

# Chemical Reactions Controlling Copper Transportation in the Upper Clark Fork of the Columbia River

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## Abstract

Water samples were collected from the Clark Fork of the Columbia River in Montana and analyzed for major components as well as copper. A model was developed to interpret the copper toxicity and the transport of copper through the study area. Major complexing of the copper(II) was by carbonate and sulfate. Water hardness reduces the copper (II) toxicity by at least a factor of 10.

## Introduction

The transport of a trace metal through an aquatic surface system depends on many variables. Some of these include temperature, flow rate, amount and type of other chemicals, and the nature of any suspended materials. This dependence reflects the chemical species that are toxic and those less toxic (1-4, 6-9, 11). In the Clark Fork River headwaters all of these variables are important and must be considered. Our area of interest is approximately 25 miles long extending from Warm Springs downstream to Garrison, Montana. Our study was done using samples collected from the Galen area, about 4 miles downstream from Warm Springs. The river is formed through the combination of three general surface waters: surface creeks coming in from the surrounding areas, the drainage from the smelted material near Anaconda, and Silver Bow Creek. These sources make a sizable chemical contribution to the river. Our sampling was done downstream from these sources and therefore included chemicals contributed from all of them.

## Methods

The sample area lies about 1 mile east of Galen and is accessible by road (fig. 1). The samples were collected 30 m upstream from the river bridge near Galen. Samples were obtained in the middle of the river approximately 30 cm below the surface. A portion of each sample was filtered through 0.22  $\mu$ m filters and acidified. The amount of material filtered off was in the 20 mg/L range. A portion of the nonfiltered samples was also acidified to about pH 2. The samples were kept on ice during transport from the sampling area to Montana State University Chemistry Department. Temperature of the samples at time of collection was obtained in the field. Laboratory analyses included specific conductance, pH, calcium, magnesium, sodium, bicarbonate, sulfate, and copper. The major analytical procedure was recommended by the U.S.

Environmental Protection Agency. Copper (II) concentration was monitored by an ion selective electrode. A concentration of Cu lower than approximately  $10^{-7}$  M is difficult to monitor in the pH 8 range and thus one cannot achieve accurate measurements. Acidification of the sample converts the copper species to  $\text{Cu}^{2+}$  so that analyses of total copper can be made.

## Results

Eight river samples were taken between August 8, 1984, and February 18, 1985. The analytical results are listed in table 1. The analysis is not yet complete but it does include sufficient information to calculate the copper species distribution. From this group of samples, seven of the eight were collected when it was cold, whereas the first one (August 1984) was collected when it was warm. In addition, the first sample followed a large localized rainstorm that caused a fish kill in the river. As a consequence, most of the comparisons are made using the samples obtained in the winter.

In general, the pH does not vary substantially and is somewhat greater than 8.1. The major cations are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$ . The anions are dominated by bicarbonate and sulfate. The concentration of copper in the February samples was greater in the afternoon than in the morning. For example, the three morning samples averaged  $1.16 \times 10^{-6} \text{ M}$ , whereas the afternoon samples averaged  $2.23 \times 10^{-6} \text{ M}$ . The stream water temperature did not rise during the day and thus the increase in total copper was probably associated with snow ice melt during the day. If copper was present only as  $\text{Cu}^{2+}$  the water would have been very toxic and, in fact, would kill all of the trout in a very short period of time. Since there are many complexing reactions they need to be included for copper(II).

## Discussion

We found that the total copper is somewhat variable and the total concentration is high enough to be very toxic if the water is acid. However, in the Clark Fork River, copper is found in a variety of complexes and thus many of the species are not toxic. The species and thermodynamic stability constants are summarized in table 2. The water temperature is much below  $25^{\circ}\text{C}$  and, as a consequence, values that are more appropriate at  $5^{\circ}\text{C}$  were used in table 2.

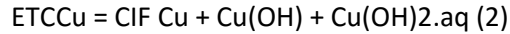
Some reactions are more stable at lower temperature; i.e., Cu complexation, whereas others are not; i.e.,  $\text{Ca}^{2+}$ . In addition, the pH changes from 14.0 to 14.5. To do the calculations, representative concentrations were utilized. The values are as follows:  $\text{CuT} = 2.0 \times 10^{-6} \text{ M}$ ;  $\text{pH} = 8.15$ ;  $\text{pOH} = 6.4$ ;  $\text{HCO}_3^- = 2.5 \times 10^{-3} \text{ M}$ ;  $\text{SP} = 1 \times 10^{-5} \text{ M}$ , (5). The results of the calculations are shown in table 3.

