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Combining ballast water treatment and ballast water exchange: Reducing colonization pressure and propagule pressure of phytoplankton organisms

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1 **Title:** Ships' Ballast Water Treatment by Chlorination Can Generate Toxic Trihalomethanes

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5 **Abstract**

6 The International Maritime Organization (IMO) will enforce a new abundance-based
7 performance standard for ballast water in September, 2017. Strong oxidants, like chlorine, have
8 been proposed as a method for achieving this standard. However chlorine treatment of ballast
9 water can produce hazardous trihalomethanes. We assessed maximum trihalomethane production
10 from one chlorine dose for three types of ballast water (fresh, brackish and marine) and three
11 levels of total organic carbon (TOC) concentration (natural, filtered, enhanced). While the
12 current standard test considers a five day voyage, there is a high possibility of shorter trips and
13 sudden change of plans that will release treated waters in the environment. Water source and
14 TOC significantly affected trihalomethane production, with the highest amounts generated in
15 brackish waters and enhanced TOC concentration. The concentration of brominated
16 trihalomethanes increased from background levels and was highest in brackish water, followed
17 by marine and fresh water.

18 **Keywords:** THMs, seawater, brackish, freshwater, TOC, IMO D-2 standard

19 Vessels use ballast water to preserve buoyancy and maneuverability (Carlton 1987); by design,
20 ballast tanks hold a volume sufficient to equal the tonnage of dry cargo (IMO 2008a). It is
21 estimated that three to five billion tons of ballast water are transported every year (Globallast
22 IMO 2015). Large vessels like bulk carriers and tankers can discharge between 15,000 and
23 113,000m³ of treated ballast water in a single event, thereby posing an invasion risk for recipient
24 ports. New global regulations for ballast water management will be globally implemented
25 beginning September, 2017. These regulations are designed to reduce the movement of non-
26 indigenous species by setting numerical limits for abundance of two planktonic groups and three
27 health-related bacteria of concern (IMO 2016). Different alternatives to achieve these limits
28 exist, including use of strong oxidants such as chlorine (e.g. Werschkun *et al.* 2012; Zhang *et al.*
29 2013). Chlorine may be applied to ballast water either directly or indirectly via in situ electro-
30 chlorination of sea water.

31 Chlorine is the most widely used chemical for disinfection of fresh water, as it eliminates active
32 pathogens. However, chlorine treatment of water is associated with undesirable by-products,
33 some of which have carcinogenic effects (Boorman *et al.* 1999). Trihalomethanes (THMs),
34 which result when three halogen atoms are substituted for hydrogen atoms in the methane
35 molecule, are the most commonly observed by-product (Budziak *et al.* 2007).

36 THMs formation depends on the availability of both chlorine and natural organic matter (NOM).
37 Limiting production of THMs by pre-treatment to reduce NOMs is a common practice in public
38 utilities (Bull *et al.* 1995). This capability does not extend to ballast water, where large volumes
39 of water are loaded and discharged, and little space exists for on-board pre-treatment.
40 Consequently, ballast water treatment has focused on control of the oxidant dose (Tsolaki *et al.*
41 2010; Paolucci *et al.* 2015). Salinity of ballast water varies according to the geographic location
42 where it is loaded.

43 Formation of THMs requires dissolved NOM such as humic substances and/or fulvic acid
44 (Madabhushi 1999) and halogens dissolved in water. Both humic and fulvic acids constitute the
45 largest portion of dissolved organic carbon (DOC) in waters. In addition to DOC, natural waters

46 contain particulate organic carbon (POC) produced by plants and animals. The availability of
47 NOM and POC in water plays a key role in the quantity of THMs generated; however, there is a
48 large list of organic compounds that constitute NOM and POC in water, with the compounds
49 varying with the water source (Liu *et al.* 2015). The sum of DOC and POC equals total organic
50 carbon (TOC) and is typically used as a proxy for the potential reactive pool for THMs
51 generation (Bruchet *et al.* 1990; Singer 1999).

