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# Risk assessment of human health from exposure to the discharged ballast water after full-scale electrolysis treatment

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The presence of disinfection by-products (DBPs) releasing from ballast water management systems (BWMS) can cause a possible adverse effects on humans. The objectives of this study were to compute the Derived No Effect Levels (DNELs) for different exposure scenarios and to compare these levels with the exposure levels from the measured DBPs in treated ballast water. The risk assessment showed that when using animal toxicity data, all the DNELs values were approximately $10^3$–$10^{12}$ times higher than the exposure levels of occupational and general public exposure scenarios, indicating the level of risk was low (risk characterization ratios (RCRs) < 1). However, when using human data, the RCRs were higher than 1 for dichlorobromomethane and trichloromethane, indicating that the risk of adverse effects on human were significant. This implies that there are apparent discrepancies between risk characterization from animal and human data, which may affect the overall results. We therefore recommend that when appropriate, human data should be used in risk assessment as much as possible, although human data are very limited. Moreover, more appropriate assessment factors can be considered to be employed in estimating the DNELs for human when the animal data is selected as the dose descriptors.



## 1. Introduction

The introduction of invasive marine species into new environments via ships' ballast water has been identified as one of the greatest threats to the world's oceans (Bax et al., 2003; Ricciardi, 2006; Molnar et al., 2008; Hulme, 2009; Bradie et al., 2010; Carbona et al., 2010; Bailey et al., 2011). Upon discharge during de-ballasting, nonindigenous invasive species (NIS) may develop and become established in the new receiving environment with high propensity, causing serious ecological problems (Briski et al., 2013; Pam et al., 2013). Many experts consider invasive marine species to pose a greater threat to the environment than oil pollution (North of England P&I Association, 2009). Furthermore, aquatic NIS are a significant and growing contributor to the global spread of red tide blooms (Briski et al., 2013), and cause enormous ecological and economic damage (Ruiz et al., 2000). To reduce the risk of ballast water introductions, the International Maritime Organization (IMO) has proposed discharge standards limiting the maximum concentrations of living organisms (Miller et al., 2011). As a result, developers and manufactures have been producing onboard ballast water management systems (BWMS).

The predominant technologies for ballast water treatment generally consist of filtration plus electrolysis, UV irradiation, cavitation and/or ozonation (Lloyd's Register, 2012). Both electrolysis and ozonation are highly effective for the removal of harmful organisms; however, the majority of these systems generate disinfection by-products (DBPs) in varying amounts (Banerji et al., 2012). Several DBPs have been proven to be carcinogens and mutagens to humans (Wang et al., 2013; Delacroix et al., 2013). Consequently, humans may be exposed to treated ballast water containing DBPs in the workplace (occupational exposure) or from the use of consumer products (consumer exposure) and indirectly

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via the environment (Banerji et al., 2012; Werschkun et al., 2012). Many research studies have paid attention to the human health risks posed by trihalomethanes (THMs) in drinking water (Wang et al., 2007; Basu et al., 2011). The US Environmental Protection Agency (EPA) and the World Health Organization (WHO) have established regulations for DBPs (e.g., THMs, haloacetic acids (HAAs)) control in drinking water.

However, specific discharge standards limiting are unavailable for DBPs in treated ballast water. Although the exposure level of treated ballast water is much lower than drinking water, seawater generally has higher brominated DBPs formation potentials, most likely because the amounts of bromide ion and natural organic substances are higher than those in drinking water (Delacroix et al., 2013). Echardt and Kornmuller (2009) reported that the concentrations of THMs, HAAs and bromate generated by electrolytic chlorination BWMS were as high as 338.25, 69.64 and 55.25 μg/L, respectively. For ozone-based BWMS, the concentration of bromate was as high as 490 μg/L when the total residual oxidant (TRO) level was 6.4 mg/L as $Cl_2$ in seawater (Maritime Environment Protection Committee, 2012), which is 49 times higher than the WHO guideline value of 10 μg/L (World Health Organization, 2011).

According to Lloyd's Register (2012), 29% of the technologies are based on electrolysis; while 27% are applying UV irradiation as the main disinfection process and 44% other technologies are based on ozonation, deoxygenation, heating and nonchlorine chemical disinfection (Delacroix et al., 2013). This means that electrolysis-based BWMS are dominant technologies in this marked. Biological inactivation by electrolysis-based BWMS achieved the D-2 performance standard of the Ballast Water Convention (i.e., discharging less than 10 viable organisms $\geq$ 50 μm per $m^3$; less than 10 viable organisms $\geq$ 10 to $<$50 μm per mL; less than 1 colony forming unit (cfu) of toxicogenic *Vibrio cholerae* (O1 and O139) per 100 mL; less than 250 cfu of *Escherichia coli* per 100 mL; and less than 100 cfu of intestinal Enterococci per 100 mL) (International Maritime Organization, 2004) when the TRO level was approximately 7.5–9.5 mg/L as $Cl_2$ (Maritime Environment Protection Committee, 2009). In addition, aquatic toxicity tests for organisms of three trophic levels were conducted to confirm that there were no detectable toxic effects on algae, invertebrates, or fish, indicating that the effects of treated ballast water were acceptable when discharged (Maritime Environment Protection Committee, 2009). According to IMO G9 procedure (International Maritime Organization, 2008a), electrolysis-based BWMS have to provide human health risk assessment, and many of these health risk assessments provided limited toxicological information on many DBPs or used only animal toxicity data required for effects assessment (Banerji et al., 2012).