This speciation has important implications for fish life. The most important is the contribution of  $\text{CuCO}_3\text{.aq}$ ; it takes up 90% of the total Cu and this complexing gives the fish marked protection. The toxic species, or at least most toxic species, are  $(\text{Cu} + \text{Cu}(\text{OH}) + \text{Cu}(\text{OH})_2\text{.aq})$  which collectively constitute about 6.3% of the total. The other ones do not make major contributions to toxicity but they do contribute to the nontoxic species.

The concentration of the three toxic species, which is equal to  $8.0 \text{ ug/L}$ , is high enough to cause 96-hour toxicity (I) if it is not shielded away. When water contains hardness components, the trace metals toxicity is reduced (7). This is referred to as CIF, concentration inhibition factor. This factor is calculated using the following:

$$\text{CIF} = 1/(1 + K_m \text{Ca}^{2+} + \text{Mg}^{2+})^{-3} \quad (1)$$

The total hardness concentration in the system is near  $3.5 \times 10^{-3} \text{ M}$  and thus  $\text{CIF} = .054$ . The value of  $K_m$  is  $5 \times 10^3 \text{ M}^{-1}$ . Coupling this to the toxicity relationship provides the following:



Combination of the two factors, CIF = 0.056 and copper species = 8.0 ug/L, provides an effective concentration of 0.45 ug/L which apparently is below that required to kill the fish.

In summation, there is a large variety and fairly high concentration of chemics in the water. If the buffer capacity was weaker, and if the hardness components did not protect the fish, there would be excessive toxic copper species present; as a result, the river could not support a fish population.

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Figure 1. Study area on upper Clark Fork of the Columbia River.

Table 1.--Analyses results for samples collected near Galen, Montana

Date	8/8/84	11/13/84	1/26/85	2/16/85
Time	--	1 pm	1 pm	4 pm
pH	8.36	8.31	8.29	8.14
S.C., $\mu\text{mhos/cm}$	232	246	648	630
T °C	23	9	-1	0
Ca, mg/L	26.5	66	83	75
Mg, mg/L	5.4	24	32	32
Na, mg/L	12	13	11	11
HCO <sub>3</sub> , mg/L	118	161	161	141
SO <sub>4</sub> , mg/L	63	76	114	117
10 <sup>6</sup> x total copper*, M	.94	**6.57	1.25	1.88

Date	2/17/85	2/17/85	2/18/85	2/18/85
Time	11 am	5 pm	10 am	11 am
pH	8.12	8.16	8.14	8.30
S.C., $\mu\text{mhos/cm}$	704	702	717	673
T °C	0	0	0	0
Ca, mg/L	79	82	78	76
Mg, mg/L	40	33	30	30
Na, mg/L	10	11	10	10
HCO <sub>3</sub> , mg/L	152	142	143	146
SO <sub>4</sub> , mg/L	121	128	119	125
10 <sup>6</sup> x total copper*, M	1.32	2.58	1.13	1.02

\*Sample acidified to pH 2.

\*\*Contains contribution from sediment.

Table 2.--Stability constants for copper(II) and other species

Species	Log stability constant	Reference
Cu(OH) <sup>+</sup>	6.3	10
Cu(OH) <sub>2</sub> .aq	12.8	10
Cu(OH) <sub>3</sub>	15.0	10
CuCO <sub>3</sub> .aq	6.8	11
CuHCO <sub>3</sub> <sup>-</sup>	2.7	10
CuSO <sub>4</sub> .aq	2.3	11
Cu-SP (10 <sup>-5</sup> molar)	5.0	12
HCO <sub>3</sub> <sup>-</sup>	-10.5	11
CO <sub>2</sub> .aq	-6.5	11
CaSO <sub>4</sub> .aq	2.3	10
MgSO <sub>4</sub> .aq	2.2	10
pK <sub>w</sub>	14.5	10

Table 3.--Calculated copper species distribution

Species	Total concentration	Percent
$\text{Cu}^{2+}$	$2.54 \times 10^{-8}$	1.28
$\text{Cu}(\text{OH})^+$	$2.01 \times 10^{-8}$	1.01
$\text{Cu}(\text{OH})_2.\text{aq}$	$8.03 \times 10^{-8}$	4.04
$\text{Cu}(\text{OH})_3^-$	$1.6 \times 10^{-12}$	<0.10
$\text{CuCO}_3.\text{aq}$	$179 \times 10^{-8}$	90.00
$\text{CuHCO}_3^+$	$3.2 \times 10^{-8}$	1.61
$\text{CuSO}_4.\text{aq}$	$1.5 \times 10^{-8}$	0.75
$\text{Cu-SP}$	$2.5 \times 10^{-8}$	1.26
$\text{Cu total}$	$2.0 \times 10^{-6}$	