching of the waste manure in the river water. It can be further corroborated by the fact that K_2O, copper sulfate, Co and Ti are commonly used ingredients in fertilizers (Anke, 2004b; Momčilović, 2004; Schrauzer, 2004; Anke and Seifert, 2004), whereas some of the metals which were found increased are common contaminants of NPK fertilizers, e.g. V and Rb (Vachirapatama et al., 2002; Senesi et al., 1983). The number of enterococci in the river water at the sites 7 and 8 was also appreciably increased at October 14th (approximately 50 times; Fig. 5), as well as the concentrations of total N (1.12 mg L^{-1}) and total P (0.48 mg L^{-1}; Table 2). Agriculture is a major source of phosphorus, nitrogen and enterococci to aquatic ecosystems (Carpenter et al., 1998; Lata et al., 2009). Increased number of enterococci, which indicate the presence of feces from warm blooded animals in the water (http 5), in conjunction with the described prominent increases of specific trace element, macro element and nutrient levels in the river water, supported the assumption that nearby husbandries influence the river water quality.

3.2.2. Diffuse source water contamination

At four upstream sampling sites, both pH and DO were significantly lower compared to downstream sites (Table 1). A high organic content, confirmed by increase of total P level (Table 2), or high microbial activity (Fig. 5), as observed at upstream sites of the river Sutla, will tend to decrease pH. As microorganisms break down organic material, oxygen will be consumed out of the water and the produced CO_2 will dissolve and equilibrate with water forming carbonic acid and causing the lowering of the pH value (Bellingham, http 4). At downstream sites (Fig. 4), i.e. at the sites with higher oxygen saturation, the decrease of Mn and increase of U concentrations was observed. It can be explained by the fact that under highly oxygenated conditions Mn is mainly present in the water in the form of insoluble oxides, such as MnO_2 (Förstner and Wittmann, 1979; Stumm and Morgan, 1981), whereas U(VI), present under oxic conditions, is much more soluble than U(IV), present under anoxic conditions (Melo and Burkart, 2004). In addition, at the pH around 7, such as measured in our study, Sachs et al. (2007) reported significant formation of uranium complexes with humic substances, which are abundant organic ligands of natural origin, and made up approximately 60% of the carbon dissolved in aquatic systems (Peña-Méndez et al., 2005). As a consequence of the increased use of fertilizers in the modern agriculture, additional input of humic substances into the river water can occur due to their use as additives to fertilizers (Peña-Méndez et al., 2005), which could resulted in uranium complexation and further concentration increase in the river water at agriculturally impacted downstream sites. Fertiliziers can also be a source for the accumulation of potential mineral contaminants, such as Ba and Sr, in the upper layer of cultivated soils (Senesi et al., 1983). This is in agreement with generally higher concentrations of Ba, Sr and V observed at downstream sampling sites in the river Sutla (Fig. 4). Therefore, there is a possibility that slight increase of several elements towards downstream sites could be associated to more developed agricultural activity, i.e. leaching of both humic substances and specific metals from the soil, whereas the results collected at the upstream sites implied diffuse non-specific organic pollution.

3.3. Comparison with other rivers and European regulations

3.3.1. Macro and trace elements

The concentrations of macro and trace elements measured at the least and at the most contaminated sites of the Sutla River (site 1 and site 4, respectively) were at first compared with the concentrations previously reported for two rivers in Croatia, pristine river Una and urban and industrially impacted river Sava (Dautović, 2006; Table 5). Despite the known anthropogenic influences, even the concentrations of dissolved trace metals in the Sava River water were defined as not significantly above the natural level (Dautović, 2006; Dragun et al., 2009). The concentrations of trace and macro elements in the Sutla River at the site 1 were mainly between the levels reported for the rivers Una and Sava, and thus the site 1 could be regarded as the reference site, with baseline metal levels. Contrary, the metal concentrations measured in the river Sutla at the site 4 were mostly manifold higher even compared to the river Sava. Considering that the Sava River has 100-200 times higher water discharges than the Sutla River (Table 3), it is more probably the consequence of higher dilution capacity of the Sava River than of the higher input of contaminants into the Sutla River water. To put the results in broader perspective, we have carried out the comparison with several world rivers (Table 5). As the results presented here for the river Sutla correspond to period of baseflow, the comparison with baseflow metal concentrations in differently contaminated rivers of comparable water discharges to Sutla seemed appropriate (rivers Tweed, Great Ouse and Wear in UK; Neal and Robson, 2000). The macro and trace element concentrations at the contaminated site 4 of the river Sutla were mainly in the line with the concentrations reported for agriculturally impacted river. The exception were somewhat higher Fe and Mn levels, comparable to industrially impacted river, whereas several metals (Mo, Pb, Sb and Sn) exceeded even those concentrations, 3-10 times. To obtain the more complete insight in the possible river water contamination, comparison was further made with the metal concentrations reported for both pristine and highly contaminated rivers, even though they have much higher discharges than Sutla. The site 1 was again proved as a good reference site, due to metal levels comparable even to pristine river Lena (Martin et al., 1993), which has average discharge of 17000 $m^3 s^{-1}$, and therefore also very high dilution capacity. Although the contaminated site 4 had somewhat higher concentrations of several metals, especially Cd and Pb, compared to agriculturally impacted Yamaska River in Canada (Cooper and Fortin, 2010), its metal concentrations were still far below metal levels reported for highly contaminated rivers, such as Nanyang River in China contaminated by electronic waste (Wong et al., 2007), or mining impacted rivers like Luda Yana in Bulgaria (Rabadjieva et al., 2009).