52 THMs are continuously produced if NOM is present and the halogen supply is not exhausted
53 (Stack *et al.* 2000). The most abundant halogen used in ballast treatment is chlorine because it is
54 inexpensive and can be readily added from sources such as sodium hypochlorite (NaClO). If the
55 ballast is fresh water, CHCl_3 may constitute the most abundant THM, based upon utility plant
56 experience (Ivahnenco and Zogorski 2006). However, THMs abundance and composition
57 changes in the presence of bromine. High concentrations of bromine result in brominated THMs
58 even when chlorine is added as the active substance of disinfection (Bull *et al.* 1995). Ballast
59 from brackish and marine waters may produce brominated THMs owing to the higher bromine
60 content of these water sources (Ged and Boyer 2014). Speciation of THMs occurs when bromine
61 is present in the water, leading to the formation of CHCl_2Br , CHClBr_2 , and CHBr_3 , with the sum
62 of these plus CHCl_3 equalling total THMs (TTHMs; Singer 1999). The ratio of chlorinated to
63 brominated species can be estimated based on molar ratios and then extrapolated using
64 probability models when analysis is limited to final concentration of TTHMs and not initial
65 doses of chlorine and bromine (Chang *et al.* 2001).

66 Here we evaluate potential TTHMs production in ballast water treated with chlorine at doses
67 recommended for use to reduce target organisms in ballast water (see Paolucci *et al.* 2015),
68 specifically exploring the effects of both water salinity and NOM. Experiments were performed
69 using natural water sources representative of freshwater and brackish waters from shipping ports
70 and marine water derived from a ballast sample. In addition, we augmented samples with humic
71 acids to explore effects of NOM concentration on THM generation.

72 **Materials and Methods**

73 Water samples were collected from two different ports and one vessel according to their salinity
74 as a follow-up to a larger ballast water treatment experiment (see Paolucci *et al.* 2015). Sampled
75 water included fresh water (0.1 practical salinity units; PSU) from Trois Rivières, Québec and
76 brackish water (11.3 PSU) from Port Alfred, Québec, and marine water (34.0 PSU) was collected
77 from a ballast tank of a general cargo vessel whose water was exchanged in the North Atlantic
78 region (38°08.7' N, 67°23.1' W) according to its ballast water management record. All samples
79 were kept in the dark at 4°C until day of analysis. Water in amber glass bottles at ambient
80 temperature was used hereafter to mimic light exposure in a ballast tank.

81 The experimental design was full factorial with two fixed factors: source of water (according to
82 salinity) and organic matter content. Three conditions for organic content were tested: i) natural
83 condition (water as it was collected); ii) removal by filtration (POC and other suspended solids
84 were removed) with a 0.45 µm glass fibre filter; and iii) enrichment with humic acid (HUMICan
85 100, AgroCare Canada) to increase content of TOC to 25 mg L⁻¹. The resulting 3x3
86 combinations were prepared in a 500mL sterilized, amber glass bottle with a Teflon lined cap.
87 Five hundred mL were measured with a volumetric flask and dosed (single pulse) to 10 mg Cl L⁻¹
88 using commercial pool bleach (sodium hypochlorite 10%, Pool Sanitizer, Cul-Mac Industries,
89 Inc., Wayne, MI, USA) at 10% weight-to-weight (w/w) solution. All nine treatments (3x3
90 combinations) were analyzed in triplicate (3 replicates per treatment) across three time intervals

91 (t₁≈1 hour, t₂≈5 hours, and t₃≈25-26 hours) to assess THMs maximum production. TOC was
 92 measured prior to incubation using an **in-line** TOC analyzer (Shimadzu, model VCSH, Kyoto JP)
 93 with a detection limit of 1 mg L⁻¹ and chlorine (estimated detection limit 0.1 µg L⁻¹) using a Hach
 94 Pocket Colorimeter™ II (Hach, Loveland, CO, USA).

