

Edited by Barbara Werschkun, Thomas Höfer, Matthias Greiner

Emerging Risks from Ballast Water Treatment



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1 Ballast Water: Challenges for Consumer Protection, Activities, and Cooperations

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The Ballast Water Management Convention, adopted by the international community in 2004, is expected to enter into force within the next one or two years. From then on, more than 50,000 ships world wide will have to be equipped with on-board installations for ballast water treatment to meet the requirements of the Convention for the maximum number of living organisms in ballast water upon discharge.

From the view point of health protection, both treated and untreated ballast water may be associated with potential hazards to human health. On the one hand, the spread of human pathogens or toxin-producing algae may pose direct threats to biological safety and safety in the food chain. On the other hand, the envisaged countermeasure of biocidal treatment may lead to new risks with regard to chemical safety - not only from the use of chemicals and the generation of by-products on board the ships themselves, but also from the release of these substances into fishing waters or recreational areas.

With these challenges in mind, BfR scientists over the years have contributed to the international efforts directed at the ballast water problem in various ways: Within the setting of the Ballast Water Management Convention, the BfR has evaluated many application documents for the approval of ballast water management systems with regard to their human health risks and has continuously contributed to the development and improvement of international guidelines within the bodies of the International Maritime Organization. Based on insights from the regulatory risk assessment and the identification of open questions, the BfR initiated its own research activities, both in the office and in the laboratory, with particular focus on the formation of hazardous disinfection by-products and the exposure of humans to hazardous substances from ballast water treatment systems.

Ballast water transport is a challenge of global dimensions that affects many sectors, and its solution requires interdisciplinary scientific efforts. Communication and cooperation is therefore of paramount importance. In the regulatory arena, the BfR is part of a stable national network under the auspices of the Federal Ministry of Transport, Building and Urban Development and coordinated by the Federal Maritime and Hydrographic Agency. International contacts have emerged from our work in the bodies of the International Maritime Organization and the collaboration within the EU Interreg project North Sea Ballast Water Opportunity. Participation in the international discussion and presentation of the ballast water work in the scientific community has helped to enlarge these existing networks and to establish new contacts with scientists in all disciplines concerned with water treatment and marine resources, regulators and stakeholders in the fields of shipping and transport, public health and marine environmental protection.

The collection of articles in this volume provides a cross-sectional overview of various issues, sectors, and scientific disciplines that are either affected by the ballast water problem themselves or that can benefit the further development of ballast water solutions by a transfer of experiences made in their respective fields.

2 Ballast Water Risks and the History of Regulation

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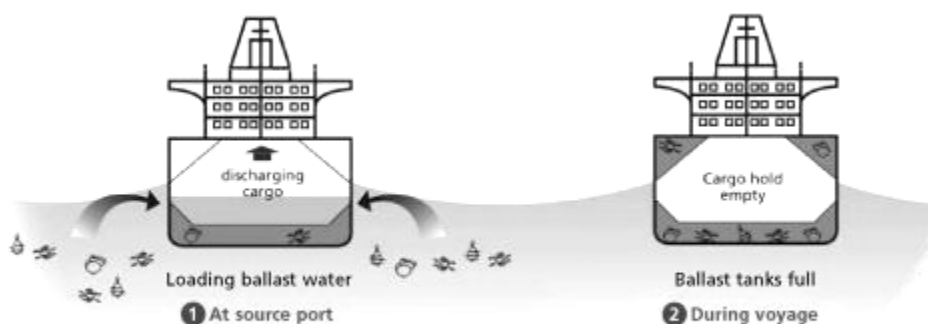
2.1 Abstract

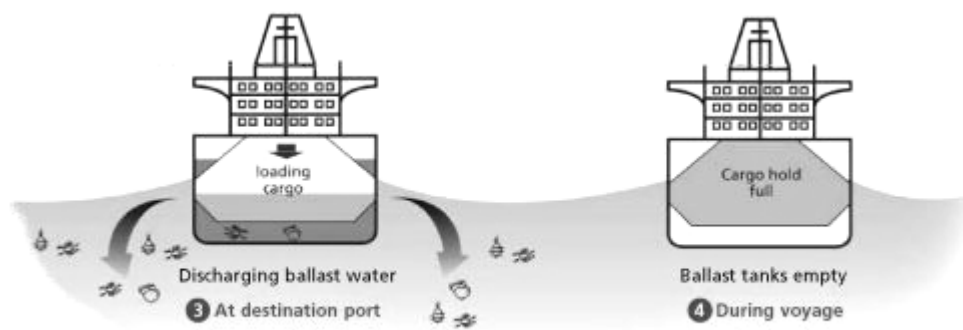
The hazards of ballast water discharge for hygiene and public health had already been identified in 1918. Many decades later more and more ecological effects and health risks were identified. It was in particular the GloBallast project that initiated a diplomatic conference in 2004 resulting in an international regulation. The hazards of biocidal treatment of ballast water became clear asking for detailed assessment of the environmental and health risks including a regulatory system for the approvals of methods using active substances. A specific evaluation of the ballast water treatment by-products became an essential part of the approval procedure. There are now many systems approved by the International Maritime Organization and thus being available for ships. There is a need to compile the existing knowledge, the scientific discussions and the proposals for further regulatory measures in respect to the emerging risks from ballast water treatment.

2.2 Introduction

Ballast water is essential for the maritime world. Oceangoing ships need ballast water not only for their capability to stay on the water and be able to manoeuvre, but for many ships it is also necessary for the stability of the ship itself. For decades, if not longer, it has been very clear that with the ballast water organisms are travelling as stowaways in ships from one continent to the other (see figure 1).

Figure 1: Loading and discharging ballast water (© GloBallast)





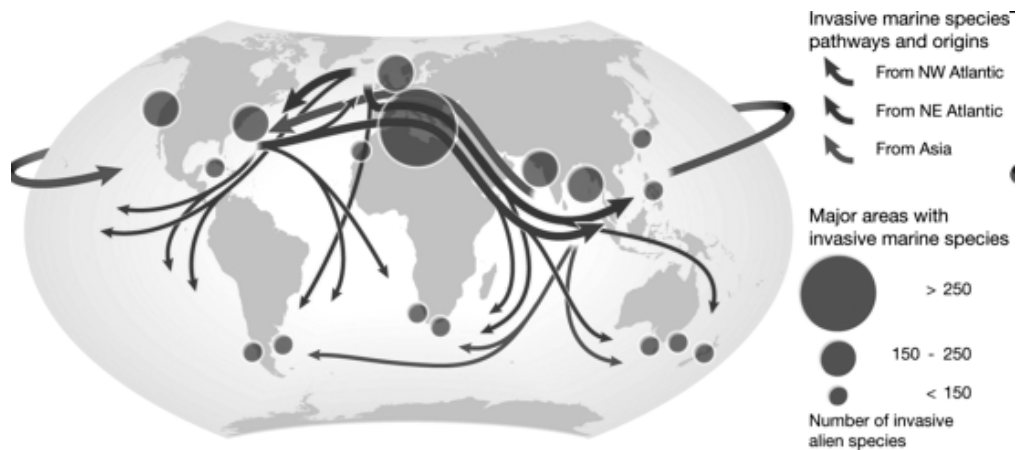
2.3 The Challenge

Human health risks – aspects of hygiene and public health – were part of the arguments for a regulation of ballast water discharge and ballast water treatment that was advocated about 80 years ago in an article published by the US National Institute of Health (Ferguson, 1932), referring to a report of the International Joint Commission on the Pollution of Boundary Waters from 1918. Already at that time it was recognized that there were risks associated with the unrestricted discharge of ballast water, which was described as “often seriously contaminated”. The discussion was centred around ships travelling along the US American and Canadian coast and the Great Lakes. In 1932, a chlorination method using sodium hypochlorite was proposed for all ships using ballast water. In view of the anticipated side effects, it was proposed to reduce chlorination by “dividing harbour waters into classifications on the basis of plate counts of total bacteria and specifying a chlorine dosage for each class.”

At that time, ballast water volumes ranged between 750 and 7000 tonnes per ship. Today, the maximum volume in large vessels carrying solid or liquid bulk materials (ore, mineral oil) is more than 100,000 tonnes. With 90,000 vessel visiting US harbours discharging at least 70,000,000 tonnes ballast water per year (Steichen et al., 2012), the risk of introducing pathogens has multiplied, and the current situation is hardly comparable to the risk identified in 1932.

Ships have not only become larger but also faster, travelling along shipping routes around the globe, and the importance of cargo shipping has changed dramatically. Today, shipping transfers approximately 2 to 3 billion tonnes of ballast water each year. There is significant transfer of ballast water from one continent to another continental shelf and also between oceans (see figure 2).

Figure 2: Global transfer of ballast water (© GloBallast)



2.4 Regulatory developments

It was one of the most important achievements of the so-called GloBallast project, funded and organized jointly by the Global Environmental Fund, the United Nations Development Programme and the International Maritime Organization (IMO), to bring the diplomatic delegations within IMO, representing more than 160 nations, to recognizing the risks from ballast water transfer about ten years ago. As a consequence, the Ballast Water Management Convention and associated regulatory provisions were developed.

Within the IMO committees and working groups the treatment of ballast water has been discussed since 2002. The input of GESAMP¹ to the ballast water challenge was born at that time. The GESAMP Working Group on the Evaluation of Harmful Substances Carried by Ships published a scientific statement, advising the 48th session of IMO's Marine Environmental Protection Committee (IMO, 2002a). This advice on the hazards of biocidal treatment of ballast water became a part of the more comprehensive counsel of GESAMP, the common organisation created by the United Nations' agencies for scientific work on marine pollution (IMO 2002b).

At that time, the use of biocides as a ballast water treatment option for a large fraction of the global fleet seemed unrealistic. Nevertheless, operators of older vessels that would not be able to install alternative treatment technologies should be enabled to use chemical dosing systems for contingency purposes rather than being refused entry to certain ports. Similarly, GESAMP outlined that biocide use might be sanctioned by some port states as an emergency measure in cases where the alternative treatments available were not considered adequate and where serious risks to the environment or human health were imminent. Thus, it seemed prudent to clarify the conditions under which biocides should, or should not, be used and the precautions appropriate for such practices.

However in an annex, GESAMP became much more explicit on the issue: The use of chemical treatment to kill or inactivate organisms contained in ballast tanks was seen as attractive because, *inter alia*, it may be effective against a wide range of life forms at low concentrations and the equipment required for dosing was thought to be comparatively simple and inexpensive. GESAMP expressed the view that no biocide should be used to treat ballast water if the active ingredient, or any of its metabolites, have the potential to accumulate in suspended matter, sediments or biota. The aim should be to ensure that neither toxic effects nor any persistent metabolites endure following ballast water discharge. This would require extensive environmental fate testing for any biocidal product under consideration for ballast

¹ GESAMP stands for „IMO/FAO/UNESCO-IOC/WMO/UNIDO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection“.

water treatment. A key factor in the selection of a ballast water treatment product, according to GESAMP in 2002, would be the availability of analytical methods for the substance and any breakdown products in seawater and, as appropriate, in sediments and biological tissues. GESAMP asked IMO to develop criteria for evaluating the suitability of particular chemicals and categories of chemicals.

In these early years, many of the regulators and experts on invasive species shared the view of GESAMP that environmentally friendly technologies, such as high performance filters, ultrasound, or deoxygenation, could achieve sufficient purification of ballast water. However, it soon became clear that active chemistry or radiation would be needed, resulting in many chemical side products, so-called disinfection by-products.

During the International Conference on Ballast Water Management for Ships in 2004, the Netherlands lobbied for a regulation that ballast water management systems which make use of active substances should be approved by IMO (IMO, 2004a). As shipping has the longest history of any global business, and any regulation on discharge from ships into the oceans has to be in line with the United Nations Convention on the Law of the Sea (UNCLOS), it was clear that an international approval system, an IMO stamp, had to be created. A regulatory system for the approval of ballast water management systems had to be established.

