

A study on copper speciation in Uittamo marina, Finland

Introduction

Copper, although ubiquitously present in the marine environment, is sometimes found in elevated concentrations in shallow, coastal areas such as estuaries, harbours and marinas. One anthropogenic source of copper loading into these areas is the copper-based antifouling paints used on the hulls of vessels. The speciation of copper is extremely important when considering copper bioavailability and toxicity. It is widely accepted that the free ion concentration (i.e. Cu^+ and Cu^{2+}) is the most bioavailable and thus most toxic form. Copper toxicity decreases with the binding of copper to inorganic ligands and becomes non-toxic when bound to organic matter. With the aim of studying copper bioavailability in connection with the marina, a sampling survey was conducted in Uittamo Marina, situated in the South West coast of Finland, to assess the concentrations of the total dissolved and labile fractions of copper in seawater.

Materials and methods

Sample location

The sampling survey took into account various physical factors such as particle loading, organic matter and flushing rate. Water samples were collected quarterly over a one-year period to include all seasonal weather variations and different boat activities.

The 4 sampling sites varied in their proximity to anthropogenic inputs (i.e., from the centre of a marina outwards to a reference site, Figure 1).



Figure 1: Aerial view of Uittamo marina located in Turku, Finland. Red circles denote sampling sites

Water sampling

Water samples (500ml and 125ml) were collected using a Winchester sampler at 2 depths: one at surface level and one at 1m above the seabed for copper and dissolved organic carbon (DOC) analyses. A triplicate sample was taken at site 2 during Spring and Summer to provide information on the reproducibility of the sampling and analytical methods. Water samples were stored in nalgene bottles and kept cool prior to filtration. All the physico-chemical parameters were measured on site (dissolved oxygen (DO), pH, temperature) using a Multiline P4 Universal pocket meter (Figure 2 and 3).



Figure 2: Water sampling in Summer



Figure 3: Water sampling in Winter

Filtration

Water samples were filtered within 48 hours of sample collection using a nucleopore 0.4µm filter. Suspended Particulate Matter (SPM) was determined gravimetrically and the filtered water samples were either analysed immediately for total and labile copper or frozen at -20°C until analysis.

Copper analysis

Total dissolved copper (TDCu)

A sub-sample of the filtrate was acidified and UV-digested over 12 hours prior to TDCu determination by Differential Pulse Anodic Stripping Voltammetry at a Hanging Mercury Drop Electrode (DPASV-HMDE), Metrohm Computrace 767 Multimode electrode system (Figure 4).

Labile copper (LCu)

LCu was determined from the remaining filtrate by DPASV on a Thin Mercury Film at a Rotating Glassy Carbon Disk Electrode (TMF-RGCDE), Voltammeter EG&G Instruments Model 394, Rotating glassy carbon electrode Model 616 (Figure 5).

Figure 4: HMDE



Figure 5: TMF-RGCDE



Results and discussion

TDCu

Concentration of TDCu ranged from 0.662 to 3.89µg/l, with the highest concentration found in the Summer at site 2. Generally, the lowest TDCu concentrations were recorded in spring for all 4 sites (Figure 6). No correlation was observed between surface TDCu concentrations with those from 1m above the seabed for any site or season.

Analysis of the triplicate samples revealed good reproducibility of the analytical method for spring samples (0.94 ± 0.15) with only a slight variability for winter samples (2.77 ± 0.93).

No TDCu value exceeded the Environmental Quality Standards for copper in marine waters (5µg/l).

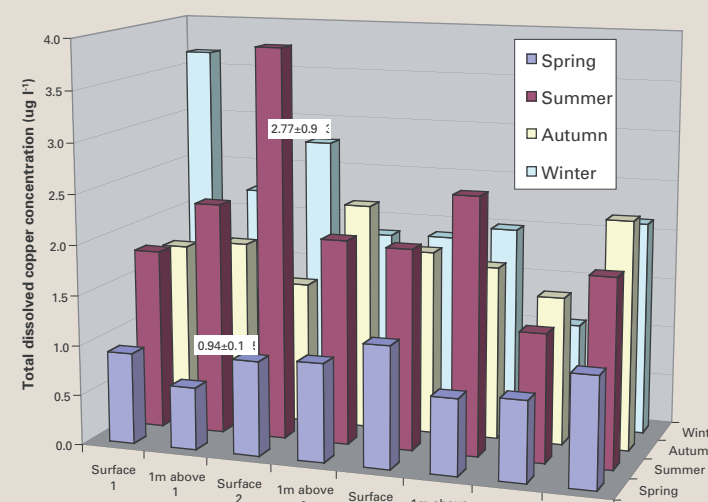


Figure 6: TDCu in seawater samples at each site and season

LCu

The majority of LCu values were measured within or around 1 µg/l with an exceptional high LCu concentration recorded during winter at site 1 (surface=2.066 µg/l). As for TDCu, LCu concentrations were lowest during spring, increasing in summer and autumn and peaking in winter (0.4422 to 2.066 µg/l, Figure 7).

Similar reproducibility was obtained for LCu when compared to TDCu data for the triplicate samples.

