Field testing of copper alloy cages in British Columbia: comparison of measured copper to ambient water quality criteria.

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Problem

- Antifoulant coated nylon nets
  - Net integrity is a concern
- Easily damaged due to predator attacks
  - Product loss or animal stress
- Decreased pen size during “storm events”
  - Overcrowding and poor oxygen levels
- High costs associated with maintenance, repairs and replacement of nylon nets.
  - Biofouling

Copper-Alloy Cages

- Currently in use in several countries
  - Chile (70)
  - Australia (28)
  - Asia (200 - 300)
- Trials are also being conducted
  - Scotland, China, Panama, South Africa, Turkey, United States
- Copper-alloy cages are used for a variety of species
  - Salmon, Trout, Sea Bream, Sea Bass, Cod, Cobia….

Copper Alloys in Marine Aquaculture (2011) Report by European Copper Institute, International Copper Association, EcoSea.

Copper-Alloy Cages

Advantages of Copper Alloy Pens

- High strength
  - Prevent the loss of fish through escapes and predator attack
- Rigid flexibility
  - Maintain shape during “storm events”
- Cages remain in water for life expectancy
  - 6 - 8 years (3 - 4 production cycles)
  - Minimal *in situ* cleaning (1 – 2 /annum)


[1]

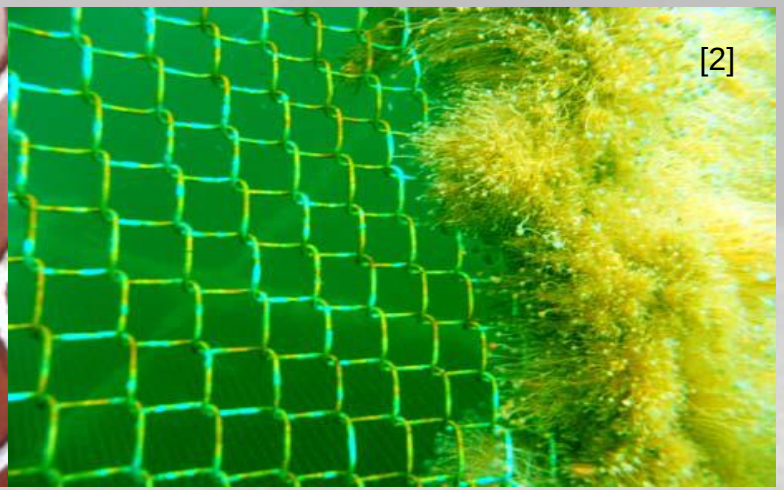

[2]

Photo Credit: [1] EcoSea; [2] University of New Hampshire.

Copper

- Useful and important component in industry
  - Copper is an essential micro-nutrient
    - Necessary for normal metabolism in both plants and animals
    - Fish food and dietary supplements
  - At high concentrations is toxic to aquatic species
    - Antifouling paints

Copper Guidelines

- Water Quality Guidelines for British Columbia[1]
  - 30-day average concentration ≤ 2 µg Cu/L
  - Maximum concentrations cannot exceed 3 µg Cu/L
    - Total copper

- Alaska[2,3]
  - Protected Waters
  - 4-day average concentration (chronic) - 3.1 µg Cu/L
  - 24-hour average concentrations (acute) - 4.8 µg Cu/L
    - Dissolved copper

[1] Water Quality Criteria for Copper (Ministry of the Environment, Government of British Columbia)
[2] Alaska Water Quality Criteria Manual for Toxic And Other Deleterious Organic and Inorganic Substances (Department of Environmental Conservation)
[3] U.S. EPA, 2007

Objectives

- To assess the potential for ecological risk from the introduction of copper alloy nets to a site in British Columbia
  - monitor Cu concentrations (contributions above background)
  - assess the potential for impacts.

Installation

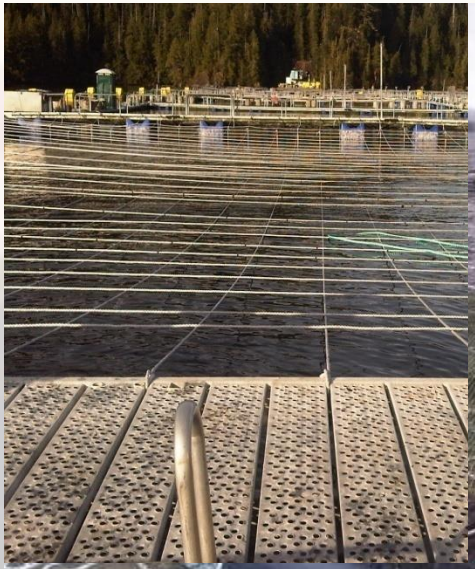


Photo Credit: Langley Gace and [4, 5] EcoSea

Sampling Locations

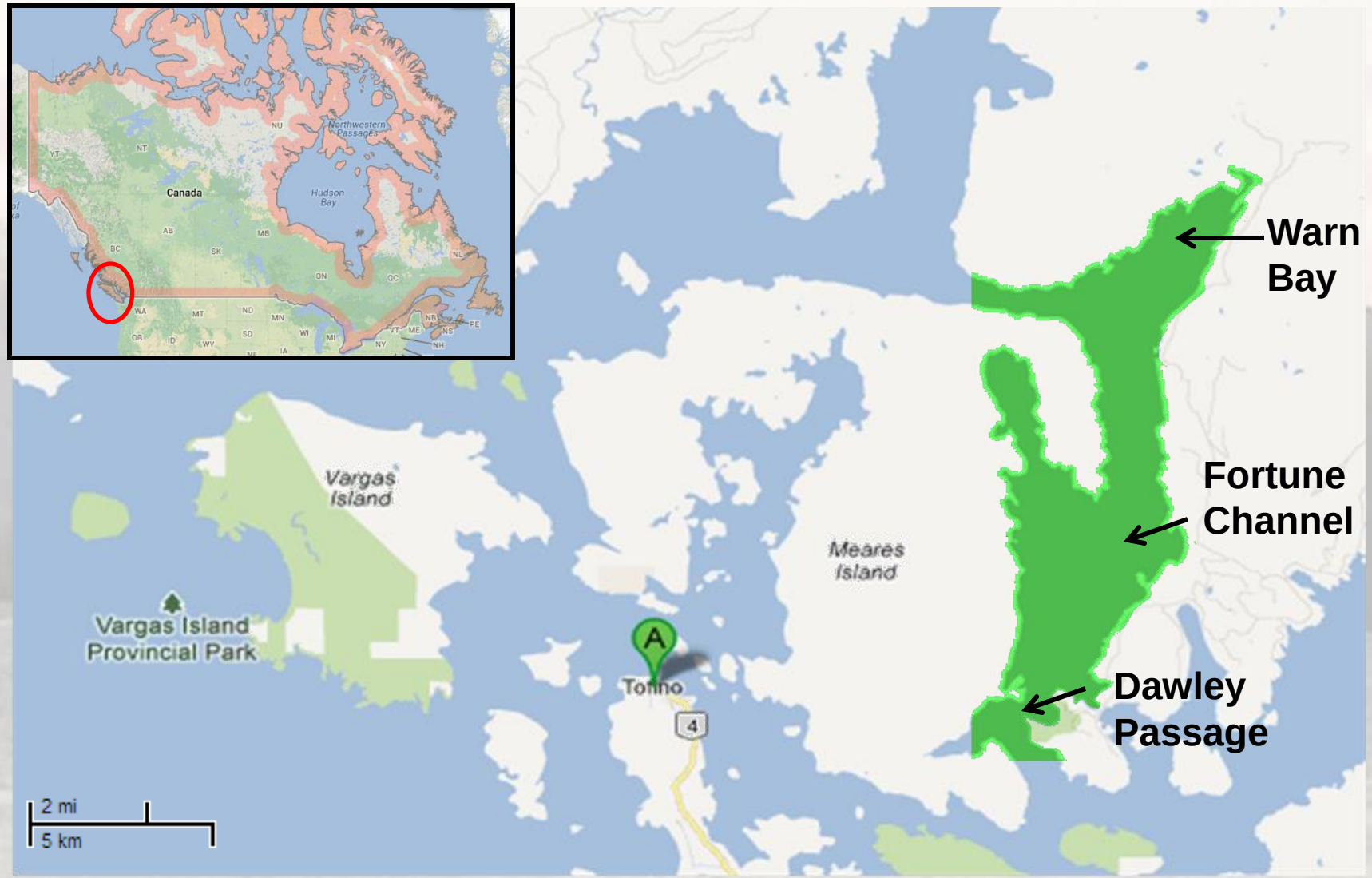
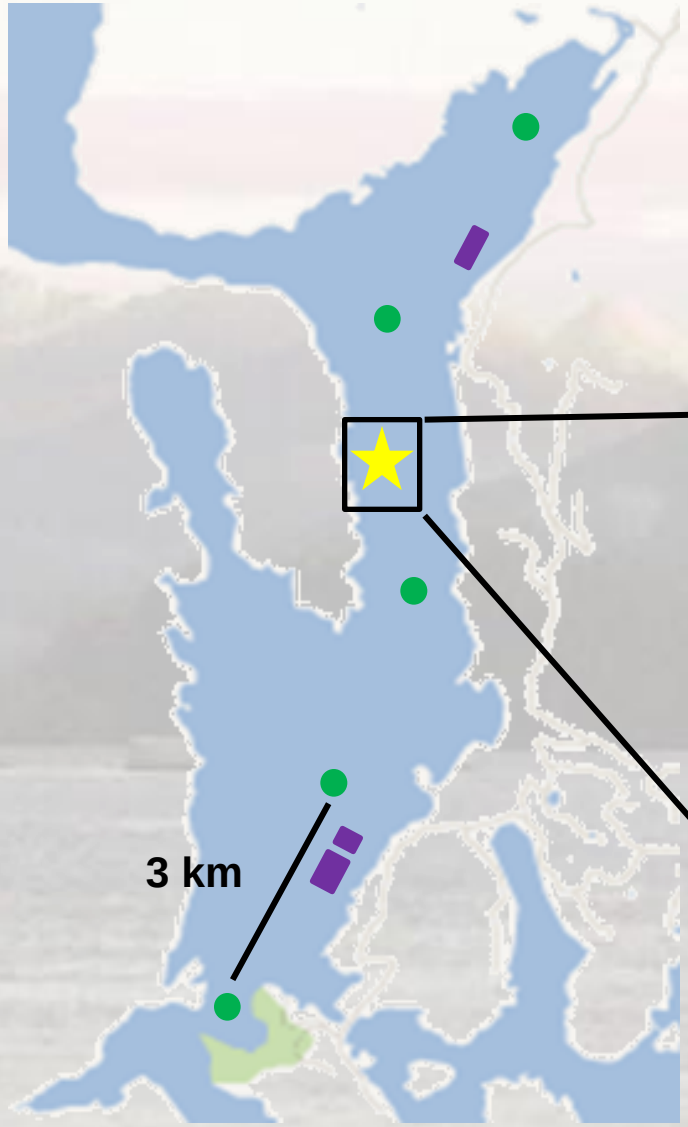