95 At sampling, THMs were extracted from water samples using the method of headspace solid-
 96 phase microextraction (SPME) followed by analysis by GC-MSD (Stack *et al.* 2000; Zhao *et al.*
 97 2004). **A SPME fiber (75µm CAR/PDMS, 24 Ga.; Supelco, Bellefonte, PA, USA,), mounted in a**
 98 **manual holder, was used to transfer the extracted analytes.** The fibre was conditioned at 300°C
 99 for 5 min before and after each extraction. SPME extraction was performed by transferring 20g
 100 of water sample from a given incubation vessel into a precleaned amber VOA vial with screw
 101 cap and **PTFE/silicone** septum (EPA VO vials, Supelco part # 23189), containing 7.2g of NaCl
 102 and spiked with a mix of recovery surrogate standard solution containing p-bromofluorobenzene
 103 and d8-Toluene [CPL-PS-4X, AccuStandard, New Haven, CT, USA (concentration: 2 µg mL⁻¹;
 104 10 µL)]. The sample was vortexed for 1 min, following which a SPME needle (protecting fibre)
 105 was slid through the pierced septum and into the vial. Needle depth was adjusted to keep the
 106 fibre above the liquid layer in the headspace environment. The SPME extraction was initiated
 107 after exposing the fibre into the headspace and heating the vial indirectly at 45°C ± 1°C with
 108 constant stirring at 300 rpm for 20 min. Our methods differed slightly from those of Stack *et al.*
 109 (2000) and Zhao *et al.* (2004), the former because we used moderate stirring for 20 min as
 110 opposed to low stirring for a longer period, and the latter because we increased temperature.
 111 Volatiles were absorbed/adsorbed to the fibre and concentrated, followed by retraction of fibre
 112 into the needle. Thermal desorption of THMs from the fibre occurred when the needle was
 113 directly introduced to the GC inlet, followed by the extension of the fibre from the needle and the
 114 introduction of the fibre into the hot GC inlet.

115 **Analytes were identified and quantified using a gas chromatograph with a mass selective**
 116 **detector (GC/MSD) (Hewlett Packard HP 6890/5973, Wilmington, DE, USA) equipped with a**
 117 **capillary** column [VF-624ms; 30m x 0.25mm I.D. x 1.4µm film thickness (Agilent J&W, Santa
 118 Clara, CA, USA)]. The inlet was set at 250°C in a splitless mode and carrier gas (UHP) at a flow
 119 rate of 0.8 mL min⁻¹ with column head pressure 4.8 psi. The MSD operated in EI SIM mode.
 120 Oven temperature was set at 40°C for an initial time of 2.0 min and increased at a rate of 7°C
 121 min⁻¹ and held at 130°C for 1.0 min. The total analysis time was 15.86 min with equilibration
 122 time at 0.5 min. Calibration was carried out with the same procedure replacing the sample water
 123 with 20 mL of buffer solution [sodium chloride (360g) in Milli-Q water (1L) fixed at pH 2.0 with
 124 ortho-phosphoric acid (85% weight/weight)].

125 Known concentrations of THMs were loaded into 20 g of water using the THM standard mix
 126 (M-501-10X, AccuStandard, New Haven, CT, USA) to generate a calibration curve. **Method**
 127 **detection limits (MDLs) for the THMs were based** on a signal-to-noise ratio (S/N*5) at low
 128 concentration and were between 0.04 to 0.05 µg L⁻¹ for CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃.
 129 **The recovery rate** for our surrogate was 94.3%. However, it was not used in MDLs determination
 130 because it was within the acceptable range for volatiles.

131 **Table 1.** Mean (SD) total organic carbon (TOC; mg L⁻¹), pH, salinity (PSU) and TTHMs (mg L⁻¹)
 132 measured before dosing samples with chlorine.

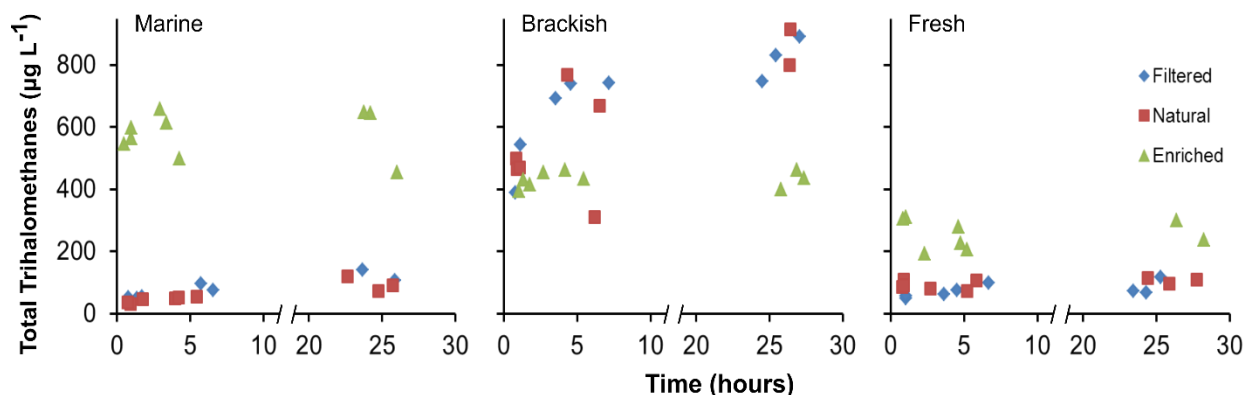
| Water Source | Natural | Filtered | Enriched | pH | Salinity | TTHMs |
|--------------|------------|-----------|------------|-----------|------------|-------|
| Fresh | 15.6 (0.8) | 7.3 (0.0) | 23.9 (3.2) | 8.2 (0.2) | 0.1 (0.0) | 0 (0) |
| Brackish | 11.4 (0.4) | 8.6 (0.2) | 26.1 (2.4) | 7.2 (0.2) | 11.3 (0.2) | 0 (0) |

