Copper in the Ocean Environment

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SUMMARY

A number of studies were reviewed that investigate copper concentrations in ocean water, sediments and organisms. The purpose of reviewing the studies was to compare natural versus anthropogenic copper concentrations. It was found that large variations in concentrations do occur in ocean water, sediments and organisms due to both naturally occurring and anthropogenic copper. Copper is an essential micronutrient to both plants and animals. As such, organisms were found to have mechanisms to deal with copper levels in their environment from both natural and anthropogenic copper within the ranges studied. It was also concluded that when studying copper in the environment both natural varying copper levels and varying concentrations due to anthropogenic copper must be considered.

INTRODUCTION

Copper has been a principal biocide used in antifouling marine paints for over 100 years. Even with the advent of TBT, copper was still used in the paint along side the TBT biocide. With the pending ban in 2003 on the use of TBT as a marine antifouling biocide, copper is also coming under increased scrutiny for this use. This paper looks at the broader view of copper's existence as a natural occurring substance in the ocean environment as well covering anthropogenic copper some of which is introduced from antifouling marine paint. The purpose of this broader view is to develop an understanding of the relationship of both natural and anthropogenic copper in the ocean environment. With this understanding, scientific data can be better utilized to make critical decisions as to the future role of copper in antifouling coatings.

STUDIES ARE REVIEWED AND SUMMARIZED

This paper reviews data from numerous studies of both natural and anthropogenic levels of copper in marine water, sediments and organisms. The studies cover varying concentrations of copper. A partial summary of the results of each study is presented and briefly discussed. For a complete review of the study the reader is directed toward the references.

RESULTS AND DISCUSSION

To begin this review we must start with some fundamental facts about copper in the environment. Copper occurs both naturally and anthropogenically. There is no difference in the two forms. Copper is ubiquitous in the environment with 50 ppm in the Earth's crust and 0.25 ppb in Ocean water (1) to over 100 ppm in sediments.

Copper is introduced in to the aquatic environment through a number of natural methods. Copper is also a very useful substance for man. When these uses occur some of that copper is also introduced into the aquatic environment. The sources of copper in the aquatic environment are (2):

- Minerals in soil and weathered rock that form the sediments and suspended particles in the water.
- Extraction of copper from rock into a dissolved state.
- Biological particles, including both living and dead organic material.

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- Hydrothermal systems in which heated or chemically altered water are found. This includes volcanic action and thermal vents.

- Input from sediments.

- Anthropogenic inputs - either directly into the water or leached after deposition on land.

- Deposition from the atmosphere – a major source here is anthropogenic.

Copper is introduced from all these sources into the marine aquatic environment but not equally in all areas. It exists in water, sediments and organisms. The amount in each can vary widely for a number of reasons as the following studies and calculated facts reveal.

An estimated 0.34 billion metric tons of copper currently exists in the ocean's waters based on a concentration of 0.25 ug/L and a volume of 1.338 x 10^9 km^3 (3). Inputs into the ocean include atmospheric inputs accounting for 22 x 10^6 kg/yr, riverine input including dissolved copper at 58 x 10^6 kg/yr and particulate copper at 1500 x 10^6 kg/yr (4) and antifouling copper estimated as 15 x 10^6 kg/yr (5). Based on these input rates, it would take 213 years to put as much copper into the oceans' waters as they currently contain. Also it would take 23,000 years for the current antifouling copper input to equal the existing copper in the world's oceans. These numbers put in perspective the limited addition of antifouling copper on a macro scale but does not address concerns of anthropogenic copper introduction on a smaller scale such as in enclosed estuaries.

Copper is also removed over time from the oceans' water via the formation of sediments. This can occur via biological or physiochemical processes or by particulate settling. Biological activity can remove copper when organisms utilize copper and excrete that copper in fecal material, or when organisms die or molt and these biogenic materials become sediment. If all dissolved copper in the ocean margins were removed through biological processes it is estimated it would take 600 years to be completely removed. If total copper, both dissolved and particulate in the deep oceans continues to be removed at the current rate deep sea sediments are formed, it would take 1500 years to completely remove it (6).

