

Evaluation of Copper Ion Generator for Effects on Settlement of Veligers and Impact on Adult Quagga Mussels – Lower Colorado River

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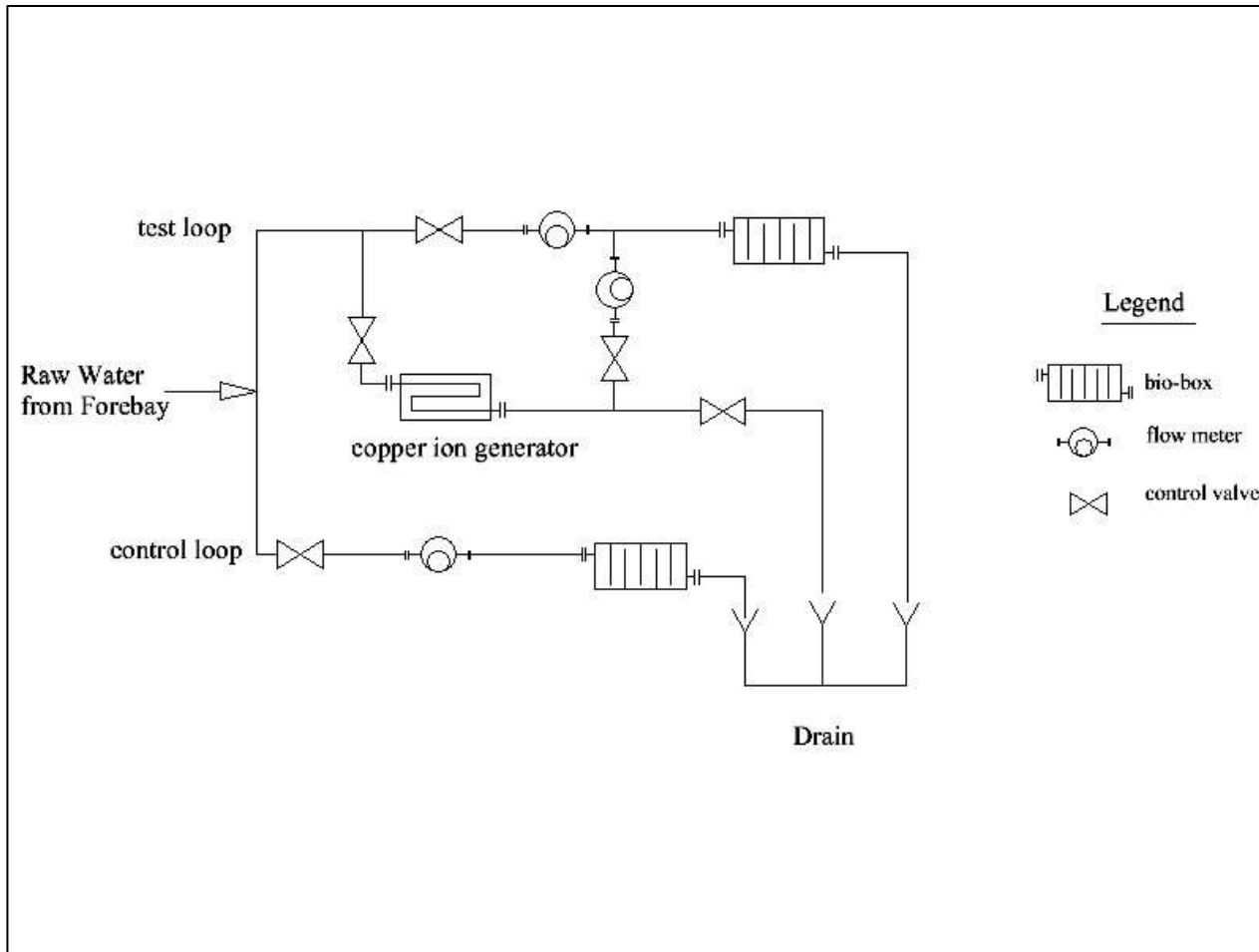


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Background

- Toxicity of copper to marine life has been recognized for centuries
- Use of copper ion generator technology for the control of invasive mussels has been promoted for over 20 years
- Last independent evaluation done in 1994 on the Great Lakes
- Mixed reviews from users
- Need to re-evaluate the copper ion levels needed in water with different chemistry
- Need to evaluate the performance of the generator under field conditions