The highest metal concentrations were often reported at baseflows, i.e. a slight flow dilution is most common, usually at sites where concentrations are relatively high, like the sites influenced by point sources of pollution, such as industrial and sewer outlets (Robson and Neal, 1997; Sherrell and Ross, 1999). Therefore, it could be presumed that high metal concentrations measured in the river Sutla at the sites impacted by point sources, would be diluted during the periods of increased water discharge in the rainy part of the year. However, the increase of metal concentrations in the river water at high discharge is also possible, since metals can be flushed from soils into streams (Sherrell and Ross, 1999), e.g. in the areas with more developed agriculture. Therefore, it is important to characterize the contamination of the river water both during the periods of low and high flow, taking in consideration the specificity of the land use, geological characteristics and the characteristics of the pollution sources. Still, the baseflow levels of total dissolved metals and other contaminants in the Sutla River water present relevant information even on their own, considering that aquatic organisms in the Sutla River water are exposed to the conditions of the baseflow during two thirds of the year (Fig. 2). However, since total dissolved metal levels also comprise the colloidal fraction, which passes through standard 0.45 μm filter, and which contribution to total dissolved level can be different for each metal, they are not regarded as fully bioavailable. Therefore, it would be of great importance to additionally evaluate the baseflow metal exposure of aquatic organisms, for example by analysis of metals accumulated in specific fish tissues.

Finally, the comparison with European regulations revealed that even the concentrations of dissolved Cd, Pb, Ni and Cu measured at the contaminated site 4 were considerably lower than acceptable annual average (AA) values defined in the environmental quality standards (EQS) for total dissolved metals in the inland surface water (Table 5; Crane et al., 2007;

EPCEU, 2008). Since EQS were not set for the remaining metals, several other elements found in notably increased concentrations at specific sites of the Sutla River were compared to currently available literature:

- *Sn*: in natural freshwaters inorganic Sn is present in the concentrations below 10 ng L^{-1}, but may reach 1 μg L^{-1} in certain polluted areas (Alzieu and Michel, 1998); Sn concentrations measured in the river Sutla, downstream from the glass production facility, occasionally reached even 10-30 μg L^{-1} indicating considerable water contamination with this metal; however, if Sn is present in the water in the inorganic form it does not appear to accumulate in the living organisms due to its low solubility (Anger, 2004);
- *Sb* concentrations may measure only a few ng L^{-1} in unpolluted waters, whereas in industrial areas they may increase by a factor of thousand (Filella et al., 2002); Sb concentrations of 3-12 μg L^{-1} measured at site 4 are comparable with industrially impacted rivers, such as the River Thames (0.15-38 μg L^{-1}; Neal et al., 2000); considering that Sb is defined as a pollutant of priority interest by USEPA (1999a), it is also convenient to point out that maximal Sb concentrations measured in the river Sutla occasionally exceeded the USEPA (1999b) and EU (1998) regulations for drinking waters (6 and 5 μg L^{-1}, respectively);
- *Mo* concentration in drinking water varies in the range from <0.5 to >30 μg L^{-1}, whereas near industrial sources Mo concentrations may reach 200-400 μg L^{-1} in the surface water (Anke, 2004a); since Mo is an essential component of the animal enzymes (Anke, 2004a), and its concentrations in the river Sutla were always below 25 μg L^{-1}, observed increases of Mo concentrations at the specific sites could not be considered as troublesome;
- *As* concentrations in unpolluted freshwaters commonly range from 1 to 10 μg L^{-1} (Mandal and Suzuki, 2002); even the highest As concentrations measured in the river Sutla fell within this range;

- *Rb*: the highest Rb concentration measured in the river Sutla of 10 μg L^{-1} was comparable with mean Rb concentration in drinking water in Germany (11 μg L^{-1}; Anke et al., 1997);
- *Sr*: maximal Sr concentration measured in our study (~0.50 mg L^{-1}) was within the range reported for Canadian drinking water, which amounted to 0.19-3.20 mg L^{-1} (Skoryna, 1981).

3.3.2. Bacterial counts

The microbiological quality of the Sutla River was compared to the river Sava (within Black Sea drainage basin) as a river under strong anthropogenic influence, and the river Krka (within Adriatic drainage basin) as a representative of relatively unpolluted watercourses (Table 6; Kapetanović et al., 2009; Kapetanović, unpublished results). For this comparison, the sampling sites incorporated in this study were divided into two groups: the contaminated sites (sites 2-4 for *fecal bacteria*; site 3 for HPC) and the remaining sites with 10-30 times lower bacterial counts. Comparison with the Krka River revealed the slight fecal contamination along the entire stretch of the Sutla River flow, since not only the contaminated but also the remaining sites usually had higher fecal indicators than reported for Krka. At contaminated Sutla River sites, the bacterial counts were as much as 30-500 times higher than in the unpolluted Krka River, depending on the parameter. On the other hand, the anthropogenic pressure on the Sutla River was still less prominent than on the Sava River. Only the contaminated Sutla River sites had approximately 5-10 times higher bacterial counts compared to the main stream of the river Sava (from Otok Samoborski to Jasenovac), but still 2-15 times below the number obtained in the Sava River at the sites downstream from the municipal sewage outlets. The exception was the number of heterotrophic bacteria, which was unambiguously the highest at the sampling site 3 of the Sutla River (Fig. 5). Comparison with standards and directives for bathing water quality (Kohl, 1975; Kavka and Poetsch, 2002; CEC, 1976; and EPCEU, 2006) indicated critical fecal and organic pollution at contaminated

Sutla River sites, whereas even the remaining Sutla River sites showed moderate fecal and organic pollution.

