METALS CONCENTRATIONS IN WATER AND SEDIMENT FROM THE DANUBE RIVER

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KONCENTRACIJA METALA U VODI I SEDIMENTU REKE DUNAV

Apstrakt

Voda je osnov opstanka živog sveta koji je u njoj i nastao. Dve trećine zemljine površine je pod vodom. Bez obzira na značaj vode na opstanak živog sveta ljudska vrsta prema vodi nema odgovarajući odnos. O tome govore podaci o zagađenju okeana, mora, vodotokova (reke, potoci) i jezera. Antropogeno zagađenje vode, dakle, poreklom od čoveka, javlja se kao posledica direktnog ili indirektnog ispuštanja zagađivača u vodu, bez adekvatnog postupka sa štetnim i opasnim jedinjenjima. Najčešći zagađivači vode posledica su otpadnih voda i voda koje dolaze sa površina zemlje (naročito obradivih površina). Zagađenost vode je blisko povezana za povećanim potrebama stanovništva za vodenim resursima. Povećane potrebe rastu sa porastom stanovništva, razvoja privrede i tehnologije. Veća potrošnja vode znači i veću količinu otpadnih voda. Dospevanjem u reke otpadne vode menjaju fizička (boja, miris, ukus, providnost), hemijska (sastav) i biološka svojstva (živi svet reka). Naša zemlja nema odgovarajuće propise za procenu kvaliteta sedimenta pa se, zbog toga, koriste standardi kvaliteta prema kanadskom zakonodavstvu, preporuke ICPDR-a (International Commission for the Protection of the Danube River), a pojedini parametri se procenjuju korišćenjem holandske metodologije. Prema kanadskom zakonodavstvu definisane su dve vrednosti: niža vrednost ISQGs (Interim Sediment Quality Guideline) predstavlja privremene preporuke koje su dobijene teorijskim putem i iznad kojih je moguć uticaj na akvatične organizme, dok je druga, viša, vrednost PEL (Probable Effect Level), vrednost iznad koje je uticaj na akvatične organizme verovatan. Poređenjem sa kanadskim preporukama, sadržaj žive je prekoračen na skoro svim ispitanim lokalitetima, prema ISQG vrednosti. Viša PEL vrednost ukazuje na verovatno prisutne negativne toksične efekte na akvatične organizme i sedimente u dva ispitivana profila u Dunavu (profil A i profil

B). Pojava žive u sedimentu je posledica ispuštanja industrijskih otpadnih voda (naročito iz pogona za proizvodnju hlora), upotrebe živinih pesticida za zaštitu semena, upotrebe živinih jedinjenja u upaljačima eksplozivnih sredstava (posledice ratnog konflikta 1999. godine) i upotreba žive u mernim uređajima (u toku razaranja industrijskih postrojenja za vreme konflikta 1999. godine uništen je deo ove merne opreme). Arsen je poznat po negativnim ekotoksičnim efektima, a negov sadržaj u sedimentu reke Dunav nije bio iznad ICPDR vrednosti. Sadržaj drugih teških metala, cinka, bakra, kadmijuma i olova (profil B) je bio u ispod vrednosti propisane ICPDR. Kako se sam proces zagađivanja vode teško može sprečiti, zaštita voda, prvenstveno, je usmerena na smanjenje uticaja, a u najboljem slučaju, potpuno uklanjanjanje uticaja teških metala. To se postiže kroz opšte ekološke (radne akcije, ekološki aktivizam) kao i specifične mere (obrazovanje, sredstva javnog informisanja). Najvažnije je utvrđivanje kvaliteta vode i mogućnosti vodotoka da primi otpadne vode, registovanje svih mogućih zagađivača (njihova lokacije i stepen zagađivanja), obavljanje stalnih kontrola otpadnih voda u blizini vodotokova, prečišćavanje otpadnih voda i izmeštanje industrije na mesta na kojima će zagađivanje biti minimalno.

