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ASSESSMENT OF SEDIMENT POLLUTION USING CHEMICAL AND BIOLOGICAL TRAIT APPROACH

Natasa VARGA[1], Dejan KRCMAR[1], Bozo DALMACIJA[1], Sonja GVOZDENAC[2], Jelena TRICKOVIĆ[1], Srdjan RONCEVIC[1] & Miljana PRICA[3*]

[1]University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia, natasa.varga@dh.uns.ac.rs;
[2]Institute of field and vegetable crops, Maksima Gorkog 30, 21000 Novi Sad, Serbia, sonja.gvozdenac@nsseme.com
*[3]University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia, miljana@uns.ac.rs, *Corresponding author*

Abstract: The chemical and biological trait approach have been applied to sediment pollution assessment of the Veliki Bački canal (Serbia) –VBC. For this assessment, pseudo-total metal contents, pollution load index (PLI), contamination factor (CF), enrichment factor (EF), sequential extraction procedure (SEP), pore water metal concentrations, geoaccumulation factor (I_{geo}), sediment quality guidelines (SQGs) and risk assessment code (RAC) have been used. Furthermore, the phytotoxic effects of the contaminated sediment have been assessed according to the physiological and morphological trait changes of the test plant species (maize, white mustard, barley and cucumber) in a bioassay. The chemical analysis has shown that an assessed sediment from VBC is extremely polluted with Cd, Zn, Ni whereas pore water is polluted with Cu, Zn, Ni. The results which have been acquired in plant bioassays indicate the different sensitivity of the plants. While pore water from the contaminated sediment had no effect on maize traits, it considerably inhibited the physiological and morphological traits of barley, cucumber and white mustard. These species are potentially good indicators of impaired sediment quality.

Keywords: metals; sediment; pollution; contamination criteria; phytotoxic effects; test plants

1. INTRODUCTION

Concentration of heavy metals in aquatic systems have drastically increased as a result of human production and consumption activities causing pollution by heavy metals, which is a serious environmental threat (Pap et al., 2016; Ilie et al., 2017). Sediments are the main sink for these elements in aquatic systems.

Over the past few years, several chemical approaches have been developed (Bing et al., 2013, Malik et al., 2015) for assessing heavy metal contamination of sediment. Due to the fact that chemical methods for assessing contamination of sediment do not provide information on the direct impact of pollutants and/or interactions with living organisms (Leitgib et al., 2007; Baran et al., 2016) when applied solely, they may be insufficient for the overall evaluation of risk. In order to evaluate the risk of particular pollutants, it is necessary for chemical methods to be complemented with toxicological i.e. biological methods (Vaajasaari et al., 2002; Leitgib et al., 2007). Not only can such integrated methodology give information about the quality and content of contaminants, but it can also provide information about its bioavailability and biological status (Leitgib et al., 2007). Bio-assays that involve the use of agricultural plants as indicators are of great importance for water and sediment quality evaluation in agricultural production (Liu et al., 2005). In addition, they give an overview of the impact of polluted water on relevant plant species (Gvozdenac et al., 2016).

Large quantities of sediments are commonly dredged during seasonal maintenance of irrigation canals in order to restore their desired functionality. Currently in Serbia, the dredged sediment, which is usually overloaded with nutrients and hazardous or other undesirable substances, is being disposed of in landfills. All these can have a very negative effect on the environment in the canals as well as on their banks and in their wider area. Moreover, the capacity of the landfill is limited and the dredged sediment can cause a serious threat due to a number of contaminants that can be re-suspended and become accessible to organisms (Wasserman et al., 2013). It is highly desirable to remove water from contaminated dredged sediments in Confined Disposal Facilities since this reduces the volume occupied by the sediments (Smith et al., 2009). In order to assess the risk realistically and to develop the adequate remediation approach, the information on metal concentrations in pore water is necessary due to the effects of metal mobility and bioavailability. Sediments frequently contain about 20–50% water, and the chemistry of this pore water is considerably different between water above the sediment and in the sediment. Moreover, the dissolved metals in pore water, which pose an extensive threat, are generally in the fractions that are most bioavailable to benthic organisms (Burbridge et al., 2012).

