

LONG-TERM EFFECTS OF COPPER  
ADDITIONS TO LAKES

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## Management Perspective

Figure Eight Lake (Peace River district) was treated with copper sulphate from 1980 to 1984 to suppress algal growth. Although the application dose was typical of most treatments in Canada, concern over the long-term effects was expressed when the quality of the fishery declined, and benthic invertebrates that are important fish food became rare. Fisheries biologists wanted proof that a cause and effect relationship existed between the use of copper sulphate and the demise of the fishery.

Analysis of the lake indicated that the lake sediments were still toxic a year after the copper sulphate treatment. Heterotrophic activity in the sediments was suppressed. The inhibition of sulphate reducing bacteria blocked pyrite formation and resulted in a doubling of the sulphate content of the water column.

A year after the last copper sulphate treatment, copper phosphorus, and ammonia were released from the sediments into the water column. Sediment nutrient release usually enhances algal growth; however, the algal bloom was suppressed. Much of the sediment copper was mobile and toxic to algae; thus, it was bioavailable. Moreover, copper concentrations in the water column exceeded values needed to kill sensitive invertebrates. The concentration of bioavailable copper in the surface sediments prior to the sediment release could have killed many invertebrates, especially juvenile forms. Unfortunately, in some lakes, the long-term toxicity of copper sulphate can interfere with fisheries.

## Perspective - gestion

De 1980 à 1984, on a traité le lac Figure Eight (district de Peace River) au sulfate de cuivre afin de supprimer la croissance des algues. Même si la quantité utilisée était à peu près la même que pour la majorité des traitements semblables faits au Canada, on a commencé à s'inquiéter des effets à long terme lorsque l'on a constaté que la qualité de la pêche diminuait et que les invertébrés du benthos, essentiels à l'alimentation des poissons, se raréfiaient. Les biologistes des pêches ont voulu obtenir la preuve qu'il existait une relation de cause à effet entre l'utilisation du sulfate de cuivre et le déclin des pêches.

En procédant à des analyses dans le lac, on a découvert que les sédiments étaient encore toxiques une année après le dernier traitement au sulfate de cuivre et que l'activité hétérotrophique dans les sédiments avait cessé. L'inhibition des bactéries réductrices de sulfate empêchait la formation de pyrite et, par conséquent, la concentration de sulfate dans la colonne d'eau doublait.

Une année après le dernier traitement au sulfate de cuivre, on a remarqué que du phosphore de cuivre et de l'ammoniaque étaient libérés par les sédiments dans la colonne d'eau. En général, une libération de nutriments par les sédiments favorise la croissance des algues mais, dans ce cas particulier, on a constaté que cette croissance était supprimée. La plus grande partie du cuivre dans les sédiments était mobile et toxique pour les algues; le cuivre était donc biodisponible. De plus, les concentrations de cuivre dans la colonne d'eau étaient suffisamment élevées pour tuer les invertébrés plus fragiles. Le cuivre biodisponible dans les sédiments de surface avant la libération par les sédiments était suffisamment concentré pour détruire de nombreuses espèces d'invertébrés, surtout les formes juvéniles.

Malheureusement, dans certains lacs, la toxicité à long terme du sulfate de cuivre peut nuire aux pêches.

## SOMMAIRE

Le traitement des lacs eutrophes au sulfate de cuivre dans le but de limiter la croissance des algues est utilisé depuis longtemps.<sup>1,2</sup> En même temps, les charges de cuivre ont augmenté dans les lacs situés près des régions industrialisées.<sup>3</sup> On sait que le cuivre versé dans un lac disparaît rapidement de la colonne d'eau<sup>4</sup> et demeure dans les sédiments<sup>5</sup>. On a déjà signalé certains effets négatifs de ces ajouts de cuivre<sup>1,2,6-8</sup>, mais on possède très peu d'informations sur les effets à long terme de l'augmentation des charges de cuivre sur les processus du benthos ou sur les organismes en eau libre. Le présent document constitue le rapport d'une étude sur un lac qui a été traité au sulfate de cuivre pendant une période de quatre ans. Une année après le dernier traitement, nous avons découvert que, en conditions de réduction au milieu de l'été, du cuivre était libéré par les sédiments. Il semble que ce cuivre détruit la biomasse des algues. De plus, on a découvert que l'activité bactérienne était bloquée dans la couche de sédiments où le cuivre s'était accumulé. Par conséquent, les accumulations de cuivre dans les sédiments de lacs peuvent avoir des effets graves autant sur les étendues d'eau libre que sur les processus qui se déroulent dans les sédiments.

