Inputs of disinfection by-products to the marine environment from various industrial activities: Comparison to natural production

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ABSTRACT

Oxidative treatment of seawater in coastal and shipboard installations is applied to control biofouling and/or minimize the input of noxious or invasive species into the marine environment. This treatment allows a safe and efficient operation of industrial installations and helps to protect human health from infectious diseases and to maintain the biodiversity in the marine environment. On the downside, the application of chemical oxidants generates undesired organic compounds, so-called disinfection by-products (DBPs), which are discharged into the marine environment. This article provides an overview on sources and quantities of DBP inputs, which could serve as basis for hazard analysis for the marine environment, human health and the atmosphere. During oxidation of marine water, mainly brominated DBPs are generated with bromoform ($CHBr_3$) being the major DBP. $CHBr_3$ has been used as an indicator to compare inputs from different sources. Total global annual volumes of treated seawater inputs resulting from cooling processes of coastal power stations, from desalination plants and from ballast water treatment in ships are estimated to be 470–$800 \times 10^9 \, m^3$, $46 \times 10^9 \, m^3$ and $3.5 \times 10^9 \, m^3$, respectively. Overall, the total estimated anthropogenic bromoform production and discharge adds up to 13.5–21.8×10^6 kg/a (kg per year) with contributions of 11.8–20.1×10^6 kg/a from cooling water treatment, 0.89×10^6 kg/a from desalination and 0.86×10^6 kg/a from ballast water treatment. This equals approximately 2–6% of the natural bromoform emissions from marine water, which is estimated to be 385–870×10^6 kg/a.

1. Introduction

Marine water is subject to disinfection for several purposes. In cooling water circuits, disinfection strives to mitigate biofouling and clogging to guarantee good thermal exchange efficiency and reduce maintenance efforts (Rajagopal, 2012). In desalination plants for potable water production, disinfection seeks to limit biofouling and to avoid clogging of in-take pipes in membrane-based and thermal treatment trains (Kim et al., 2015). Ballast water treatment aims to prevent, minimize and ultimately eliminate the risks resulting from the discharge of potentially invasive and harmful aquatic organisms and pathogens from ships to the environment and to human health (David and Gollasch, 2015). In municipal wastewater disinfection as well as for seawater toilet systems, which are used in some coastal areas with limited freshwater supply, with the city of Hong Kong being the only large-scale case worldwide, the main purpose of treatment is to limit the discharge of pathogens to the aquatic environment (Jacangelo and Trussell, 2002, Liu et al., 2016; Ng, 2015). Furthermore, oxidative treatment is performed in various sectors such as aquaculture and seawater aquaria to control animal diseases and improve water quality (Qiang et al., 2015). However, while these latter applications may be locally relevant, they are less important as sources of disinfection by-products (DBPs) on a global scale and are not further addressed here.

Different chemical oxidants can be used for disinfection purposes; they can either be added from storage tanks or be generated *in situ*. For treatment of ocean or brackish waters containing bromide, some disinfection techniques (including electro-chlorination, chlorination and ozonation) generate hypobromous acid (HOBr) as secondary oxidant in ocean and brackish water (HOBr) and thus produce similar patterns of DBPs (Heeb et al., 2014). Other oxidation processes (e.g., chlorine dioxide, peracetic acid and hydrogen peroxide) typically produce different patterns of DBPs (Shah et al., 2015b). However, the relative composition and absolute concentrations of DBPs also depend on process parameters such as the concentration of active substances, reaction time, as well as the chemical and physical characteristics of the treated water (salinity, organic matter, temperature, etc.) (Shah et al., 2015a). Therefore, DBP generation typically varies between different applications and sites even if similar or identical processes are applied.

So far, more than 700 anthropogenic DBPs have been identified in oxidative water treatment, mainly haloorganic compounds (also named organohalogens). Haloorganic compounds are also part of the spectrum of naturally generated compounds with more than 5000 compounds described to be formed by marine organisms (Gribble, 2010). Most of these compounds are distinct from DBPs and are formed in small quantities by specialized organisms. However, some of the DBPs with the highest concentrations in oxidative seawater treatment are also produced as natural organohalogens, with bromoform being a major DBP and similarly a major natural haloorganic product in the marine environment (Quack and Wallace, 2003). Phytoplankton and macroalgae have been identified as main sources (Carpenter and Liss, 2000; Hepach et al., 2015).

The aim of this study is to identify sources and quantify the inputs of major DBPs through anthropogenic activities such as industrial cooling units, desalination plants, ballast water treatment in ships and wastewater treatment/seawater toilets to the marine environment. To this end, an overview on the most prominent treatment processes and regimes, i.e. oxidant concentrations and reaction times is provided for the different industrial processes. Data on DBP concentrations from different industrial activities is provided with a focus on the most abundant DBPs of each compound class to enable a comparative assessment. Furthermore, as the major DBP, bromoform is also produced naturally in the marine environment, this study also provides an overview on its production from natural processes. A quantitative comparison of the anthropogenic bromoform production relative to its overall production is carried out, which could serve as a basis for the estimation of potentially harmful impact of anthropogenic DBPs to aquatic organisms in the marine environment, to human health and the atmosphere.