First, the aim of this study is to determine the level of metal pollution (Cd, Cu, Ni, Zn, Cr, Pb) in the sediment from Veliki Bački canal (VBC) in Serbia, based on the different sediment chemical contamination criteria. Next, the effects of the pore water from contaminated sediment on cultivated plants are assessed (maize, barley, cucumber and white mustard), based on the changes in physiological and morphological traits in bioassays performed according to a slightly modified filter paper method (ISTA, 2011). Finally, the study explores the degree of correlation between the chemical and biological assessments of sediment quality.

2. MATERIALS AND METHODS

2.1. Study Area

Samples were collected from the VBC, part of the Danube-Tisa-Danube canal network (DTD-HS). The canal (119 km long) connects the Danube and Tisa rivers, consists of several sluices and locks, and has numerous and diverse purposes: irrigation, water supply, drainage, receiving wastewater, fisheries, tourism and recreation, shipping etc.

As a result of the discharge of untreated or only partially treated wastewater into the canal from a lot of industrial facilities such as two sugar refineries, a metal works, an edible oil refinery, a tannery, slaughter houses etc., it has ultimately became more polluted. The total organic pollution from industry is 36.6 t COD day^{-1} (chemical oxygen demand) or 17.9 t BOD_5 day^{-1} (biochemical oxygen demand), together with 1329 kg COD day^{-1} or 619 kg BOD_5 day^{-1} from municipal wastewaters. The high load of wastewaters in the canal along a 6 km stretch has consequently formed about 400,000 m^3 of sediment. The canal is approximately 3 m deep, with the depth of sediment depending on the proximity of wastewater discharges, varying from 1 to 2.5 m.

2.2. Sample collection

Composite sediment samples were taken from three locations from the middle of the canal and the left and right banks. Samples entail vertical sediment cores taken over the entire depth of the sediment (VBC: 100 to 160 cm).

All materials used for sampling, treatment and storage of samples and solutions were carefully chosen, acid-cleaned and conditioned to minimize sample contamination (US EPA, 2004). Immediately after collecting, all samples were split and placed into plastic bags prior to analysis. The samples were stored at 4 °C and transported to the laboratory. Pore water was obtained by centrifuging under laboratory conditions (US EPA, 2001). The pore water was filtered (0.45 µm), acidified with ultrapure nitric acid to pH<1 and stored in polyethylene sample tubes at 4°C.

2.3. Analytical Methods

Sediment samples were pretreated in accordance with method ISO 11464:2006. The protocol for chemical extraction for determination of pseudo-total content of metals in sediment was performed in accordance with US EPA method 3051A (US EPA 2007b). Extraction was carried out with a microwave oven (Milestone, Start E microwave). The sediment extracts were analyzed for Ni, Zn, Cd, Cr, Cu and Pb by flame atomic absorption spectrometry-FAAS (Perkin Elmer, AAnalyst 700) in accordance with US EPA method 7000b (US EPA 2007a).

Pore-water metal (Zn, Cu, Cr, Pb, Cd, Ni) concentrations were also determined by AAS. The microwave assisted sequential extraction procedure (SEP) was performed using identical operating conditions applied to each individual modified BCR fraction (Jamali et al., 2009).

Through each complete procedure, blanks (containing reagent but no samples) were analysed. In order to evaluate the accuracy of the method, a certified reference material BCR 701 (European Commission, Brussels) was used. The analytical precision, expressed as relative standard deviation (RSD), was generally better than 5% for all metals. Method accuracy was also satisfactory, with the values obtained during this study differing less than 2 standard deviations from the certified values (BCR-701). There is less than 10% difference between the sum of the four sequential steps from the procedure and the pseudo-total metal content. Therefore, the acquired results for the extractable heavy metal amounts validate the applied microwave assisted SEP.

The microwave assisted SEP was carried out in the following steps: step 1 (F1, exchangeable fraction) - 0.11M CH_3COOH, microwave induced time 60-90 sec; Step 2 (F2, reducible fraction) - NH_2OH-HCl 0.5 M, pH 1.5, microwave induced time 90-120 sec; Step 3 (F3, oxidisable fraction) – H_2O_2 (8.8 M) heat to 85^0C for 1 h (twice) and then add CH_3COONH_4 1M (pH 2), microwave induced time 70-90 sec; Step 4 (F4, residual fraction) – aqua regia digestion (HCl/HNO_3, 3:1) (Jamali et al., 2009).