Ključne reči: sediment, voda, Dunav, teški metali
Keywords: sediment, water, Danube, heavy metals

INTRODUCTION

Chemical elements belong to the most common environmental pollutants, and they are equally undesirable in the air, water and soil (Mendil et al., 2010). Nowaday, environmental pollutants of aquatic ecosystems, especially heavy metals are the major problem. In aquatic systems, they are deposited into the sediments (Monroy et al., 2014). Metal pollutants can accumulate in aquatic organisms from water, sediments or through the food chain. Some metals like Cu, Zn or Fe are important for many biochemical processes in living organisms. Also, they are essential elements for aquatic plants and animals. Presence of pollutants in the Danube is the topic of many previous researches and international treaties and agreements, such is the Danube Convention issued by the International Commission for the Protection of the Danube River (Milenković et al., 2005; Pajević et al., 2008). Serbia is the full member of this association since August 2003, which stipulates monitoring of water quality as well as ecosystem. The aims of the study was to measure concentrations of heavy metals in samples of sediment and water.

MATERIAL AND METHOD

The samples were taken from the river Danube in Belgrade region, near Vinča - Profile A (N 44º 40', E 20º 43') and Belegiš - Profile B (N 45º 01', E 20º 20'). Sediments samples were collected during 2013. The samples of sediments were first dried at 110 ºC for 24 h and then were mechanically homogenized to a powder. Amounts of 0.5 g of each sample of dry sediments were wet digestion with nitric acid and hydrogen peroxide in a microwave closed system on temperature program of 180 – 240 ºC for 35 min. All reagents used in the analysis were of reagent grade. Double-deionized water (18.2 $M\Omega cm^{-1}$ resistivity at 25ºC) obtained using a Milli-Q system (Millipore, Bedford, USA) was used for all dilutions. Chemicals used for microwave digestion (nitric acid, HNO_3, 65%) and hydrogen peroxide (H_2O_2, 30%) were of high pure quality (Merck, Germany). The element standard solutions (Merck, Germany) that were used for the calibrations were prepared by diluting the stock solutions of 1000 mg/L concentration. Sample digestion was carried out using a microwave closed system Berghof MWS-2 (Berghof Products+ Instruments GmbH, Eningen, Germany). After digestion, concentrations of heavy metals were analyzed by absorption spectroscopy using the GBC 932 plus atomic absorption spectrometer (GBC Scientific Equipment, USA). Detection of Cu, Fe, Zn and Ni were determinate in air-acetylene flame, while analysis of Pb and Cd were conducted by graphite furnace (GBC SensAA spectrometer with Hyper-Pulse background corrector) with an auto sampler. Mercury and arsenic were analyzed by the cold vapor technique with a flow injection system. The operating parameters for the working elements were set as recommended by the manufacturers, and are that were given in Table 1.

Water samples (n=74) were collected at the depth of 20-30 cm under the water surface with a 5 l Friedinger bottle (SCHOTT DURAN®, Elmsford, North America), and mixed. A 500 ml subsamples were bottled in the pre-cleaned plastic flasks. The sampled material was stored in darkness at 4 °C, and before analyses all water samples were filtered through Whatman filters (Sigma-Aldrich Co, United Kingdom) to remove suspended particulate matter.

Table 1. Instrumental analytical conditions for measurement heavy metals recommended by FAAS

Element	Acetylene (L/min)	Air (L/min)	Wavelength (nm)	Slit width (nm)
Fe	2.0	17.0	248.3	0.2
Cu	2.0	17.0	324.7	0.5
Zn	2.0	17.0	213.9	0.5
As	2.0	17.0	193.7	1.0

Instrumental conditions	Pb	Cd
Wavelength (nm)	217.0	228.8
Slit width (nm)	1.0	0.5
Argon flow (mL/min)	250	250
Sample volume (μL)	20	20
Heating program temperature (°C)		
Drying 1	80 (10,10)[a]	80 (10, 10)
Drying 2	120 (20, 5)	120 (20, 5)
Pyrolysis	400 (5, 15)	300 (5, 15)
AZ (auto zero)	400 (0.5, 1)	300 (0.5, 1)
Atomization	1600 (1, 2)	1700 (0.9, 2)
Cleaning	2100 (1, 1)	2100 (1, 1)

Conditions for GFAAS [a] - ramp time (s), hold time (s)

The analyses were performed by included the assessment of concentrations of the following elements: As, Al, Zn, Fe, Cu, As, Sd, Hd, Pb. The concentrations of heavy metals were compared with the probable effect levels (PELs). According to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, PELs for Zn, Cu, As, Sd, Hg and Pb are 315 mg kg^{-1}, 197 mg kg^{-1}, 17.0 mg kg^{-1}, 3.5 mg kg^{-1}, 0.486 mg $kg^{-1,}$ 91.3 mg kg^{-1} dw, respectively.

