

A preliminary study of a DGT-labile trace metals distribution in the stratified Krka River estuary (Croatia)

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Ana-Marija Blatarić¹, Cédric Garnier², Dario Omanović¹, Véronique Lenoble², Neven Cukrov¹, Stéphane Mounier², Jean-Louis Gonzalez³, and Ivanka Pižeta¹

¹ Ruđer Bošković Institute, Center for Marine and Environmental Research, PO Box 180, 10002 Zagreb, Croatia, ablatar@irb.hr

² Laboratoire PROTEE, Université du Sud Toulon - Var, BP 20132, 83957 La Garde, France

³ IFREMER, Département Biogéochimie et Ecotoxicologie, B.P.330 Zone Portuaire de Bregallon, 83507 La Seyne/mer cedex, France



A preliminary study of the determination of DGT-labile trace metals in the Krka River estuary and near coastal area (Croatia) has been performed. Two previous sites were selected for the monitoring site "S" (representing a "clean" site located in the bay of Ruđer Bošković water station "Mokrišćica") and "Zadurba" site "Z" within the industrial center. ICP-MS analysis during 50 years history and local measurement was carried out (down to 80 nM) at each site. Based on measured salinity gradient, were selected for the DGT monitoring. Three (2008) and four (2009) days deployment period of diffusive and extracted DGT devices was undertaken. At each depth, three DGT replicates were used and additional three devices were used for blank estimation. Salinity, temperature and pH were measured at the deployment sites with regularity (at least twice per day) by automatic. Average temperature obtained by in-situ temperature sensor (well consisted to average discrete manual measurements) were used in the calculations of DGT labile concentrations. Each day, two grab samples (in the morning and in the afternoon) were taken at each of subsurface, which were used for the determination of dissolved organic carbon (DOC), dissolved and total metals, of dissolved inorganic fraction of copper complexing capacity (CuCC), as well as for the accumulated in DGT complexing resin were eluted in 1 M HNO₃. Metals present according to usual protocol for measurement by HR-ICP-MS, and differential pulsed anodic stripping voltammetry (DPASV) was used for the determination of total unfiltered and total dissolved metal concentrations in composite samples.



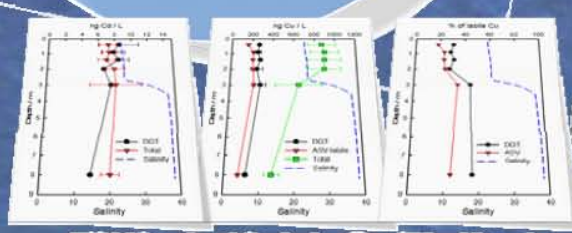
Krka River estuary with locations of sampling/deployment sites

Vertical profiles of salinity, temperature, pH and DOC show typical distribution already identified in Krka River Estuary. In middle, freshwater-seawater interface layer (FSI), a characteristic increase of temperature, DOC, as well as concentration of some metals is usually formed, consistent with our profiles shown on figures below.

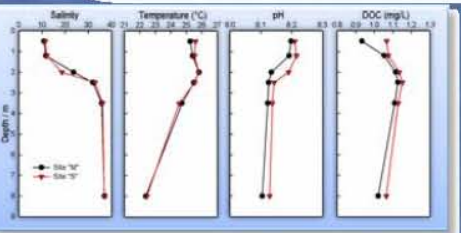
For most of the investigated metals very precise DGT replicate results were obtained. Exception is zinc with high variability, most probably as a result of contamination during DGT handling and preparation. Average DGT-blanks ranged from ~0.2% for Mn, up to ~50% for Zn.

For all DGT concentrations, values are expressed with standard deviation (SD) of triplicate DGT devices, while for dissolved and total metal concentrations with a 95%-confidence intervals.

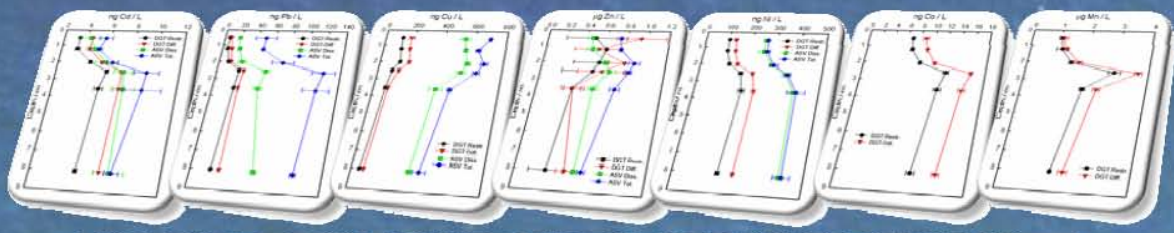
Campaigns performed in 2008 and 2009 (both in July) show relatively different vertical distribution for most of the investigated metals. While for the 2008 campaign, relatively uniform vertical distributions of DGT-labile metal concentrations were obtained, 2009 campaign show existence of relationship with salinity.



