



Disinfection by-products and ecotoxicity of ballast water after oxidative treatment – Results and experiences from seven years of full-scale testing of ballast water management systems

Stephanie Delacroix^{*}, Christian Vogelsang, August Tobiesen, Helge Liltved

Norwegian Institute for Water Research, Gaustadalleen 21, 0349 Oslo, Norway

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ABSTRACT

Since 2005, five different ballast water management systems (BWMSs) based on chlorination treatment have been tested by Norwegian Institute for Water Research (NIVA) according to guidelines from the International Maritime Organization (IMO). 25% and >50% of all the tested discharge samples exhibited acute and chronic toxic effects on algae, respectively. In most cases this toxicity was plausibly caused by a high free residual oxidant (FRO) level (>0.08 mg Cl/l). Of the 22 disinfection by-products (DBPs) that were identified in treated water at discharge, four compounds were at times found at concentrations that may pose a risk to the local aquatic environment. However, there seemed to be no clear indication that the measured DBP concentrations contributed to the observed algal toxicity. The addition of methylcellulose instead of lignin in the test water to comply with IMO requirements seemed to limit the formation of DBP.

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1. Introduction

More than 80% of world's commercial products are transported overseas by ships also carrying between 3 and 5 billion tons of ballast water around the world each year (Globallast, 2000). An estimated 7000 different marine and coastal species are transported as stowaways across the world's oceans every day in ballast water (Carlton, 1999), and 84% of the world's marine ecoregions have already reported findings of so-called "invasive marine species" (WWF, 2009). The discharge of ship's ballast water has been recognised as a major vector for invasive aquatic species spreading into new environments (Ruiz et al., 1997). Invasive marine species discharged into a new environment may threaten the native ecological balance, affect local economic activities such as fisheries, and even cause human fatalities. For example, the European zebra mussel has infested over 40% of internal waterways in USA (Globallast, 2000). By invading and clogging water intake pipes, water filtration and electric generating plants, the mussel might cause 1 billion dollars cost per year (Pimentel et al., 2005).

In order to address this challenge, the International Maritime Organisation (IMO) has adopted the international convention for the control and management of ships ballast water and sediments (IMO, 2004). This convention requires that ballast water quality shall meet strict standards regarding number of viable organisms and residual toxicity at the time of discharge.

An estimated number of 57,000 maritime vessels will have to install a type-approved ballast water management system (BWMS) by the end of 2020 if the convention is finally ratified (Royan, 2010). The convention will come into force 12 months after 30 countries representing 35% of the world merchant shipping tonnage have ratified it. To date, 37 countries representing 29% of the world merchant tonnage have signed.

According to Lloyd's register, a total of 68 different ballast water treatment systems were available to serve this marked in September 2012. Of these, 21 systems apply UV irradiation as the main disinfection process, 23 systems apply electrochlorination by electrolysis of saline water, 6 are based on ozonation, 5 apply deoxygenation, 3 apply chlorination using a chlorine containing solution and 10 other technologies are applying heating or non-chlorine chemical disinfection. This means that 30% of the technologies are based on UV treatment, while 45% are using chlorine as the active substance.

If active substances are used as disinfectant, IMO requires the manufacturers to document the potential toxicity risk of treated ballast water to the aquatic environment and to human health, including the ship crew and swimmers (IMO, 2008c,d). According to the guidelines, all BWMS should be tested at a land-based testing facility by an independent part using at least two different test water types (seawater, brackish water and/or freshwater) with elevated content of dissolved and particulate organic matter, and a minimum of five test cycles should be conducted with each water type. Both ecotoxicological tests and chemical assessment of DBPs in ballast water at discharge have to be included.

^{*} Corresponding author.

E-mail address: sde@niva.no (S. Delacroix).

The chemistry of chlorinated fresh water is very different to the chemistry of chlorinated seawater and brackish water. In fresh water, applied chlorine will be hydrolysed into hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), which are the main active substances and will co-exist in a pH dependent equilibrium. By introducing chlorine to seawater systems, a series of redox-reactions take place, and several reactive intermediates are formed. Chlorine can rapidly oxidise bromide ion (Br^-) and iodide ion (I^-) to form aqueous bromine (HOBr/OBr^-) and aqueous iodine (HOI/OI^-), respectively (Westerhoff et al., 2004). The bromide ion, in concentrations of 60–70 mg/l in seawater, gives a high formation potential of bromine (HOBr/OBr^-) which is the main active substances in chlorinated seawater. In seawater with a typical pH of 8, hypobromous acid (HOBr) will predominate and be the most important disinfectant with a half-life of hours to days dependent on light conditions and water quality characteristics (Liltved et al., 2006).

