I. The experiment

The three-electrode setup was used for measurements using alternating current voltammetry (ACV), cyclic voltammetry (CV), differential pulise anodic stripping voltammetry (DP-ASV) and square-wave voltammetry (SWV). The reference electrode was Ag/AgCl (3 mol dm^{-3} KCl), the counter electrode was Pt and the working electrode was hanging mercury drop electrode (HMDE). The capacitive current of the double layer formed between an HMDE and electrolyte (aqueous 0.55 mol dm^{-3} NaCl + 0.01 mol dm^{-3} borate buffer) solution containing 0.66 µmol dm^{-3} BCS were recorded by means of phase-sensitive alternating current voltammetry (ACV) using µ-Autolab (Electrochemical Instruments Eco Chemie, The Netherlands) connected to a 663 Stand Metrohm mercury electrode (electrode surface, A=1.68 x 10^{-3} cm^2). All other parameters used during ACV and SWV measurements (e.g. deposition potential and time, scan rate, etc.) are given in Figures description in the main manuscript and Supplementary information. All measurements using described three-electrode set up were done under the N_2 atmosphere.

The Cu(I) stock solution was prepared daily by dissolving CuCl in N_2 degassed MQ water containing high concentrations of HCl and NaCl (0.1 and 1 mol dm^{-3}, respectively). The Cu(II) standard solution was prepared by dissolving copper(II)-sulfate ($CuSO_4$; VWR BDH Prolabo Chemicals, Radnor, PA, USA) in MQ water. All supporting electrolyte solutions (0.55 mol dm-3 $NaClO_4$ or 0.55 mol dm^{-3} NaCl) were buffered at pH of ~8.2 by borate buffer with the final concentration of 0.01 mol dm^{-3}. Bathocuproine sulfonate disodium salt (BCS) was purchased from Thermo Scientific (purum >97%). Cu(I)Cl salt was supplied from the Alfa Aesar (purum >97%), ortho-Boric acid from VWR, NaOH from LACH NER, NaCl and HCl were supplied from Merck.

Total dissolved Cu concentration in Krka River estuary sample was measured by DP-ASV using the standard addition method. The sample was filtered (0.45 µm pore size, Sartorius) and acidified HNO_3 s.p. to pH < 2 preceding UV digestion for at least 24 hours prior measurements. Each standard addition measurement was performed twice. The voltammograms were processed using the ECDSOFT (ElectroChemical Data SOFTware) software developed in our laboratory (https://sites.google.com/site/daromasoft/home/ecdsoft). The peak height was used as the signal value.

II. The data

AC voltammetry

The AC voltammetry data are under the zip file: AC voltammetry. The uploaded excell file consists of the uploaded raw AC voltammetry cuves and in the first row the accumulation times are indicated. The data are presented as Figure 1 in the Manuscript.

Increase accumulation

The Square Wave Voltammetry (SWV) raw date are under the zip file:increase_accumulation. The raw SWV cuves are marked accordingly (.nox extension, e.g. BCS_Cu_NaCl_90) showing solution composition and accumulation time. The data are presented as Figure 2 in the Manuscript and S3in Supplement.

pH variation

The Square Wave Voltammetry (SWV) raw date are under the zip file:pH_variation. Within the zip two folders: pH dependence_BCS and pH dependence_BCS_Cu(I) are present. In each folder the raw SWV curves are marked (.nox extension, e.g. BCS_pH_5.7_45) showing solutin composition, pH and accumulation time. The data are presented as Figure 3 in the Manuscript and Figure 2S in Supplement.

SWV_back_forw

The Square Wave Voltammetry (SWV) raw date are under the zip file:SWV_back_forw. The raw SWV curves are marked (.nox extension, e.g. BCS) showing solutin composition. The data are presented as Figure 4 in the Manuscript.

Sample

The Square Wave Voltammetry (SWV) raw date are under the zip file: seawater. The raw SWV curves are marked (.nox extension, e.g. seawater_60) showing solution composition and accumulation time. The data are presented as Figure 5 in the Manuscript.

Amplitude and frequency variation

The Square Wave Voltammetry (SWV) raw date are under the zip file:amplitude_frequency_variation. The raw SWV curves are marked (.nox extension, e.g. 0.001) showing changes in amplitude or frequency. The data are presented as Figure 5S in the Supplement.

Method validation

The Square Wave Voltammetry (SWV) raw date are under the zip file: method_validation. The raw SWV curves are marked (.nox extension, e.g BCS_EDTA_Cu(I)) showing solution compsition. The data are presented as Figure 6S in the Supplement.

Sample standard addition

The Square Wave Voltammetry (SWV) raw date are under the zip file: sample_st_addition. The raw SWV curves are marked (.nox extension, e.g staddition_1_1) showing solution compsition and number of standard addition. The data are presented as Figure 1S in the Supplement.

Cu(I)_increasingBCS

The Square Wave Voltammetry (SWV) raw date are under the zip file: Cu(I)_increasingBCS. The raw SWV curves are marked (.nox extension, e.g BCS_1.3x10-6) showing BCS concentration added. The data are presented as Figure 4S in the Supplement.