4. Conclusions

A comprehensive study conducted on the Sutla River in Croatia during the baseflow conditions indicated that combination of various water analyses facilitates the detection of different pollution sources. The influence of several point sources on the river water quality, such as medium industrial facility, household or thermal bath discharges, as well as diffuse source water contamination by agricultural runoff were recognized along the watercourse. Since the water discharge and dilution capacity of this river are rather low, especially during the baseflow which intermittently lasts approximately two thirds of the year, the point sources causing the water contamination should be well characterized and continuously monitored to prevent more serious pollution. The presented results emphasize the incidence of increased water contamination in the rivers with low dilution capacity, even under moderate anthropogenic influence. This is a problem of general significance, since it may be equally represented in any small or medium watercourse in the world.

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Figure captions

Figure 1. The map of the Sutla River with marked sampling sites.

Figure 2. The Sutla River water discharges (m^3 s^{-1}) for the period from January 1st to December 31st 2009.

Figure 3. The concentrations (mg L^{-1}) of dissolved macro elements (Na, K, Ca, Mg) in the Sutla River water at eight sampling sites. The results are presented as box-plots whose boundaries indicate 25th and 75th percentiles; a square within the box marks the median value; whiskers above and below the box indicate the non-outlier minimum and maximum. The statistically significant differences between sites according to ANOVA (levels of significance indicated in the figure) followed by *post-hoc* Tukey's test ($p<0.05$) are indicated by different letters.

Figure 4. The concentrations (µg L^{-1}) of dissolved trace elements (Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V) in the Sutla River water at eight sampling sites. The results are presented as in the Figure 3.

Figure 5. The counts of indicator microbes in the Sutla River water at eight sampling sites: *Escherichia coli* (MPN / 100 mL), total coliforms (MPN / 100 mL); enterococci (MPN / 100 mL), and heterotrophic bacteria (HPC). The results are presented as in the Figure 3. *MPN*: the most probable number; *cfu*: colony forming units.

Table 1. The list of sampling sites with coordinates, number of samplings per site (n), and physico-chemical parameters of the river water measured in September-October period of 2009 (average ± standard deviation).

Sampling site	Site coordinates	n	pH	Dissolved oxygen / %	Conductivity / $\mu S\ cm^{-1}$	Water temperature / °C
1 - Hum na Sutli	N 46° 13,339' E 15° 43,187'	4	7.85±0.06	56.3±14.3	497.9±36.2	12.9±5.0
2 - Hum na Sutli: glass production facility	-	3	7.84±0.13	56.0±22.1	523.0±62.7	11.4±4.6
3 - Hum na Sutli-Rogatec: state border crossing	-	[a]3-4	7.82±0.03	60.4±9.0	694.0±103.5	16.2±4.0
4 - Donje Brezno	N 46° 11,532' E 15° 39,269'	4	7.88±0.05	48.2±6.8	1010.4±145.5	13.3±4.1
5 - Kumrovec	N 46° 04,377' E 15° 40,562'	4	8.23±0.05	91.8±9.5	604.9±28.8	13.2±4.2
6 - Klanjec	N 46° 02,728' E 15° 44,237'	4	8.19±0.04	91.9±3.7	596.9±34.1	13.0±4.6
7 - Ključ Brdovečki	N 45° 52,433' E 15° 41,426'	4	8.19±0.06	83.8±11.6	610.5±40.7	12.8±4.8
8 - Drenje Brdovečko	N 45° 52,133' E 15° 41,768'	4	8.24±0.06	98.5±16.7	612.3±45.9	14.2±4.6

[a] three samplings for physico-chemical parameters and microbiological analyses, and four for dissolved metal analyses

Table 2. The concentrations of nutrients at eight selected sites in the Sutla River water during September-October, 2009 (medians, with minimum and maximum values in the bracketts).

