Conférence Méditerranéenne Côtière et Maritime
EDITION 4, SPLIT, CROATIA (2017)
Coastal and Maritime Mediterranean Conference
Disponible en ligne – http://www.paralia.fr – Available online

Spatial distribution and mobility of trace metals in sediments of the Krka River estuary (Adriatic Sea, Croatia)

Nuša CUKROV [1], Cédric GARNIER [2], Duc Huy DANG [3], Ana-Marija CINDRIĆ [1], Dario OMANOVIĆ [1], Neven CUKROV [1]

1. Ruđer Bošković Institute, Division for Marine and Environmental Research, Bijenička cesta 54, 10000 Zagreb, Croatia.
   cukrov@irb.hr, ana-marija.cindric@irb.hr, omanovic@irb.hr, ncukrov@irb.hr

2. Laboratoire PROTEE, Université de Toulon, CS 60584, 83041 Toulon Cedex 9, France.
   cgarnier@univ-tln.fr
2. Trent University, Water Quality Centre, 1600 West Bank Drive, Peterborough, Ontario, K9L 0G2, Canada.
   huydang@trentu.ca

Abstract:
Estuarine sediments act as a sink for metal contaminants in aquatic system. As a consequence of biogeochemical processes which influence metal mobility, those sediments could become secondary source of metal contaminants for the environment.
The objectives of this study were to evaluate trace metal content and mobility in sediments from the Krka River estuary. Surface sediments were sampled at 40 locations scattered through entire estuary, allowing the determination of trace metal distribution with high resolution. Mobility was assessed using two approaches: (1) pore water extraction by centrifugation and (2) diffusive gradient in thin films (DGT) sediment probes.
Surface sediment analysis revealed three main pollution sources, all located in the lower part of the estuary: former ferromanganese industry, phosphate transhipment harbour and nautical marina. Mobility in the sediments is controlled by early diagenesis processes.

Keywords: Sediments, Estuary, Trace metals, Porewater, Diffusive gradients in thin films, Early diagenesis.

1. Introduction

The Krka River, located on the Eastern Adriatic coast, is considered as a pristine river. However, lower part of its estuary is under anthropogenic influence of the Šibenik town. It is the largest settlement in the region (~50 000 inhabitants) and a main source of

https://dx.doi.org/10.5150/cmcm.2017.020

contamination (waste waters, ferromanganese industry, harbour…), see figure 1. In recent years most of the town's sources of contamination are closed or modernized. Currently, the nautical tourism (~1000 permanent berths) is considered as a serious seasonal anthropogenic treat for the estuary ecosystem (CINDRIĆ *et al.*, 2015).

2. Experimental

Surface sediment samples were collected on 40 locations along the entire estuary and analysed for major/minor/trace elements. To gain information about vertical distribution and mobility of trace metals in estuarine sediments, a couple of technics were used: (1) classical ex-situ method including sediment core sampling, slicing each cm and extracting pore water and (2) *in situ* application of DGT (diffusive gradients in thin films) probes.

All solid sediment samples (surface samples and core samples) were frozen, freeze dried and sieved <2mm. Mercury concentrations were determined in untreated samples (~30-100 mg) using an Advanced Mercury Analyzer AMA 254 (LECO Corporation), while all other elements (Al, As, Ba, Be, Bi, Cr, Cs, Cu, Cd, Co, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V, Zn) were determined in acid digested samples (using microwave) by using High Resolution Inductively Coupled Plasma Mass Spectrometer (HR ICP-MS, Element 2, Thermo). A certified material PACS-2 (National Research Council of Canada) was used for validation of the analysis.

Porewater extraction was conducted under inert atmosphere (N_2) to prevent oxidation. All porewater samples were filtered (0.22 μm syringe filters, cellulose acetate, Sartorius). Dissolved Organic Carbon (DOC) concentrations were determined using a TOC-VCSH analyser (Shimadzu). A satisfactory accuracy of analyses was validated using certified reference material MISSIPPI-03 (Environment Canada). Trace elements were determined using HR ICP-MS.

Two DGT sediment probes (exposure window 150×18 mm, diffusive gel 0.08 mm) (DGT Research Ltd) were placed in sediment *in situ* for 94 hours. After retrieval, probes were rinsed with MQ water (18.2 MΩ cm^{-1}, Millipore, USA), disassembled and sliced using Teflon-coated razor blades with resolution of 5 mm. Each slice was extracted in 1.5 mL 1 M HNO_3 (suprapur). Extracted metals (Fe, Al, Mn, Ti, Co, Cr, Pb, Ti, Cu, Ni, and Cd) were analysed by HR-ICP-MS.