| | | | | | | |
|--------|------------|------------|------------|-----------|------------|-------|
| Marine | 18.8 (1.8) | 11.4 (0.1) | 22.1 (2.1) | 7.8 (0.1) | 34.0 (0.1) | 0 (0) |
|--------|------------|------------|------------|-----------|------------|-------|

133 A univariate general linear model was conducted on the production of TTHMs using two fixed
 134 factors (water source and TOC content), and a covariate (time after dose). We also tested for an
 135 interaction between the fixed factors. Additionally, we performed an independent sample t-test
 136 for TOC content between natural and filtered for all sources of water. All statistical analyses
 137 were carried out with IBM SPSS Statistics version 23 (IBM Corp., Armonk, OK, USA).

138 Results and Discussion

139 Filtered and natural TOC concentrations were low in both natural and filtered water for fresh and
 140 brackish waters, and slightly higher in marine waters (Table 1). There were no detectable
 141 concentrations of TTHMs in vessels prior to chlorine addition in vessels (Table 1). Total THM
 142 production varied significantly by water source and by TOC content at the outset of the
 143 experiment, and by an interaction of these parameters (Table 2). Fresh water produced on
 144 average less TTHMs than any other source, while marine water produced an intermediate
 145 amount of TTHMs and brackish water the highest amount (Table 2, Fig. 1).



146
 147 **Fig. 1** Concentrations of total trihalomethanes (TTHMs; $\mu\text{g L}^{-1}$) over time for all replicates
 148 analyzed. Individual panels display water types commonly used as ballast, and the series depict
 149 different TOC concentrations.

150 Enrichment of TOC increased TTHMs production for fresh and marine waters but not for
 151 brackish water (Table 2; Fig. 1). Filtering significantly reduced TOC concentration versus
 152 natural conditions ($t = 5.17$, $df = 16$, and $p < 0.001$). Although non-significant, filtered samples
 153 yielded the highest production of TTHMs for brackish water (Table 2; Fig. 2).

154 TTHMs maximum production was achieved very quickly (i.e. within 1 hour) and was sustained
 155 over the 24-hour follow-up measure in all TOC concentrations for fresh and marine water (Fig.
 156 1, right and left panels). Brackish water almost doubled TTHMs in the first hours after dose for
 157 natural and filtered concentrations, and sustained the same levels in the enriched concentration
 158 (Fig. 1, middle panel).

159 CHCl_3 was the major constituent of TTHMs in fresh water, whereas brackish or marine water
 160 treatments had a higher ratio of brominated to chlorinated species of THMs owing to the very
 161 low presence of bromine in fresh water (Table 2). Most production in natural or filtered fresh
 162 water was by CHBrCl_2 (Table 2). By contrast, marine and brackish water produced more CHBr_3
 163 but under different conditions, with the former being greatest in the enhanced TOC concentration
 164 and the latter in natural and filtered concentrations (Table 2).

165 The World Health Organization (WHO) limits TTHMs to $200\mu\text{g L}^{-1}$; with individual conditions
 166 for chloroform (CHCl_3) to $200\mu\text{g L}^{-1}$, bromoform (CHBr_3) to $100\mu\text{g L}^{-1}$, dibromochloromethane

167 (CHClBr₂) to 100 µg L⁻¹, and bromodichloromethane (CHCl₂Br) to 60 µg L⁻¹ (Stack *et al.* 2000).
 168 We found concentrations of TTHMs in fresh water ballast for natural and filtered concentrations
 169 were well below the 200 µg L⁻¹ limit, and thus compliant with WHO regulations for continental
 170 waters (Agus *et al.* 2009; Werschkun *et al.* 2012). It is likely that a source of fresh ballast water
 171 with a maximum TOC concentration of 16mg L⁻¹ would produce similar or lower concentrations
 172 for TTHMs with doses of Cl⁻¹ ≤ 10 mg·L⁻¹.

