Distribution of mercury, cadmium, lead, copper and zinc in sediments of the Rijeka harbour as record of pollution

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Abstract

Distribution of Hg, Cd, Pb, Cu and Zn were determined in sediment samples (first 9 centimetres) from 3 locations in area of the Rijeka Harbour.

In the first and the second location vertical distribution of the metal concentration in investigated sediments is uniform. In third one the vertical distribution reveals increase of metal concentration from surface down the sediment column (Hg 1,73-5,65 µg/g; Cd 1,28-8,54 µg/g; Pb 383-1206 µg/g; Cu 232-1156 µg/g and Zn 562-2225 µg/g), indicating reduction of pollution in the last decade.

Concentrations of cadmium, copper, lead and zinc were determined by differential pulse anodic stripping voltammetry (DPASV), while mercury by the cold vapor atomic absorption spectrometry (CVAAS).

As National Regulation on the sediment quality chemical criteria does not exist, measured metal concentrations in sediment were compared with ones in some Croatian (Šibenik) and world's harbours (Apra, Kaohsiung, Napoli, Sydney) as well as with ones in the North Adriatic Sea. Results comparison shows that concentrations of ecotoxic metals in sediments of Rijeka Harbour are comparable with results in others harbours but also significantly above natural values of North Adriatic Sea.

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 and different complex. It is important to distinguish between the introduction of metals by anthropogenic activities and through the natural weathering processes. The one side sediments are a sink for pollutant, but also a potential source the toxicity source for aquatic organisms. Therefore, monitoring of trace metals in sediments is necessary to provide insight of pollution in the water column and appearance of toxic metals in sediments

The Port of Rijeka is a typical example of mixed diffuse and concentrated sources of ecotoxic metals. The Port of Rijeka is integrated in the city of Rijeka pointing all city (waste and communal waters, industry) and port activity influences.

2 Experimental

2.1 Sampling and sampling preparation

Sediment samples were collected in November 2006 by a scuba diver using hand-driven acrylic corers (ϕ14 cm). First 9 centimetres of sediment were sampled at 3 locations (first one is Container and RO-RO Terminal, the second at the entry into the Sušak Port and the third one at the entry into the Rijeka Harbour). Sampling locations shown in Figure 1 were determined by GPS instrument Garmin GPSMap 76 CSx (Kansas City, USA) with the accuracy of ± 5 m.

Sediments were wet sieved using 0,063 mm standard Retsch sieves (Haan, Germany) and the fine fraction (<63 µm) was separated for future analysis. It is known that fine fraction bind more pollutants and that it is recommended for valuation of sediment quality in terms of pollution (Förstner 2004). Dried sediments were digested and concentrations of cadmium, copper, lead and zinc were determined by differential pulse anodic stripping voltammetry (DPASV) according to the method based on norm DIN 38406 E-16, while mercury by the cold vapour atomic absorption spectrometry (CVAAS).

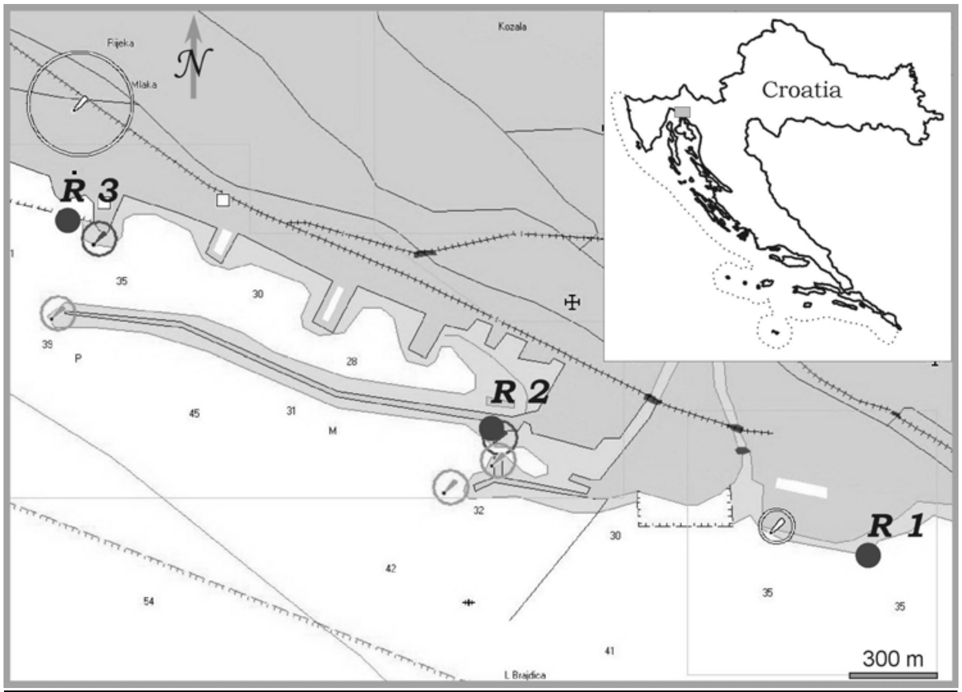

Figure 1. Map of the Rijeka Harbour showing the locations of sampling

3 Results & discussion

The concentration of mercury, cadmium, lead, copper and zinc in sediments of the Rijeka Harbour are present in Figure 2.

