Updated Recommendation for Approval of the Request to Grant a Promising Technology Waiver for Using the Ecochlor® Ballast Water Treatment System on the Moku Pahu

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Executive Summary

The Ecochlor® Ballast Water Treatment System (BWTS) combines Purate® (active ingredients: sodium chlorate and hydrogen peroxide) with sulfuric acid to generate 2,500 ppm of chlorine dioxide (ClO_2) which is fed into the ballast water intake stream to produce a ClO_2 concentration of about 5 mg/L in the ballast water. Sodium sulfate, oxygen, and water are also formed by the reaction. The Water Quality Program (WQP) predicts that a discharge of ballast water treated with the Ecochlor® BWTS will be environmentally safe based upon toxicity test results and the physical controls in the BWTS. Therefore, the WQP recommends that the Washington Department of Fish and Wildlife (WDFW) approve the application for a waiver for use of the Ecochlor® BWTS on the Moku Pahu to allow further evaluation of its effectiveness and environmental safety. The conditions for maintaining waiver approval must include installing and maintaining the physical controls described below. Further toxicity testing of treated ballast water is also a condition of waiver approval and discussed below. Questions about the recommendation or conditions should be directed to Randall Marshall at rmar461@ecy.wa.gov or 360-407-6445.

Results of Toxicity Testing of Seawater Treated by the Ecochlor® BWTS

Toxicity tests assessed chlorine dioxide effects on survival and growth for silverside minnows (*Menidia beryllina*) and mysids (*Americamysis bahia*), survival and normal development for mussel (*Mytilus sp*.) and Pacific herring (*Clupea pallasi*) embryos, germination and germ tube length for giant kelp (*Macrocystis pyrifera*) zoospores, 96-hour population growth for diatoms (*Skeletonema costatum*), and 96-hour survival for Pacific herring larvae. The most sensitive test endpoints were mussel normal-survival with an EC_{50} of 0.22 mg/L ClO_2, kelp germination with an EC_{50} of 0.20 mg/L ClO_2, and kelp germ tube length with an EC_{50} of 0.21 mg/L ClO_2. Herring 96-hour larval survival was the second most sensitive endpoint with an LC_{50} of 0.35 mg/L ClO_2. Mysids were also sensitive with a 7-day survival LC_{50} around 0.5 mg/L ClO_2.

To demonstrate that chlorine dioxide toxicity would degrade under conditions similar to a ballast tank, a lab dosed a San Francisco Bay water sample with ClO_2, stirred it in the dark at 12º C until no ClO_2 was detectable, and tested its toxicity to topsmelt (*Atherinops affinis*), mysids, and mussels. Topsmelt 96-hour survival and mussel normal-survival were unaffected. However, mysid 48-hour survival was only 5% in 100% test solution and 40% in 50% test solution. Freshly prepared test solutions in both the mysid and topsmelt tests had dissolved oxygen and pH gradients. Dissolved oxygen increased by as much as 2 mg/L from the control to 100% test solution while pH decreased by about 0.21 units. This is unexpected and did not occur in the mussel test on treated bay water or in any of the tests on ClO_2 described above. The test temperature was 15º C for mussels, 20º C for topsmelt, and 26º C for mysids. The dissolved oxygen and pH gradients in the mysid and topsmelt tests may be indications of supersaturation of gases due to stirring at 12º C and then warming to test temperature. Supersaturation of gases could have killed the mysids. Mussels are more sensitive to ClO_2 than mysids, and the lack of toxicity to mussels in the simulated ballast water indicates ClO_2 was below its toxic threshold for mysids. Untreated bay water tested concurrently had 100% mysid survival showing that there was no toxicity in the original bay water sample.

To assess the toxicity of an actual ballast water discharge from an Ecochlor® BWTS onboard a ship, two samples of treated ballast water from the Atlantic Compass were tested for toxicity to mysids and mussels and a sample from the Moku Pahu was tested for toxicity to giant kelp and silverside minnows. Testing on one sample from the Atlantic Compass was begun about 95 hours after treatment and testing on the other sample was begun around 195 hours after treatment. Neither sample from the Atlantic Compass adversely affected mussel survival or development. The two Atlantic Compass samples reduced mysid 48-hour survival to an equal degree (NOEC = 25% sample, LOEC = 50% sample, and LC_{50} = 38% sample). Neither mysid test had a dissolved oxygen gradient as described in the paragraph above. The sample from the Moku Pahu was tested 125 hours after treatment and produced no adverse effects to kelp germination or germ tube length or to silverside minnow 7-day survival and growth as measured by biomass. The difference in biomass between the treated ballast water and a lab control was slight (only 15%) but statistically significant. However, treated ballast water biomass was not significantly different from the untreated ballast water biomass providing another indication that the apparent biomass effect may be spurious and not linked to ballast water treatment.

