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VIA EMAIL: lippelaw@sonic.net

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Re: Comments on City of Napa's CEQA Initial Study and Mitigated Negative Declaration: Use of Copper to Control Aquatic Weeds at the Milliken Diversion Dam and Lake Hennessey. (February 21, 2006)

Dear Thomas:

I have reviewed the above document at your request and provide my professional opinions regarding the potential environmental effects of copper applications as a best management practice (BMP) to control algae and aquatic weeds in the above mentioned water supply reservoirs, Milliken Diversion Dam and Lake Hennessey. I am an expert on inorganic chemistry in natural aquatic systems. Both my dissertation and current professional research focus upon the biogeochemical interactions of nutrients and trace metals on the primary producer community. The City of Napa intends to continue applications of copper sulfate (CuSO_4) to control the rate and magnitude of primary production in an aquatic ecosystem. In my professional opinion, the application of CuSO_4 to natural waters is an unnecessarily harmful BMP that solely provides a very short term band-aid solution to system-wide nutrient loading and eutrophication problems. The potential for negative impacts to the resident biota within the treated waters, as well as to the downstream resources, are significant and I urge that the City of Napa be encouraged to develop an Environmental Impact Report, complete with alternatives to managing the primary producer community (phytoplankton and aquatic weeds) that are less damaging to the environment. Below I explain the scientific processes upon which I base my opinion. Peer-reviewed scientific references are also provided.

"Dilution is the solution to pollution"

"Dilution is the solution to pollution" was a pollution best management practice 50 years ago, and decades of data are now available on the ecological and environmental effects of contaminants, including copper (Cu), in the environment. Rachel Carson's *Silent Spring* (1963) is the classic example of the devastating effects of toxic pollutants on ecosystems. The Negative Declaration continually asserts that the long-term impacts of copper applications will be mitigated by dilution, where concentrations in the water column return to pre-application levels on the order of days. Where does the copper go that it is removed from the water column so rapidly?

Accumulation of copper in the sediments

The cupric ion possesses a 2^+ charge, and thus has a high affinity to adsorb to negatively-charged clay particles in fresh water columns, a process known as electrostatic attraction (Stumm and Morgan 1996). Copper can also be removed from solution by adsorption or uptake by organic particles (Beck et al 2002). The concentration of free copper (Cu^{2+}) in the water column therefore rapidly decreases following applications in natural waters. This is the reason why weekly applications of copper sulfate are necessary to control the phytoplankton and aquatic weeds (primary producers) as practiced by the City of Napa. However, the copper becomes bound to organic or inorganic particles that settle to the sediment and accumulates

there. In systems where copper applications have been historically used to treat primary production rates, elevated concentrations of copper are observed in the sediments (Haughey et al 2000). Copper in the sediments is not a permanent sink of Cu^{2+} , as it can go through a series of particle desorption and adsorption processes depending upon: 1) the relative concentrations of copper in the sediments and bottom waters (diffusion) (Gee and Bruland 2002), 2) the pH of the sediments and/or overlying waters (Stumm and Morgan 1996), and 3) sediment resuspension events (e.g. storms, floods and other physical disturbances) that mobilize copper enriched surface sediments and transport them downstream (Haughey et al 2000), potentially increasing the water concentrations of free copper. The localized and surrounding environmental and ecological effects of copper applications in reservoirs around the world have been documented. One peer-reviewed example is Van Hullebusch et al 2003 (*Copper accumulation in a reservoir ecosystem following copper sulfate treatment*), who studied a reservoir in the center of France following copper sulfate treatments. The authors estimated 17% of the copper applied to the reservoir was exported downstream within 70 days following applications. The predictable bioaccumulation of Cu by resident moss communities allowed the researchers to track the transport of Cu to the stream system below, with Cu concentrations in the moss decreasing with distance from the reservoir outlet. Other relevant references documenting the accumulation of copper in the sediments of systems chronically treated with CuSO_4 include Elder and Horne 1978, Hanson and Stefan 1984, and many others.

Copper Toxicity

The obvious toxic effects of copper on primary producer communities are the reason that copper sulfate application is such an effective herbicide to control algal growth in natural waters. However, the primary producer community (particularly the phytoplankton, i.e. floating single-celled organisms) is the base of the food chain. Changes in this community structure and dynamics will resonate upward through the trophic levels. Copper sulfate applications can result in a shift of the primary producer community assemblages and create a stressed environment selecting for more tolerant species to survive in the treated waters. Tolerant phytoplankton can grow at faster rates in more inclement conditions and may not be the preferred food source for the secondary grazing community. Thus copper treatment can, in theory, exacerbate the eutrophic conditions they are intended to alleviate by adversely impacting all levels of the food chain.

