

## Emerging risks from ballast water treatment

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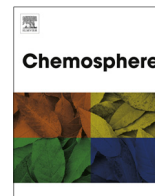
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## Review

## Emerging risks from ballast water treatment: The run-up to the International Ballast Water Management Convention



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## HIGHLIGHTS

- Potential impacts of the International Ballast Water Management Convention are discussed.
- Chemical ballast water treatment effectively reduces the risk of aquatic species invasions.
- Oxidative water treatment forms disinfection by-products that may harm humans and marine biota.
- The established risk assessment disregards multiple exposures and long-term sub-lethal effects.
- Holistic assessment of ballast water management needs to cover many additional factors.

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## ABSTRACT

Uptake and discharge of ballast water by ocean-going ships contribute to the worldwide spread of aquatic invasive species, with negative impacts on the environment, economies, and public health. The International Ballast Water Management Convention aims at a global answer. The agreed standards for ballast water discharge will require ballast water treatment. Systems based on various physical and/or chemical methods were developed for on-board installation and approved by the International Maritime Organization. Most common are combinations of high-performance filters with oxidizing chemicals or UV radiation. A well-known problem of oxidative water treatment is the formation of disinfection by-products, many of which show genotoxicity, carcinogenicity, or other long-term toxicity. In natural biota, genetic damages can affect reproductive success and ultimately impact biodiversity. The future exposure towards chemicals from ballast water treatment can only be estimated, based on land-based testing of treatment systems, mathematical models, and exposure scenarios. Systematic studies on the chemistry of oxidants in seawater are lacking, as are data about the background levels of disinfection

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Risk assessment  
Ballast water treatment

by-products in the oceans and strategies for monitoring future developments. The international approval procedure of ballast water treatment systems compares the estimated exposure levels of individual substances with their experimental toxicity. While well established in many substance regulations, this approach is also criticised for its simplification, which may disregard critical aspects such as multiple exposures and long-term sub-lethal effects. Moreover, a truly holistic sustainability assessment would need to take into account factors beyond chemical hazards, e.g. energy consumption, air pollution or waste generation.

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## 1. Introduction

Almost two thirds of traded goods worldwide are transported by ship (Kumar and Hoffmann, 2002). To ensure ship buoyancy, stability and manoeuvrability, oceangoing ships need ballast water. Based on an estimation that the world seaborne trade in 2013 amounted to 9.35 billion tons of cargo, the global ballast water discharges in 2013 are estimated to about 3.1 billion tonnes (David, in prep.). There is significant transfer of ballast water between different continents and oceans, and it has been known for decades that ballast water also transports organisms into new ecosystems, where, under favorable conditions, they can become invasive (Carlton, 1985; Williams et al., 1988). The introduction of invasive aquatic species into new environments has been identified as one of the four greatest threats to the world's oceans. When including terrestrial species, invasive species were identified as key factor in 54% of all known species extinctions as documented in the Red List database maintained by the International Union for Conservation of Nature (Clavero and Garcia-Berthou, 2005). Aquatic invasions are virtually irreversible and, once the newcomers are established, their impacts may also increase in severity over time. The transfer of invasive species does not occur only over larger distances, between continents, but also as a secondary spread in regional seas (David et al., 2013).

Invasive aquatic species can result in ecosystem changes and disruptions of ecosystem services (Vilà et al., 2010). Invasive species management in marine and coastal environments are major challenges. In European Seas alone, more than 1000 alien species are known. A list of the 100 most impacting species introduced into European waters was prepared within the project “Delivering Alien Invasive Species Inventories for Europe (DAISIE)” (Vilà et al., 2009). Ecological impacts were categorized, e.g. competition with native species, hybridization with native species, use of resources, or habitat modification. Among the top scorers of overall impact, for which ballast water could be identified as a major vector, are organisms from different taxonomic groups originating from different native ranges. Two species in particular, which were

introduced by ballast water and are widespread in Europe, illustrate the possible impact of invasion: The first is the Chinese mitten crab (*Eriocheir sinensis*), a decapod crab, which is native in Asia. The crab, which reaches a size of approx. 7 cm body length, reproduces in marine waters, juvenile crabs migrate up to 1000 km upstream where the adults live for two years in lakes and rivers before they migrate back to the sea for reproduction. This invader was first recorded in Europe in 1912 in the Aller River (Germany). Mass development of this crab in several decades of the last century highlighted its negative impact. Fishermen were affected by the crabs preying upon fish caught in nets and they damaged fishing nets by rope cutting. It was also observed that the crabs clogged commercial water intakes and increased the river bank erosion by burrowing. A “beneficial” impact was also documented as the crabs are considered an Asian delicacy and are sold to Chinese restaurants. Today this species is found from Portugal to Norway and Russia (Gollasch and Rosenthal, 2006). A second example is the comb jelly (*Mnemiopsis leidyi*), which is a more recent case of a drastically impacting invasive species. This species originates from the East Coast of the USA and the Caribbean Sea and was introduced in the 1980s to the Black Sea where it caused, in combination with pollution and overfishing, a devastating reduction in fish catches (Shiganova and Bulgakova, 2000). Since then, the comb jelly spread further and is today also found in the Mediterranean, Baltic and North Seas, luckily without causing a comparable negative impact.

In 2004, the GloBallast programme – a cooperative initiative of the International Maritime Organization (IMO), the United Nations Development Programme, and the Global Environment Facility – undertook an initial scoping study on the global economic impacts of invasive aquatic species (Hassell, 2003; GEF-UNDP-IMO GloBallast Partnerships Programme and IUCN, 2010). Direct economic impacts due to currently known aquatic invasions, including costs from reductions in fisheries and aquaculture production, physical impacts on coastal infrastructure, loss of income for the shipping industry, and impacts on recreational areas and tourism, are estimated to exceed US\$ 100 billion per

year. Additional costs will be incurred by response measures, such as prevention, control and eradication of pests, research and monitoring, education and communication, compliance monitoring and enforcement, as well as costs of the development and onboard installation of ballast water treatment technologies.