Methodology







- Copper ion level in the test biobox was set using HACH DR-900 colorimeter and the porphyrin method for free copper. The instrument range was between 4 and 200ppb of copper with accuracy of +/- 6ppb. Portion of the water sample was sent to one, sometimes two independent environmental laboratories to verify the Hach instrument readings.
- Copper levels verified and adjusted weekly.
- Copper background level fluctuated between 0 and 10ppb in raw water
- Water parameters as temperature, pH and DO were measured weekly using Hach HQ40d Multiprobe handheld instrument.

- Settlement of new juveniles allowed to proceed for 4 weeks – 5 weeks before evaluation.
- Each biobox had 100 captive adult mussels introduced at the start of the experiment. Mortality checked weekly.
- Experiment repeated 6 times at different copper ions levels

Experimental Test Cycles

Test Cycle	Copper Objective	Start	End
C	13 to 15ppb	August 16, 2013	September 20, 2013
C1	13 to 15ppb	September 20 th .	October 1 st - October 29 th
C2	13 to 15ppb	November 6 th , 2013	December 3 rd , 2013
C3	13 to 15ppb	January 3 rd , 2014	February 3 rd
C4	20 to 30 ppb	February 28 th	April 15 th , 2014
C5	15 to 20 ppb	April 16 th , 2014	May 13 th , 2014
C6	10 to 15 ppb	May 14 th ,2014	June 9 th , 2014

Results

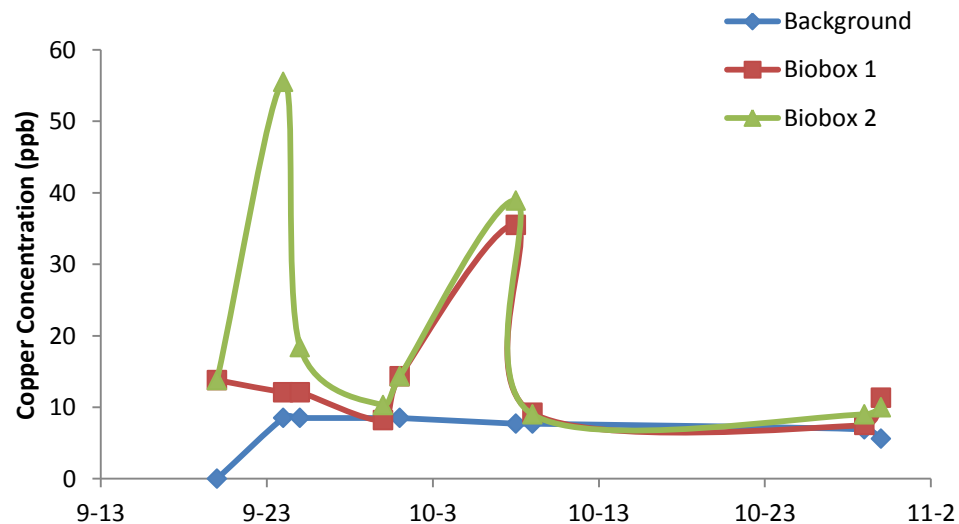
Cycle C - Electrical outage caused loss of flow and resulted in an overdose for several days. The copper levels found during the next visit were 50ppb in the treated biobox. All adults were dead as were all settlers on the test plates.

C1 - initiated Sept. 20th. Copper level 13 - 15ppb with background level measured between 0 and 3ppb. On October 1st we received a work stop order due to US Government shutdown. The shutdown continued until October 17, 2013. On October 29th we were able to re-enter the facility and terminate the experiment.

