MONITORING DISSOLVED COPPER
CONCENTRATIONS IN CHESAPEAKE BAY, U.S.A.

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(Received September 1987)

Abstract. Dissolved copper and selected water chemistry parameters were monitored for 11 months in Chesapeake Bay, U.S.A. Dissolved copper concentrations in four recreational marinas, a large harbor, two major river systems, and a heavily used shipping canal ranged from below detectable levels to 80 μg L⁻¹ (X = 11.7 μg L⁻¹). Dissolved copper was detected >91% of the time at five locations. Lowest copper concentrations were found in Potomac River, Baltimore Harbor, Pier One Marina, and C&D Canal (X = 6–10 μg L⁻¹); slightly higher levels of dissolved copper were found in Choptank River (X = 12 μg L⁻¹). Highest levels of copper were detected in Port Annapolis, Hartge, and Piney Narrows Marinas (X = 13–18 μg L⁻¹), with the highest values observed in the study (70 and 80 μg L⁻¹) found in two of these marinas. Copper in the three marinas with highest dissolved copper levels could have been toxic to some of the more sensitive aquatic species. Intensive study of one marina indicated that a likely source of dissolved copper was the recreational boats housed in the marina.

1. Introduction

Copper is one of the most toxic metals to estuarine organisms (U.S. EPA, 1980). Although an essential trace element for many aquatic organisms, copper is often toxic at concentrations just above levels required for growth and reproduction of some species (Harrison, 1982; U.S. EPA, 1985). Copper has also been shown to accumulate in marine and estuarine sediments and bioata (Huggett et al., 1973; 1975).

Copper toxicity to aquatic biota is believed to be related primarily to the dissolved cupric (Cu²⁺) ion and possibly to some hydroxyl complexes (Sunda and Guillard, 1976; Howarth and Sprague, 1978; Chakoumakos et al., 1979; Dodge and Theis, 1979; Peterson, 1982; Pagenkopf, 1983; Florence and Stauber, 1986). The free cupric ion forms complexes and precipitates with organic and inorganic components of natural waters. The toxicity of copper in its complexed, precipitated, and adsorbed form is thought to be less than that of the free ionic form.

Copper concentrations in surface waters are highly variable and influenced to a large degree by local geology and point-source inputs. In a review of copper concentrations in the marine environment, Schmidt (1978) reports a range of 0.06–6.7 μg L⁻¹, stating concentrations are generally higher near shore. Dissolved
copper concentrations of main body Chesapeake Bay were consistently reported as being about 2 μg L\(^{-1}\) by Kingston \textit{et al.} (1978, 1983) and Greensberg and Kingston (1983). Dissolved copper concentrations of selected Chesapeake Bay tributaries were < 1 to 72 μg L\(^{-1}\) (Hall \textit{et al.}, 1985, 1987a, b).

Major copper inputs to marine and estuarine environments are atmospheric deposition, industrial and municipal wastes, urban runoff, rivers and shoreline erosion. Chesapeake Bay receives more than 1810 kg of copper per day from these sources (U.S. EPA, 1983). Copper also enters Chesapeake Bay due to its use as the active agent in antifouling bottom paints applied to watercraft. Many boats, especially leisure craft, painted with copper-based bottom paints are housed in harbors and marinas which receive little flushing. These paints, designed to slowly release copper to kill bottom fouling organisms, represent a potential toxic input which may affect non-target organisms. Copper-based paints may become more widely used as tributyltin-based bottom paints are being restricted in some areas of the U.S.

The primary objective of this study was to monitor dissolved copper concentrations in upper Chesapeake Bay, U.S.A. Seasonal patterns in copper concentrations and general water chemistry conditions were also evaluated. A recreational marina was monitored intensively to better define the extent and possible source of high levels of copper in that area. Dissolved copper was monitored because it is believed that the most toxic forms of metals reside in the aqueous phase.