Photo Credit: Google Maps

Sampling Locations



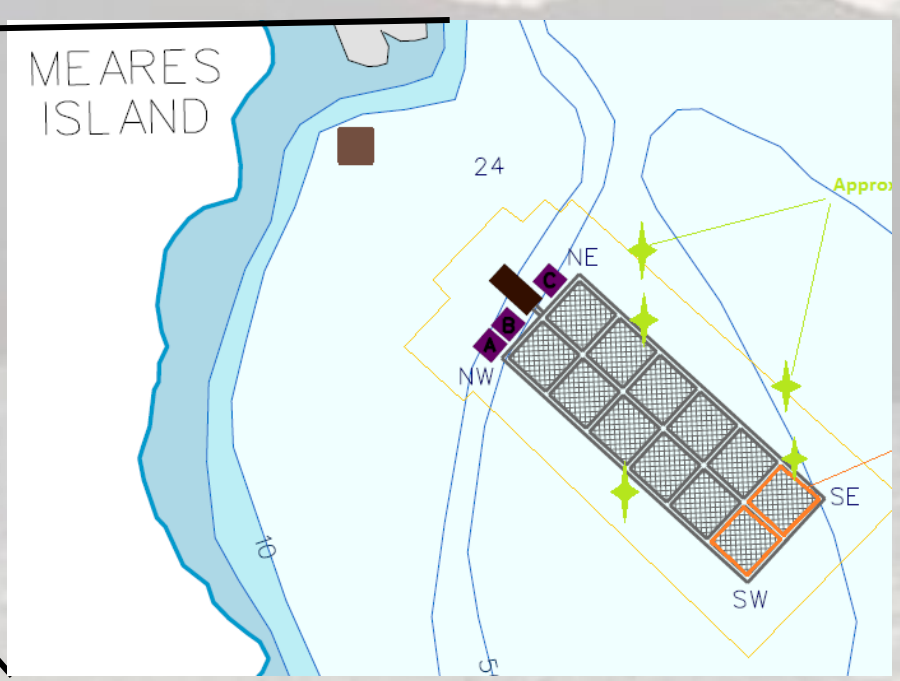
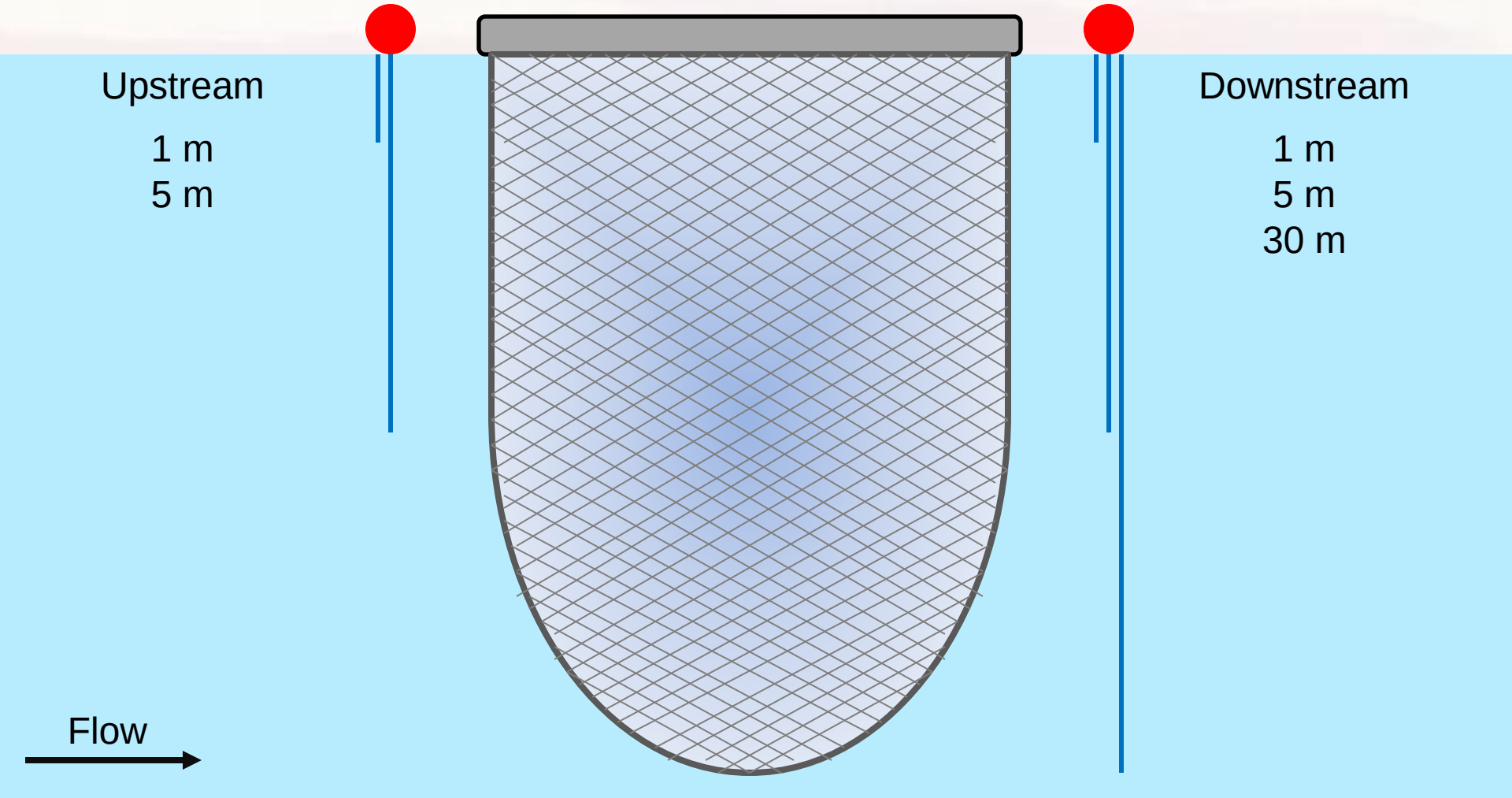


Photo Credit: Google Maps and Mainstream Canada

Sampling Method

- Samples for background concentrations were collected prior to cage installation
- Sampling occurred daily once installation commenced
  - Only intermittent sampling during install of cage two
- Sampling linked to tidal cycle
  - Flood
  - Slack
  - Ebb

Sampling Method



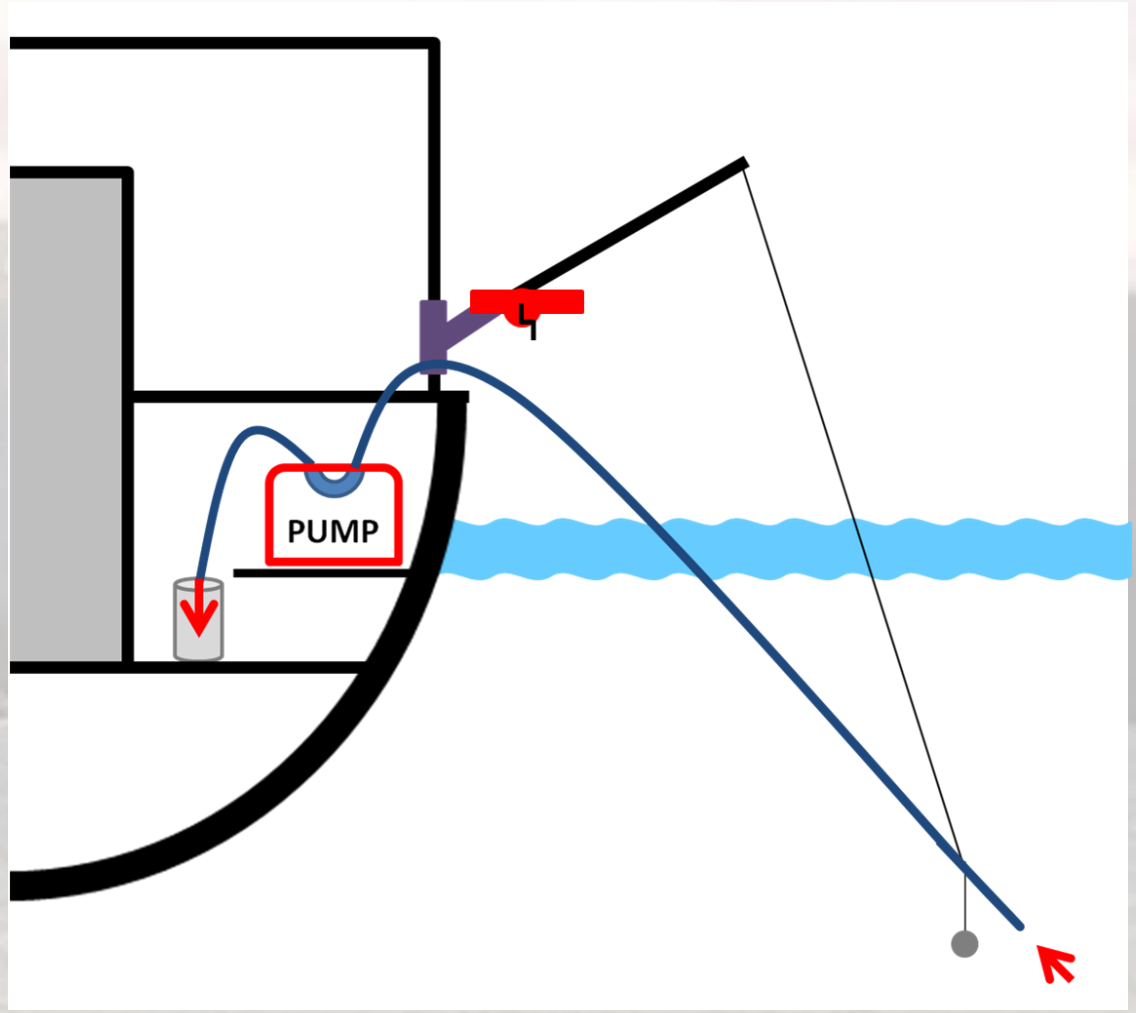
Sampling Method

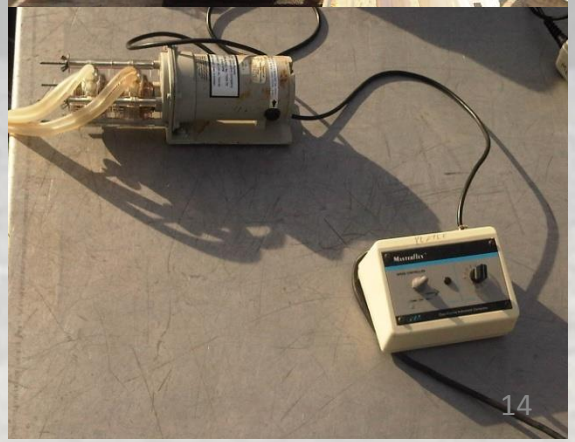
- U.S. EPA (2004) SOP 1229 TRACE METAL CLEAN SAMPLING OF NATURAL WATERS
  - derived from EPA Method 1669, Sampling Ambient Water for Determinations of Metals at EPA Water Quality Criteria Levels
- Polytertrafluorethylene (PTFE) Tubing
- Samples were collected into pre-cleaned PTFE bottles
  - Filtered samples were filtered on site
  - 0.45 µm membrane filter

On Site Measurements:
- Salinity
- Temperature

Sample Shipping Preparation:
- Acidified (trace metal grade)
- Sealed Bottles (Parafilm®)