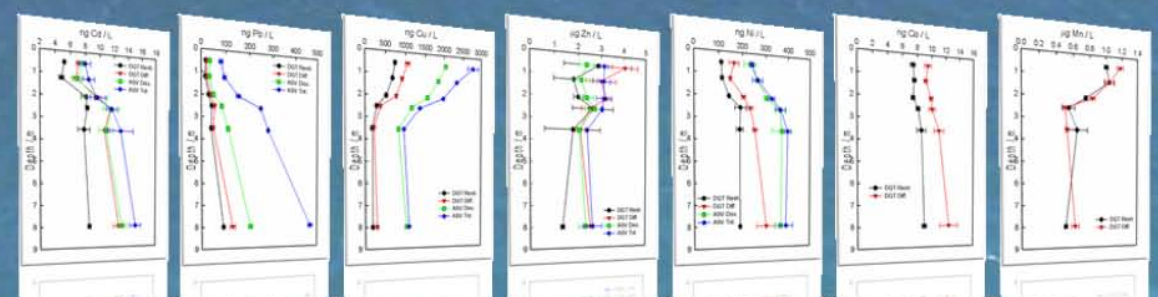
DGT-labile and total dissolved profiles of Cd and Pb, and percentage of DGT- and ASV-labile Cu (2008, site "W")



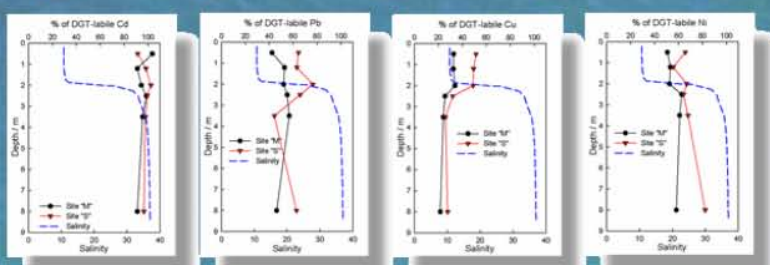
Average salinity, temperature, pH and DOC vertical profiles (2009)



Vertical distribution of DGT-labile, dissolved and total concentrations of Cd, Pb, Cu, Zn, Ni, Co and Mn at site "W" (2009)



Vertical distribution of DGT-labile, dissolved and total concentrations of Cd, Pb, Cu, Zn, Ni, Co and Mn at site "Z" (2009)



Percentage-profiles of DGT-labile (inorganic and weak organic complexes) metals (2009)

As expected, dissolved and total metal concentrations are higher than measured by DGT. Exception is cadmium, because of its relatively low affinity to organic ligands and strong ability to form chloro-complexes. Different vertical profiles of metals reflect their concentrations in upper fresh/brackish water (Krka River) and bottom seawater, respectively.

During summer period estuary is under heavy touristic boat traffic, which has consequence of higher copper concentrations in upper brackish layer (copper is used as antifouling agent). Higher concentrations of most trace metals at site "Z" are in direct relation to fact that the site is located in industrial center with numbers of yachts. Interesting is manganese profiles for which higher concentrations are registered at "clean" site "W". This is a consequence of the vicinity of former ferromanganese factory. During our experiment an action of slag removal was in progress, which produced dust particles spreading, and consequently, increased Mn concentrations at site "W".

For all studied metals, very good correlation of vertical concentration profiles of restrictive and normal DGT, as well as of dissolved and total metal concentrations was achieved. From this data, metal speciation could be directly determined just by comparing DGT and total dissolved metal concentration profiles. Anyway, for more in depth study of dissolved organic matter/copper interactions, calculation models will be applied on the complexation experiments (CuCC) already performed. Vertical percentage profiles for lead and nickel for both sites show that DGT-labile parts for both metals ranged between 40% and 80%, without well expressed correlation with salinity. However, correlation of DGT-labile portions with salinity is obvious for copper. Contrary to 2008 campaign, where percentage of labile copper was lower at brackish layer, in 2009 higher portions of labile copper were registered in seawater layer.

Very low concentrations of most metals and low concentrations of DOC show that Estuary is not under permanent anthropogenic influence, although remote zones (like site "Z") could be subjected to elevated metal concentrations, leading to free metal levels potentially higher than toxic limits.^{1,2}

Unfortunately, because of limited time, detailed analysis, comparison and speciation calculation is not yet accomplished. This story will continue...

1. J. Y. Louis, C. Garnier, V. Lenoble, S. Mounier, N. Cukrov, D. Omanović, I. Pižeta, Mar. Chem. 114 (2009) 110-119.
2. V. Turic and T. Legović, Nature, 328 (1987) 612-614.
3. W.B. Swadlow, K.A. Weber, S.A. Hurlbert, Mar. Biol. 94 (1987) 205-210.