Another aspect of species transfer by ballast water concerns the spreading of organisms with potentially harmful effects on human health, such as toxin-releasing algae (Baldwin, 1992; Doblin et al., 2004; Hallegraeff and Bolch, 1991; Lilly et al., 2002) or pathogenic bacteria (Ruiz et al., 2000). Eighty years ago, concerns about hygiene and public health already prompted the U.S. National Institute of Health to advocate a regulation of ballast water discharge and ballast water treatment (Ferguson, 1932). Discharged ballast water at that time was described as “usually seriously contaminated”, and ballast water treatment with sodium hypochlorite was proposed for all ships travelling along the North American Coast and the Great Lakes. In view of the anticipated side effects, the chlorine dosage was to be controlled by “dividing harbour waters into classifications on the basis of plate counts of total bacteria and specifying a chlorine dosage for each class.” Although it was reported that there were no “physical difficulties in the way of effectively chlorinating ballast water”, further work on this issue was discontinued in view of the more serious problems that were caused by the pollution of water with discharged vessel sewage.

Since the 1930s, ships have become larger and faster, and the importance of global cargo shipping has changed dramatically. Ballast water moved back onto environmental and public health agendas. While some countries, i.e. Australia and Canada, which were particularly affected by aquatic invasions, put in place national regulations for ballast water management, it was also clear that the global nature of shipping would require a global response to the ballast water problem. In the 1990s, the IMO developed guidelines for the control and management of ships' ballast water, while at the same time preparing for a binding international treaty. This was finally put into practice at a diplomatic conference in 2004, which adopted by consensus the “International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention)” (IMO, 2004). The BWM Convention enters into force twelve months after the date on which not less than 30 states with combined merchant fleets of not less than 35% of the gross tonnage of the world's merchant shipping have signed it. At the end of April 2014, 38 states constituting 30.38% of the world's tonnage had ratified the Convention.

The BWM Convention provides a set of management tools through which the maritime industry can be regulated. At its core are two different protective ballast water management regimes with a sequential implementation: 1. Ballast Water Exchange Standard (Regulation D-1) requiring ships to exchange a minimum of 95% ballast water volume at least 50 nautical miles from the nearest shore and in waters of 200 m depth or more; 2. Ballast Water Performance Standard (Regulation D-2), which requires that discharged ballast water contain viable organisms only in numbers below specified limits (Table 1). In order to ensure uniform

implementation of the Convention, a set of regulatory and technical guidelines were needed, which the IMO developed together with representatives of the member states, industry, and other organizations. As it was already foreseen that one option of ballast water treatment would be the use of active chemicals or radiation to achieve the D-2 standards, regulations had to be put into place to make sure that the employment of such treatment methods would not cause unacceptable risks to the aquatic environment, human health, or the safety of the ship itself. Hence, IMO guideline G8 (IMO, 2008a) outlines the approval requirements of ballast water management systems (BWMS) by competent flag state authorities and IMO procedure G9 (IMO, 2008b) controls the approval of specifically those BWMS that make use of active substances, which must be endorsed by the IMO Marine Environment Protection Committee (MEPC). To review and evaluate the often-confidential documents, which BWMS manufacturers provide with regard to the properties of their systems, MEPC established a technical group of experts, the GESAMP Ballast Water Working Group (GESAMP BWWG; GESAMP stands for “Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection”, a UN advisory body).

Today, we look back on eight years of experience with the IMO approval procedure. During this time MEPC granted Final Approval to 31 BWMS that make use of active substances (as of May 2013). Both G8 and G9 have meanwhile been revised, and the GESAMP BWWG has further developed its “Methodology for information gathering and the conduct of work” (IMO, 2012). Once the BWM Convention finally enters into force, >50000 ships will need to be equipped with BWMS. Prior to that seems to be the right time to summarize the experiences and observations made and to critically analyze, whether the existing protocols and practices for BWMS testing and approval provide sufficient protection from the environmental and health risks that have so far been identified for the application of these technologies. The German Federal Institute for Risk Assessment (BfR), which recently published two studies with particular relevance to human health (Banerji et al., 2012; Werschkun et al., 2012b), has initiated an extension of the ballast water discussion to a wider circle of scientists, administrators, and stakeholders in the areas of water treatment and marine resources, public health and marine environmental protection (Werschkun et al., 2012a). This paper intends to reflect the current state of understanding and invites further discussion of this issue.

## 2. Ballast water management systems

Many different water treatment technologies are available for municipal and industrial applications. However, when applying them without modifications for ballast water treatment, none of these technologies has shown the capability to achieve the treatment level required by the BWM Convention D-2 standard. However, the soon expected entry into force of the Convention is an important driving force for ballast water treatment technology developments worldwide (David and Gollasch, 2008). While there are still concerns regarding certain types of vessels and regarding the retrofitting capacity of shipyards, many different BWMS are already on the market and others are under development (Dobroski et al., 2009; Gregg et al., 2009; American Bureau of Shipping, 2010; California State Lands Commission, 2010; Lloyds Register, 2012; Witherby Seamanship International, 2011; David and Gollasch, 2012). By July 2012, information on 95 different systems was brought together as background information for the EU FP7-funded project VECTORS. Of these, 23 systems were already type approved with others being in different stages of testing and approval processes (David and Gollasch, 2012). The system capacities range predominantly from 50 m<sup>3</sup> h<sup>-1</sup> to more than

**Table 1**

The BWM Convention ballast water performance standard (Regulation D-2) for maximum limits of viable organisms per defined volume of discharged ballast water.

Group of organisms	Counts per volume
≥ 50 µm	<10 per m <sup>3</sup>
≥ 10 µm < 50 µm	<10 per mL
<i>Vibrio cholerae</i>	<1 cfu per 100 mL or
(O1 and O139)	<1 cfu per 1 g (wet weight)
	zooplankton samples
<i>Escherichia coli</i>	<250 cfu per 100 mL
Intestinal Enterococci	<100 cfu per 100 mL

10000 m<sup>3</sup> h<sup>-1</sup>, while five manufacturers announced a capacity of 20000 m<sup>3</sup> h<sup>-1</sup> and higher. BWMS footprints occupy from less than 1 m<sup>2</sup> up to 145 m<sup>2</sup>; some operate without electricity, while others may consume up to 0.2 kW h m<sup>-3</sup> (David and Gollasch, 2012). Since the completion of this summary, even more BWMS became known so that the total number is now higher than one hundred.