Sampling site	n	$^{**}NH_4^+$ / mg N L^{-1}	NO_2^- / mg N L^{-1}	$^{*}NO_3^-$ / mg N L^{-1}	Total N / mg N L^{-1}	Total P / mg P L^{-1}
1 - Hum na Sutli	4	0.045 (0.031-0.054)	0.002 (0.000-0.003)	0.015 (0.000-0.070)	0.10 (0.00-1.30)	0.29 (0.20-0.41)
2 - Hum na Sutli: glass production facility	3	0.086 (0.070-0.094)	0.026 (0.013-0.092)	0.040 (0.030-0.100)	0.60 (0.20-0.60)	0.37 (0.21-0.39)
3 - Hum na Sutli-Rogatec: state border crossing	3	0.072 (0.067-0.105)	0.003 (0.001-0.104)	0.020 (0.020-0.060)	1.40 (0.90-1.50)	0.27 (0.16-0.34)
4 - Donje Brezno	4	0.105 (0.071-0.120)	0.013 (0.002-0.087)	0.075 (0.020-0.120)	0.65 (0.20-1.40)	0.22 (0.03-0.39)
5 - Kumrovec	4	0.056 (0.020-0.080)	0.006 (0.000-0.014)	0.010 (0.000-0.050)	0.85 (0.00-2.50)	0.17 (0.04-0.30)
6 - Klanjec	4	0.042 (0.033-0.051)	0.005 (0.000-0.007)	0.010 (0.000-0.010)	0.15 (0.00-3.20)	0.19 (0.09-0.25)
7 - Ključ Brdovečki	4	0.035 (0.020-0.060)	0.001 (0.000-0.004)	0.020 (0.000-0.060)	0.05 (0.00-1.12)	0.18 (0.09-0.47)
8 - Drenje Brdovečko	4	0.046 (0.034-0.051)	0.001 (0.000-0.024)	0.015 (0.000-0.030)	0.60 (0.000-1.11)	0.20 (0.05-0.48)

* statistically significant differences between sites ($p<0.05$)
** statistically significant differences between sites ($p<0.0001$)
n - number of samplings per site

Table 3. Hydrological information for the rivers Sutla and Sava in the September-October period of 2009: water discharge ($m^3\ s^{-1}$).

Date	Sutla - Zelenjak	Sava - Zagreb
September 14th	0.879	106
September 15th	0.984	156
September 16th	0.984	235
October 9th	0.829	87.0
October 14th	1.21	152
October 21st	0.879	88.5
Annual minimum	**0.733**	**78.6**
Annual maximum	**68.8**	**2219**

Table 4. The HR ICP-MS method quality control was performed using 10 times diluted quality control sample for macro elements (QC Minerals, Catalog number 8052, Lot Number 41751-41752, UNEP GEMS, Burlington, Canada) and the certified reference material SLRS-4 (river water from Ottawa River, Ontario, Canada, distributed by the National Research Council Canada). The average values and standard deviations are based on 2 and 4 independent measurements, respectively, performed simultaneously with the metal determination in the river water samples. Limits of the quantification (LOQ) are also presented in this table.

Certified reference material	Metal	LOQ μg L^{-1}	Certified values μg L^{-1}	Measured values μg L^{-1}
QC Minerals (10 times diluted)	Na	-	3310±71.8	3791±54.1
	K	-	837±3.69	889±38.3
	Ca	-	2410±18.9	2665±15.0
	Mg	-	234±1.26	257±7.3
SLRS-4	Li	0.033	-	-
	Rb	-	-	-
	Cs	-	-	-
	Sr	0.067	26.3±3.2	27.2±2.7
	Ba	0.067	12.2±0.6	12.0±1.2
	Ti	0.067	-	-
	V	0.007	0.32±0.03	0.32±0.06
	Cr	0.017	0.33±0.02	0.29±0.03
	Mo	0.067	0.21±0.02	0.19±0.02
	Mn	0.033	3.37±0.18	3.20±0.39
	Fe	0.333	103±5	103±8.2
	Co	0.003	0.033±0.006	0.034±0.002
	Ni	0.067	0.67±0.08	0.59±0.06
	Cu	0.033	1.81±0.08	1.75±0.21
	Cd	0.003	0.012±0.002	0.016±0.003
	Al	0.333	54±4	50.6±10.4
	Tl	0.007	-	-
	Sn	0.003	-	-
	Pb	0.067	-	-
	Sb	-	-	-
	U	0.003	0.050±0.003	0.055±0.009
	As	0.017	0.68±0.06	0.85±0.08

Table 5. The comparison of average macro (Na, Mg, Ca and K) and trace element concentrations measured in the river Sutla at the least and the most contaminated sites (Hum na Sutli (site 1) and Donje Brezno (site 4), respectively) with the concentrations reported for the rivers in Croatia, several differently polluted world rivers, and the environmental quality standards (EQS) proposed by EU WFD.

