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Preliminary assessment of total dissolved trace metal concentrations in Sava River water

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Abstract

This study provides the preliminary data set for total dissolved trace metal concentrations in the surface water of the Sava River in Croatia, and the assessment of Sava River water quality status. The highest levels of total dissolved metals were observed for Fe, Mn and Zn (12.6 ± 7.8 μg L^{-1}, 3.44 ± 3.95 μg L^{-1}, and 2.27 ± 1.53 μg L^{-1}, respectively), the intermediate concentrations for Ni, Cu and Cr (0.59 ± 0.14 μg L^{-1}, 0.54 ± 0.14 μg L^{-1}, and 0.32 ± 0.06 μg L^{-1}, respectively), and the lowest levels for Co, Pb and Cd (0.064 ± 0.022 μg L^{-1}, 0.055 ± 0.051 μg L^{-1} and 0.011 ± 0.004 μg L^{-1}, respectively). The results refer to the grab water samples taken at five sites in the period from March to June, 2006. For four trace metals (Mn, Pb, Zn and Fe) the high temporal variability within one season was observed. It can present a problem for reliable evaluation of total dissolved concentrations of these metals in the river water, if the assessment is based on the occasional grab water sampling. The comparison of results obtained in this study with previously reported data for several unpolluted rivers indicated that Sava River water reflects a certain anthropogenic impact. However, according to the levels proposed by European regulations, it still can be classified as water containing total dissolved trace metals in concentrations not significantly above the natural level.

Key words: metals, dissolved fraction, Sava River, water, regulations

1. Introduction

A large number of metals are present in the environment as a result of human activities (e.g. industries, agriculture, mining, transport, oil spills). Because of the metal toxicity, persistence and bioaccumulation, metal contamination is of major concern in many industrialized countries. In the aquatic environment, metals may be present in different forms, as ions, simple inorganic complexes, complexes with organic macromolecules (e.g. humic substances), as well as in the form of the metals adsorbed on the surface or within microorganisms and suspended matter (Buffle *et al.*, 1997). The most common categorization of metals in water is based on separation into dissolved and particulate metal fractions. The fraction collected by the 0.45 μm filter is termed as particulate, while the fraction that passes through this filter is conventionally defined as dissolved (INAP, 2002). The dissolved fraction comprises the free metal ions, labile inorganic and organic complexes, as well as inert high molecular organic metal complexes and colloids. It is commonly accepted that the concentrations of trace metals in surface water, which are available to aquatic organisms, are lower than the total concentrations of those metals (Cleven *et al.*, 2005). The biological response is very often proportional to the labile metal concentrations (Campbell, 1995), which are therefore usually regarded as bioavailable metal concentrations.

In the course of the European Union Sixth Framework Programme project (SARIB project, INCO-CT-2004-509160), the bioavailable metal levels were measured in the surface water of River Sava, an important European watercourse and the largest tributary of the Danube River. The 95551 km^2 catchment area extends over Slovenia, Croatia, Bosnia and Herzegovina and Serbia. Its source is in the Alpine region of Slovenia, while its confluence with the Danube

River is in Serbia. The Sava River is the longest river in Croatia, whose basin is the main source of water for this country, as well as for the reparian countries.

The bioavailability of metals in the Sava River water was assessed based on two approaches: the measurement of metals in the gill cytosol of European chub (*Squalius cephalus* L.) as bioindicator organism (Dragun et al., 2007), and the measurement of labile metal concentrations in river water using the diffusive gradients in thin films (DGT) (Dragun et al., 2008). However, bioavailable metal concentrations are not yet included in legislation, and the Environmental Quality Standards set by European Union's Water Framework Directive (WFD) (EPCEU, 2000; CEC, 2006) define the acceptable concentrations only for dissolved metal species in surface water. Therefore, to obtain a better estimate of Sava River metal pollution status, it was advisable to supplement the collected data set referring to bioavailable metal levels (Dragun et al., 2007; Dragun et al., 2008) with the information on total dissolved metal concentrations in river water, since they are commonly reported in environmental monitoring programmes.

The data on dangerous and priority substances established by WFD, including four trace metals (Cd, Hg, Ni and Pb), are still lacking for Sava River Basin due to insufficient financing and recent warfare. Therefore, the objective of this study was to provide preliminary data set on total dissolved concentrations of the same trace metals (Fe, Mn, Zn, Cu, Ni, Cr, Co, Pb and Cd) which were measured by DGTs in the Sava River water. Further aim was to define the metal pollution status of this river by comparison with several unpolluted rivers, as well as with the concentrations defined as acceptable by WFD.