## 2.1. Treatment methods

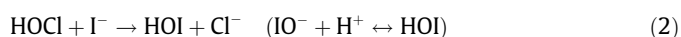
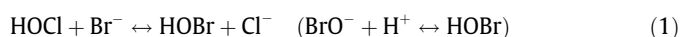
Measures for ballast water treatment can be divided into mechanical–physical and chemical processes (Fig. 1). Practically all identified BWMS employ a combination of two or more different processes. In most cases, mechanical separation of larger particles by filters or hydrocyclones constitutes the first treatment step. Automatic, self-cleaning filter systems with mesh sizes of about 40 µm are frequently employed, leaving smaller organisms in the water. Other physical measures are (a) the application of ultrasound and cavitation, which lead to the mechanical destruction of particles and organisms, (b) high energy techniques, such as heating or (c) UV irradiation. With the combination of high performance filters and UV radiation, there are several type-approved BWMS on the market that rely entirely on physical treatment methods to achieve the IMO D-2 standard. While these systems have no potential to cause chemical hazards to humans or the environment, their downsides are high energy consumption and potential performance problems in waters of high turbidity or a high content of dissolved organic matter (DOM), which may reduce the penetration of UV light.

The majority of BWMS make use of “active substances”, which are defined, according to the IMO, as “substances that have a general or specific action on or against harmful aquatic organisms and pathogens”. There is not always agreement about the interpretation of this definition. While a number of UV systems underwent the complete G9 risk assessment and approval procedure, even though not employing any “substance” in the common sense, another BWMS is currently side-stepping the G9 procedure, which relies on the so-called ‘inert gas’ technology: A gas mixture, which is generated by the combustion of high purity fuel, is released into the ballast tanks, where its main purpose is to replace oxygen and thus create an anoxic environment, in which many organisms cannot survive. At the same time, however, elevated carbon dioxide levels in the combustion gas decrease the pH in the water, and a number of trace compounds such as sulfur and nitrogen oxides or aldehydes may contaminate the treated water. Even though this system, as any other BWMS approved in accordance with IMO guideline G8, must undergo the same ecotoxicity testing of treated water as required by IMO procedure G9 for active substances, the study reports need to be submitted to the competent flag state authority, only. Thus, no detailed data about the exact composition of the combustion gas mixture or the

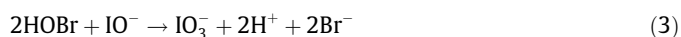
composition and toxicity of discharged ballast water resulting from this treatment have so far been made publically available.

Chemical disinfectants act by a variety of mechanisms at the molecular level. One approved BWMS utilizes ionic interactions to combine fine particles, colloids, and dissolved matter into removable aggregates by the addition of the common flocculants iron(III) oxide, polyaluminium chloride, and polyacrylamide. Most agents inhibit biological processes by chemical reactions with biomolecules such as membrane constituents, proteins or nucleic acids. Applications in ballast water treatment have been discussed for metal ions (silver or copper), aldehydes (formaldehyde, acrolein), and quaternary ammonium compounds, but no system based on any of these compounds has so far entered the IMO approval process. By far the largest group of active substances used are oxidizing agents. Systems based on chlorine (either generated *in situ* by seawater electrolysis or from hypochlorite stock-solutions) clearly predominate, followed by ozone, peracetic acid, and chlorine dioxide (in this order). The application of chloramine is under development. Strong oxidants, due to their high reactivity, not only react with the organisms to be inactivated but also with a number of other water matrix components.

In freshwater, the reactivity of chemical oxidants with matrix components has been of interest since the 1970s when trihalo-methane formation was discovered following chlorine addition (Rook, 1974). Many more compounds, i.e. disinfection byproducts (DBPs), have been identified since this time. In general, DBPs form through the reaction of oxidants with organic matter (i.e. humic and fulvic acids) and/or various inorganic species (e.g. bromide and iodide). Halides are of particular importance because they can form additional oxidizing species. Chlorine (HOCl) reacts with bromide and iodide to form the oxidizing species HOBr and HOI, respectively (reactions (1) and (2); Kumar and Margerum, 1987; Nagy et al., 1988), but, may also generate lower levels of oxidants such as Br<sub>2</sub>, BrCl, BrOCl, and even Cl<sub>2</sub> given the high concentration of chloride present in saline waters (0.54 M; Eigen and Kustin, 1962; Wang and Margerum, 1994; Liu and Margerum, 2001; Margerum and Huff Hartz, 2002).



HOBr, formed by reaction (1), also reacts fairly quickly with IO<sup>-</sup> to iodate (IO<sub>3</sub><sup>-</sup>) (reaction (3); Criquet et al., 2012), a non-toxic sink for iodide (Bürgi et al., 2001). This reduces the chance to form iodo-organic compounds significantly (Criquet et al., 2012).



Similar processes may also be observed in the presence of ammonia in which chloramines (NH<sub>2</sub>Cl, NHCl<sub>2</sub>, and NCl<sub>3</sub>) are initially formed. Monochloramine (NH<sub>2</sub>Cl) may then further react with bromide and iodide to form bromamines/bromochloramine (Hofmann and Andrews, 2001; Duirk and Valentine, 2007; Trofe et al., 1980) and HOI (Bichsel and von Gunten, 1999), respectively. Formation of such brominating/iodinating oxidants generates species that are often more reactive than the initial applied oxidant (Sivey and Roberts, 2012; Sivey et al., 2013) and form brominated/iodinated DBPs in the reaction with dissolved organic matter.

Ozone is also affected by the presence of halides. Initially, ozone reacts with bromide and iodide to form HOBr and HOI (reactions (4) and (5)), respectively, but can further oxidize BrO<sup>-</sup> to bromate (BrO<sub>3</sub><sup>-</sup>; reaction (6), simplified; Haag and Hoigne, 1983; von Gunten and Hoigné, 1994; von Sonntag and von Gunten, 2012). Since the reaction of ozone with HOBr/BrO<sup>-</sup> is relatively slow, this oxidant may react with the dissolved organic matter to form brominated organic compounds. In contrast, ozone reacts quickly with

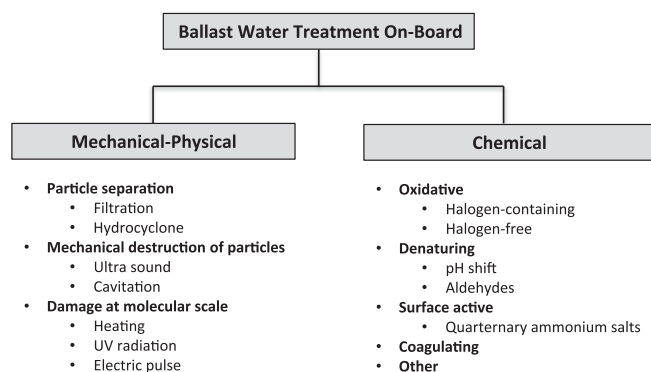
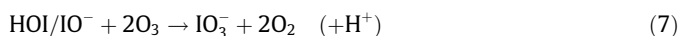


Fig. 1. Overview of ballast water treatment measures on board a ship.