Analytical grade reagents were used for preparation of the extracting solutions. Standard solutions of metals were prepared by diluting 1000 ppm certified standard solutions from Fluka Kamica (Buchs, Switzerland). The hydroxylammonium chloride solution was prepared immediately prior to use. 100 ml acid-washed polyethylene centrifuge tubes were used in order to perform the extraction, while 100 ml polyethylene vessels were used for storing the extracts. All results are expressed with reference to sediment dry matter.

Background metal concentrations were obtained from literature data (Zeremski-Škorić, 2005). Due to the lack of data on the background concentrations of the examined sediment, the mean concentrations of heavy metals in uncontaminated soils in the study area were used as background values in this paper (for VBC: Pb 19.3 mg kg^{-1}, Cu 17.5 mg kg^{-1}, Cr 41.9 mg kg^{-1}, Ni 3.6 mg kg^{-1}, Cd 0.1 mg kg^{-1}, Zn 40.8 mg kg^{-1}).

2.4 Assessment of sediment contamination

2.4.1. Chemical approach

In this study the sediment metal pollution was compared with sediment quality guidelines, contamination factor (CF), geoaccumulation factor (I_{geo}), enrichment factor (EF), pollution load index (PLI) and Risk Assessment Code (RAC), whereas for the pore water, the pore water criteria toxic units (IWCTU Index Water Criteria Toxic Units) have been applied.

The government of Serbia has adopted a regulation on limiting pollutants in surface and ground waters and sediments (Official Gazette of RS, 2012). The regulation on emission limit values for sediment is based on the Dutch classification system (Ministry of Transport and Public Works, 1994), which consists of four classes of sediment pollution, from 0 (clean) to 4 (heavily polluted).

Three sets of additional sediment quality guidelines, the TEL (threshold effects level) and PLE (probable effects level), LEL (lowest effects level) and SEL (severe effects level) and ERL (effects range low) and ERM (effects range medium) were used for determining whether the concentrations of detected heavy metals in sediments pose a threat to aquatic life (US EPA, 2002; Sundaray et al., 2011). These three sets of numerical SQGs (without normalization) were used to evaluate the potential risk caused by heavy metal contamination in the sediments in the study area.

The CF is the ratio obtained by dividing the concentration of each metal in the sediment by the baseline or background value - the concentration in uncontaminated sediment (1) (Kalender & Cicek Ucar, 2013):

$$CF= C_{heavy\ metal} / C_{background} \quad (1)$$

CF values are to be interpreted as proposed by Hakanson (1980) and Varol (2011) where: CF < 1 means low contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 means very high contamination.

For the whole sampling site, the PLI was determined as the *nth* root of the product of the n CF (2):

$$PLI= (CF_1 \cdot CF_2 \cdot CF_3 \ldots CF_n)^{1/n} \quad (2)$$

This empirical index is considered to provide simple, comparative assessment of the level of heavy metal pollution. Pollution exists when PLI > 1; otherwise, if PLI < 1, there is no metal pollution (Tomlinson et al., 1980; Varol, 2011). The geoaccumulation index (I_{geo}) is defined by the following equation (3), (Varol, 2011):

$$I_{geo}= Log_2(C_n)/1.5(B_n) \quad (3)$$

In this equation, C_n represents the concentration of metals in sediment samples and *Bn* is the chemical background concentration of the metal (n). The factor 1.5 is the background matrix correction factor caused by lithospheric effects. There are seven classes defined by the geoaccumulation index. Class 0 (practically unpolluted): $I_{geo} \leq 0$; Class 1 (unpolluted to moderately polluted): $0 < I_{geo} < 1$; Class 2 (moderately polluted): $1 < I_{geo} < 2$; Class 3 (moderately to heavily polluted): $2 < I_{geo} < 3$; Class 4 (heavily polluted): $3 < I_{geo} < 4$; Class 5 (heavily to extremely polluted): $4 < I_{geo} < 5$; Class 6 (extremely polluted): $5 > I_{geo}$.[23]

The normalized enrichment factor (EF) is used to differentiate metal sources originating from natural and anthropogenic means and involves normalization of the sediment with respect to reference elements: Al, Fe, Mn, Ti, Sc, Li and Cs (Zahra et al., 2014; Charzyński et al., 2016). Geochemical normalization is also widely used for calculating enrichment and reducing heavy metal variability caused by grain size and mineralogy of sediments (Zahra et al., 2014). There are several reasons why Fe is used as the reference element for geochemical normalization in this study: firstly, Fe is linked to fine solid surfaces. Secondly, the geochemistry of Fe is similar to that of many trace metals. Finally, Fe has a tendency to have uniform natural concentrations. The EF is calculated using the following relationship (4):

$$EF = (Me/Fe) \cdot Sample / (Me/Fe) \cdot Background \qquad (4)$$

Where, (Me/Fe) is the ratio of concentration of the element of concern (Me) to that of Fe in the sediment sample and (Me/Fe) is the same ratio in an unpolluted reference sample.

