

A complementary approaches for speciation of trace metals in the stratified Krka River estuary (Croatia): DGT vs. voltammetry

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The distribution and speciation of selected trace metals (TM) (Cd/Pb/Cu/Ni/Co) were studied in the water column of the highly stratified estuary by using stripping voltammetry and diffusion gradient in thin films (DGT) techniques.

A very good agreement between the vertical profiles of DGT-labile and dissolved TM concentrations were obtained. DGT-labile fraction ranged from >90% for Cd, to <20% for Cu. ASV speciation of Cu showed the presence of two types of organic ligands that form strong (L_1 , $9.6 < \log K_1 < 11.9$) and weak (L_2 , $7.8 < \log K_2 < 9.9$) complexes. Concentration of free Cu ions at ambient conditions is regulated primarily by the complexation with strong ligands (L_1). Relatively good correlation between vertical profiles of ASV-labile and DGT-labile concentrations of Cu were obtained (Fig 1).

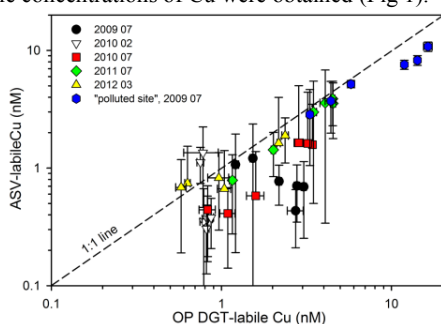


Figure 1: Relationship between ASV- and DGT-labile Cu

Modelling of Cu speciation within the salinity gradient showed that interpretation of the type of ligands which form Cu-org complexes should be carefully examined due to the fact that change in sample composition (major ions) have strong influence on estimated experimental conditional stability constant ($\log K'$), and eventually on the prediction of free Cu concentration.