



## Long-term algal toxicity of oxidant treated ballast water

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### ABSTRACT

National and international regulations require that ships' ballast water is treated to minimize the risk of introducing potentially invasive species. A common approach employed by commercial ballast water management systems is chlorination. This study presents the algal toxicity findings for three chlorination-based BWMS and their implications to environmental safety of port waters receiving treated ballast water from ships. Discharged treated ballast water from all three BWMS was toxic to algae with IC25s (25% growth inhibition) ranging from 9.9% to 17.9%, despite having total residual oxidant concentrations below 0.02 mg/l, based on Whole Effluent Toxicity assays. When held at 4 °C, some of the ballast water samples continued to exhibit toxic effects with no observed effect concentrations as low as 18% after a 134 day holding time. Thirteen individual disinfection by-products were measured above the detected limit at the time of discharge. No correlation between DBPs and algal toxicity was observed.

### 1. Introduction

Ballast water is used by modern ships to maintain balance, maneuverability and structural integrity. However, the discharge of ballast water can lead to the release of a variety of non-indigenous species (NIS) at ports around the world (Ruiz et al., 1997). Introduced NIS propagules can lead to invasions and result in extensive economic, ecological, and human health impacts (Carlton, 1985; Ruiz et al., 1997, 2000; Drake et al., 2007). Although there are a number of unquantified variables (NRC, 2011), the implementation of ballast water management strategies, such as open ocean ballast water exchange (BWE) and ballast water treatment, can limit invasion success by reducing the number of propagules discharged in ballast water. Assuming a dose-response relationship for propagule pressure and establishment success, a reduction in establishment of new invasive species is expected with reduced propagule supply (Ruiz and Carlton, 2003; Lockwood et al., 2005).

To address this significant environmental and economic problem, the U.S. Coast Guard and the International Maritime Organization (IMO) have established ballast water regulations to minimize the introduction of potentially invasive species from ships. The International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention) of the IMO (IMO, 2004, 2008a, 2017a), and similar regulatory instruments implemented by individual countries (e.g. USCG 33 CFR 151, 2012; USEPA Vessel General Permit, 2013;

NZMPI, 2016), require ships to treat their ballast water with certified Ballast Water Management Systems (BWMS) and to meet numeric discharge standards for live organisms in different size classes. To date, over 70 BWMS have been Type Approved by IMO, and the USCG has Type Approved six systems. Approximately 26% of the 69 IMO Type Approved BWMS use some form of chlorination (e.g. electrochlorination, dichloroisocyanurate dihydrate, hypochlorite), and almost all of these systems have the ability to neutralize treated water before discharge. Procedure (G9) of the BWM Convention, "Procedures for the Approval of Ballast Water Management Systems That Make Use of Active Substances" (IMO, 2004), calls for an overall review of BWMS including environmental safety of discharged ballast water. Under Procedure (G9), BWMS are evaluated following a methodology specifically designed for evaluating BWMS (IMO, 2012). The Methodology calls for toxicity testing of discharged ballast water with a vertebrate, invertebrate and algal species according to internationally accepted toxicity test methods (e.g. OECD, ISO, USEPA).

Toxicity test results from scientific presentations (Ziegler et al., 2010) and peer-reviewed journal articles (Delacroix et al., 2013; Park et al., 2017), as well as toxicity test data submitted by BWMS manufacturers for Procedure G9 review ([www.imo.org](http://www.imo.org)), show frequent algal toxicity of discharged ballast water when strong oxidants are employed as the treatment biocide. Algal toxicity testing outside of the ballast water realm has also shown that chlorinated water can remain toxic to micro algae after the loss or neutralization of TRO (Gentile et al., 1976;

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Sanders, 1984; Ziegler et al., 2010; Lee et al., 2015; Rhie, 2016).

The chemistry of chlorinated fresh water is complicated, involving a cascade of reactions which can lead to small, well defined disinfection by-products (DBPs), as well as larger halogenated organic molecules that are not typically identified during DBP analysis (Richardson, 2003). The production of DBPs results from the interaction between oxidants and natural organic matter (NOM) in water (Westerhoff et al., 2004). The addition of chlorine to fresh water results in rapid hydrolysis, forming active chlorine ( $\text{HOCl}$  and  $\text{OCl}^-$ ) and leading to chlorinated DBPs in fresh water, with the inclusion of brominated DBPs (after reaction with  $\text{HOBr}$  and  $\text{OBr}^-$ ) in estuarine and marine waters (Ichihashi et al., 1999; Nokes et al., 1999; Werschkun et al., 2012; Shah et al., 2015). The quantity and type of DBPs can vary and is related to multiple factors including oxidant type/dose, contact time, dissolved organic matter (DOM) concentration and composition, temperature, bromine content and pH (Chowdhury et al., 2009; Shah et al., 2015; Hao et al., 2017). Research has identified smaller traditional DBPs as well as over 600 higher molecular weight DBPs in drinking water (Richardson, 2011; Zhai and Zhang, 2011; Ding et al., 2013), and 462 brominated DBPs in ballast water following treatment by electrochlorination (Gonsior et al., 2015). There is also the possibility of oxidant reactions with other pollutants found in urban waters which can result in additional halogenated compounds (Benitez et al., 2011; Acero et al., 2013; Heeb et al., 2014).