2. Materials and methods

2.1. Selected sites and periods for water sampling

This investigation was performed as a part of the study on bioavailable metal concentrations in Sava River water. The water was sampled for the determination of total dissolved trace metals at the same sites where fish were caught (Dragun et al., 2007) and DGTs were deployed (Dragun et al., 2008). Those sites, exposed to different anthropogenic impact, included Sava in Zagreb, Oborovo and Lukavec Posavski (pollution sources are described in Table 1). However, since the municipal sewage outlet of city Velika Gorica (VG) is in the immediate vicinity of the sampling site Oborovo, in the Oborovo area the investigation was performed at three locations to examine the influence of direct point source of pollution on river water quality. Two sites were located 0.5 km upstream and 0.5 km downstream of the VG sewage outlet, while the third one was just upstream of the ferry, which is located ≈5 km downstream of the sewage outlet. The selected water sampling sites are presented in Figure 1, while the coordinates recorded with GPSMAP 76CS (Garmin International, USA) are given in Table 1. Unlike the DGT deployments which were carried out in two seasons (autumn 2005 and spring 2006; Dragun et al., 2008), the sampling period for total dissolved trace metals was limited to only one season (spring 2006).The river water was sampled in the period from March 28th to June 16th, 2006, with 8-11 samplings per site.

2.2. Determination of the total dissolved metal concentrations

The plastic bottles (high or low density polyethylene) for river water samples were rinsed with nitric acid (v/v 10%, *p.a.*) and Milli-Q water prior to sampling. River water samples were filtered through a cellulose nitrate filter (0.45 μm pore diameter, Sartorius), acidified with nitric acid (v/v 1%, *Suprapur*), and then stored at +4°C. Total dissolved concentrations of nine metals (Fe, Zn, Mn, Ni, Cu, Cr, Co, Cd and Pb) were measured using high resolution inductively coupled plasma-mass spectrometry (HR ICP-MS, Element 2, Thermo Finnigan, Germany), with indium (1 μg L^{-1}) as internal standard (Dautović, 2006). The detection limits for metals measured by HR ICP-MS in filtered and acidified water samples were (in μg L^{-1}): Fe: 0.100; Zn: 0.100; Mn: 0.010; Ni: 0.020; Cu: 0.010; Cr: 0.005; Co: 0.001; Cd: 0.001; and Pb: 0.020. The accuracy of metal determination was controlled with the certified river water reference material for trace metals (SLRS-4), and the results are presented in Table 2. A generally good agreement was observed between our data and the certified values.

2.3. Hydrological and physico-chemical parameters

The water-level values were taken from the web page of the Public Enterprise "Hrvatske vode" (http://www.voda.hr). For three Oborovo sampling sites, the water-level was recorded every hour at common nearby station Rugvica (Table 1) and the average daily values are presented on Figure 2. The water-level measuring stations for the remaining sampling sites, Sava-Zagreb and Lukavec Posavski, are located in Zagreb and in Gušće, respectively (Table 1). The river water was periodically sampled in the plastic bottles for the determination of pH (pH-meter MP120, Mettler Toledo) and conductivity (conductivity meter S30 Seven Easy, Mettler Toledo), and the results are presented in Table 3. The periodical measurements of the dissolved oxygen level in river water were carried out *in situ*, using the portable device MO 128 (Mettler Toledo). The water temperature was recorded continuously, with one reading every 15 minutes, using temperature data loggers StowAway® Tidbit® (Onset Computer Corporation) deployed in river water together with DGTs (Dragun et al., 2008).

2.4. Statistical analyses

The descriptive statistics, correlation analysis and Kruskal-Wallis test were performed using the standard statistical package SigmaStat for Windows, Version 1.0.

3. Results and discussion

3.1. The short-term temporal variability of total dissolved metal concentrations in Sava River water

Total dissolved trace metal concentrations in the surface water of Sava River in spring 2006 (Table 4) showed the comparable increasing order as reported for labile metal species (Dragun et al., 2008):

Cd, Co, Pb < Cr, Ni, Cu < Zn, Mn, Fe.

Previous reports have indicated that dissolved concentrations of Mn and Fe show significant differences between seasons (Shiller, 1997). Our measurements were performed only during the spring period of 2006, and showed significant variation of total dissolved metal concentrations within one season, and even within few days. High relative standard deviations (RSD) within each sampling site (Table 4) were observed for Mn, Pb, Zn and Fe (average RSD: 104%, 94%, 65% and 45%, respectively). By contrast, in the same period relatively low RSDs were obtained for Co, Cd, Cu, Ni and Cr total dissolved concentrations (average RSD: 32%, 29%, 26%, 23% and 16%, respectively). Our results are consistent with the previous reports on high temporal variability of dissolved Mn and Fe in rivers (Gaillardet et al., 2004), as well as with report on low Cd variability in New Jersey streams (Sherrell and Ross, 1999).

High short-term temporal variability of total dissolved concentrations of several metals can present a serious problem for reliable assessment of river water contamination with metals, if it is based on grab water sampling with a frequency of once or twice a month.

The variability of total dissolved metal concentrations in water can be the result of different factors. The wastewater inflow or soil leaching can result in the actual increase of the total metal concentrations in the river water, while the changes of physico-chemical conditions in water can cause the metal redistribution between dissolved and particulate phase. Due to the stability of pH (RSD <3%) and conductivity (RSD: 6-12%) measured in Sava river water during the study period (Table 3), these physico-chemical parameters were not considered as the possible cause of short-term variability of total dissolved metal concentrations. On the other hand, the Sava River has a very dynamic hydrological regime (Figure 2). Therefore, for four metals that exhibited the highest short-term temporal variability (Mn, Pb, Zn and Fe), we have compared the changes of the water-level measured at Rugvica with the changes of total dissolved metal concentrations in the river water measured in the vicinity of the sewage outlet.