Ballast water contains various amounts of natural organic substances that, dependent on local conditions, may be oxidised to halogenated organic compounds such as trihalomethanes (THMs) and other disinfection by-products (DBPs). The DBPs most frequent found in chlorinated seawater are bromoform, dibromoacetic acid, bromoacetonitrile and traces of bromophenols (Fabbicino and Korshin, 2005; Bowmer and Linders, 2010; Shi et al., 2013). Several DBPs might be harmful to aquatic animals and humans because of their potential carcinogenic and mutagenic effects (Richardson et al., 2007), and are regulated in drinking water and bathing water standards (WHO, 2003, 2011). Some DBPs can be persistent in the marine environment and may bio-accumulate in food chains (Gregg et al., 2009). The amount of organic DBPs in chlorinated ballast water is mainly dependent on the oxidant type and dosage and on the type and concentration of natural organic matter in the local ballast water (Gregg et al., 2009; Ichihashi et al., 1999). The high reactivity of hypobromous acid can create a variety of brominated DBP compounds in chlorinated and ozonated marine water (Werschun et al., 2012). In order to address this DBP formation potential when active substances are used for ballast water treatment, the joint Group of Experts on the Scientific Aspects of Marine Environmental Protection-Ballast Water Working Group GESAMP-BWWG has suggested a preliminary list of 18 compounds to be assessed in all BWMS tests before final approval (IMO, 2009a).

Several authors have addressed the formation potential of DBPs in chlorinated and ozonated ballast water (Gregg et al., 2009; Bowmer and Linders, 2010; Tsolaki and Diamadopoulos, 2009). However, there is a lack of information about the causes and mechanisms of DBP formation, and the effects of different DBPs to the marine aquatic environment. These deficiencies have also been pointed out by Werschun et al. (2012). Previous work do not address the effect of concentration and nature of organic precursors on DBP formation potential, and do not compare observed toxicological effects to concentration levels of DBPs in an attempt to explain causes of toxicity. It is evident that the formation potential of different DBPs may vary considerably from test site to test site dependent of the nature of additives used to comply with the requirements regarding organic content of test water. Additives used include natural sediments from the seafloor, lignin, humic acids and a starch mixture. No previous published work has focused on the connection between the nature of the organic additive used and the abundance of various DBPs found in chlorinated ballast water.

Since 2005, five different ballast water management systems (BWMS) based on chlorination treatment have been tested at the Norwegian Institute for Water Research's (NIVA) test facility according to guidelines from the IMO. In this paper, the results from toxicity tests and DBP analyses of chlorinated ballast water during the full scale testing of these BWMS are presented. The objective of the work was to evaluate a possible correlation be-

tween measured concentrations of various DBPs detected in treated ballast water and the oxidant dosage used or the oxidant consumption by the ballast water, as well as attempting to identify the main factor causing elevated levels of certain DBPs in ballast water at the time of discharge. A further objective was to find out if the DBPs found in treated ballast water could pose a risk to the marine aquatic environment.

2. Material and methods

2.1. Tested ballast water management systems

The five BWMS reported here all included treatment with active substances (e.g. hypochlorous acid, hydroxyl radicals) in combination with cavitation, ultrasonic treatment or similar, and always with filtration as pre-treatment. The active substances were introduced either by direct injection or by in situ production. The latter was done by electro-chlorination or similar. During discharge, only physical treatment or neutralisation was applied, except for one BWMS that did use active substances, hence increasing the level of total residual oxidants (TRO) to a maximum of 2.0 mg/l at discharge. Each BWMS was operated by its vendor, but with inspection during operation by NIVA staff personnel to confirm and report operating parameters.

2.2. Test site facilities for full scale land-based tests

NIVA's test site facility located at Solbergstrand 20 km south of Oslo with direct access to seawater was used for the full scale land-based tests. The facility consists of four circular glass-fibre reinforced polyester tanks; one of 516 m³ for test water preparation, and three others of 231 m³ each for treated and control water (Fig. 1). The surfaces of the tanks are coated with coatings for ships (Balloxy HB light, Jotun, Norway).

2.3. Chemical water quality of test waters used in full scale land-based tests

Test waters with high and medium range salinities were prepared following the requirements stated in the IMO G8 guidelines (IMO, 2008a,b,c). The chemical requirements to the two test water types are shown in Table 1. Seawater for the tests was pumped up from 60 m depth in the Oslofjord. To obtain the required salinity content of the brackish water (20–22 PSU), water was prepared by mixing seawater from 1 m depth in the fjord with freshwater.

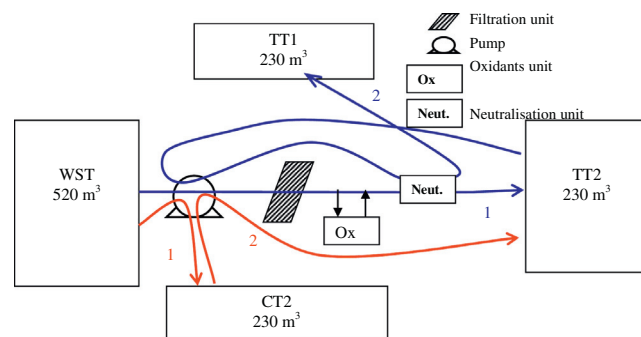


Fig. 1. Transfer of test water during a test cycle with a BWMS including filtration, oxidation (chlorination) and neutralisation units. Blue line 1 indicates the day 0 ballasting operation of treated water, whilst blue line 2 indicates the day 5 discharge operation of treated water. Red line 1 indicates the day 0 ballasting operation of control water. Red line 2 indicates the day 5 discharge operation of control water. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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