Ecotoxic metals in water and sediment of the southeastern part of the of Šibenik harbor, Croatia

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Abstract

Šibenik harbor is located in the lower part of the Krka river estuary. During last fifty years in the southeastern part of the Šibenik harbor (southern shore of the peninsula Mandalina) military port and repair shipyard were located. Currently, there has been building-out of nautical centre. Long-lasting port and shipyard activities contaminated surrounding aquatic environment with ecotoxic metals. Intention of this research was to identify present ecotoxic metals concentrations in water and sediment as a result of this contamination.

In order to define its influence on the environment, we measured total mercury, cadmium, lead, copper and zinc concentrations in the water columns from three sampling sites. Measured concentrations were compared with ones from referent site located in the western part of the Šibenik harbor (Martinska). Concentrations of the ecotoxic metals were also analyzed in bulk and the fine fractions (< 63µm) in the sediment.

Ecotoxic metals concentrations found in the water were not significantly elevated indicating weak anthropogenic influence.

On the other hand, measured concentrations of the ecotoxic metals in sediment samples are significantly higher of naturally present concentrations. That is consequence of strong input of

ecotoxic metals in the past period. These elevated metal concentrations in sediment are high threat for benthic communities.

1 Introduction

Industrial, agricultural and domestic wastes are continuously discharged into water-bodies. Pollutants in those wastes, particularly heavy metals, can endanger public health by becoming part of the food chain. Heavy metals are not biologically degraded like many organic pollutants, hence, they tend to accumulate, especially in sediments associated with organic and inorganic matter, and involve formation and adsorption of different complexes. It is important to distinguish between the introduction of trace metals by anthropogenic activities and through the natural weathering processes.

All aquatic ecosystem sediments are trace metals ultimate sinks, with possibility of their remobilization due to physico-chemical changes, into the water column (Ouyang et al., 2006). Sediments are not only reservoir for contaminants through the adsorption and absorption processes, but also a source of toxicants for aquatic organisms through the water column which is in direct contact with precipitated layer on the bottom (Long et al., 1996; Fichet et al., 1998). Therefore, monitoring of trace metals in sediments is necessary to provide insight of recent as well as early pollution, which is directly connected with the pollution level in the water column above the sediments.

Krka River is situated in the karst region of Croatia and its estuary was formed during the Holocene transgression. Located between the Skradinski Buk waterfalls (calc-tufa barrier) through the Prokljan Lake to the St. Ante Channel, the estuarys' total length is to about 22 km. It is typical stratified estuary with fresh-brackish surface layer moving seawards and bottom seawater layer as counter-current, moving upwards. Input of clastic material of terrigenous origin in the Krka estuary, is small (Juračić and Prohić, 1991), because the number of waterfalls along the Krka River, significantly reduce suspended material transport (Cukrov et al., 2004). Main input of the terrigenous material in the Krka River estuary originates from a Guduča creek. That material is mostly settled in upper part of the estuary (Cukrov and Barišić, 2006). Krka River estuarine sediments are generally unpolluted, according to the literature (Bogner et al. 2004; Cukrov et al., in press; Martinčić et al. 1989; Martinčić et al., 1990; Prohić and Juračić, 1989). Calculated sedimentation rate was 2 mm/a upstream of the Prokljan Lake, 4 - 5 mm/a at the Guduča Creek mouth in Prokljan Lake and 3 - 4 mm/a in other parts of the lake. Downstream of the Prokljan Lake to the lower area, sedimentation rate was 1 - 2 mm/a. In the lower part of estuary, sedimentation rate was very small, less than 1 mm with exceptions in deepest parts of estuary in front of city Šibenik where sedimentation rate was approx. 3 mm/a (Cukrov et al., 2007).

Šibenik harbor is located in the lower part of the Krka river estuary. During last fifty years in the southeastern part of the Šibenik harbor (southern shore of the peninsula Mandalina) military port and repair shipyard were located.

Long-lasting port and shipyard activities are a typical example of mixed diffuse and concentrated sources of ecotoxic metals. Also, that is integral part of the city of Šibenik and, therefore, all urban (waste and communal waters, industry) and port activities influence the pollution present in the seawater and sediments.

Basic evaluation factor of trace metals in natural sediments is their toxicity, which is connected with their concentration levels. Trace metals in elevated concentrations have various toxicological effects on biota in natural water ecosystems, and indirectly on humans.