After the sudden water-level increases (Figure 2), the pronounced increases of total dissolved Mn concentrations (from ~0.4 $\mu g\ L^{-1}$ to ~15 $\mu g\ L^{-1}$) were observed in the River Sava at three sites in the Oborovo area, which are influenced by municipal sewage outlets (Figure 3a). The positive connection between Mn and water-level at these sites was further confirmed by correlation analysis (Table 5). Since the sediment serves as the sink for metals and organic pollutants (Luoma, 1989; Kļaviņš et al., 2000), it can be hypothesized that the sediment resuspension and subsequent remobilization of precipitated Mn occurs during the periods of high water-level. The increase of dissolved concentrations as a consequence of the increasing water flow is characteristic for the redox sensitive trace elements associated with the particulate phase, especially Mn and Fe (Neal et al., 2000). Contrary to high Mn concentrations occasionally measured at the sites close to the sewage outlet (up to 15 μg L^{-1}), maximal total dissolved Mn concentrations were much lower at the sites which are not influenced by the point sources of pollution (Sava-Zagreb: 6 μg L^{-1}; Lukavec Posavski: 4 μg L^{-1}).

At three locations in Oborovo area, total dissolved Fe concentrations have exhibited the opposite temporal trend to Mn concentrations, as seen from negative correlations obtained between these two elements (Table 5). Iron increased following the decrease of the water-level, with the highest concentration (~30 μg L^{-1}; Figure 3b) associated to the low water-level in June 2006, at the site directly influenced by the sewage outlet (Figure 2). Negative association of Fe with water-level was also confirmed by correlation analysis, presented in Table 5. This phenomenon can be explained by the fact that metals which are introduced into the river water through point sources, like sewage outlets, tend to concentrate under the conditions of the decreasing water level (Robson and Neal, 1997; Sherrell and Ross, 1999; Neal et al., 2000; Neal et al., 2006). Higher average total dissolved Fe concentrations downstream from VG sewage outlet compared to the most of the remaining sampling sites (Table 4) additionally confirmed that municipal sewage outlet is a significant source of Fe in river water.

The question is why, at the sites influenced by sewage outlets, Mn and Fe total dissolved concentrations change in an opposite manner, with the high concentrations of total dissolved Mn and low concentrations of total dissolved Fe measured after the water level increases, and *vice versa*. It is not possible to give definite explanation simply based on the present data set, and without the adequate speciation analyses. It can only be hypothesized that higher water discharge which causes sediment resuspension due to enhanced river water mixing, would also result in higher level of oxygen in the bottom water. On a large time scale (seasonal variations) both Mn and Fe fluxes from sediment depend on redox conditions in bottom water; when bottom water is oxic, dissolved Mn and Fe become oxidized and precipitate. However, at pH ≈7 (characteristic for Sava River water, Table 3) the oxidation rate of Fe(II) is fast, while it is very slow for Mn(II) (Stumm and Morgan, 1970). Therefore, on the short time scale (few days), Mn fluxes do not depend on oxygen concentration, because for dissolved Mn the rate of oxidation is much slower than the rate of release from the sediment. By contrast, oxidation of released dissolved Fe occurs very rapidly under bottom oxic conditions, right after its release from the sediment (Pakhomova et al., 2007). Consequently, in our study, the resuspension of sediment possibly resulted in the release of both metals into the solution, followed by rapid precipitation of oxidized Fe.

In the opposite conditions of the low water-level, the organic material which enters the river flow through the sewage outlet tends to concentrate in river water, as described for autumn 2005 (Dragun et al., 2008). Due to enhanced oxygen consumption by bacteria in the process of biodegradation of the increased content of dissolved organic matter, the dissolved oxygen level in river water decreases (Harrison, 1995; Koukal *et al.*, 2004). In such conditions it can be expected that both Fe and Mn will be released into the solution as a consequence of the reduction of their oxyhydroxides. However, total dissolved Mn level was mainly very low at the sites influenced by sewage outlet during the periods of low water-level, and therefore probably present in the oxidized form. It was previously reported that oxidation of Mn may be strongly promoted by bacteria (Tebo, 1991; Pakhomova et al., 2007), which amplified presence can be expected near the sewage outlets (Kapetanović et al., 2008), especially associated to the low water discharge.

The reduction of Fe oxyhydroxides would also cause the release of adsorbed metals into the solution, and the subsequent increase of their dissolved levels in the river water, exactly as we have observed for total dissolved Pb concentrations at the sites influenced by the point sources of pollution during the low water-level (Figure 3c). The association of Fe and Pb was confirmed by positive, statistically significant correlations (Table 5). It was also an indication of Pb input in river water by sewage outlet, which is consistent with the previous reports (Mikac and Branica, 1994). However, this hypothesis should be further investigated, since total dissolved Pb concentrations were comparable at all five sampling sites (Table 4, Figure 4d).

