

June 23, 1994

Mr. Tom Bauman  
 Department of Natural Resources  
 Bureau of Wastewater Management  
 101 S. Webster Street  
 P.O. Box 7921  
 Madison, WI 53707

Re: Flambeau Mining Company WPDES Permit No. WI-0047376-1

Dear Mr. Bauman:

Flambeau Mining Company (Flambeau) is submitting this letter as a follow-up to the Toxicity Reduction Evaluation (TRE) reports submitted to the Department on January 11, 1994 and March 18, 1994. The TRE reports indicated that minor operational adjustments resulted in an increased treatment efficiency of Flambeau's wastewater treatment plant (WWTP) and that Flambeau has continued to pass the bioassay test provisions in its WPDES permit.

Bioassay tests in subsequent to March 18 have also passed all permit requirements. Table 1 summarizes the results of acute bioassays conducted since December 1993. All of these test batteries have shown full compliance with Flambeau's permit limits.

Table 1. Acute Bioassay Results.

DATE	Mean Survival (%)			Mean Survival (%)		
	100% Effluent			50% Effluent		
	<i>C. dubia</i>	<i>D. magna</i>	<i>P. promelas</i>	<i>C. dubia</i>	<i>D. magna</i>	<i>P. promelas</i>
Dec. 21 - 25, 1993	85	100	100	100	100	100
Jan. 6 - 10, 1994	100	100	100	100	100	100
Jan. 20 - 24, 1994	100	85	100	100	100	100
April 14 - 18, 1994	100	100	100	100	100	100
April 28 - May 1, 1994	100	100	90	100	100	100
May 19 - 22, 1994	85	100	100	100	100	100
June 9 - 13, 1994	85	100	95	100	100	95

Flambeau's WWTP has consistently generated an effluent which is below WPDES chemical specific permit limitation. Further efforts to improve WWTP efficiency have resulted in a continued reduction in the concentration of copper in the effluent. Figure 1 shows graphically the decrease in copper concentrations in Flambeau's effluent since December 1993.

Nevertheless, because of Flambeau's ongoing commitment to environmental protection, we have undertaken additional research to continue full compliance with the WPDES permit. In our literature review, numerous studies have shown that the availability and toxicity of trace metals such as copper to aquatic organisms is influenced by the degree of chelation (Sprague, 1985; Winner, 1985). Chelation is the complexing of metal ions with organic compounds.

After evaluating various ways to apply the chelation process, Flambeau determined that utilization of citric acid as a source of an organic complexing agent, decreased the bioavailability of copper. Flambeau reached this conclusion by performing bench scale studies using samples taken from the clarifier overflow. The pH of the samples was adjusted with a combination of citric acid and dilute sulfuric acid; the latter is currently used for pH adjustment in the WWTP sulfide treatment process. These samples then underwent the remaining wastewater treatment process on a bench scale. The samples were then spiked with varying concentrations of copper. An independent lab performed acute bioassays on these samples using *C. dubia* as the test organism. Table 2 summarizes the copper/citric acid bioassays .

Table 2. Copper/Citric Acid Research Bioassays.

DATE	Copper LC <sub>50</sub> (ppb)	Citric Acid (ppm)
May 19-22, 1994	25	1.15
May 19-22, 1994	50	3.03
June 2-4, 1994	75.2	5.50
June 2-4, 1994	>184	11.01

The copper/citric acid research showed consistent dose/response results. Flambeau concluded from this research that the use of relatively low quantities of citric acid in the treatment process would result in increasing the LC<sub>50</sub> of copper to a concentration greater than Flambeau's current chemical specific limitation for copper.

In addition, Flambeau also determined that the use of citric acid would have minimal impact on the Flambeau River with respect to either the nonpurgeable organic carbon [NPOC] content in the river or the potential biochemical oxygen demand [BOD]. Table 3 compares these constituents in the Flambeau River on May 31, 1994 with the simulated effluent. The simulated effluent treated with this quantity of citric acid very closely equates with these characteristics of the Flambeau River. Thus, there would be no negative impact on the Flambeau River with the use of citric acid as well as dilute sulfuric acid for pH adjustment.