Sampling

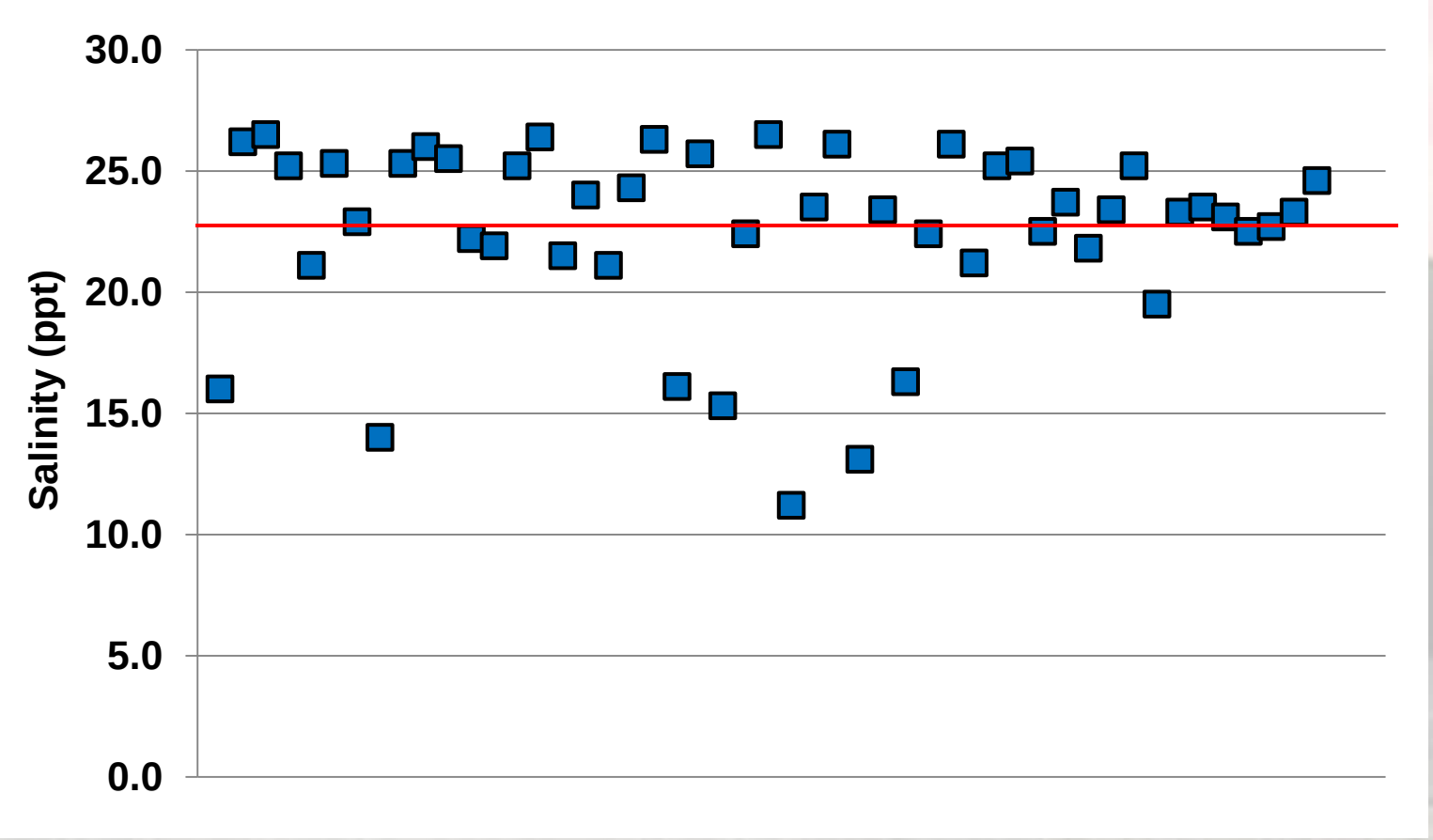




Experimental Methods

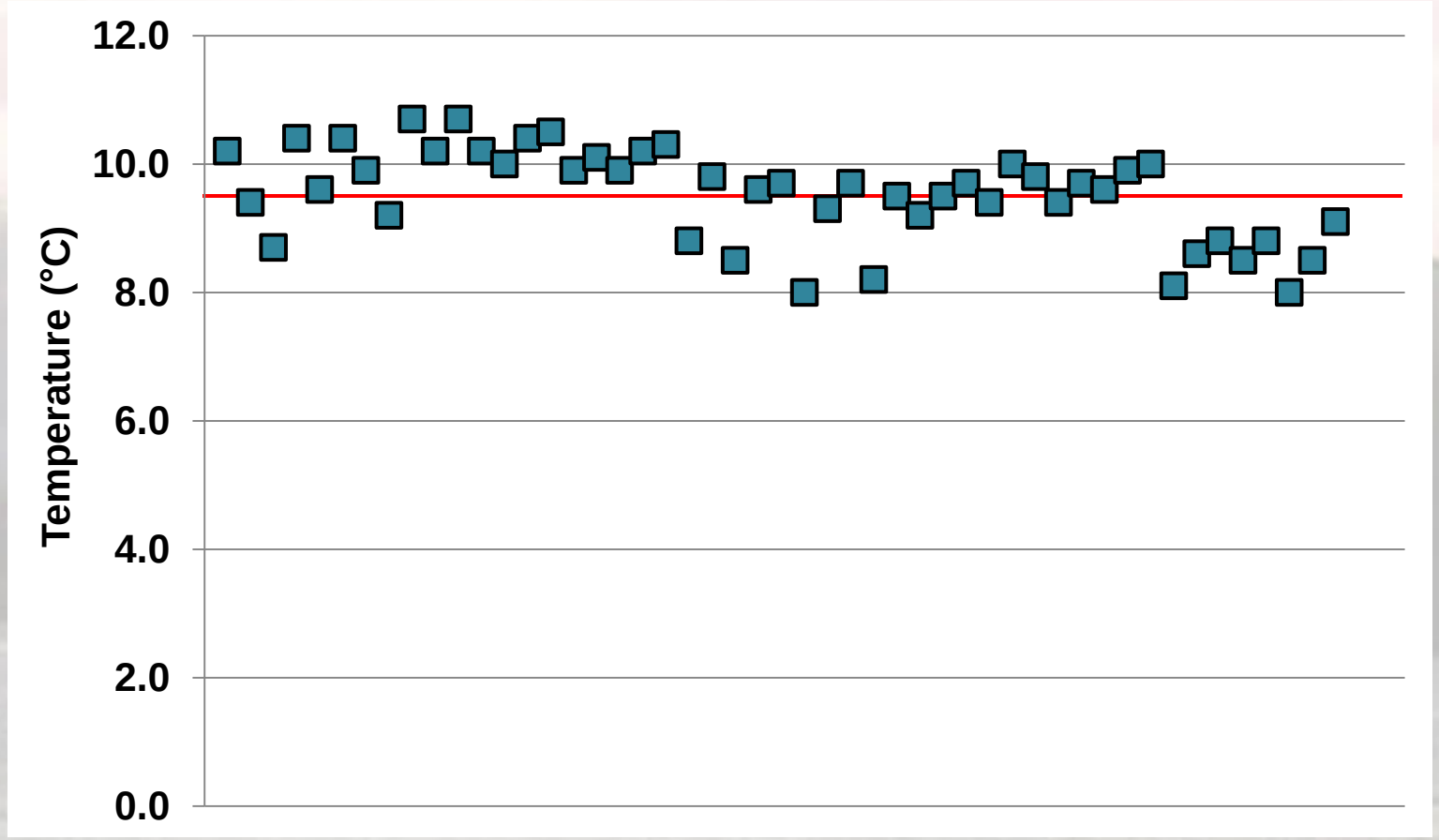
- Total and Dissolved Cu Measurements
  - Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)
    - Maxxam Analytical
  - Anodic Stripping Voltammetry (ASV)
    - Wilfrid Laurier University
- Total and Dissolved Organic Carbon
    - Wilfrid Laurier University