EF values have been interpreted as indicated by Sakan and Đorđević (2010) where: EF < 1 means no enrichment; <3 is minor enrichment; 3–5 is moderate enrichment; 5–10 is moderately severe enrichment; 10–25 is severe enrichment; 25–50 is very severe enrichment; and >50 is extremely severe enrichment.

RAC denotes possibilities of the risk to the aquatic life by applying a scale to the percentage of metals presented in the exchangeable and carbonate fractions, i.e. the labile phases. According to the RAC, if this fraction is <1%, there is no risk to the aquatic system, 1–10% exhibits low risk, 11–30% medium risk, 31–50% high risk, and >75% very high risk (Jain, 2004). The distribution of metals in the different phases using the sequential extraction procedure indicates their availability. Consequently, this allows the assessment of the risk they pose to the aquatic environment.

IWCTU has been used for the examination of pore water qualities for each single metal. IWCTU for single metals have been derived from the following prediction model relationships (5) (Ankley et al., 1996):

$$IWCTU = [Md]/[FCVd] \qquad (5)$$

Md - is the total dissolved pore water concentration of a metal

FCV_d- is the final chronic value of metals applied total dissolved metal concentration

2.4.2. Biological approach - Plant Phytotoxicity Bioassay

Test species for the bioassay were chosen as representatives of monocotyledonous: maize (*Zea mays L.*) variety NS 6030 and barley (*Hordeum vulgare* L.) variety Novosadski 525; and of dicotyledonous: cucumber (*Cucumis sativus* L.) variety Tajfun and white mustard (*Sinapis alba* L.) variety Torpedo. Sediment quality from the canal was evaluated according to changes in physiological (germination - %) and morphological traits (root and shoot length - cm and biomass - fresh and dry weight of roots and shoots - g), and for the bioassay, sediment pore water was used.

The bioassay was carried out according to the standard filter paper method, with slight modifications (ISTA, 2011). For germination assessment, 50 maize and 100 barley, cucumber seeds were placed in plastic boxes on pleated filter paper, previously moistened with 25 ml of pore water and distilled water for the control. White mustard seeds were placed in Petri dishes (Ø15 cm), on previously moistened filter paper with 10 ml of pore water and distilled water for the control. Seeds were incubated in the dark at 25±2 °C for three (white mustard) or four days (other species) after which 10 seedlings were taken from each replicate and placed on filter paper lanes (14 x 60 cm) previously moistened with 30 ml of pore water and distilled water in the control, rolled up, packed in PVC bags and placed back in the incubator. Boxes with the remaining seeds were also returned to the incubator until the final germination assessment. After seven (maize, barley and white mustard) and eight (cucumber) days, germination was recorded and length of seedlings roots, shoots and their fresh weight were measured. After drying to constant mass, the dry weight was also measured. The experiment was carried out in four replicates.

Data were processed using Student's t test at 95% confidence interval in statistical software SPSS 19.

3. RESULTS AND DISCUSSION

3.1 Assessment of Contamination Based on Comparison with the Sediment Quality Guidelines

The results presented in Table 1 are discussed with reference to Serbian regulations (Official Gazette of RS, 2012).

There are four numerical levels included in the Serbian regulations: the target, limit, verification and remediation values. The target value or the baseline concentration value is the lower level below which the natural properties of the sediment are presumed not to be affected by compounds and/or elements. Values between the target, limit and verification values indicate that the sediment is polluted to a slight degree, while the values between the verification and remediation values show that the sediment is polluted. The remediation value represents maximum tolerable concentration above which remediation is required and it is the highest level. The measured values for heavy metals are dependent on the clay and/or organic matter content. The Serbian system defines the class limits for “standard sediment”, with 10% of organic matter and 25% of clay. In assessing sediment quality, the values for the standard sediment are compared by scaling the values of the actual sediment concerned on the basis of the measured organic material (measured by percentage weight lost on volatilization, on the total dry weight of the sediment) and clay content (the percentage by weight of the total dry material comprising mineral particle matter with a diameter of less than 2 μm). The Serbian national evaluation scheme was used for classification of the metal concentrations of the sediment, which have first been corrected to the standard sediment based on the correction formulas. The "worst class" sediment parameter(s) are used to establish the overall quality of a sediment at a particular location. In the VBC sediment, concentrations of Cd (13 mg kg^{-1}), Zn (503 mg kg^{-1}) and Cu (255 mg kg^{-1}) were above the remediation values. It is shown by the content of Ni (58 mg kg^{-1}) that the contaminated sediment is above the verification level and below the remediation level and based on the content of Cr (113 mg kg^{-1}) this sample was be below the limit value. Pb (67 mg kg^{-1}) in the sediment is below the target value.