Also it is important to note that the vast majority of input of copper into the ocean environment comes from riverine particulate and 90-95% of that is removed as sediments in the ocean margins. Therefore 80-90% of total copper input into ocean water is removed as sediments in ocean margins.

The concentration of copper in open ocean salt water and in estuary water can vary greatly. This can be due to both natural and anthropogenic copper. In the San Diego Bay area there is an elevated level of dissolved copper, 5.4 ug/L, primarily due to antifouling paints, in the crowded Shelter Island Yacht Basin versus 1.5 ug/L in the bay outside the marina (7). While the world's oceans naturally contain approximately 0.25 ug/L of total copper, the Red Sea median valley naturally contains approx. 1000 ug/L due to high evaporation of the sea as a whole and high water temperature in the deep-water trench, thus creating a brine type environment (8).

There is also a large difference between total and dissolved copper, often an order of magnitude. In the North Sea and Baltic Sea Region dissolved copper was determined to be 0.25 ug/L (9) while total copper was found to be 1.6 ug/L (10). Dissolved copper is most often defined as the amount of copper remaining after filtration through a fine filter. In the San Diego Bay study it was defined as measured copper passing through a 0.45-micron filter.

There are also large variations in copper concentrations in estuarine and marine sediments. These variations are again due to both natural and anthropogenic copper. In the Havana City – Littoral Zone in Cuba, sediments defined as contaminated contained 97-978 ppm copper while 4-29 ppm were found in those areas defined as uncontaminated (11). In mid-ocean areas where presumably very little anthropogenic copper is present, copper in sediments has been found to range from relatively low levels such as 46 ppm in the North American Basin(12) to relatively high levels such as 1200 ppm in the Mid-Pacific Mountains - Ore Crusts (13). Again there is an extremely highly concentrated naturally level of 3100 ppm in the Red Sea median valley sediments.

Sediment concentration can also be used to track the increase or decrease the relative levels of copper in the marine environment over time. In samples taken off the southern coast of Norway, sediments dated as 380 years old had 21 ppm Cu while those dated 35 years old and taken at a different site had 25 ppm Cu. It was noted in this report by the North Sea Task Force that copper concentrations were not becoming significantly more elevated (14).

Multiple sediment samples taken both inside and outside the Port Townsend Marina in Washington State were measured for copper and TBT concentrations (15). The copper was found to be 62 ppm in the marina and 29.2 ppm outside the marina while TBT was found to be 46.5 ppb inside the marina and 1.9 ppb outside the marina. Therefore the level of copper inside the marina was approximately twice that of outside the marina, while the level of TBT was 24 times greater inside versus outside the marina. The study concluded that TBT levels were significantly higher inside versus outside the marina relative to copper because the sediments in the entire port have a significant natural copper concentration level of approximately 29 ppm. The study stated that only 1% of the copper in the bay outside the marina was from antifouling.

Copper is an essential element required for normal growth in all plants and animals. As such, it is considered a normal constituent in the ecosystem in both soil and water where its presence is partially due to the metabolic by-products of plants and animals as previously discussed. The amount of copper required for normal metabolism is small, and for this reason the metal is considered a micronutrient. At both high and low concentrations copper can be detrimental to organisms. **Figure 1** depicts a typical dose-response curve for micronutrients such as copper, showing the range of concentrations spanning defiency, adequacy and toxicity.

