

# Effect of a Spring Phytoplankton Bloom on Dissolved Copper Speciation in Bedford Basin

D. E. SLAUENWHITE, P. J. WANGERSKY and B. D. JOHNSON

*Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J1*

The concentration and speciation of dissolved copper was measured in Bedford Basin, Nova Scotia during the spring phytoplankton bloom of 1987 using *in situ* extraction techniques. The data demonstrated that there was little change in the concentration of copper bound by organic chelators extractable by reverse phase techniques during the growth period of the bloom. The concentration of total dissolved copper and organic bound copper in this system was found to be controlled by local fresh water inputs. The total concentration of copper was found to vary from 5 nM to 10.5 nM, concentrations typical of coastal waters.

There have been several mechanisms proposed to control the concentration of trace metals in seawater since Goldberg (1954) and Krauskopf (1956) found that these metals were undersaturated in seawater relative to their least soluble compounds. Krauskopf's initially proposed a method that involved adsorption onto iron and manganese oxide and hydroxide particles. He also suggested removal by major ion sulphide precipitation in conjunction with organic reactions. In our current understanding, the primary control of trace metal speciation appears to be biologically mediated, specifically uptake or chelation by phytoplankton blooms (Wangersky, 1986).

This hypothesis was proposed to explain trace metal profiles which exhibit nutrient like behavior in the open ocean (Bruland, 1980; Moore, 1981; Jeandel *et al.*, 1987) as well as sediment trap data showing trace metal enrichments in falling biogenic particles (Brewer *et al.*, 1980; Anderson *et al.*, 1983; Noriki *et al.*, 1985).

In addition to the effects of phytoplankton blooms on trace metal speciation, there are conversely the effects of the trace metals on phytoplankton. Several studies on the toxicological effects of metals such as copper on phytoplankton (Anderson and Morel, 1978; Gavis *et al.*, 1981). They have suggested that phytoplankton during a bloom can decrease the concentration of toxic free copper ions by releasing organic chelates that coordinate the copper and thereby detoxify the water. To study the effects of a phytoplankton bloom on copper speciation and concentration in the natural environment, copper organic complexes and uncomplexed copper were measured in the surface waters of Bedford Basin during the spring bloom of 1987.

## Sampling Site

Bedford Basin is a small marine inlet with an area of 17 km<sup>2</sup> and a maximum depth of 70 m at the sampling station (Fig. 1). The water exchange exhibits estuarine type circulation, occurring through a shallow inlet with an effective sill depth of 20 m and maximum width of 375 m. The major fresh water input is the Sackville River in the northern end of Bedford Bay.

Drainage from the surrounding urban areas of Halifax, Dartmouth, Bedford and Sackville, especially during the spring, also accounts for a significant fresh water input.