2 Experimental

Sampling and sampling preparation

Water samples were collected in January 2008. The samples were taken in 1L in pre-cleaned high density polyethylene bottles (HDPE) for determination Cd, Pb, Cu and Zn and in 1 L pre-cleaned SIMAX Sklárny Kavalier borosilicate glass reagent bottles (Sázava, Czech Republic) for Hg, respectively, all by scuba diving (Kniewald et al. 1987). Salinity was determined by the Atago refractometer S-10E (Tokyo, Japan), while pH were determined by the Mettler Toledo MP 120 (Schwerzenbach, Switzerland).

Total Cu, Cd, Pb and Zn concentrations were measured in unfiltered samples. Prior to analysis, water samples for measuring Cu, Cd, Pb, Zn and Hg total concentrations were acidified with extra clean nitric acid (Merck, Darmstadt, Germany) at $pH < 2$ and UV treated during 24 hours in order to digest organic matter (150 W Hg lamp).

Cu, Cd, Pb and Zn concentration measurements were performed on the ECO Chemie μAUTOLAB multimode potentiostat (Utrecht, The Netherlands) connected with a three-electrode system Metrohm 663 VA STAND (Herissau, Switzerland). Electrochemical method used (Branica, 1990; Bard and Faulkner, 2001) was differential pulse anodic stripping voltammetry (DPASV). Method detection limit in seawater samples was in the range of 1 do 10 ng/L, depending on metal. Total Hg was measured by cold vapour atomic absorption spectrometry (CVAAS) with detection limit 0.015 ng/L (Kwokal and Branica, 2000).

Sediment samples were collected in January 2008 by a scuba diver using hand-driven acrylic corers (Φ14 cm). Surface sediment were sampled at 4 locations (SP 1 to SP 3 at the location of the future nautical centre, and ref sample in front of the Martinska located in the western part of the Šibenik harbor (Figure 1).

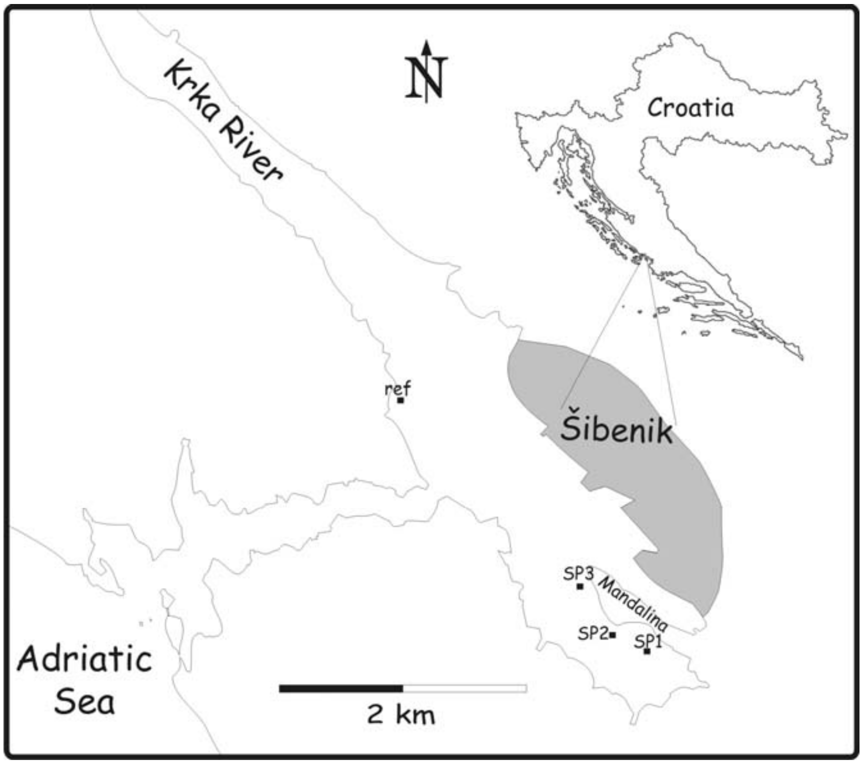

Figure 1. Map of the Šibenik harbor with sampling locations

Half of the sediments were wet sieved using Sieve shakers AS 200 Digit with 0.063 mm standard Retsch sieves (Haan, Germany) and the fine fraction (<63 µm) was separated for future analysis. Sieved sediment and other half of sediment (bulk) were dried at the 50°C until constant mass. The analyses were performed at Activation Laboratories Ltd of Canada for major and trace elements determinations from dried samples, using an ultratrace 2 package (ICP + ICP/MS) with Aqua Regia Extraction and Code 1 G (cold vapor AA) for Hg determination. Techniques and procedures can be found at www.actlabs.com.