After the finalization of the Ballast Water Management Convention, including a regulation on the use of “active substances” (the term introduced by the Netherlands for biocidal treatment), Japan, the Netherlands and Germany worked together on the drafting of guidance for the evaluation of management technologies. The first Japanese draft identified in particular the hazards of halogenated by-products: “Active substances ... should not contain ... organohalogen compounds and substances which may form such compounds in the aquatic environment.” A list of further compounds that should be regulated in a similarly strict manner, derived from existing U.S. clean water regulations, was part of the draft guidance in June 2004. Furthermore, not readily biodegradable as well as carcinogenic, mutagenic or reprotoxic components should not be used. The hazard evaluation of components of active substances and their discharged ballast water treatment by-products was based on the ratings resulting from the revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships (Bowmer et al., 2002). However, during further consultations, in particular under the influence of the European regulative principles for biocides, these ideas did not prevail. The resulting proposal (IMO, 2004b) was the birth of the present IMO Guideline 9 (IMO, 2005a; IMO, 2008a).

A “think tank” composed of regulatory scientists from very active countries in this field, like Germany, and a number of MEPC delegates and IMO secretaries gathered in informal sessions in 2005 at the office of Jean Claude Saintlos, at that time the director of the Marine Environment Division at the IMO. During these sessions it became clear that confidential documents from industry would have to be evaluated. Public IMO committees would not be able to handle such confidential proprietary information. In addition, scientific advice independent from economical and political interests was deemed essential for assessing the risks of ballast water management systems. The procedural involvement of GESAMP in the ballast water regulation was born at that time and was later officially introduced as the “Technical Group” into the regulatory system under the Convention (IMO, 2005b).

2.5 Future challenges

Today, we have more than five years of practical experience with the risk evaluation process under IMO Procedure G9 (IMO, 2005a; IMO, 2008a) and the “Methodology for information gathering and the conduct of work of GESAMP-BWWG “ (IMO, 2008b), and we have more systems evaluated and approved than ever anticipated. We can now look into all of the dos-

siers and evaluations and ask ourselves: What is the core information? Are there general common data, dominating the risk assessments? Are these data solid enough in this respect? Do we need any measurements in the field to validate the results from land-based testing? The first of such evaluations has already been published (Werschkun et al., 2012). We do hope that more will come.

In this respect, assessing the risks of individual systems within the approval procedures may not be enough. With more and more information on treatment technologies coming up and the 50,000 ships which have to be equipped with ballast water treatment technology within the upcoming years, the public has the right for clear risk information: What are the emerging risks for the public health, for the supply with healthy sea food and for all aspects of the marine and coastal environment?

Some of the ships, that is common knowledge for those involved in maritime regulations, will not always run the technology in the approved way. We just need to look at the illegal discharges of oil, cargoes and garbage on the open seas from all kinds of ships. Some ballast water management systems will be installed on passenger ships and ferries – or may create additional risks for crews already living under often lax occupational health protection, for example on tank ships and solid bulk carriers. We have to keep this in mind when talking about risks.

Today, there are about 30 ballast water management systems being finally evaluated under the IMO approval procedure (see also papers by Pughuic, David and Gollasch, and Kacan in this volume). We now know that most of the systems, and in particular the highly effective ones, will be based on technological principles that produce halogenated disinfection by-products – a situation already foreseen in 1932. Several of those by-products are known to be carcinogenic, many are mutagenic and some are even toxic to reproduction. Little is known about the long-term impact of these halogenated hydrocarbons on the marine environment, on fish, marine mammals, or even less so on invertebrates. What is the health risk along the shipping lanes in those areas where ships de-ballast? Will the concentrations of all those substances together stay below the threshold of toxicological concern? How does such discharge relate to integrated maritime policies in Europe and world-wide and how does this go with the HELCOM policies (e.g. Baltic Sea Action Plan), where the Baltic Sea countries have committed themselves to achieve a “Baltic Sea with life undisturbed by hazardous substances”.

Already in 2002, GESAMP (IMO, 2002a) stated: “In ports frequented by tankers and large freight vessels, huge volumes of ballast water are regularly discharged within relatively small areas. Thus, if biocidal treatments become a regular feature of ballast water management, there is scope for local marine ecosystems to be constantly exposed to chemicals remaining in the ballast water when discharged. Even if residual concentrations are undetectable (chemically and/or biologically), or considered acceptably low, the possibility of chronic effects from long-term exposure cannot be discounted. Accordingly, environmental protection authorities of port states should consider periodic monitoring in the vicinity of ports to detect any abnormalities within benthic communities (e.g. loss of biodiversity, reductions in recruitment etc.).”

Are we good enough with our risk evaluation today? Do we have enough data generated by industry? Did we look deep enough into the scientific debates and results of similar areas of public and environmental health, like other uses of treatment systems in land-based installations, power stations, swimming pools and last but not least drinking water disinfection? How safe is the current risk assessment? The collection of articles presented with this volume should add knowledge on these questions.

It might be possible that relevant emerging risks from the treatment of ballast water with active chemicals cannot be excluded. However, we also have to keep in mind the risks created

by invasive species for the environment, for human health and the sustainability of our coastal ecosystems. A strong ballast water regulation is clearly one element of sustainable shipping. We might have to balance the risks created by any transfer of organisms and infection with those risks created by newly introduced toxic chemicals. Only with such risk balance we might be able to report on sustainability.

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3 Ballast Water Management Convention – an Immediate Call for Action

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The views expressed in this paper are those of the author and should not be construed as necessarily reflecting the views of IMO or its Secretariat.

3.1 Abstract

Towards the end of the last century, scientists, governments, shipping industry and environmentalists have all acknowledged the issue of transferring harmful aquatic species and pathogens between ecosystems. As ships' ballast water was perceived as one of the main vectors for such transfers, the International Maritime Organization (IMO) was urged by the World Summit on Sustainable Development in 2002 to finalize the development of an international treaty to address the problem. Once again, IMO demonstrated pragmatism, vision and determination and, in February 2004, its Member States adopted the International Convention for the Control and Management of Ships' Ballast Water and Sediments. Considering the enormous scientific and technological challenges and the highly complex and multi disciplinary nature of the problem, not to mention the impact on the shipping industry and international trade, the development of this new instrument is, perhaps, one of the most significant achievements of the Organization in the first decade of this century. The new Convention and its associated guidelines provide the much needed framework for developing an integrated approach to ballast water management, which includes ballast water exchange, new shipboard treatment technologies, new infrastructures, such as port reception facilities and new ship designs, to name a few. Met with circumspection in 2004, at a time when no viable solutions for treatment appeared to be available, the ratification process benefited from the timely development of a comprehensive set of guidelines and gathered momentum during the last few years – the treaty being currently ratified by 28 countries representing nearly 27 per cent of the world's merchant fleet tonnage. Nevertheless, the issue remains as complex as the biology of marine organisms and some aspects like sampling and monitoring tools, enforcement procedures, verification and approval of ballast water management systems, and risk assessment are still in their infancy and need further attention from all the stakeholders in the shipping community. The paper provides an overview of the implementation process, touches upon the treatment technologies, emphasizes the importance of wide engagement to ensure sustainability, and represents a call for immediate action by the shipping industry.

3.2 Introduction

The introduction of invasive aquatic species into new environments has been identified as one of the four greatest threats to the world's oceans. Ships move enormous quantities of ballast water across the planet and, in doing so, facilitate the transfer of harmful organisms and pathogens from one bioregion to another. When all factors are favourable, the transferred species may survive to establish a reproductive population in the host environment – become invasive, out-compete native species and multiply into pest proportions. Invasive species, in general, are considered the second greatest threat to global bio-diversity after habitat loss and, once established, their impacts increase in severity over time. If environments affected by oil pollution recover in time, as appears to be the case with Torrey Can-

yon in Europe or Exxon Valdez in the United States, in contrast, aquatic invasions are virtually irreversible.

The global economic impacts of invasive aquatic species have not been quantified but are likely to be in the order of tens of billions of US\$ per year or more. Human health can also be affected by the transfer and spread of pathogens and toxic organisms, such as harmful algae in ships' ballast water. In 2004, the GloBallast Programme (a cooperative initiative of the IMO, Global Environment Facility and United Nations Development Programme), undertook an initial scoping study on the global economic impacts of invasive aquatic species. The study identified the current state of knowledge in relation to both direct economic impacts and the costs involved in responding to invasive aquatic species. Direct economic impacts are the actual monetary costs caused by the species in their invaded environments, including costs from: reductions in fisheries production, closure/reductions in aquaculture, physical impacts on coastal infrastructure (fouling), loss of income for the shipping industry, and impacts/closure of recreational/tourism beaches. The data relating to seven specific invasions indicated that the direct economic impacts of these alone, are more than US\$10 billion per year (GloBallast, 2004). It was estimated that the economic loss due to currently known aquatic invasions may be an order higher (US\$ 100 billion per year). The response costs identified by the study were the costs incurred by society in responding to the problem including prevention, control and eradication, research and monitoring, education and communication, compliance monitoring and enforcement, as well as costs of developing new ballast water treatment technologies. Overall, the projected costs to respond globally were estimated at up to four per cent of the total loss.

3.3 Global response

The transfer of invasive aquatic species in ballast water is, perhaps, one of the biggest environmental challenges the shipping industry was confronted with. There have been numerous global calls for action at the international level and the international law provides a strong mandate for the adoption of remedial measures. The United Nations Convention on the Law of the Sea (UNCLOS) requires states to work together "to prevent, reduce and control human-caused pollution of the marine environment, including the intentional or accidental introduction of harmful or alien species to a particular part of the marine environment." Controls on the introduction of alien species that threaten the ecosystems are also mandated under the Convention on Biological Diversity, and targeted for action in the Plan of Implementation adopted at the World Summit on Sustainable Development of 2002. In recognition of the severe impacts of invasive species, a number of UN agencies have taken action to address this challenge through specific guidelines, specialized training or cross-sectoral co-operation, mainly based on voluntary acceptance. Demonstrating once again its proactive character and its determination to address the environmental challenges, the International Maritime Organization (IMO) successfully managed to develop the first and probably the only international treaty to prevent the transfer of invasive species. The International Convention on Control and Management of Ships' Ballast Water and Sediments (Ballast Water Management Convention), adopted by IMO member states in early 2004, demonstrates the effectiveness of governments working together under the right auspices.

3.4 The Ballast Water Management Convention

Considering the enormous scientific and technological challenges, and the highly complex and multi-disciplinary nature of the problem, the development of the Ballast Water Management (BWM) Convention is, perhaps, one of the most significant global environmental achievements in the early part of this century.

Although structured in the traditional IMO format, inspired from the widely accepted MARPOL 73/78 Convention, the new instrument clearly links with the United Nations Convention on the Law of the Sea (UNCLOS) and recognizes the precautionary approach, the principle of sustainable development and the integrated management practices promoted by the World Summit on Sustainable Development in its Plan of Implementation. Traditionally, IMO conventions aim at the improvement of ships equipment and procedures on board ships and are mainly directed at flag states. Many of the requirements under the BWM Convention fall into this category. However, this is the first IMO instrument where reliance on modern equipment and ballast water treatment technologies is combined with an adequate understanding of the impact of ballasting operations on coastal waters and risk assessment. It is a unique situation where engineering challenges are addressed in conjunction with the biology of marine organisms.

The Convention provides a critically needed set of management tools through which the maritime industry can be regulated in a manner that is predictable, transparent and responsive with regard to environmental benefits, technological achievability and international consistency. Moreover, the Convention also provides for processes through which the ballast water performance standard may be adjusted, based on the availability of technology to meet that standard, which again is a unique feature of this “unconventional” Convention.