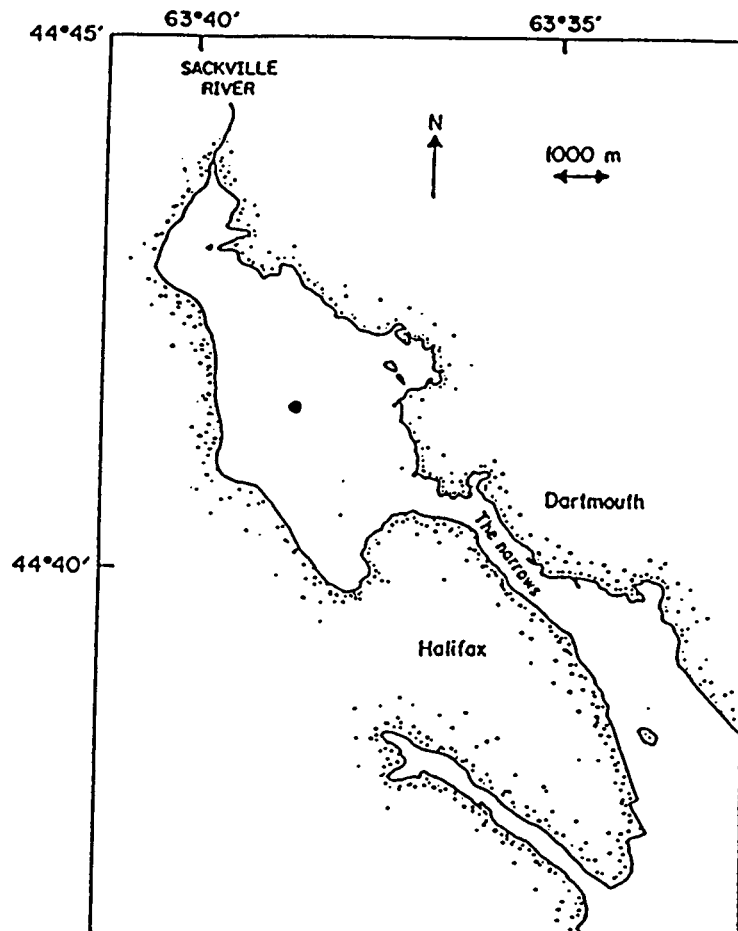


Figure 1. Bedford Basin, Halifax, Nova Scotia with sampling station ( ) used in this study. Sampling depth is 5 m.

### Sampling and Analysis

All materials that come into contact with samples to be analysed for trace metals were scrupulously washed and leached for at least 2 days in 5 N nitric acid (Baker, Reagent) and rinsed with distilled, deionized water (Millipore

Super-Q) before use. Sampling for copper was performed using the battery operated, messenger activated Johnson-Wangersky *in situ* pump (Johnson *et al.*, 1987) attached to a hydrowire from the research vessel R.V. Sigma-T. The pump was deployed at 5 m depth. The inlet of the pump was a 50 cm Teflon tube leading to a polycarbonate filter holder. The filter, Millipore HA (47 mm diameter, 0.45  $\mu\text{m}$  pore size), was cleaned by leaching for 2 days in 2 N hydrochloric acid (Baker Ultrex) and washing with Super-Q. The sample, which varied from 300 - 600 ml, was then pumped through the filter and the two extraction columns in sequence at a flow rate of about 10 ml/min. The first column was C<sub>18</sub> Sep-Pak, a reverse phase adsorbant which has been shown to extract organic-copper complexes (Mills *et al.*, 1982; Mills and Quinn, 1984; Donat *et al.*, 1986; Slauenwhite and Wangersky, 1990). These columns were obtained commercially prepared (Millipore Waters) and cleaned by passing 10 ml of methanol (BDH Omnisolve) followed by 10 ml of Super-Q. They were eluted using 6 ml of a methanol:Super-Q mixture (50:50 vol:vol) and the eluate stored frozen in 30 ml polyethylene bottles with screw caps until analysis.

The second column consisted of porous silica gel onto which had been chemically bonded 8-hydroxyquinoline, designed to extract copper passing through the C<sub>18</sub> column. This column was prepared and cleaned according to the modified method of Slauenwhite *et al.* (1985). Elution was accomplished with 10 ml of 1 N hydrochloric acid/ 0.1 N nitric acid (Baker Ultrex) mixture. The samples were stored frozen and analysed without further preconcentration using a Perkin-Elmer 403 atomic absorption spectrophotometer with a PE 2200 graphite furnace and AS-1 autosampler with uncoated tubes and manufacturers recommended instrument settings. Precision is 5-10 % for all samples analysed in this manner.

Salinity, nutrients, particulate organic carbon (POC), and chloropigment samples were collected in acid rinsed 5 l Niskin Go-Flo bottles. Salinity was measured using a Guildline Salinometer with the appropriate standard. Nutrients and chloropigments were analysed by the spectrophotometric and spectrofluorometric methods respectively, outlined by Strickland and Parsons (1972), adapted for the small sample sizes. POC was analysed by a dry combustion method (Wangersky, 1976), using a 2000-4000 ml sample filtered through Gelman GF/C glass fiber filters that had been previously combusted at 450 C for 12 hours.