Copper sulphate has long been applied to eutrophic lakes to suppress algal blooms (Effler et al., 1980; Hanson and Stefan, 1984). As well, copper loadings have increased to lakes near industrialized centres (Ouellet and Jones, 1983). Copper added to the lake reportedly disappears rapidly from the water column (Wagemann and Barica, 1979) and remains in the sediments (Elder and Horne, 1978). Although some negative effects of copper additions have been reported (Beers et al., 1977; Whitaker et al., 1978; Effler et al., 1980; Hanson and Stefan, 1984; Hedtke, 1984; Winner, 1985; Collvin, 1985) little is known about the long-term effects of increased copper loading on benthic processes or open water organisms.

The residual effects of copper additions were investigated during the summer of 1985 on the sediments and water of Figure 8 Lake, situated 48 km northwest of Peace River, Alberta. It is a small (37 ha) and shallow (mean depth 3.1 m) eutrophic lake with one inlet stream which flows briefly in April, a control structure on the outlet, a moderate-sized drainage basin ( $4.5 \text{ m}^2$ ) and lake water residence time of  $\approx 4$  yr. Annual precipitation is low (long-term average is  $446 \text{ mm}\cdot\text{yr}^{-1}$ ). (Environment Canada, 1951-1980). The region is far from any heavy industrialized activities. Chemistry of the lake water was similar to many shallow eutrophic prairie lakes (Prepas and Trew, 1983), pH of the surface waters in summer averaged 9.2 and this water was moderately alkaline ( $92 \text{ mg}\cdot\text{l}^{-1} \text{ CaCO}_3$ ) with conductivity of  $202 \text{ }\mu\text{S}\cdot\text{cm}^{-1}$ . The phytoplankton community was dominated (>95% by weight) by the blue-green algae, Aphanizomenon flos-aquae.

Figure 8 Lake was treated a total of 4 times with copper sulphate from 1980 through 1984 (Table 1). The amount of copper added was typical of many treatments (Whitaker et al., 1978) and sufficient to depress algal biomass for 1 to 6 wk.

On July 30 and October 26, 1985, nine cores were collected with a modified Kajak-Brinkhurst corer (CCIW, unpublished) from the deepest spot in each of the two main basins (depths 6 and 5 m) of the lake. Cores were analyzed as follows: Cu was determined after acid dissolution by atomic absorption (McKeague, 1978), org C was measured with a Leco furnace after removal of the carbonate carbon (Kemp, 1971), water content was determined after freeze-drying, iron in  $\text{FeS}_2$  was determined by Mössbauer spectrometry (Manning and Ash, 1979; Manning et al., 1979) and net acetate uptake was measured with  $^{14}\text{C}$ -acetate (Burnison et al., 1987) on samples less than 72 h old. Analyses of four complete cores and surficial sediments from two additional cores revealed that there was a layer of sediment high in copper which extended from 1 cm below the surface to a depth that varied from 5 to 8 cm (Fig. 1). This band of copper would represent the period of copper sulphate application and suggests a sedimentation rate of  $\approx 1 \text{ cm}\cdot\text{yr}^{-1}$ . Analyses of all the cores collected revealed that in this same band, there was relatively little organic carbon (8 to 10% as compared with 15 to 19% deeper in the cores), and depressed water content (as low as 82% as compared with 86 to 90% deeper in the cores). Pyrite formation, a process which is dependent upon bacterial reduction of sulphate was inhibited in this band and  $^{14}\text{C}$ -acetate uptake was depressed

(Fig. 1). These results strongly suggest that bacterial activity was suppressed in the sediments during the 4 yr when copper was applied to the lake, as well as for at least 1 yr after the treatment stopped. In addition, the sediments reflect reduced algal productivity during the period when copper was added.