Statistical analysis of the results were elaborated using software GraphPad Prism version 5.00 for Windows, GraphPad Software, San Diego California USA, www.graphpad.com.

RESULTS AND DISCUSSION

Presence of chemical elements in water depends on many environmental factors, like the influence of industry and other forms of pollutions (Adhikari et al.,2009). The obtained results may be explained by the fact that several rivers flow into the Dunabe near the sampling site, but also large cities lying on this river, as well as the industry, can be serious polluters of the environment (Subotić et al., 2013). Concentration of the metals in samples of sediments and water from Danube river are presented in table 2.

Table 2. Heavy metal concentration in water samples (mg L) and sediment (mg kg^{-1}) from river Danube, expressed as means±deviation (range)

Metals	Profile A		Profile B	
	Water (mg/L)	Sediment (mg kg^{-1})	Water (mg/L)	Sediment (mg kg^{-1})
Zn	0.032±0.002	270.40±17.98	0.063±0.007	139.4 ± 8.71
Fe	0.33±0.02	17530.00±971.7	0.41±0.01	16104 ± 1068.0
Cu	0.004±0.001	50.93±3.34	0.004±0.001	35.95 ± 1.40
As	0.004±0.001	13.89±1.05	0.006±0.001	8.90 ± 0.25
Cd	ND	1.69±0.13	ND	0.61 ± 0.11
Hg	ND	0.80±0.09	ND	0.69 ± 0.08
Pb	ND	64.92±2.39	ND	32.58 ± 2.61

Legend: *ND- not detected

It was found that the environmentally mobile elements were arranged in the order Fe> Zn> Pb>Cu>As> Cd> Hg in samples collected in the examined profile A. In profile B, elements were arranged Fe> Zn> Cu>Pb>As> Hg> Cd. Vasiljevic and Tomasevic (1985), 30 years ago, were conducted a survey on the heavy metal concentrations in the Danube sediments in Serbia. They selected six sites, two of which corresponded to those investigated in this study (Veliko Gradiste and Tekija), thus allowing a direct comparison between the sites over the intervened time period. Their results also showed higher concentrations at those sites, where higher sedimentation occurs due to slowing down of the river.

Zinc concentration in profile A and profile B did not exceed PeLs prescribed by Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Comparing with the profile examined in 2001 (Škrbić et al., 2004), zinc concentration increased during the same period. Copper concentrations were below the PeLs in profile A and profile B, but it was higher in profile A. Crnković et al. (2008) found that copper concentration was below the

PELs. In 2005, the obtained results for copper concentration were in agreement with the data presented in the study of copper content in Sava sediment around Belgrade (Ščančar et al., 2007). Arsenic concentrations were below PELs prescribed by Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. In 2001 (Škrbić et al. 2004) arsenic concentration increased in sediment from Novi Sad. In the study of Crnković et al. (2008) it was found the arsenic concentration always below PELs value. Cadmium concentration has been below the PELs value. In 2001, on Novi Sad spot, Šrkbić et al., 2004 noted that the examined profile in their work contained higher amount of cadmium. According to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life the concentration of mercury in profile A (0.80±0.09 mg kg-1) and profile B (0.69 ± 0.08 mg kg-1) exceed PELs, which are 0.486 mg kg^{-1}. The obtained results are not in argeement with the previous studies of mercury content in sediment of Danubian tributaries around Belgrade (International Commission, 2000). In the study of Crnković et al. (2008) concentration of mercury was above the PELs.

CONCLUSIONS

This study provides information about heavy metals content in water and sediment from the Danube river. Sediment samples contained mercury above the PELs prescribed by the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.

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