The Impacts of Copper use in Lily Bulb Cultivation on Juvenile Coho Salmon in the Smith River Plain

Ethan Villalta[2], Logan Wolfe[1,2], Peter Bright[1], Matthew Hurst[1]

[1] *Department of Chemistry, Cal Poly Humboldt, Arcata CA 95521*

[2] *Department of Geology, Cal Poly Humboldt, Arcata CA 95521*

Abstract

Copper is used as a fungicide in the lily bulb industry and is water soluble. Previous laboratory studies have shown that acute copper toxicity in juvenile salmonids can occur at extremely low copper concentrations. These low levels of copper induce predatory avoidance behavior and the loss of olfactory sensory function, which lowers the survival rates of the juvenile salmonids. The objective of this study was to provide scientific information to determine whether the copper levels in the Smith River Plain are toxic to juvenile Coho salmon. Electrochemical techniques were used to measure the copper bioavailability (Cu^{2+}) in the site-specific conditions found in the Smith River Plain. Dissolved copper (dCu), hardness, dissolved organic carbon (DOC), and other water quality parameters were also measured to determine how lily bulb cultivation is altering the water chemistry in fish habitat. The study found that dCu levels were higher downstream of agricultural fields when compared to upstream measurements. However, DOC and hardness also increased, and the addition of these constituents lowered the bioavailability of copper to levels that were below the threshold that induces a toxic response in juvenile salmonids. The findings will be shared with the lily bulb farmers in effort to guide best practices in land management which will lead to improved water quality in the Smith River Plain.

Background

The lily bulb industry in the Smith River Plain employs hundreds of workers and contributes 5-7 million dollars to the economy of Del Norte County, California. It is estimated that 95% of all Easter lilies in the world are grown in this area. Water quality is an important component of fish habitat and must be considered in order to maximize restoration efforts and economic cost-benefit balance within this system (Fig. 1). The Smith River region is the ancestral lands of the Tolowa Dee-ni' Nation, who are the original stewards of these lands. These waterways are also important habitat and spawning and rearing grounds for the federally threatened Coho salmon, which are essential to the life and nutrient cycling of the river, are an integral part of the culture and tradition of the Tolowa Dee-ni' Nation.

Smith River and Coho Salmon

The waterways in the Smith River Plain of Del Norte County, California consist of a network of streams and tributaries that dissect agricultural land used for Easter lily bulb cultivation (Fig. 4). The industry is highly dependent upon pesticides to combat nematodes and fungi. The primary fungicide used is a copper hydroxide salt, which is sprayed throughout the spring when foliage is aboveground. The copper is water soluble and is transported to the waterways during rain events. With respect to Coho salmon, it has been shown that they are very sensitive to elevated dissolved copper (dCu) levels (Fig. 3). Three successive studies have measured elevated levels of dCu in the tributaries below the agricultural fields in the Smith River Plain and the dCu levels are more than a magnitude higher than those shown in laboratory studies to cause salmonids to experience predator avoidance behavior and loss of olfactory sensory function (Sandahl *et al.*, 2007; McIntyre *et al.*, 2008). McIntyre *et al.* (2008) demonstrated that the presence of dissolved organic carbon (DOC) in sufficient quantities in a waterway has the potential to mitigate the toxic effects of dCu on juvenile Coho salmon. The amount of DOC in the runoff decreases the bioavailability of the copper by changing the copper speciation or form. Pesticide and copper use in the lily bulb industry over the last five decades and its potential effects on the water quality in the Smith River Plain raises many concerns.

Figure 1: Juvenile Coho salmon (left) and Easter lilies in full bloom in the Smith River Plain.

References

McIntyre, J.K., D.H. Baldwin, J.P. Meador, and N.L. Scholz. 2008. Chemosensory deprivation in juvenile coho salmon exposed to dissolved copper under varying water chemistry conditions. Environmental Science and Technology 42:1352-1358.

Sandahl, J. F., D. H. Baldwin, J. J. Jenkins, and N. L. Scholz. 2007. A sensory system at the interface between urban stormwater runoff and salmon survival. Environmental Science and Technology 41:2998–3004.