In July, 1985, Figure 8 lake was thermally stratified. Water samples were collected and analyzed as outlined in Prepas and Trew (1983). During this period, water over the deeper sediments (>3 m) was anoxic (i.e. dissolved oxygen was  $0 \text{ mg}\cdot\text{l}^{-1}$ ) and total phosphorus increased to  $750 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ . In August the lake mixed completely, the phosphorus-rich waters over the sediments were mixed into the surface waters, and total phosphorus in the surface waters increased from  $92 \text{ }\mu\text{g}\cdot\text{l}^{-1}$  in mid-July to  $223 \text{ }\mu\text{g}\cdot\text{l}^{-1}$  in late August (Fig. 2).

This dramatic increase in total phosphorus in August is common in shallow prairie (freshwater) lakes and is always associated with an increase in chlorophyll a (an index of phytoplankton biomass) (Prepas and Trew, 1983; Riley and Prepas, 1984) as illustrated in Fig. 2b. However, in Figure 8 Lake, as total phosphorus levels increased, chlorophyll a levels decreased from  $47 \text{ }\mu\text{g}\cdot\text{l}^{-1}$  in mid-July to  $23 \text{ }\mu\text{g}\cdot\text{l}^{-1}$  in late August (Fig. 2a). Thus the infusion of phosphorus (mainly in an available form) to the euphotic zone in August did not enhance chlorophyll in Figure 8 Lake and even appeared to suppress it.

We looked at whether the depressed chlorophyll levels could be related to copper. Analysis (Environment Canada, 1979) showed that copper accumulated (up to  $36 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ ) over the sediments

when the lake was thermally stratified and the water overlying the sediments was anoxic. This accumulated copper (Cu) was mixed into the surface waters in August: the average in the surface waters in August was  $11 \mu\text{g}\cdot\text{l}^{-1}$  Cu with levels as high as  $25 \mu\text{g}\cdot\text{l}^{-1}$  recorded at a depth of 1 m below the surface. By November, 1985 lakewater copper had returned to background levels of  $<2 \mu\text{g}\cdot\text{l}^{-1}$ . The Cu levels recorded in the surface waters of Figure 8 Lake were sufficiently high to cause a serious depression in chlorophyll a (Steeman-Nielsen and Laursen, 1976; Sundra and Guillard, 1977; Whitaker et al., 1978). Thus, there was a residual effect of copper additions 1 yr after the last application.

Our data show for the first time that copper can be released from lake sediments during summer. Analysis of copper fractions (Krantzberg and Stokes, 1981, 1985) in the Figure 8 Lake sediments indicated that more than 80% of the sediment copper is tied up with organic matter or resistant inorganic forms. Thus, one explanation for the data from Figure 8 Lake is that biological modification of these sediments by benthos burrowing activity could release copper into the overlying waters (Krantzberg and Stokes, 1985) during the warm summer months.

The copper levels observed in the surface sediments of lakes located near large industrial centres can be at least 3 times the maximum level recorded for Figure 8 Lake ( $180$  vs.  $60 \mu\text{g}\cdot\text{g}^{-1}$ ). Thus, the problem of copper toxicity could potentially extend to many lakes. Further work is urgently needed to document the extent and duration of copper toxicity in lakes.



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TABLE I

Copper<sup>†</sup> added to Figure 8 Lake, 1980 to 1984.

Date	Total Cu added#	Cu concentration* ( $\mu\text{g}\cdot\text{l}^{-1}$ )
June 11, 1980	80.4	71.2
August 11, 1983	28.0	24.8
June 25, 1984	21.6	19.1
August 14, 1984	34.4	30.5
Total	164.4	

<sup>†</sup>Source D. Walty, Alberta Fish and Wildlife.#Copper added as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , units kg of Cu.

\*Assumes complete mixing.

## FIGURE LEGENDS

Fig. 1. Copper (Cu) content, organic carbon (org C) levels, water content and iron (Fe) in pyrite ( $\text{FeS}_2$ ) in the top 20 cm of core #8 collected from the north basin of Figure 8 Lake, July, 1985 and net acetate assimilation in the top 8 cm of a core collected from the same basin in October, 1985.

Fig. 2a. Total phosphorus (TP) and chlorophyll a (Chla) levels in the euphotic zone (0 to 3 m) of Figure 8 Lake in July and August, 1985. Data represent composite samples collected from five sites on the lake. b. Similar data from the euphotic zone (0-1.2 m) of Nakamun Lake (Riley and Prepas, 1984) a shallow eutrophic prairie lake which had not been treated with copper.