HOI/OI<sup>−</sup> to iodate (IO<sub>3</sub><sup>−</sup>) (reaction (7); Bichsel and von Gunten, 1999). Thus, the formation of iodinated DBPs is minimized (Allard et al., 2013; von Sonntag and von Gunten, 2012).



The impact of halides on other oxidants such as chlorine dioxide and peracetic acid remains less clear. Chlorine dioxide, while well documented to generate the inorganic DBPs chlorite and chlorate, does not react with bromide but does react with iodide (Hoigné and Bader, 1994). This was followed by a study in which chlorine dioxide-treated water containing 2 mg L<sup>−1</sup> bromide and 17–18 µg L<sup>−1</sup> iodide did not generate brominated DBPs while formation of iodinated DBPs remained inconclusive (Richardson et al., 2003). Only very limited evidence is available on peracetic acid, suggesting that DBPs such as chlorophenols and bromophenols form from phenol-spiked final effluent wastewater in the presence of chloride and bromide, respectively (Booth and Lester, 1995).

## 2.2. Testing

As long as the BWMS Convention is not implemented, we derive our knowledge about BWMS performance and side effects from prototypes that are already installed on board ships and from BWMS testing in land-based facilities. The primary scope of land-based testing as described in IMO guideline G8 (IMO, 2008a) is to evaluate the effectiveness of BWMS in removing or killing organisms. BWMS that make use of active substances must additionally undergo toxicity testing as detailed in IMO procedure G9 (IMO, 2008b). Land-based tests are conducted at flow rates of 200 m<sup>3</sup> h<sup>−1</sup> and a minimum holding time of 5 d for treated water. A control experiment with untreated water is conducted in parallel. However, the holding tanks used for land-based testing differ significantly from a ship's ballast water tank in size and design. Tanks used for land-based testing usually have less internal structures than a vessel's ballast water tank, which influence the movement of the water within the tank, while filling and discharging. Furthermore, the role of sediment cannot be assessed during land-based certification, since the protocols call for cleaning of the tanks between each test. Water samples are generally taken on intake and on discharge. In order to get reliable and representative samples, land-based test facilities are equipped with numerous sampling points at different locations. Analysis of the samples focuses on biological parameters. In addition, basic parameters characterizing the water matrix such as salinity, temperature, organic carbon and particulate matter content, pH and oxygen are measured. Additional samples can easily be taken, for instance for toxicity testing or for the analysis of nutrients or chemicals.

The IMO guidelines G8 and G9 are generic in nature, and at the time the first versions were released in 2004/2005, there were no standard methods available. Test facilities had to find their own means of putting the guidelines into practice. Harmonization efforts, e.g. via the GloBallast programme or the North Sea Ballast Water Opportunity project show that the different test facilities in general developed quite similar approaches to the problem (Gollasch, 2010). Almost all test facilities use ambient, natural water. However, the degree to which this water is altered varies. To ensure sufficient function of BWMS even under challenging conditions, guideline G8 requires that test water used for land-based testing must contain specified minimum concentrations of living organisms as well as abiotic matter. Test facilities that are located

in biologically highly productive and turbid areas need less manipulation of their water to fulfil these criteria. Others, who either do not have suitable water conditions or want to test independently of surrounding conditions, add surrogate organisms and suspended and/or dissolved matter. Working with natural water makes the tests less predictable, while working with heavily modified waters increases the possibility of artefacts. When analysing data from certification tests of BWMS, it is important to keep in mind that the preparation of test water and water chemistry might have an influence on studies performed for toxicological risk-assessment, e.g. through differences in by-product formation.

## 3. Hazards

Chemical hazards associated with BWMS can be divided into acute effects from the action of strong oxidants and long-term effects from DBPs. While the employed oxidants generally act as corrosives on living tissue, the concentrations handled on board are mostly below toxicological concern, especially when generated *in situ*. Only in a few cases concentrated chemicals are carried on board – ready-made hypochlorite solutions, peracetic acid, and starting materials for the generation of chlorine dioxide (hydrogenperoxide, sodium chlorate, 70% sulfuric acid) – and pose potential danger to the crew. The aquatic environment is protected from strong oxidants by the requirement to keep total residual oxidant concentrations in discharged treated water below 0.2 mg L<sup>−1</sup>, which is achieved by reaction with reducing agents such as sodium bisulfite or thiosulphate. The generated mixtures of DBPs present far more complex toxicological challenges, both to human health and natural biota.

### 3.1. Long-term toxicity of disinfection by-products

Many DBPs are associated with severe health hazards, such as the potential to cause cancer and reproductive and developmental effects (Nieuwenhuijsen et al., 2000; Richardson et al., 2007; Savitz et al., 2005; Villanueva et al., 2004; Waller et al., 1998). Chloroform and other trihalomethanes (THMs) were the first DBPs identified in chlorinated drinking water in 1974 (Rook, 1974; Bellar et al., 1974). Soon after their discovery, the THMs were found to cause cancer in laboratory animals (National Cancer Institute, 1976). As a result, they became regulated in the United States in 1979 (U.S. EPA, 1979), and later in several other countries. A few additional DBPs are now regulated in the U.S., including five haloacetic acids (HAAs), chlorite, and bromate (U.S. EPA, 2006).

Over the last 30 years, significant research efforts in the field of drinking water disinfection have been directed towards increasing our understanding of DBP formation, occurrence, and health effects. More than 600 DBPs have now been reported in the scientific literature (Richardson, 1998, 2011). However, only less than 100 have been addressed either in quantitative occurrence or toxicity studies (Richardson et al., 2007). More than 50% of the halogenated DBP material formed during the chlorination of drinking water, and more than 50% of the DBPs formed during ozonation of drinking water are still not accounted for (Krasner et al., 2006; Richardson et al., 2008a), and nothing is known about the potential toxicity of many of the DBPs present in drinking water. Much of the previous health effects research has focused on cancer, genotoxicity, mutagenicity, or cytotoxicity (Richardson et al., 2007). There are concerns that the types of cancer observed in animal studies (primarily liver cancer) for the regulated DBPs do not correlate with the types observed in human epidemiology studies (primarily bladder cancer). Therefore, studies on DBPs beyond those that are currently regulated are needed.