## Results

The chlorophyll and POC data suggest that the 1987 spring bloom occurred as a single sharp pulse (Fig. 2a and 2b), similar to the classical concept of a spring bloom. The chlorophyll started to increase rapidly on Julian Day (JD) 72 from 2.9 nM to a maximum of 24 nM on JD 84. The POC increased from 150  $\mu\text{g/l}$  to 1700  $\mu\text{g/l}$  over this same time period. Complimenting these data, the reactive silicate and phosphate showed steep declines in this same period (Fig. 2d and 2c). The concentration of phosphate dropped from 1.5  $\mu\text{M}$  to 0.5  $\mu\text{M}$  and silicate dropped from 8  $\mu\text{M}$  to 1  $\mu\text{M}$ , indicating a diatom bloom. This was confirmed by microscopic examination. The peak of the POC and chlorophyll maxima coincided with the peak of the nutrient minima.

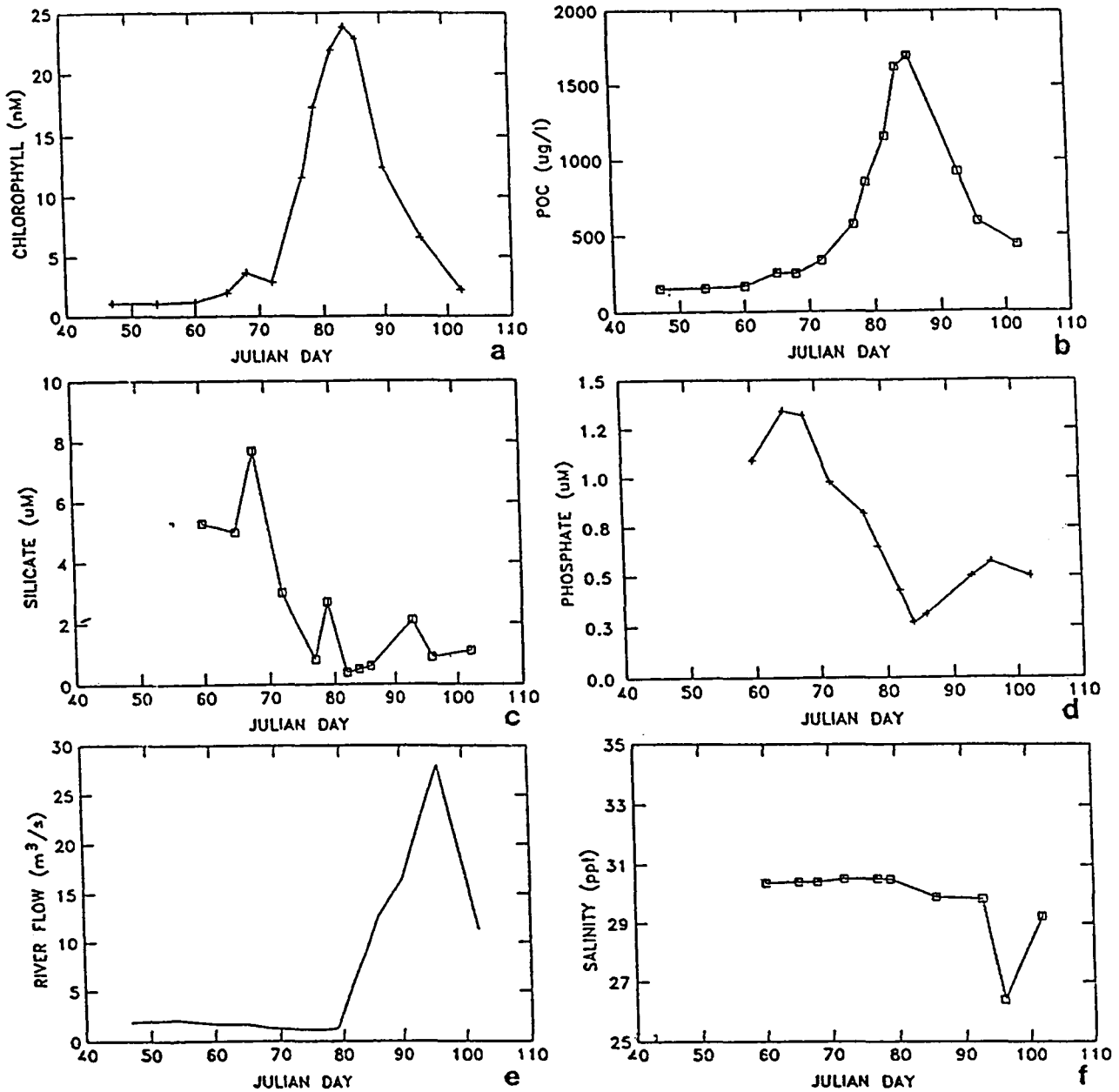


Figure 2. Temporal variation of chlorophyll (2a), POC (2b), reactive phosphate (2c), silicate (2d), Sackville River runoff (2e), and salinity (2f) in Bedford Basin during the spring bloom.