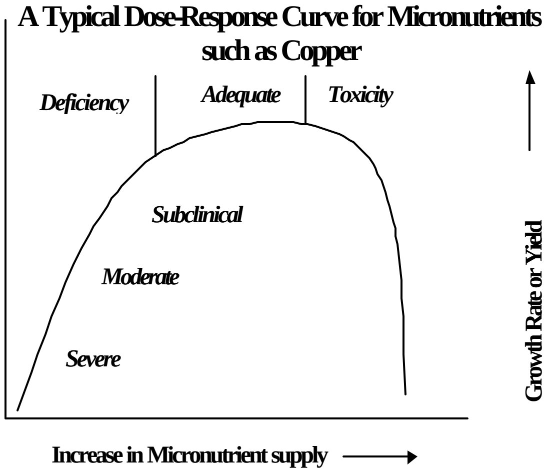


***Figure 1**. Typical Dose Response Curve*

Aquatic organisms acquire the copper that they require for metabolic processes from soluble copper in the water and in interstitial water in the sediments, adsorbed copper on particles in the water or sediments, and copper in the food of the animal. **Figure 2** depicts a schematic relationship between copper in the water and sediments and that in organisms throughout the food chain.

The relationship between copper in the organism and in its environment is complex as it depends on the particular organism and on the bioavailability of the copper. Not all copper in the environment is bioavailable to the organism.

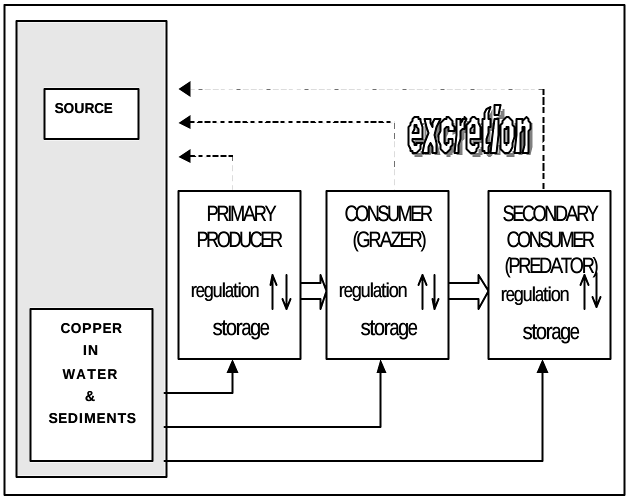


Figure 2. *Relationship between copper in the water and sediments and in organisms*

Antarctic krill were studied to determine levels of copper in their systems over time (16). It was found that there was a seasonal natural variation with February (Antarctic summer) being a particularly high month **Figure 3**. It was speculated that this may be due to seasonal changes in feeding habits and food availability.

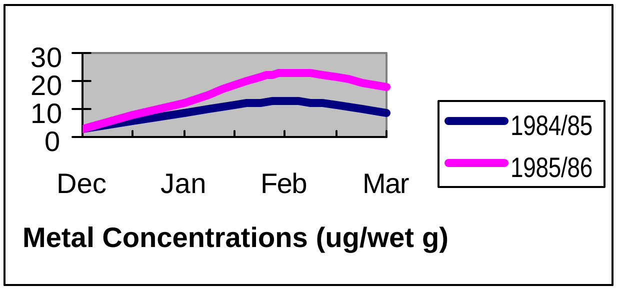


Figure 3. *Levels of copper in Antarctic Krill*

The copper then declined in the krill and it was speculated that this decline was probably due to the ability of the krill to expel copper through the synthesis of the copper containing respiratory protein haemocyanin. It was concluded that natural seasonal variation in bioaccumulation must be considered when looking at copper concentration in krill and in higher tropic animals in this region.

Copper levels in Blue Crab were studied in relation to molt cycle (17). Blue crab blood naturally contains a high level of copper, just as human blood contains elevated levels of iron. The crabs used in this study were not exposed to elevated levels of copper. Therefore, changes in metal concentration of the hemolymph, **Figure 4**, are associated with a normal molting cycle. It was found that there was as much as a 300% natural variation of copper concentration in the hemolymph during the molt cycle. It was determined that this variation in copper content of the hemolymph is a function of the metallothionein protein that is naturally produced by the crab to regulate copper metabolism.