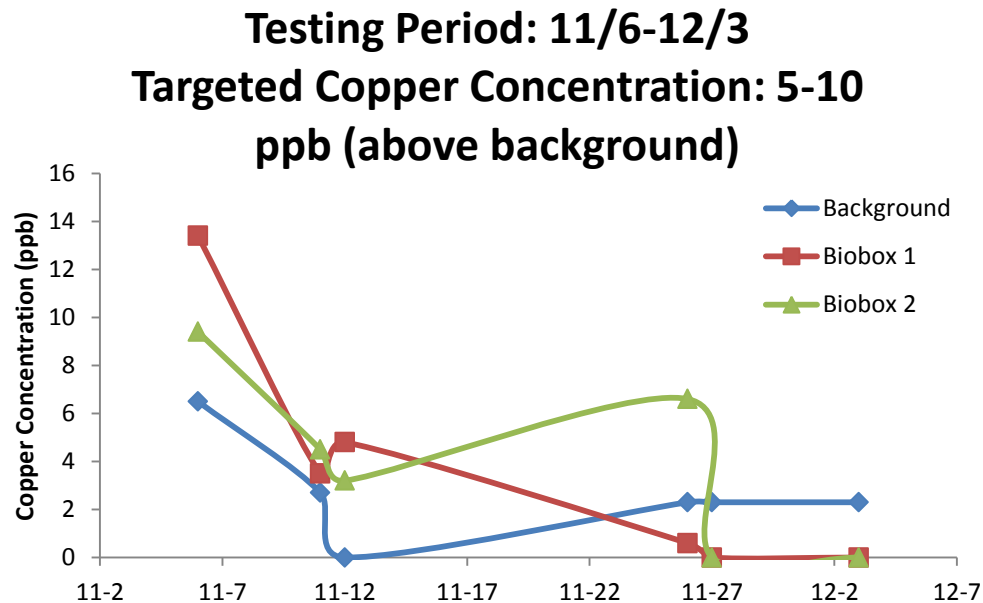
Settlement present in both test and control bioboxes but significantly lower in test.

96% adults dead in the test biobox, 4% dead in control

Testing Period: 9/20-10/30
Targeted Copper Concentration: 13-15
ppb (above background)

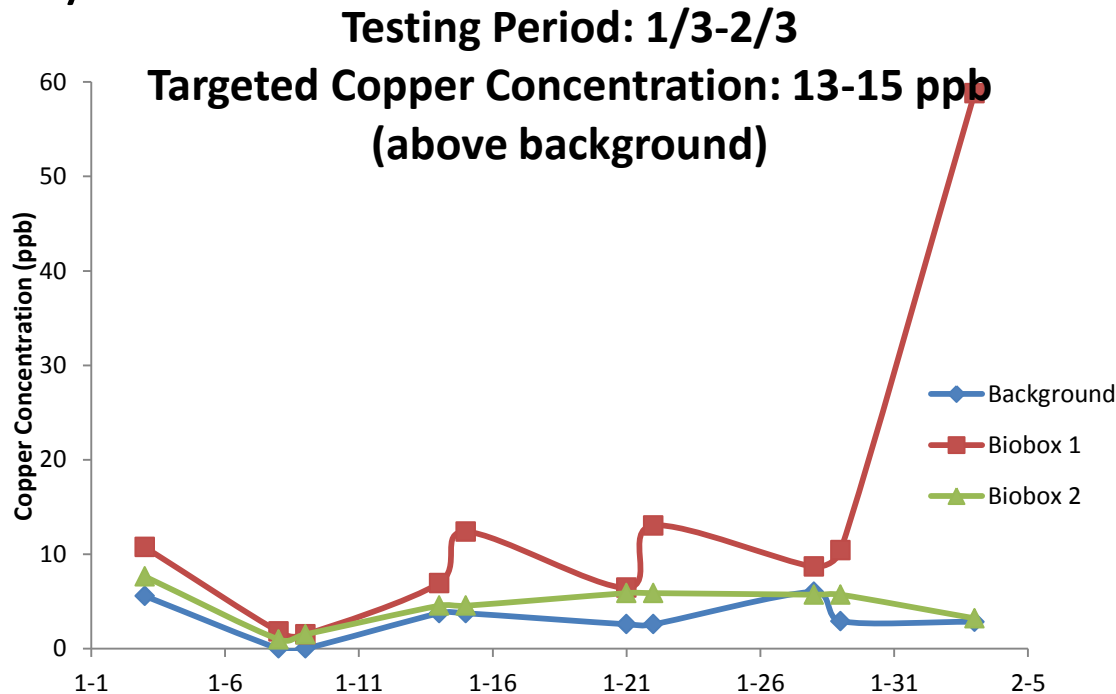


C2 - November 6, 2013 to December 3, 2013. Objective 13 - 15ppb in the test biobox. The actual copper levels achieved were below this target. The ambient temperature during the experiment was between 16.9 °C and 12 °C. There was settlement in both the treated and control systems. No significant difference in adult mortality.