**Figure 1. Outfall 001 Copper Concentrations  
Flambeau Mining Company**

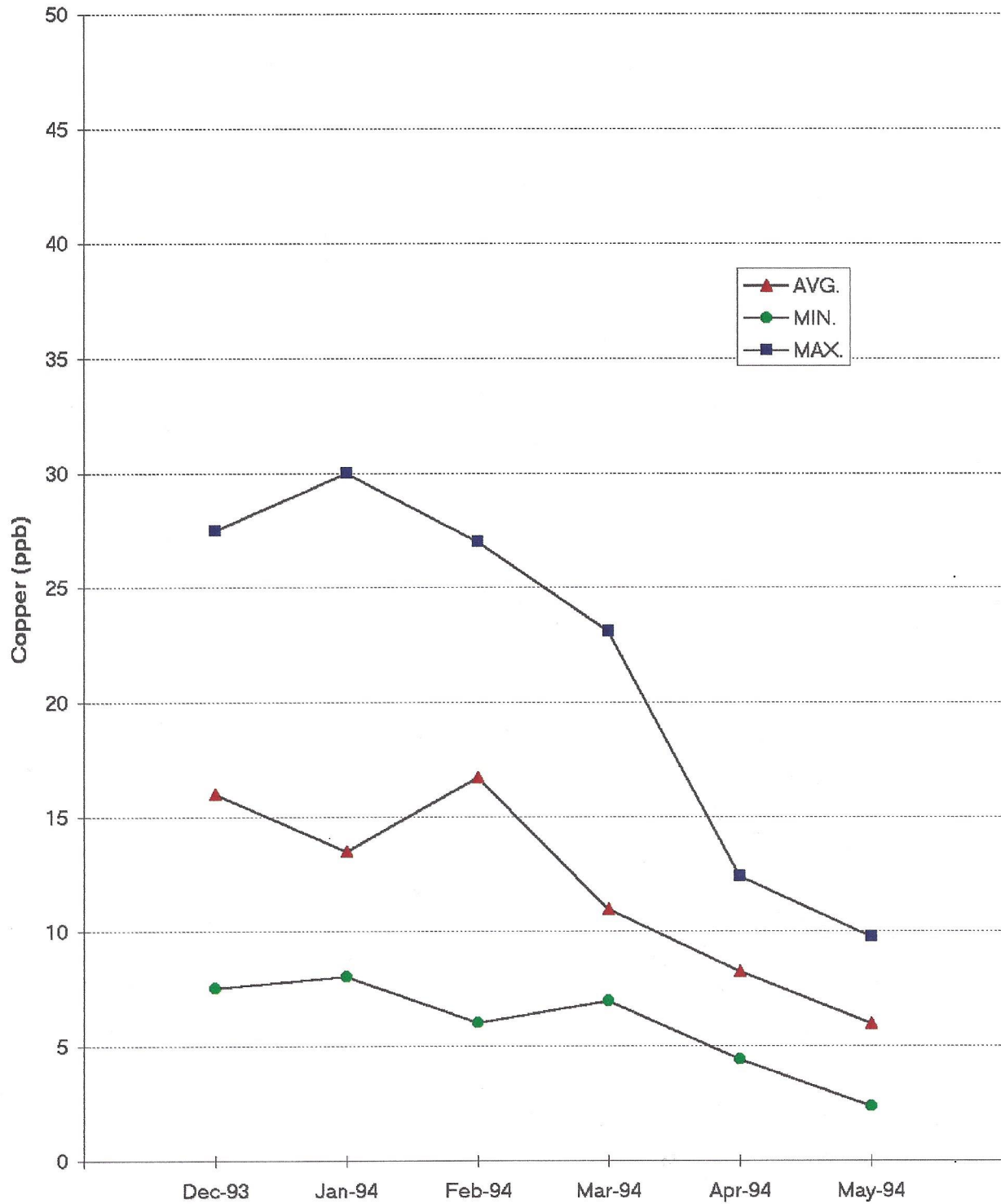


Table 3. Citric Acid/Flambeau River Constituents.

	NPOC (ppm)	BOD (ppm)
Flambeau River	7.0	<6.0
Citric Acid (5.5 ppm)	3.0	<6.0

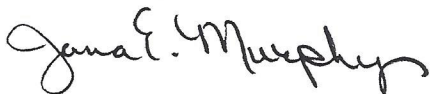
Based upon the foregoing analysis, Flambeau believes that the use of citric acid in addition to sulfuric acid for pH adjustment within the treatment process would reduce bioavailable copper to a concentration which would result in a continuance of full compliance with the WPDES permit.