3.5 The implementation guidelines

The complexity of the problem posed by invasive aquatic species in ships' ballast water required further work to develop guidelines and procedures for the timely and uniform implementation of the BWM Convention. IMO member states, together with industry representatives and other organizations in consultative status with IMO, have dedicated important resources and time to this process and, in a record period of time, adopted fourteen sets of guidelines needed for the smooth implementation of the instrument. Table 1 provides the list of the implementation guidelines with reference to the relevant resolutions through which they have been adopted by IMO's Marine Environmental Protection Committee (MEPC). The guidelines are available on the IMO website [http://www.imo.org/KnowledgeCentre/HowAndWhereToFindIMOInformation/IndexofIMOResolutions/Pages/Marine-Environment-Protection-Committee-\(MEPC\).aspx](http://www.imo.org/KnowledgeCentre/HowAndWhereToFindIMOInformation/IndexofIMOResolutions/Pages/Marine-Environment-Protection-Committee-(MEPC).aspx) or alternatively, can be ordered from IMO Publishing under the sales number 1621E.

Table 1: BWM Convention implementation guidelines

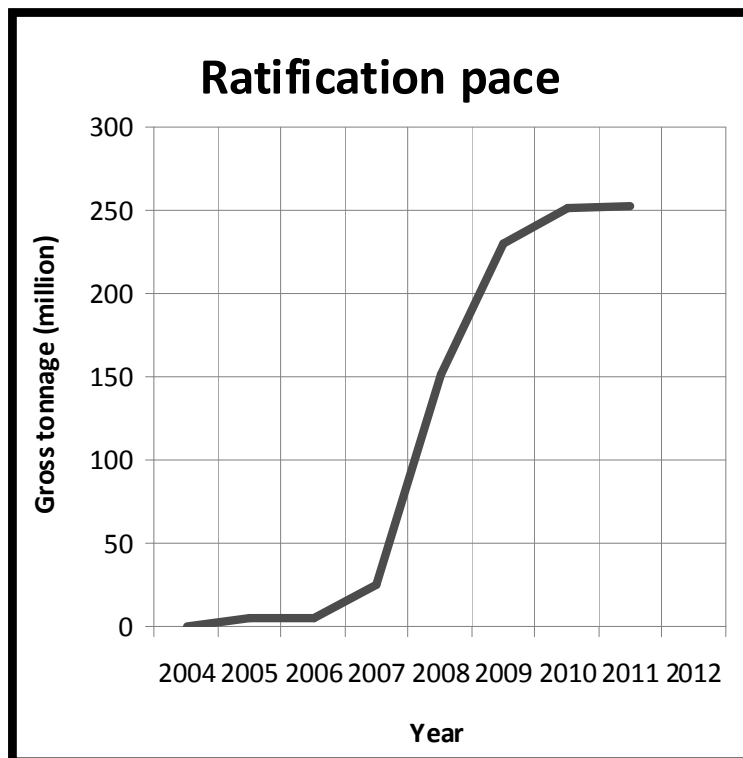
Name of the guidelines	Relevant MEPC resolution
Guidelines for sediments reception facilities (G1)	Resolution MEPC.152(55)
Guidelines for Ballast Water Sampling (G2)	Resolution MEPC.173(58)
Guidelines for ballast water management equivalent compliance(G3)	Resolution MEPC.123(53)
Guidelines for Ballast Water Management and Development of Ballast Water Management Plans (G4)	Resolution MEPC.127(53)
Guidelines for ballast water reception facilities (G5)	Resolution MEPC.153(55)
Guidelines for Ballast Water Exchange (G6)	Resolution MEPC.124(53)
Guidelines for Risk Assessment under Regulation A-4 (G 7)	Resolution MEPC.162(56)
Guidelines for approval of Ballast Water Management Systems (G8)	Resolution MEPC.174(58)
Procedure for Approval of BWM systems that make use of Active Substances (G9)	Resolution MEPC.169(57)
Guidelines for approval and oversight of prototype ballast water treatment technology programmes (G10)	Resolution MEPC.140(54)
Guidelines for Ballast Water Exchange Design and Construction Standards (G11)	Resolution MEPC.149(55)
Guidelines for sediment control on ships (G12)	Resolution MEPC.150(55)
Guidelines for additional measures including emergency situations (G13)	Resolution MEPC.161(56)
Guidelines on designation of areas for ballast water exchange (G14)	Resolution MEPC.151(55)

The tremendous effort of the IMO member states and the Secretariat to accomplish the tasks related to the implementation of the BWM Convention clearly indicates the importance attached by the international community to this issue and the determination to vigorously address the threats posed by aquatic invasive species.

3.6 Ratification process

Due to the lack of proper technologies to treat the ballast water at the time of its adoption, the conditions for entry into force of the BWM Convention were established at thirty states with a combined merchant fleet which constitute not less than thirty five per cent of the world's gross tonnage. Some observers found these conditions too drastic and difficult to be met and predicted a long coming into force process. Because of the inter-related engineering, technical, scientific, environmental, economic and social implications, the ballast water issue is far more complex than most of the other ship-based pollution problems that IMO member states and the shipping industry have faced and, during the first two years after the adoption of the instrument, the ratification pace was very slow. The governments were assessing the various requirements and, in particular, the capability to comply with the performance standard contained in regulation D-2 of the Convention, which establishes a numeric threshold of organisms accepted at discharge. Figure 3 illustrates the pace of ratification during the last seven years in relation to the gross tonnage of the contracting governments.

Figure 3: Ratification of the BWM Convention



The development of the first ballast water treatment technologies and the approval of the first ballast water systems in 2008, brought a new impetus to the process and the number of contracting governments increased visibly approaching to date the requirements for entry into force. With 28 ratifications representing almost 27 per cent of the world's tonnage, there is a wide expectation for the BWM Convention to enter into force during the next two years. There are still concerns regarding the treatment technologies for certain types of vessels with high

ballast water capacity and high flow rate and regarding the retrofitting capacity of the shipyards. However, the increasing number of new technologies coming to the global markets sent an encouraging message to the international community and to the shipping industry.

3.7 Response by industry

IMO has been working very closely with the industry ever since the matter was brought to the attention of international community by Canada and Australia. The maritime industry has recognized the problems posed by aquatic invasive species and their translocation in ship's ballast water and participated actively to the global process emphasizing the need for environmentally sound and technologically achievable solutions. Taking into account the significant commitments that will be borne by shipping, such solutions need to be practical and economically viable. The effective implementation of the BWM Convention could be severely restricted, if appropriate and approved technologies and management systems that meet the requirements of the Convention are not available or if sufficient capacity to install them on ships is missing.

Despite the fact that in 2004, when the Convention was adopted, the challenges involved in finding appropriate engineering solutions appeared to be insurmountable, the technology developers have been rising to the challenge and some steady progress has been achieved over the last five years. A recent review by MEPC, aimed at assessing the status of technology developments, concluded that ballast water treatment technologies are available and are currently being fitted on board ships. While the outcome of this review appears to be positive, some difficulties still remain and the shipping industry will continue to play a key role to ensure meaningful progress on a global basis.

3.8 Ballast water treatment technologies

Ballast water management systems (BWMS), designed to treat the ballast water, are, as most of the other shipboard equipment, approved by national administrations before their installation on ships. Due to the fact that one of the fundamental principles embedded in the BWM Convention is that any measure to manage ships' ballast water should not cause greater harm than it prevents, BWMS that make use of active substances must be approved by IMO first and only after being granted final approval by the organization they can be type approved by the respective administrations and offered to the markets.

It is increasingly believed that the use of active substances in ballast water treatment will become a condition to comply with the provisions of the Convention. Active substances accomplish their intended purpose through action on aquatic organisms and pathogens in ships' ballast water and sediments. However, if the ballast water is still toxic at the time of discharge into the environment, the organisms in the receiving water may suffer unacceptable harm. A cautious approach needs to be taken by developers of such BWMS, and thorough toxicity testing is required to determine if an active substance can be used and under which conditions the potential of harming the receiving environment or human health is acceptably low. The approval of BWMS that make use of active substances consists of a two-tier process and involves extensive consultations among IMO member states.

Out of 26 systems currently approved, 20 are using active substances to treat the ballast water and they went through a thorough process of detailed scrutiny by the GESAMP² Ballast Water Working Group (BWWG) and approval by the MEPC. Apart from being a new

²GESAMP stands for „IMO/FAO/UNESCO-IOC/WMO/UNIDO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection“.

challenge for IMO, the process proved to be complex and time-consuming and the approval of 20 systems in less than three years would not have been possible without the hard work and wholehearted dedication of the GESAMP-BWWG and the GESAMP main body. The main task of the GESAMP is to advise the MEPC with regard to the potential risks posed by the treated ballast water when discharged in the loading port. This involves a detailed identification of the chemicals and their concentrations, a risk characterization based on toxicity tests followed by a final evaluation of the risks.

A large number of BWMS are based on production of active substances in situ by electrolysis of the seawater to produce chlorine and its oxidizing derivatives. These processes are combined with filtration or other means of separation and are followed by a neutralization step before discharge. Other treatment methods include ozonation, adding biocides, oxygen deprivation or removal of organisms through flocculation. Table 2 provides a list of all the type-approved BWMS up to September 2011 and a brief description of the technologies employed. The information on systems 11 to 17 is based on communications received from the respective administrations.

Table 2: Type approved BWMS, as of September 2011

	Approval date	Administration	Name of the BWMS	Technology used	Active substance employed
1	June 2008	Det Norske Veritas, on behalf of Norway	PureBallast	Advanced oxidation (UV + TiO ₂)	Free radicals
2	10 June 2008	Germany	SEDNA®	Chemical treatment	Peraclean® Ocean
3	31 December 2008	Republic of Korea	Electro-Clean™	Electrolysis	Chlorine/HOCl
4	17 April 2009	Det Norske Veritas, on behalf of Norway	OceanSaver®	Cavitation, N ₂ super-saturation, electrolysis	Chlorine/HOCl
5	24 November 2009	Republic of Korea	NK-O3 BlueBallast (Ozone)	Ozone in situ production	Ozone
6	4 December 2009	Republic of Korea	GloEn-Patrol™	MPUV treatment	N/A
7	5 March 2010	Japan	Hitachi (ClearBallast)	Flocculation	Fe ₃ O ₄ , PAC and PASA
8	28 January 2011	China	BalClor™	Electrolysis	Chlorine/HOCl
9	26 May 2010 and 25 March 2011	Japan	JFE BallastAce®	Chemical treatment	NaOCl
10	19 April 2011	South Africa	Resource Ballast Technologies System	Cavitation chemical disinfection	Ozone and chlorine/HOCl
11	2 September 2008 and 19 January 2010	Marshall Islands and Malta	NEI Treatment System VOS-2500-101	O ₂ deprivation	N/A
12	29 April 2009	Lloyd's Register, on behalf of the UK	Hyde GUARDIAN™	UV treatment	N/A
13	12 November 2009	Det Norske Veritas, on behalf of Norway	OptiMarin Ballast System (OBS)	UV treatment	N/A
14	16 February 2011	China	Blue Ocean Shield	UV treatment	N/A
15	10 March 2011	Norway	PureBallast 2.0 and PureBallast Ex	UV treatment	N/A
16	28 March 2011	China	BSKY™	UV treatment	N/A
17	6 August 2011	Marshall Islands	NEI Treatment System VOS 500 to VOS 6000	O ₂ deprivation	N/A

The considerable efforts of the research and development community to find solutions to the ballast water problem should be applauded and fully supported, and the shipping companies should be strongly encouraged to fit and test alternative systems in real-life operational situations as an essential part of the process. The shipping industry has again an important role in leveling the playing field and maximizing the entry into the marketplace of as many as possible new technologies. A prompt reaction of the industry will help in creating the mechanisms to encourage new research and, at the same time, will reward those who had the vision to invest in ballast water treatment technologies.