According to the US EPA, three sets of recommendations are used (TEL-PEL, SEL-LEL, ERL-ERM) (Sundaray et al., 2011; US EPA, 2002). The first set recommend that Cr and Pb amounts should be between the TEL-PEL values, which may sporadically be linked to adverse biological effects. However, Zn, Cd, Cu and Ni are above the PEL value, which are frequently associated with harmful biological effects. Following the recommendations of the second set, only Pb has a moderate impact on the environment (value was between the LEL-SEL), while the impact from all the other metals is severe (> SEL). Based on the third set of recommendations, Cu, Cr and Pb cause occasional negative effects (the value was between ERL-ERM), while with Zn, Cd and Ni (> ERM) adverse effects are frequent.

3.2. Assessment of Contamination Based on the CF, PLI, EF and I_{geo}

The CF, PLI, EF and I_{geo} values for the VBC are presented in Table 2. A “very high contamination” is indicated by Cd, Cu, Ni and Zn, all of which had the highest CF values found in the VBC. As for the CF values for Pb, the sediment is considered substantially polluted, while chromium levels show predominantly “moderate contamination”. There are high pollution levels in the VBC, since the PLI is 6.6. According to Zhang & Liu (2002), the metal is completely from crustal materials or natural processes if EF values are between 0.05 and 1.5, whereas with EF values higher than 1.5, the sources are more likely to be anthropogenic. Since the mean EF values for all metals in the sediment were >1.5, this points to an anthropogenic impact on the metal levels in the canal.

The “extremely severe enrichment” was the EF value for Cd, which was above 50. The value for Cu shows “severe enrichment” and the EF value for Zn indicates a “moderately severe enrichment”. The EF values for other metals indicate “moderate enrichment”. Based on I_{geo} values, the sediment from the VBC is not polluted with the other metals, except for Cd, for which the I_{geo} class was “extremely polluted”.

Table 1. Contents of Cd, Cr, Cu, Ni, Pb and Zn in the sediment of the VBC with the Serbian and USEPA guidelines

Metal	VBC[k]		Serbian limits			USEPA guidelines				
	1[a]	2[b]	TV[c]	IV[d]	TEL[e]	PEL[f]	LEL[g]	SEL[h]	ERL[i]	ERM[j]
	mg kg^{-1}									
Cd	13	*13*	0.8	12	0.68	4.21	0.6	9	1.2	9.6
Cr	113	*222*	100	380	52.3	160	26	110	81	370
Cu	255	*352*	36	190	18.7	108	160	42.8	112	4.21
Pb	67	*83*	85	530	30.2	112	31	110	46.7	218
Ni	58	*193*	35	210	15.9	42.8	16	50	20.9	51.6
Zn	504	*899*	140	720	124	271	120	270	150	410

[a]measured value, [b]value corrected for organic matter and clay contents, [c]target value, [d]intervention value, [h]threshold effects level, [f]probable effects level, [g]lowest effects level, [h]severe effects level, [i]effects range low, [j]effects range medium, [k]VBC

Table 2. Metal contamination factors (CF), enrichment factor (EF) geoaccumulation index (I_{geo}), pollution load indices (PLI) and pore water criteria toxic units (IWCTU)

	Cd	Cr	Cu	Pb	Ni	Zn
CF	145	2.7	15	3.3	16	12
EF	61.7	3.78	14.9	3.90	3.93	8.32
I_{geo}	8.4	0	0.1	0.1	0.3	0
IWCTU	0	0.98	15.8	0.7	3.8	1.1
PLI	6.6					

3.3. Assessment of Contamination Based on Pore Water Metal Concentrations

During longer time periods, the pore water is in contact with sediment surfaces resulting in possible contamination due to partitioning of the contaminants from the surrounding sediments. The factors which influence this contamination of the pore waters are various: flow, residence time and other physicochemical factors (e.g., pH, temperature, redox potential, organic carbon, sulphides, carbonates, mineralogy). This makes pore water useful for the contamination level assessment as well as the associated toxicity (Ankley et al., 1996; US EPA, 2001).

