

Copper speciation in natural waters by CLE-AdCSV - a methodological uncertainties

SAŠA MARCINEK^{1*}, ANA-MARIJA CINDRIĆ¹, JASMIN
PAĐAN¹, CÉDRIC GARNIER², DARIO OMANOVIC¹

¹Ruđer Bošković Institute, Center for Marine and
Environmental Research, Bijenička 54, Zagreb, Croatia
(*correspondence: smarcin@irb.hr; ana-
marija.cindric@irb.hr; jpadjan@irb.hr; omanovic@irb.hr)

²Université de Toulon, Aix Marseille Univ, CNRS, IRD,
MIO, France (cgarnier@univ-tln.fr)

Copper (Cu) is a naturally occurring micronutrient of eco-toxicological concern in natural waters. Approximately 99% of total dissolved copper (dCu) exists in marine waters as relatively stable, organic complexes. Characterization and discrimination of trace metal-organic ligand complexes in natural waters commonly rely on determination of their conditional stability constants ($K'MLi$) and concentrations of corresponding discrete ligand classes, $[Li]T$ [1]. Competitive ligand exchange-adsorptive cathodic voltammetry (CLE-AdCSV) is most widely used electrochemical technique for these studies. It is based on the re-distribution of metal between the natural organic ligands present in the sample and added competitive ligand (AL) which forms the electroactive complex with known stability constant [2].

In this work we examined different aspects of the entire protocol related to the CLE-AdCSV method of Cu speciation which could influence the estimation of complexation parameters: the concentration of added ligand (AL), the range of the titration, the number of titration points, the treatment of signal intensities (e.g. area, height, 1st derivative), the estimation of proper sensitivities, various combinations of fitting models. Study was performed on simulated data, as well as on real experimental data obtained in samples from the salinity gradient of the Krka River estuary (Croatia). It was shown that obtained complexation parameters may significantly vary in relation to all above mentioned parameters. The reported results and associated uncertainties should be critically evaluated and adequately presented.

Acknowledgement: This research was realized within the MEBTRACE project (IP-2014-09-7530), financially supported by the Croatian Science Foundation.

- [1] Buck *et al.* (2012), *Limnol. Oceanogr.: Methods* **10**, 496–515. [2] I. Pižeta *et al.* (2015), *Mar. Chem.* **173**, 3–24