This study was initiated by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP, 2022), an expert group of ten UN Organizations, which strives to support sustainable governance of the marine environment by providing a multidisciplinary, scientific advice on marine ecosystems and human activities that affect them. GESAMP is involved in the assessment of risks resulting from ballast water treatment. To broaden the perspective towards potential risks of DBP discharges to the marine environment from other sources, a workshop was organized involving experts from different backgrounds and a report on the outcomes will be published (GESAMP in preparation). The present study provides a comprehensive compilation of the main aspects related to the quantification of DBP inputs.

2. Generation of disinfection by-products in marine waters

Various chemical oxidants are used in water treatment for disinfection purposes, with chlorine (Cl_2) being the most widely applied in large industrial processes. In marine and brackish waters, the applied oxidants react with bromide to form various bromine species with hypobromous acid/hypobromite ($HOBr/OBr^-$) being the most important ones. The formation of bromine by chemical oxidants such as chlorine, ozone and peracetic acid and its reactions with inorganic and organic compounds have been reviewed by Heeb et al. (2014). Depending on the characteristics of the treated waters, a large fraction of the applied or formed secondary oxidants reacts with dissolved organic matter (DOM) leading to the formation of DBPs. Processes involved in DBP formation through reaction with DOM have been reviewed (Li and Mitch, 2018; Richardson and Ternes, 2018; Sedlak and von Gunten, 2011; von Gunten, 2018). In waters with high bromide levels, mainly brominated DBPs are formed (Shah et al. 2015a).

Because DBPs were first discovered in chlorinated drinking water, most of the initially discovered DBPs were chlorine-containing (Rook, 1974). Later on, when bromide-containing waters were investigated including marine waters, many bromo-analogues of chlorine-containing DBPs were identified (Rook et al., 1978). Bromine-containing compounds represent the largest group of DBPs detected in marine waters (Manasfi et al., 2019; Werschkun et al., 2012). The types and concentrations of the brominated DBPs depend strongly on the specific oxidation conditions (oxidant, dose, reaction time, temperature, etc.) and on the characteristics and the concentrations of the dissolved organic matter.

Trihalomethanes (THMs) are the most important group of DBPs generated during chlorination of both freshwater and marine water (WHO, 2017). In freshwater containing low levels of bromide, chloroform ($CHCl_3$) is the major THM generated, whereas its brominated analogue bromoform ($CHBr_3$) predominates at high bromide levels (Richardson et al., 1999). The four major chlorinated/brominated THMs ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) have been detected in chlorinated marine water, with chloroform being very minor and bromoform being by far the major THM (Shah et al., 2015a).

Haloacetic acids (HAAs) typically represent the second largest group of DBPs formed in oxidative processes. In marine water, dibromoacetic acid (DBAA) is observed as the compound with the second highest concentration after bromoform followed by tribromoacetic acid (TBAA) (Shah et al., 2015a). Other HAAs can be detected in considerably lower concentrations, including monobromoacetic acid (MBAA), mono-, di- and trichloroacetic acid along with bromochloro-, bromodichloro- and dibromochloroacetic acids (Fabbricino and Korshin, 2005). HAAs are often summarized as the sum parameter HAA_5 (sum of concentrations of monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), MBAA and DBAA) or HAA_9, which include HAA_5 and the sum of the concentrations of bromochloroacetic acid (BCAA), bromodichloroacetic acid, chlorodibromoacetic acid and TBAA.

Haloacetonitriles (HANs) typically occur at higher concentrations in

chlorinated and chloraminated drinking waters than many other nitrogen-containing DBPs (*N*-DBPs) such as nitrosamines, halonitromethanes, and haloacetamides (Krasner et al., 2006). In chlorinated seawater, HANs constitute only a small portion of the formed halogenated DBPs with dibromoacetonitrile (DBAN) being the predominant HAN (Fabbricino and Korshin, 2005). The formation of HANs is related to the presence of nitrogenous precursors (e.g., amino acids) in water.

Bromate formation mainly occurs during ozonation (Shah et al., 2015a; von Sonntag and von Gunten, 2012). Chlorination typically does not lead to bromate formation, unless it is in electro-chlorination treatment or when the process is catalyzed by metal oxides such as copper oxide (Jung et al., 2014; Liu et al., 2012).

Numerous aromatic DBPs have been detected in chlorine-treated, bromide-rich drinking water samples (Pan and Zhang, 2013) and disinfected saline wastewater effluents (Ding et al., 2013). In chlorinated seawater cooling effluents of power stations, 2,4,6-tribromophenol (TBP) has been detected as the most important aromatic DBP (Allonier et al., 1999b; Boudjellaba et al., 2016).