In the investigated sediment from the first and the second sampling site, the vertical distribution of cadmium, lead, copper and zinc concentration is uniform. However, concentrations of mercury are higher in deeper layers in the sampling site 1 and in middle layers in the sampling site 2. In the sampling site 3 sediments taken at the entry into the Rijeka Harbour, where all investigated metal concentrations are highest, the vertical distribution reveals increase of metal concentration from surface through the sediment column (Fig.2.). This vertical distribution of trace metal concentrations indicates decrease of the pollution in the last decade.

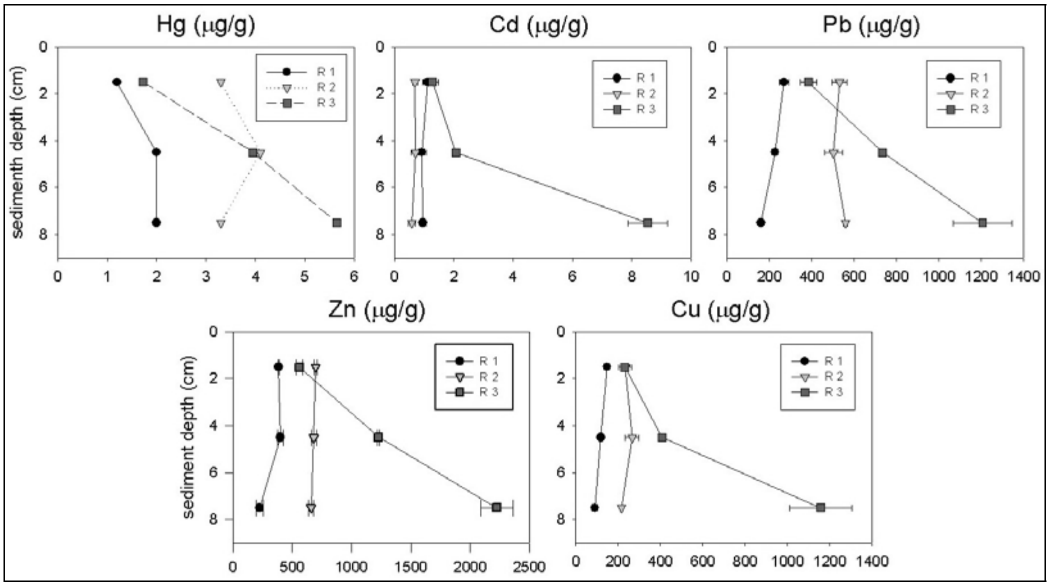

Figure 2. Vertical distribution of trace metal in the sediment of the Rijeka Harbour

As the National Regulation of the sediment quality does not exist, measured metal concentrations in sediments were compared with ones in the Šibenik Harbours, North Adriatic and some world's harbours of (Apra, Kaohsiung, Napoli, Sydney)(Table 1).

Table 1 – Concentrations of the trace metals (dry weight) in the sediments of worlds harbours ([1] Chen et al. 2007, [2] Sprovieri et al. 2006, [3] McCready et al. 2006, [4] Denton et al. 2005, [5] Martinčić at al. 1989, [6] Cukrov 2006)

	Grain size	Hg (µg/g)	Cd (µg/g)	Pb (µg/g)	Cu (µg/g)	Zn (µg/g)
Kaohsiung Taiwan [1]	< 1 mm	0,1 - 8,5	0,1 - 6,8	9,5 - 470	5 - 946	52 - 1369
Naples har. Italy [2]	< 2mm	0,01 – 139	0,01 - 3	19 - 3083	12 - 5743	17 - 7234
Sydney har. Australia [3]	bulk	0,1 - 5,9	0,2 - 10	5 - 1420	3 - 1060	17 - 11300
Apra har. Micronesia [4]	< 1 mm	0,1 - 0,8	0,07 - 2,2	1,1 - 194	1,7 - 153	3 - 552
North Adriatic sea [5]	< 0,063 mm	0,1 - 0,4	0,1 - 0,4	25 - 44	10 - 21	76 - 140
Šibenik har. [6]	< 0,063 mm	0,9 - 2,6	12,7 -23	215 -408	120 -186	2299 - 4713
Rijeka Harbour	< 0,063 mm	1,2 - 5,65	0,6 - 8,5	160 - 1206	91 - 1156	226 - 2225

Results comparison shows that concentrations of ecotoxic metals in sediments of the Rijeka Harbour are comparable with results in others harbours, but also significantly above natural values of the North Adriatic Sea. Additionally, in the Rijeka Harbour only fine fraction (< 0,063 mm) that bind most pollutants was analysed. In the bulk sediment concentration of trace metal are usually lower.