3. Results and discussion

Surface sediment analysis demonstrated that generally there are three main pollution sources: former ferromanganese industry (Mn, Pb, Bi, Ba, Co, Sb, Cu, Zn), phosphate transhipment harbour (U, Cd, Bi, Cr, Ag, Sb, Cu) and nautical marina (Hg, As, Cu, Zn, Sb); which differently contribute to the sedimentary deposits, see figure 1. No elevated metal concentrations were found in the upper part of estuary. For example, in the upper part of the estuary mercury concentration were found in range 0.06-0.4 μg g^{-1}, while in

the lower part of the estuary values go as high as 12.4 µg g^{-1} (figure 1). If we compare this values to various Sediment Quality Guidelines (ERL value 0.15 µg g^{-1}, ERM values 0.7-1.3 µg g^{-1}) (BURTON, 2002), we can see that highest mercury value is far above ERM value.

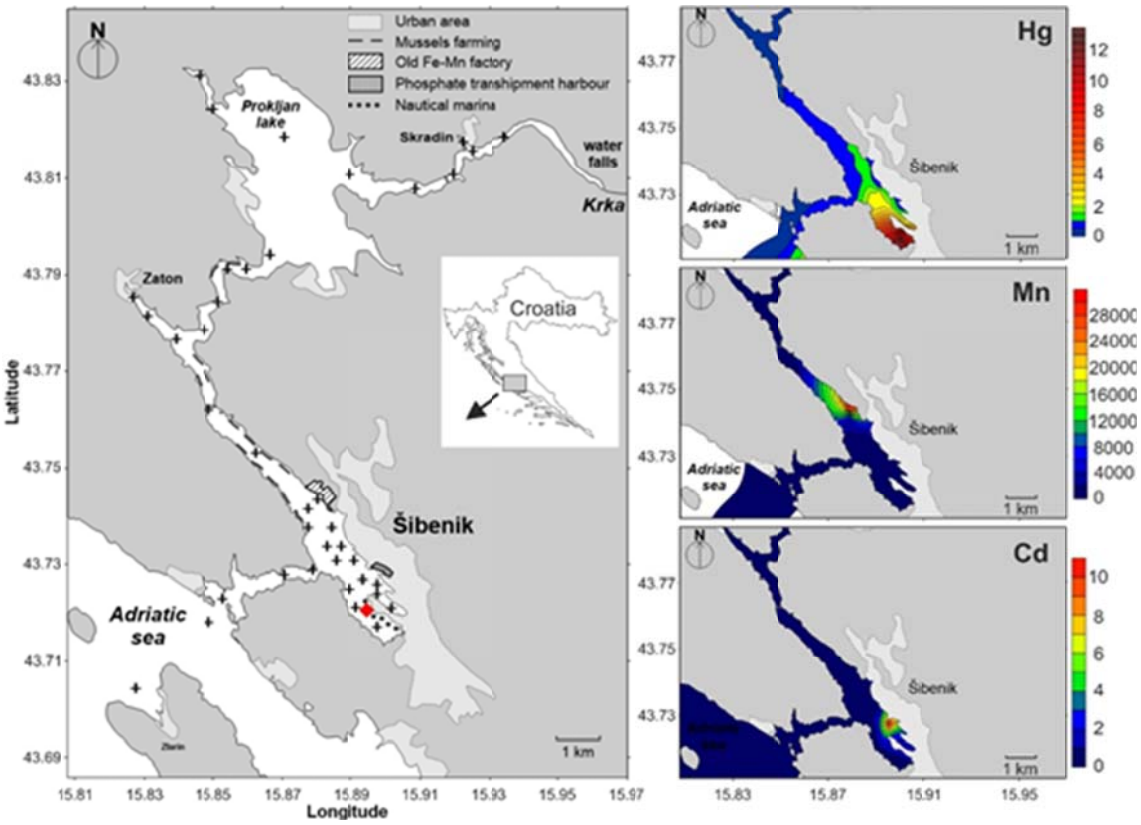

Figure 1. Map of the Krka River estuary with marked surface sediment (crosses) and sediment core and DGT probe (diamond) sampling sites (on left); distribution of Hg, Mn and Cd in the surface sediment of the lower part of the Krka River estuary (on right). Values are expressed in µg g^{-1}.

Sediment from the core sampled in the marina is characterized with relatively high contents of trace metals (data not shown), as expected from the sediment surface mapping. When normalized to lithogenic element (Li), most of the trace metals (Bi, Co, Cu, Hg, Pb, Sb, Sn, and Zn) show a maximum in surface followed by a continuous decrease with depth, suggesting relatively recent anthropic inputs.

In porewater, classical diagenetic sequence can be observed, with subsurface peak of Mn (-2 cm), followed by Fe (maximum at -8 cm) related to Mn and Fe oxyhydroxides reduction, see figure 2. Gradual increase of Ba is related to organic matter mineralisation. Profile of Co is well correlated with Mn profile, as often observed (DANG *et al.*, 2015). Remobilisation of Cu follows profile of Mn at subsurface, while

at deeper layers those of Fe and DOC. Increase of Pb along the depth is well linked to Fe profile. DOC shows subsurface maximum with a continuous decrease down to -7cm followed by a peak at ~-8cm. Despite that most of the metals show two maxima (around -2 cm and -8 cm); the observed peculiar vertical profiles are related to different early diagenesis processes. This is even more evidenced by the DGT profiles, which are well correlated with the porewater profiles, with the former one allowing getting higher depth resolution.