173 Similarly, we expect that marine water will be below permissible limits set by WHO regulations
 174 for TTHMs. However, under conditions of enhanced TOC concentration, we anticipate that
 175 production of TTHMs would increase greatly (Table 2) and possibly exceed these regulations.
 176 Production of TTHMs in enriched marine water was almost 10 times higher than in filtered or
 177 natural water (Table 2). It is apparent that the largest limiting factor for THMs production in
 178 marine ballast water used in this experiment is NOM in the water.

179 Brackish water produced less TTHMs under enrichment than under natural or filtered conditions.
 180 We propose that an inhibitor may have prevented the oxidation process in water collected at Port
 181 Alfred. Further, we propose that some macromolecules may sequester chlorine in the natural
 182 condition, because filtering removes suspended particles above 0.45 µm in size. It has been
 183 documented that ammonia reduced THMs production during chlorination despite the presence of
 184 humic substances (Amy *et al.* 1984). High production of TTHMs in brackish versus marine or
 185 fresh water has been documented in at least five ballast water treatment systems (OceanSaver,
 186 CleanBallast, Greenship, TG, OceanGuard) (Werschkun *et al.* 2012). Similar results were also
 187 found when the OceanGuard system was tested on land, with CHBr₃ accounting for almost 90%
 188 of the total 670 µg L⁻¹ TTHM produced (Werschkun *et al.* 2012).

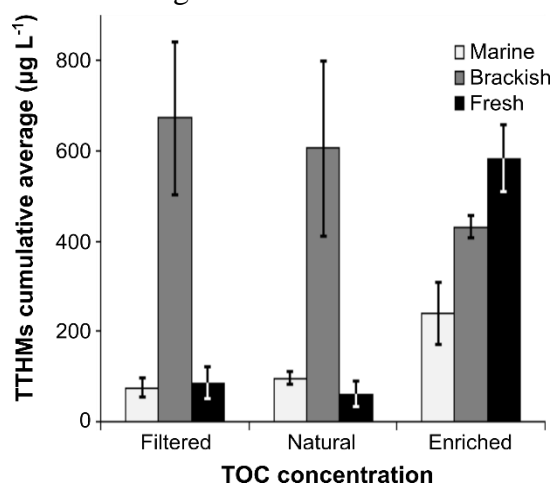
189 **Table 2.** Mean (SD) production of THMs (µg L⁻¹) in each combination of fixed factors.

| Water source | TOC | CHCl ₃ | CHBrCl ₂ | CHBr ₂ Cl | CHBr ₃ | Total THMs |
|--------------|----------|-------------------|---------------------|----------------------|-------------------|---------------|
| Marine | Enriched | 0.9 (0.3) | 15.0 (0.5) | 32.9 (7.0) | 545.6 (64.2) | 581.1 (71.3) |
| Marine | Filtered | 1.3 (0.9) | 5.7 (0.6) | 7.7 (10.7) | 75.7 (32.7) | 86.6 (33.1) |
| Marine | Natural | 0.6 (0.1) | 2.2 (0.1) | 3.4 (1.2) | 57.4 (27.3) | 61.6 (28.6) |
| Brackish | Enriched | 2.7 (1.4) | 128.1 (5.3) | 73.5 (11.9) | 341.8 (27.3) | 432.2 (25.6) |
| Brackish | Filtered | 1.6 (0.9) | 21.2 (0.4) | 34.7 (6.0) | 633.4 (163.1) | 672.0 (168.1) |
| Brackish | Natural | 0.8 (0.5) | 14.7 (0.5) | 28.1 (7.4) | 575.0 (187.5) | 605.5 (194.2) |
| Fresh | Enriched | 169.8 (73.9) | 113.0 (6.2) | 14.9 (20.4) | 43.3 (65.5) | 240.5 (67.2) |
| Fresh | Filtered | 31.9 (17.5) | 97.6 (4.7) | 7.4 (2.6) | 25.4 (8.7) | 75.6 (21.6) |
| Fresh | Natural | 40.2 (21.5) | 119.4 (2.8) | 10.0 (4.0) | 33.3 (15.0) | 96.8 (14.7) |