Salinity



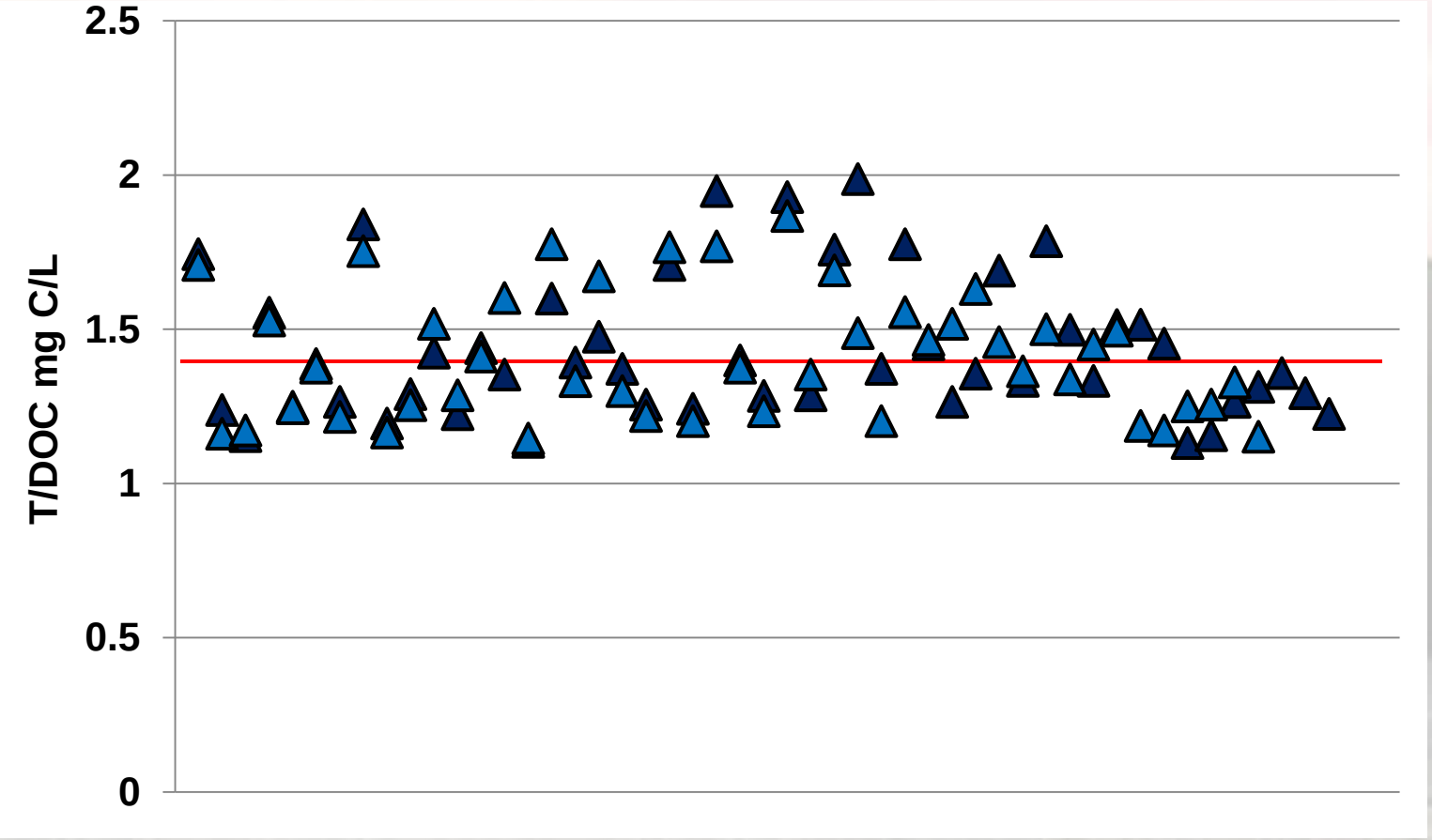
22.6 ± 3.8 ppt
N = 48

Temperature



9.5 ± 0.7 °C
N = 48

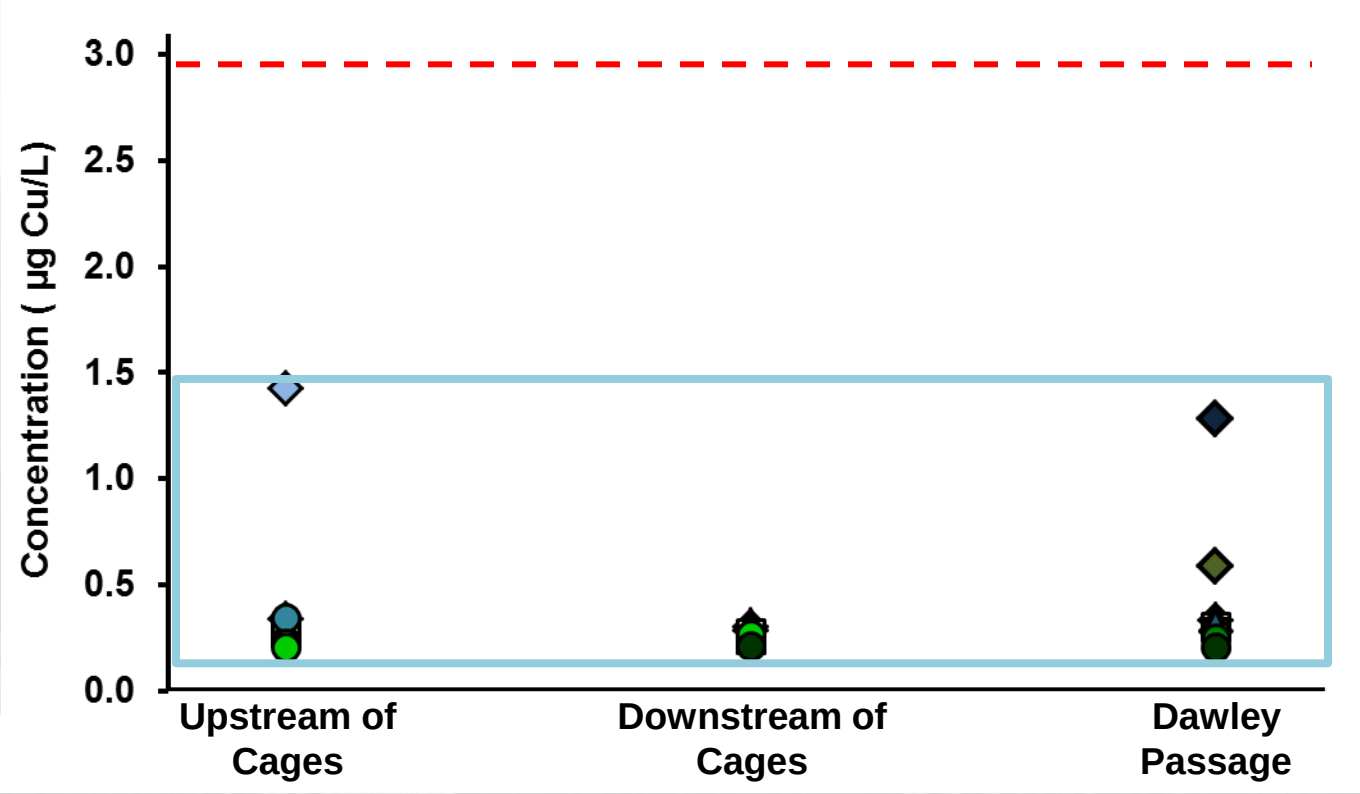
Total and Dissolved Organic Carbon



TOC 1.432 ± 0.2 mg C/L
N = 48

DOC 1.411 ± 0.2 mg C/L
N = 42

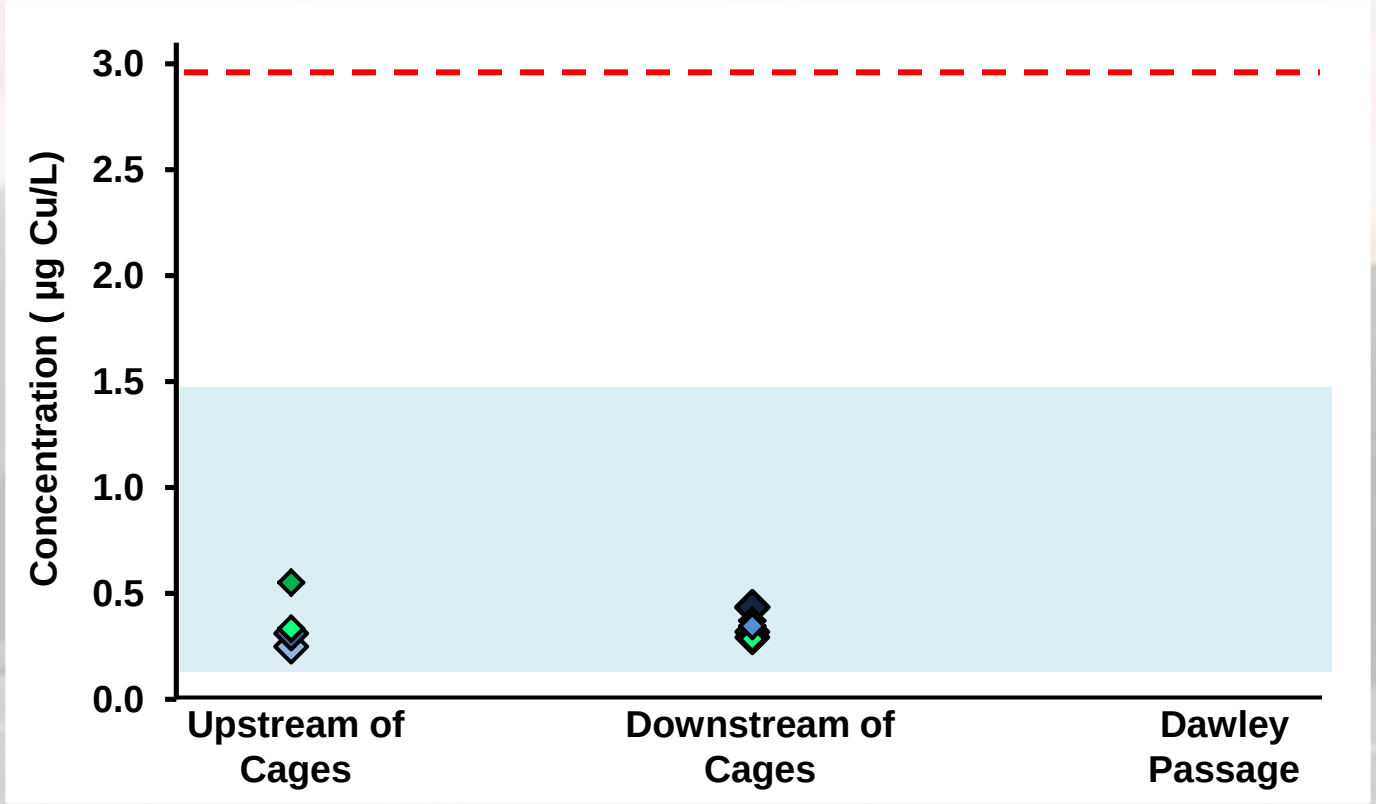
Background Cu Levels



$[Cu]_{Total}$
- Day 1 (Nov. 26)
- Day 2 (Nov. 27)

$[Cu]_{Dissolved}$
- Day 1 (Nov. 26)
- Day 2 (Nov. 27)

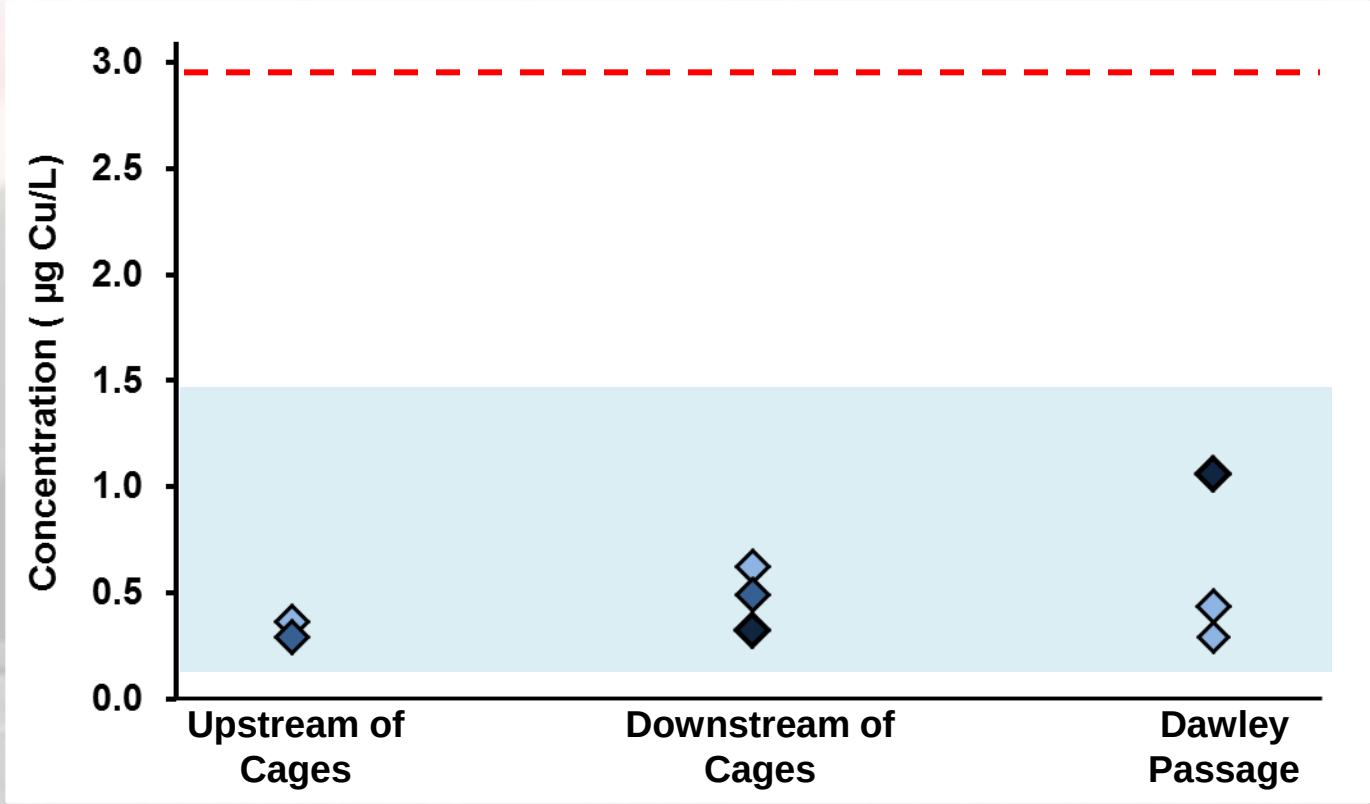
Day 6 and 8 (Dec. 4 and 6)



- Day 6
  - Walls of cage was installed
  - Floatation pipes were delivered for cage 1
- Day 8
  - Floatation device installed
  - Lift bag was removed

