Potential Toxicity of Ballast Water Treatment Systems Employing Chlorination of Ballast Water

Gregory P. Ziegler[1] , Daniel J. Fisher[1], and Mario Tamburri[2]

University of Maryland

[1]Wye Research and Education Center

[2]MERC, Chesapeake Biological Laboratory

Maritime Environmental Resource Center
MERC

ABSTRACT

Ballast water treatment technologies are being developed as an important tool in the prevention of invasive species introductions from ballast water discharges. In addition to being effective at killing potential invasive species, a ballast water treatment system must be non toxic to receiving water flora and fauna upon discharge. To satisfy this requirement, the Marine Environmental Protection Committee of the IMO has established the "Procedures for the Approval of Ballast Water Management Systems That Make Use of Active Substances" guidelines (G9). These guidelines include the toxicity testing of algae according to OECD testing method 201, "Algal, Growth Inhibition Test". Several treatment systems involve the chlorination, or electrochlorination, of ballast water followed by either storage until residual active chlorine is minimized, or dechlorination upon discharge to reduce reactive chlorine.

Toxicity testing has revealed that under certain circumstances previously chlorinated water remains toxic to algae after the loss of Total Residual Oxidant (TRO). All toxicity tests were conducted on samples that were chlorinated and stored for five days in the dark. The continued toxicity of dechlorinated estuarine water is species specific with the golden brown algal species *Isochrysis galbana* exhibiting decreased growth after TRO is at, or below detection (DPD method). In contrast similarly treated water was non toxic to the diatom *Phaeodactylum tricornutum*. Toxicity was found in samples that were chlorinated and aged for five days with high initial TRO (8-12 mg/L) and a dechlorination step, as well as in samples with low initial TRO (2 mg/L) and no dechlorination step before testing. Two dechlorinating compounds (sodium thiosulfate and sodium bisulfate) were toxic whether initial chlorination step was by electrochlorination or sodium hypochlorite addition. Neither dechlorinating compound, however, was toxic alone at relevant concentrations, with NOECs of 100 and 200 mg/l for sodium thiosulfate and sodium bisulfite, respectively.

Here we present results from a series of algal toxicity tests conducted to investigate the cause, as well as the extent, of chlorine toxicity to multiple algal species. This toxicity study is part of a larger multi-year project conducted by Maritime Environmental Resource Center, and affiliated institutions, to test ballast water treatment technologies.

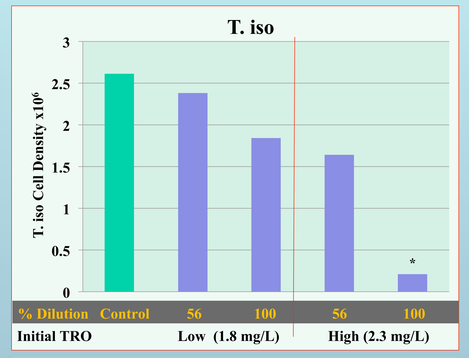

Figure 1. Algal toxicity (T. iso) of sodium hypochlorite in control water. * Statistically different from control. Final TRO ≤ 0.2 mg/L.

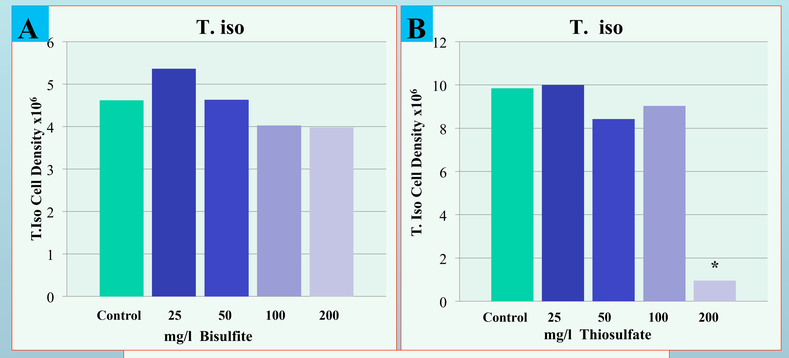

Figure 2. Algal toxicity (T. iso) of sulfur compounds in control water. * Statistically different from control.