In the Table 2 are presented approved trace metal concentrations values permited in Australia & New Zealand, USA & Canada. ERL (Effects Range Low) values should be used primarily as estimates of the concentrations below which toxicity is least likely, and ERM (Effect Range Median) values are indicators of concentrations which are associated with toxicity effects.

Table 2 – Guideline values for trace metal toxicity (**ERL** – Effects range low, **ERM** – Effect range median). [1]Australia & New Zeland, [2]National Oceanic and Atmospheric Administration, [3] University Waterloo, Canada.

	Hg (μg/g)		Cd (μg/g)		Pb (μg/g)		Cu (μg/g)		Zn (μg/g)	
	ERL	ERM	ERL	ERM	ERL	ERM	ERL	ERM	ERL	ERM
ANZECC [1]	0,15	1	1,5	10,0	50	220	80	270	200	410
NOAA [2]	0,15	0,71	1,2	9,6	46,7	218	34	270	150	410
UWC [3]	0,20	2	0,2	10,0	31	250	16	110	90	200

Table 3 presentes Average and Median concentrations of trace metals in the sediments from the Rijeka Harbour.

Table 3 – Average and Median concentrations of trace metal in sediment from the Rijeka Harbour

Luka Rijeka	Hg (μg/g)	Cd (μg/g)	Pb (μg/g)	Cu (μg/g)	Zn (μg/g)
Average	3,03	1,87	508,02	319,10	785,08
Median	3,30	0,96	502,97	231,69	658,92

Comparing average and median Hg concentrations in the sediments it is evident that these concentrations in the Rijeka Harbour are above concentrations that are associated with possible toxicity effects (Table 2 and Table 3). Concentrations of Cd are just about ERL values. Pb, Cu and Zn concentrations in the Rijeka Harbour sediments are above ERM values.

4 Conclusions

In general, concentrations of trace metals (Hg, Cd, Pb, Cu & Zn) are significantly elevated in the sediments of the Rijeka Harbour, but similar with results in others world harbours.

In the sediments at the Rijeka Harbour entrance (R 3) ecotoxic metals concentrations are highest, especially in the deepest sediment layers. Higher concentrations in deeper layers indicate reduction of the ecotoxic metals input in the last decade.

Acknowledgements

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Raspodjela žive, kadmija, olova, bakra i cinka u sedimentima luke rijeka kao podaci o zagađenju

Sažetak

Istraživana je raspodjela ekotoksičnih metala žive, kadmija, olova, bakra i cinka u uzorcima sedimenta s tri postaje (prvih 9 cm) u akvatoriju Luke Rijeka.

Vertikalna distribucija koncentracija metala u sedimentima sa prve i druge lokacije je ujednačena. Na trećoj lokaciji, vertikalna raspodjela pokazuje povećanje koncentracije metala s dubinom duž stupca sedimenta (Hg 1.73-5.65 µg/g; Cd 1.28-8.54 µg/g; Pb 383-1206 µg/g; Cu 232-1156 µg/g and Zn 562-2225 µg/g), što upućuje na smanjenje zagađenja u posljednjem desetljeću.

Koncentracije bakra, cinka, kadmija i olova bile su mjerene diferencijalno pulsnom voltammetrijom anodnog otapanja(DPASV), dok je koncentracija žive bila mjerena atomskom apsorpcijskom spektrometrijom metodom hladnih para (CVAAS).

S obzirom da u Hrvatskoj zakonskoj regulativi ne postoji uredba o kemijskoj kvaliteti sedimenta, izmjerene koncentracije metala u sedimentima bile su uspoređene s onima iz nekih Hrvatskih (Šibenik) i svjetskih luka (Apra, Hamilton, Kaohsiung, Napulj, Sydney), kao i sa koncentracijama istih u Sjevernom Jadranskom moru. Usporedba rezultata pokazuje da su koncentracije ekotoksičnih metala u sedimentima Luke Rijeka usporedive s rezultatima drugih spomenutih luka, ali su značajno povišene u odnosu na prirodne koncentracije u Sjevernom Jadranskom moru.