Cycle 3 - January 3, 2014. The targeted copper level was 13 to 15 ppb. February 3, the generation unit which supplied raw water to the test loops went out of service. The readings in biobox 1 were almost 50ppb on February 3. The average ambient water temperature was 11.5° C.

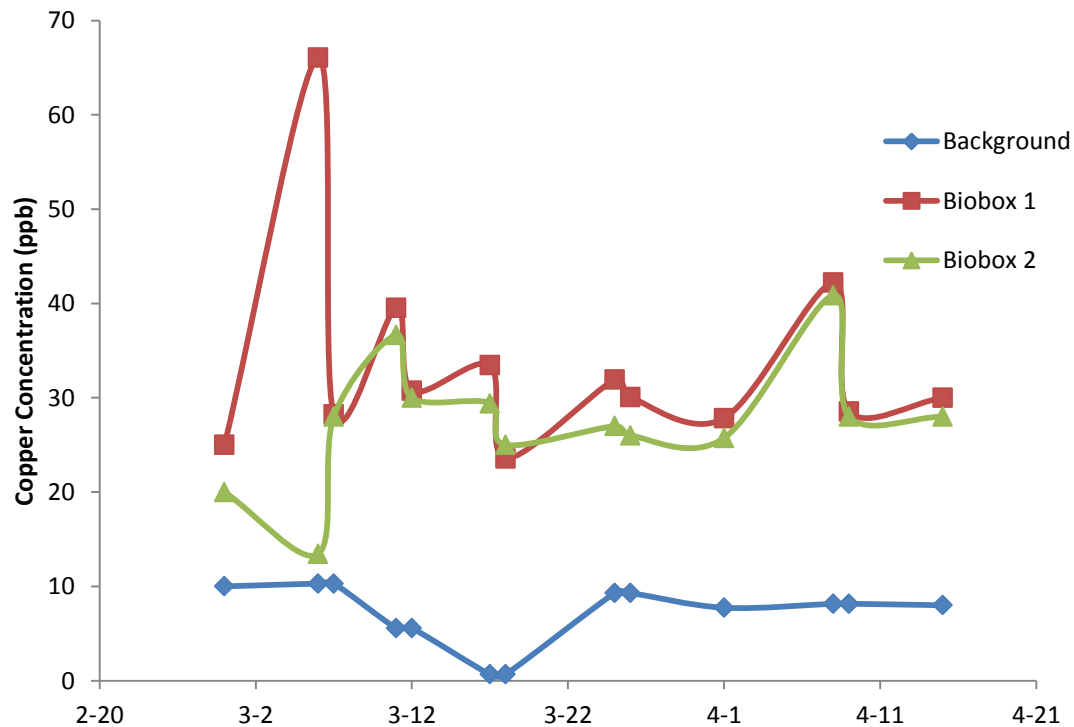
Settlement in both control and test biobox. No difference in adult mortality.



C4 - initiated on February 28th until April 15th. The target for copper level was 20 and 30ppb. Actual levels measured in the biobox were between 25 and 65ppb. The average ambient temperature was 15° C.