		Na	Mg	Ca	K	Li	Rb	Cs	Sr	Ba	Ti	V	Cr	Mo
		mg L^{-1}				µg L^{-1}								
Sutla - site 1	this study	11.3	18.6	58.8	3.79	1.96	2.38	0.002	216.1	18.8	<LOQ	0.18	<LOQ	0.55
Sutla - site 4	this study	88.3	27.1	77.3	13.4	34.2	9.63	0.110	417.8	37.1	0.099	0.72	0.27	11.96
	[a]Ratio, site 4:site 1	**7.8**	**1.5**	**1.3**	**3.5**	**17.4**	**4.0**	**73.3**	**1.9**	**2.0**	**1.5**	**4.0**	**15.9**	**21.7**
Rivers in Croatia														
Una, Croatia	pristine river; Q_{av}: 221 m^3 s^{-1} (Dautović, 2006)	2.12	9.3	73.9	0.40	0.36	-	-	125.0	8.74	0.018	0.55	0.15	0.49
Sava, Croatia	urban, industrially impacted river; Q_{av}: 255 m^3 s^{-1} (Dautović, 2006)	10.6	19.5	91.1	3.20	1.16	-	-	128.0	21.4	0.153	0.54	0.59	0.81
World rivers														
Lena, Russia	pristine river; Q_{av}: 17000 m^3 s^{-1} (Martin et al., 1993)	-	-	-	-	-	-	-	-	-	-	-	-	-
Tweed-Teviot, UK	rural river; at low flow: 2.32 m^3 s^{-1} (Neal and Robson, 2000)	16.1	17.04	41.1	2.15	4.0	1.52	-	166.4	123.3	-	-	0.349	0.33
Great Ouse, UK	agriculturally impacted river; at low flow: 1.53 m^3 s^{-1} (Neal and Robson, 2000)	81.0	8.76	124.0	14.36	14.2	7.57	-	499.5	18.7	-	-	0.346	2.39
Yamaska, Canada	agriculturally impacted river; Q_{av}: 83 m^3 s^{-1} (Cooper and Fortin, 2010)	29	14.4	62	5.8	-	-	-	-	-	-	-	-	-
Wear, UK	industrially impacted river; at low flow: 1.98 m^3 s^{-1} (Neal and Robson, 2000)	105.9	35.06	80.7	12.28	197.9	35.71	-	748.6	60.3	-	-	0.550	0.90
Nanyang, China	impact of electronic waste (Wong et al., 2007)	-	2.65	18.7	-	3.22	-	-	196	-	161	1.26	1.21	1.75
Luda Yana, Bulgaria	influence of copper mine; at low flow (Rabadjieva et al., 2009)	5	16.8	29	3.5	-	-	-	-	-	-	-	-	-
EQS	(CEC, 2006; *Crane et al., 2007)	-	-	-	-	-	-	-	-	-	-	-	-	-

[a] for metal concentrations which were below LOQs at the site 1, the ratios were calculated relative to LOQs

Table 5. continued

	Mn	Fe	Co	Ni	Cu	Cd	Al	Tl	Sn	Pb	Sb	U	As
							μg L^{-1}						
Sutla - site 1	17.1	36.7	0.068	0.45	0.49	0.007	2.12	<LOQ	<LOQ	<LOQ	0.082	0.55	0.79
Sutla - site 4	51.5	51.8	0.347	1.86	0.93	0.117	7.27	0.028	1.60	0.901	6.47	0.79	3.83
[a]Ratio, site 4:site 1	**3.0**	**1.4**	**5.1**	**4.1**	**1.9**	**16.7**	**3.4**	**4.0**	**533.3**	**13.4**	**78.9**	**1.5**	**4.8**
Rivers in Croatia													
Una, Croatia	1.64	1.63	0.016	0.14	0.10	0.005	1.33	0.005	-	0.077	-	0.57	0.17
Sava, Croatia	8.72	14.1	0.068	0.56	1.27	0.015	6.66	0.005	-	0.045	-	0.70	0.41
World rivers													
Lena, Russia	-	24	-	0.38	0.76	0.006	-	-	-	0.019	-	-	-
Tweed-Teviot, UK	6.2	10.0	0.150	1.35	5.98	-	7.02	-	0.212	0.217	0.134	0.630	0.72
Great Ouse, UK	2.3	27.2	0.696	5.95	5.06	-	3.60	-	0.234	0.316	0.666	0.560	2.41
Yamaska, Canada	50	30	-	1.69	2.2	0.012	40	-	-	0.14	-	-	0.75
Wear, UK	79.9	48.6	1.050	4.75	2.71	-	3.74	-	0.162	0.292	0.488	0.450	0.73
Nanyang, China	199	318	3.62	52.4	50.8	0.315	510	-	-	1.81	18.7	-	4.74
Luda Yana, Bulgaria	100	1010	-	-	8780	103	-	-	-	1680	-	-	-
EQS	-	-	-	20.0	8.2*	0.150	-	-	-	7.2	-	-	-