2. Methods

2.1. SAMPLING SITES

Dissolved copper samples were collected monthly during an 11 month period in four recreational marinas, a large harbor, a major shipping canal, and two major river systems. Stations were located on the eastern and western shores of upper Chesapeake Bay, U.S.A. Temperature, pH, dissolved oxygen, salinity and conductivity were determined at each sampling site following collection of copper samples.

2.2. SAMPLING

Ambient water samples were collected in a plastic bucket from a depth of approximately 1 m. Duplicate samples of > 100 mL were filtered through 0.45 μm filters to separate the dissolved copper fraction (APHA \textit{et al.}, 1985). Copper samples were placed in Nalgene\textsuperscript{R} high density polyethylene bottles containing 1 mL of Ultrex nitric acid (J. T. Baker). These bottles were also used to carry deionized water and 1 mL acid on sampling trips to serve as blanks. Bottles had been washed in laboratory detergent then rinsed with tap water and distilled water, soaked overnight in 10 percent Ultrex, rinsed thoroughly with distilled water and allowed to dry before use.
2.3. ANALYSES

Analysis of copper samples was carried out on a Perkin Elmer model 2380 or model 5000 atomic absorption spectrophotometer equipped with an HGA-500 graphite furnace. A standard additions technique was employed. A detection limit of \( \leq 10 \mu g \text{ L}^{-1} \) was obtained for samples collected during the 11 month study, and a detection limit of \( 2 \mu g \text{ L}^{-1} \) obtaining during an intensive study of one marina. Standard water chemistry parameters were determined after copper samples were collected. Dissolved oxygen concentrations at approximately 1 m were determined with a YSI Model 57 dissolved oxygen meter. Salinity, conductivity, and pH were determined from water samples collected from a depth of approximately 1 m. Salinity and conductivity, and pH were determined with a Beckman model TS5-3 induction salinometer, and Orion research grade model 231 pH meter, respectively.

2.4. STATISTICS

A parametric analysis of variance (ANOVA) tested for significance (alpha = 0.05) between station, date, and any interaction effects between station and date. Duncan’s Multiple Range Test determined statistically different copper values for each station and date. Copper samples determined to be below \( 10 \mu g \text{ L}^{-1} \) detection limits were entered as random values ranging from zero to \( 10 \mu g \text{ L}^{-1} \). This technique helps to satisfy homogeneity of variance assumptions inherent in ANOVA testing.

2.5. INTENSIVE MARINA STUDY

Dissolved copper was monitored at seven stations in an intensive study of a marina found to contain high levels of copper. The marina was on the Western Shore of Chesapeake Bay, in Annapolis, Maryland. Copper sampling points were located among boats housed in the marina, in the marina channel, and in the adjacent open waters of the receiving system. The study was conducted during high marina use periods on falling tides to monitor dissolved copper in the marina, marina channel, and receiving system as waters flowed from the marina into open waters. It was hoped that evaluating spatial distribution of dissolved copper under these conditions would provide some clue as to the source of high copper concentrations in this marina.

3. Results

3.1. COPPER ANALYSES

Results of dissolved copper analyses from the 11 month study are presented in Table I. The mean dissolved copper concentration for all stations was 11.7 \( \mu g \text{ L}^{-1} \). Copper concentrations observed during the study ranged from below detectable levels to 80 \( \mu g \text{ L}^{-1} \). In three of eight blanks, levels of copper at detection limits (10 \( \mu g \text{ L}^{-1} \)) were found, indicating a possibility of occasional trace-level contamination. The significance of this apparent contamination is hard to assess since copper concentrations in blanks were just at detection limits. Other investigators have noted
### TABLE I