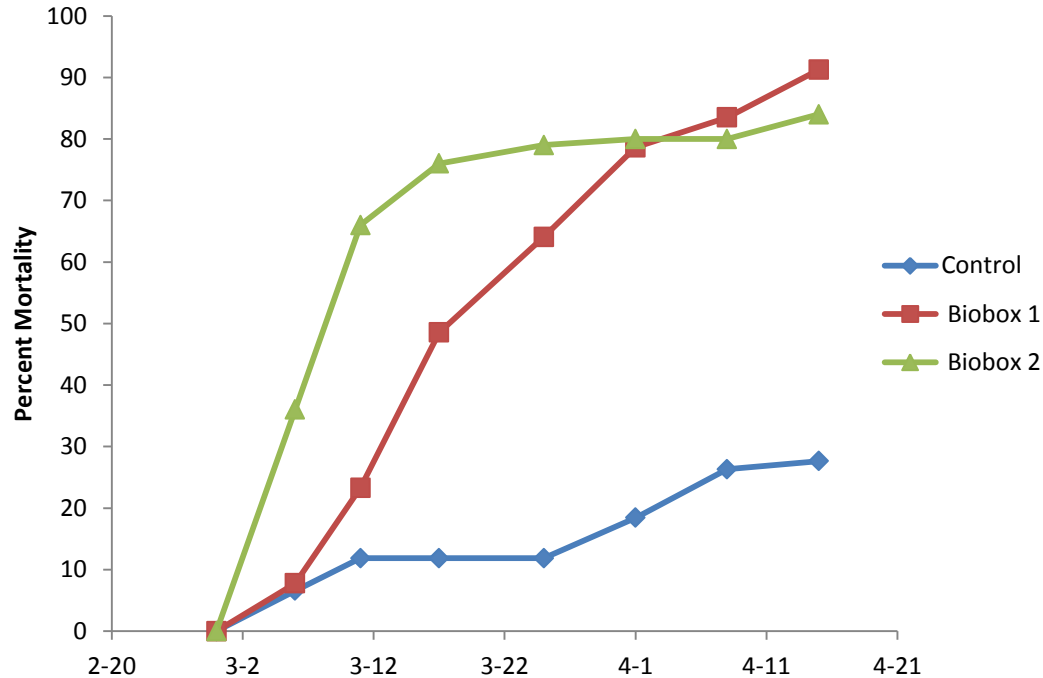
Settlement was present in the treated bioboxes but no settler was larger than 0.5mm. In the control biobox settlers ranged from 0.5mm to 5mm.

Target 20-30ppb



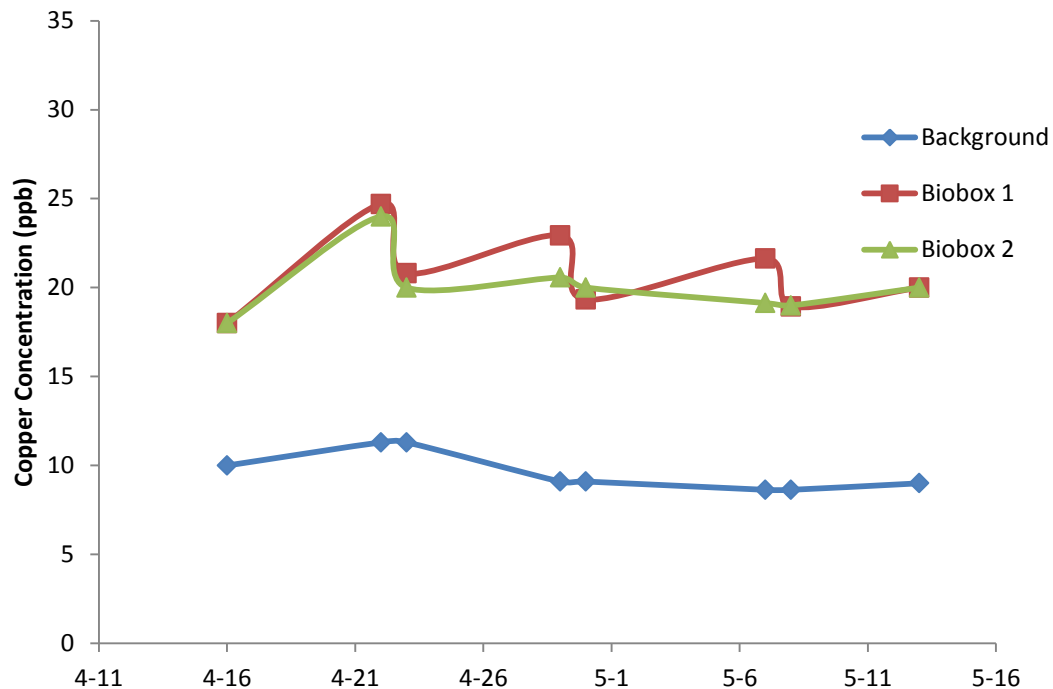
Adult mortality began after the first week of treatment. At the end test biobox 1 had almost 90% mortality of adults, while control had just over 20% mortality of adults.