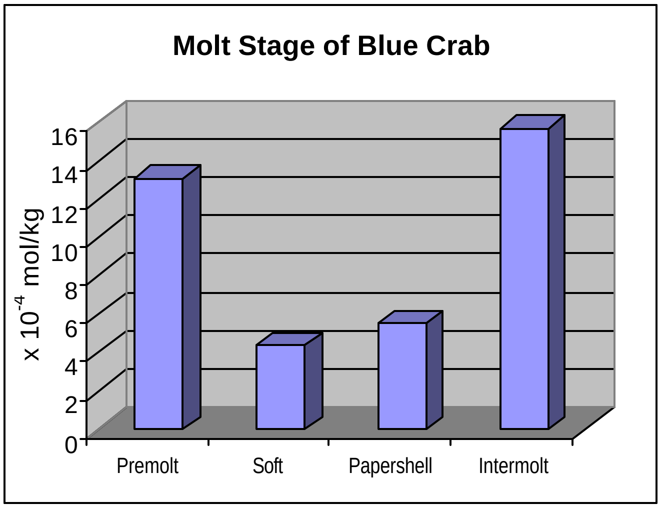


Figure 4. *Copper Level in Blue Crabs*

There are also cases where activities of humans create copper concentration variation in organisms. In a study performed on copper levels in the brown seaweed *Fucus vesiculosus* (18), commonly called bladderwrack, samples of the bladderwrack were taken at various distances from a fish farm, **Figure 5a**. The fish farm used enclosures treated with copper containing antifouling paints. Concentration measurements were taken over an entire year, **Figure 5b**. The data lead to several conclusions. First, it was determined that there was a general tendency for increased levels of copper in bladderwrack located closer to the fish farm. However, there was again seasonal variation just as in the Antarctic krill study.

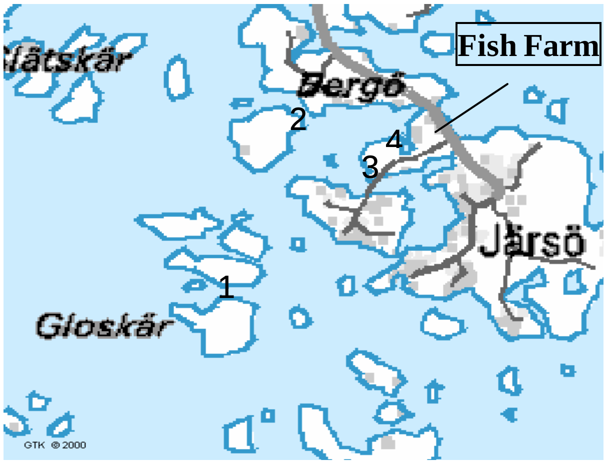


Figure 5a. *Location of fish farm and sampling locations.*

Also, it was found that levels of Fe, Zn and Mn also increased substantially in the bladderwrack near the fish farm and it was hypothesized that higher levels of all four metals in the bladderwrack may have been due to the anoxic condition in the areas' sediments due to the high concentration of organic matter. The conclusions were that contents of copper in the bladderwrack normally vary seasonally and that this organism can be used to indicate copper availability.

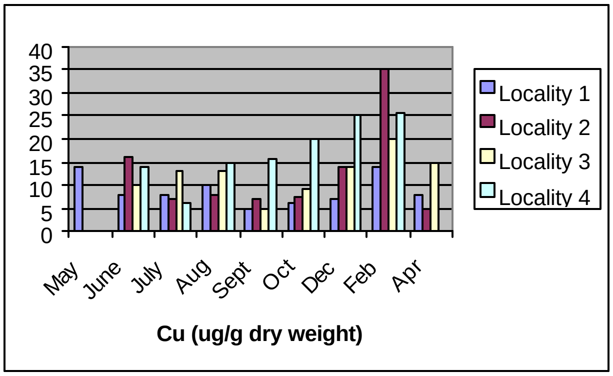
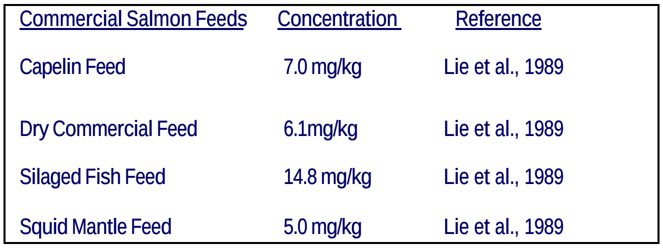


