TRACE METAL DYNAMICS IN THE STRATIFIED KRKA RIVER ESTUARY (CROATIA): AN INTEGRATED APPROACH BY VOLTAMMETRY, DGT AND FLUORESCENCE SPECTROSCOPY

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Abstract

Trace metal dynamics in the stratified Krka River estuary (Šibenik bay, Croatia) has been studied by combination of different analytical and modelling tools for sampling campaigns 2007-2009. Results showed an increased metal content at the estuary surface layer in summer, especially for Cu due to antifouling paint release associated to strong boat traffic. Contrary to March-April period for which the organic ligands are sufficient to maintain the free Cu concentration at non-toxic level in the whole water column, in summer this limit is over-passed in the surface layer for at least one order of magnitude, particularly at locations close to nautical marina.

Keywords: Analytical Methods, Chemical Speciation, Estuaries, Metals, Organic Matter

Experimental

The Krka River estuary water column is permanently stratified because of a sheltered geography and the low tidal range of the Adriatic Sea. Due to low anthropogenic activities, this estuary is oligotrophic with ultratrace levels of heavy metals. However, during summer touristic period, the total Cu concentration increases, mainly because of Cu leaching from the antifouling paints [1]. According to depth variations of physico-chemical parameters ($T/S/pH/\%O_2$), samples were collected by scuba diving in April-2007 and March-2008, at 4 depths in front of the scientific marine station Martinska (site M). Additionally, in March-2008, samples were collected in the Krka River and the Adriatic Sea to obtain the 2 end-members of the estuarine water mixing. These samples were studied to (1) characterize the dissolved organic matter (DOM) by dissolved organic carbon (DOC) content and 3-D fluorescence spectroscopy (with PARAFAC analysis), (2) determine the dissolved metal concentrations by DPASV, and (3) study the DOM/Cu interactions by logarithmic titration with analysis of the ASV-labile Cu fraction and further modelling to define the DOM binding parameters by the classical at-equilibrium approach and by an innovative kinetic approach [2]. Furthermore, 2 field campaigns were performed in July-2008 and 2009. Diffusive- and restrictive-DGT were deployed during 3-4 days at 6 depths (according to physico-chemical parameters depth variation), at 2 distinctive sites: the "clean" site M, and a "polluted" one in a nautical marina (site S). DGT-labile metal levels were determined by HR-ICP-MS. In addition, water samples were collected 1-2 a day at each DGT-depth, leading to discrete and composite samples analysed for DOM, total/dissolved metal and DOM/Cu interactions by the previously described techniques.

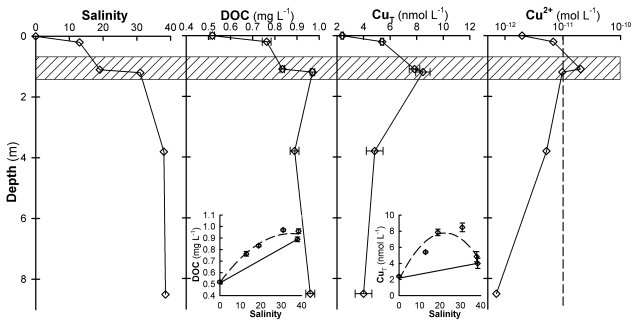

Fig. 1. Salinity, DOC, total dissolved Cu and calculated free Cu concentration depth profiles of samples taken in 2008; marked area represents the depth range of fresh/marine water interface. Vertical dashed line: the Cu toxicity limit of 10 pM [3]. Insets: Same parameters in relation to salinity; Full and dashed lines represent conservative and parabolic variations, respectively.

Results and discussion

DOC and Cu concentrations measured in April-2007 and March-2008 showed non-conservative variations, with a clear enhancement at the fresh/marine water interface (Fig.1). The main source of fluorescent material in the estuary is due to terrestrial inputs, and the additional OM produced by biological activities did not show any specific fluorescent signature. The increasing Cu concentration at the freshwater/seawater interface seemed to be controlled by the organic ligands (probably produced by biological activity), leading to calculated free-Cu concentrations lower than the toxicity limit of 10^{-11} M [3] (Fig.1). Our results validated the applicability/reliability of the kinetic approach in the determination of apparent stability constants and ligand concentrations, and additionally allowed the calculation of the association/dissociation rate constants, i.e. the dynamic of DOM/Cu interactions. In summer, important metal contamination of the estuary surface has been recorded, due to increasing boat traffic [1]. Under such conditions, predicted free-Cu concentrations over-passed the toxicity level in the whole water column, except at the bottom. Results obtained for the summer campaigns demonstrated that site S is more polluted than site M for Cd, Cu, Pb and Zn, but showed quite comparable values for Co, Cr, Mo, Ni and U (partly seen in Fig.2). Exception is for Mn which presented higher concentrations for site M, due to the vicinity of a former ferromanganese factory. Metal speciation could be directly determined by comparing DGT (diffusive/restrictive) and total/dissolved metal concentration profiles (Fig.2). Additionally, the binding parameters determined by the study of DOM/metal interactions allowed a more detailed definition of the metal speciation and the prediction of metal behaviour in different physico-chemical conditions.

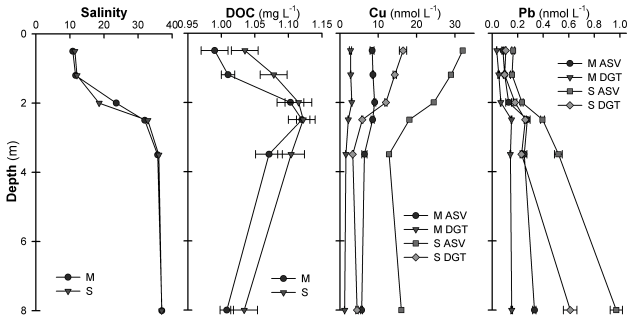

Fig. 2. Salinity, DOC, total dissolved Cu and Pb (by DPASV) concentration depth profiles of composite samples taken in 2009 and diffusive DGT-labile Cu and Pb concentrations depth profiles at both sampling sites

References

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