# Starry Stonewort Pilot Treatment

Tully Lake Property Owners Association Meeting



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### Agenda

- Brief Background on SSW
- Goal of Pilot Project
- Copper Comparison
- Environmental Safety
- Case Study Info
- Proposed Pilot Site Details & Water Uses
- Question & Answer
- Proposed Next Steps

### Starry Stonewort (*Nitellopsis obtusa*)

- Macro algae (appears similar to some vascular aquatic plants)
- Whorls of four to six branchlets with blunt tips
- Star shaped bulbils produced at nodes and on rhizoides
- Reaches 2 meters in length
- In North America SSW reproduces asexually

### Impacts

- Forms dense mats of vegetation
- Crowds and outcompetes native aquatic plant species
- Can produce odors
- Clogs areas used for swimming, boating, angling
- End of season decomposition consumes oxygen





### Risk of Spread

- Easily fragments and spreads to new locations via wind and water currents
- Easily transported on watercraft and gear
- Bulbils easily spread and persist in sediments for years

### Pilot Project Goal

Evaluate efficacy of Komeen Descend on SSW in Tully Lake

### **Benefits**:

- Allows access and usability of water
- Limits spread and impacts of this invasive species

### **Risk-based Analysis**

#### Copper

- Essential nutrient for life
  - Part of enzymes/proteins
  - Suggested Daily Intake (2mg)
- 1,300 µg/L is MCL in drinking water
- 26<sup>th</sup> most abundant element in Earths Crust
- Does not bio-accumulate
- Transfers to less available sediment forms through time
- No swimming/ drinking/ irrigation restrictions on USEPA approved labels (such as Komeen Descend)

Copper is an essential nutrient that is incorporated into a number of metalloenzymes: (over 30 enzymes known; Flemming and Trevors 1989)

- cytochrome c oxidase
- dopamine β-monooxygenase
- superoxide dismutase,
- ferroxidases,
- monoamine oxidase,

Given the role copper plays as an essential element to the human body, its ubiquitous nature in food and drinking water, the long-standing tolerance exemptions for the pesticidal use of copper on growing crops, as well as on meat, milk, poultry, eggs, fish, shellfish, and irrigated crops, and the lack of systemic toxicity resulting from copper, a quantitative acute toxicity assessment was not conducted for acute dietary, dermal, oral or inhalation exposures.

#### 1. Background on Copper

Copper is a naturally-occurring, ubiquitous element in the environment. Copper is found in water, air, and occurs naturally in various foods including organ meats, seafood, beans, nuts, and whole grains. In most foods, copper is bound to macromolecules rather than as a free ion. For many animals, copper is essential for the homeostasis of life. The role of copper in maintaining normal health both in humans and animals has been recognized for many years. Copper is an essential cofactor for approximately a dozen copper-binding proteins for the proper regulation of copper homeostasis in humans. A deficiency of copper or a defect in coppercarrying proteins may result in symptoms such as anemia, defective blood vessel development, growth retardation, a compromised immune function or connective tissue symptoms.

USEPA reregistration eligibility

document copper. Page 26

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## Copper Modes of Action on Algae

- Disrupt respiration; ATP production; electron transport chain (Jursinic and Stemler 1983)
- Combine with glutathione (GSH) prevents cell division (Stauber and Florence 1997)
- Inhibits enzyme catalase and others, free radical susceptibility (Stauber and Florence 1997)
- Pigment synthesis inhibition
- Interfere with cell permeability and binding of essential elements (Sunda and Huntsman 1983)

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### **Copper sulfate selects for tough algae**