There is indication that brominated DBPs may be more carcinogenic than their chlorinated analogues (Richardson et al., 2007), and

early evidence in epidemiologic studies also gives indication that brominated DBPs may be associated with reproductive and developmental effects (Savitz et al., 2005; Waller et al., 1998). New studies are indicating that iodinated compounds are even more toxic than their brominated analogues (Plewa et al., 2004a; Richardson et al., 2007, 2008b). Moreover, many emerging DBPs are nitrogen containing (the so-called “N-DBPs”), which are generally more genotoxic and cytotoxic than those without nitrogen (Plewa et al., 2008). Specific DBPs that are of current interest include iodo-acids, bromonitromethanes, iodo-THMs, haloamides, halofuranones, halopyrroles, haloquinones, haloaldehydes, halonitriles, and nitrosamines. Several of these DBPs are carcinogenic, including MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) and several of the nitrosamines including N-nitrosodimethylamine (NDMA). Many emerging DBPs show stronger genotoxic or cytotoxic effects in mammalian or human cells (in vitro) than DBPs that are currently regulated (Attene-Ramos et al., 2010; Plewa et al., 2008). For example, iodoacetic acid, the most genotoxic DBP studied to-date, is two times more genotoxic than bromoacetic acid (Plewa et al., 2004a), which is regulated. Throughout the series of haloacetic acids, the toxic potency increases from chloro- to bromo- to iodo-derivatives (Plewa et al., 2010). Recently published research revealed an association between the toxicity of monohaloacetic acids and their capacity to induce oxidative stress (Pals et al., 2013). Iodoacetic acid also caused neural tube defects in mouse embryos (Hunter and Tugman, 1995), and recent data shows that it is also tumorigenic in mice (Wei et al., 2013).

While most toxicity studies to-date have been conducted on individual chemicals only, DBPs in treated water are always present as mixtures. As a consequence, a collaborative study of the four national laboratories and centres of the U.S. EPA was conducted to investigate the toxicity of these complex DBP mixtures, as well as defined mixtures containing regulated DBPs (Pressman et al., 2010; Simmons et al., 2008). A battery of in vitro and in vivo assays was used to investigate the toxicity, with an emphasis on reproductive and developmental effects. Seventy priority DBPs were quantified, and more than 100 were comprehensively identified. In the tested concentrates (~136× drinking water concentrations), major in vivo effects were not observed, but a number of more subtle effects (such as lower sperm counts, and delayed puberty) were found. Complete toxicology results for this work have recently been published (Narotsky et al., 2013). In Europe, the HIWATE project combined chemical analysis of DBPs in drinking water samples from five different countries with both in vitro cytotoxicity tests and epidemiological studies on adverse pregnancy outcomes (Jeong et al., 2012). Poor correlation between chemical analyses and genotoxic responses observed in this study indicates an unidentified influence and emphasizes the need to further evaluate the toxicity of complex mixtures.

In view of the multitude of potentially occurring DBPs, a bio-test-based test strategy might be a feasible alternative or addition to chemical analysis for the hazard assessment of treated water. A number of comparatively simple in vitro tests may already give important indications of the toxicological properties of most concern. Kirkland et al. (2011) have shown that none of the known genotoxic carcinogens would have remained undetected by a simple combination of a bacterial gene mutation assay (Ames test) and an in vitro micronucleus test. Both assays are already applied for regulatory purposes in the German waste water regulation (German Federal Ministry of Justice, 1997).

### 3.2. Implications for natural biota

Given the universal make-up and functionality of DNA, it is generally accepted that qualitatively the induction of genetic damage following exposure to environmental contaminants across

phylogenetically disparate groups of organisms is the same (Dixon et al., 2002; Jha, 2004). Genotoxic effects are considered to be important for the initiation and promotion of carcinogenesis, and several studies have linked the induction of pre-neoplastic and neoplastic lesions in fish and invertebrates with genotoxic effects (e.g. DNA adducts, DNA strand breaks, induction of micronuclei) following exposure to a range of contaminants in the natural environment (Myers et al., 1998; Lyons et al., 2004; Frenzilli et al., 2004; Vogelbein et al., 1990; Hesselman et al., 1988; Gardner et al., 1991; Bolognesi and Hayashi, 2011; Theodorakis et al., 2012). Whilst cancer is one of the major health concerns in the human health arena, this disease until now has not been considered important for natural biota - despite the fact that under the microscope neoplasia whether in humans or in natural biota (e.g., fish or mussels) have similar mechanisms of induction and pathological features. In natural biota, with enormous reproductive surplus, the occurrence of neoplasia has in the past not been considered relevant for environmental risk assessment. This paradigm is however being scientifically challenged for two reasons (a) induction of genetic damage in natural biota could serve as a sentinel for risks to human health by environmental contamination and (b) induction of genetic damage (whether in somatic or germ cells) indicates a potential threat to biodiversity (Jha, 2004, 2008; Bickham et al., 2000). Even the fixation of mildly deleterious mutations could significantly contribute to a loss of Darwinian fitness and could eventually lead to the extinction of small populations (Lynch et al., 1995; Lande, 1998).

Whilst there is a large number of studies using bacterial systems (e.g., Ames test, SOS chromo test, etc.) to determine the intrinsic genotoxic potential of DBPs, there have been very few studies to determine expressed genotoxic effects on natural biota in vivo, taking into account the environmentally realistic routes of exposure, metabolism, excretion and DNA repair capabilities of the organisms. In freshwater, erythrocytes from the larvae of urodele amphibian (newt), *Pleurodeles waltl*, suggested that chlorine levels of 0.125 and 0.25 ppm in water disinfected with sodium hypochlorite led to significant elevations in micronuclei (Mn). The level of Mn also increased with an increasing concentration of monochloramine (Gauthier et al., 1989). While evaluating the genotoxicity of five chlorinated propanones identified in several chlorinated waters, the newt Mn assay detected clastogenic/aneugenic effects only for two compounds - 1,3-dichloropropanone and 1,1,3-trichloropropanone (Curieux et al., 1994). In order to compare the relative genotoxicity of classic disinfectants (e.g., sodium hypochlorite and chlorine dioxide) and an alternative disinfectant (e.g., peracetic acid), induction of DNA damage (using the comet assay) and micronuclei was carried out in the haemocytes of zebra mussels, *Dreissena polymorpha* under *in situ* conditions. Results suggested the two chlorinated compounds to be positive for the endpoints whereas peracetic acid did not show any genotoxic effects (Bolognesi et al., 2004). Examination of kinetics, tissue specific concentrations and effects on enzyme systems has been carried out for dichloroacetic acid, a product of chlorine disinfection, in rainbow trout, *Oncorhynchus mykiss* showing differential tissue specific responses (Fitzsimmons et al., 2009) but more work is required to further elucidate these mechanistic aspects.