After the peak of the bloom, the POC and chlorophyll concentrations decreased rapidly, and the phosphate levels increased slightly. The decrease in POC and chlorophyll is probably due to the organisms undergoing nutrient stress and subsequent death and settling out of the water column. The increased phosphate levels could be due to fresh water inputs or to remineralization of the phytoplankton remnants. As the bloom accelerated, the fresh water input from the Sackville River increased as well (Fig. 2e), with significant fresh water inputs beginning by JD 80. The fresh water input from the river, increasing by 20-fold over the next 10 days, is reflected in the surface salinity (Fig. 2f) which decreases from 30.54 to 26.62 ppt at the peak of the fresh water runoff.

The total concentration of extractable copper remained relatively constant at about 5 nM until JD 85-90, when the total approximately doubled over the next 10 days (Fig. 3a). The peak of total copper concentration occurred on JD 96, when the concentration reached 10.5 nM. The organic complexed copper and unbound copper also show significant increases on these days (Fig. 3b), with the complexed copper increasing from 2.5 nM to 4.9 nM and the unbound copper from 2.5 nM to 5.9 nM.

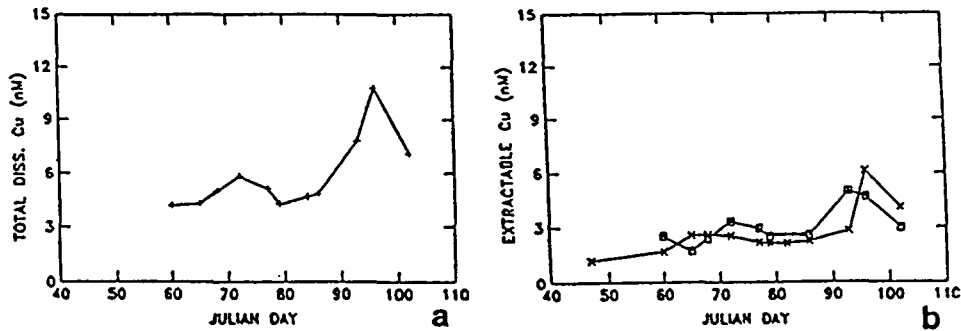


Figure 3. Temporal variation of total dissolved copper (3a) and organic bound copper ( ) and unbound ( ) extractable copper (3b) from Bedford Basin. Total copper is the sum of bound and unbound copper.

### Discussion and Conclusions

Progression of the Bedford Basin bloom can be divided into two distinct phases. The first phase of the bloom occurred between JD 47 and JD 80, and was marked by an increase in primary productivity as demonstrated by the increased POC and chlorophyll concentrations and the concomitant decrease in nutrient concentrations. The second phase of the bloom occurred after JD 80. While the diatom bloom was still progressing and then peaking in this phase, the dominant process was the increased fresh water flux as indicated by the decrease in surface salinity.

The copper data for the first phase showed no measurable variation in concentration or speciation. The concentration of total dissolved copper remained constant at about 5 nM, indicating no significant uptake onto phytoplankton. The concentration of 5 nM is a typical near shore copper concentration this, despite the fact that metropolitan Halifax dumps all of its sewage in the raw form directly into Bedford Basin and adjacent Halifax harbour. In this area most of the metal contamination seems to be rapidly transported out of the water column. Sinks include incorporation into the sediments or dilution and flushing by tidal mixing with incoming Atlantic Ocean shelf waters. The organic bound copper (OrgCu) was constant at 2.5 nM as was the unbound copper (UnbCu). 50 % of the total copper in these waters is extractable by  $C_{18}$  techniques. This proportion remained constant throughout the bloom, demonstrating that this phytoplankton bloom did not have an important influence on the relative amount of OrgCu in the water column.