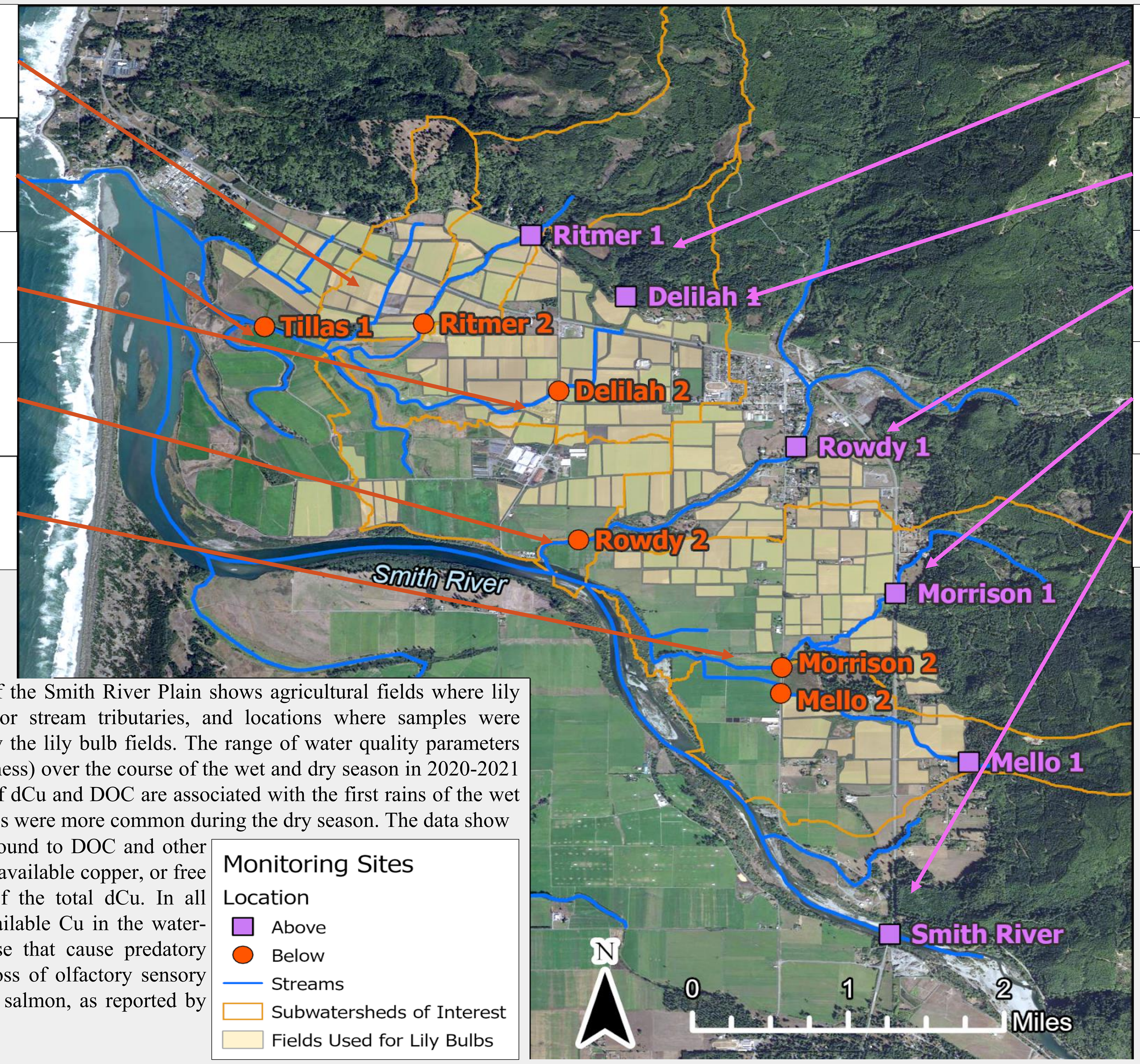
dCu: 0.37 - 1.41 µg/L
Cu^{2+}: 0.2 - 3.2 (x 10^{-14}) M
DOC: 0.79 - 5.71 mg/L
Hardness: 20 - 38 mg/L

dCu: 0.44 – 2.77 µg/L
Cu^{2+}: 0.2 – 3.2 (x 10^{-14}) M
DOC: 3.41 – 12.9 mg/L
Hardness: 20 – 1090 mg/L

dCu: 1.10 - 6.86µg/L
Cu^{2+}: 3.0 - 5.3 (x 10^{-14}) M
DOC: 1.01 - 4.39 mg/L
Hardness: 14 – 73 mg/L

dCu: 0.15 - 0.38 µg/L
Cu^{2+}: 0.7 - 1.7 (x 10^{-14}) M
DOC: 0.49 - 3.72 mg/L
Hardness: 29 - 54mg/L

dCu: 0.28 - 0.68 µg/L
Cu^{2+}: 1.1 - 1.4 (x 10^{-14}) M
DOC: 0.97 - 2.42 mg/L
Hardness: 17 - 22mg/L