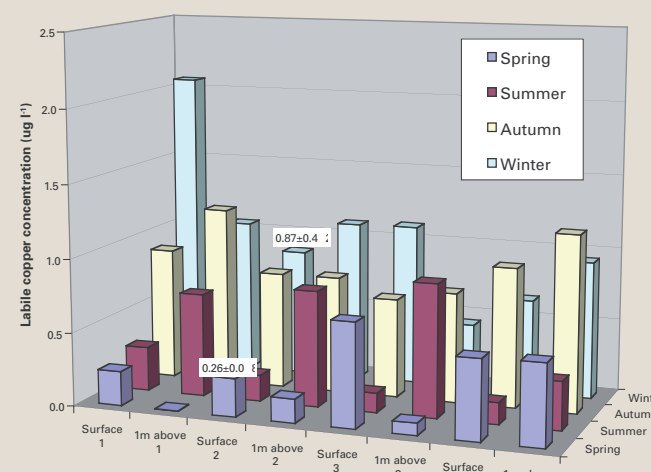


Figure 7: LCu concentrations at each site and season

Ratio of LCu:TDCu

LCu to TDCu ratio ranged from 0.003 to 0.677, with most values being close to 0.5. Although the proportion of LCu to TDCu was higher in the autumn and winter samples, no overall pattern in the LCu:TDCu ratio with increasing TDCu was observed (Figure 8). This might indicate the presence of complexing agents in the water column (dissolved organic matter, inorganic ligands and suspended particulates) that actively bind with the labile copper, therefore decreasing the toxicity of copper present. However, measurements of DOC (Figure 9) did not show an increase in value with the increasing TDCu, indicating that DOC may not correlate with TDCu but the complexation of copper resulted from a number of factors such as DOC, SPM, DO, pH, temperature.

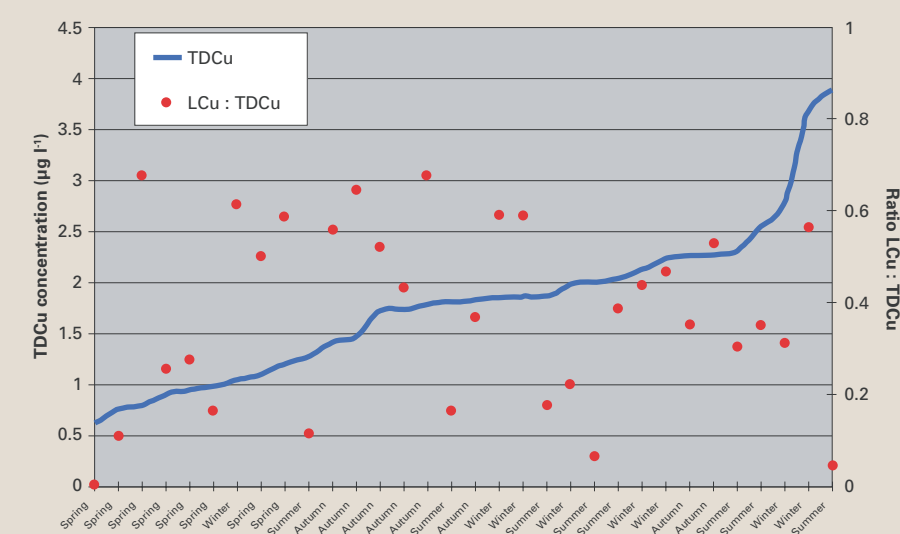


Figure 8: Ratio of labile to total dissolved copper in relation to TDCu. Data plotted as ranked by increasing TDCu concentration

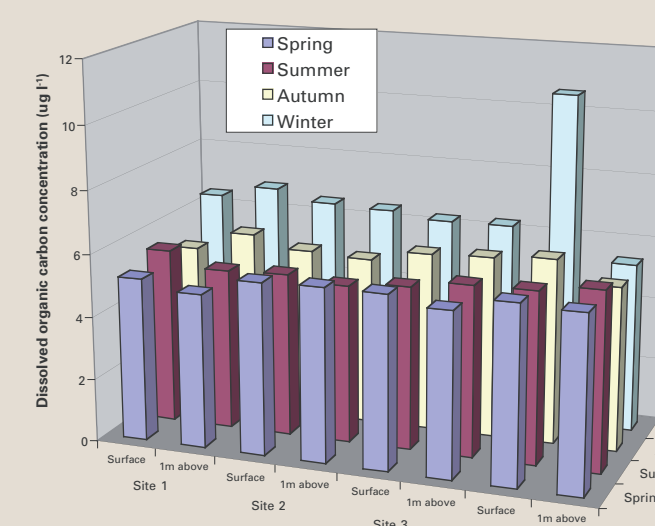


Figure 9: Dissolved organic carbon concentrations at each site and season

Conclusions

This study has demonstrated the following:

- No TDCu value exceeded the Environmental Quality Standards for copper in marine waters (5µg/l).
- The speciation behaviour of copper in the marine water column is very complex.
- A significant number of variables (e.g., DOC, SPM, DO, pH, temperature) contribute to the bioavailability and speciation of copper.

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