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# The effects of chemical additives on the production of disinfection byproducts and ecotoxicity in simulated ballast water

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ABSTRACT

The management of ship ballast water is essential to stemming the introduction of non-indigenous species. Approval for onboard installation of a system to treat ballast water requires rigorous land-based testing as dictated in the G8 guideline by the International Maritime Organization. However, this testing lacks standardization—most notably augmentation of organic carbon for influent water by adding chemical additives. Electrochlorination is a popular treatment method for ballast water, in which chlorinated oxidants react with organisms and organic matter in water. The additives could thus affect the treatment efficacy of the ballast water. Here, we examined the effects of several candidates of organic carbon additives on the consumption of total residual oxidant (TRO), the production of disinfection byproducts (DBPs), plankton survival, and ecotoxicity. The TRO consumption over five days of storage was higher in electrochlorinated seawater amended with lignin and Metamucil when compared with seawaters with other organic carbon compounds. DBP production varied by almost two orders of magnitude as a function of the various additives. This was largely attributed to the production of tribromomethane and dibromoacetic acid. The survival of *Artemia franciscana* was significantly different across waters of different organic carbon additives. Algal toxicity testing with the marine haptophyte *Isochrysis galbana* significantly reduced growth in lignin- and Metamucil-treated seawaters, but not with other organic carbon compounds. Bioluminescence in *Vibrio fischeri* sharply declined in electrochlorinated seawaters with all types of organic carbon compounds, but no toxicity was manifested once the electrochlorinated seawaters were neutralized with sodium thiosulfate. The varying degrees of outcome suggest that it might be better to eliminate the requirements of adding organic carbon to test water as long as natural water was used for land-based testing of BWMS. If needed, the additives could be used in proportion to the composition of the organic matter in water being tested.

## 1. Introduction

Ballast water is widely recognized as one of the principal vectors for the introduction and spread of non-indigenous species (NIS). The daily global transport of organisms through ballast water is estimated to be in excess of 10,000 species per day (Carlton, 1985, Carlton, 1999, Ruiz et al., 1997 and Ruiz et al., 2000). The introduction of NIS by international commercial ships including toxin-producing phytoplankton and marine invertebrates can have potentially devastating impacts on recipient ecosystems (Choi et al., 2005, Cohen and Carlton, 1995, Duggan et al., 2005 and McCarthy and Crowder, 2000).

The International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention) (IMO, 2004) is an international effort and a key instrument to address the problem of unwanted organism transport via ship ballast water. The convention, once implemented, requires that qualified vessels be installed with a flag state certified ballast water management system (BWMS). It also dictates that discharged ballast water at the port-of-call contains viable organisms in numbers below specified limits, i.e., the Ballast Water Performance Standard (Regulation D-2). The convention comes with many guidelines including G8 (IMO, 2008) that specifically outlines the approval requirements of BWMS by flag state authorities and G9 by

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IMO (IMO, 2012) for BWMS producing disinfection byproducts.

One of the core elements of the G8 guideline is a regulation on water conditions for BWMS performance testing. The challenge water condition requires specified levels of dissolved organic carbon (DOC) and particulate organic carbon (POC) as well as biological concentrations for test water (e.g., > 5 mg $L^{-1}$ for both dissolved and POC for brackish and seawater). In the event that these concentrations do not meet the required level, additives can be supplemented to augment the organic carbon concentration to meet the challenge water conditions. Although the G8 guidance dictates the concentrations of POC and DOC for test water, it does not specify the chemical additive(s) that should be used to augment water quality. Different land-based test facilities use different additives for this purpose (e.g., lignin, methyl-cellulose, sodium acetate, sodium citrate and glucose, among others) (Delacroix et al., 2013, MEPC 2014).

Various ballast water treatment technologies have been tested at land-based test facilities. Electrochlorination is a popular treatment technology accounting for more than a third of all BWMSs installed on ships (Lloyd's Register, 2012). Electrochlorination relies on the total residual oxidant (TRO) produced during electrolysis of salts in water. The TRO disintegrates over time, but it is sufficiently stable to react with and kill or inactivate organisms. TRO also reacts with organic matter in water to produce disinfection by-products (Gonsior et al., 2015 and Werschkun et al., 2014). Despite these concerns, some studies show that DBPs produced during electrochlorination pose no or low risk to humans or marine/aquatic organisms (Delacroix et al., 2013 and Nanayakkara et al., 2011).

The natural organic carbon content of the water used at the test facility can affect the formation of DBPs. However, the chemicals used to meet test conditions can greatly affect DBP formation because the quantity of the organic carbon added can produce concentrations that are much higher than would be found naturally. The use of various additives has raised concerns from the perspective of the Regulation D-3 of the BWM Convention, which dictates the Final Approval by IMO of BWMS using active substance (e.g., DBPs). The addition of different chemicals at different facilities may produce varying levels and compositions of DBPs even for testing the same BWMS depending on which chemical is added during testing. This can subsequently affect the outcome of human and environmental risk assessments addressing the DBPs. The different concentrations and compositions of DBPs might also affect the performance of BWMSs in terms of killing or inactivation of planktons in test water. These effects would make it difficult to compare the performance of different BWMSs. The best choice for organic carbon additives would be one that consumes TRO and produces DBPs as closely as possible to natural seawater.