Dissolved copper concentrations (μg L⁻¹) in replicate samples collected during 11 month study. Station and monthly means with same letters are not statistically different.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aug</td>
<td>Sept</td>
<td>Oct</td>
<td>Nov</td>
<td>Dec</td>
<td>Jan</td>
<td>Feb</td>
<td>March</td>
<td>Apr</td>
</tr>
<tr>
<td>Hartge</td>
<td>12,10</td>
<td>8,30</td>
<td>10,30</td>
<td>20,20</td>
<td>30,BD</td>
<td>70,2C</td>
<td>10,10</td>
<td>10,10</td>
<td>20,10</td>
</tr>
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<td>Port Annapolis</td>
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<td>13,20</td>
<td>30,20</td>
<td>10,80</td>
<td>10,BD</td>
<td>10,2C</td>
<td>20,10</td>
<td>20,BD</td>
<td>70,BD</td>
</tr>
<tr>
<td>Piney Narrows</td>
<td>16,18</td>
<td>14,10</td>
<td>10,20</td>
<td>10,10</td>
<td>BD,10</td>
<td>20,10</td>
<td>BD,BD</td>
<td>20,BD</td>
<td>10,20</td>
</tr>
<tr>
<td>Choptank River</td>
<td>17,20</td>
<td>1,10</td>
<td>10,10</td>
<td>10,BD</td>
<td>10,BD</td>
<td>10,2C</td>
<td>10,BD</td>
<td>20,20</td>
<td>10,10</td>
</tr>
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<td>C and D Canal</td>
<td>10,6</td>
<td>13,10</td>
<td>BD,10</td>
<td>10,10</td>
<td>10,10</td>
<td>10,BD</td>
<td>BD,BD</td>
<td>10,10</td>
<td>10,10</td>
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<td>Pier One</td>
<td>47,16</td>
<td>10,BD</td>
<td>BD,BD</td>
<td>BD,10</td>
<td>BD,BD</td>
<td>BD,BD</td>
<td>BD,BD</td>
<td>BD,BD</td>
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<td>Baltimore Harbour</td>
<td>14,12</td>
<td>14,10</td>
<td>10,10</td>
<td>BD,BD</td>
<td>BD,BD</td>
<td>BD,BD</td>
<td>BD,BD</td>
<td>BD,BD</td>
<td>10,10</td>
</tr>
<tr>
<td>Potomac River</td>
<td>10,8</td>
<td>15,BD</td>
<td>BD,BD</td>
<td>10,BD</td>
<td>10,10</td>
<td>10,BD</td>
<td>BD,BD</td>
<td>BD,BD</td>
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</tr>
<tr>
<td>Monthly Mean</td>
<td>15.3A</td>
<td>12.2A</td>
<td>12.0A</td>
<td>14.8A</td>
<td>9.2A</td>
<td>13.7A</td>
<td>9.3A</td>
<td>10.2A</td>
<td>7.9A</td>
</tr>
</tbody>
</table>

BD = Below Detection (< 10 μg L⁻¹).
— = Not measured.
the lack of documentation of contaminant-free trace metal samples (Bender and Gagner, 1976) and historical difficulties in obtaining contaminant-free environmental copper samples (Boyle, 1979).

Detectable levels of dissolved copper were found in Potomac River waters and at Pier One Marina on only 45% of sampling dates. Baltimore Harbor had detectable levels of copper 64% of the time, while the remaining sites had copper detected with 91 to 100% frequency. Highest copper concentrations (70 and 80 $\mu$g L$^{-1}$) were detected at Port Annapolis Marina and Hartge Marina. Lowest levels of dissolved copper (<15 $\mu$g L$^{-1}$) were found in Potomac River and Baltimore Harbor. Trends evident in Table I are that Hartge and Port Annapolis Marinas often had dissolved copper concentrations >20 g L$^{-1}$ while concentrations at Piney Narrows Marina, Choptank River, and C & D Canal were generally between 10 and 20 $\mu$g L$^{-1}$. With the exception of one sample (47 $\mu$g L$^{-1}$), Pier One Marina had dissolved copper concentrations similar to Baltimore Harbor and Potomac River (<20 $\mu$g L$^{-1}$). The only stations with detectable levels of copper in at least one replicate at all times sampled were Hartge Marina, C & D Canal, and Choptank River. This indicates that copper can be consistently present in a system regardless of levels of copper in the system.