Since only a fraction of DBPs has been identified, sum parameters such as adsorbable organic halide (AOX) or total organic halide (TOX) can be used to quantify the total organohalogen content (Hua and Reckhow, 2006; Kristiana et al., 2009; Langsa et al. 2017). For the same source water, the toxic potency of the disinfected water has been reported to be positively correlated with the TOX level of the disinfected water (Han and Zhang, 2018). The measured individual DBPs account for about 40–70% of TOX in chlorinated water (Chen et al. 2015; Krasner, 2009). Hence, there is a need of sum parameters to evaluate the overall content of halogenated DBPs. One major challenge is that not all DBPs are amenable to extraction methods and chemical analyzes commonly used in the determination of DBPs. Moreover, among the extracted DBPs many are still unknown. This results in a gap between quantified DBPs and the sum of organohalogens (e.g., TOX). Accordingly, a considerable portion of DBPs remains to be discovered by new analytical techniques including improved methods for sample preparation.

Chlorine is used as oxidant for most large-scale applications. However, because concentrations of generated DBPs and ratios of different DBPs depend on process parameters (oxidant concentration, reaction time, etc.) and water characteristics (DOM type and concentration, salinity, etc.), each technical installation likely generates specific levels of DBPs. In the subsequent sections, an overview on the process parameters, volumes of treated water and DBPs generated is provided for major technical applications of oxidative treatment of marine and brackish waters.

2.1. Cooling waters

All industrial cooling systems using seawater are affected by excessive macrofouling (settlement and development of sessile marine organisms such as barnacles and mussels) that may block condensers, or microfouling (formation of biofilms) that limit heat exchange. Fossil fuel and nuclear power stations at the seaside are particularly affected by biofouling because of the large water volumes required and the large size and complexity of the cooling systems (Jenner et al., 1997). To maintain water flow and heat exchange at the required level and to avoid disruption of operation of the cooling systems, it is necessary to apply anti-fouling measures.

Hypochlorite addition represents the most common antifouling treatment in industrial cooling water systems (Rajagopal, 2012), either injected from a hypochlorite storage tank or produced on-site electrochemically. A low-level chlorination process requires to maintain a residual oxidant concentration of about 0.2 mg Cl_2/L at the outlet of all heat exchangers such as condensers and auxiliary exchangers (Khalanski and Jenner, 2012). The applied chlorine dose depends on the water quality (such as dissolved organic carbon (DOC) concentration and oxidant demand), the growth pressure (such as concentration of

organisms and season) and specificities of the circuits. Typical chlorine doses range between 0.5 and 1.5 mg Cl_2/L.

The most extensive study on DBPs in power plant cooling water covers 90 analyzes of cooling water in 10 different coastal power stations in the United Kingdom, France and the Netherlands (Jenner et al., 1997). Since then, some additional data from these sites and additional analyzes were presented (Allonier et al. 1999a; Taylor, 2006). Additionally, studies on cooling waters of two Korean, an Indian and a Swedish power station were published (Fogelqvist et al., 1982; Padhi et al., 2012; Sim et al., 2009; Yang, 2001). The main results from these studies are summarized in Table S1 (supporting information, SI). The analyzes of chlorinated cooling water samples show large variations that are not only explained by differences in water quality but also by the variability in circuits' complexity and their operation. Furthermore, quantitative comparison of DBP concentrations produced is hampered by differences in study design and quality (grab samples vs. multiple sampling, information on target or effective chlorine dose). Despite the shortcomings of this heterogeneous data set, average concentrations reported are relatively consistent with estimated DBP concentrations based on formation yields of bromoform and other major DBPs linked to chlorine dosage assuming an average chlorine dose in power plant cooling water of 0.75 mg/L as described by Khalanski (2003). Average concentrations of selected DBPs representing different compound groups in power station effluents provided in Table S1 are used as reference for the assessment: 25 (3.1–100) μg/L for bromoform, 9 (7, 4–10.3) μg/L for DBAA, 1.1 (<0.1–3.6) μg/L for DBAN and 0.16 (0.002–0.37) μg/L for TBP.

In 2016, approximately 25,000 terawatt hours (TWh) of electricity were produced worldwide (IEA, 2018). In thermal electricity production accounting for 18,900 TWh, an important fraction of the energy is transformed to heat, which needs to be dissipated. In coastal power stations once-through cooling (so-called open loop) is used for cooling by heating water by ΔT of 10–15°C and subsequent rejection into the surrounding water. In total, the ratio of dissipated heat into cooling water compared to electricity produced amounts to 1.2 and 2.1 for fossil fuel and nuclear power stations, respectively (Hartmann et al., 2011). This results in water consumption of approximately 20–30 m^3/s and 33–50 m^3/s for fossil fuel or nuclear power stations of 1000 MW, respectively. The produced electricity thus allows an estimate of the dissipated heat and subsequently the volumes of required cooling water. Based on an analysis of geographic information, Maas et al. (2021) identified that about one fourth of the power plant capacities are located at the coast and estimated a global volume of discharged cooling water of 8×10^{11} m^3/a into the marine environment. This emission estimate is based on an assumption of a high cooling requirement independent of energy source. Taking into account the lower cooling requirements of fossil power production compared to nuclear power production, an alternative value for the annual discharge of 4.7×10^{11} m^3 was estimated. Details on this estimate are provided as supplementary information (Table S6 and associated text). These two values serve as an estimate of range of discharges into marine waters from energy production.