Incorporation of biomarkers into regulatory environmental risk assessment is lacking and the focus continues to be on chemical measurements in the context of environmental quality standards, although some of the international treaties (e.g., the Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR) recommend the use of biomarkers for environmental monitoring programmes (Hagger et al., 2006). Similarly, the water framework directive of the European Union (Directive 2000/60/EC) emphasizes the need for biological elements as well as physicochemical and hydromorphological components for the

determination of good ecological status. Sub-lethal effects inadvertently affect the Darwinian fitness, including reproductive success of the organisms (Jha, 2008), which will ultimately impact short- and long-term survival of the exposed species and hence environmental sustainability. Therefore, there is a growing need to develop a strategy to determine the sub-lethal toxicity (including genotoxicity) of environmental contaminants in a range of ecologically relevant species at different trophic levels.

#### 4. Exposure

Human and environmental exposure to ballast water related chemicals is first and foremost determined by the quantities of chemicals that may be released by BWMS. While quantities of active substances applied are defined in the operational schedule of BWMS, quantities of generated DBPs need to be determined analytically in treated water during BWMS testing. As indicated above, most data available at the present comes from land-based testing and is at least summarily published in the course of the IMO procedure G9 for the approval of BWMS that make use of active substances. A recent review article summarizes the DBP data reported for ten internationally approved BWMS based on chlorine or ozone as active substance (Werschkun et al., 2012b). As can be expected in marine waters (see Section 2.1), brominated compounds are predominately formed. The dominating individual substances detected in treated ballast water are bromoform (up to  $670 \mu\text{g L}^{-1}$ ), dibromoacetic acid (up to  $120 \mu\text{g L}^{-1}$ ), tribromoacetic acid (up to  $99 \mu\text{g L}^{-1}$ ), bromoacetic acid (up to  $86 \mu\text{g L}^{-1}$ ), bromate (up to  $70 \mu\text{g L}^{-1}$ ), dibromochloromethane and dibromoacetonitrile (each up to  $21 \mu\text{g L}^{-1}$ ). Only a limited range of substances has so far been investigated, mainly chlorinated and brominated methanes, phenols, acetic acids, and acetonitriles. The available database suffers from a number of information gaps and uncertainties, and systematic investigations of DBP formation in sea water in relation to water quality or operational parameters are missing.

##### 4.1. Environmental exposure

For the assessment of environmental acceptability of a BWMS the predicted environmental concentration (PEC) of all discharged substances needs to be determined. The PEC needs to account for different harbour types worldwide and should be a realistic worst case representation of the harbour properties, the processes causing renewal of the harbour water masses, the average treated ballast water emissions and the environmental fate of the different released substances. For this purpose, the software MAMPEC (Marine Antifoulant Model to Predict Environmental Concentrations), originally developed for the exposure calculation of leaching antifoulants, was adapted to the specific requirements of ballast water assessment and includes a specified model harbour. A systematic sensitivity analysis (Zipperle et al., 2011) determined that the original MAMPEC assumption of constant and homogeneous emissions underestimates the maximum concentrations of fast decaying substances as compared to the more realistic assumption of spatial and temporal heterogeneity of ballast water discharges. In particular for the calculation of maximum exposure to substances with half-lives shorter than 1 d near-field analysis is therefore proposed as a more fitting approach. In the 'near-field', which addresses an individual discharge and ship rather than an entire harbour, discharge characteristics control the mixing behavior (Doneker, 2002). Modelling of different case studies showed that the dilution factor at the end of the near-field zone increases (i.e. the maximum concentration of substances decreases) with increasing ambient current velocities, increasing discharge depths, and decreasing ballast water discharges. Under stagnant conditions, e.g., in a confined harbour basin, a dilution factor as low as

5 may result. In all environmental assessments of rapidly reacting substances, e.g., oxidants, it is important to apply the same consideration of decay for exposure calculation as for the assessment of toxicity values used in risk assessment (see also Section 5).

At the moment, there are no field data for ballast water related chemicals to verify the validity of exposure models, since the substances in question (see Table 2) are not currently included in established monitoring programmes for the marine environment, which mainly target persistent organic pollutants (POPs), such as polychlorinated and polybrominated hydrocarbons, dibenzodioxins and -furans, or perfluorinated compounds. Classical POPs are semi-volatile to non-volatile and evaporate slowly in air. As they are predominantly non-polar they show a high bioaccumulation tendency and are concentrated at solid phases of suspended matter or sediments. Therefore, they are eliminated quite rapidly from the water phase by sedimentation. In contrast, most BWMS compounds are either rather volatile (halogenated hydrocarbons, acetonitriles, and amines) or non-volatile and polar (halogenated phenols and acetic acids). Compounds of the first category evaporate quite readily from the water, whereas the polar group members remain in the water column. They do not accumulate on suspended matter or sediments and exhibit little bioaccumulation potential. Thus, they can be transported by currents over large distances if they are persistent. The different chemical and environmental characteristics of classical POPs and ballast water treatment chemicals have significant effects on monitoring parameters such as the monitoring matrix, concentration ranges, and spatial objectives. Classical POPs are often monitored in sediments and biota because they have a tendency to accumulate in these matrices. Due to this accumulation, a safety margin is often applied to water concentrations and to the evaluation of effect levels. The monitoring of ballast water treatment chemicals, on the other hand, will concentrate on the water phase, with medium to low concentrations, and on local and regional distribution.

Concentrations of the most important DBPs produced in BWMS (THMs and HAAs) were calculated as up to  $100 \mu\text{g L}^{-1}$  for 5-times dilution from the ship outlet and as up to  $5 \mu\text{g L}^{-1}$  for 100-times dilution (Zipperle et al., 2011). These concentrations are about 2–4 orders of magnitude higher than those of classical POPs in the marine environment. Within the dense plume from the emitting ship (5-fold dilution) direct analysis, e.g. gas or liquid chromatography coupled with mass spectrometry, without a pre-concentration step will be possible for major constituents. However, with increasing distance and increasing dilution, the analysis will become more and more difficult and additional enrichment and pre-concentration steps will be necessary. The most challenging problem of future monitoring strategies for ballast water compounds will be sampling at locations other than the immediate point of discharge because of the temporal and spatial variability of emissions. Time-integrated sampling using passive samplers might be a promising approach. With increasing distance from the land, i.e. along shipping routes or in open sea areas, even this may only be feasible for persistent compounds in the higher concentration ranges. A differentiation from background concentrations arising from natural or other anthropogenic sources will be important, in order to properly distinguish contributions from BWMS.