- Shift to copper tolerant Aphanizomenon in Femont Lake
  - Hanson, J.M. & Stefan, H.G. 1984. Side Effects of 58 years of Copper Sulfate Treatment of the Fremont Lakes, Minnesota. Water Resource Bulletin 20(6):889-899
- Shift to copper tolerant Phormidium in Lake Mathews, CA
  - Izaguirre, G. (1992). A copper-tolerant Phormidium species from Lake Mathews, California, that produces. 2-methylisoborneol and geosmin. Wat. Sci. Tech., 25(2), 217–224.
- Spontaneous mutation in *Microcystis aeruginosa* to Cu++
  - Diminished fitness, smaller
    - García-Villada, L.; Rico, M.; Altamirano, M.A.; Sánchez-Martín, L.; López-Rodas, V.; Costas, E. Occurrence of copper resistant mutants in the toxic cyanobacteria microcystis aeruginosa: Characterisation and future implications in the use of copper sulphate as algaecide. Water Res. 2004, 38, 2207–2213

Long-term effects of copper on the structure of freshwater periphyton communities and their tolerance to copper, zinc, nickel and silver

Diana Soldo, Renata Behra \*





## Biotic ligand model USEPA (2003)



### Formulation makes a big difference

- Chelating agents
  - Stability, corrosivity, water chemistry
  - Degree of interaction with water chemistry
- Toxicity to targets
  - Lipid soluble can diffuse through membrane
    - Stauber and Florence 1987
  - Membranes impermeable to charged/polar species
    - Sunda 1989
  - EDA
    - Miscible with polar substances
    - Solubilize proteins
    - Bidentate chelating ligand
    - Allows penetration through algae wall/membranes

Biological membranes are virtually impermeable to charged or polar species, and free metal ions are usually taken up into cells by binding to specialized transport ligands associated with the cell membrane (Sunda 1988, 1989). This transport follows in general the Michaelis-Menten kinetics for facilitated or active transport, as has been observed experimentally in phytoplankton (Anderson and Morel 1982, Sunda and Huntsman 1985, 1986).



HO-Cú-

Fig. 1. Effect of pH on concentrations of  $Cu^{2+}$ , inorganic copper complexes, trichanolamine Cu complexes (TEA<sup>-</sup> Cu complexes), and total dissolved copper ( $Cu_D$ ). Conditions: aqueous solution; 25°C; total alkalinity, 100 mg  $|^{-1}$ ; sulface, 2.5 mg  $|^{-1}$ ; tricthanolamine, 0.000074 M.

Lipid-

soluble complexes can diffuse directly through the membrane into the cell, where both copper and the ligand may exert separate toxicity.

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## Chelated copper safety

- Komeen
  - Delta smelt
  - LC<sub>50</sub> 1.4 mg Cu/L
- Komeen/Nautique
  - Bluegill/bass/shiner/perch
  - LC<sub>50</sub> 5.4-496 ppm Cu
- Nautique
  - 96 hr LC<sub>50</sub> > 20 mg Cu/L
  - Trout, fathead minnow
  - Wagner et al. 2017

ACUTE TOXICITIES OF HERBICIDES USED TO CONTROL. WATER HYACINTH AND BRAZILIAN ELODEA ON LARVAL. DELTA SMELT AND SACRAMENTO SPLITTAIL by. Frank *Riley and Sandra Finlayson*. California Department of Fish and Game. Aquatic Toxicology Laboratory

catfish (LC50 = 0.064 ppm Cu for Cutrine®) and ornamental carp like koi and goldfish. Based on the available evidence Komeen® and Nautique<sup>TM</sup> may be moderately toxic to practically non- toxic (LC50 = ~0.1 ppm on salmonids and LC50 = 5.4 to ~500 ppm on most other species of fish) while K-Tea<sup>TM</sup>, Cutrine®, Copper Control® Clearigate® and Captain<sup>TM</sup> are generally more toxic to the sensitive species but highly toxic to moderately toxic to other species (LC50 = ~0.01 to ~0.03 ppm on salmonids, striped bass and channel catfish, and 0.2 to ~6 ppm Cu on most other species of fish). In soft, low alkalinity water (<50 ppm CaCO<sub>2</sub>) the toxicity of the commercial conper-complexes may be high

> WA DOE Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides volume 6: copper