The IWCTU values for VBC are presented in Table 2. The toxicity in the sediment is rather serious as the IWCTU for Cu, Ni and Zn were higher than 1. Due to the fact that Cu was mainly present in the second phase of SEP, it could be concluded that the release and activity of Cu were enhanced, which was most likely induced by the variation or redistribution in the sediment. The contents of Ni and Zn in the pore water are in agreement with the results of the SEP concentrations.

3.4. Assessment of Contamination Based on the Sequential Extraction Procedure (SEP)

The results of the fractionation study evidently indicate that the metals in the sediments are bound to different fractions with different strengths. The risk concerning the type of bounding of metals in sediment or the type of association, is described by the RAC (Jain, 2004).

The results of the SEP for the VBC sediment are presented in figure 1. Significant proportions of the Cd, Ni and Zn in the VBC are present in exchangeable forms and bound to carbonates in the first fraction, correlating with the results of the pseudo-total concentration and pore water criterion. This is extremely harmful to the environment as the Cd (53%), Ni (58%) and Zn (63%) in the carbonate phases are highly dangerous and can easily enter the food chain (Jain, 2004). Pb and Cu, which were mainly present in the second phase (54 and 85%), are associated with hydrated iron oxides and manganese (moderately mobile metal fractions) which may be released due to the changes in the reduction conditions. The amount of Cr in the first phase was <10%, and according to RAC, it represents a low risk or possibility of mobility of metals from sediments into the aqueous phase. It is typical of Cr to be mostly present in the oxidisable fraction (65%) due to its clear tendency for complexation with organic matter and sulphides and shows medium risk (Jain, 2004).

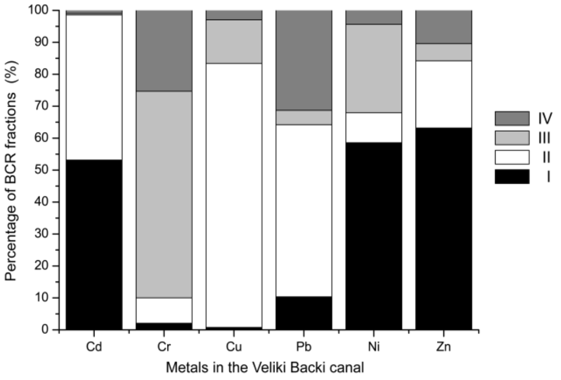

Figure 1. Results of the SEP for the VBC sediment

3.5. Assessment of Contamination using Test Plants

The results of the pore water effect on physiological and morphological traits of maize, barley, cucumber and white mustard are presented in Table 3.

Pore water did not affect germination of maize, barley, cucumber and white mustard (t=3.01ns; 4.88ns; 12.9ns; 4.90ns, p>0.05, respectively) since all values were on the same level of significance with the controls. It is evident that the bioavailable contaminants detected in the sediment (Cd, Zn, Ni) and pore water (Cu, Zn, Ni) were below the levels that cause effects on germination of the tested plant species. Results indicating seed tolerance to pollution and high levels of heavy metals have also been presented by a number of other authors (Chen et al., 2001; Yildiz, 2005; Mahmood et al., 2005; Pandey et al., 2008; Ma, 2010; Wang et al., 2010; Gvozdenac et al., 2011; Soydam et al., 2012; Gvozdenac et al., 2014).

Root length of maize seedlings was not influenced by the heavy metals from the sediment (t=1.07ns, p>0.05), while roots of barley, white mustard and cucumber were significantly inhibited by pore water from the canal (t=14.11**, 10.68*, p<0.01/ p<0.05).

Table 3. Physiological and morphological parameters of maize, barley, cucumber and white mustard in pore water from the VBC and in the control.