Total dissolved Fe and Pb concentrations, furthermore, exhibited a gradual increase toward summer months (Figure 3b-c and Figure 4c-d). Increased concentrations of total dissolved Cd and Co in the river water were also measured in June at all sites (Figure 4e-f), while total dissolved Cu concentrations, although rather stable throughout the spring period (RSD 26%), exhibited the slight gradual increase from March to June (Figure 4g). In the study performed in river Seine, the highest concentrations of Mn, Cu, Cd and Pb were also measured during summer months (Elbaz-Poulichet et al., 2006). This phenomenon was explained by the elevated water temperature which reduces the solubility of oxygen, and also enhances the activity of the bacteria responsible for oxygen consumption. The result is the decrease of dissolved oxygen level which causes the reduction of Fe and Mn oxides and release of the associated metals into the solution (Elbaz-Poulichet et al., 2006). This explanation is possible for the conditions observed in river Sava, since the increase of total dissolved Fe, Pb, Cd, Co and Cu concentrations (observed in Period 3, Figure 4c-g) was accompanied by the increase of water temperature at all sites (Figure 4a), and the decrease of dissolved oxygen level at four sampling sites (Figure 4b). Although the temporal variability of total dissolved metal concentrations presented in this study is confined to only one season, it still can serve as the basis for the future research. However, to make the final conclusions on the influence of water discharge, temperature and dissolved oxygen level on total dissolved metal concentrations in the River Sava, the systematic measurements during at least one whole year are required.

Contrary to total dissolved concentrations of Mn, Fe, Pb, Cd, Co and Cu, high variability of Zn concentrations during the spring period (RSD 65%) could not be associated either to the hydrological or to the analyzed physico-chemical conditions in the river water. It was previously reported that, in some rivers, the dissolved Zn concentrations increase from late afternoon to early morning (Jones et al., 2004; Nimick et al., 2003).Therefore, the pronounced variability of total dissolved Zn can be partly a result of the river water sampling at different times of the day, or it can be a consequence of the sample handling. Further investigation is thus required to clarify the causes for high short-term variability of total dissolved Zn in river water.

3.2. The spatial variability of total dissolved metal concentrations in the Sava River water

The studied section of the Sava River is influenced by several point sources of pollution, including the municipal and industrial wastewater outlets of cities Zagreb, Velika Gorica and Sisak. The previous investigations indicated that the untreated wastewater of city Zagreb present a significant source of metal input into the river Sava (Mikac and Branica, 1994; Dautović, 2006). In this study, according to Kruskal-Wallis test, the concentrations of Pb, Cu, Ni and Zn have not differed significantly between sites, while in the case of Cd and Cr, the differences were statistically significant (*p*<0.10 and *p*<0.01, respectively), with decreased concentrations observed at Lukavec Posavski. The VG sewage outlet was identified as a source of metal input in river water for Mn, Fe and possibly Pb (as discussed in the section 3.1.). Increased concentrations of total dissolved Co were also found at the site downstream of the VG sewage outlet (Table 4 and Figure 4f). However, Kruskal-Wallis test confirmed the influence of the sewage outlet only for the concentrations of Mn (*p*<0.10), Fe and Co (*p*<0.05). The total dissolved concentrations of these three metals decreased with the distance from the point source of pollution. Due to their adsorption on suspended particles and subsequent precipitation, the increased concentrations of several metals can be expected in the river sediment, and not necessarily in the water (Koukal et al., 2004). The contribution of the VG sewage outlet to total dissolved concentrations of Cd, Cr, Cu, Ni and Zn in the surface water of river Sava, therefore, was not observed in the spring period of 2006, while the influence on dissolved Pb concentrations should be further studied.

3.3. The comparison with the unpolluted rivers and the water regulations

The average total dissolved concentrations of nine metals in Sava River measured in our study during spring period of 2006 were comparable to total dissolved metal levels reported for the same section of Sava River in January 2005 (Dautović, 2006; Dautović et al., 2007) (Table 6). The metal levels in the river water obtained in our study were compared with previously published data for several rivers, regarded as pristine aquatic environments, which are compiled in Table 6. Total dissolved concentrations of Cd, Co, Cr, Ni, Cu, Zn, Mn and Fe in the selected section of river Sava in Croatia were mostly higher compared to the unpolluted rivers Krka and Una in Croatia, and Lena in Russia, indicating to the probable anthropogenic impact on Sava River water quality. However, Gaillardet et al. (2004) have reported the world average levels of total dissolved metals for so called ″natural″ river systems (Table 6), based on the metal concentrations in major world rivers, but excluding the heavily polluted ones. The average total dissolved metal levels in the Sava River were comparable or even lower than the world average for all metals except Zn. Furthermore, the average levels of total dissolved Cr were lower than the Cr concentrations defined for unpolluted freshwater (<2 μg L^{-1}) (Pawlisz et al., 1997).

The obtained results were also compared with the environmental quality standards (EQS) for total dissolved metals in the inland surface water (Table 6) (CEC, 2006). The maximum allowable concentrations (MAC) were derived on the basis of the acute toxicity only for Cd and Hg, while the annual average (AA) values were defined for Cd, Hg, Pb and Ni. The AA values were also proposed for Cu, Zn and Fe in the unpublished draft UK reports (Crane et al., 2007). As a part of preliminary assessment of Sava River water quality status we have compared our data with the defined annual average levels, although the concentrations measured in this study refer to only one season. Total dissolved Cd concentrations in the river Sava were approximately 40 times lower than MAC defined by EQS for Cd (≤0.45 μg L^{-1}). The average total dissolved Fe concentrations were comparable to proposed Fe AA level, while the average values of Cd, Pb, Ni, Cu and Zn were lower (7, 130, 34, 15 and 3 times, respectively) than their respective AA levels defined by EQS.