C4: Adult mussel mortality

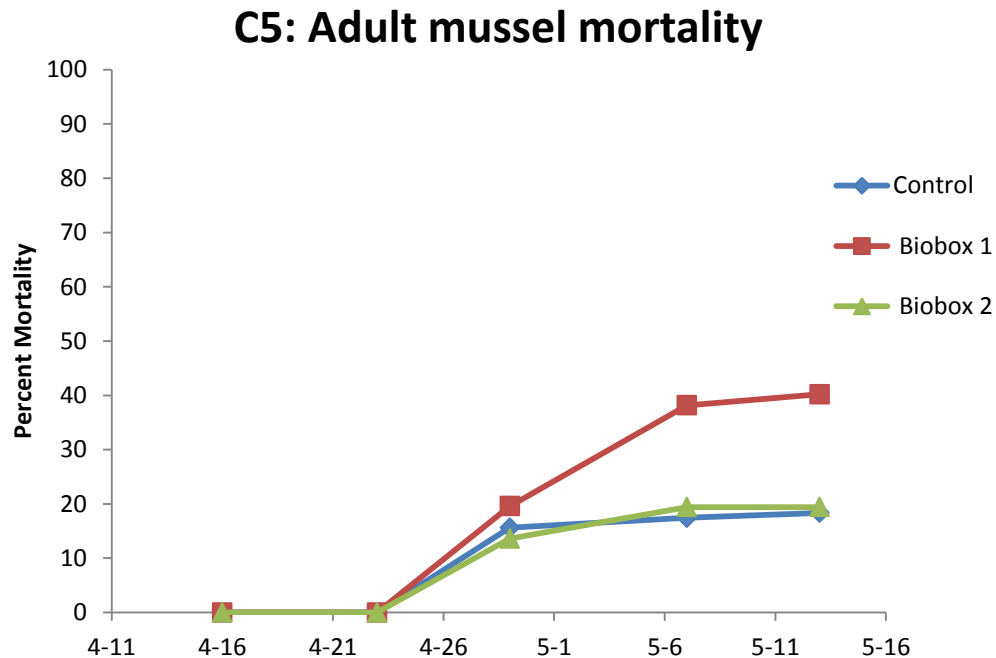


C 5 - started on April 16th, 2014 and ended on May 13th, 2014. The copper level was targeted between 15 and 20ppb. The ambient water temperature was 17°C.

Settlement was present in the treated bioboxes but no settler was larger than 0.5mm while the settlers in the control bioboxes ranged from 0.5mm to 5mm. In terms of absolute settlement numbers there was a significant difference between the treated system and control (p-value 0.03).