2.2. Desalination

Desalination processes contribute to the water supply in arid regions around the world. The global capacity for water production by desalination has been estimated to be 9.5×10^7 m^3/d in 2018 (Jones et al., 2019). However, capacity and production are predicted to rapidly increase in the future (Hanasaki et al., 2016) due to rapid population growth and droughts induced by climate change. The largest number of desalination plants is present in the Middle East including the Arabian Gulf, Saudi Arabia and the United Arab Emirates (Jones et al., 2019). Important capacities are installed in the Mediterranean Basin, East Asia and the Pacific as well as the United States (Jones et al., 2019). Before 2013, around 60% of global desalination capacity treated seawater;

while the remainder treated brackish (21%) and less saline water (19%) (Bennett, 2013). The share of seawater has become larger according to the more recent data published by Jones et al. (2019).

Desalination is either based on reverse osmosis (RO) or distillation (i. e., thermal desalination) representing 63% and 31% of the world's treatment capacity, respectively (Gude, 2016). To prevent bacterial growth and biofouling in the intake structures and to improve the performance of filters, chemical disinfectants are used as a pre-treatment before multi-media filtration or membrane filtration. Hypochlorite is the most commonly used disinfectant for pre-treatment as well as final disinfection. Chloramine, ozone, and chlorine dioxide are alternative disinfectants used less frequently in this context, typically for specific treatment objectives (Kim et al., 2015). For RO desalination plants, the chlorine dose and contact time vary with the chlorination mode (continuous, intermittent or shock treatment), the location and the objectives (intake pipe can be used for other applications e.g., power plants). A dose in the range of 0.2–2 mg Cl_2/L is typically applied continuously to protect the intake pipe, although doses of up to 5 mg Cl_2/L are used in some installations (Kim et al., 2015). The chlorine contact time can reach 45–60 min followed by an injection of sulfite to quench residual chlorine prior to RO filtration to avoid damage to membranes. For distillation plants, chlorine doses of approximately 2 mg Cl_2/L are applied targeting a residual chlorine concentration of 0.2–0.3 mg Cl_2/L at the heat rejection section and no sulfite injection is required in the production line. As a result of disinfection, DBPs are formed during desalination processes.

It is important to distinguish between the produced desalinated water, which might be dedicated to human consumption and the wastewater typically called brine, which is discharged into the sea. Depending on the treatment process, different concentrations of DBPs can accumulate in the different water fractions. In this paper, the brines are the main focus as they represent the main source of DBP inputs into the marine environment resulting from desalination. DBP occurrences in brine produced from distillation and RO seawater desalination plants from several previous publications are provided in Table S2 (SI). In addition to THMs, HAAs, and HANs, low levels of iodinated THMs and brominated phenols were reported in a few RO concentrates (Agus and Sedlak, 2010; Le Roux et al., 2015). Due to the heterogeneity of the installations and studies, it is difficult to draw general conclusions on DBP concentrations in discharged brines. Therefore, systematic DBP studies in full-scale seawater desalination plants are warranted to provide generalizable information of THMs and HAAs as well as other DBPs for each process. From several available studies, mean concentrations of major DBPs were calculated (Table S2, SI). Average concentrations of selected DBPs representing different compound groups in power station effluents are provided in Table S2 are used as reference for the assessment: 19 (0.2–104) μg/L for bromoform, 3.6 (0.6–11.6) μg/L for DBAA, 0.7 (0–1.2) μg/L for DBAN and 0.75 (0.53–0.96) μg/L for TBP.

Jones et al. (2019). estimate a global brine production and discharge of 1.42×10^8 m^3/d taking into account specificities of combination of desalination technology and different feedwater qualities. 1.25×10^8 m^3/d comes from seawater desalination plants situated close to the coastline. This equals a total estimated discharge of treated water from desalination plants into the marine environment of 4.6×10^{10} m^3/a.

2.3. Ballast water treatment

Ballast water is taken up by ships when cargo is unloaded and discharged when cargo is loaded. It is an essential measure to stabilize vessels at sea and it is therefore essential for safe and efficient shipping operations. However, discharged ballast water can lead to the introduction of non-indigenous species into the receiving environment, potentially becoming invasive and possibly causing severe ecological, economic and human health impacts (Gollasch, 2006; Ruiz et al., 2000). To address this problem, the International Maritime Organization (IMO) adopted the *International Convention for the Control and Management of*

Ships' Ballast Water and Sediments (BWMC, 2004), which entered into force in 2017. The Convention sets a maximum permissible concentration standard for living organisms in discharged ballast water for all ships in international traffic.

