

DETERMINATION OF THE DISSOLVED COPPER FRACTION COMPLEXED WITH SOLUBLE ORGANIC LIGANDS IN COASTAL WATERS OF THE SARONIKOS GULF, GREECE

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Abstract

This work deals with speciation of dissolved copper in seawaters of two sites in the Saronikos Gulf namely the Gulf of Elefsis and the coast of Piraiki. The samples were UV irradiated in order to determine the inert fraction of dissolved copper corresponding to copper complexed with dissolved colloidal organic carbon. The determined concentration of kinetically inert as for Chelex-100 resin dissolved copper ranges widely from 1.3 to 32.1 nM, corresponding to a percentage fluctuating between 8% and 67%, with a mean value of 37%, of the total dissolved copper.

Keywords: copper, speciation, UV irradiation, Greece

Introduction

The chemical forms under which metals exist in seawater affect their bioavailability and toxicity and therefore the determination of the different species of dissolved metals is of great interest. Organic complexation with natural organic ligands in seawaters is significant for trace metals such as copper [1], since it may prevent metal scavenging by suspended particulate matter and/or formation of insoluble inorganic metal complexes, maintaining thereby enhanced dissolved trace metal concentrations in seawater. The main purpose of the present study is the description and evaluation of the method employed for copper speciation and the preliminary reporting of the results obtained.

Methodology

Five coastal sampling locations were chosen in the Saronikos Gulf, four of which within the Elefsis Gulf (Aspropyrgos, Elefsis port, Loutropyrgos, Nea Peramos), an industrialized area near Athens and one station at the Piraiki coast, near Piraeus, the biggest port of Greece. From the sampling area of Loutropyrgos seawater samples were taken both from the surface and from near the sea-bottom. All stations were characterised by the presence of a significant biomass of the macroalga *Ulva rigida*. Nine samplings were carried out between May and October 1998, the period when the highest biodegradation rate of the macroalga *Ulva* was observed.

Immediately after collection and transfer to the laboratory seawater samples were filtered through 0.45µm pore size acid-washed cellulose nitrate filters (Millipore), kept in darkness in low-density polyethylene containers and analysed within 24h. For the determination of the dissolved labile copper, 500ml of each sample were pumped through a Chelex-100 resin (200-400 mesh; Bio-Rad laboratories, Richmond California; contact time of the sample with the resin 7sec) and eluted with 10ml of HNO₃-HCl 2:1M. The concentration of copper was measured by a flameless atomic absorption spectrophotometer (VARIAN SpectrAA 640 Z) equipped with Zeeman background correction. For the determination of the total dissolved metal, the filtered sample was UV irradiated for 100min before the preconcentration step. UV digestion of samples was carried out by irradiation of solutions using a 400 W medium pressure lamp (Cleo HPA, Philips), positioned in an aluminum lamp housing device built in purpose, placed inside a fume cupboard cooled by a fan. Each sample was put into a teflon beaker with quartz glass cap, where the distance between the light source and the beaker was 2 cm. The sample was stirred continuously employing a magnetic stirrer. The efficiency of the procedure was tested with the analysis of CASS-4 certified reference seawater (certified copper value 0.592 ± 0.055 µg/l, measured value 0.568 ± 0.067 µg/l) as well as with synthetic solutions of Salicylic acid (1.5 mg/l; >90% decomposition) and commercial humic acid (1.0 mg/l; Fluka Lot 45729/1) containing a Cu(II) concentration. Although UV irradiation for 100min resulted in the decomposition of approximately 60% of the humic acid contained in the samples, the complexed Cu was almost fully released, as shown by Cu analysis with DPASV. DOC was measured by a Shimadzu-5000A TOC analyser.

Results and discussion

The concentrations of kinetically inert, as for Chelex-100 resin dissolved copper, which is calculated by subtracting the concentration of the labile fraction of dissolved copper from total copper, were found to range from 1.3 to 32.1 nM in a total of 52 samples analysed.

The mean concentrations were 5.8 nM for Piraiki, 9.0 nM for Aspropyrgos, 8.4 nM for the port of Elefsis, 5.4 nM for surface and 8.5 nM for bottom samples of Loutropyrgos and 8.1 nM for Nea Peramos. These concentrations correspond to a percentage of inert fraction of dissolved copper over the total dissolved copper ranging from 8% to 67% with a mean value of 37%. By correlating these results to those of researches from other seas [2, 3] it becomes evident that UV irradiation accelerates the release of a major part of the inert fraction of dissolved copper which corresponds to copper bound predominantly to organic colloids. The percentage of this fraction in the aforementioned cases was around 44%. Lewis and Landing [4] showed that in seawater samples from the Black Sea following preconcentration in a series of sequential columns where Chelex-100 was included, the percentage contribution of organically bound copper was never less than 50%.

The concentrations of DOC ranged from 38 to 338 nM. There was no correlation observed between the concentrations of inert dissolved copper and those of DOC ($r=0.15$), due to the contribution of a single part of dissolved organic matter to the complexation of dissolved copper.

Inert dissolved copper measured in bottom seawater samples taken from Loutropyrgos (mean value 8.5 nM) were higher compared to the corresponding concentrations (mean value 5.4 nM) of surface seawater samples. This difference is attributed to the decomposition of the *Ulva rigida* biomass accumulated at the seabed. The dissolved organic matter released aggregates forming colloids or even particulate matter, either through biotic mechanisms including bacterial activity or by abiotic procedures such as adsorption on solid surfaces, increasing the copper complexing capacity of seawater.

It is noteworthy that other researchers [5] attribute the stable complexation of copper to relatively low molecular weight colloidal organic ligands. The phenomena recorded require further investigation which is currently under way.

References

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