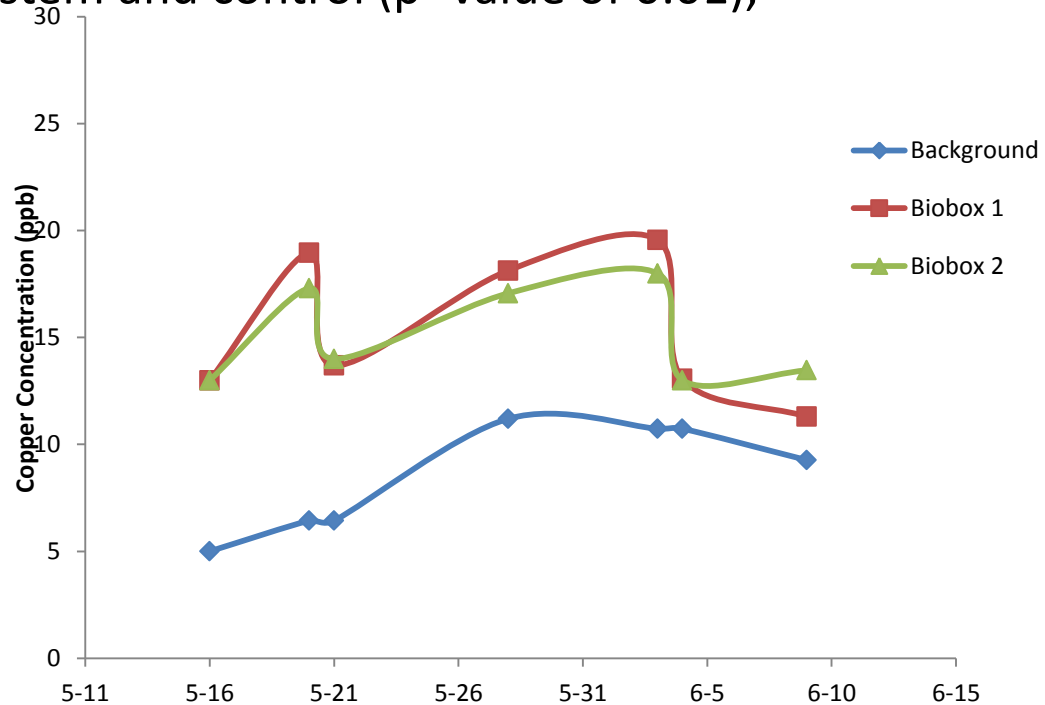


Adult mortality began after the third week of treatment. By the end test biobox had just over 40% mortality of adults, while control had just under 20% mortality of adults.



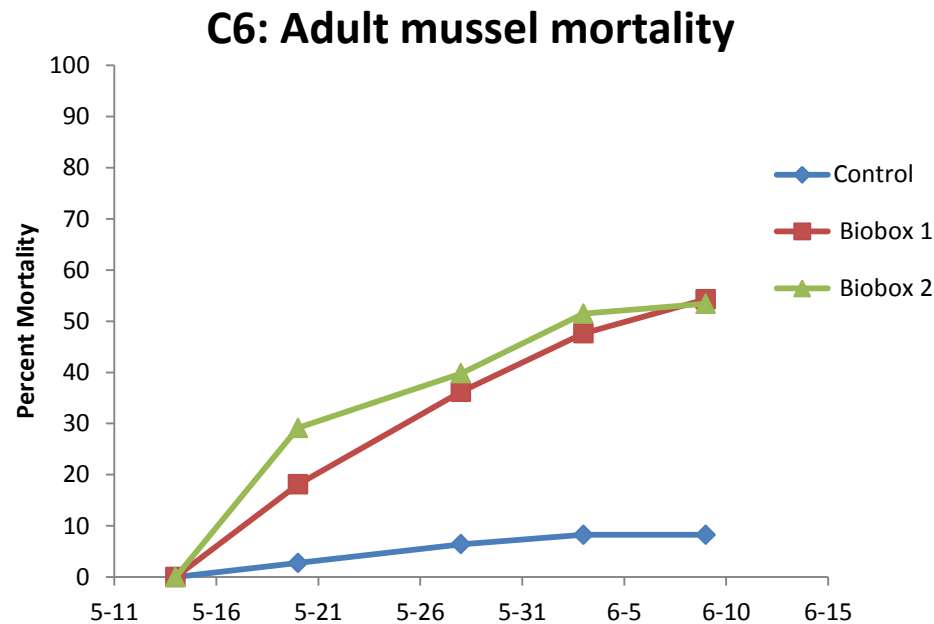
C6 - started on May 14th and terminated unexpectedly on June 9th. An electrical spike appeared to have destroyed the fuse in the copper ion generator and this shut down the copper addition. The copper level targeted was between 10 and 15ppb but has moved between 15 and 20ppb. The ambient water temperature was 19.3° C.

Settlement was present in the treated bioboxes but no settler was larger than 0.5mm while the settlers in the control bioboxes ranged from 0.5mm to 5mm. In terms of absolute settlement numbers there was a significant difference between the treated system and control (p- value of 0.01),





Adult mortality began after the first week of treatment. By the end of the cycle both treated bioboxes had over 50% mortality of adults, while the control had just under 5% mortality of adults.



Summary of Results

- 15 to 20ppb range of copper ions ready to settle veligers settle but quickly expire, hence the lack of size increase on the test settlement plates. Therefore, settlement is inhibited. At this level there appears to be 50% mortality of adult quagga mussels in 4 weeks at ambient temperature of 19°C. However, given the fluctuation in the background levels of copper and the +/- 6ppb reading error of the instrument, it is prudent to speak about an effective concentration range rather than a specific copper ion level.
- 50 ppb range of copper ions appears to cause mortality in adult quagga mussels within days at the same ambient temperature.