dCu: 0.16 - 0.80 µg/L
Cu^{2+}: 0.3 - 4.5 (x 10^{-14}) M
DOC: 0.66 - 5.17 mg/L
Hardness: 15 - 23 mg/L

dCu: 0.11 - 0.31 µg/L
Cu^{2+}: 0.1 - 0.6 (x 10^{-14}) M
DOC: 0.51 - 2.30 mg/L
Hardness: 10 - 16 mg/L

dCu: 0.13 - 0.32 µg/L
Cu^{2+}: 0.2 - 3.8 (x 10^{-14}) M
DOC: 0.41 - 5.31 mg/L
Hardness: 28 - 52 mg/L

dCu: 0.18 - 0.32 µg/L
Cu^{2+}: 0.1 - 1.4 (x 10^{-14}) M
DOC: 0.80 - 2.01 mg/L
Hardness: 18 - 23 mg/L

dCu: 0.13 - 0.38 µg/L
Cu^{2+}: 1.5-2.2 (x 10^{-14}) M
DOC: 0.52 - 4.09 mg/L
Hardness: 48 - 64 mg/L

Figure 2: The site map of the Smith River Plain shows agricultural fields where lily bulbs are cultivated, major stream tributaries, and locations where samples were collected above and below the lily bulb fields. The range of water quality parameters (dCu, Cu , DOC and hardness) over the course of the wet and dry season in 2020-2021 are listed. Higher values of dCu and DOC are associated with the first rains of the wet season and the lower values were more common during the dry season. The data show that the dCu is strongly bound to DOC and other ligands, decreasing the bioavailable copper, or free Cu^{2+}, to just a fraction of the total dCu. In all cases, the levels of bioavailable Cu in the waterways are lower than those that cause predatory avoidance behavior and loss of olfactory sensory function in juvenile Coho salmon, as reported by McIntyre et al. (2008).

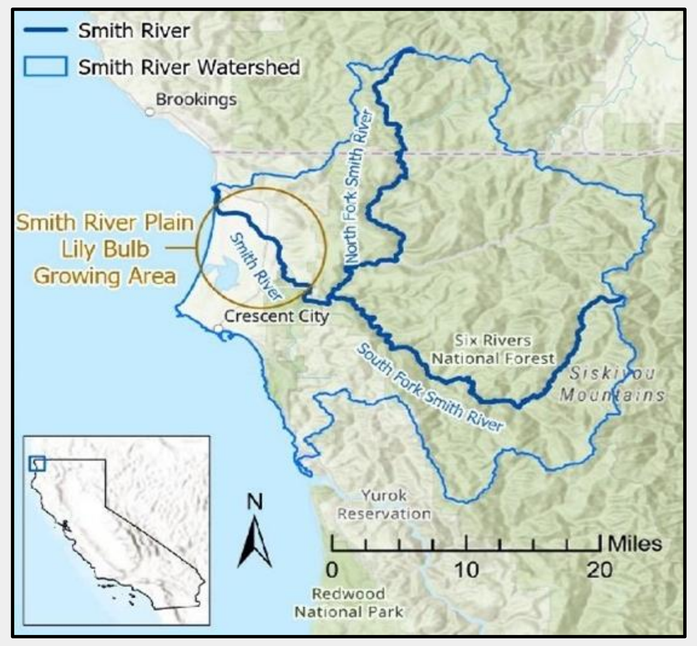


Figure 4: Site Map of the Smith River watershed and the Smith River Plain.