Sampling locations shown in Figure 1 were determined by GPS instrument Garmin GPSMap 76 CSx (Kansas City, USA) with the accuracy of ± 5 m, while sampling depths were determined by the dive computer Uwatec Aladin Tec 2G (Henggart, Switzerland) with a depth accuracy of ± 5 cm..

3 Results and discussion

The total concentration of mercury, cadmium, lead, copper and zinc in the water columns at three locations of the future nautical port Mandalina-Kuline and referent site (Fig 1.) are presented in the Figure 2.

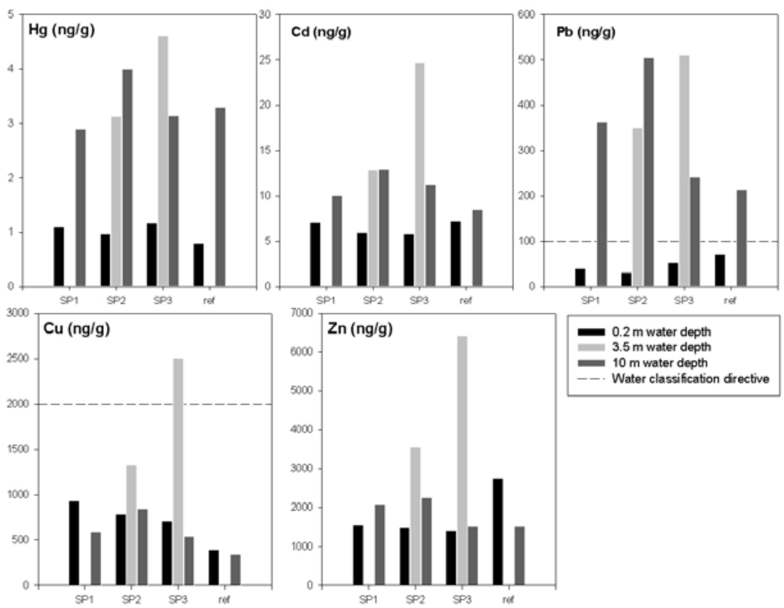

Figure 2. Total concentrations of Hg, Cd, Pb, Cu and Zn (ng/L) in water columns

In all water samples Hg, Cd and Zn concentrations qualified estuarine water into first class of natural water according to Croatian water classification directive (1998). Cu concentration in water sample from 3.5 m depth at the sampling station SP3 qualified water into second class, while Cu concentrations in all other water samples qualified into first class. Only Pb concentrations found in surface water samples qualified water into the first class, while Pb content in deeper water samples qualified to second class. It is interesting to notice elevated concentrations of all metals at the 3.5 m water layer from SP3 sampling station. These elevated concentrations were consequence of stratification of the estuary waters (Bilinski et al., 2000).

The concentration levels of mercury, cadmium, lead, copper, zinc, chromium, nickel, arsenic and silver in surface sediment are presented in Figure 3. As the Croatian National Regulation on the sediment quality does not exist, measured metal concentrations in sediments were compared with Sediment Quality Guidelines from National Oceanic and Atmospheric Administration, USA (1999). ERM (effect range low) and ERM (effect range median) were calculated for 9 trace metals (Hg, Cd, Pb, Cu, Zn, Cr, Ni, As & Ag). ERL guideline represent concentrations below which effect were rarely observed, while ERM guideline represent concentrations above which toxic effect frequently occur.