4. Conclusions

The preliminary metal pollution study performed in the Sava River in Croatia in spring 2006 lead to the following conclusions:

- The total dissolved concentrations of several metals, namely Mn, Pb, Zn and Fe, exhibit high short-term variability within one season. The evaluation of metal concentrations in the river water based on the conventional approach, which relies on grab water sampling with frequency of once or twice a month, is therefore not suitable for the above mentioned metals.
- The total dissolved metal concentrations in the selected section of the Sava River reflect certain level of anthropogenic impact on river water quality. However, based on the comparison with the Environmental Quality Standards set by WFD, and with the world average concentrations, they can still be defined as concentrations not significantly above the natural level.
- The sewage outlets were identified as the significant sources of Co, Mn, Fe and possibly Pb input into the river water, and therefore, the continuous monitoring of the river water in their vicinity is recommended.

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Figure captions

Figure 1. The map of the studied section of the river Sava in Croatia (the sampling sites are marked with stars). *The site legend*: **SZ** - Sava-Zagreb; **OB** - Oborovo (three locations - upstream and downstream of the sewage outlet of the city Velika Gorica, and near the ferry); **LP** - Lukavec Posavski.

Figure 2. Daily water-levels (average±standard deviation) for the Sava River measured near Oborovo (in Rugvica) during spring period of 2006 (arrows point to the sampling dates).

Figure 3. The changes of total dissolved metal concentrations (**a)** Mn; **b)** Fe; **c)** Pb) in the Sava River water at three locations influenced by the point source of pollution during the spring 2006.

Figure 4. The comparison of the variability of **a)** river water temperature (continuously monitored) and of **b)** dissolved oxygen percentage (measured at the beginning and the end of each period), with the changes of total dissolved concentrations of five metals (**c)** Fe; **d)** Pb; **e)** Cd; **f)** Co; **g)** Cu) at five sites. For total dissolved metal analyses water was sampled 2-5 times per period.

Table 1. Water sampling sites, with defined point sources of pollution and the coordinates recorded with GPSMAP 76CS (Garmin International, USA)

Water sampling site	Point sources of pollution	Coordinates	Water-level measuring station
Sava-Zagreb (SZ) (upstream of Zagreb sewage outlet)	none	N 45° 46.572' E 15° 56.524'	Zagreb
Upstream of VG sewage outlet (UP-VGSO)	approximately 10 km downstream of Zagreb municipal wastewater outlet and 0.5 km upstream of VG sewage outlet	N 45° 43.095' E 16° 12.756'	Rugvica
Downstream of VG sewage outlet (DS-VGSO)	approximately 0.5 km downstream of VG sewage outlet	N 45° 42.499' E 16° 13.589'	Rugvica
Oborovo-ferry (OB-F)	approximately 5 km downstream of VG sewage outlet	N 45° 41.286' E 16° 14.875'	Rugvica
Lukavec Posavski (LP)	approximately 11 km downstream of city Sisak, receiving effluents from chemical industry, domestic sewage and oil refinery	N 45° 24.036' E 16° 32.576'	Gušće

Table 2. The HR ICP-MS method quality control was performed by the analysis of the certified reference material SLRS-4 (river water from Ottawa River, Ontario, Canada) from the National Research Council Canada. The average values and standard deviations are based on 8 independent measurements.

Certified reference material	**Metal**	**Certified values μg L^{-1}**	**Measured values μg L^{-1}**
SLRS-4	Cd	0.012±0.002	0.017±0.001
	Cr	0.33±0.02	0.29±0.01
	Co	0.033±0.006	0.034±0.001
	Cu	1.81±0.08	1.91±0.21
	Fe	103±5	96±8
	Pb	0.086±0.007	0.090±0.005
	Mn	3.37±0.18	3.31±0.12
	Ni	0.67±0.08	0.61±0.05
	Zn	0.93±0.10	0.94±0.10

Table 3. The pH and conductivity of Sava River water measured at five sampling sites on several occasions in spring 2006

Water sampling sites	pH	Conductivity / µS cm^{-1}
SZ	7.67±0.15	463±39
UP-VGSO	7.60±0.12	477±54
DS-VGSO	7.51±0.20	503±54
OB-F	7.63±0.14	479±56
LP	7.71±0.20	465±28

Table 4. The total dissolved concentrations of nine metals in Sava River water at five locations measured during spring 2006 (average±standard deviation, with relative standard deviations in brackets)