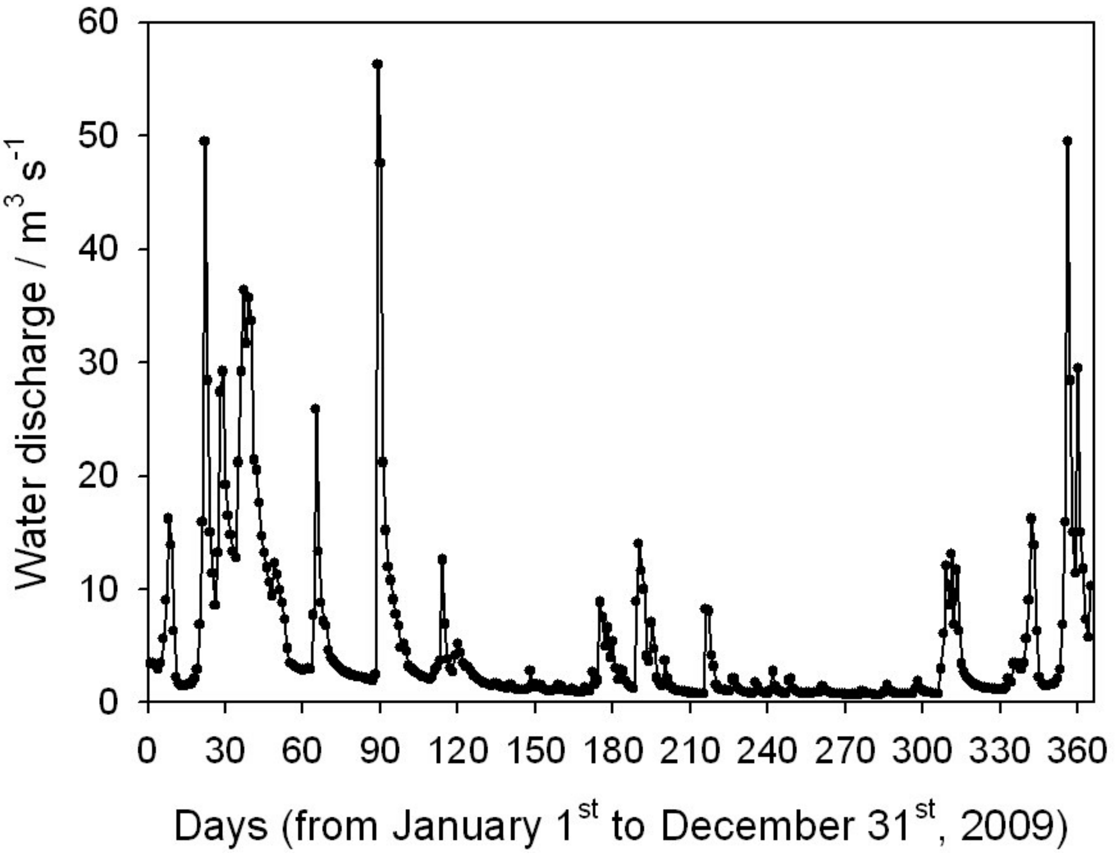
[a] for metal concentrations which were below LOQs at the site 1, the ratios were calculated relative to LOQs

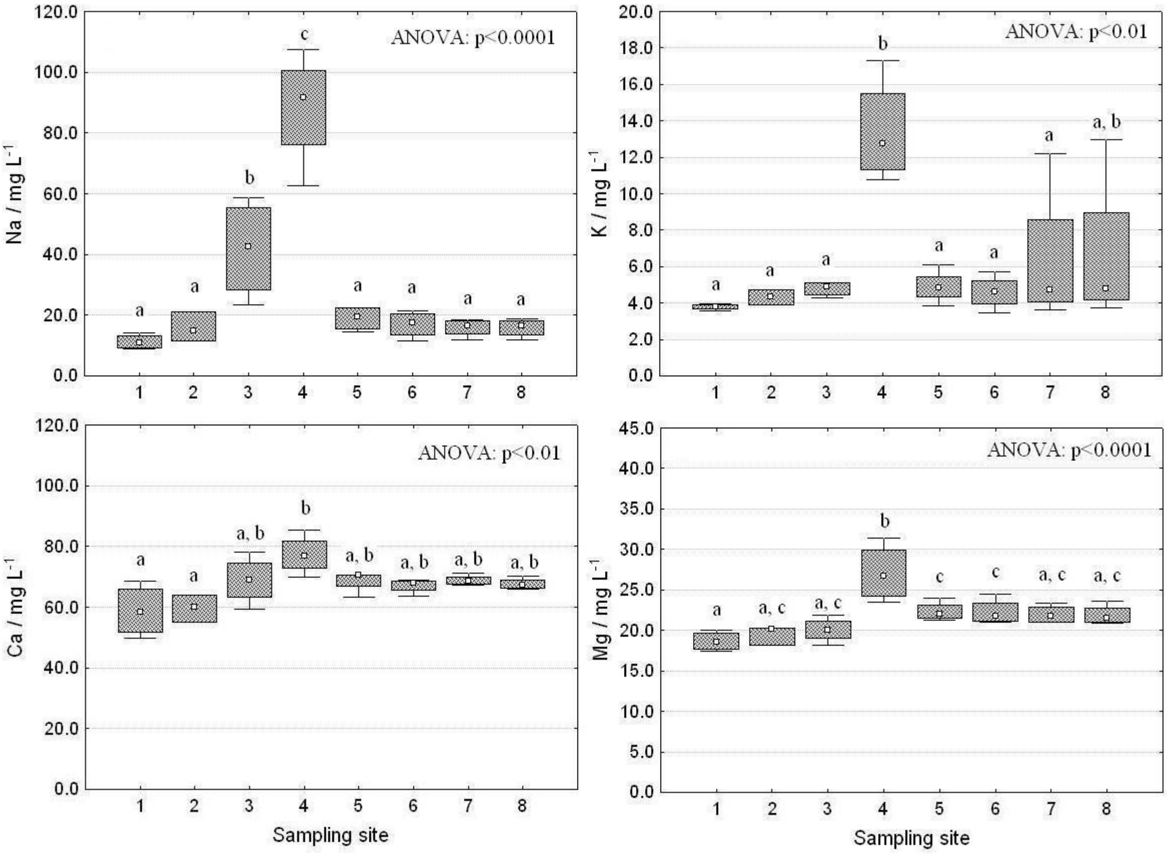
Table 6. The comparison of microbiological quality of the river Sutla with the data reported for the river Sava and river Krka (medians).