Materials and Methods

Algae

- *Isochrysis aff. Galbana* (T. iso) and *Phaeodactylum tricornutum* were obtained from Univ. of Texas: Culture Collection of Algae.
- T. iso is a flagellated golden-brown species.
- *P. tricornutum* is a pinnate diatom.
- Both species were cultured in f/2 media at 15 ppt and tested between 12 and 15 ppt (silicates were added to diatom f/2 media).

Chlorination

- Reagent grade sodium hypochlorite was used for laboratory chlorination.
- Ballast water chlorination (treatments A and B) was achieved by passing a current through a brine slurry following separate proprietary electrochlorination processes.
- Treatment A uses high levels of chlorination (8-12 mg/L) and a dechlorination step (bisulfite or thiosulfate).
- Treatment B uses low levels of chlorination (1.4-3.0 mg/L) and no dechlorination step.

Bioassays

- Tests complied to ASTM guidelines for the testing of microalgae (ASTM, 2006).
- Four replicates were used for each test concentration.
- Final cell counts were made on a hemocytometer and converted to cells per ml for statistical analysis.

Chemical Analysis

- TRO was measured by the DPD method.
- Salinity was measured with a handheld refractometer.

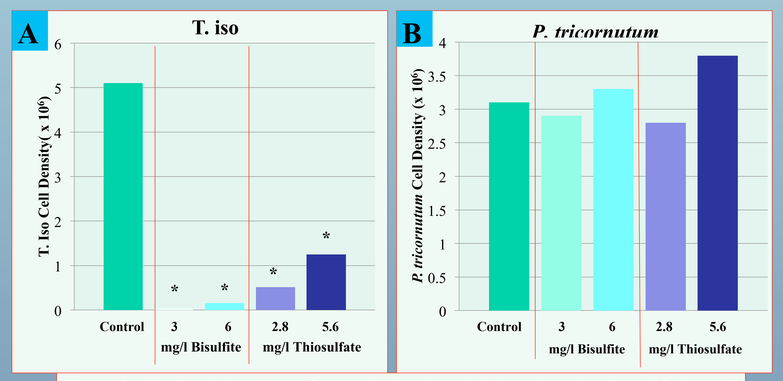

Figure 3. Algal toxicity of control water that has been chlorinated (sodium hypochlorite) and de-chlorinated (sulfur compounds) after 5 days. Initial TRO = 6.9 mg/L. Test species T. iso and *P. tricornutum*. * Statistically different from control.

Results

- Chlorinated (sodium hypochlorite) estuarine water with an initial TRO of 2.3 mg/L remained toxic to T. iso after 5 days holding time with a final TRO ≤ 0.2 mg/L (Fig. 1).
- Bisulfite had no statistically significant effect on the growth of T. iso at any concentration tested (Fig. 2A), while thiosulfate had an effect (Fig. 2B) at the highest concentration (200 mg/l).
- Chlorinated (sodium hypochlorite) estuarine water remained toxic to T. iso after dechlorination with both bisulfite and thiosulfate (Fig. 3A) while showing no toxicity to *P. tricornutum* (Fig. 3B).
- Treatment A caused a reduction in T. iso growth in all 5 trials (Fig. 4) with several trials causing toxicity in ballast water dilutions down to 32% (trials 3 and 4).
- Treatment B caused a reduction in T. iso growth in 3 out of 5 trials (Fig. 5), but only in the 100% concentrations.