Conclusion

Chlorine dioxide is commonly used by the dairy, beverage, pulp and paper, fruit and vegetable processing, and meat industries to control the growth of microbes. It is also frequently used in municipal potable water treatment facilities and for treating industrial waste. Chlorine dioxide can neutralize or degrade pollutants such as phenols, sulfides, cyanides, thiosulfates, and mercaptans. Unlike conventional chlorination or bromination, ClO_2 does not tend to produce halogenated organics.

The EC_{50} results for the most sensitive test endpoints (mussel normal-survival, kelp germination, and kelp germ tube length) were around 0.2 mg/L ClO_2. The toxic thresholds were sharp and effects disappeared when concentrations reached 0.15 mg/L. Such a sharp threshold makes it easy to set a maximum discharge concentration so that toxicity disappears immediately in the receiving environment. Appendix H, *Establishing the Environmental Safety of Ballast Water Biocides*, of Ecology Publication No. WQ-R-95-80 contains the option of setting a maximum discharge concentration equal to twice the EC_{50} when the toxic threshold is sharp. This option provides a ClO_2 maximum discharge concentration of 0.4 mg/L (twice an EC_{50} of 0.2 mg/L), and somewhere between 1:2 and 1:3 dilution in the receiving water would take 0.4 mg/L ClO_2 below the toxic threshold. A similar amount of dilution would remove the toxicity seen in the 48-hour mysid survival test results from ballast water treated on the Atlantic Compass.

A toxicant other than ClO_2 may have caused the toxicity to mysids seen in the treated San Francisco Bay water and treated ballast water from the Atlantic Compass. Testing on ClO_2 in clean lab water showed mussels to be more sensitive than mysids and yet mussels showed no reaction to the treated Atlantic Compass ballast water or San Francisco Bay water. The lack of toxicity to mussels is not surprising given that the ballast water was aged and the bay water was stirred to allow ClO_2 to react or evaporate from solution. The toxicity to mysids is surprising but not a concern because some toxicity at discharge is good for discouraging living organisms from ballast water and minimal dilution in the environment will readily remove the toxicity. The chemicals used to generate ClO_2 in the lab were different from the chemicals used in the Ecochlor® BWTS on the Atlantic Compass and Moku Pahu and this difference in chemicals could have caused differences in toxicity.

Approval Conditions

Documentation shall be kept and made available to WDFW or Department of Ecology inspectors for verification that the conditions listed below are being met.

Physical controls:

1. The precursor chemicals, Purate® and sulfuric acid, shall only be stored in tanks constructed of compatible materials and provided with secondary containment at least equal to the volume of the tanks. The refill of the precursor chemicals shall only be done by Ecochlor-trained personnel.
2. The programmable logic controller shall be set to provide a ballast water ClO_2 concentration of 5 mg/L. The Ecochlor® system shall also be setup to measure and record chlorine dioxide residuals as a verification of target dose to supplement the operational parameters used to calculate dosage.
3. The pressure transmitter and automatic shut down shall be inspected and maintained so that the system will quickly shut down if the vacuum inside the reaction column is lost.
4. Dedicated logs shall be kept on board and made available of system flows, chemical usage, chlorine dioxide residual, and all system maintenance activities.
5. Ballast water may only be discharged to state waters if it contains 0.4 mg/L or less ClO_2.

Toxicity testing:

6. Any reports on ballast water toxicity testing conducted to meet requirements in the U.S. EPA Vessel General Permit or required by the International Maritime Organization shall also be submitted at the same time to the Washington State Department of Ecology.
7. Once during the promising technology waiver period a mysid (*Americamysis bahia*) 48-hour survival test shall be conducted on a composite of three grab samples taken near the beginning, middle, and end of a treated ballast water discharge.
8. The Department of Ecology may require additional ballast water toxicity tests if deemed necessary to protect state waters.