Although, a wide range of treatment technologies have been assessed to meet the standards, two treatment technologies are currently evolving as the major market shares: ultraviolet radiation (UV) and chemical oxidation, mainly hypochlorite added as a chemical or generated *in situ* by electrolysis (i.e., electro-chlorination), both combined with filtration. Typically, the treatment is performed during the uptake of the ballast water. Oxidant doses ranging from 2 to 20 mg Cl_2/L are used in IMO-approved ballast water management systems (BWMS). The reaction in the ballast water tank continues as long as residual oxidants are available and can last up to the total holding time of the ballast water, which may be as long as 21 d. Many systems aim to maintain a certain concentration of residual oxidants over the total ballast water holding time to maintain the biocidal potential and prevent the re-growth of organisms. To prevent a release of residual oxidants into the environment, often reducing agents such as thiosulfate or sulfite are added prior to or during the discharge of treated ballast water.

David et al. (2018) analyzed data on DBP concentrations in 36 BWMS submitted to the IMO approval process and assessed according to the established methodology (GESAMP, 2019). Bromoform was detected in discharged water of all investigated BWMS, whereas DBAA, dibromochloromethane and MBAA were detected in the discharged water of 34, 33 and 30 out of the 36 BWMS, respectively. Less frequently, 24 other DBPs were detected. An overview on relative frequencies of occurrences and mean and maximum concentrations in ballast water discharge during the test scenarios is provided in Table S3 (SI). DBP formation depends on oxidant type and concentration with most DBPs formed in systems applying hypochlorite treatment. Due to more variable water quality characteristics resulting from ship movements compared to fixed installations, a higher variability of the extent of DBP formation can be expected in operating BWMS. It should be noted that IMO regulations require BWMS to be tested under most challenging conditions, including very high concentrations of organic matter. DBP concentrations observed under these conditions are likely higher than those generated under normal operating conditions of the BWMS in natural waters. Mean concentrations of selected DBPs representing different compound groups in ballast water from this analysis are used as reference for the assessment in this study: 247 (0.08–920) μg/L for bromoform, 49 (0.14–230) μg/L for DBAA, 23 (0.28–133) μg/L for DBAN and 0.27 (0.1–0.45) μg/L for 2,4,6-TBP.

The annual global ballast water discharge from vessels in the international seaborne trade was estimated as 3.1×10^9 m^3 in 2013 (David, 2015). Another estimate provides a value of 10^{10} m^3 of ballast water per year (WHO, 2011). Today, estimates from the IMO suggest that UV treatment or electro-chlorination systems have been installed on vessels as the dominant technologies with a market share of about one-third each. The use of oxidants and other disinfection processes might represent most of the rest. It is currently unclear what percentage of ballast water volumes will be treated with oxidants in 2024, when the whole fleet will have to be equipped with BWMS. For the assessment in this study, it is assumed that a total of 7×10^9 m^3 of ballast water is taken from the aquatic environment by ships each year of which 50% is subject to oxidative treatment, resulting in an estimated total annual volume of 3.5×10^9 m^3 by 2024.

2.4. Wastewater treatment

Disinfection of wastewater prior to effluent discharge to the sea is used to preserve the health of the coastal marine environment (Yang et al., 2000) and to protect humans against exposure to waterborne pathogenic microorganisms, notably from fecal contamination (Mansilha et al., 2009). The most common treatments include oxidation (especially chlorination) and UV irradiation (Jacangelo and Trussell,

2002).

Chlorination is still the most widely used method for disinfection of municipal wastewater effluents both in Europe (Collivignarelli et al., 2017) and the USA. Krasner et al. (2009) report that wastewater treatment plants apply median chlorine doses of 2.4–2.7 mg Cl_2 /L. In the USA, wastewater chlorination is commonly followed by a dechlorination step before the discharge of the effluents to the receiving waters.

Chlorine and to a lesser extent chloramines can react with organic matter present in municipal wastewater to produce various DBPs. The wide array of formed DBPs include THMs, HAAs, and halogenated nitrogenous DBPs (Sgroi et al., 2018). Krasner et al. (2009) showed that chlorination of wastewater resulted in different DBP formation patterns depending on whether or not the treatment plant achieved good nitrification. Some results from this study are provided in Table S4 (SI).

As stated above, disinfection of municipal wastewater is applied worldwide. However, as the information is patchy, it is difficult to quantify the total volumes treated and volumes entering the marine environment. Therefore, for this study, no reliable information on the volumes of oxidatively treated sewage water discharged into the marine environment could be compiled. Since the relevance of these inputs is unknown for estimating DBP inputs into the marine environment at this point, they are not further considered here.

2.5. Seawater toilets

To mitigate the shortage of freshwater supply, seawater is used for toilet flushing in different coastal areas including Hong Kong, the city of Avalon (California), and several Pacific regions including the Marshall Islands and Kiribati (Boehm et al., 2009; Mirti and Davies, 2005; Tang et al., 2007). In Hong Kong, where this practice has been extensively implemented since the 1950s, a total of 2.7 $\times$ 10^8 m^3 of seawater is supplied every year (HK WSD, 2018). The seawater is treated with chlorine or hypochlorite generated on-site before being pumped to service reservoirs and distributed to consumers and then mixed with other domestic sewage and enters the sewage systems in Hong Kong where it is again treated with chlorine prior to discharge.