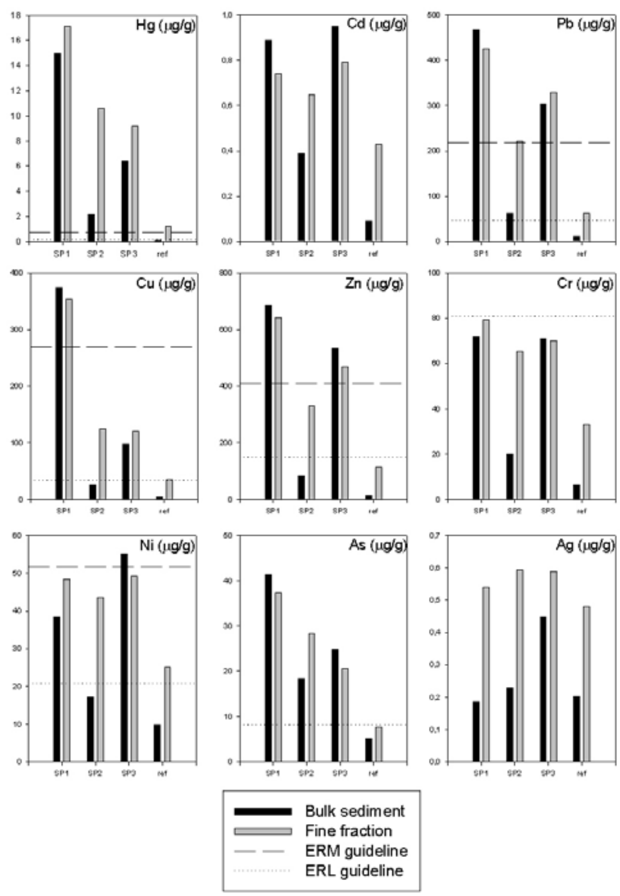

Figure 3. Concentrations of Hg, Cd, Pb, Cu, Zn, Cr, Ni, As and Ag (µg/g) in the sediments from Šibenik harbor with Sediment Quality Guidelines from National Oceanic and Atmospheric Administration, USA (1999).

It is clearly notable difference between sediment metals concentrations levels from planned nautical port (SP1 to SP3) and referent site which contains significantly lower metal levels. Also, concentration levels of ecotoxic metals in sediment from referent site are at the same level as one measured there 20 years ago (Martinčić et al. 1989; Martinčić et al., 1990; Prohić and Juračić, 1989). The concentration levels of mercury were extremely elevated (few times above ERM guidelines) in fine fraction and bulk sediment from future nautical port. However, elevated metal concentration were also found in the sediment from the other side of the Šibenik harbor, where fine fraction was above ERM guidelines, while bulk sediment was below ERL guidelines.

The concentration of lead, copper, zinc and nickel in the sediments from planned nautical port were elevated and partly above ERM guidelines (Figure 3), but fine fraction of sediment were completely above ERL guidelines. The arsenic concentrations in sediments from future nautical port were above ERL guidelines, while in sediments from referent sampling stations were below ERL guidelines, according arsenic concentrations. The concentrations of cadmium, chromium and silver were below ERL guidelines (Figure 3).

It is important to understand that these guidelines (ERM & ERL) were not derived as toxicity thresholds. That is, there is no assurance that there will be a total lack of toxicity when metal concentrations are less than the ERL values. Similarly, there is no assurance that samples in which ERM values are exceeded will be toxic. Toxicity, or a lack thereof, must be confirmed with empirical data from toxicity tests.

4 Conclusions

In general, trace metals concentrations (Hg, Cd, Pb, Cu and Zn) in the water from area of the planned nautical port are lightly elevated, but similar with results in others parts of the Krka River estuary. Particularly, trace metal concentrations were elevated in a mixed water layer.

The concentration levels of ecotoxic metals (of Hg, Cd, Pb, Cu, Zn, Cr, Ni, As and Ag) in surface sediment from future nautical port Mandalina-Kuline were significantly elevated as a consequences of long-lasting port and shipyard activities. These elevated concentrations of ecotoxic metals can be associated with toxic effects in the investigated aquatic ecosystem.

5 Acknowledgements

The financial support of the Ministry of Science, Education and Sports of the Republic of Croatia, under Project 098-0982934-2720, Physical Chemistry of Trace Metals in Aquatic Systems, is gratefully acknowledged.

References

[1] Bard, A.J. and Faulkner, L.R. (2001) Electrochemical methods: fundamentals and applications. John Wiley & Sons, inc., New York, USA.
[2] Bogner, D., Ujević, I., Zvonarić, T., Barić, A., 2004. Distribution of selected Trace metals in coastal surface sediments from the middle and south Adriatic Sea. Fres. Environ. Bull. 13, 1281-1287.
[3] Branica, M., (Ed.) 1990. Environmental research in aquatic systems. Forschungszentrum Jülich GmbH, Jülich, Germany.
[4] Bilinski, H., Kwokal, Ž., Plavšić, M., Wrischer, M., Branica, M., 2000. Mercury distribution in the water column of the stratified Krka river estuary (Croatia): importance of natural organic matter and of strong winds. Water Research, 34, 2001-2010.
[5] Cukrov, N., Barišić, D., Branica, M., 2004. Content of the 40K, 232Th, 226Ra, 238U & 137Cs in the recent sediments of the Krka river estuary. In: Briand, F. (Ed.), Rapp. 37 Congress CIESM, Barcelona, p. 20.
[6] Cukrov, N., Barišić, D., 2006. Spatial Distribution of 40K and 232Th in Recent Sediments of the Krka River Estuary. Croat. Chem. Acta 79, 115-118.
[7] Cukrov, N., Barišić, D., Juračić, M., 2007. Calculated Sedimentation Rate in the Krka River Estuary using Vertical Distribution of 137Cs. In: Briand, F. (Ed.), Rapp. 38 Congress CIESM, Istanbul, p. 81.
[8] Cukrov, N., Frančišković-Bilinski, S., Mikac, N., Roje, V., in press. Natural and anthropogenic influences recorded in sediments from the Krka river estuary (Eastern Adriatic coast), evaluated by statistical methods. Fres. Environ. Bull.
[9] Fichet, D., Radenac, G., Miramand, P., 1998. Experimental studies of impacts of harbor sediments resuspension to marine invertebrates larvae: bioavailability of Cd, Cu, Pb and Zn and toxicity. Marine Pollution Bulletin, 36, 509-518.
[10] Juračić , M., Prohić , E., 1991. Mineralogy, sources of particles, and sedimentation in the Krka River Estuary (Croatia). Geol. Vjesnik 44, 195-200.
[11] Kniewald, G., Kwokal, Ž., Branica, M., 1987. Marine sampling by scuba diving. 3. Sampling procedure for measurement of mercury concentrations in estuarine waters and seawater. Mar. Chem. 22, 343-352.
[12] Kwokal, Ž., Branica, M., 2000. Determination of dissolved monomethylmercury in saline, estuarine and fresh waters of Croatia. Croat. Chem. Acta 73, 97-109.
[13] Long, E.R., Robertson, A., Wolfe, D.A., Hameedi, J., Sloane, G.M., 1996. Estimates of the spatial extent of sediment toxicity in major US estuaries. Environ. Sci. Techn. 30, 3585-3592.