The vast majority of available information on toxicity of chlorination based BWMS is from dossiers submitted to IMO (IMO, 2016a) during the IMO approval process under Procedure G9 (IMO, 2008b). Typically, DBP analysis and toxicity testing of treated ballast water is conducted at 0, 1 or 2 days, and 5 days (to link with IMO G8 Guidelines for efficacy testing), and is assumed to incorporate the “worst case scenario” for DBP concentrations. Ballast water risk assessments include possible toxic effects of individual DBPs measured in ballast water, while combined effects of DBPs and any residual oxidant are addressed with whole effluent toxicity (WET) testing, which is considered a more realistic measure of mixture toxicity of effluents (Johnson et al., 2006).

The persistence of algal toxicity in discharged ballast water after 5 days has not been addressed scientifically. A review of available data revealed that there can be an increase in some DBPs over a 5-day holding time (IMO, 2014), presumably as a result of the continuing interaction between organics and TRO, or as breakdown products of larger halogenated molecules. To the authors' knowledge, no long-term (i.e. > 5 days) toxicity testing or DBP analysis of treated ballast water has been conducted. Here, we present the results of algal toxicity tests conducted in 2015 and 2016 from 3 different oxidant-based BWMS, investigating the longevity of treated ballast water toxicity after storage at 4 °C. BWMS tests were conducted in accordance with the collaborative USEPA/USCG, Environmental Technology Verification (ETV) Protocol (USEPA, 2010). Smaller traditional DBP compounds (haloacetic acids (HAAs), haloacetoneitriles (HANs) and trihalomethanes (THMs)) were only measured at the time of discharge in an attempt to correlate observed toxicity to the initial concentration of DBPs.

## 2. Materials and methods

### 2.1. Test site facility

The test site facility was located in Port Covington, Baltimore, Maryland, USA, adjacent to a large commercial port in an industrial area of Baltimore City. Estuarine salinities at this location are typically in the range of 5–11 psu. The testing of each BWMS was carried out following USCG performance standards outlined in the ETV protocol (Table 1). Control and treated ballast tanks were thoroughly cleaned by pressure washing between all treatment events, and all piping was flushed with potable water from a municipal source.

### 2.1.1. Uptake

Test waters were drawn from the surface of Winans Cove (Baltimore, MD, USA) through a flexible inlet pipe allowing uptake from different depths. There was no manipulation or addition to the natural plankton community. However, dissolved organic carbon (DOC), total suspended solids (TSS), and particulate organic carbon (POC) were enhanced to coincide with ETV challenge water conditions. Amendment of uptake water included the addition of sodium citrate dihydrate (Fisher Scientific, USA), Arizona fine test dust (Arizona Powder Technology, Inc.; Burnsville, Minnesota) and Micromate-micronized humate (Mesa Verde Resources; Placitas, New Mexico) for increasing DOC, TSS, and POC, respectively (Table 1). A slurry containing TSS, POC and DOC amendments was injected during ballast water uptake before separating into untreated and BWMS treated ballast water lines. The slurry was mixed with a propeller mixer (Brawn™ Mixer Inc., model MD75-870) in a cone-bottom HDPE tank (1.1 m<sup>3</sup>). Delivery of slurry into the ballast water uptake line was by peristaltic pump (Eccentric Pumps LLC, model SLP-218). The exact slurry recipe was based on estimates of ambient water conditions, targeted flow rate through the intake pipe, and tank volume. Water was taken from the surface with no manipulation of ambient salinity. Control and treated waters were delivered to independent control and treated water ballast tanks, and held for 48 h (Systems 1B, 2 and 3), or 72 h (System 1A) in closed ballast tanks.

### 2.1.2. Discharge

At discharge, untreated water samples were collected in 20-l polycarbonate carboys directly from a hatch on the untreated ballast tank for use as control and dilution water in toxicity tests. A continuous, time integrated sample of treated ballast water was collected by an in-line sample port and delivered to a 100-l fiberglass sample container. The treated water sampling was conducted during the entire treated water discharge process of approximately 1 h. When necessary to meet the local TRO discharge standard, treated water was neutralized by the BWMS before sample collection. Treated samples were collected from the 100-l container by gravity flow into 20-l glass carboys, which were immediately transferred to ice filled coolers for transport to the University of Maryland Wye Research and Education Center (WREC) for toxicity testing.

## 2.2. Ballast water management systems

Three BWMS (Systems 1, 2 and 3) were tested that employed filtration and treatment with strong oxidants (Table 2). Systems 1 and 3 employed in-situ electrochlorination, and System 2 used sodium dichloroisocyanurate dihydrate (DICD) granules dissolved in water with direct injection of the disinfecting solution. Each BWMS had a target TRO dose, or an initial TRO dose range, for treatment of ballast water during uptake. System 1 was tested at two different target TRO doses, 6 mg/l (System 1A) and 8 mg/l (System 1B). System 2 had a target TRO dose between 11 and 13 mg/l, and System 3 had a target TRO dose of 15 mg/l (Table 2). After treatment, water was held in ballast tanks for 2 days (Systems 1B, 2 and 3) or 3 days (System 1A). Each system had the ability to add neutralizer during discharge to keep the TRO below 0.1 mg/l, the local maximum acceptable discharge limit, in accordance with the local discharge permitting authority, the Maryland Department of the Environment (MDE). Neutralization of TRO in discharged ballast water with sodium sulfite (System 1A) or sodium bisulfite (Systems 1B, 2 and 3) injection was adjusted by the BWMS.

## 2.3. Chemical analysis

### 2.3.1. POC, DOC and TSS

Chemical analyses of POC, DOC and TSS were carried out for each BWMS on water collected at uptake, both before and after the addition of compounds, to reach ETV minimum POC, DOC and TSS

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