Cage 1 in water

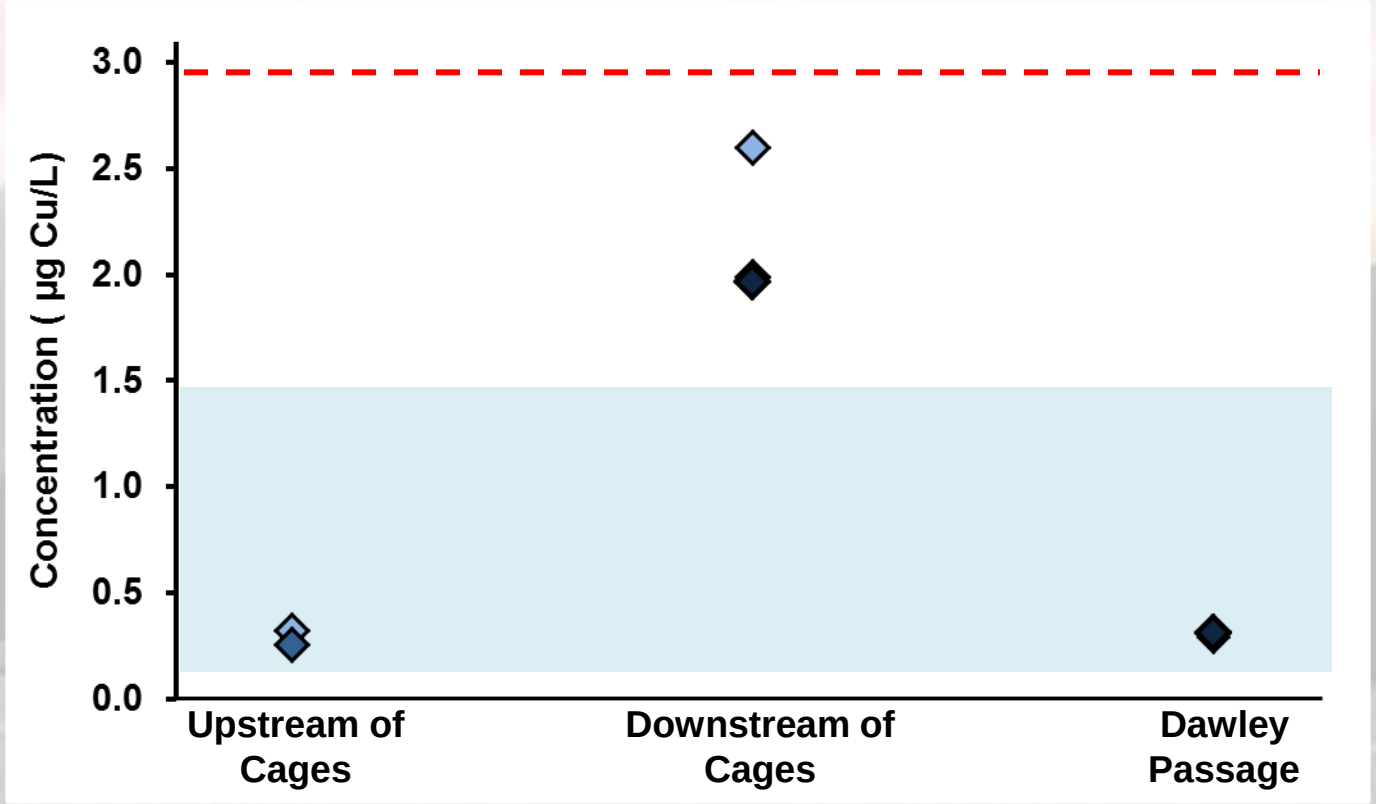
Day 9 (Dec. 7)



- Bottom of Cage 2 installed

Cage 1 in water for 24 hours

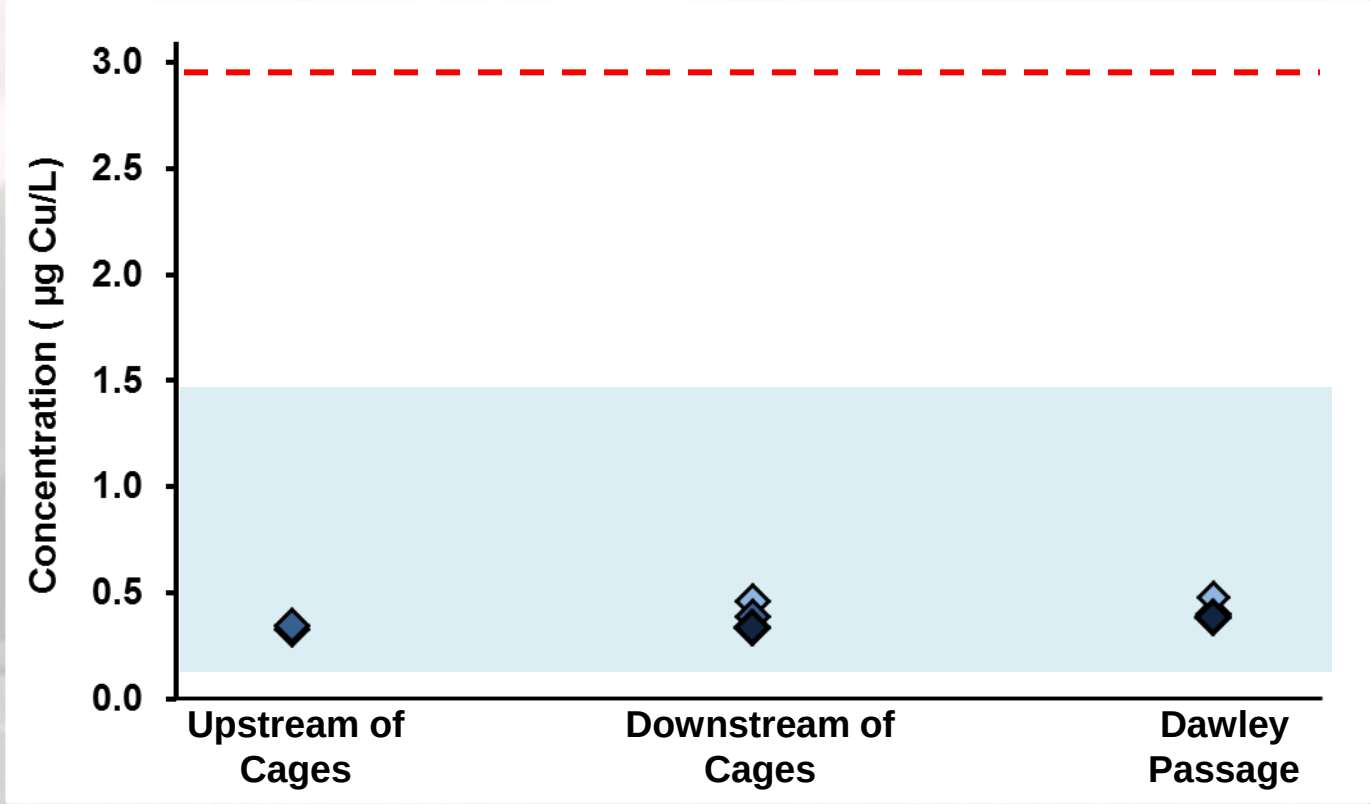
Day 15 (Dec. 13)



- Floatation device installed
- Lift bag was removed

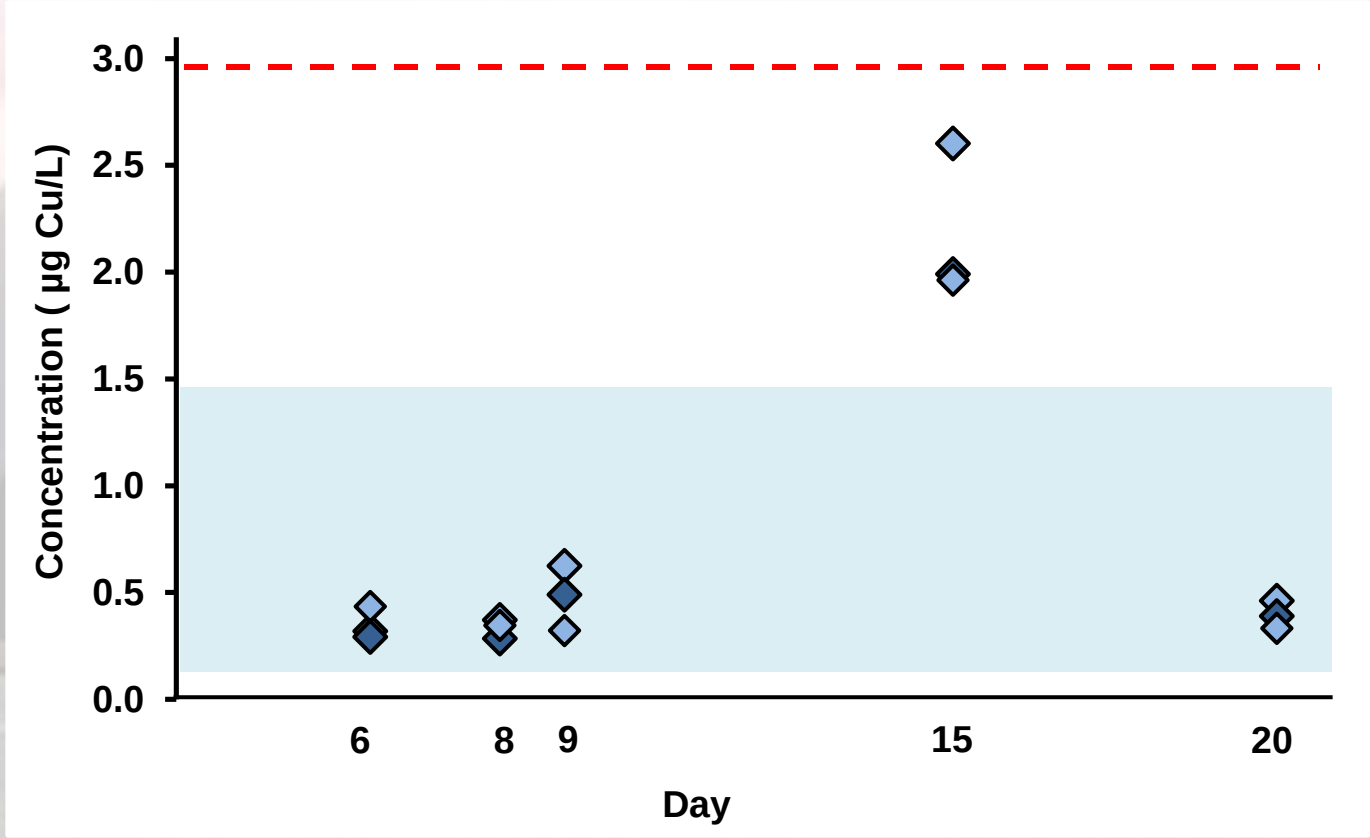
Cage 1 and Cage 2 in water

Day 20 (Dec. 18)