With your concurrence, Flambeau proposes the following schedule for implementing the use of citric acid.

Date	Evaluation	Implementation
8/1/94	<ul style="list-style-type: none"> <li>•Additional studies of effect upon sulfide treatment;</li> <li>•Stability of citric acid in dilute sulfuric acid;</li> <li>•Locate effective feed point;</li> <li>•Chronic effect on <i>C. dubia</i></li> </ul>	
9/1/94		<ul style="list-style-type: none"> <li>•Install necessary equipment to feed citric acid;</li> <li>•Establish procedures for mixing citric acid.</li> </ul>
10/1/94	<ul style="list-style-type: none"> <li>•Process monitoring to include determination of suitable citric feed rate;</li> <li>•BOD analyses 3X/week for one month after implementation.</li> </ul>	<ul style="list-style-type: none"> <li>•Adjustment of feed rates or feed points as determined by process monitoring.</li> </ul>

If you believe that the above application of citric acid would require an approval under Wis. Stat. 144.04, please advise and we can provide additional information. Should you have any other questions or concerns regarding this information, please feel free to contact me at (715) 532-6690, extension 717. We look forward to your favorable response to our proposal.

Sincerely,



Jana E. Murphy  
 Supervisor of Environmental Affairs

Mr. Tom Bauman  
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cc: Greg Fauquier, Flambeau Mine  
Cindy Emmons, Kennecott Mineral Mines  
Bob Gothblad, WDNR  
Jim Hansen, WDNR  
Larry Lynch, WDNR  
Ken Markart, WDNR  
Bernice Dukerschein, Rusk Co.  
Al Christianson, City of Ladysmith  
Melvin Spencer, Rusk Co. Zoning  
Tom Riegel, Town of Grant  
Jim Hutchison, Foth & Van Dyke  
Steven Canton, Chadwick & Assc.  
Paul Kent, DeWitt, Porter, *et al*

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#### LITERATURE CITED

- Sprague, J.H. 1985. Factors that modify toxicity, p. 124-163. *In* G.M. Rand and S.R. Petrocolli [ed.] *Fundamentals of aquatic toxicology: methods and applications*. Hemisphere Publishing Corp., New York, N.Y.
- Winner, R.W. 1985. Bioaccumulation and toxicity of copper as affected by interactions between humic acid and water hardness. *Water Res.* 19:449-455.

Rec'd 7-11-94

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Subsidiary of Kennecott Corporation  
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(715) 532-6690  
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**Kennecott**

July 8, 1994

Mr. Tom Bauman  
Department of Natural Resources  
Bureau of Wastewater Management  
101 S. Webster Street  
P.O. Box 7921  
Madison, WI 53707

RE: Flambeau Mining Company WPDES Permit No. WI-0047376-1  
Amendment to June 23, 1994 Submittal

Dear Mr. Bauman:

Flambeau Mining Company (Flambeau) submitted to the Department the third Toxicity Reduction Evaluation (TRE) report in a letter dated June 23, 1994.

Flambeau has realized that a minor amendment must be made to Table 2 located on page 2 of the June 23 report. The changes are not substantial and do not affect Flambeau's original conclusions in the least. As you can see in the following table, minor changes were made to the Citric Acid concentration column for the test conducted during May. Please ensure this amendment is attached to the original June 23 report.

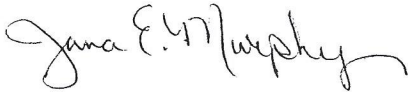
Table 2. Copper/Citric Acid Research Bioassays.

Date	Copper LC <sub>50</sub> (ppb)	Citric Acid (ppm)
May 19-22, 1994	25	3.06
May 19-22, 1994	50	8.08
June 2-4, 1994	75.2	5.50
June 2-4, 1994	>184	11.01

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If you should have any questions or concerns regarding this amendment or any previous TRE submittal, please feel free to contact me at 715-532-6690 Ext. 717.

Sincerely,



Jana E. Murphy  
Supervisor of Environmental Affairs

cc: Greg Fauquier, Flambeau  
Cindy Emmons, Kennecott Mineral Mines  
Bob Gothblad, WDNR  
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