Wagner et al. 2017



Nautique™ was significantly less toxic to brook trout and fathead minnows than the other formulations (Table 3). With time and concentration held constant, the percentage of brook trout that died

#### **Copper Sulfate**

- Copper sulfate is <u>not</u> readily passed to internal toxic sites of action and can desorb from external binding sites (Kadukova and Vircikova 2005; Flemming and Trevors 1989)
- Copper sulfate is greatly impacted by water chemistries in terms of algaecidal availability (USEPA 2003)
- Environmental conditions like colder temperatures can decrease ability of copper to reach critical toxic sites of action
- Copper sulfate cannot overcome numerous algae defense mechanisms
- Adaption to ionic copper (copper sulfate source) has been documented with algae leading to decreased toxicological response

#### **Chelated copper**

- Chelated copper provides increased infusion (passive transport not facilitated active) of copper into the target algae biomass to act on multiple internal modes of action and elicit greater algaecide activity
  - Masuda and Boyd 1993; Stauber and Florence 1987
- Chelated copper provides effectiveness independent of environmental conditions, growth characteristics and water chemistries
- Chelated copper can increase the stability of copper in the water column by decreasing the potential for precipitation with inorganic compounds
  - Masuda and Boyd 1993; Murray-Gulde et al. 2002
- Chelated copper products can have a greater affinity for the target species and control at lower treatment copper concentrations
- Chelated copper has documented decreased toxicity to non-target fish/invertebrate species

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### Sediment fate

- Background sediment copper concentrations (10-50mg/kg average)
  - Flemming and Trevors 1989, Wilis and Bishop 2016
- Lithic biogeochemical cycle
- Rapid sediment partitioning and transfer after controls algae (ultimate fate)
  - - Gallagher et al. 2005; Nor 1987; Button and Hostetter 1977, Liu et al 2006
- Residual copper from algaecides and herbicides can transform to less bioavailable forms through time as well as dilute by natural mixing and sediment accretion
  - - Jones *et al*. 2008
- Adverse effect require >197 mg Cu/kg by the National Oceanic and Atmospheric Administration's screening quick reference tables or SQuiRTs (SQuiRTs 1999)
  - Difficult to attain with any algaecide treatment program allowed

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### Gallagher et. al. 2005 (JAPM)

 No sediment toxicity found after Komeen applications



Figure 3. Response of *H. azteca* to ten-day Komeen®-amended sediment exposure. The "control" represents un-amended Lake Murray Marina sediment.

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Based on accumulation in top 5 cm (and no accretion), takes >65 applications (decades of treatments) at 1mg Cu/L (max label rate) to go from 16.3 to 180mg/kg



## Former Technology

Improved spatial targeting and depth performance





### **Komeen**\* LOOKING FORWARD SEPRO



### Komeen formulation works on SSW

#### **Publications**

- Pokrzywinski, K, WM Bishop, C Grasso, K Volk, and K Getsinger. 2021. Chemical Management Strategies for Starry Stonewort: A Mesocosm Study. USACE Report Number: ERDC/EL TR-21-10 <u>http://dx.doi.org/10.21079/11681/42040</u>
- Glisson WJ, R Contreras-Rangel, WM Bishop, DJ Larkin. 2022. Laboratory evaluation of copper-based algaecides for control of the invasive macroalga starry stonewort (*Nitellopsis obtusa*). Management of Biological Invasions. 13 (2): 303-325
- <u>https://doi.org/10.3391/mbi.2022.13.2.04</u>



Figure 5. Bulbil viability 24 hours after harvesting. In A, representative TTC assay images. In B, bars represent the average rank 0 to 3, where lower values indicate white, dead bulbils and higher values indicate pink, active/viable bulbils (B inset). Error bars represent the SEM.

### And can kill bulbils..

Figure 4. Biomass changes 6 DAT for both mesocosm trials combined. Bars represent the average wet weight (A) and dry weight (B) for all tested mesocosms. Error bars represent the SEM of both trials combined. Statistical significance is denoted by asterisks where \*; p < 0.05.