Sampling site	**No. of samplings**	**Cd**	**Pb**	**Co**	**Cr**	**Ni**	**Cu**	**Zn**	**Mn**	**Fe**
		µg L^{-1}								
SZ	8	0.012±0.004 *(33%)*	0.053±0.049 *(93%)*	0.050±0.015 *(30%)*	0.324±0.110 *(34%)*	0.529±0.130 *(25%)*	0.475±0.205 *(43%)*	2.00±1.27 *(64%)*	1.64±1.99 *(121%)*	8.35±3.58 *(43%)*
UP-VGSO	9	0.012±0.004 *(33%)*	0.057±0.053 *(93%)*	0.068±0.017 *(25%)*	0.338±0.034 (10%)	0.558±0.112 *(20%)*	0.569±0.102 *(18%)*	2.40±1.49 *(62%)*	3.77±3.71 *(98%)*	10.17±3.89 *(38%)*
DS-VGSO	9	0.011±0.003 *(27%)*	0.058±0.051 *(88%)*	0.080±0.023 *(29%)*	0.331±0.029 *(9%)*	0.553±0.118 *(21%)*	0.546±0.074 *(14%)*	2.76±2.37 *(86%)*	6.26±5.61 *(90%)*	14.32±7.63 *(53%)*
OB-F	11	0.012±0.003 *(25%)*	0.042±0.038 *(91%)*	0.065±0.021 *(32%)*	0.336±0.045 *(13%)*	0.632±0.185 *(29%)*	0.552±0.100 *(18%)*	2.33±1.27 *(55%)*	3.77±3.83 *(102%)*	9.67±3.49 *(36%)*
LP	8	0.008±0.002 *(25%)*	0.068±0.071 *(104%)*	0.055±0.024 *(44%)*	0.248±0.033 *(13%)*	0.646±0.134 *(21%)*	0.527±0.193 *(37%)*	1.72±1.02 *(59%)*	1.27±1.37 *(108%)*	21.46±11.72 *(55%)*

Table 5. Spearman correlation coefficients (r) for the selected pairs of variables measured at three locations influenced by the point source of pollution ($^{+}$ p<0.10; * p<0.05; ** p<0.01; *** p<0.001).

	UP-VGSO	**DS-VGSO**	**OB-F**
Mn - water level	*0.733	0.500	**0.736
Fe - water level	-0.517	***-0.850	*-0.664
Pb - water level	-0.467	-0.367	**-0.780
Fe - Mn	-0.350	-0.450	-0.373
Fe - Pb	*0.650	$^{+}$0.617	***0.940

Table 6. The total dissolved concentrations of nine metals in several rivers considered as pristine aquatic environments, the world average for ″natural″ river systems, as well as the acceptable metal levels in the river water stated by Water Framework Directive

	Cd	**Co**	**Pb**	**Cr**	**Ni**	**Cu**	**Zn**	**Mn**	**Fe**
	ng L^{-1}		**μg L^{-1}**						
Sava, Croatia (this study) Average Min-Max	11 3-20	64 23-136	0.055 0.003-0.234	0.32 0.07-0.43	0.59 0.31-1.07	0.54 0.06-0.88	2.27 0.09-8.74	3.44 0.35-14.72	12.6 0.65-44.5
Sava, Croatia (Dautović, 2006; Dautović et al., 2007)	15	68	0.045	0.59	0.56	1.27	2.77	8.72	14.1
Krka, Croatia (Elbaz-Poulichet et al., 1991)	5	-	0.017	-	0.15	0.11	-	-	1.35
Una, Croatia (Dautović, 2006; Dautović et al., 2007)	5	16	0.077	0.15	0.14	0.10	0.22	1.64	1.63
Lena River, Russia (Martin et al., 1993)	6	-	0.017	-	0.31	0.62	0.35	-	22.9
World average (Gaillardet et al., 2004)	80	148	0.079	0.70	0.80	1.48	0.60	34.0	66.0
***AA for total dissolved metals in inland surface waters** (CEC, 2006)	≤80	-	7.2	-	20	8.2^{+}	7.8^{+}	-	16.0^{+}

*AA: annual average stated by WFD;

$^{+}$ Proposed WFD EQS (AA) for Cu, Zn and Fe are taken from the unpublished draft UK reports, cited by Crane et al. (2007)

Figure 1.


30 km
Slovenia
Hungary
river Sava
SZ
OB
Zagreb
Velika Gorica
Sisak
LP
Croatia
river Sava
Bosnia and Herzegovina

Figure 2.