Bioaccumulation of Cu up the food chain is a significant potential impact of CuSO_4 treatments. Benthic and bottom dwelling organisms can be impacted if the sediment and/or overlying water copper concentrations exceed the toxic threshold of the resident organisms. Harrahy and Clements 1997 (*Toxicity and bioaccumulation of a mixture of heavy metals in chironomus tentans (Diptera:Chironomidae) in synthetic sediment*) exposed a benthic invertebrate species (chironomids) to sediments with elevated levels of trace metals for 14 days and found that bioaccumulation increased with respect to Cu and the concentrations of metals in chironomids were significantly correlated with exposure time in the uptake phases. There is a high potential for bioaccumulation of Cu in invertebrates at the Milliken and Hennessy reservoirs. There is a significant potential ecological effect to the higher trophic organisms, particularly fish species, as benthic organisms are the primary source of food for trout and other larger fish species.

Elevated copper in the food supply can be toxic to fish as documented by numerous scientific publications including:

- Berntssen et al 1999 (*Toxic levels of dietary copper in Atlantic salmon (Salmo salar L.) parr*) exposed young salmon to elevated Cu treated food sources for 4 weeks, documenting increased liver and intestinal concentrations in the exposed salmon

in comparison to the control subjects. The authors conclude “Cu-exposed Atlantic salmon parr (young) showed an onset of adaptive responses (increase of intestinal PCNA, apoptosis, and MT levels) at concentrations of 35 and 700 mg Cu kg⁻¹ dry feed, indicating that stress responses are induced at these dietary Cu concentrations.”

- Handy 1993 (*The effect of acute exposure to dietary Cd and Cu on organ toxicant concentrations in rainbow trout, Oncorhynchus mykiss*) fed rainbow trout Cd and Cu enriched food for 28 days and found Cu toxicity did occur. The authors suggest “that fish will ingest heavily polluted food until toxicity occurs. Wild fish may therefore be at risk from contamination via the diet after pollution incidents.”

Application rates and existing water quality data

Microsoft excel files of limited water sampling data were provided and reviewed in addition to the material provided in the Negative Declaration document. The existing water quality monitoring data is too limited spatially and temporally to assess if the historic applications of CuSO₄ have had a significant effect on the surrounding environment and ecology. Based on the limited water quality data provided, I have the following comments:

1. The City of Napa’s target Cu concentration in the surface waters during applications is presented as a range of 0.12 to 0.5 ppm. These surface water concentrations are an order of magnitude higher than the Toxic Reference Value (TRV) calculated by the authors of the Negative Declaration (Appendix E) for fish (0.013 ppm).
2. The application instructions for EarthTEC provided in the Negative Declaration (Appendix C) state that 0.1 ppm of free copper is required for treatment of the phytoplankton species targeted in the subject reservoirs. The City of Napa is requesting to apply amounts exceeding the manufacturer’s recommended dosages.
3. The analytical detection limits for sampling at Milliken is reported in the Excel data file to be 0.05 ppm. These analytical detection limits are much too high to properly monitor the persistence or the potential risk of Cu²⁺ in the water column following treatment and in between treatments. As stated above, the TRV for fish provided by the applicant is 0.013 ppm. Beck et al (2002) documented that algae/phytoplankton growth rates were significantly inhibited when Cu²⁺ was 0.00065 ppm in a controlled microcosm experiment, three orders of magnitude lower than the targeted concentrations provided by the applicant. The existing analytical techniques are clearly not able to detect Cu at concentrations appropriate for proper monitoring.
4. The stability of copper bound to sediments is highly dependant upon the pH of the system, and a lower pH will facilitate a greater dissolution of Cu²⁺ into the water column (Stumm and Morgan 1996). The water quality data provided from Milliken Reservoir documents pH values below 7 in the surface waters. No pH data from the deep waters of Milliken Reservoir were provided, but pH will typically decrease with increasing depth in eutrophic waters. This effect is documented in the vertical profile water quality data provided from Hennessey Reservoir. A lower pH in the bottom waters suggests that solely monitoring surface waters for copper does not provide a complete evaluation of the persistence of CU²⁺ following treatment.
5. To my knowledge, there has not been any sediment monitoring for Cu concentrations where the chronic applications of Cu have been accumulating. Vertical sediment cores (3-4 ft in depth) should be extracted from 3-4 locations within each of the reservoirs, with at least one location located above suspected CuSO₄ treatment influences. Sub-samples of the cores should be extracted every 0.5’ and submitted to an analytical laboratory for copper analysis. Efforts should be made to complete

cores deep enough to extend to the sediments representing pre-treatment conditions, thus providing a baseline sediment copper concentration expected in these systems and supplementing upstream sampling results.

6. Additionally, to my knowledge no surface water and sediment sampling has been conducted along a distance gradient downstream from the reservoirs to evaluate any persistent downstream effects of historic applications of copper.
7. To my knowledge, no biotic assessments have been conducted to systematically evaluate if ecological effects from CuSO_4 can be detected.

Water resource managers around the country have been developing alternative approaches to reducing eutrophication in fresh water reservoirs and lakes. Long-term source control efforts to reduce nutrient sources can be combined with aeration, circulation and innovative water exchange techniques. Variations in the temporal and spatial locations of water intake and water releases from reservoirs have also been implemented. Many opportunities exist to obtain effective alternatives to copper sulfate treatments that will not have the same potential ecological and environmental impacts.

Sincerely,

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