Subject: Draft Irrigation System and Aquatic Weed Control General Permit

Prepared for: State of Washington, Department of Ecology (WADOE)

Executive Summary

We appreciate the opportunity to review and comment on the prepared draft entitled: *Irrigation System Aquatic Weed Control General Permit*. This document provides justification to support alteration of two sections of the permit; 1) differentiation between copper sulfate from complexed or chelated copper formulations, 2) corresponding alteration of discharge limits and monitoring requirements.

Overview

Permitted aquatic pesticide discharges of treated water at the point of compliance are limited to specific concentrations. These concentrations are based on a risk assessment to ensure negligible risks to humans and the environment. The current General Permit states a discharge limit of 25 μ g/L of copper (dissolved). This listing is too generic to appropriately represent chelated or complexed forms of copper and how they behave in the aquatic environment following application to surface waters. The concentration also seems to be based on toxicity assessments with copper sulfate pentahydrate and not representative of other forms of copper which act very differently and may be in completely different (and better) toxicity categories.

Differentiation of chelated copper from copper sulfate

USEPA (2009) has designated Pesticide Chemical (PC) codes for different active ingredients and those actives must be listed on corresponding pesticide labels. USEPA has numerous different PC codes for different copper compounds such as copper sulfate pentahydrate (024401) and copper ethanolamine complex (024409). Similarly, different Chemical Abstracts Service (CAS) numbers exist for those same chemicals, 7758-99-8 and 14215-52-2, respectively.

The registrant of a specific copper product is required to provide specific environmental data, per the USEPA data call-in, to satisfy the registration applicability. These data are required to match the listed active copper chemical compound (and not just copper sulfate). USEPA treats copper compounds differently in terms of toxicity and labeling. These USEPA registration review requirements for copper compounds support the request that separate assessments and restrictions should be considered in the General Permit in the State of Washington.

Other state regulatory agencies have also distinguished copper into chelated/complexed and copper sulfate/blue stone (Virginia Cooperative Extension 2009) and conducted toxicity assessments based on the chelated formulation and not just reliant on copper sulfate data (Riley and Finlayson 2004).

It is also important to note, the WADOE has come to a similar conclusion per their environmental impact assessment on copper stating that: "All formulations of commercial copper products may not be similar in toxicity on an elemental copper equivalence basis". Further, WADOE assessment highlights some large differences in ecotoxicity among copper formulations stating "...while the commercial coppercomplexes have a fairly low acute toxicity to most fish and aquatic invertebrates" and "Komeen® and Nautique™ may be moderately toxic to practically non-toxic" where copper sulfate would be categorized as highly toxic. The differences in ecotoxicity are further reinforced in this statement "Copper ethylenediamine products like Komeen® and Nautique™ are not highly toxic to most species of fish."

Peer-reviewed literature supports the findings of WADOE. In one example, chelated copper (i.e. Nautique), showed significantly more favorable ecotoxicity profile (over an order of magnitude less toxic) on three species of juvenile freshwater mussels (Popp et al. 2018). The same formulation was also two orders of magnitude less toxic than copper sulfate to juvenile brook trout and fathead minnows (Wagner et al 2017). Additionally, significant differences in toxicity to Ceriodaphnia dubia and Pimephales promelas was shown with multiple chelated copper formulations compared with copper sulfate (Murray-Gulde et al. 2002). The stability of the chelated form has also been measured in the water-column (Masuda and Boyd 1993). Upon request from WADOE, we can provide additional data about chelated coppers related to enhanced efficacy, sorption, labeled approved use sites and application types, etc.

First permit alteration proposed

S4. THE APPLICATION OF PRODUCTS AND DISCHARGE LIMITS B. Authorized Discharges (page 18 and 19, text and table 2)

With the scientific evidence differentiating chelated copper from copper sulfate, we recommend WADOE impose separate discharge limits for copper depending on its specific active ingredient, as is the case with all other active ingredients included in this General Permit.

Specifically, the scientific data supports an authorized discharge limit of $50 \mu g/L$ of copper from a chelated formulation (dissolved) and a discharge limit of 25 $\mu g/L$ of copper (dissolved) for copper sulfate applications (as currently proposed in the General Permit).

Second permit alteration proposed

S5. MONITORING REQUIREMENTS (page 29)

- **B.** Special Situations
- 2. Reduced monitoring for a specific pesticide
- b. Treatment events when copper is applied i
- b) Permittees must have the results of water hardness analysis for one (1) full permit cycle of monitoring. (A full permit cycle is five (5) years.)
- c) All water hardness results are > 50 mg/l.

The draft General Permit reads, "to be eligible for reduced monitoring for copper sulfate use, permittees must have 5 years of water hardness results that are all over > 50 mg/l". In addition to the afore mentioned data demonstrating lower toxicity of chelated copper products, it is also documented in low alkalinity and low hardness water (Straus and Tucker 1993) compared to copper sulfate.

The data supports a less stringent hardness level and monitoring period for when chelated copper is used compared with copper sulfate. We propose additional language stating, if chelated copper is being used, water hardness results for one year are needed and those results need to be > 25mg CaCO₃/L.

References

- Masuda, K., C..E Boyd (1993) Comparative evaluation of the solubility and algal toxicity of copper sulfate and chelated copper. Aquaculture 117:287-302.
- Murray-Gulde, C. L., J. E. Heatley, A. L. Schwartzman and J. H. Rodgers Jr. 2002. Algicidal effectiveness of Clearigate, Cutrine-Plus, and Copper Sulfate and margins of safety associated with their use. Environ. Contam. Toxicol. 43:19-27.
- Popp, A., Cope, W. G., McGregor, M. A., Kwak, T. J., Augspurger, T., Levine, J. F., & Koch, L. 2018. A Comparison of the chemical sensitivities between in vitro and in vivo propagated juvenile freshwater mussels:

 Implications for standard toxicity testing. Environmental Toxicology and Chemistry, 37(12), 3077–3085
- Riley and Finlayson. 2004. Acute Toxicities of Herbicides Used To Control Water Hyacinth And Brazilian Elodea On Larval Delta Smelt And Sacramento Splittail By. California Department of Fish and Game. Office Of Spill Prevention and Response Administrative Report 04-003
- Stauber, J. L. and T. M. Florence (1987) Mechanism of toxicity of ionic copper and copper complexes to algae. Marine Bio. 94:511-519.
- Straus, D.L., C.S. Tucker (1993) Acute toxicity of copper sulfate and chelated copper to channel catfish Ictalarus punctatus. J World Aquacult Soc 24(3):390-395.
- United States Environmental Protection Agency (2009) Reregistration Eligibility Decision for Coppers. 738-R-09-304. 176 p.
- Virginia Cooperative Extension. 2009. Pesticides and Aquatic Animals: A Guide to Reducing Impacts on Aquatic Systems. Publication 420-013. http://hdl.handle.net/10919/48060
- WA DOE Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides volume 6: copper
- Wagner JL, Townsend AK, Velzis AE, Paul EA. 2017. Temperature and toxicity of the copper herbicide (Nautique) to freshwater fish in field and laboratory trials. Cogent Environmental Science 3:1339386