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# MicroCRYSTAL<sub>IM</sub> Technology

- Benefits of both liquids and pellets •
  - Ease of application of a liquid, though targeted delivery to the plant ٠

**MicroCRYSTAL** 

- Avoid complications with granules ٠
- Dust clumps, moisture content, coverage, sink into sediment •
- More efficiency out of the product, less offsite movement •
- Sprayable, yet precision release liquid applied



### LOOKING FORWARD SEPRO



### Komeen<sup>®</sup> Descend **Aquatic Herbicide**





#### Starry Stonewort algaecide treatments on Medicine Lake

Case Study - Plymouth, MN

The Problem

uth, MN) in 2018. The infestation of





#### Case Study - Plymouth, MN

NDNB staff along with Three Bive



SSWBIO1	Komeen Descend	194.15	9.58	4.70	95.07	97.54
SSWBIO2	Komeen Descend	189.51	29.79	3.39	84.28	9821
SSWBIO4	Hydrothdi/ copper sulfate	374.31	77.79	63.12	79.22	8314
SSWBIOS	Hydrothal/ opper suitate	217,28	90.84	98.92	58.19	54.47



Project Overview ocation: Medicine Lake MN

oject Objective: Evaluate !









- 1. Novel chelated copper microcrystal formulation
  - Sprayable, Ease of application of a liquid
- 2. Benefits of both liquids and pellets
  - Targeted delivery and control

### 3. More efficiency

Less offsite movement



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# Komeen<sup>®</sup> Descend

### 1189.225



For use in still or flowing wester it a including, golf course, ornamental, fish, and fire ponds;

No Water Use Restrictions for:

- Swimming
- Fishing
- Boating
- Recreation





Pre







Copper 30x rest of pond at 30 min after treatment OOKING FORWARD





### Medicine Lake, Hennepin County

- SSW infested lake
- Treatment Date: 8/11/2023
- 2 treatment areas: 5+ acre sites, adjacent and separated by bulrush
- Treatment Area A: Komeen Descend
- Treatment Area B: CuSo4/Hydrothol 191







### **Biomass Sampling Results**

Sample ID	Chomical	Bie	omass (gran	ns)	% Reduction After	% Reduction After 6
	Chemical	8/7/2023	8/24/2023	9/21/2023	2 Weeks	Weeks
SSWBIO1	Komeen Descend	194.15	9.58	4.78	95.07	97.54
SSWBIO2	Komeen Descend	189.51	29.79	3.39	84.28	98.21
SSWBIO4	Copper Sulfate/Hydrothol	374.31	77.79	63.12	79.22	83.14
SSWBIO6	Copper Sulfate/Hydrothol	217.28	90.84	98.92	58.19	54.47







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# Komeen<sup>®</sup> Descend

Aquatic Herbicide Field Observations – sago pondweed 4 WAT





### Potential Treatment Area

St. Charles Bay

1.5 acre treatment area

Significantly infested area

Access to bay is limited

Avoids NYSDEC Freshwater Wetland zone or check zone



NYSDEC Dilution model suggests product will be diluted within a 5-acre area

Dilution area avoids NYSDEC Freshwater Wetland zone

#### Komeen Diluton Area

Komeen will Dilute to <200ppb within a 5 acre dilution zone



- Komeen Descend Dilution Area
- SSW Pilot Treatment Area (1.5 acres)

Lake

N

SSW Pilot Treatment Area (1.5 acres)

Google Earth

### Questions

### Solutions to Preserve our most Precious Natural Resource...Water

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> Alga Corner

Host:

The Sepres Stewards

### Next Steps

- Board Vote on Resolution
- LBE submit Permit Applications to NYSDEC
- Pre-treatment Survey (July)
- Komeen<sup>®</sup> Descend Treatment (July)
- Post-treatment Survey (August-Sept)