To further verify the health acceptability of electrolysis-based BWMS, this study was conducted to evaluate the risk to human health associated with occupational and general public exposures due to operation of the electrolysis-based BWMS. This study followed a risk assessment procedure that consisted of four basic steps, hazard identification, dose–response assessment, exposure assessment, and risk characterization. Briefly, the first step was to identify the potential DBPs in treated ballast water at discharge. The Derived No Effect Levels (DNELs) of the measured DBPs were then derived on the basis of available dose descriptors from human epidemiology and/or animal toxicity studies such as the No Observed Adverse Effect Level (NOAEL). We next linked the measured DBPs levels in different exposure scenarios with risk. In the interim, MAMPEC-BW (Marine antifouling model to predict environmental concentrations-ballast water) model version 3.0 was used to calculate the predicted environmental concentrations (PECs) of the measured DBPs. Finally, the acceptable levels of risk for human health were determined by comparing the exposure levels to various DNELs.

## 2. Materials and methods

### 2.1. Test water

According to the IMO Guidelines, brackish water was tested to verify BWMS efficiency in a wide salinity range (International Maritime Organization, 2008b). During the experiment, brackish water (salinity 3-32 PSU) was achieved by mixing natural seawater (Qingdao, China) with municipal tap water. The initial salinity, temperature and pH of the influent brackish water were 21.3 PSU, 12.6 °C and 8.1, respectively. To meet the required water quality indexes of the IMO Guidelines (International Maritime Organization, 2008b), commercial humic acid, globigerina and kieselguhr were added to make the concentrations of dissolved organic carbon (DOC), particulate organic carbon (POC) and total suspended solid (TSS) of 6.14, 5.41 and 73.3 mg/L, respectively. Compared to natural seawater (DOC = 3.82 mg/L; POC = 2.29 mg/L; TSS = 2.15 mg/L), water quality conditions of brackish water was considered to be relatively bad due to high DOC, POC and TSS contents. Plankton densities were adjusted by adding concentrated natural populations from the harbor into the influent water; the target densities for organisms $\geq$50 μm and $\geq$10 to $<$50 μm were at least $10^5$ individuals (ind.)/$m^3$ and $10^3$ cells/mL, respectively (International Maritime Organization, 2008b).

### 2.2. Identification/description of unit operations in the BWMS and experimental procedure

To perform human health risk assessment for occupational exposure, a description of the ballast water treatment process associated with the system as a set of unit operations is a basic step to identify which individual system components are likely to lead to human exposure to the BWMS related DBPs (International Maritime Organization, 2012). The system regarded as a set of unit operations based on the treatment process is shown in Fig. 1. Filtration unit (1) and Sampling unit (5) were set in the engine room; Electrolysis unit (2) and Neutralization unit (4) were installed in the equipment room; and the BWMS were operated automatically in cargo control station. During ballasting, the influent brackish water with a flow rate of 250 $m^3$/h was filtered using an automatic self-cleaning filter to remove particles and organisms larger than 50 μm, after which a side stream of filtered seawater (approximately 5.5 $m^3$/h of 250 $m^3$/h) was subjected to an inactivation step employing an electrolytic cell where active substances (mainly sodium hypochlorite and sodium hypobromite) were produced, and then was injected back into the main ballast stream after degas. The range of TRO concentration measured by TRO analyzer 1 (CLX-XT, HF Scientific, USA) was 8.0–9.5 mg/L as $Cl_2$ (Fig. 1). During de-ballasting, the filter and the electrolytic cell were by-passed. Treated ballast water was neutralized using sodium thiosulphate ($Na_2S_2O_3$) upon discharge if the TRO content measured by TRO analyzer 2 (CLX-XT, HF Scientific, USA) was larger than 0.2 mg/L as $Cl_2$ (Fig. 1). The present study was conducted to measure 25 types of DBPs (Table S1, Supporting Information). According to Guideline G8 of the IMO (International Maritime Organization, 2008b), treated ballast water was stored in the tank for at least 5 days. Chemical analysis for DBPs in treated ballast water were carried out immediately after treatment (day 0), as well as each day over the 5-day storage period. Two sampling points were arranged as shown in Fig. 1. Treated water samples were collected from SP1 immediately after treatment, while samples of discharged water were collected from SP2. Three replicate samples of influent and/or treated water at discharge were collected over the period of uptake and/or discharge (e.g., beginning, middle, end). All samples were poured into 1-L sample containers, preserved with $Na_2S_2O_3$ to