

Copper speciation survey from UK marinas, harbours and estuaries

Bryn Jones *, Thi Bolam

Cefas Burnham Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex CM0 8HA, United Kingdom

Abstract

The use of copper in antifouling paints has increased in the UK in the last 20 years as TBT and several other organic biocides have been phased out. To assess the probable impact of copper on estuarine systems a survey was undertaken to measure the different fractions of copper present in the water column at current usage. The different fractions measured were; labile copper, (LCu) considered as both the free copper ions and inorganically bound copper, the total dissolved copper (TDCu) present, and the difference between them taken as the organically bound likely non-toxic copper fraction. The survey considered sites with different levels of boat use, namely marinas, harbours and estuaries, differing physical parameters of suspended and dissolved organic matter, different seasons of the year and different depths in the water column all of which control speciation behaviour.

Suspended particulate matter (SPM) values were measured at all sites and increased from West to East coast locations (5.7–34.4 mg/l). Dissolved organic matter (DOM) values ranged from 0.58 to 2.2 mg/l C. The total dissolved copper concentrations ranged from 0.30 to 6.68 $\mu\text{g/l}$, with labile fraction ranging from 0.02 to 2.69 $\mu\text{g/l}$, and most labile copper concentrations below 1 $\mu\text{g/l}$. None of the yearly mean copper measurements exceeded the 76/464/EEC EQS of 5 $\mu\text{g/l}$. Of the 306 measurements, only one dissolved copper value in one season was above 5 $\mu\text{g/l}$.

This ratio of labile to total copper was between 10 and 30%. The results from this survey suggest that if toxicity of copper is due to the labile fraction then using the total dissolved copper concentrations as an indicator of impact overestimate the risk by a factor of four times.

Crown Copyright © 2007 Published by Elsevier Ltd. All rights reserved.

Keywords: Copper; Labile copper; Total dissolved copper; Marinas; Harbours; Estuaries

1. Introduction

Despite our knowledge on the toxicity and speciation mechanisms, there is surprisingly little data on the copper species present in marine systems close to sources of copper inputs and the changes in ratios of different forms, and hence toxicity, of copper as it disperses. We conducted surveys to measure the different forms of copper present in marine waters around the UK using a simple fractionation system. The different fractions measured were: (i) labile copper, considered as both the free copper ions and inorganically bound copper, (ii) total dissolved copper and the difference between these measurements assigned (iii)

organically bound copper fraction. The survey evaluated the spatial distribution of copper at sites with different levels of vessel use, namely marinas, harbours and estuaries with inherent differing physical parameters, which are considered to affect speciation behaviour. This survey also included temporal measurements to evaluate seasonal changes of concentrations.

Because of the ban on use of tributyltin antifouling coatings, copper use within these coatings has increased to maintain the biocide properties. Concerns are growing that copper has an adverse effect on the environment but it also realised that measurements of total dissolved copper may provide an over estimation of toxicity as the organically bound copper is considered to be largely non-toxic.

Copper is a ubiquitous element present in all compartments of the marine environment. It may exist in many different chemical species from free copper ions, inorganic

* Corresponding author. Tel.: +44 1621 787273.
E-mail address: bryn.jones@cefas.co.uk (B. Jones).

salts and organically bound copper. It is an essential element, required by most organisms for normal metabolic function, only becoming toxic when an organism is unable to regulate excessive concentrations. The free Cu^+ and Cu^{++} ions are the most toxic forms to marine life, with toxicity decreasing in the order, Cu^+ and Cu^{++} > inorganic copper > organic copper. Many marine organisms have inducible detoxification systems (Bryan and Langston, 1992) and have adapted to thrive in different concentrations of copper, even to the extent that organisms from the same species are able to adapt and tolerate different concentrations at different locations (Qixing et al., 2003).

Coating manufacturers have exploited the short-term toxic effects of copper as an antifouling agent in paint on marine vessels. Free copper ions released at the surface of the paint prevent organisms from attaching to the vessel, however on entry to the water column free copper is quickly complexed to carbonates, hydroxides and bound by organic ligands, reducing its effect on the marine species (Tubbing et al., 1994).