Parameter	Sample	maize	barley
germination (%)	VBC^a	99.0 ±0.76 a	91.0 ±0.20 a
	Control	100.0 ±0.38 a	98.0 ±0.40 a
	t value	3.01ns	4.88ns
root length (cm)	VBC^a	14.25 ±1.49 a	11.62 ±1.36 b
	Control	15.24 ±0.81 a	14.47 ±0.45 a
	t value	1.07ns	14.11**
root fresh weight (g)	VBC^a	6.86 ±1.30 a	1.18 ±0.18 b
	Control	5.33 ±0.40 b	1.68 ±0.16 a
	t value	5.21*	15.32**
root dry weight (g)	VBC^a	0.59 ±0.05 a	0.18 ±0.05 a
	Control	0.54 ±0.05 a	0.21 ±0.01 a
	t value	1.14ns	1.75ns
shoot length (cm)	VBC^a	5.94 ±0.64 a	12.70 ±1.58 a
	Control	6.61 ±0.42 a	12.82 ±0.39 a
	t value	5.35ns	4.09ns
shoot fresh weight (g)	VBC^a	4.12 ±0.93 a	2.78 ±0.22 a
	Control	3.94 ±0.24 a	2.32 ±0.22 a
	t value	2.09ns	4.81ns
shoot dry weight (g)	VBC^a	0.32 ±0.06 a	0.20 ±0.01 a
	Control	0.23 ±0.01 a	0.19 ±0.01 a
	t value	2.53ns	7.56ns
germination (%)	VBC^a	91.0 ±1.04 a	88.0 ±1.41 a
	Control	86.0 ±0.89 a	83.2 ±2.50 a
	t value	12.19ns	4.90ns
root length (cm)	VBC^a	9.12 ±0.67 b	3.28 ±0.86 b
	Control	10.86 ±0.77 a	4.04 ±0.89 a
	t value	10.68*	4.12 **
root fresh weight (g)	VBC^a	0.41 ±0.06 b	0.02 ±0.80 a
	Control	0.88 ±0.06 a	0.01 ±0.01 b
	t value	9.71**	7.91*
root dry weight (g)	VBCa	0.04 ±0.00 a	0.01 ±0.01 a
	Control	0.04 ±0.02 a	0.01 ±0.01 a
	t value	1.70ns	0.373ns
shoot length (cm)	VBC^a	11.95 ±2.37 a	9.40 ±1.63 a
	Control	9.53 ±0.61 b	3.49 ±0.23 b
	t value	8.31*	22.97**
shoot fresh weight (g)	VBC^a	4.88 ±0.98 a	0.80 ±0.23 a
	Control	4.23 ±0.45 a	0.29 ±0.05 b
	t value	6.08ns	3.62*
shoot dry weight (g)	VBC^a	0.25 ±0.02 a	0.13 ±0.03 b
	Control	0.24 ±0.02 a	0.36 ±0.00 a
	t value	4.05ns	9.88**

Student's test (t value) ±SD; values with the same letter in the column are on the same level of significance for the confidence interval 95%; **$p<0.01$;* $p<0.05$; NS $p>0.05$, ^{a}- VBC

Since the sediment samples are complex in terms of toxicity assessment and heavy metals are not solely responsible for the toxic effects, the levels of N (14600 mg kg^{-1}), P (4100 mg kg^{-1}), COD (926 gO$_2$ kg^{-1}) and BOD (66.6 gO$_2$ kg^{-1}) should also be taken into consideration when interpreting these results. Gvozdenac et al., (2014) report the phytotoxic effect of water containing high levels of ammonium ion, total nitrogen, organic matter with low degradability and TOC, on maize and barley. Several authors emphasize that heavy metals (Cd, Cr, Zn, Ni, Cu) cause root growth inhibition of a number of plant species (Breckle, 1991; Chen et al., 2001; Nocito et al., 2002; Pandey et al., 2008; Ma, 2010; Wang et al., 2010; Soydam et al., 2012).

Inhibition or activation of root elongation was considered to be the first effect of metal toxicity in the tested plants. On the basis of the results of the bioassay, we may speculate that the presence of elevated levels of heavy metals and their interactions in sediment from the VBC inhibited root elongation in some tested species.