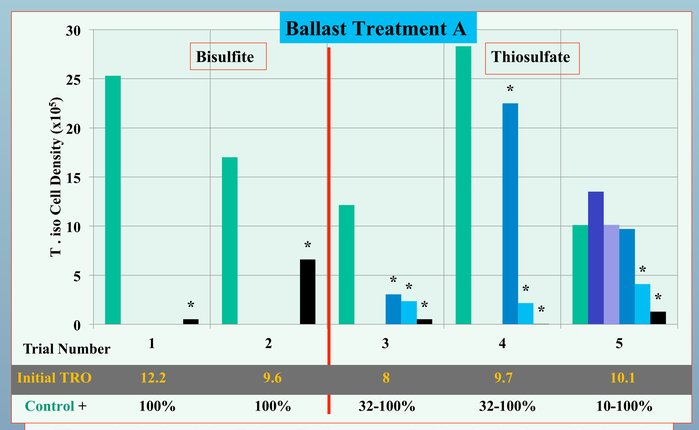

Figure 4. Algal toxicity (T. iso) of ballast water (5 trials) that has been chlorinated (electrochlorination), and de-chlorinated (sulfur compounds) after 5 days in ships ballast. Final TRO < 0.02 mg/L. * Statistically different from control.

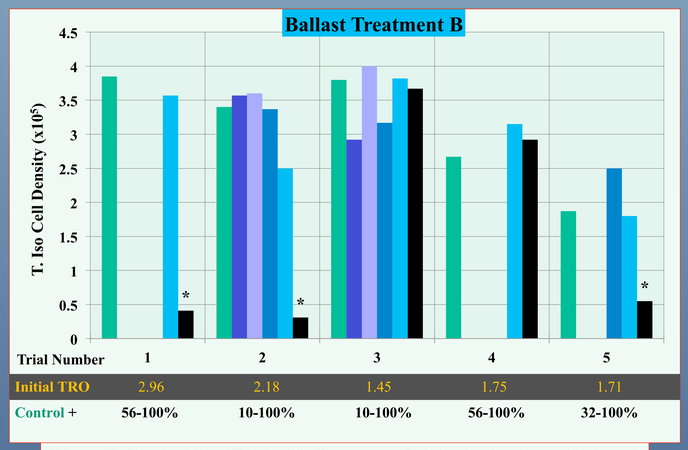

Figure 5. Algal toxicity (T. iso) of ballast water (5 trials) that has been chlorinated (electrochlorination) at a low level (1.4-3.0 mg/L) and held for 5 days. Final TRO < 0.02 mg/L. * Statistically different from control.

Statistical Analyses

- Algal cell counts were converted into cell densities for statistical analysis.
- Statistical analyses was conducted with ToxCalc (TSS, 2006).
- Datasets were tested for normality (Chi Square Test) and homogeneity of variance (Bartlett's Test).
- A *p* value of 0.01 was used for testing the assumptions of normality and homogeneity of variance.
- Mean density values were tested for growth reductions compared to the control treatment with a one-tailed Dunnett's test.
- A *p* value of 0.05 was used for all hypotheses testing .
- NOECs and LOECs were found for average cell density.

Conclusions

- Sulfur compounds that are used to reduce total residual oxidant were not toxic to T. iso at relevant concentrations (Fig. 2). 200 mg/l is several orders of magnitude greater than that used by Ballast Treatment A for dechlorination (~2-6 mg/l) .
- Estuarine water that was chlorinated with both sodium hypochlorite (Fig. 1) and electrochlorination of a brine solution (Fig. 5) remained toxic to T. iso after 5 days and after total residual oxidant was below the detection limit (DPD method).
- Post chlorination toxicity seems to be species specific (Fig. 3) which may result in driving natural algae assemblages toward species which are resistant to the harmful effects of unspecified residual chlorination compounds.
- Treatment A (Fig. 4), with higher levels of TRO, and a dechlorination step, was consistently more toxic to algae than the lower levels of TRO in Treatment B (Fig. 5).
- Toxicity seems to be reduced when initial TRO is below approximately 2 mg/L. This was the case with electrochlorination, as seen in Treatment B (Fig. 5), as well as with sodium hypochlorite (Fig. 1).

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Literature Cited

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