3.9 Conclusion

The ballast water issue is an international problem calling for international solutions. Shipping cannot operate without ballasting or de-ballasting. Despite the significant progress achieved in the last ten years in terms of developing an international regulatory regime, and despite the early ratification of the Convention by several countries and the promising signals emerging from technology developers, the road ahead is long and challenging. The immediate challenges include the issues associated with lack of effective compliance monitoring and enforcement tools, lack of associated capacity in many developing countries, and difficulties related to technology transfer. While the challenges appear to be significant, they are not insurmountable. The indications are that, with effective and intelligent use of resources and through an integrated collaborative approach, the answers to these challenges are being found. IMO will continue, through the Integrated Technical Co-operation Programme, to assist its members in their efforts towards the implementation of effective measures to address aquatic invasions. However, all these efforts are futile without the most important ingredient – the determination of the member states. The international community needs vision, foresight, purpose and strength of will. All the stakeholders and, in particular, the shipping industry need to act now pro-actively, positively and with due sense of responsibility in preserving our planet for the future generations.

3.10 References

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4 Ballast Water Treatment Systems – a Summary

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4.1 Abstract

Ballast water treatment systems (BWTS) developed to meet the standards set forth in the Ballast Water Management Convention adopted by the International Maritime Organization (IMO) were summarized here considering existing and developing BWTS. The systems need to be applied in very different settings onboard (e.g. different vessel types, flow rates and waters to be treated) so that fundamentally different BWTS are considered. The most common treatment technologies and basic technical requirements are outlined, also documenting the availability of certified BWTS.

4.2 Introduction

Noting the problems caused by alien species introduced with ballast water the International Maritime Organization (IMO) worked towards an instrument to reduce the rate of new species introductions. Firstly voluntary ballast water management guidelines were prepared (IMO, 1993, 1997) and eventually the International Convention on the Management of Ships' Ballast Water and Sediments (BWM Convention) was adopted in 2004 as a mandatory instrument (IMO, 2004). The BWM Convention introduces two different protective ballast water management regimes with a sequential implementation:

- 1) Ballast Water Exchange Standard (BWE) (Regulation D-1) requiring ships to exchange a minimum of 95% ballast water volume;
- 2) Ballast Water Performance Standard (Regulation D-2) which requires that ballast water discharged has the number of viable organisms below specified limits.

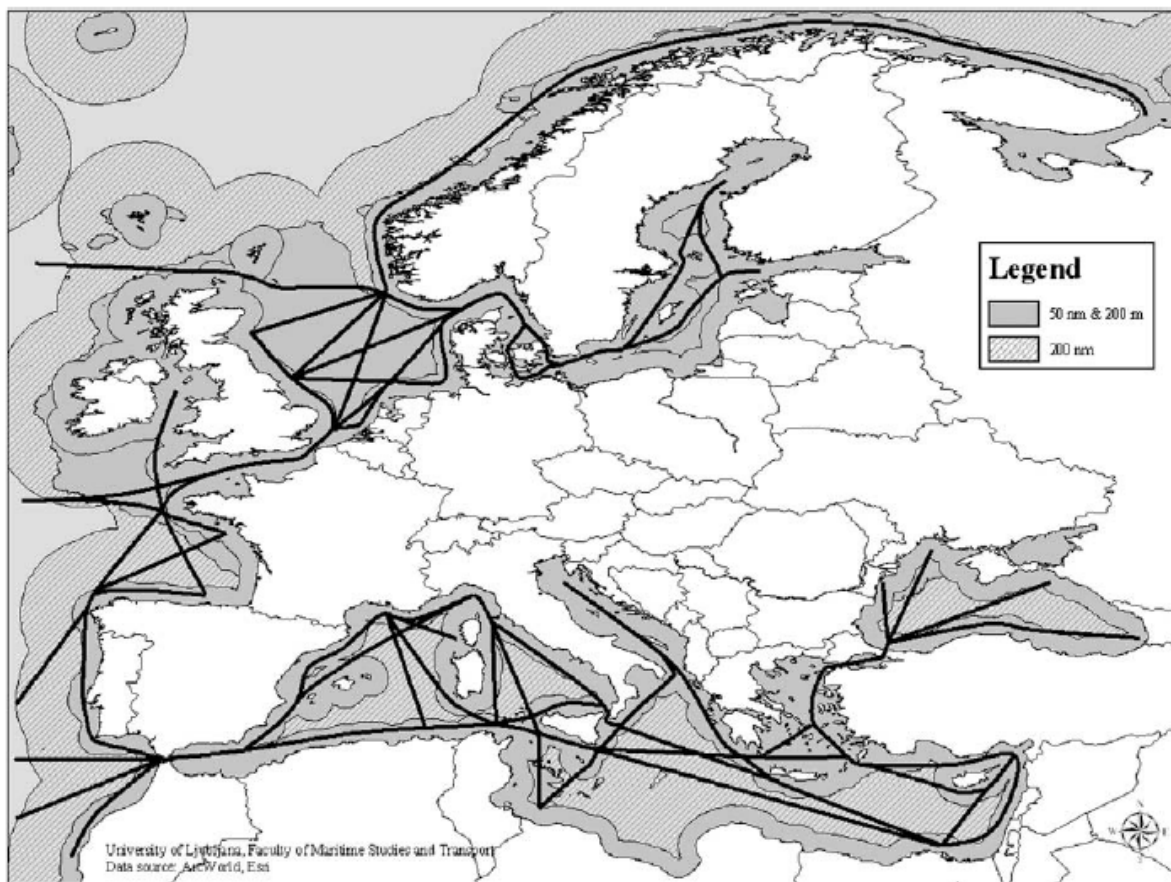
As required by IMO, BWE should be undertaken at least 200 nautical miles from the nearest land and in water depths of at least 200 m. If this is impossible, then BWE should be undertaken as far from the nearest land as possible, and in all cases at least 50 nautical miles from the nearest land and in water at least 200 m in depth (Fig. 4). In sea areas where these parameters cannot be met, the port state may designate a BWE area, in consultation with adjacent or other states, as appropriate. In addition to the IMO requirements national BWE requirements should also be considered. In general, a ship should not be required to deviate from its intended voyage and the voyage should not be delayed. However, a port state may require a ship to deviate, which may result in a delay in case a designated BWE area has been established.

Noting that species introductions are an increasing problem, voluntary BWE requirements are in place in Europe, as is published elsewhere (David and Gollasch, 2008). It was understood the BWE is of lower efficiency regarding the risk reduction to introduce new alien species and therefore the more stringent ballast water performance standard as outlined in Regulation D-2 of the BWM Convention was agreed (see below).

The BWM Convention enters into force twelve months after the date on which not less than 30 States with a combined merchant fleets of not less than 35% of the gross tonnage of the

world's merchant shipping have signed it. As reported by the IMO (see www.imo.org, Status of the conventions), 30 States constituting 26.44 % of the gross tonnage had ratified the BWM Convention in January 2012. In Europe, the BWM Convention has been signed by only four of the 27 EU Member States, i.e., France, Netherlands, Spain and Sweden. Several EU countries have announced that they are aiming to ratify the BWM Convention by 2012, or at the latest in 2013. As the limit for the entry into force is approaching rapidly industry becomes more and more aware of the commercial opportunities of ballast water treatment. These become obvious when noting the high number of vessels which need to be equipped with treatment systems (see below).

Figure 4: The European seas with the 50 nautical miles and 200 m depth limit shown in dark grey, and light grey shaded the 200 nautical miles limit. The main shipping routes are shown as black lines (from David and Gollasch, 2008).



There are many different treatment technologies available, and most were previously developed for municipal and other industrial applications. However, when applying them without modifications and improvements to the ballast water treatment purpose, none of these technologies have shown the capability to treat the ballast water to the level required by the BWM Convention D-2 Ballast Water Performance Standard. The standard in Regulation D-2 of the BWM Convention requires a discharge of a low number of organisms per water volume according to two size classes, and specific human health standards for indicator bacteria:

- 1) *Ships conducting Ballast Water Management in accordance with this regulation shall discharge less than 10 viable organisms per cubic metre greater than or equal to 50 micrometres in minimum dimension and less than 10 viable organisms per millilitre less than 50 micrometres in minimum dimension and greater than or equal to 10 micrometres in minimum dimension; and discharge of the indicator microbes shall not exceed the specified concentrations described in paragraph 2.*

2) *Indicator microbes, as a human health standard, shall include:*

- a) *Toxicogenic Vibrio cholerae (O1 and O139) with less than 1 colony forming unit (cfu) per 100 millilitres or less than 1 cfu per 1 gram (wet weight) zooplankton samples;*
- b) *Escherichia coli less than 250 cfu per 100 millilitres;*
- c) *Intestinal Enterococci less than 100 cfu per 100 milliliters.*

Currently it is believed that the only way to achieve the discharge requirements of the D-2 standard is with the installation of a BWTS. The soon expected entry into force of the BWM Convention is an important driving force for ballast water treatment technology developments worldwide (David and Gollasch, 2008) and it is expected that the demand for these systems will soon greatly increase. The phase-in of the D-2 standard was agreed at IMO according to ballast water capacity and ships age (see Figure 5).

Figure 5: Phase-in of the ballast water performance standard (Regulation D-2) per vessel age and ballast water capacity in relation to the ballast water exchange standard (Regulation D-1) (from David and Gollasch, 2008)

Ships built	BW capacity (m ³)	Phase in of the D-1 and D-2 standards of the BWM Convention								
		2009	2010	2011	2012	2013	2014	2015	2016	
<2009	1500 - 5000	D-1 or D-2					D-2			
<2009	<1500 >5000	D-1 or D-2							D-2	
2009	<5000	D-1 or D-2		D-2						
2010	<5000	D-2								
2009 <2012	>5000	D-1 or D-2							D-2	
2012	>5000	D-2								

4.3 Ballast water treatment systems

Many different BWTS are currently available 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, 2011; Witherby Seamanship International, 2011; the authors experience in shipboard tests of BWTS).

By July 2011 information of 87 different systems was brought together as background information for the FP7-funded Project VECTORS (David and Gollasch, 2011, see Acknowledgements) and was briefly summarized elsewhere (David and Gollasch, submitted). Many of these BWTS are in the (early) development stage, hence information about some systems is limited or not available and therefore not included in other summaries of BWTS. Information on some BWTS is not ready to be published, yet, and in order to be able to include this information, the system manufacturers names are not given, but are marked as "confidential" in Tables 3 and 4.