Highest mean dissolved copper concentrations for all stations occurred during August, and August and September were the only months in which all stations had detectable levels of dissolved copper in at least one replicate. Highest copper concentrations reported at the three low-level sites (Potomac River, Baltimore Harbor, Pier One Marina) were also found during August and September. Higher levels of copper observed in these months could, at least at some sites, represent a natural phenomenon rather than increases due to anthropogenic inputs.

ANOVA demonstrated significant station effects but no significance between dates or between date X station interactions. Duncan's Multiple Range Test separated statistically different stations. Port Annapolis Marina, Hartge Marina, Piney Narrows Marina, and the Choptank River had the highest mean dissolved copper concentrations and were not statistically different. Dissolved copper concentrations from the Choptank River were not statistically different from those at any other station. Lowest copper concentrations were found at the Potomac River, Baltimore Harbor, Pier One Marina, and C & D Canal.

3.2. WATER CHEMISTRY

Results of physicochemical parameters monitored during the study are summarized in Table II. Ranges observed were: temperature, 0–29.5 °C; pH, 6.3–8.87; dissolved oxygen, 3.7–14.8 $\mu$g L$^{-1}$; salinity, 0.1–15.1‰; and conductivity, 200–26,200 $\mu$mhos cm$^{-1}$. With the exception of three readings, station pH was always >7.0, generally ranging from 7.2 to 8.5. The C & D Canal had a relatively low pH ($\bar{X}=7.3$) compared to other stations. Dissolved oxygen concentrations were generally >5 mg L$^{-1}$ at all stations. Lowest dissolved oxygen concentrations occurred
TABLE II
Mean and Range of physicochemical parameters monitored during 11 month study

<table>
<thead>
<tr>
<th>Station</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Dissolved oxygen (mg L⁻¹)</th>
<th>Salinity (%)</th>
<th>Conductivity (µmhos cm⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>Baltimore</td>
<td>14.7</td>
<td>8.00</td>
<td>9.2</td>
<td>7.4</td>
<td>10,647</td>
</tr>
<tr>
<td>Harbor</td>
<td>(2.5–26)</td>
<td>(7.30–8.75)</td>
<td>(3.7–12.2)</td>
<td>(2.2–12.2)</td>
<td>(2,500–21,000)</td>
</tr>
<tr>
<td>C &amp; D Canal</td>
<td>13.5</td>
<td>7.31</td>
<td>9.4</td>
<td>2.0</td>
<td>3,445</td>
</tr>
<tr>
<td>(0–27.5)</td>
<td>(6.80–7.58)</td>
<td>(6.1–14.0)</td>
<td>(0.1–5.2)</td>
<td>(200–8,100)</td>
<td></td>
</tr>
<tr>
<td>Choptank River</td>
<td>15.3</td>
<td>8.19</td>
<td>10.8</td>
<td>12.3</td>
<td>17,323</td>
</tr>
<tr>
<td>(1–28.5)</td>
<td>(7.29–8.70)</td>
<td>(7.8–14.8)</td>
<td>(9.4–14.6)</td>
<td>(11,000–25,500)</td>
<td></td>
</tr>
<tr>
<td>Piney Narrows</td>
<td>14.2</td>
<td>7.79</td>
<td>10.2</td>
<td>10.8</td>
<td>15,421</td>
</tr>
<tr>
<td>Marina</td>
<td>(0.5–27.5)</td>
<td>(7.16–8.34)</td>
<td>(4.5–14.6)</td>
<td>(5.0–14.1)</td>
<td>(7,520–24,600)</td>
</tr>
<tr>
<td>Pier One Marina</td>
<td>14.5</td>
<td>7.92</td>
<td>10.2</td>
<td>10.7</td>
<td>15,160</td>
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<tr>
<td>Potomac River</td>
<td>14.7</td>
<td>7.65</td>
<td>8.7</td>
<td>7.8</td>
<td>11,411</td>
</tr>
<tr>
<td>(0–29)</td>
<td>(7.13–8.31)</td>
<td>(3.8–14.2)</td>
<td>(4.3–11.6)</td>
<td>(5,800–20,700)</td>
<td></td>
</tr>
<tr>
<td>Port Annapolis</td>
<td>14.7</td>
<td>8.36</td>
<td>10.7</td>
<td>10.5</td>
<td>15,540</td>
</tr>
<tr>
<td>Marina</td>
<td>(1.5–28.5)</td>
<td>(7.24–8.80)</td>
<td>(5.3–13.4)</td>
<td>(5.3–14.0)</td>
<td>(8,380–24,600)</td>
</tr>
<tr>
<td>Hartge Marina</td>
<td>15.1</td>
<td>8.36</td>
<td>10.0</td>
<td>10.8</td>
<td>16,043</td>
</tr>
<tr>
<td>(1–29.5)</td>
<td>(6.88–8.87)</td>
<td>(4.5–14.2)</td>
<td>(6.0–14.2)</td>
<td>(9,620–25,200)</td>
<td></td>
</tr>
</tbody>
</table>
during September when values were below 5 mg L\(^{-1}\) in 50% of sampling sites. Lowest dissolved oxygen concentrations were detected in Baltimore Harbor and the Potomac River. The most frequently observed dissolved oxygen concentrations of <5 mg L\(^{-1}\) occurred in the Potomac River (3) and Hartge Marina (2). Lowest salinity and conductivity occurred in the C & D Canal.