Here we used various organic carbon additives for TRO consumption and DBPs produced during electrochlorination of seawater to examine which additives behave in TRO consumption and DBP production similar to natural seawater. We also tested the effects of additives on zooplankton survival and ecotoxicity for standard alga and bioluminescent bacteria. The ultimate goal was to recommend chemical additives for land-based testing for ballast water management system based on the comprehensive results such that the outcome enables objective comparisons of chlorination-based BWMSs.

## 2. Materials and methods

### 2.1. Preparation of test water for electrochlorination

An electrochlorination system capable of treating 1 $m^3$ of seawater per hour was set up on a pier at the Korea Institute of Ocean Science and Technology (KIOST) in Jangmok Bay, Korea. Test seawater (1 $m^3$, salinity 31–32) was prepared for each experiment by pumping the surface water of Jangmok Bay into a 1 $m^3$ polyethylene water tank on the pier. The seawater was pre-filtered through 50-μm mesh Nytex filters to remove large zooplankton. If required, the water temperature was raised to 15 °C with a submersible thermostatic regulator (LifeTech Inc., China).

Natural seawater served as a control with no chemical augmentation, and the other seven test seawaters received additives to increase the level of organic carbon. Starch (Sigma-Aldrich Co., St. Louis, MO, USA, 5.3 g $m^{-3}$) has low solubility (< 2% at room temperature, Takahashi and Seib, 1988), and it was added to all waters except for the seawater control. Six different chemical additives were also used to increase the carbon concentration in each seawater with starch: glucose (Sigma-Aldrich Co., St. Louis, MO, US, 3.3 g $m^{-3}$), lignin (Yugin Chemical Co., Korea, 31.5 g $m^{-3}$), sodium acetate (Junsei Chemical Co., Japan, 20.5 g $m^{-3}$), sodium citrate (Daejung Chemicals & Metals Co., Korea, 22.2 g $m^{-3}$), Metamucil (known as Psyllium seed husks, P & G, Cincinnati, OH, USA) and methylcellulose (Sigma-Aldrich Co., St. Louis, MO, US, 17.1 g $m^{-3}$).

Pre-cultured *Artemia franciscana* is a brine shrimp (INVE aquaculture, Nonthaburi Thailand) that was added at > $10^5$ individuals per $m^3$. *Tetraselmis suecica* is a marine green alga and was also added as food for *A. franciscana* at 500–700 cells $mL^{-1}$ to each tank with different additives and control. The *Artemia franciscana* were hatched from dehydrated cysts. During cyst development, a water bath was used to maintain a temperature of ~25 °C for 2 days with continuous aeration (Madhu, 2009). The freshly hatched cysts were then carefully separated from the remaining cysts. The zooplankton culture was added to the seawater immediately before electrochlorination.

### 2.2. Electrochlorination and TRO and DBP production

Next, 1 $m^3$ of the eight different test waters (1 seawater control, 1 seawater with starch added, and each of 6 different additives) was injected at 1 $m^3$ $h^{-1}$ into a 4.5 L electrochlorination chamber consisting of a $TiO_2$ electrode coated with ruthenium (NewWater Tech Inc., Korea) at a current density of 4.7 A on average ( ± 0.3 for standard error) to produce 10 ppm TRO. The contact time of the seawater with the electrodes in the chamber was about 15–16 s. At an interval of 20 min, the electrochlorinated seawater was collected in 10 L jars separately (three replicates in total), and these were then stored at 20 °C for 5 days in the dark as required by IMO G8 and G9 guidelines (IMO 2008; IMO, 2012). The TRO would react with organic carbon in the seawater and produce DBPs during the storage period until TRO is exhausted. Glass amber bottles (1 L, DURAN Group GmbH, Germany) were used to collect electrochlorinated waters. Following the 5-day incubation in the dark, the chlorinated waters were immediately neutralized by adding sodium thiosulfate (40 g $L^{-1}$) at 1:500 volume/volume ratio into the bottles.

The preparation of test water and the experiments could not be done simultaneously; they lasted about 2 weeks. The bay water contained low concentrations of DOC (< 2 ppm) and POC (~1–2 ppm) (Cha et al., 2015) with little temporal variation (e.g., no high discharge of freshwater during the experiments). Therefore, the variability of DOC in the natural seawater would have little effect on the electrochlorination results.

### 2.3. Water quality parameter measurements

A YSI 6000 multi-parameter water quality Sonde with temperature, salinity, dissolved oxygen, and pH sensors (YSI Inc., Yellow Springs, OH, USA) was placed in the test water tank during each treatment cycle. The temperature and salinity of the test waters were recorded prior to each test. The electrochlorinated water was collected every 10 min into 500 mL glass beakers. The TRO concentrations (e.g., free hypobromous and hypochlorous acid/ion and chloramines) in the electrochlorinated waters were measured by the colorimetric DPD-method (Hach Method 8167) (Buchan et al., 2005). The TRO concentrations varied only slightly over one-hour of operation for each test (< 1 ppm for standard deviation, Fig. 1). The method is based on the oxidation of *N*,*N*-diethyl-*p*-phenylendiamin (DPD), which turns to a