Performance of the Copper Ion Generator

- Simple to install
- Small current draw
- Difficult to maintain pre-set level of copper ion addition
- Only manual compensation for increase or decrease in volume of water being treated
- No feed back loop as to how much copper is being generated
- Difficult to inspect the internal state of the generator
- No means of knowing if copper electrodes need to be changed

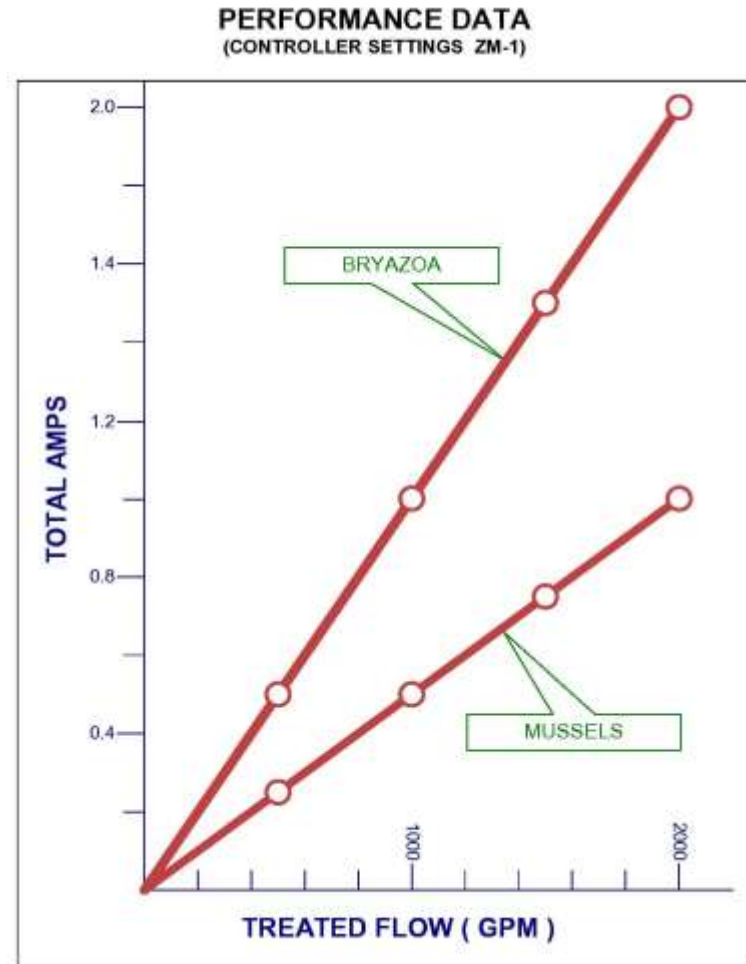
The raw water flow through the generator was set to 13 gpm and the current was adjusted to 1 ampere. Throughout the duration of the evaluation the flow and current were monitored once per day and adjusted as necessary. The flow was in the range of 11 -13.5 gpm which was within the manufacturer's recommended range of 10 - 15 gpm. The current variation during the evaluation was in the range of 0.9 to 1.3 amps.

At the start of the experiments , the discharge water stream from the copper ion generator typically had copper ion concentration of 145 ppb with occasional excursions down to 100 and up to 195 ppb. Based on the concentration of the discharge from the ion generator and a desired concentration of 10 ppb above background, the ZM01 unit should be capable of treating a total flow stream of no more than 200 gpm. This is significantly lower than what we would expect based on the manufacturers manual, which suggests that 1 ampere of impressed current the ZM01 unit would be capable of treating 2000 gpm.

By the end of the experiment the discharge from the ion generator had deteriorated to 80-90ppb while the raw water flow and current were still being maintained within the manufacturer's recommended values.

Performance Evaluation of the Copper Ion Generator

No feedback loop



Copper Generation

Based on the measure concentration of copper from the discharge from the ion generator, if no more than 10 ppb of copper above background was required, the ZM01 unit would be capable of treating a total flow stream of no more than 200 gpm. This is significantly lower than what would be expect based on the manufacturers manual, which suggests that 1 ampere of impressed current the ZM01 unit would be capable of treating 2000 gpm.

State of the Ion Chamber