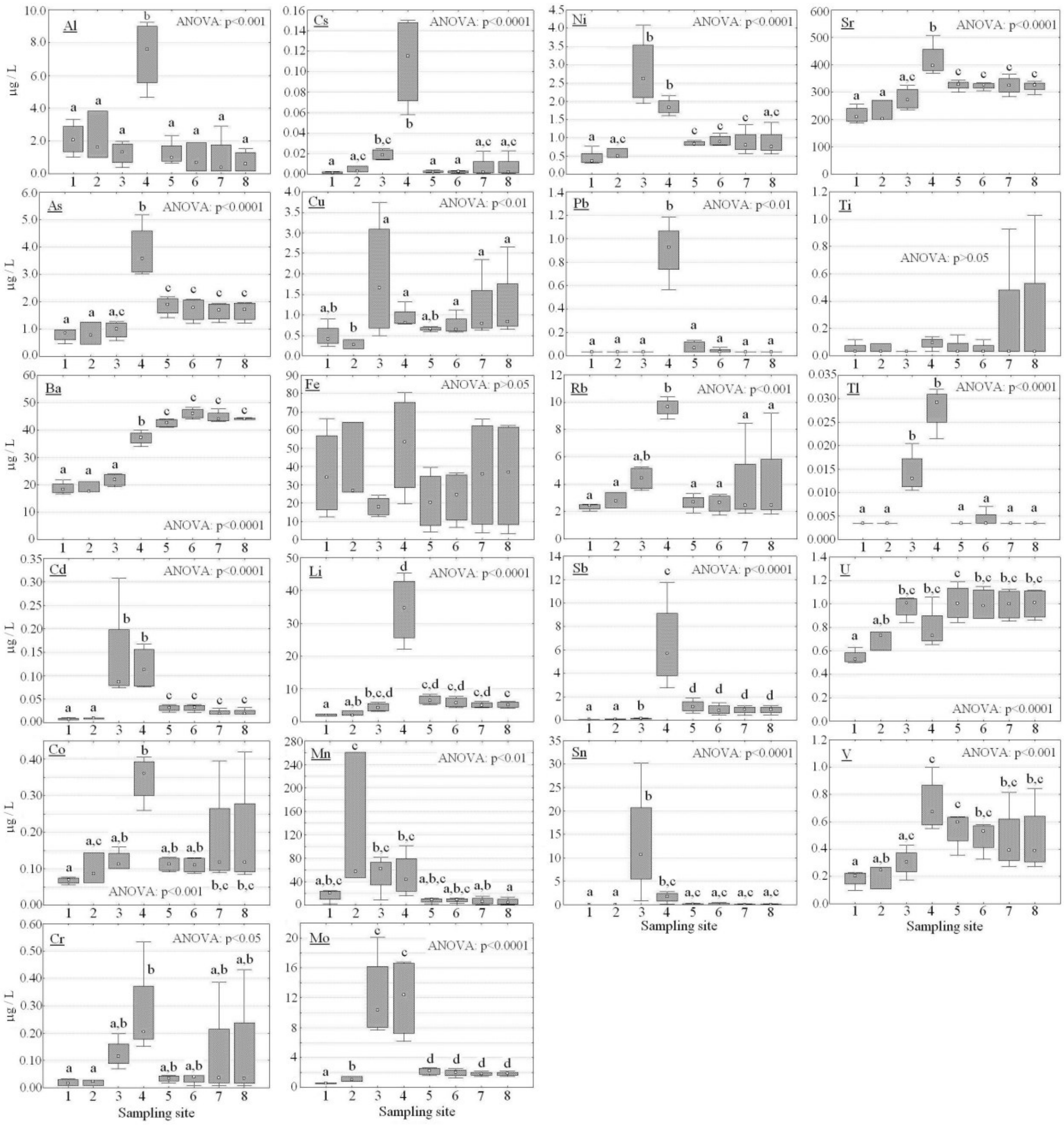
River	E. coli *MPN / 100 mL*	Total coliforms *MPN / 100 mL*	Enterococci *MPN / 100 mL*	HPC *cfu / mL*
[a]Krka	10	1017	20	3050
[b]Sutla – contaminated sites	4888	45307	1303	94000
[c]Sutla – remaining sites	439	2427	66	3500
[d]Sava – sites directly affected by municipal sewage outlet	29790	666810	2530	35000
[e]Sava – main stream	995	13870	100	8717