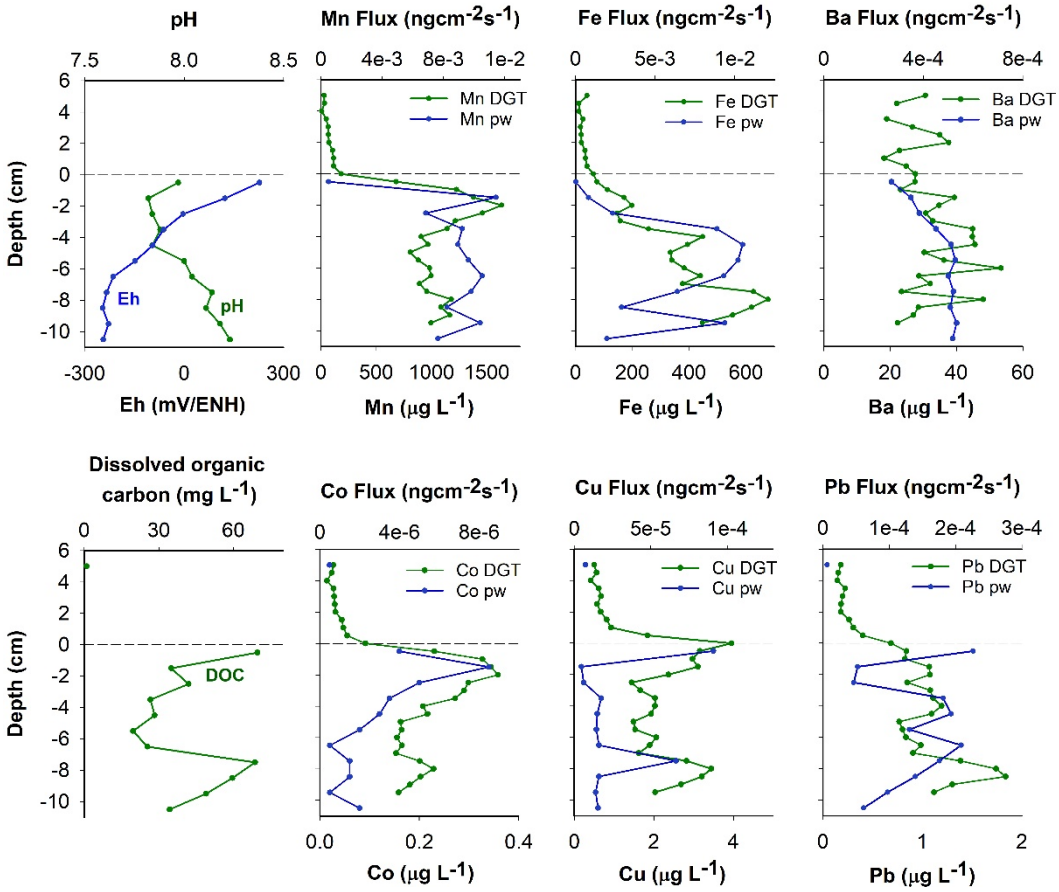

Figure 2. Depth profiles of pH/Eh, Mn, Fe, Ba, DOC, Co, Cu and Pb, in comparison to DGT fluxes (for Mn, Fe, Ba, Co, Cu and Pb).

4. Conclusion

According the trace metals distribution in surface sediments, estuary is divided into two sections: (1) non-impacted upper estuary and (2) lower estuary with various sources of anthropogenic pollution. Detailed analysis of the sediment profile at the marina, by two complementary approaches (porewater/solid fraction, DGT) demonstrated the control of early diagenesis processes on the trace metals mobility, with significant gradient at the sediment/water interface, suggesting potential transfer to the water column.

5. References

BURTON Jr. G. A. (2002). *Sediment quality criteria in use around the world*. Limnology, Vol. 3, pp. 65–75. https://doi.org/10.1007/s102010200008

CINDRIĆ A.M., GARNIER C., OURSEL B., PIŽETA I., OMANOVIĆ D. (2015). *Evidencing the natural and anthropogenic processes controlling trace metals dynamic in a highly stratified estuary: The Krka River estuary (Adriatic, Croatia)*. Marine Pollution Bulletin, Vol. 94, pp. 199-216. http://dx.doi.org/10.1016/j.marpolbul.2015.02.029

DANG D.H., LENOBLE V., DURRIEU G., OMANOVIĆ D., MULLOT J.U., MOUNIER S., GARNIER C. (2015). *Seasonal variations of coastal sedimentary trace metals cycling: Insight on the effect of manganese and iron (oxy)hydroxides, sulphide and organic matter*. Marine Pollution Bulletin, Vol. 92, pp. 113-124. http://dx.doi.org/10.1016/j.marpolbul.2014.12.048.