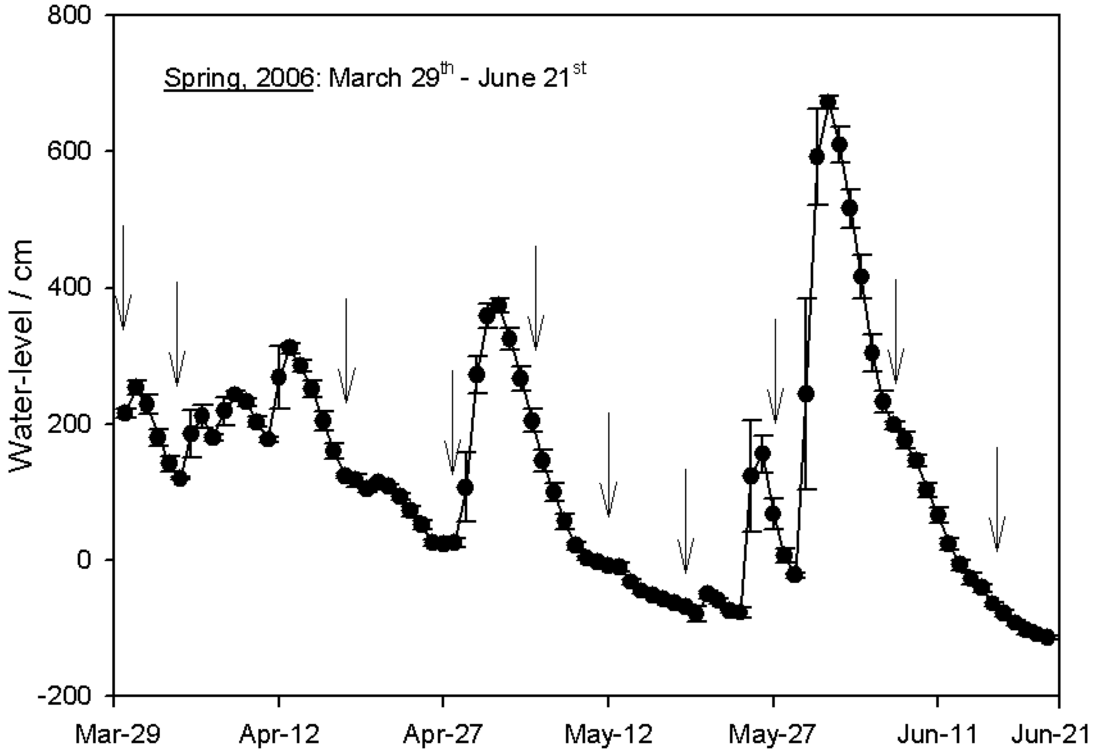

Spring, 2006: March 29th - June 21st
Water-level / cm
800
600
400
200
0
-200
Mar-29
Apr-12
Apr-27
May-12
May-27
Jun-11
Jun-21

Figure 3.