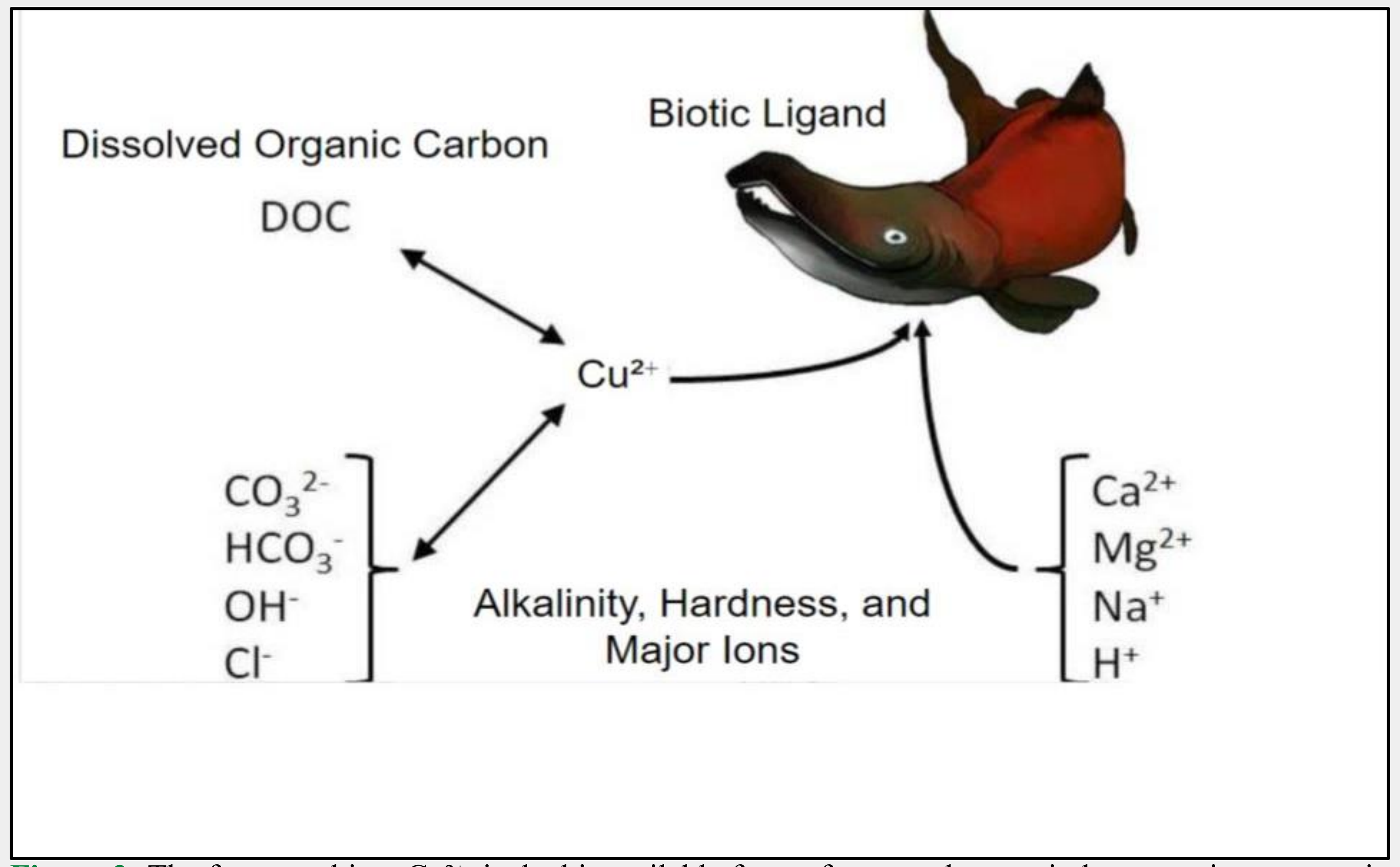


Figure 3: The free metal ion, Cu^{2+}, is the bioavailable form of copper that can induce a toxic response in many aquatic species. This form of copper can be actively bound to other molecules (i.e., ligands) in the environment. This sets up a competition between natural ligands found in the environment (estimated in this study using hardness, alkalinity, and DOC) with the biotic ligands in the organism. The greater the concentration of natural ligands and their affinity for Cu^{2+}, the less bioavailable the copper will be. The DOC can bind copper very strongly and helps protect sensitive species from it toxic effects.

Results

The copper bioavailability in water samples collected in November 2020, March and May (2021) was measured using competitive ligand equilibration – adsorptive cathodic stripping voltammetry (CLE-AdCSV). It was determined that 99.9% of the dCu was strongly bound to natural ligands. The free Cu^{2+} concentration was on the order of 10^{-14} M, which was more than an order of magnitude lower than the threshold that causes a toxic response in juvenile Coho salmon (Fig. 2). Although the added copper from lily bulb cultivation does not appear to raise concern with respect to copper toxicity, the agricultural practices are altering the water quality in the stream tributaries of the Smith River Plain.

Conclusion

The Smith River watershed is one of the most pristine rivers in the continental United States, except for the waterways dissecting the agricultural fields in the Smith River Plain. The study has shown the effects of Easter lily bulb cultivation on the water quality in the stream tributaries. It provides the Tolowa Dee-ni' Nation, government agencies, and lily bulb growers a water quality baseline that defines the current health of their waterways. These stakeholders are all working to improve the environmental conditions in the region and additional monitoring of dCu and other pesticides is needed to show progress and benefits from changes in land management practices.

Acknowledgements

This work was supported by the California State University - Agricultural Research Institute (CSU-ARI) and the Tolowa Dee Ni` Nation. We would like to thank the staff at Cal Poly Humboldt and UC Santa Cruz for providing technical support during the fieldwork preparation and chemical analysis phases of the project.