[14] Martinčić, D., Kwokal, Ž., Branica, M., 1990. Distribution of zinc, lead, cadmium and copper between different size fraction of sediments. II The Krka River Estuary and the Kornati islands (Central Adriatic Sea). Science of Total Environment, 95, 217-225.
[15] Martinčić, D., Kwokal, Ž., Stoeppler, M., Branica, M., 1989. Trace metals in sediments from Adriatic sea. The Science of the Total Environment, 84, 135-147.
[16] NOAA (1999).National Oceanic and Atmospheric Administration, Sediment Quality Guidelines developed for the National Status and Trends Program (http://archive.orr.noaa.gov/cpr/sediment/SPQ.pdf)
[17] Ouyang, T. P., Zhu, Z. Y., Kuang, Y. Q., Huang, N. S., Tan, J. J., Guo, G. Z., Gu, l. S., Sun, B., 2006. Dissolved trace elements in river water : spatial distribution and the influencing factor, a study for the Pearl River Delta Economic Zone, China. Environ. Geol. 49, 733-742.
[18] Prohić, E., Juračić, M., 1989. Heavy Metals in Sediment - Problems Concerning Determination of Anthropogenic Influence. Study in the Krka River Estuary, Eastern Adriatic. Environ. Geol. Water Sci. 13, 145-151.
[19] Water classification directive. (1998) Narodne novine - Official Gazette of the Republic of Croatia, No. 77.

Ekotoksični metali u vodi i sedimentu jugoistočnog dijela šibenske luke, hrvatskaž

Sažetak

Šibenska luka smještena je u donjem dijelu estuarija rijeke Krke. Tijekom zadnjih pedesetak godina u jugoistočnom dijelu Šibenske luke (južna obala poluotoka Mandalina) djelovali su vojna luka i vojno remontno brodogradilište. Dugogodišnje lučke i remontne aktivnosti opterećivale su okolni akvatorij ekotoksičnim metalima. Cilj ovog istraživanja bio je ispitati posljedice tog opterećenja, odnosno odrediti sadašnje stanje koncentracija ekotoksičnih metala. Trenutno je u tom akvatoriju, u tijeku izgradnja nautičkog centra, te je za potrebe izrade studije utjecaja na okoliš nautičkog centra istraživana raspodjela ekotoksičnih metala žive, kadmija, olova, bakra i cinka u vodenim stupcima na tri postaje. Nađene koncentracije su uspoređene s koncentracijama s referentne postaje u zapadnom dijelu Šibenske luke (Martinska). Na istim postajama određena je i koncentracije ekotoksičnih metala u površinskim uzorcima sedimenta. Određene su koncentracije u ukupnom sedimentu i njegovoj najfinijoj frakciji (< 63μm).

Koncentracije ekotoksičnih metala u vodi nisu značajno više od prirodnih razina što ukazuje na trenutno neznatno antropogeno opterećenje. S druge strane koncentracije ekotoksičnih metala u sedimentu su znatno više od prirodnih. To je posljedica intenzivnog unosa tih metala u okoliš u prijašnjem razdoblju. Vrijednost koncentracije ekotoksičnih metala u sedimentu ukazuju na veliku vjerojatnost negativnog utjecaja na betonske zajednice.