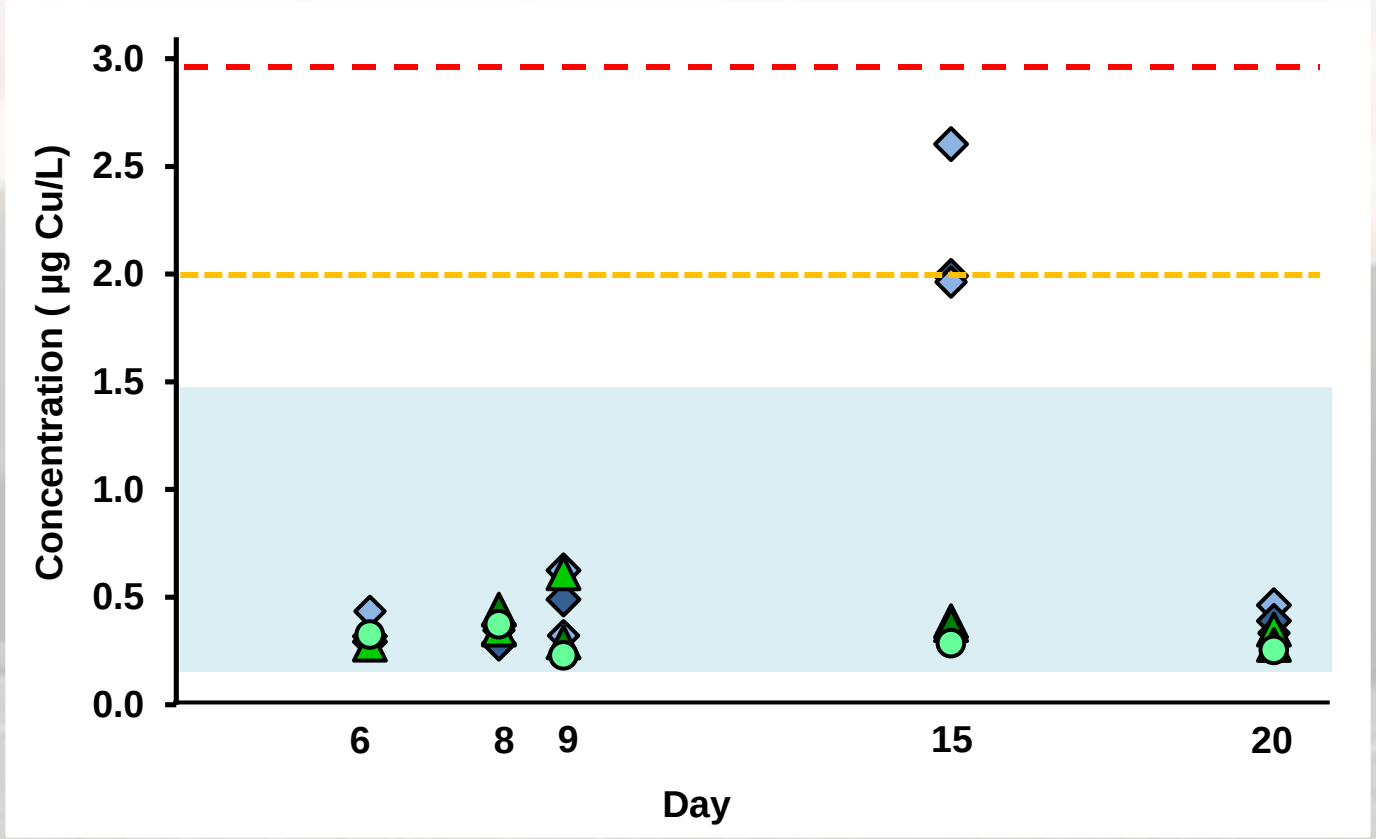


Cage 1 and Cage 2 in water for 4 days

Downstream Samples Over Time



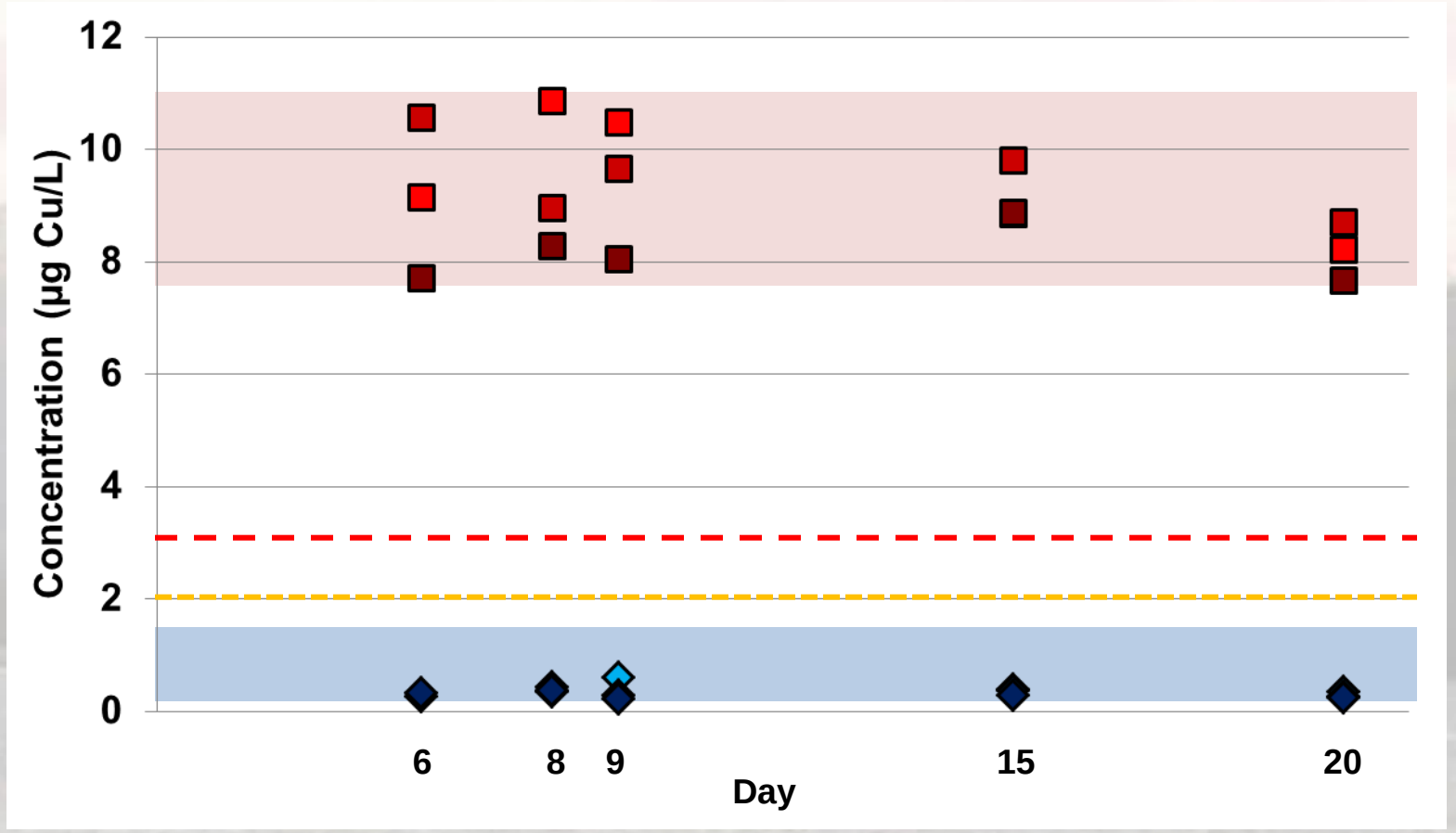
Downstream Samples Over Time



◆ $[Cu]_{Total}$

● $[Cu]_{Dissolved}$

Downstream Dissolved Cu Concentrations



-Species Mean Acute Value (SMAV)

- Average of EC50 data
- *Mytilus edulis*
  - Most sensitive organism in marine database

Conclusions

- Measured values are below applicable British Columbian water quality standards for copper.

- No consistent patterns to indicate detectable amounts of copper are being released from the newly-installed cages.

Acknowledgements

- Eddie Frank
- Rodrigo Fuenzalida
- Site Manage (Ron)
- Jessie Cunningham
- Tara Tait

Copper-Alloy Composition

-Brass

- Copper and Zinc

Mitsubishi Shindoh Co. Ltd. (Sambo Copper Alloy Co. Ltd.) provides technical information about the alloy UR30 on its internet website.

Element	Cu	Sn	Ni	Zn
Content, wt. -%	64.0	0.6	0.3	bal.

According to Mitsubishi Shindoh's data sheet, at least one further mircoelement is added to the CuZn-alloy.

Copper-Alloy

Physical Properties

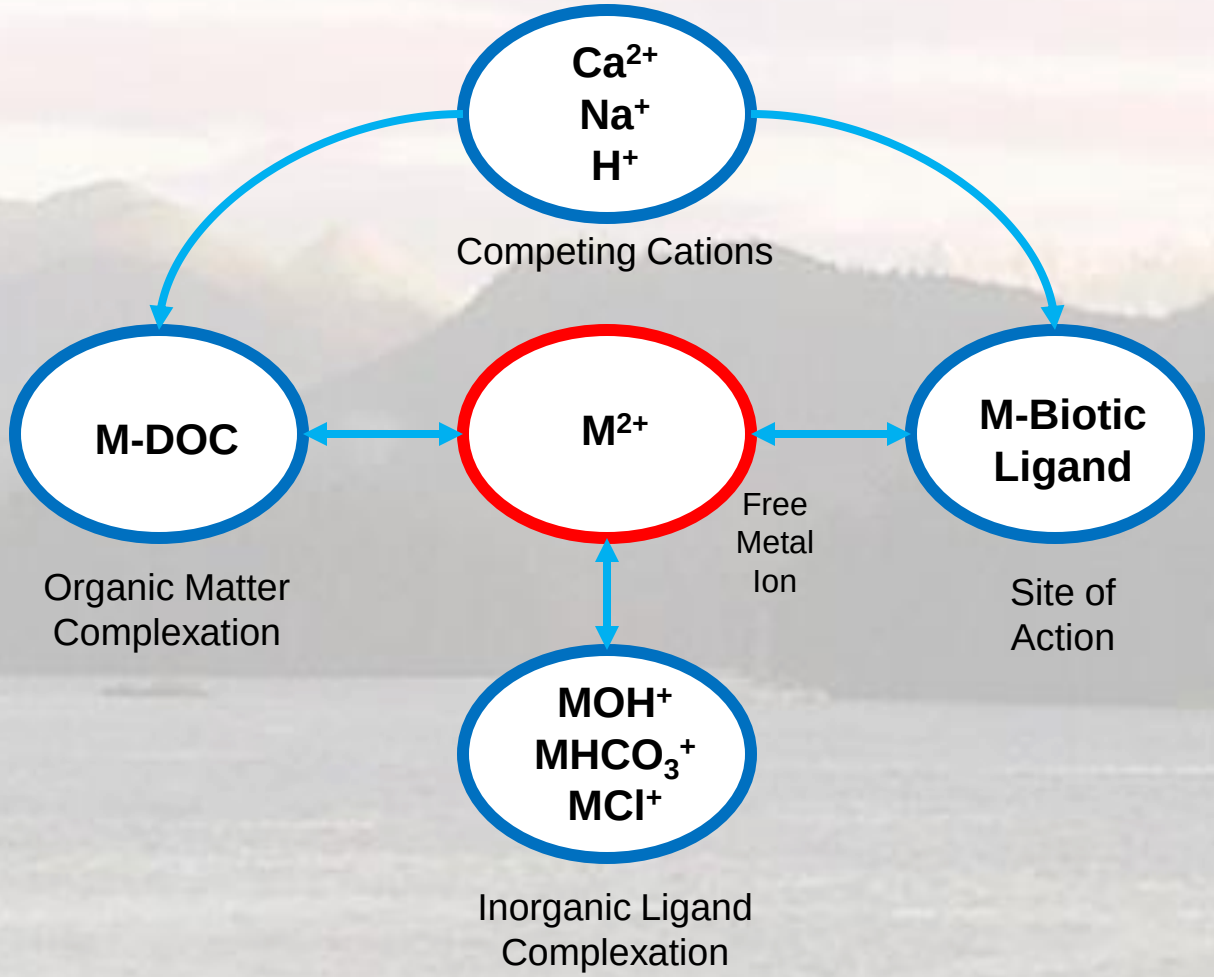
Melting Point	Specific Weight	Electrical Conductivity	Coefficient of Thermal Expansion
920 °C	8.4 g/cm^3	26% IACS	21 x 10^{-6} / °C