Table 3: BWTS manufacturers and known commercial names of the systems in alphabetical order

Nr.	Manufacturer	System name
1	21st Century Shipbuilding Co., Ltd	ARA Ballast (Blue Ocean Guardian BOG)
2	Alfa Laval Tumba AB	PureBallast (2.0)
3	Aquaeng Co. Ltd.	AquaStar BWMS
4	Aquaworx ATC GmbH	AquaTriComb
5	atgUVTechnology (ATG Willand)	
6	ATLAS-DANMARK	ATLAS-DANMARK ABTS
7	Auramarine	CrystalBallast
8	BaWaPla (development stopped)	
9	Brillyant Marine	
10	Cavipure (Jetsam)	
11	China Ocean Shipping Company (COSCO)	Blue Ocean Shield
12	Coldharbour Marine	Coldharbour BWT
13	confidential	
14	confidential	
15	confidential	
16	confidential	
17	confidential	
18	confidential	
19	confidential	
20	confidential	
21	confidential	
22	confidential	
23	confidential	
24	confidential	
25	confidential	
26	DESMI Ocean Guard AS	DESMI Ocean Guard BWMS
27	Ecochlor Inc	Ecochlor
28	Ecologiq	BallaClean
29	Electrichlor Inc	Electrichlor
30	EltronWaterSystems	PeroxEgen
31	Environmental Technologies Inc	ETI
32	Envirotech and Consultany PTE ltd.	BlueSeas BWMS
33	Envirotech and Consultany PTE ltd.	BlueWorld BWMS
34	Erma First SA	Erma First BWMS
35	Evonik (formerly Degussa)	PeracleanOcean
36	Ferrate Treatment Technologies	Ferrator BW
37	Gauss (stopped development)	
38	GEA Westfalia	BallastMaster
39	Hamann AG (Evonik) (development stopped)	Sedna (using PeracleanOcean)
40	Hamworthy Greenship	Greenship Sedinox
41	Headway Technology Co., Ltd.	OceanGuard
42	Hi Tech Marine Pty Ltd	Ballast water disinfection
43	Hitachi	ClearBallast
44	Hyde Marine Inc -Hyde Guardian	Hyde Guardian
45	Hyde Marine Inc -Seakleen TM (Vitamar)	
46	Hyundai Heavy Industries	EcoBallast
47	Hyundai Heavy Industries	HiBallast
48	JFE Engineering Corporation	JFE BWMS (uses TG Ballastcleaner)
49	JFE Engineering Corporation	JFE BallastAce BWMS
50	Kashiwa Kuraray Co.Ltd. (ref doc 61/2/6)	Microfade
51	Katayama Chemical inc.	Sky-System with PeracleanOcean
52	Kwang San Co., Ltd.	En-Ballast
53	Mahle NFV GmbH	Ocean Protection System OPS

Table 4: BWTS manufacturers and known commercial names of the systems in alphabetical order – continued

Nr.	Manufacturer	System name
54	Marenco Technology Group Inc	Marenco BWTS
55	Maritime Solutions Inc.	
56	Mexel Industries	
57	MH Systems Inc	MH Systems BWTS
58	Mitsubishi Heavy Industries	
59	Mitsui Engineering & Shipbuilding	Special Pipe SP-Hybrid BWMS
60	NEI Treatment Systems LLC	Venturi Oxygen Stripping
61	NK Company	NK-03 BlueBallast
62	Nutech 03	Mark III
63	Oceansaver AS	Oceansaver
64	Optimarin AS	OptiMarin Ballast System OBS
65	Panasia	GloEn-Patrol
66	Permascand, RWO	EctoSys
67	Pinnacle Ozone Solutions	
68	Qwater	
69	RWO GmbH Marine Water Technology	CleanBallast (uses EctoSys)
70	Samsung Heavy Industries	PuriMar
71	Samsung Heavy Industries	NEO-PuriMar
72	Sea Knight Corporation	
73	Sea Reliance Marine Services	
74	Seair	
75	Severn Trent De Nora	BalPure
76	Siemens	SiCURE
77	Sincerus	Sincerus maritime
78	SPO System	Special Pipe Hybrid BWMS with PeracleanOcean
79	STX Metal Co. Ltd.	Smart Ballast
80	Sumetomo Electric Industries Ltd.	SEI BWMS
81	Sunrui Corrosion and Fouling Control Company (Sunrui CFCC)	BalClor BWMS (Sunrui BWMS)
82	Techcross	ElectroClean System ECS
83	TechwinEcoCo.,Ltd.	Purimar
84	Toagosei Group	TG Ballastcleaner
85	Vitamar, LLC-Seakleen TM	
86	Wilhelmsen Technical Solutions / Resource	Unitor Resource BWTS

In total, 86 BWTS manufacturers were identified and of these, 67 use some form of pre-treatment technology (51 use filtration, others use different other methods to mechanically separate organisms or a combination of these as pre-treatment). As secondary treatment step the majority of systems (60) use some kind of an “Active Substance”³. The most frequently used active substances are generated by electrolysis/electrochlorination (25 systems), which is mostly applied in combination with other techniques. By these methods the active substances are either generated in the full water flow or in a sidestream and then re-injected into the vessel ballast water pipe. The second frequent method is UV (24 systems); 16 of these systems use UV as the only secondary treatment step, while eight systems use UV in combination with one or more other techniques (i.e., TiO₂, ultrasound, ozonation, electrolysis, plasma). In total 20 BWTS use two or more treatment steps, while 64 rely on one secondary treatment step (no information for three BWTS).

³“Active Substance” means a substance or organism, including a virus or a fungus that has a general or specific action on or against harmful aquatic organisms and pathogens.

4.4 BWTS – size and dimensions

BWTS need to meet vessel requirements like different water flow capacities and technical profiles, the system footprint onboard and power consumption. This review revealed that the current BWTS capacities range from 50 m³/h to more than 10,000 m³/h and two manufacturers indicated that their systems are (will be) able to treat 20,000 m³/h or more. The footprint requirements of the systems range from less than 1 m² to 145 m² and possibly more. Some BWTS work without electricity requirement, and others may consume up to 200 kW per 1,000 m³/h treated water.

4.5 BWTS testing and approvals

All BWTS need to be type approved by a flag state before commercialisation. When making use of Active Substances a more thorough certification process needs to be followed to obtain Basic and Final Approval by the IMO Marine Environment Protection Committee (MEPC), as is described in detail e.g. in the articles by Pughiuc and by Linders in this volume. The approval process and the data requirements to document the environmental acceptability of such systems, is described in the IMO Procedure G9 (IMO, 2005). A group of independent experts (GESAMP Ballast Water Working Group) is evaluating the environmental acceptability of these systems and the group makes its recommendations, whether or not Basic and Final Approvals may be given, available to MEPC.

All systems, no matter if they use active substances or not, need to be tested in a land-based test-bed setting with challenging water conditions (see also the article by Fuhr in this volume). Further, at least three successful test cycles need to be conducted onboard of commercial vessels to document the BWTS seaworthiness. For further details the IMO G8 Guideline (IMO, 2008) may be consulted. At present the BWTS are in different stages of tests and approval processes, while 16 were already type approved by different administrations (China, Germany, Japan, Korea, Norway, South Africa, and the United Kingdom). Some of the system listed above are far advanced and are nearing type approval also with new administrations being involved (e.g. Denmark, Greece, the Netherlands).

4.6 Conclusions

With today's knowledge and experience it seems that the only possible way to meet the discharge requirements outlined in the D-2 standard is by using a BWTS. The entry into force of the BWM Convention is expected soon and this will be an important driving force for treatment technology developments worldwide, because, after its entry into force, BWTS systems need to be installed on vessels.

As shown above, many different technologies are considered for ballast water treatment. However, only a combination of different treatment technologies resulting in at least a two-step treatment process, so far showed the capability to treat the ballast water to the level required by the D-2 standard. Consequently, BWTS manufacturers developed different systems as a combination of a primary and secondary treatment based upon different technologies.

In this paper, 86 BWTS manufacturers are identified. Most systems are applied at ballast water uptake, but 39 systems treat the ballast water during both, at uptake and discharge. In total, 67 systems use pre-treatment step (51 use filtration), others selected different methods or use a combination of two or more pre-treatment steps. The majority of systems (60) use an active substance and the most frequently applied technique is electrolysis/electrochlorination (25 systems). The second most commonly used technology is UV ra-

diation (24 systems), which is considered as a non-active substance system. The system capacities range predominantly from 50 m³/h to more than 10,000 m³/h, although two vendors announced a capacity of 20,000 m³/h and higher. BWTS footprints occupy less than 1 m² up to 145 m², depending on their capacity and treatment technologies used, and some operate without electricity, while others may consume up to 200 kW per 1,000 m³/h.

Before the sales begin, all systems need to be type approved by a flag state according to the IMO G8 Guideline, also considering the procedure G9 as appropriate. Currently BWTS are in different stages of the testing and approval processes, but 16 BWTS vendors completed the certification requirements and obtained already the type approved certificate by an administration.

The BWM Convention is nearing its entry into force which is anticipated for 2013. Thereafter, more than 50,000 vessels need to be equipped with BWTS (IMO, 2010) and BWTS production and shipyard capacities may become a bottleneck. A proactive approach, i.e. to install BWTS already today, may reduce the risk of delayed compliance due to the installation limitations.

4.7 Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under Grant Agreement No. 266445 for the project "Vectors of Change in Oceans and Seas Marine Life, Impact on Economic Sectors" (VECTORS).

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5 Overview of Ballast Water Treatment Principles

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5.1 Abstract

According to the Ballast Water Management Convention (BWMC) the distribution of non indigenous species by ships' ballast water has to be prevented. How to do this is a challenge for scientists, engineers, ship builders, and ship owners. A treatment of ballast water is inevitable. Since the passage of BWMC in 2004 many innovative ideas for ballast water treatment were presented and in a large part already converted into technologies feasible for shipping. In general, the proposed treatment technologies can be divided into two main categories: mechanical- physical water treatment and treatment with active substances. Many ballast water treatment systems have their origin in drinking water purification. Currently the use of fine-mesh filter systems, UV-radiation and chlorination are the most important practices for ballast water treatment. Beyond that, interesting other methods complement the tools for the prevention of further species distribution all over the world by ships' ballast water. This article gives an overview of different treatment principles which are already on the market or in the stage of development. The advantages and disadvantages are briefly discussed.

5.2 Introduction

Since wooden ships were replaced with steel-hulled vessels in the second half of the 19th century natural water has been used for ships' ballast. Water can be easily pumped in and out of ballast tanks. Ships' ballast is important for stability and trim of a vessel. Ballast (water) remarkably contributes to the safety of ships, crew, and cargo. The centre of buoyancy of a common vessel is way beyond the water level. (The cruise ship Queen Mary II has a draught of about 10 m and is about 40 m high above the water level.) So, a vessel actually would be capsized easily. Ballast is used to tare a vessel like a skipjack. A ship has to upright itself in any possible situation it may encounter. Furthermore, ships' ballast prevents torsion of a vessel's hull and determines the posture of a ship in the water (Shama, 2011). The world's shipping fleet carries billions of tonnes of ballast water each year. Depending on the size and number of ships entering a harbour a huge amount of ballast water might be discharged into the environment. Because of the natural origin of ballast water several living organisms (bacteria, algae, juvenile and adult animals) are highly abundant in this water. By shipping these organisms are distributed all over the world.

Ecosystems are a complex and very sensitive network of species interactions, established over long historical periods. Non-indigenous species introduced e.g. by ships' ballast water, could seriously threaten the biodiversity and stability of such evolved aquatic bionetworks. Beyond that, the invaders could lead to substantial economic consequences. For example, the comb jelly *Mnemiopsis leidyi* (Agassiz, 1865) was introduced in the Black Sea in the late 1980ies. That caused a drastic reduction in zooplankton, ichthyoplankton, and zooplanktivorous fish populations in that area. A collapse of local anchovy fishery around the Black Sea ensued from this decline in zooplankton and fish populations (e.g. Kideys, 1994; Shiganova et al., 1998, 2001).

Ballast water could also be a source and a vector for human and animal pathogens. The outbreak and the rapid spreading of the cholera epidemic in the 1990ies in Latin America was

traced to ballast water (e.g. WHO, 1992; McCarthy et al., 1992; DePaola et al., 1992; Wilson, 1995). Toxins responsible for the disease paralytic shellfish poisoning were detected in France in 1998. The organism releasing these so called saxitoxins was identified as *Alexandrium catenella* ((Whedon & Kofoid) Balech, 1985). Morphological characteristics, DNA sequencing and toxin analyses demonstrated that the strains of *A. catenella* detected in France were closely related to populations of the same species found in the Western Pacific. The most likely scenario is the introduction of these strains to French waters via ships' ballast water (Lilly et al., 2002).

Scientists and politicians have already publicized the threat posed by invasive organisms many times. In 2001, William A. O'Neil, the former Secretary General of the International Maritime Organisation (IMO), stated: "The introduction of harmful aquatic organisms and pathogens to new environments, including via ships' ballast water, has been identified as one of the four greatest threats to the world's oceans." As a consequence, "The International Convention for the Control and Management of Ships Ballast Water & Sediments" (Ballast Water Management Convention, BWMC) was adopted by consensus at a diplomatic IMO conference in 2004. The aim of this convention is to stop the further invasion of harmful organisms by ships' ballast water and to reduce the sedimentation of particles in ballast tanks. Regulations for the control and management of ships' ballast water and sediments can be found in the annex of the convention. Regulation D determines standards for ballast water management to prevent the introduction of alien species. Especially the Ballast Water Performance Standard (D2) provides limits of viable organisms per defined volume that are allowed to discharge with ballast water (see also the article by David and Gollasch in this volume). To achieve the D2-standard a treatment of ships' ballast water is needed.