3.3. INTENSIVE MARINA STUDY

Dissolved copper concentrations observed at sampling stations in the selected marina are presented in Table III. Blanks used on each date had copper concentrations ≤ 2 \(\mu\)g L\(^{-1}\), indicating no or minimal contamination. High dissolved copper concentrations (38 and 32 \(\mu\)g L\(^{-1}\)) were again observed in this marina. A pattern of increasing dissolved copper concentrations from the inner marina to marina channel, then decreased concentrations in the receiving system was evident on each sampling date and for means observed at each station.

<table>
<thead>
<tr>
<th>Date</th>
<th>Inner Marina</th>
<th>Marina Channel</th>
<th>Receiving system</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 26</td>
<td>8.9</td>
<td>12.16</td>
<td>8.8</td>
</tr>
<tr>
<td>September 9</td>
<td>9.10</td>
<td>—</td>
<td>13.12</td>
</tr>
<tr>
<td>September 22</td>
<td>11.7</td>
<td>6.10</td>
<td>38.8</td>
</tr>
<tr>
<td>Station Mean</td>
<td>9.0</td>
<td>11.0</td>
<td>15.2</td>
</tr>
</tbody>
</table>

When considering all copper data from these monitoring efforts one must remember that means represent values calculated using random numbers rather than values of zero for samples containing below detectable levels of copper. Additionally, it is not known why copper was not detected in blanks during the intensive marina study (detection limit 2 \(\mu\)g L\(^{-1}\)) but was occasionally detected in blanks in the 11 month study (detection limit 10 \(\mu\)g L\(^{-1}\)). Thus, copper concentrations of 10 \(\mu\)g L\(^{-1}\) in samples from the 11 month study may represent values of some uncertainty due to the inherent variability in values near the detection limit of a standard curve. Nevertheless, trends in copper concentrations at the eight sampling sites are evident when the whole data set is considered.

Mean dissolved copper concentrations in Potomac River, Baltimore Harbor, Pier One Marina, and C & D Canal were within or just above the range of values reported for unpolluted surface waters and oceans (Schmidt, 1978; Boyle, 1979). However, dissolved copper concentrations determined in this study were generally higher than those reported by other investigators for Chesapeake Bay (Kingston et al., 1978, 1983). Copper concentrations are generally higher in near-shore areas such as those sampled in this study, while other investigators examined open waters of Chesapeake Bay. Dissolved copper concentrations observed in this study agree well with
the values reported by Hall et al., (1985; 1987a,b) for Chesapeake Bay tributaries.