190 Experiments with chlorination in marine water, as a means to control biofouling, used doses
 191 from 0.5 to 1.5 µg L⁻¹ and resulted in TTHMs concentrations of 2.5 to 18.5 µg L⁻¹ (Boudjellaba
 192 *et al.* 2016). However, the IMO D-2 performance standard targets two planktonic groups that
 193 will require a larger dose to achieve lethality in larger organisms (Gregg *et al.* 2009). Our TTHM
 194 production results for marine water were an order of magnitude greater than those of Boudjellaba
 195 *et al.* (2016). Other studies that have evaluated differences in TTHM production using nearshore
 196 and deep-ocean waters revealed that TTHM production differed by orders of magnitude, with
 197 nearshore water having the highest TTHM production (Fabbricino and Korshin 2005).

198 Werschkun *et al.* (2012) reported that three commercial ballast water treatment systems
 199 (CleanBallast, TG and OceanGuard), tested with marine water and a lower chlorine dose,
 200 experienced TTHMs production just below 200 µg L⁻¹ over a five day cycle (as required by IMO
 201 G9; IMO 2008b). OceanSaver produced relatively less TTHMs, yielding results similar to ours

202 (Fig. 1 left panel). Cowman and Singer (1996) documented a shift of brominated species in
 203 disinfection by-products, where hypochlorous acid continuously integrated bromide into THM
 204 formation. The free chloride from the completion of this reaction restarts the process. Marine
 205 water produced more TTHMs when enriched compared with fresh water. Symons *et al.* (1993)
 206 found that chlorine (as low as 3 mg L⁻¹) in the presence of precursors (DOC and bromide) in
 207 fresh water, will promote production of brominated species until complete exhaustion of one
 208 precursor. In contrast, production in fresh water will stop when hypochlorous acid no longer can
 209 react with organic matter.



210 **Fig. 2** TTHMs cumulative average and standard deviation (µg L⁻¹) for all TOC concentrations
 211 and ballast water sources.
 212

213 Chlorination is an effective alternative to ballast water exchange under the new IMO ballast
 214 water standard. Bench-scale experiments like ours allow inferences to be made regarding
 215 patterns and trends, though care must be taken when extrapolating to the field. Paim *et al.* (2007)
 216 spiked fresh water with humic acids to 23.7 mg L⁻¹ and, using a 5 µg L⁻¹ chlorine dose, reported
 217 a maximum production of CHCl₃ of 18 µg L⁻¹. Our experiments with fresh water, conducted
 218 under laboratory conditions and 10 µg L⁻¹ Cl⁻¹ and 23.9 mg L⁻¹ TOC, revealed much higher
 219 production of TTHMs (Fig. 1) during the first hours. This large difference might stem from the
 220 higher chlorine dose and its apparent immediate impact on CHCl₃ production. It is apparent that
 221 filtering will remove the particulate fraction, yet it had little or a net positive effect on
 222 subsequent TTHMs production because the dissolved fraction of organic carbon was involved in
 223 reactions that produced TTHMs. Liu *et al.* (2015) observed that only four species of organic
 224 carbon (glycolic, alginic, citric, humic acids and urea) enhanced TTHM production. While it will
 225 be difficult for crew and port authorities to analyze what species of organic carbon is in the
 226 water, the option exists to adjust the dose. In addition, it is possible to track free chlorine in real
 227 time using electronic sensors in the tanks (Zimmer-Faust *et al.* 2014).

228 This study assessed the importance of ballast water source and its organic carbon content to
 229 production of TTHMs. By IMO convention (IMO 2008b), analyses of TTHMs are only made
 230 during final discharge of ballast water; our study reveals patterns of TTHM production and
 231 attenuation prior to discharge. We observed clear differences in TTHM production in brackish,
 232 fresh and marine water, which has strong implications for where ballast water should be loaded
 233 and its likely generation of TTHMs. Ballast water loaded in freshwater ports - even if TOC load
 234 is high - may pose less risk of TTHM production than that loaded in brackish or marine water.
 235 However, many global ports are brackish or marine (Werschkun *et al.* 2014), thus by-product

236 generation of TTHMs may pose a problem, particularly in carbon-enriched marine or filtered
237 brackish water for voyages shorter than five days (see guidelines G8 and G9; IMO 2008a, b).
238 Our results suggest that if treated ballast water is discharged within the first two days there is a
239 risk of releasing sufficient TTHMs to cause environmental harm.

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