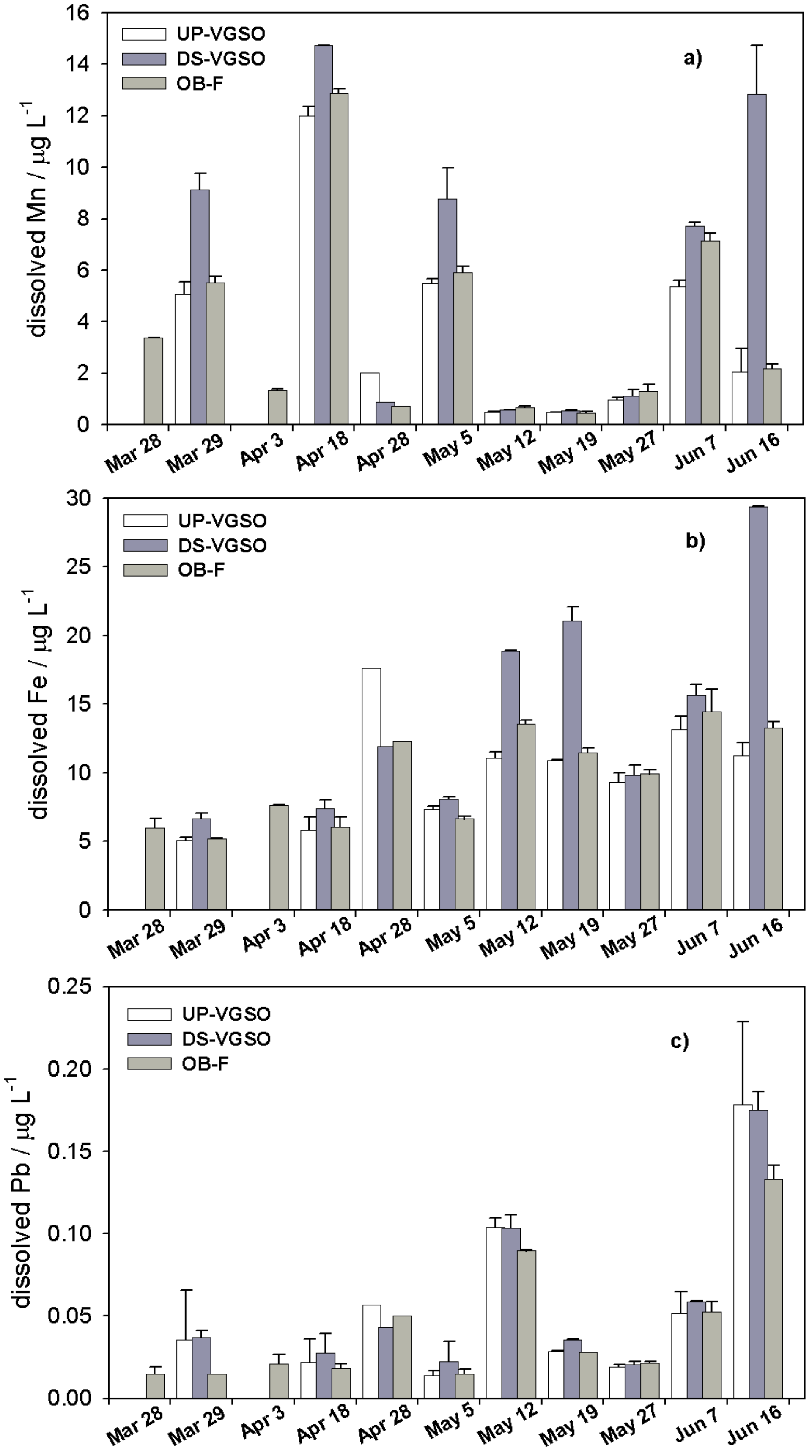
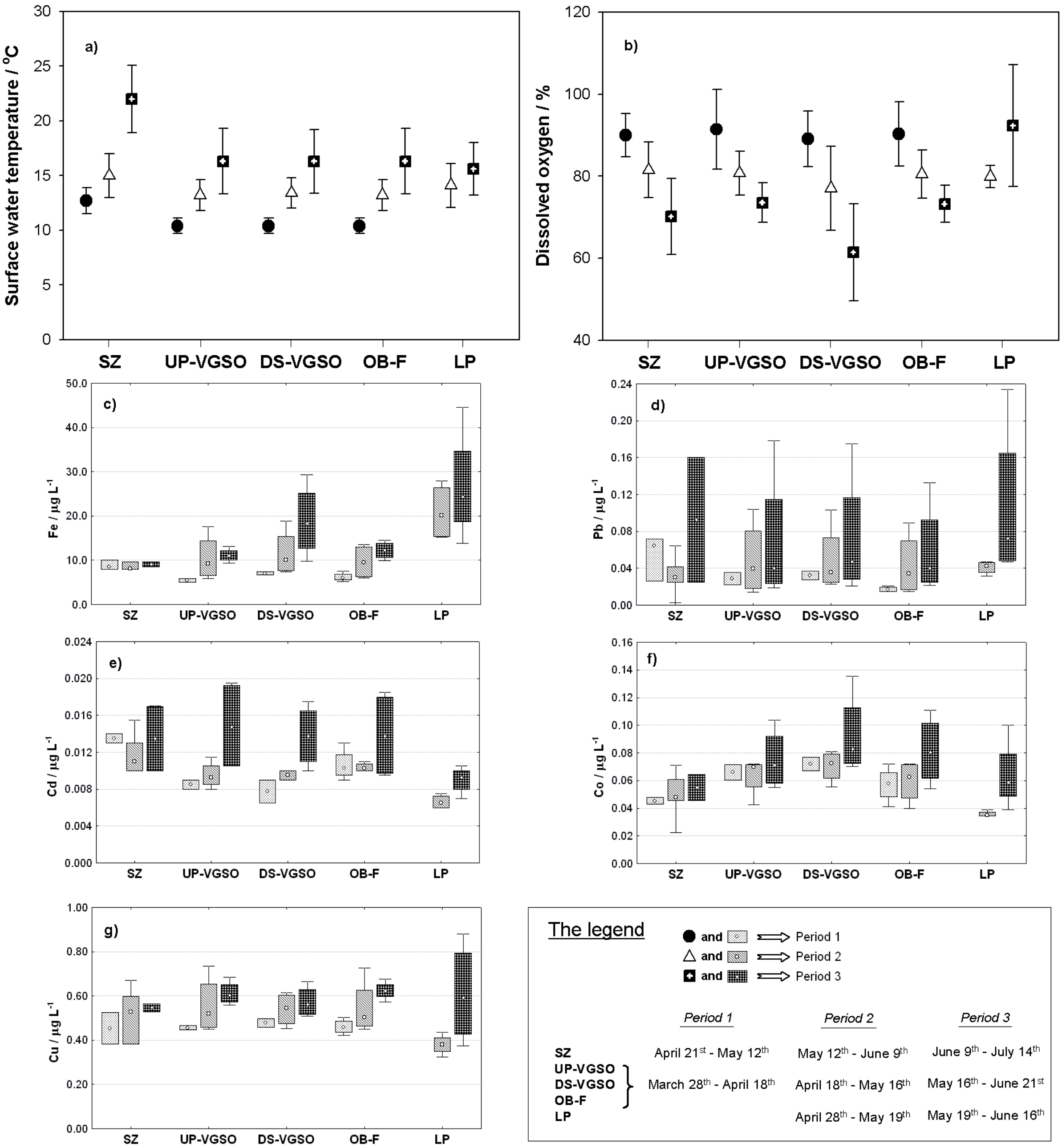

a)
UP-VGSO
DS-VGSO
OB-F
dissolved Mn / μg L^{-1}
0
2
4
6
8
10
12
14
16
b)
dissolved Fe / μg L^{-1}
0
5
10
15
20
25
30
c)
dissolved Pb / μg L^{-1}
0.00
0.05
0.10
0.15
0.20
0.25
Mar 28
Mar 29
Apr 3
Apr 18
Apr 28
May 5
May 12
May 19
May 27
Jun 7
Jun 16

Figure 4.



	Period 1	*Period 2*	*Period 3*
SZ	April 21st - May 12th	May 12th - June 9th	June 9th - July 14th
UP-VGSO DS-VGSO OB-F	March 28th - April 18th	April 18th - May 16th	May 16th - June 21st
LP		April 28th - May 19th	May 19th - June 16th