Copper toxicity can be altered by the physicochemical environment. Copper toxicity would be expected to be increased by increased temperatures, decreased pH, decreases in copper complexing agents (carbonates, organics), and decreases in ions competing with copper for exchange sites at membrane surfaces (i.e. decreases in salinity, conductivity). Dissolved copper as measured in this study may be in a form with different toxicity than that measured in some toxicity studies. Dissolved copper measured in this study would represent Cu$^{2+}$ and any copper associated with dissolved ligands. The toxicity of copper bound to dissolved materials would likely be less than that of the free cupric ion. Thus, interpreting the dissolved copper data in terms of possible toxicity to aquatic organisms is complex.

Consistently low or non-detectable levels of dissolved copper were found in Potomantic River, Baltimore Harbor, and Pier One Marina. For this reason alone, these areas are least likely to have been impacted by copper. Detectable dissolved copper concentrations were found in C & D Canal and Choptank River on all sampling periods. The likelihood of toxic effects at each station is hard to assess since lower copper concentrations were generally found in the more dilute C & D Canal while higher copper concentrations were found in the Choptank River where higher pH, high salinity, and high conductivity would reduce potential copper toxicity. The consistent presence of dissolved copper in these areas raises the possibility of adverse effects on aquatic life. However, the Choptank River represents a healthy eastern shore river with few anthropogenic inputs. Thus, copper concentrations in the Choptank River may represent “background” levels which do not have adverse effects under high pH and high ionic strength conditions.

Port Annapolis, Hartge, and Piney Narrows Marinas had the highest mean dissolved copper concentrations and detectable levels of dissolved copper in 91–100% of samples. Mean dissolved copper concentrations (18 µg L$^{-1}$) of these marinas where above toxic effects levels for phytoplankton (Davey et al., 1973; Ibragin and Patin, 1975), flatfish growth (Saward et al., 1975), early life stages of mussel and oyster (Martin et al., 1981), and the estuarine copepod Acartia tonsa (Sosnowski and Gentile, 1978). Highest dissolved copper concentrations of 70 and 80 µg L$^{-1}$ in Hartge and Port Annapolis Marinas are close to or above toxic effects levels for oyster larvae (Calabrese et al., 1977), a polychaete worm (Pesch and Morgan, 1978) and a mysid shrimp (U.S. EPA, 1985). Salinity, pH, and conductivity were generally high in these marina areas and would have reduced copper toxicity as previously discussed. However, copper toxicity to the above and other species could have been exerted due to the continuous presence of copper and the occasionally very high dissolved copper concentrations. Occasional reductions in dissolved oxygen concentrations at Hartge and Piney Narrows Marinas and the presence of other toxicants such as butyltins (Hall et al., 1987c) and boat fuels commonly associated with marinas could increase copper toxicity. Since copper was consistently detected at Port Annapolis, Hartge, and Piney Narrows Marinas the potential for chronic effects
exists. Little information is available on chronic effects of copper to estuarine organisms, but the fact that mean dissolved copper concentrations in these marinas were above acute effects levels for some species makes chronic effects even more likely. However, which species are present in these marinas and their sensitivity relative to those used in toxicity tests is unknown. Species present at these sites may be more resistant than those used in toxicity tests. Acclimation of organisms to toxicants is well known and copper acclimation by a saltwater organism has been documented (Pesch and Hoffman, 1982).

Although no casual relationship can be drawn it seems that a likely source of the high levels of copper in the marinas is the anti-fouling bottom paints used on boats housed in these marinas. The intensive study of one marina would seem to support this. Highest copper concentrations detected in that marina were found in the two middle stations of the marina channel. Distributions of copper observed during the intensive marina study seemed to indicate that copper was ‘flushing’ from boats on each side of the marina, through the marina channel, and into open waters.

Acknowledgements

We would like to thank the State of Maryland Department of Natural Resources for sponsoring this research with a subcontract to JHU/APL. Special consideration is extended to the University of Maryland for serving as the prime contractor. We acknowledge Dr E. S. Perry for statistical analysis of data.

References