Mechanical Properties (wire, Ø 4 mm)

Temper	R_{pO2}	R_m	Elongation	Young's Modulus
1/8 H	330 MPa	440 MPa	22 %	100 GPa

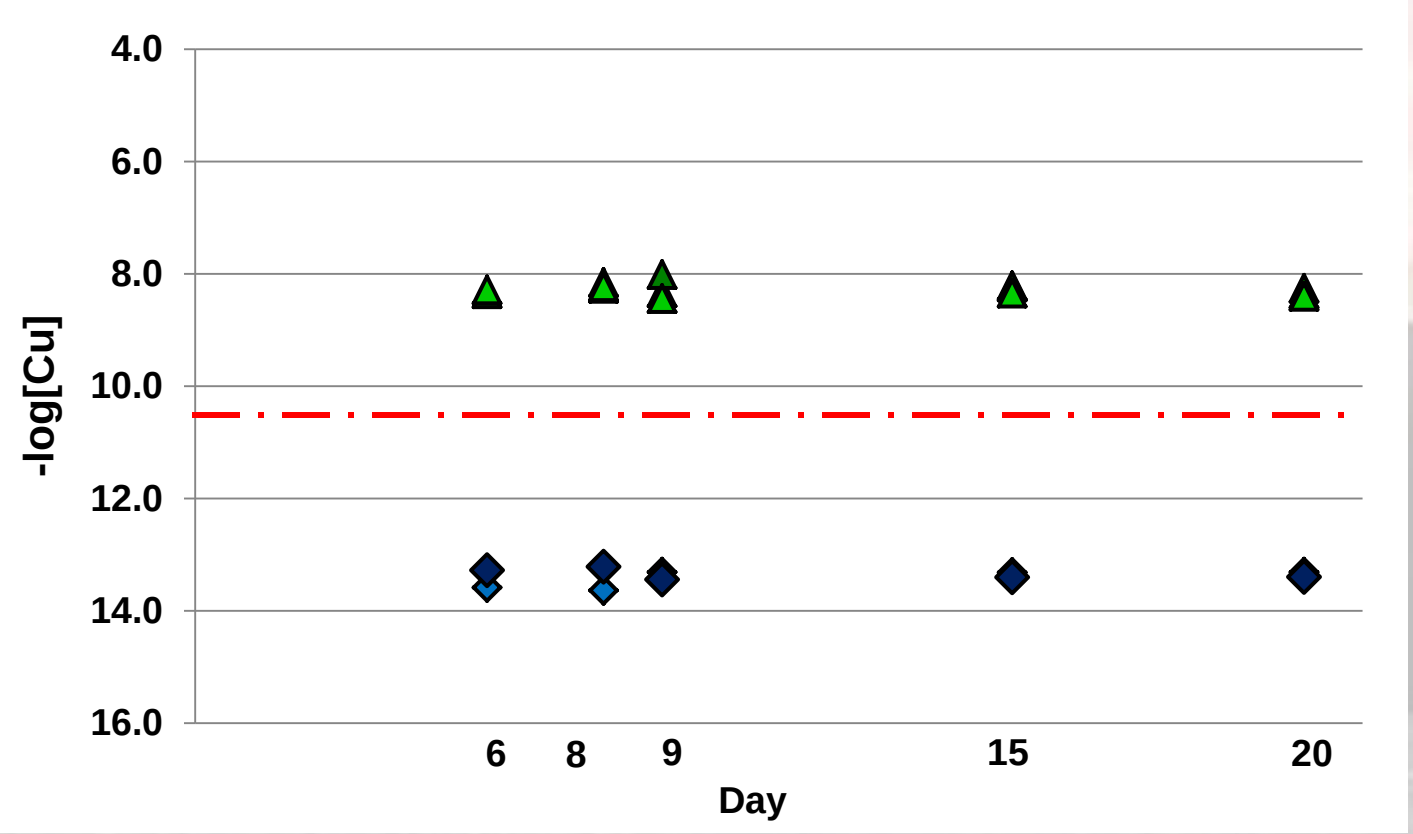
Corrosion resistance:
-Excellent resistance against dezincification
-Corrosion in seawater after 5 years exposure: max. corrosion depth 20 µm, mean corrosion depth 10µm.

Biotic Ligand Model (BLM)



Di Toro et al., Environ. Toxicol. Chem., 20 (2001), pp. 2383–2396.

Bioavailable Cu Concentrations



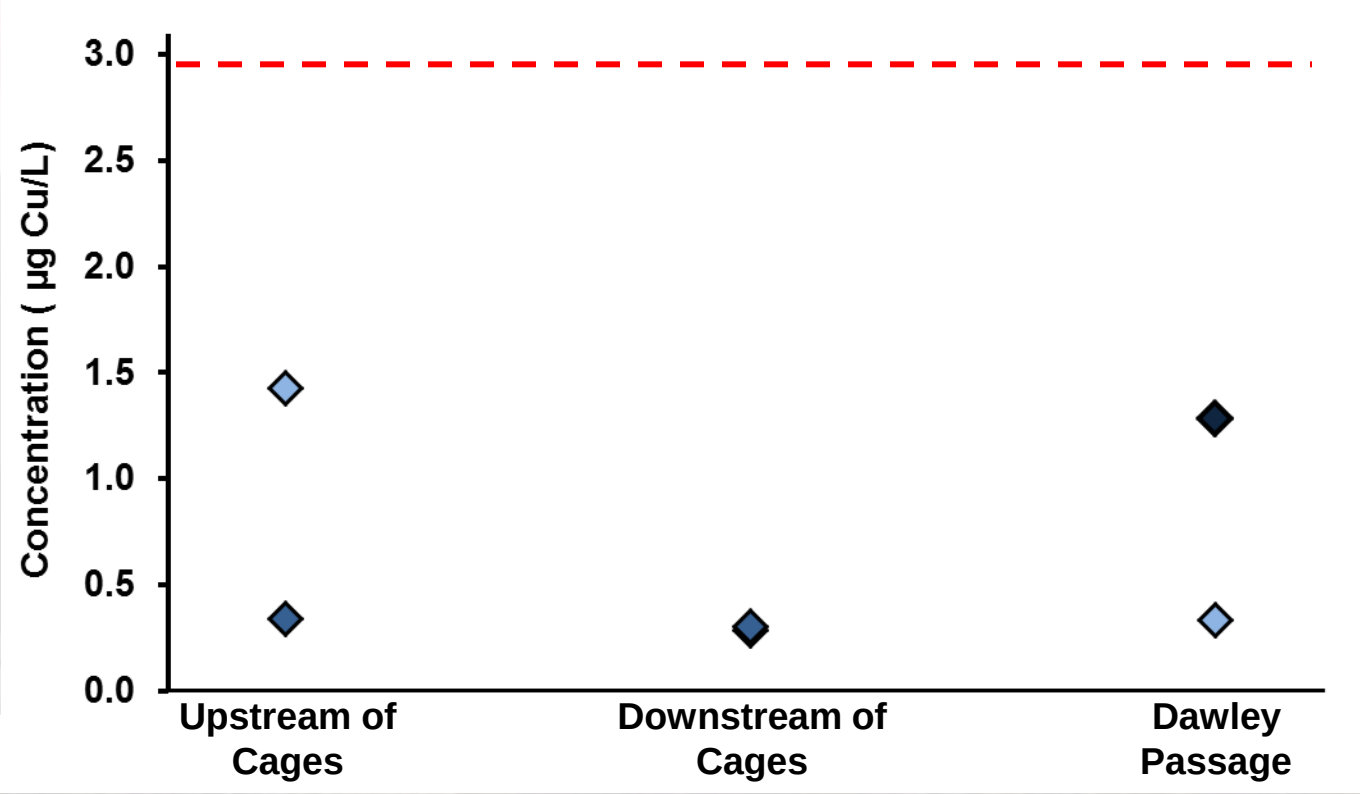
-Species Mean Acute Value (SMAV)

- Average of EC50 data
- *Mytilus edulis*
  - Most sensitive organism in marine database

Still in progress…

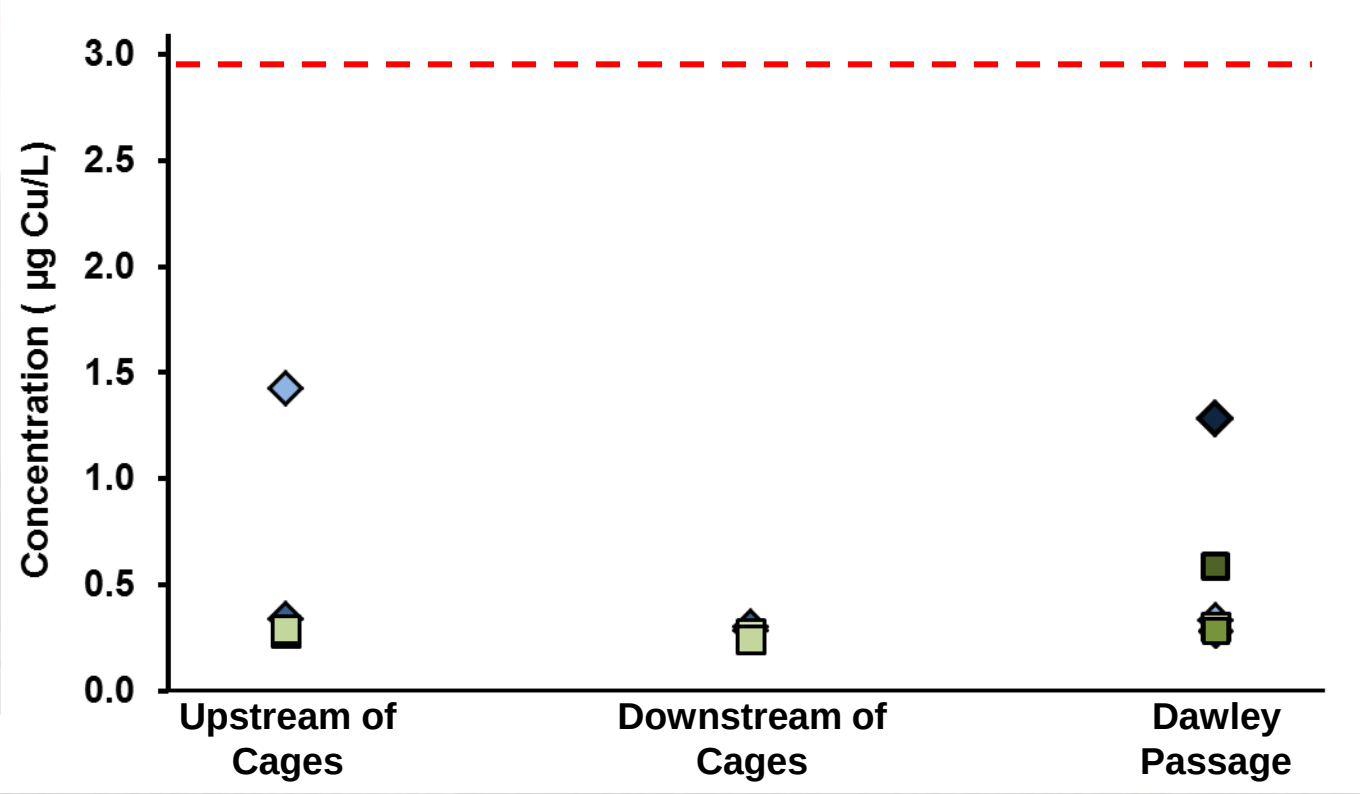
- Still measuring samples:
  - 518 samples (filtered and unfiltered)
  - Flood and Ebb tidal samples
    - Anodic Stripping Voltammetry (ASV)