##### 4.2. Human exposure

Potential exposure to chemicals from BWMS can be anticipated in particular for the ship's crew and for port state inspectors, but also for the general public. The GESAMP BWWG (IMO, 2012) and Banerji et al. (2012) compiled comprehensive lists of exposure scenarios and equations for the quantification of exposure. The most important information is summarized in Table 3. Many specific

**Table 2**

Frequent by-products and other chemicals observed in BWMS effluents.

Relevant chemicals	Molecular formula	Relevant chemicals	Molecular formula
<b>Halogenated Methanes</b>		<b>Halogenated Phenols</b>	
Trichloromethane	CHCl <sub>3</sub>	2,4-Dibromophenol	C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub> O
Tetrachloromethane	CCl <sub>4</sub>	2,6-Dibromophenol	C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub> O
Tribromomethane	CHBr <sub>3</sub>	2,4,6-Tribromophenol	C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub> O
Dibromochloromethane	CHBr <sub>2</sub> Cl	<b>Halogenated Acetic Acids</b>	
Dichlorobromomethane	CHBrCl <sub>2</sub>	Monochloroacetic acid	CH <sub>2</sub> ClCOOH
<b>Halogenated Hydrocarbons</b>		Dichloroacetic acid	CHCl <sub>2</sub> COOH
1,2-Dibromoethane	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	Trichloroacetic acid	CCl <sub>3</sub> COOH
1,1,1-Trichloroethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	Monobromoacetic acid	CH <sub>2</sub> BrCOOH
Tetrachloroethene	C <sub>2</sub> Cl <sub>4</sub>	Dibromoacetic acid	CHBr <sub>2</sub> COOH
1,2,3-Trichloropropane	C <sub>3</sub> H <sub>4</sub> Cl <sub>3</sub>	Tribromoacetic acid	CBr <sub>3</sub> COOH
1,2-Dibromo-3-chloropropane	C <sub>3</sub> H <sub>4</sub> Br <sub>2</sub> Cl	Bromochloroacetic acid	CHClBrCOOH
2-Chlorotoluene	C <sub>7</sub> H <sub>7</sub> Cl	Dibromochloroacetic acid	CBr <sub>2</sub> ClCOOH
4-Chlorotoluene	C <sub>7</sub> H <sub>7</sub> Cl	Bromodichloroacetic acid	CBrCl <sub>2</sub> COOH
1,2,3-Tribromobenzene	C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub>	<b>Inorganics</b>	
<b>Halogenated Acetonitriles</b>		Chlorite ion	ClO <sub>2</sub> <sup>-</sup>
Chloroacetonitrile	CH <sub>2</sub> ClCN	Chlorate ion	ClO <sub>3</sub> <sup>-</sup>
Dichloroacetonitrile	CHCl <sub>2</sub> CN	Bromate ion	BrO <sub>3</sub> <sup>-</sup>
Trichloroacetonitrile	CCl <sub>3</sub> CN	Nitrite ion	NO <sub>2</sub> <sup>-</sup>
Monobromoacetonitrile	CH <sub>2</sub> BrCN	Nitrate ion	NO <sub>3</sub> <sup>-</sup>
Dibromoacetonitrile	CHBr <sub>2</sub> CN	<b>Neutralization</b>	
Tribromoacetonitrile	CBr <sub>3</sub> CN	Sodium bisulfate	NaHSO <sub>4</sub>
Bromochloroacetonitrile	CHBrClCN	Sodium sulfite	Na <sub>2</sub> SO <sub>3</sub>
<b>Halogenated Amines</b>		Sodium thiosulfate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Monochloramine	NH <sub>2</sub> Cl	Sodium sulfate	Na <sub>2</sub> SO <sub>4</sub>
Dichloramine	NHCl <sub>2</sub>		

**Table 3**

Scenarios and pathways for human exposure to chemicals from BWMS.

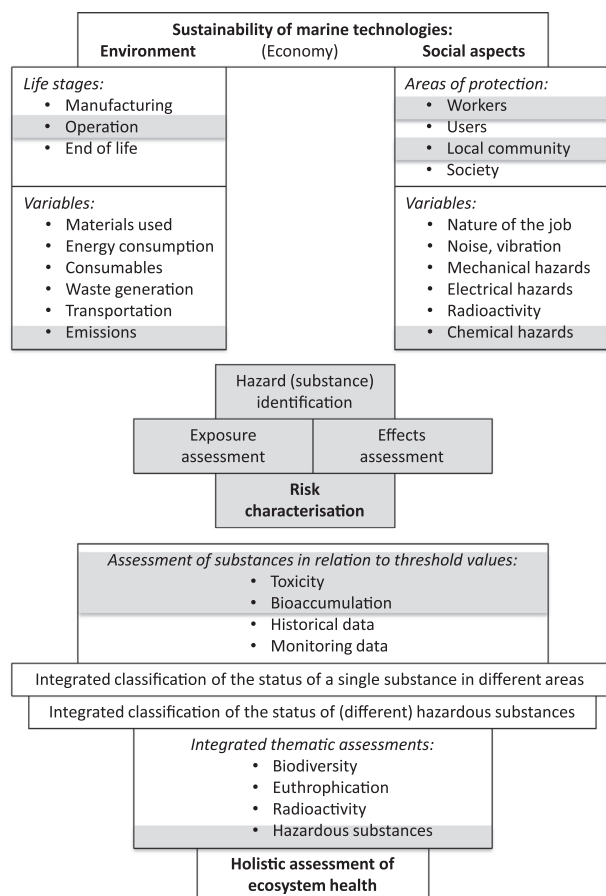
Activity	Exposure	Quantification (IMO, 2012)
<i>Crew</i>		
Handling of chemicals	Dermal/inhalation (leakages, spills)	100 mg (0.1 mL)/container
Starting of BWMS	Type-specific	Case by case
BW treatment	Type-specific	Case by case
Ballasting/routine deck work	Inhalation (BW tank exhaust)	1 h d <sup>-1</sup> over 6 mth <sup>-1</sup>
De-ballasting	Dermal/inhalation (spray drift)	Not considered
Tank cleaning	Dermal (whole body)/inhalation	8 h d <sup>-1</sup> on 5 d wk <sup>-1</sup> ; 1 wk y <sup>-1</sup>
Other maintenance work	Type-specific	Case by case
Malfunctions, accidents	Inhalation/dermal	Not considered
<i>Port state control</i>		
Sampling (compliance control)	Inhalation/dermal (hands)	2 h d <sup>-1</sup> on 5 d wk <sup>-1</sup> ; 45 wk y <sup>-1</sup>
Tank inspection	Inhalation	3 h d <sup>-1</sup> on 1 d mth <sup>-1</sup>
<i>General public</i>		
Swimming/recreational activities	Inhalation/dermal/oral	5 h d <sup>-1</sup> on 14 d y <sup>-1</sup>
Seafood consumption	Oral	~200 g d <sup>-1</sup>