2. Methods

A number of studies have utilised electrochemical methods to titrate the excess (free copper ions) with organic material and to therefore derive the free copper content, (Van den Berg, 1984; Donat et al., 1992; Donat et al., 1994; Lucia et al., 1994). For this study, the approach taken was to measure the electrochemical (labile) copper by anodic stripping voltammetry, which is selective for the free copper ions and inorganic copper species together. Total dissolved copper, the copper present after filtration, acidification and UV digestion was also measured by electrochemical means. This measures both the free labile, inorganic and organic copper species. The difference between the two methods is taken as the organically bound copper.

3. Survey sites

The study design considered 4 sites around the UK, with selection based upon physical factors such as particle loading, organic matter and flushing rates (Fig. 1).

Three scenarios were considered: – commercial harbours, estuarine harbours, and marinas. The classification is taken from conditions described in the MAMPEC model, a computer-based simulation of predicted environmental concentrations of antifouling biocides (Van Hattum, 1999). For each of the scenarios, sites were chosen where possible to include a range of conditions from putative low suspended solids at locations on west coast rising to high-suspended solids on the east coast. Similarly sites with organic enrichment were expected in the southern sites and lower levels of organic ligands elsewhere. Samples were collected quarterly over a period of one year to include all four seasons and therefore differing boat usage and weather conditions.

At each site, three stations were sampled at three depths (i.e. surface, 1 m under surface and 1 m above substrate) to provide a putative concentration gradient away from the likely source of copper. For example at each harbour site one sampling station would be in the inner harbour, one in middle of the harbour and one located outside the harbour mouth.

Three commercial harbours were sampled, Milford Haven harbour, a traditional fishing harbour which now berths both fishing and pleasure yachts. The site is located on the west coast and generally has a low level of solids suspended in the water column. Devonport a naval harbour situated on the river Tamar on the southern coast with medium to low suspended solids, berths a range of military vessels from small craft to large ships. Harwich harbour located on the east coast with very high-suspended loads, is a very large commercial container-ship terminal and lies opposite to a number of continental ferry terminals.

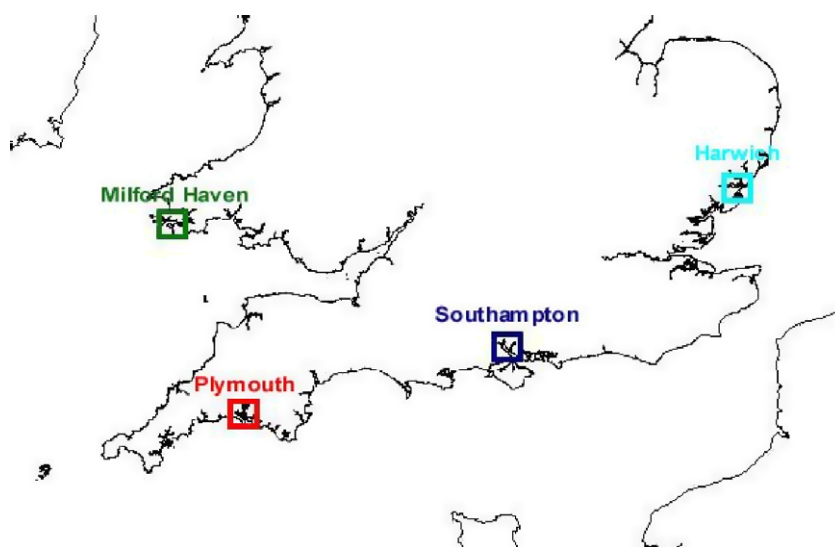


Fig. 1. Sampling sites around UK coast.

Download English Version:

<https://daneshyari.com/en/article/4477835>

Download Persian Version:

<https://daneshyari.com/article/4477835>

[Daneshyari.com](https://daneshyari.com)