In Hong Kong's seawater supply, typical chlorine doses are reported as 3–6 mg Cl_2 /L for the intake of seawater, 15 mg Cl_2/L (12 min contact time) for the disinfection of primary sewage effluent and 4–18 mg Cl_2/L (15–30 min contact time) for the disinfection of secondary sewage effluent (Ding et al., 2013; Gong and Zhang, 2015). As the seawater after toilet flushing is mixed with other domestic sewage and enters the sewage systems in Hong Kong, very high levels of sea salts, particularly bromide are introduced into the sewage.

Due to the variety of dissolved organic matter, including compounds derived from microorganism metabolization along with human and industrial waste, a higher complexity of DBPs can be formed in chlorinated saline sewage effluents than in chlorinated marine water. Nevertheless, commonly known DBPs such as THMs and HAAs have been reported to form in chlorinated saline sewage effluents as major compounds (Sun et al., 2009; Yang et al., 2005). An overview of the typical levels of DBPs reported in chlorinated saline sewage effluents in Hong Kong is provided in Table S5 (SI). Many polar/semi-polar brominated and iodinated aromatic DBPs have also been detected (Ding et al., 2013; Gong and Zhang, 2015; Gong et al., 2016). Mean concentrations of selected DBPs representing different compound groups in seawater toilet effluents are used as reference for the assessment in this study: 32 µg/L for bromoform, 9 µg/L for DBAA, and 0.97 µg/L for 2,4,6-TBP.

To date, only a few coastal cities have adopted seawater toilets requiring saline sewage effluents and generating halogenated DBPs. The saline sewage discharge in Hong Kong has been estimated to be 1.0 $\times$ 10^9 m^3/a. This likely represents one of the largest volumes of treated wastewater inputs into the marine environment, which might be considered as a local hotspot.

3. Overview on treatment processes, volumes and DBP concentrations

An overview on oxidant treatment conditions and estimated global volumes of water treated in the different industrial sectors is provided in Table 1. Treatment processes differ in typically applied oxidant doses and in reaction times. Along the coast, where water resources are abundant, billions of m^3 of seawater are used, mostly for cooling of power plants and other industrial installations and desalination. Global cooling water discharge to marine water is estimated in the range of 4.7 $\times$ 10^{11}–8.0 $\times$ 10^{11} m^3/a. Desalination plants treat high amounts of marine water, mostly in arid regions. The global volume of discharged concentrate (brine) is estimated to be 4.6 $\times$ 10^{10} m^3/a. More than 50% of discharge originates from desalination plants located on the Arabian Peninsula. Thus, other regions are considered to be less impacted from desalination discharge. Input of treated ballast water may add locally to the DBP concentrations around large ports (Maas et al., 2019). All applications are expected to expand due to increasing demand from economic development and population growth.

In Table 2, an overview is provided on the mean concentrations of selected DBPs representing different compound groups detected in the treated or discharged water of the different industrial activities. The data show that DBP concentrations are generally higher in ballast water compared to other sectors, e.g., for bromoform, the major DBP, a mean concentration of 247 µg/L was detected whereas only about 10% of this level is typically observed in power plant cooling water, desalination brine and wastewater effluent from seawater toilets. The relatively high concentration in ballast water is coherent with the high oxidant doses and long contact times for these treatments. Furthermore, DBPs containing chlorine, appear to be present in relatively low concentrations in power plant cooling water (Jenner et al., 1997) compared to discharge from other sectors, possibly reflecting the more constant quality of marine water treated. Ballast water and municipal wastewater may be characterized by varying water qualities and thus also varying bromide concentrations, which might shift the spectrum of generated DBPs to chlorinated species (David et al., 2018).

Based on the volumes of treated water in the different sectors (Table 1) and the observed mean DBP concentrations in the treated water or discharge (Table 2) the global production of DBPs from industrial activities can be estimated. Table 3 provides the estimated global production for bromoform. It is assumed that the major part of the produced DBPs represents direct inputs into the marine environment. Since bromoform is the most prominent DBP it may serve as a proxy to compare the inputs from different sectors. The total estimated anthropogenic bromoform production and discharge adds up to 1.35 $\times$ 10^7–2.18 $\times$ 10^7 kg/a, with contributions of 1.18 $\times$ 10^7–2.01 $\times$ 10^7 kg/a from cooling water, 8.9 $\times$ 10^5 kg/a from desalination, 8.6 $\times$ 10^5 kg/a from ballast water and 3 $\times$ 10^4 kg/a from saline sewage treatment (Hong Kong only). Most of the estimates are based on realistic assumptions for

Table 1
Oxidant doses, reaction times and total treated volumes for the different sectors.

Input	Estimated average oxidant dose [mg Cl_2/L]	Reaction times	Estimated volumes [m^3/ a]
Cooling water	0.75 (0.5–1)	2–30 min	4.7–8.0 $\times$ 10^{11}
Desalination	0.2–2	10 min–few hours	4.6 $\times$ 10^{10}
Ballast water	10 (2–20)	1–21 days	3.5 $\times$ 10^9 [a]
Seawater toilets: Saline sewage treatment	4–18	12–30 min	1.0 $\times$ 10^9
Municipal wastewater treatment	2.4–2.7	no information	no information

[a] These volumes are estimated to be treated once the global merchant fleet is equipped with ballast water management systems (by 2024).