details depend on the type of system, e.g., whether it requires the storage of chemicals on board, or whether it involves frequent cleaning and maintenance procedures. Occupational exposure to BWMS related chemicals may occur through dermal contact, which can be prevented by appropriate protective clothing and equipment, or through inhalation of volatile substances, e.g. THMs, emitted from treated ballast water into the surrounding atmosphere. For the quantitative estimation of exposure, reliable data on the concentrations of substances, in particular DBPs, in treated water are essential. As calculations based on concentrations measured during land-based testing show, inhalation of bromoform in the confined space of the ballast tank during inspection or cleaning may reach toxicologically relevant levels in the case of inadequate ventilation. In order to help ship owners to protect their crews from chemicals associated with ballast water treatment, the IMO published a guidance document detailing the potential exposure situations that should be addressed when installing a BWMS on board a specific ship (IMO, 2009).

Non-occupational exposure scenarios also include oral intake of chemicals by swallowing diluted ballast water during swimming or by the consumption of seafood from ballast water discharge areas. While substance concentrations in the water can be calculated with MAMPEC (see above), the calculation of concentrations in seafood requires substance-specific data on bioconcentration, which are mostly lacking for the substances of concern. Estimations based on physical–chemical properties, although a common practice in environmental risk assessment, may be significantly flawed, as exemplified by Taylor (2006), who reported an experimentally determined bioconcentration factor of bromoform in sea bass that exceeded the value calculated from its octanol–water partition coefficient by more than a factor of 10.

## 5. Risk assessment

IMO procedure G9 outlines the risk assessment to be performed for BWMS that make use of active substances (IMO, 2008b). A more



**Fig. 2.** Risk assessment for BWMS (centre) in relation to holistic assessments of the sustainability of marine technologies (top) and of ecosystem health (bottom). Overlaps are shaded in grey.

detailed description of the risk assessment process can be found in the “Methodology for information gathering and the conduct of work of the GESAMP Ballast Water Working Group” (IMO, 2012). Risks are evaluated with regard to the aquatic environment, human health and the safety of the ship itself. Risk assessment for human health and the environment is based on information provided by the manufacturer of the BWMS and follows the general principles of established regulatory frameworks for the evaluation of chemicals or biocides (see Fig. 2, centre). In fact, key provisions of IMO procedure G9 were modelled on the former EU directive for biocidal products (EU, 1998). Generally, the risk assessment for both the environment and human health consists of a comparison between the calculated exposure (see Section 4) and the exposure for which no adverse effect is assumed based on laboratory tests. Toxicity tests for the environment should consider short-term and long-term effects for at least three taxonomic groups of different trophic levels, i.e., algae, invertebrates, and fish. Human health effects are estimated from in vitro or animal studies on short-term and long-term toxicity, local effects on skin and eye, mutagenicity, and effects on reproduction and development. Assessment factors account for inherent uncertainties of the effects assessment. Ecotoxicity tests are also conducted with the treated ballast water, providing information on the mixture of substances present in the discharge as compared to single substances. Whole effluent tests for mammalian toxicity endpoints are not part of the G9 procedure. A frequent point of criticism towards regulatory risk assessment is its simplification and standardisation, which may not adequately reflect the complex reality, in particular with regard to multiple exposures or long-term population effects.

While the risk assessment of BWMS focuses on the future discharge of substances from a discrete source (ship), the established conventions for the protection of the marine environment, e.g., OSPAR for the North Atlantic or HELCOM for the Baltic Sea, are concerned with the status of substances present in the environment today (Fig. 2, bottom). The initial step of this assessment also includes the derivation of effect levels, which are considered safe, from toxicity testing of single substances. In this regard, regulatory risk assessment and environmental monitoring schemes are complementary. Spatial integration of the assessment for a single substance followed by the integration of status classifications obtained for different substances give a more complete picture of the status of the aquatic environment with regard to hazardous substances. This may be complemented by assessments of different ecological aspects, such as biodiversity.

A different kind of holistic approach, which includes and at the same time transcends the assessment of chemical hazards from BWMS, is provided by Basurko and Mesbahi (2014) with their proposed sustainability assessment of marine technologies (Fig. 2, top). Based on life-cycle methodologies (Klöpffer, 2003; Dreyer et al., 2006; UNEP, 2009), assessment schemes were developed for three different dimensions of sustainability – environment, economy and social impact. In addition to the toxicity of treated water and the chemicals used on board, the sustainability assessment of the technology as a whole also needs to consider factors like the materials used in the construction of the BWMS, energy consumption and related air pollution, or waste generation and management. The integration of the different dimensions of sustainability allows comparisons between different technologies or scenarios with regard to their overall impact, as well as specific variables.

## 6. Summary and outlook

Since the adoption of the International Ballast Water Management Convention in 2004, major advances were achieved in the development of ballast water treatment technologies and their approval under the auspices of IMO. While aiming at a reduction of aquatic species invasions and their negative impacts on ecosystems and resources, ballast water treatment brings about new challenges for environmental and public health protection. Compliance with the biological standard of the Convention is most effectively realized through application of chemical oxidants. These methods favor the formation of potentially toxic disinfection by-products, which has so far been insufficiently investigated in marine waters. Risk assessment of BWMS within the IMO approval procedure is primarily based on exposure estimations derived from mathematical modelling and/or physical–chemical properties in conjunction with laboratory toxicity data on a certain range of DBPs and their concentrations measured during land-based testing of BWMS prototypes. The validity of these models and assumptions may need to be closely monitored once the Convention enters into force and BWMS are installed on board ships for routine operation. In preparing for this future challenge, the maritime community can benefit from the expertise and experience available in other areas of water treatment, public health and environmental protection and monitoring. Continuation of the recently initiated exchange and discussion, which this paper summarizes, can help to identify existing knowledge gaps and initiate targeted measures in research and regulation at the right time.

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