5.3 Principles

Currently, several treatment systems for ballast water (BWTS) are under development or have already been internationally approved. In general, diverse measures are available for pre-treatment and disinfection of water. They were mainly established for drinking water purification. The primary aim for both, drinking water and ballast water treatment, is quite similar: removal of organisms, pathogens, and sediments (BWMC, 2004; WHO, 1997; and Directive 98/83/EC). So, a large number of drinking water purification technologies could be directly adopted or easily accommodated to ballast water treatment.

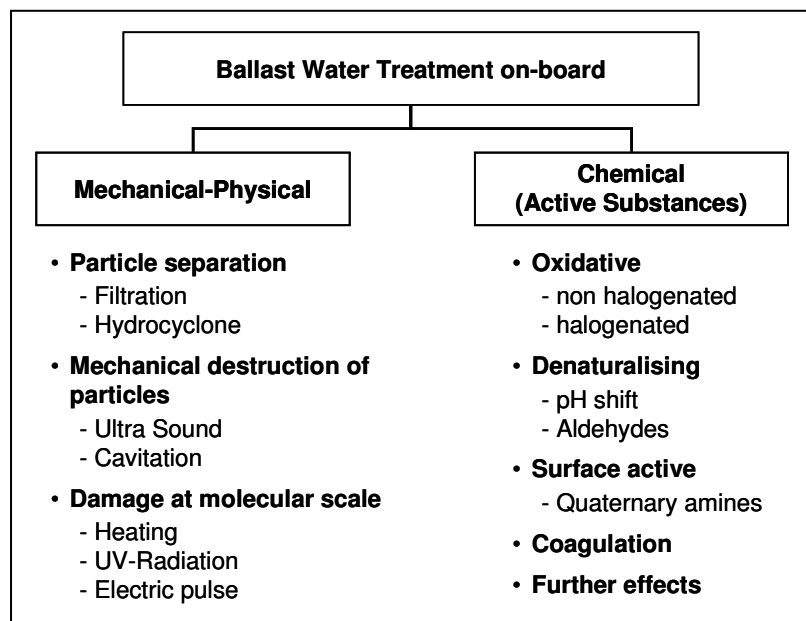
Beyond that, other principles like cleaning methods used in cooling water systems of power plants are easily conceivable for ballast water treatment. There is no lack in concepts how ballast water could be treated to reach the D2-standard or even stricter limitations. However, not all ideas are convertible into equipment that is feasible and asserting on the market. Ballast water might be treated in shore reception facilities or directly on board a ship. This article only focuses on the most important on-board ballast water treatment systems. Measures for treating ballast water can be divided into mechanical-physical and chemical processes (fig. 6).

Worldwide 60 BWTS have been in the approval process in September 2011. That includes different stages from pretesting to already type approved systems. About 70% of these systems use active substances for ballast water disinfection (Dobroski et al., 2011 and BSH internal information).

5.3.1 Mechanical-physical treatment

This group of techniques utilize the behaviour of physical bodies and the subsequent effects of these bodies on their environment subjected by forces or displacements to treat ballast water. Beyond that, the introduction of high energy into a water body could be applied as effective disinfection measure.

Figure 6: Overview of ballast water treatment measures on board a ship



Particle separation

Ballast water almost always is mechanically pre filtered by disc or screen *filters*. Automatic filter systems with mesh sizes of about 40 µm, in some cases even down to 20 µm, retain larger particles and organisms. Functional reliability in heavy turbid sea water and the deposition grade are important parameters that define the performance of a filter system.

Hydrocyclones use gravity and centrifugal force to separate solid particles from the water stream based on the ratio of their centripetal force to fluid resistance. A hydrocyclone mostly has a cylindrical section at the top. Here the water stream tangentially influxes into the container. The water emits at the conical base. The angle, and hence length of the conical section, plays a role in determining operating characteristics. Larger or denser particles are transported to the wall by centrifugal forces. Finer or less dense particles remain in the liquid and exit at the overflow side through a tube extending slightly into the body of the cyclone at the centre (Dyakowski et al., 1999; Statie et al., 2001).

Filter and hydrocyclone systems are easy to maintain. They use automatic self-cleaning procedures during operation. The separated residue can be constantly removed and discharged over board. No environmental risk is to be feared by such systems. However, despite their compact construction filter and hydrocyclone units take up some space in a vessel's engine room. The mechanical particle separation is not disinfection itself. Bacteria and pathogens could remain in the ballast water.

Mechanical destruction of particles

Particles and organisms in ballast water can be cracked mechanically with *cavitation* and *ultra sound*. In a cavitation process, numerous micron-size gas bubbles are formed and expand in the liquid. It usually occurs when a liquid is subjected to rapid changes of pressure that cause the formation of cavities where the pressure is relatively low. By imploding those bubbles they force energetic liquid into very small volumes and consequently a tremendous amount of energy is released. This creates spots of high temperature and emitting shock waves destroying particles or cell walls (Brennen, 1995). Ultrasonic treatment uses high frequency sound waves usually from 20–130 kHz to vibrate a liquid. This results in a cavitation process, too.

Such treatment systems immediately destroy particles and organisms without environmental risk. But they are very energy intense and a uniform treatment cannot be guaranteed. The treatment process in the water is difficult to control.

Damage on the molecular scale

Using high energy will not only crack particles mechanically. *Heating* and *UV radiation* even produce effects on the molecular scale. Heating acts by denaturation of essential proteins. Energy rich UV-C radiation with a wave length less than 300 nm causes damages at the DNA and proteins of living organisms. A four log reduction of germs and viruses occurs under an exposure of 400 J/m² (at 253.7 nm) to all water volume elements passing the UV system. The performance of a UV treatment prototype can be verified by biosimetric testing using suspensions of germs with a known UV susceptibility (Hoyer, 1998).

UV treatment is very effective in clear water with low turbidity at low environmental risk. A treatment system is simple to install and requires little supervision, maintenance, or space, improved safety, minimum service time, and low maintenance costs. Using UV radiation for disinfection, problems could occur in water with high levels of suspended solids, turbidity, colour, or soluble organic matter. These materials can decrease the radiation transmission or UV radiation can cause chemical transformations of these compounds. As the consequence the UV dose required for the inactivation of organisms is reduced and the disinfection performance is deficient.

Pulsed electric field (PEF) disinfection is a new technology for a non-thermal disinfection of water. Controlled high voltage impulses create pores in a cell membrane. These pores originate from dielectric breakdown of the membrane. A cell lysis is performed by application of multiple high voltage impulses on a fixed volume of liquid (Johnstone and Bodger, 1997). The use of short duration electrical pulses with pulse widths of 130–500 ns inactivates spores, bacteria, and viruses in water. A four log reduction was shown for *E. coli* at field strengths of 110 kV/cm and 70 pps, with a total energy consumption of 40 J/cm³ (Narsetti et al., 2006). Up to date there is little experience with the application of this technology in ballast water treatment. The main disadvantage for UV treatment as well as for heating and for pulsed electric field disinfection is the high consumption of energy.

5.3.2 Treatment using Active Substances

The resolution MEPC.169(57) – G9 defines “Active Substance” as “a substance or organism, including a virus or a fungus that has a general or specific action on or against harmful aquatic organisms and pathogens.” Living organisms and viruses are not considered in this article. Active chemicals react in a variety of ways to inactivate harmful aquatic organisms and pathogens in ballast water. Active substances inhibit biological processes in living cells and viruses by disrupting protein and membrane structures. They interact with the enzymatic system in living cells or tissues or they directly influence ribonucleic acids (RNA/DNA). In

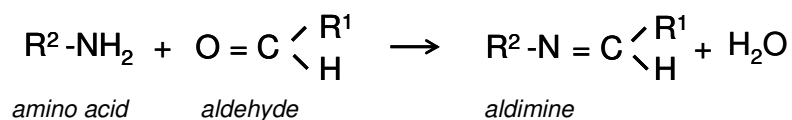
short, active substances denaturalise essential vital components in a wider sense resulting in the loss of their biological function.

Denaturalising agents

In molecular biology, protein and ribonucleic acid structure describes the various levels of organization of protein or ribonucleic acid molecules. The primary structure refers to the linear nucleotide or peptide sequence of the molecular chain. Secondary structure describes the regular local sub-structures. Secondary structure is defined by the hydrogen bonds between backbone amide and carboxyl groups in proteins and between the nitrogenous bases in ribonucleic acids. For proteins two main types of secondary structure, the alpha helix and the beta strand or beta sheets, were suggested by Linus Pauling in 1951. The tertiary structure is the three-dimensional total structure of a single molecule. This structure already is largely determined by the sequence of nucleotides and peptides. Quaternary structure is the three-dimensional structure of a multi-subunit protein and how the subunits fit together. In performing its biological function such a molecule may undergo reversible structural changes. In a narrow sense, denaturalising agents cause irreversible structural changes in proteins or ribonucleic acids associated with the loss of the biological function of that molecule.

The formation of higher level molecular structures is often pH-dependent. Consequently, a *change in the pH-value* may result in inactivation of functional molecules. That in turn results in inhibition of harmful organisms. A change in the pH value by addition of acids or bases to the water is easy to achieve. And a recovering neutralisation also is not difficult. However, for a treatment of ballast water this procedure does not react very fast and corrosion of the tanks could be one consequence.

Aldehyde compounds like acrolein have also been proposed for the use in ballast water treatment. Because of the ability of the carbonyl group to add to other compounds, *carbonyl compounds* like aldehydes and ketones are well known for their denaturalising properties. Among others, targets of the carbonyl addition in proteins could be the amino acids with amino groups that are not involved in the peptide binding (e.g. in the amino acid arginine). Under the elimination of water, the carbonyl compound will be added to the nitrogen atom of an amino group according to the following equation (Mortimer, 1996):



As the result, the cell proteins will be inactivated step by step and the affected organism dies. The use of such denaturalising agents is very effective for organisms of all sizes. However, because of its high environmental and human toxicity even in low concentrations and the potential of cancerogenicity, a release of aldehydes into the natural environment has to be prevented according to the EU Biocidal Products Directive (BPD). Furthermore, little is known about the decomposition pathways in the natural environment. Therefore, the use of aldehydes in ballast water treatment should be avoided.

BWTS using so-called *“inert gas” technologies* for ballast water treatment may also be placed into the group of denaturalising agents. The primary aim of these systems is the de-oxygenation of the treated water by the use of nitrogen. However, the *“inert gas”* is generated by combustion of highly pure fuel in a very effective combustion process. The combustion gas as well as the resulting treated ballast water are complex substance mixtures. Beside the inert nitrogen from the air that does not take part in the oxidation of the fuel, the released gas

mixture contains remarkable amounts of carbon dioxide. If carbon dioxide is discharged into the water the pH value in the treated water will be decreased by forming hydrogen carbonic and carbonic acids. Above that, numerous other compounds are produced, even in highly effective combustion processes. Compared to the amount of nitrogen and carbon dioxide these compounds only occur in (micro) traces. However, several compounds like sulphur oxides and aldehydes are highly soluble in water. Depending on the amount of the discharged gas mixture and the time the ballast water was treated, an increasing concentration of those compounds up to a suspension sufficient for disinfection may be a possible implication (personal communication by Johann-Philipp Crusius, Dept. of Technical Thermodynamics, University of Rostock, Germany). So, beside the effect of deoxygenation, the decrease of the pH value and the formation of a disinfection solution in the ballast water may be a reason for the treatment success. Unfortunately, there are so far only limited publically available data about the composition of the gas mixture and the finally dissolved compounds in the treated ballast water. Further investigations are necessary for a realistic risk assessment of such BWTS.