Table 2

Average concentrations and concentration ranges of selected DBPs representing different compound classes in the treated water (discharge concentrations).

DBP	Cooling water Average (range)μg/L	Desalination Average (range)μg/L	Ballast water Average (range)μg/L	Seawater toilets (1st/2nd treatment cycle)
Bromoform	25 (3.1–100)	19.3 (0.2–104)	247 (6–920)	27/32
DBAA	9 (7.4–10.3)	3.6 (0.6–11.6)	49 (0.1–230)	6/9
DBAN	1.1 (<0.1–3.6)	0.7 (0–1.2)	23 (0.3–133)	NA/NA
2,4,6-TBP	0.16 (0.02–0.37)	0.75 (0.53–0.96)	0.27 (0.1–0.45)	NA/0.97

"NA" indicated "not available".

Table 3

Estimated global anthropogenic bromoform production by different industrial sectors.

	Bromoform [10^6 kg/a]
Cooling water	11.8–20.1
Desalination	0.89
Ballast water	0.86
Seawater toilets:	0.03
Saline waste water treatment[a]	
Total anthropogenic production	**13.5–21.8**

[a] For wastewater treatment, no estimation is possible.

discharged water volumes and mean values for observed or estimated DBP concentrations. Therefore, this assessment does not represent a worst-case scenario.

Environmental concentrations of DBPs depend on the quantities emitted but also on the characteristics of the receiving environment and natural background concentrations. Furthermore, the fate of the individual DBPs in the surface water depends on the lifetime, solubility and volatility of the compound. The major DBP, bromoform, is volatile and expected to be outgassed relatively quickly and no long-term accumulation in the ocean is expected. Environmental concentrations can be assessed by measurements of DBPs in receiving environments or by predicting the estimated dilution of the effluents. Examples for measured environmental DBP concentrations have been reported for water in the vicinity of power plants (Polman, 2018) and in receiving seawater for treated sewage effluents (Feng et al., 2019). Environmental concentrations can also be estimated based on the knowledge about DBP concentrations in effluents and on assumptions of specific or generic dilutions. Predicted Environmental Concentrations (PEC) have been established for cooling water on the local and regional scale assuming dilution factors of the effluent of 20 and 100, respectively (Khalanski, 2003) and ballast water by model dilution of measured discharge concentrations in a generic harbour (David et al., 2018; GESAMP, 2019).

On local and short-time scales of a few days, all DBP discharges from anthropogenic activities contribute to the concentration in the aquatic environment. In continuous discharges, transient concentrations may be established reflecting an equilibrium of inputs, dilution, evaporation and degradation of compounds. Hence, at large industrial sites where ports, power plants or desalination plants are located, the DBP inputs in discharged waters can sum up and significantly increase DBP concentrations in the coastal ocean. This is important for metropolitan areas in temperate zones like Europe and North America or tropical and subtropical regions, like East and Southeast Asia.

4. Discussion

A quantitative comparison between DBP inputs from different industries is hampered by the heterogeneity of the analyzed studies having various objectives, analytical techniques and sampling strategies. Furthermore, as characteristics of the treated water are known to influence DPB formation, generalizations have to be interpreted with caution. Information on the total generated concentrations of halogenated organic compounds (i.e. in form of sum parameters such as adsorbable organic halogen, AOX) that would allow a total measure of DBP inputs is typically not available. Additional uncertainties may exist.

For instance, average bromoform concentrations observed in cooling water were used for the assessment, keeping in mind that the majority of available data was obtained from studies conducted in European power stations and may not be representative for power stations in other world regions. For a regional assessment, Maas et al. (2021) estimated higher bromoform emissions for East Asian power stations.

However, despite the uncertainties underlying the summarized data and the necessity of estimations to fill data gaps, general conclusions appear warranted when the orders of magnitude of inputs are considered.

Bromoform, which was used as a proxy for the input of DBPs into the marine environment, is also synthesized in large quantities by phytoplankton and macroalgae in the oceans (Quack and Wallace, 2003). Furthermore, bromophenols (with 2,4,6-tribromophenol most often detected) are part of the natural bromine-containing compounds of marine origin (Gribble. 2010). For most other DBPs, no or only very limited natural production has been described. Therefore, most DBPs have to be considered as mainly anthropogenic compounds with little overlap with natural compounds except for bromoform and bromophenols.

For local risk assessment for the aquatic environment typically measured or predicted environmental concentrations (PEC) of individual compounds are compared to their predicted no effect concentrations (PNEC) where a ratio of PEC/PNEC < 1 indicates that no unacceptable risks to the aquatic environment may be expected. PNEC values for the most important DBPs observed in marine water have been proposed by GESAMP (2019). As environmental DBP concentrations depend on specific discharge conditions and dilution in receiving waters, any risk assessment process is site- or scenario-specific. Thus, general conclusions on environmental risks of DBPs in marine water are not possible. Most known DBPs are not bioaccumulative and are quickly eliminated and thus not considered to bioconcentrate in aquatic organisms nor to biomagnify in the food chain (GESAMP, 2019; Khalanski and Jenner, 2012). The low bioaccumulation potential of major known DBPs and the important dilution rate in ocean water suggest that the risks for the aquatic environment posed by DBPs are low on larger scales and distances from discharge, although in specific exposure situation such as in harbours and close to industrial discharges, local effects on aquatic organisms may occur.