Background Cu Levels



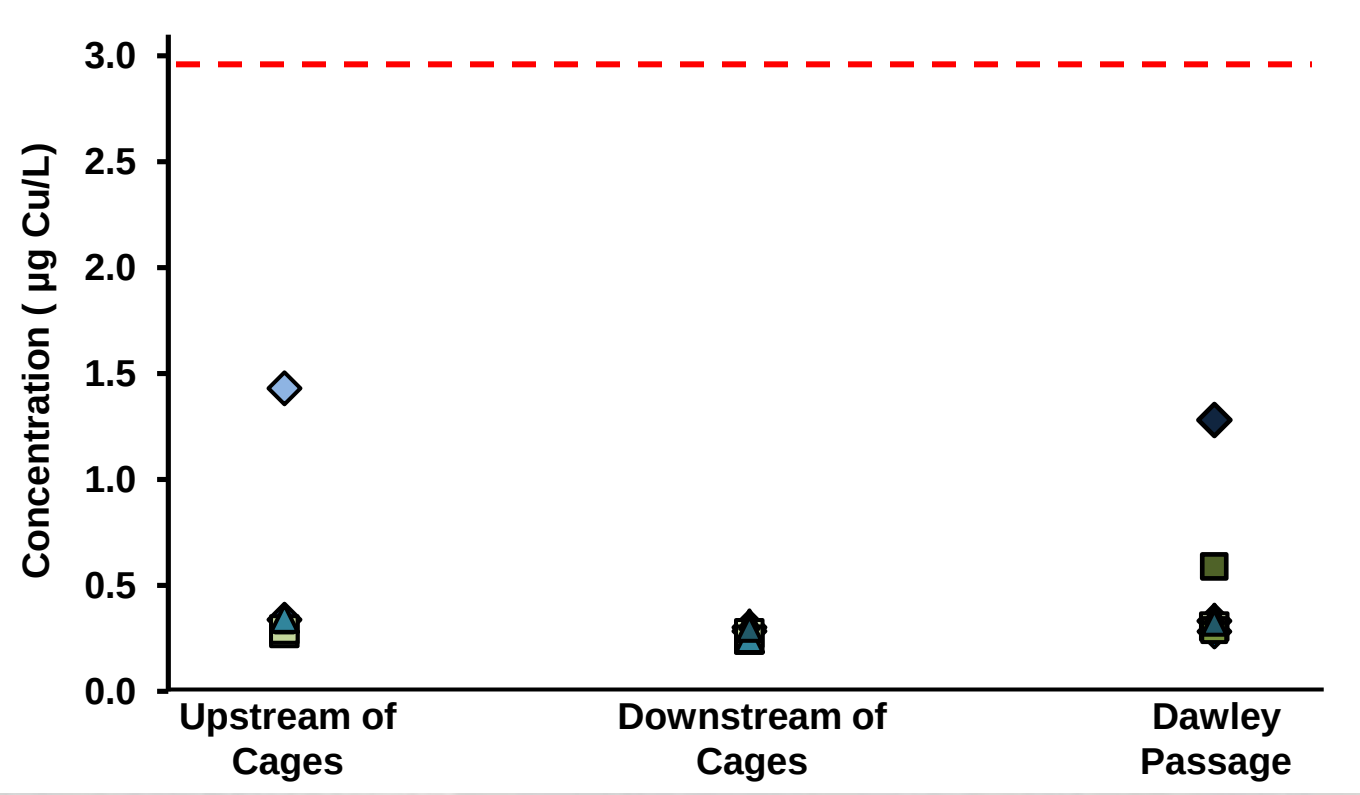
Day one from sampling for background Cu concentrations (Total Values)

Background Cu Levels



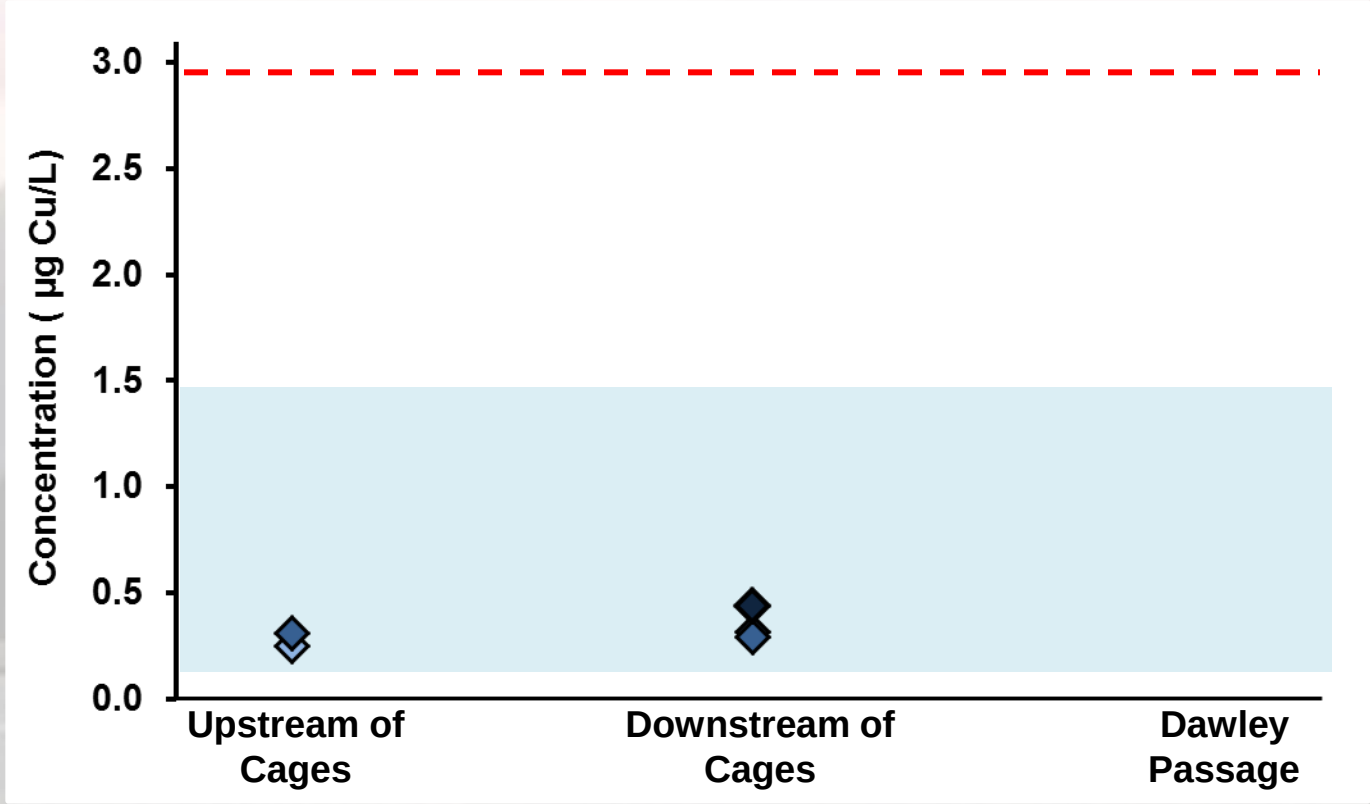
Day one and day two measurements from sampling for background Cu concentrations (Total Values)

Background Cu Levels



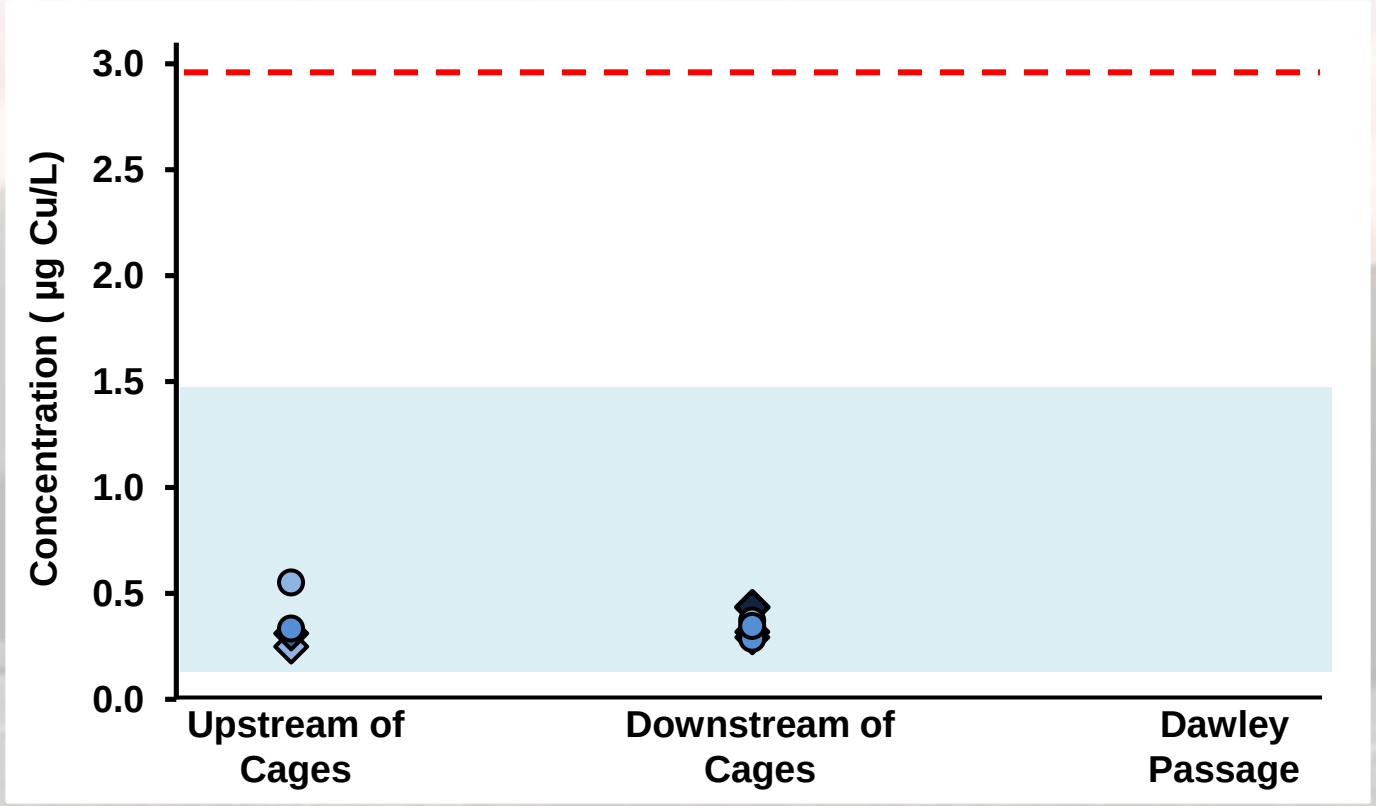
Day one and day two measurements from sampling for background Cu concentrations (Total and Dissolved Values)

Day 6 and 8 (Dec. 4 and 6)



- Walls of cage was installed
- Floatation pipes were delivered for cage 1

Day 6 and 8 (Dec. 4 and 6)



- Floatation device installed
- Lift bag was removed

Cage 1 in water