Some BWTS intend to use *metal ions (silver or copper)* for ballast water treatment. Metal ions have been well known disinfectants and food preservatives since ancient times. Silver has been used for effective water disinfection especially in Europe. The biocidal effects of silver ions have been demonstrated in several studies. The mechanisms are not completely understood, however some points of action in inactivation of bacteria are highly likely (Silvestry-Rodriguez et al., 2007). The metal ions bind to the bacterial cell walls and membranes or the ions accumulate inside the cells. Further, silver binds to cellular proteins including enzymes. Target functional groups are the sulfhydryl groups (-SH) in proteins. That leads to a disturbance of vital functions of the bacterial cells and finally to their inactivation. (e.g. Slawson et al., 1992; Bellantone et al., 2002). Interactions with cytochrome and with nucleic acids that lead to the disturbance of cell proliferation are described (Beveridge et al., 1996). Beside their toxicity metal ions are very persistent. That is one reason that the efficacy of metal ions is shifting. Organisms are able to adapt to a rising metal concentrations in a limited range. In connection with that, the accumulation of metal ions in organisms is well known. According to the BPD, the release into the environment should be avoided even in low concentrations.

Surface active agents

The use of *quaternary ammonium compounds (QACs)* as ballast water disinfectants is currently tested, too. QACs are organic compounds that contain four functional groups attached covalently to a central nitrogen atom (R_4N^+). To the QAC group belong many individual chemicals. Each QAC has its own chemical and toxicological characteristics. These chemicals strongly adsorb on suspended minerals, biomass and inorganic particles. They interact with cell membranes in living organisms and may accumulate in the membranes. So, the functionality, like the semi permeability of membranes could be disturbed heavily (Tezel, 2009). As a consequence of the extensive membrane interaction of QAC combinatory effects with other toxic compounds are likely. QACs are very toxic to aquatic organisms already at ppm levels and lower. QACs were added to molluscicides and insecticides. Because of their persistence and the hard decomposition of many QAC, their biocidal effects are long lasting, even when released into natural environments. According to the BPD the use of QACs has been restricted since 2008.

Coagulation agents

As already indicated in its full title, subjects of interests of the BWMC are the ships' ballast water and sediments. To minimise the sedimentation in ballast tanks, organisms and particles have to be removed from the up taken ballast water. Filtration could theoretically only remove particles down to a size of 1 μm . Thinly dispersed or colloidal dissolved compounds remain in the water. Again, with an effective measure from drinking water purification – the

flocculation – these compounds and larger particles could be eliminated from the water. Usually, fine particles and organisms have a negatively charged surface in consequence of several mechanisms like ionisation of functional groups. The neutralisation of the charged surface may be achieved by addition of chemical coagulants, mostly metal salts such as iron(III) or aluminium(III) sulphate ($\text{Fe}_2(\text{SO}_4)_3$ or $\text{Al}_2(\text{SO}_4)_3$) or iron chloride (FeCl_3). By addition of those salts to the water complex hydrolysis reactions occur. The Fe^{3+} or the Al^{3+} ion are highly charged counter ions to the negatively charged particles in the water. Hence, the differently charged compounds attract each other and aggregates are formed. The process is pH-dependant (Chow et al., 1998; U.S. EPA, 2005; Matilainen et al., 2010). At this stage the micro aggregates are still too small and too instable to be removed from the water. To enlarge and to stabilise the flocks, flocculant additives have to be added. Such additives are synthetic (mainly adhesive composite epoxy resins) or natural polymers (like polyacrylamide or starch). The agglomeration of micro aggregates to larger ones leads to an increased sedimentation of the particular mater. The now emerging sediments could be removed more easily e.g. by filtration or magnetic separation when iron powder was added during the treatment process (Parsons and Jefferson, 2006). Up to date, we are short on experience using this technique in ballast water treatment. However, like other metal ions aluminium and iron are very persistent in the environment. Above that, it is worth bearing in mind that aluminium is suspected as a causative agent of neurological disorders such as Alzheimer's disease and presenile dementia. Production-related heavy metal pollution may be present in inorganic flocculants. So, an adequate disposal of the removed sediment is to be recommended (Rickenbacher and Schlatter, 1983; Srinivasan et al., 1999).

Table 5: Oxidation capacity (reduction potentials) of various disinfectants in an acidic environment

Active substance	Reduction potential (eV)
Ozone	+2.07
Peracetic acid	+1.81
Chlorine dioxide	+1.57
Hypochlorous acid	+1.49
Chlorine	+1.36

Oxidants

Probably, the largest group of active substances are oxidising agents. From the chemical point of view, an oxidation is any chemical reaction in which a substance to be oxidised donates electrons. The valence of the corresponding atom in the molecule is increased. The oxidising agent is the electron acceptor, which is reduced in the reaction. The valence of the atom in the molecule is correspondingly decreased. The two partners of an oxidizing and reducing agent that are involved in a particular reaction are called a redox pair (McNaught and Wilkinson, 1997). The electron transfer is an energetic process. The energy value is specific for each redox system. This individual energy potential can be measured in comparison with the standard hydrogen electrode ($\frac{1}{2} \text{H}_2 \rightarrow \text{H}^+ + \text{e}^-$) where hydrogen is oxidized in a cell at standard state (terms of standard state: effective concentration 1 mol/L, pressure 1 bar, and temperature 25 °C). The electrode potential of each half-reaction also is known as the reduction potential, which is a measure of the tendency of the oxidizing agent to be reduced. By definition, its value is zero eV for the standard hydrogen electrode potential. For oxidizing agents which are stronger than H^+ this value is positive, and it is negative for agents which are weaker than H^+ (Petrucci et al., 2002). The standard electrode potential of the chlorine reaction $\frac{1}{2} \text{Cl}_2 + 2\text{e}^- \rightarrow \text{Cl}^-$ is +1.36 eV. The standard reduction potentials, also referred to as oxidation capacities, of some common active substances used for ballast water disinfection are listed in table 5. Beside the temperature and the pH value the concentration of the reacting compounds in a solution has an important influence on the strength of the reduction potential. Using the Nernst equation (fig. 7) the electrode potential of a redox pair at any concentration in a solution can be calculated (Mortimer, 1996).

Figure 7: The Nernst equation describes the concentration dependency of the electrode potential.

$$E = E^0 + \frac{RT}{z_e F} \ln \frac{a_{Ox}}{a_{Red}}$$

- E - half-cell reduction potential at the temperature of interest
- E^0 - standard half-cell reduction potential
- R - universal molar gas constant: $R = 8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$
- T - absolute temperature
- a - chemical activity for the relevant species, where a_{Ox} is the oxidant and a_{Red} is the reductant.
- F - Faraday constant, number of coulombs per mole of electrons:
 $F = 9.648534 \times 10^4 \text{ C mol}^{-1} = 9.648534 \times 10^4 \text{ J V}^{-1} \text{ mol}^{-1}$
- z_e - number of moles of electrons transferred in the half-reaction

The knowledge of the electrode potential of redox reactions and their concentration dependence is the basic principle behind the concept of Total Residual Oxidant (TRO) (to be discussed later on).

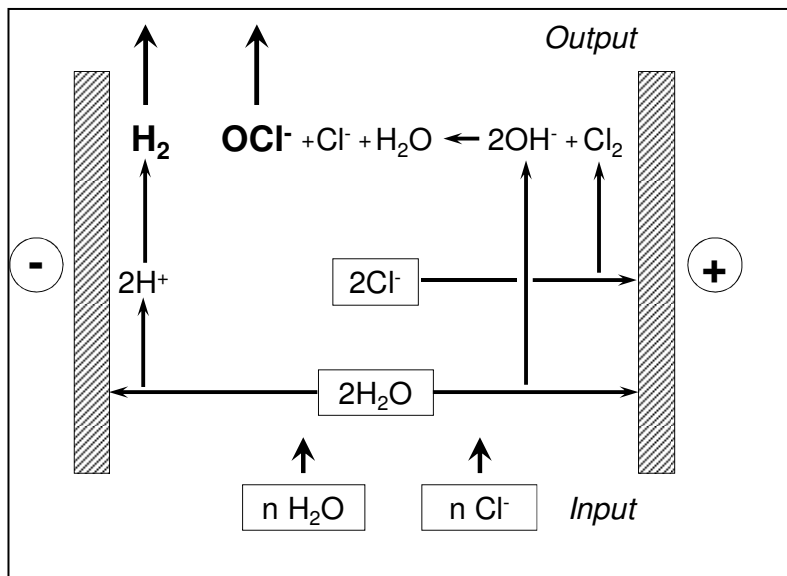
An oxidising compound compensates for the lack in electrons by electrons from substances in the surrounding environment. Frequently, reactive radicals are formed during this transfer of electrons as an intermediate step. Those radicals in turn behave as very strong oxidising agents. So, the oxidants non-specifically and extensively damage all components of a cell, including proteins, lipids, and DNA. Beyond that, some reactive oxidative species already in trace concentrations act as messengers in redox signalling in cells. A slight increase of those substances in the near environment of a cell causes disturbances in the regular cell metabolism. So, even moderate oxidation already can trigger cell death, while more intense reactions may cause necrosis, and finally the affected organism dies (Lennon et al., 1991).

Different groups of highly reactive oxidant species are in use for ballast water treatment. One major group are substances, the oxidising potential of which is mainly due to the chemical properties of oxygen present in the molecule. Compounds containing a molecular group with an oxygen-oxygen binding are known as *peroxides*. In the peroxide group the oxidation state of oxygen is -I instead of -II, which is the most stable form. The binding between the two oxygen atoms is unstable and has a disposition towards homolytic decomposition. Consequently, two reactive radicals are formed (Holleman and Wiberg, 1995). Inorganic peroxides (e.g. *hydrogen peroxide* – H_2O_2) as well as organic hydroperoxides (e.g. *peracetic acid* – CH_3COOOH) are used in water disinfection. These chemicals are effective, cheap, and easy to handle. Due to its high oxidation capacity, *ozone* (O_3) is one of the strongest known oxidising agents. Because of its effectiveness ozone disinfection has been very common in drinking and waste water treatment for decades. So, it is obvious to use ozone also in ballast water treatment. The molecule is unstable. Ozone decomposes by producing oxygen radicals ($\text{O}\cdot$) that act as active compound (Peleg, 1976). Beyond the above mentioned addition of chemicals, at certain circumstances free *hydroxyl radicals* ($\cdot\text{OH}$) can be formed in the water as disinfectant. This happens either in the reaction chain of the several (added) compounds, by electric current, or by UV radiation. These radicals and/or the oxygen containing compound itself can induce the formation of different other oxidising agents in the treated water. So, halogenated active compounds are produced by reactions with the halogenide ions present in the water.

Halogens and halogenated compounds are a second major group of powerful reactive oxidants in use for ballast water treatment. Their oxidising potential is mainly due to the chemical properties of the halogen, which is an essential atom in those molecules. Halogen atoms have two s- and five p-electrons in their valence shell ($ns^2 np^5$). So, the halogen atom needs exactly one electron to reach the stable configuration of the next noble gas following the

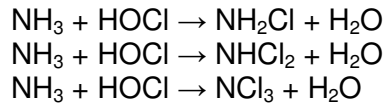
element in the periodic system. Therefore, those atoms show a strong tendency to pick up electrons from the environment (Mortimer, 1996). One of the most commonly used disinfectants for water disinfection is *chlorine* (Cl_2). When chlorine dissolves in freshwater it forms hydrochloric acid and hypochlorous acid: $Cl_2 + H_2O \rightarrow H^+ + Cl^- + H^+ + OCl^-$. The oxidation state of chlorine in the acids is +1. All these chlorine species including the corresponding anions are oxidising agents which are very effective for the deactivation of organisms and microorganisms. They react with a wide variety of biomolecules, including DNA, RNA, fatty acids, cholesterol, and proteins (see e.g. Fair et al., 1948; Prütz, 1998; Carr et al., 1997; Vissers et al., 1998). Bromine and iodine compounds have the same chemical structure and, following, similar disinfection properties. Chlorine can be easily applied, measured and controlled. It is fairly persistent and relatively cheap. Above that, the main advantage of using chlorine for ballast water disinfection is the almost universal availability of the raw material for chlorine production: natural sea water. Because of its high content of sodium chloride, seawater (or brine) can be used to produce chlorine. Electrochlorination systems work by passing seawater through an electrolytic cell, where direct current produces chlorine from the solution. Two chloride ions ($2Cl^-$) from the water are oxidized by two electrons (e^-) to form elemental chlorine (Cl_2): $2Cl^- - 2e^- \rightarrow Cl_2$. Elemental chlorine instantaneously reacts like described above (White, 1999; Casson and Bess, 2003). Nevertheless, according to Schmidt et al. (2012) the development of elemental chlorine is the basic anode reaction. Figure 8 shows a simplified electrolytic cell focussed on the most important reactions.