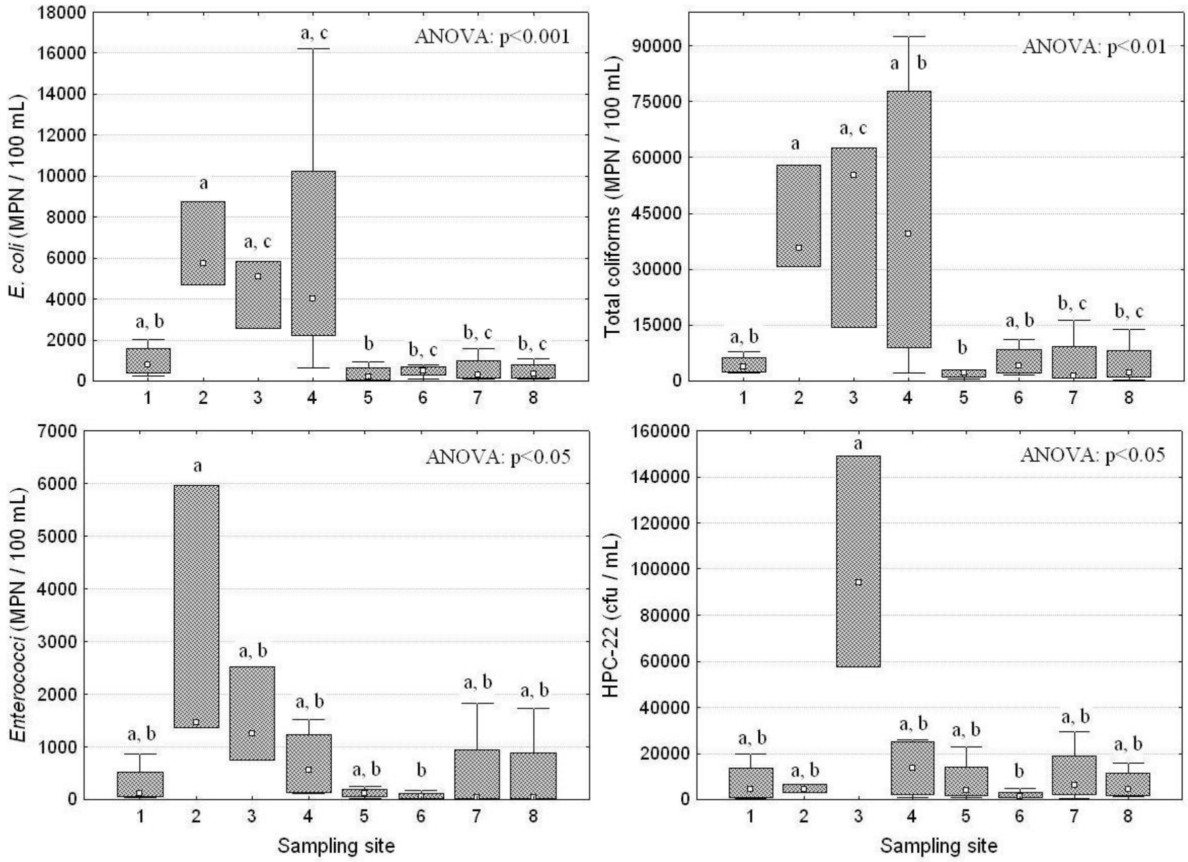
[a] number of bacteria counted along the whole stretch of the river Krka in the autumn 2006 (Kapetanović et al., 2009 and unpublished results)
[b] number of bacteria counted in the river Sutla in this study at the sampling sites 2-4, with the exception of HPC which refer only to the sampling site 3
[c] number of bacteria counted in the river Sutla in this study at the remaining sampling sites
[d] number of bacteria counted in the river Sava at the sites affected by municipal sewage outlets of cities Zagreb and Velika Gorica in spring 2006 (Kapetanović et al., 2009 and unpublished results)
[e] number of bacteria counted in the river Sava at several other sites without direct influence of point sources of pollution in spring 2006 (Kapetanović et al., 2009 and unpublished results)


Rogatec
3 2 1
Rogaška
Slatina
Hum
4 Donje
Brezno
river Sutla
5 Kumrovec
Klanjec
6
SLOVENIA
CROATIA
river Sutla
Ključ Brdovečki
river Sava
7
8 Drenje
Brdovečko
river Sava
Zagreb
14.5 km


Water discharge / m3 s-1
60
50
40
30
20
10
0
0 30 60 90 120 150 180 210 240 270 300 330 360
Days (from January 1st to December 31st, 2009)


ANOVA: p<0.0001
Na / mg L-1
ANOVA: p<0.01
K / mg L-1
ANOVA: p<0.01
Ca / mg L-1
ANOVA: p<0.0001
Mg / mg L-1
Sampling site
Sampling site


Al ANOVA: p<0.001
Cs ANOVA: p<0.0001
Ni ANOVA: p<0.0001
Sr ANOVA: p<0.0001
As ANOVA: p<0.0001
Cu ANOVA: p<0.01
Pb ANOVA: p<0.01
Ti ANOVA: p>0.05
Ba ANOVA: p<0.0001
Fe ANOVA: p>0.05
Rb ANOVA: p<0.001
Tl ANOVA: p<0.0001
Cd ANOVA: p<0.0001
Li ANOVA: p<0.0001
Sb ANOVA: p<0.0001
U ANOVA: p<0.0001
Co ANOVA: p<0.001
Mn ANOVA: p<0.01
Sn ANOVA: p<0.0001
V ANOVA: p<0.001
Cr ANOVA: p<0.05
Mo ANOVA: p<0.0001
µg / L
Sampling site


ANOVA: p<0.001
E. coli (MPN / 100 mL)
ANOVA: p<0.01
Total coliforms (MPN / 100 mL)
ANOVA: p<0.05
Enterococci (MPN / 100 mL)
ANOVA: p<0.05
HPC-22 (cfu / mL)
Sampling site
Sampling site