This result is interesting in that it is known that diatom blooms in culture

exude organic compounds during a bloom that are not the result of cell lysis, that can complex copper and are extractable by reverse phase techniques (Mantoura, 1981; Zhou and Wangersky, 1985; Seritti *et al.*, 1986). In a mesocosm experiment performed in the Dalhousie University tower tank Zhou *et al.*, (1989) found that a relatively high concentration, 40 nM, of copper complexing compounds (CCC) was released, yet Slauenwhite *et al.*, (1990) in the same experiment demonstrated only a small increase in the actual concentration of copper that was bound by these complexing agents in the water column. This result is in agreement with the results found for Bedford Basin, a natural system. It seems that there is no clear and simple relationship between the concentration of CCC and the relative amount of OrgCu. The small increase in OrgCu found by Slauenwhite *et al.*, (1990) is an effect which could be easily obscured in a natural system with many more variables than a mesocosm.

Studies have indicated that for oceanic waters Sep-Paks can allow a significant amount of copper bound by organic moieties to pass through the column (Donat *et al.*, 1986; Mills *et al.*, 1989). In this study such material would be extracted by the 8-hydroxyquinoline column and be designated UnbCu. Donat suggested that the organo-copper complexes extracted by Sep-Paks are more recalcitrant and humified than the organic chelators not extractable. He also suggests that recent phytoplankton exudates are not sufficiently humified to be extractable, and so would not partake in any measurable increase in OrgCu found by this technique, although the data of Slauenwhite *et al.* (1990) indicates some humification may occur on relatively short time scales. This may explain the lack of an increase in OrgCu over the first phase of the bloom. Given sufficient time, perhaps weeks, the newly produced chelators may have become sufficiently humified for increased extractable binding to occur, but mixing processes such as tidal dilution did not allow this to happen. This idea must be qualified in that Bedford Basin can be thought of as a pseudo-steady state system with continuous fluxes of OrgCu and UnbCu in and out of the system, as opposed to an equilibrium system as is the Tower Tank mesocosm. The forces of variability can be expected to have a significant influence in the speciation of trace materials in a real environment.

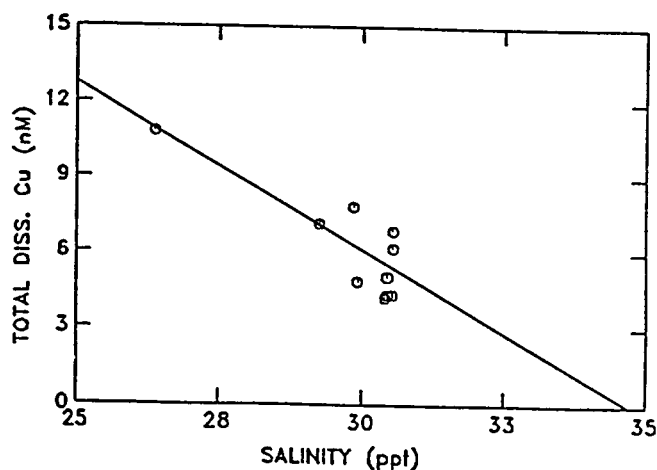


Figure 4. Plot of total dissolved copper versus salinity from Bedford Basin at the 5 m depth.

The second phase of the bloom (after JD 80) is that dominated by increased river drainage (Fig. 2e) from JD 80. In this time period the total copper increased from 5 nM to 10 nM with both OrgCu and UnbCu doubling in concentration (Fig. 3a and 3b). This type of result has been observed by other workers in different geographic areas (Anderson *et al.*, 1984; Mills *et al.*, 1984). The correlation between copper concentration and salinity is shown in Fig. 4. The plot extrapolates at 0 salinity to 45.4 nM copper, comparable to the concentration of 48.6 nM copper measured at the mouth of the Sackville River. The correlation coefficient for this data is  $r = 0.87$ , though it can be seen effectively as a 2-point plot due to the rapidity of the fresh water input. From this result it is clear that the primary mechanism controlling copper concentration in Bedford Basin during the spring bloom is fresh water input, with the effect of primary productivity secondary.

#### ACKNOWLEDGMENTS

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