Similarly, for the human health risk assessment, estimated human exposure levels are compared to Derived No Effect Levels (DNEL) and Derived Minimal Effect Levels (DMEL) for non-carcinogenic and carcinogenic compounds, respectively, where a Risk Characterization Ratio (estimated exposure level / DNEL or DMEL) (RCR) < 1 indicates that no unacceptable risks for humans may be expected. DNEL and DMEL for major DBPs are proposed by Dock et al. (2019) and GESAMP (2019). For discharge of treated ballast water, exposure from two different scenarios covering direct contact, i.e. swimming near a ship during ballast water discharge, and seafood consumption did not indicate any significant health effects (Dock et al., 2019). Similar assessments are not available for discharges from other industrial applications.

Bromoform is a major carrier of bromine from the ocean to the atmosphere (Penkett et al., 1985). If it reaches the atmospheric boundary layer it is oxidized or photo-dissociated to reactive halogen species which contribute to the depletion of tropospheric and stratospheric ozone by catalytic cycles (Saiz-Lopez and von Glasow, 2012; Tegtmeier

et al., 2020; WMO, 2018). The global bromoform emissions from marine water resulting from natural sources have been estimated to be 3.85×10^8–8.70×10^8 kg/a (Wang et al., 2019; Yokouchi et al., 2005). Therefore, based on the assessment in this study, anthropogenic bromoform discharge into the marine water resulting from the considered industrial treatments equals approximately 2–6% of those global marine bromoform emissions depending on whether higher or lower boundaries are used (Table 3). This range reflects the uncertainty of the estimated anthropogenic inputs and natural production. Potentially, the inputs could be higher in case the conducted studies on DBP concentrations in cooling water are not representative for other regions and other anthropogenic inputs may also be quantitatively relevant, e.g., emission from wastewater treatment, which could not be quantified due to missing data. Furthermore, anthropogenic emission to the atmosphere may be underestimated in this study focusing mainly on marine inputs as 90% of THMs produced in thermal desalination plants are rejected as vent gases (Le Roux et al., 2015). Therefore, an additional assessment of the overall THM production emitted to the atmosphere either from water or directly should be conducted when aiming to address potential effects on the atmosphere (Quivet et al., 2022).

5. Conclusion

This study identifies sources and quantities of inputs of major DBPs through oxidative industrial processes to marine water including industrial cooling, desalination, ballast water treatment and seawater toilets, with the following main outcomes:

- Disinfection by-products (DBPs) are produced during oxidative water treatment for disinfection purposes or biofouling control in industrial processes using marine or brackish water.
- Due to the high concentration of bromide, which is oxidized to hypobromous acid by many oxidants, brominated DBPs are most abundant in treated marine water.
- Bromoform has been identified as the major DBP in all industrial applications using oxidants in seawater. Furthermore, other DBPs, e. g., bromochloromethanes, haloacetic acids, haloacetonitriles and halophenols have been observed, with dibromoacetic acid, tribromoacetic acid, dibromoacetonitrile, 2,4,6-tribromophenol and bromate being often detected.
- Absolute concentrations and relative abundance of the different DBPs vary between different applications reflecting variable process parameters (e.g., oxidant dose and reaction time) and water quality parameters (e.g., characteristics and concentration of dissolved organic matter).
- A quantification of global discharges of DBPs from industrial processes showed that cooling water was the major anthropogenic source, followed by desalination brine and ballast water.
- Since bromoform is the most abundant DBP, it may serve as a proxy to compare the inputs from different sources. The total estimated anthropogenic bromoform discharged into marine water adds up to 1.35×10^7–2.18×10^7 kg/a which is considerably lower than the estimated natural emissions from marine water of 3.85×10^8–8.70×10^8 kg/a.
- Although there are high quality studies on individual sites, e.g., cooling circuits of some nuclear power plants and rather abundant information of DBP generation in ballast water treatment, a comprehensive risk or impact assessment is hampered by a lack of data.
- Uncertainties arise from missing information, e.g., volume of marine water used for cooling purposes worldwide, DBP concentrations in cooling water from not yet studied regions, and from unknown future developments, e.g., an increasing number of desalination plants or the fraction of ballast water management systems using oxidants to be installed. Nevertheless, the estimates from this study suggest that

industrial bromoform inputs into marine water are minor compared to the natural marine emission ($\leq 10\%$).

More harmonized studies on the different major DBPs identified in oxidant-treated effluents are warranted to allow a more systematic overview on DBP variety in the different industries and regions. Strengthening of international efforts in ocean science to build up a better database on concentrations of halogenated organic compounds in the marine environment is advised.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.118383.

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