Figure 5b. *Contents of Copper in Bladderwrack*

As mentioned earlier, copper is a natural micronutrient that is essential to normal growth. As such, aquaculture utilizes feed with the micronutrient copper in some concentration to provide organisms such as salmon with an appropriate level in their diet. **Figure 6** contains data on the concentration of copper in 4 different commercial fish feeds (19). This information is useful as we examine the data from the following two reviewed studies.



Commercial Salmon Feeds	Concentration	Reference
Capelin Feed	7.0 mg/kg	Lie et al., 1989
Dry Commercial Feed	6.1mg/kg	Lie et al., 1989
Silaged Fish Feed	14.8 mg/kg	Lie et al., 1989
Squid Mantle Feed	5.0 mg/kg	Lie et al., 1989

Figure 6. *Copper in Commercial Salmon Feed*

A study was performed to determine if pen-raised salmon were bioaccumulating copper from the antifouling coatings on the pens (20). Five pens were used - three of which were treated with cuprous oxide containing antifouling coatings and the other two were left untreated. The concentrations of copper in the muscle and liver of the salmon were measured, **Figure 7**. It was found that there was no correlation to pen treatments. It was speculated that the reason for this is the leaching of the copper was sufficiently slow such that the natural homeostasis of the fish and their detoxification processes are not compromised and that the leached Cu ion is reduced by complexation with organic and inorganic substances in the seawater. It was also hypothesized that the metabolic needs of farm salmon for copper are met from dietary sources, whose copper inputs far exceed inputs from the aqueous environment.

Copper in Farm Salmon Muscle and Liver

	Cuprous Oxide Antifouling Treated Pens			Untreated Pens	
	Pen A	Pen B	Pen C	Pen D	Pen E
Median Muscle Cu	2.0	2.0	1.4	2.1	1.7
Median liver Cu	37	97	104	89	141

(numbers shown in ug/g dry weight)

Figure 7*. Concentrations of Copper in Muscle and Liver of Salmon.*

As previously discussed, fish can pick up copper from their food source. These food sources can contain varying amounts of copper from both natural and anthropogenic sources. In the study summarized in **Figure 8** (21), fresh water tropical fish were fed three different diets:

1. a commercial feed every day,
2. tubificid worms fed bacteria from sediment where copper was not introduced followed by the commercial fish feed on alternate days,
3. tubificid worms fed bacteria from sediment where copper was introduced followed by the commercial fish feed on alternate days.

The level of copper in each food source is shown. The diet of the fish prior to the test and its copper content are unknown. The fish fed the worms that were higher in copper did have higher levels of copper in their system after 14 days. However, fish fed just the commercial fish feed, developed higher levels of copper than did the fish fed the worms that fed on low copper containing bacteria even though these worms had over twice as much copper as the commercial fish feed.

Type of Feed	Cu in feed	Young Fish Day 0	Young Fish Day 14	Old Fish Day 0	Old Fish Day 14
Unknown	Unknown	92.4		58.23	
Commercial	65.75		106.46		111.33
Tubificids fed bacteria grown without added metals	144.44		79.78		57.20
Tubuficids fed bacteria grown with added metals	231.08		199.42		146.08

Figure 8*. Passage of Metals to Freshwater Fish from their Food*

Although this was not discussed in the study, it can be hypothesized that the commercial fish food contained copper that was significantly more bioavailable to the fish than the copper contained in the tubificids.

CONCLUSIONS

Based on the studies and data reviewed the following conclusions can be drawn.

1. Copper concentrations in marine water, sediments and organisms can vary significantly both naturally and due to anthropogenic copper.

2. Organisms have mechanisms to deal with copper levels in their environment within certain ranges.

3. When studying copper in the environment both natural varying copper concentrations and varying concentrations due to anthropogenic copper must be considered.

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