Shoot lengths of maize and barley were not influenced by pore water quality (t=5.35ns, 4.09ns, $p>0.05$). However, shoots of cucumber and white mustard seedlings were stimulated by samples from VBC compared to the control (t=4.09*, 8.31*, 22.97**, $p<0.05$). This is in compliance with Gvozdenac et al., (2016), who reported that water slightly contaminated with domestic, industrial and agricultural xenobiotics can stimulate upper-parts of barely and some other cultivated species, regardless of metal content. Literature data suggests that metals rarely affect or stimulate upper-parts growth, so these changes were most probably caused by the total chemistry of the sediment sample. This can be attributed to the high P and N levels in the sediment from the VBC. These nutrients are crucial for shoot development (Kastori, 1995) and according to Marshner (2002), water rich in essential elements like nitrogen can enhance seedlings growth when used for irrigation. Oudeh et al., (2002) also reported that treatment with water containing high levels of nitrogen, Zn, Cu, Cd and/or organic matter had beneficial effects on maize and plant development. However, according to Gvozdenac et al., (2014), shoot length of barley and white mustard are not influenced by the water quality, regardless on the levels of organic and inorganic substances.

Changes in the fresh root weight of seedlings were in compliance with the results obtained for root lengths and were species-dependant. However, dry root weight was not affected by pore water quality, regardless of the tested plant species ($p>0.05$). Fresh and dry shoot weights of maize, barley and cucumber were not influenced by pore water quality. However, the fresh shoot weight of white mustard was stimulated by pore water, compared to the control (t=3.62*; $p>0.01$), while dry weight was significantly inhibited (t=9.88**, $p<0.01$) by the total chemistry and content of metals in the sediment samples.

3.6. Comparison of the Different Criteria for Assessing Sediment Contamination

The comparison of the different criteria for sediment contamination is given in Table 4. The VBC sediment is extremely polluted with metals, especially Cd, Cu and Zn (class 4) based on Serbian standards (Official Gazette of RS, 2012). Urgent sanitation measures such as dredging, disposal in special storage reservoirs and possibly sediment clean-up measures should be proposed for Class 4 sediments. These results correspond with the US EPA guidelines (Sundaray et al., 2011). Principally, CF, PLI, I_{geo}, EF values are in accordance with the Serbian and US EPA guidelines. However, based on the comparison of the results of the different criteria for sediment quality assessment and sequential extraction, it can be said that they are not entirely congruent. The sediment of the VBC is environmentally of a very high risk according to the SEP results but only for Ni, Zn and Cd.

Although, the sediment has been severely polluted by metals, the results of the bioassays demonstrate that there are no physiological and morphological changes of maize plants caused by pore water from the contaminated sediment, whereas the other species have shown different sensitivities to heavy metal pollution.

Table 4. Comparison of different pollution criteria

	Cd	Cr	Cu	Pb	Ni	Zn
Class[a]	+		+			+
>PEL[b]	+		+		+	+
>SEL[c]	+	+	+		+	+
>ERM[d]	+				+	+
CF> 6[e]	+		+		+	+
5<Igeo<6[f]	+					
EF[g]	+					
IWCTU[h]			+		+	+
SEP[i]	+				+	+
PLI> 1[j]			+			

[a]Classification according to the Serbia national evaluation scheme, showing the contaminants responsible for the designated class, [b]metal concentrations above the PEL,[c]metal concentrations above the SEL, [d]toxic effects are frequently observed in the range of concentrations above the ERM, [e]contamination factor (CF) > 6: very high contamination, [f]geoaccumulation index $5<I_{geo}<6$, class 6: extremely polluted, [h] IWCTU > 1: sediment is considered to be toxic, [i]based on the results of SEP there is high risk to the environment due to certain metals, [j]PLI > 1: pollution exists

4. CONCLUSION

Based on the results obtained in this study, the VBC sediment is polluted with heavy metals, judging by at least one criterion of sediment quality. In order to identify potentially concerning contaminants, during the problem formulation stage of the screening process, determining CF, PLI, I_{geo} and EF should be carried out in addition to the comparison with the Serbian regulation and US EPA guidelines. Risk assessment code (RAC) suggests that the concentrations of Cd, Ni, Zn in the study area pose a major risk to the environment as well as a serious threat to the ecosystem which is consistent with the results of the metal pore water concentrations.

Different sensitivities of the plant species tested is indicated by the bioassay. The results from the bioassays performed with sediment pore water show that after dredging the VBC, sediment disposal on arable land would not affect maize production. However, it is not recommended to use it on arable land with the production of barley, white mustard and cucumber, nor is the pore water suitable for the irrigation of those crops. Impaired sediment quality, i.e. pollution with Cd, Ni and Zn, was found by almost all tested species, except for maize. However, we must point out that the effect of the contaminated sediment was assessed based on the metals present in the most available fraction – the pore water.

All this should be taken into consideration when assessing sediment pollution, especially during the justification of already expensive remediation procedures.

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