Figure 8: Simplified electrolytic cell and the most important primary reactions in a reaction chain during seawater electrolysis (modified from Bommaraju et al., 2007)



⊖ — cathode; ⊕ — anode; □ — reactants; OH^- — intermediate products; OCl^- — reaction products

However, the chemistry is much more complex and there are differences between seawater and freshwater. Seawater also contains 50–70 mg/L bromide (Br^-) (White, 1999). The bromide is directly oxidized by hypochlorite to form hypobromite (OBr^-): $OCl^- + Br^- \rightarrow OBr^- + Cl^-$. Finally, after (electro)chlorination of seawater hypochlorous acid as well as hypobromous acid (hypochlorite and hypobromite) and many other compounds (like further halogenated oxyacids and their corresponding halogenate ions) will act as active disinfectants. During water chlorination, *halogenated amines* can also be formed as the result of the reaction of hypochlorous acid with ammonia in a series of competing reactions. Monochloramine (NH_2Cl), dichloramine ($NHCl_2$), or nitrogen trichloride (NCl_3) are possible reaction products (White, 1999). The simplified stoichiometry of chlorine ammonia reactions is as follows:



Halogenated amines are active oxidising agents. Currently, treatment systems that intend to use chloramines directly for ballast water disinfection are still under development. Chloramines are more stable than free chlorine. Monochloramine readily reacts with four amino acids: cysteine, cystine, methionine and tryptophan (Jacangelo et. al, 1987). So, chloramines inhibit proteins or protein-mediated processes such as respiration. Monochloramine does not produce disinfection by-products to any significant degree, although some dichloroacetic acid can be formed from monochloramine.

Chlorine dioxide (ClO_2) has been known as a powerful oxidising water disinfectant since the beginning of the twentieth century. Chlorine is in the +IV oxidation state in this compound. Due to its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO_2^-) (Hoehn et al., 1996) chlorine dioxide does not chlorinate: $\text{ClO}_2(\text{aq}) + \text{e}^- = \text{ClO}_2^-$. In contrast to the hydrolysis of chlorine gas in water, chlorine dioxide remains in solution as a dissolved gas in the pH range typically found in natural waters (Aieta and Berg, 1986). Its disinfection mechanisms are not well understood, but appear to vary by type of organism (US EPA, 1999). It is assumed that chlorine dioxide inactivates functional proteins in living cells. Chlorine dioxide reacts readily with the amino acids cysteine, tryptophan, and tyrosine, but not with RNA (Noss et al., 1983; Olivier et al., 1985). It has also been shown that chlorine dioxide reacts with free fatty acids and disrupts the permeability of the outer membrane (Ghandbari et al., 1983; Aieta and Berg, 1986). Outer membrane proteins and lipids were sufficiently altered by chlorine dioxide to increase permeability. Chlorine dioxide is more effective than chlorine and chloramines and the biocidal properties are not influenced by pH.

The cocktail of several active agents, that are finally found when natural (sea) water is treated with the above described oxidising agents, is the result of many secondary reactions. Because of its equilibrium reaction nature, a steady state of different redox processes in the treated water is obtained. It is impossible to describe any single process. So, the level of oxygen and chlorine induced oxidants is measured as *Total Residual Oxidant (TRO)* in milligram elementary chlorine or ozone equivalents per litre (mgCl_2/L , mgO_3/L). Chlorine, bromine, and iodine oxidants are formed and the standard total chlorine analytical methods do not differentiate between the oxidants. TRO is measured by standard colorimetric methods (Nielsen, 2006). To interpret the measured TRO values correctly it is important to understand the nature of the TRO concept. TRO is not a surrogate for molecular oxygen or chlorine equivalents. TRO rather is the electrode potential of treated water, expressed as an oxidative compound concentration related to the appropriate redox potential of this substance (ozone or chlorine). For example, the TRO concentration of 0.1–0.3 mg /L measured in untreated natural seawater actually is the average electrode potential of all steady state redox-processes in the water and according the Nernst equation an equivalent of the concentration of the reacting agents. This electrode potential is related to the electrode potential resulting by a chlorine concentration of 0.1–0.3 mg per litre distilled water. Discharged ballast water may at maximum show the TRO concentration of untreated natural sea water. So, ballast water treated with oxidants would require inactivation unless residual oxidants are completely reduced by the time of discharge. Sulphur compounds are commonly used for inactivation, including sodium bisulphite (NaHSO_3), sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$), and sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$). By addition of sulphur reductants, TRO forms sodium sulphate and hydrochloric acid (White, 1999).

All oxidising agents are very effective for the lasting inactivation of living organisms. They are easy to use and fairly cheap. However, oxidising disinfectants are powerful and the organic matter and halogenides naturally present in the environmental waters will be oxidized, too. So, chemical disinfection of ballast water produces an unintended hazard for human health

and the environment: the formation of disinfection by-products (DBPs). Secondary toxic effects including carcinogenicity and reproductive effects in the treated water may be linked to chemicals produced during disinfection processes. The high level of toxicity often is combined with high persistence of the occurring DBPs. Each disinfectant in use produces its own suite of chemical DBPs in the treated ballast water. More than 500 DBPs have been reported in the literature for chemical drinking water disinfection (Richardson, 1998). The reported DBPs belong among others to the groups of the trihalomethanes (e.g. trichloromethane, tribromomethane), haloacetic acids (e.g. dichloro- and trichloroacetic acid), haloacetonitriles (e.g. bromoacetonitrile and chloroacetonitrile), haloketones, haloaldehydes, and haloamides (e.g. Caughran et al., 1999; Weinberg et al., 2002; Richardson et al., 2007). Because of the enormous concentration of halogenide ions, including bromide and iodide, the amount of DBPs formed during sea water treatment with oxidative agents may be much higher than in fresh water. So, different inorganic and organic compounds containing bromine and iodine in the molecule could be expected in higher concentrations. According to the WHO (2000) there is indication that brominated DBPs may be more carcinogenic than their chlorinated analogs. And, in addition, iodinated compounds may be more toxic than their brominated analogs (Plewa et al., 2004). The great variety in the DBPs formed results in different toxicity levels of treated ballast water. Because of the multiple mixtures of produced chemicals the predictability of the resulting toxicity and the possible pathways of decomposition of the compounds in the water is not easy. Therefore, whole effluent tests are required in toxicity testing by the IMO procedure G9. The experience in approving and testing BWTS in the last years shows a further inconvenience of the DBPs. Beside their toxicity and their persistence, DBPs are not be inactivated by the use of sulphur reductants. Removing the oxidising agents, the DBPs remain in the discharged water even after the neutralisation step and may cause a more or less strong residual toxicity of the ballast water.

An ideal active substance should be very effective in ballast tanks for a long time and should not harm aquatic the environment when it is discharged. That requires a rapid inactivation of the chemical and a total degradation to harmless by-products. Substances could act in different ways at the same time or they show different reactions in combination with other chemicals. The very complex fate of a single active substance is the result of interactions of different parameters, like the chemical nature of the substance itself, the temperature, salinity, pH, the load and the quality of organic matter, and many others. Obviously, an ideal active substance for ballast water treatment does not exist. Experiences from drinking water treatment and swimming pool treatment regarding the by-products and their toxicology are a precious tool for mitigation measures of treated ballast water, too. Measures are needed to protect the sensitive ecosystems from the invasion of non indigenous species and from the harm by the used chemicals and their DBPs. Such mitigation measures are e.g. an elongation of the holding time of the water in ballast tanks or the deactivation of the active substances. A very common and efficient method is to combine different methods of ballast water treatment. Currently, a typical BWTS consists of a pre-treatment unit, like an effective filter system, followed by a disinfection unit and finally by an inactivation step if necessary.

5.4 Conclusions

For ballast water treatment an all-in-one device is searched. But in practice we do not have the ideal solution. There are always advantages and disadvantages using different ballast water treatment principles. Currently the use of fine-mesh filter systems, UV-radiation and chlorination or a combination of the different methods, are the most important practices for ballast water treatment. Beyond that interesting other methods complement the tools for the prevention of species distribution all over the world by ships ballast water.

Every ballast water treatment system is unique and shows its own performance at varying environmental conditions. This always requires a detailed evaluation of the system's per-

formance and a human and environmental risk assessment. An approval of an active substance for ballast water treatment has to consider regulations of the European Biocidal Products Directive (BPD) 98/8/EC in Europe, too. Above that, a BWTS has to fulfil requirements that result from the practical daily routine on board a ship. So, a system has to be applicable versatility at varying conditions like in retrofitting an old ship. Finally, granting an approval always is a case by case decision.

The overwhelming majority of the proposed principles for ballast water treatment unfortunately intend to kill the organisms. The BWMC is aiming at the prevention of distribution of organisms into new ecosystems. That does not mandatorily mean that the permanent inactivation of organisms is the only measure for stopping the distribution of the non indigenous by ships' ballast water. At this point it has to be remembered that most organisms are not harmful per se. The status as harmful or not depends on an enormous amount of mainly unknown variables in the natural environment and the area of interest that is affected. The BWMC recalls article 196(1) of the 1982 United Nations Convention on the Law of the Sea (UNCLOS), which provides that "States shall take all measures necessary to prevent, reduce and control pollution of the marine environment resulting from the use of technologies under their jurisdiction or control". That includes pollution by chemicals and the introduction of species which may cause significant and harmful changes in the marine environment. The rather vague term "harmful organism" may be defined more precisely. That may help to develop appropriate, fine-adjusted measures that keep the effort in preventing the distribution of organisms all over the world and the risk, e.g. by DBPs, in balance. For sustainable, environment friendly and forward-looking shipping we need more innovative ideas and concepts off of the use of the, undoubtedly very effective, ballast water treatment technologies currently in use.

5.5 References

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6 Land-Based Testing of Ballast Water Treatment Systems and its Possible Function in Risk Assessment

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6.1 Abstract

This paper describes the most important characteristics of land-based testing of ballast water treatment systems (BWTS). These general features are independent of any specific test facility. Based on this, options are presented for a closer cooperation between test facilities and entities conducting risk-assessment.

6.2 Introduction

In order to discuss the possibilities of cooperation between institutions that perform risk-assessment and those performing land-based testing of ballast water treatment systems (BWTS) it is useful to first have a closer look at what land-based testing encompasses. To avoid confusion it is necessary to clearly define the term risk in the respective context. Testing of the systems is first and foremost concerned with the risk of biological invasions via ballast water and subsequently the risk reduction through the use of the BWTS. This is a different type of risk than the risks which are addressed by the risk-assessment this and the other papers of this volume are dealing with. The latter deals with the risks that are posed by operating the BWTS itself. These risks include human health, work safety and environmental issues alike. These are the factors that will be referred to as risks from here onwards. For a more detailed discussion on these factors see the papers of Banerji, Wieck et al, and Linders in this volume.

6.3 Land-based testing of BWTS

The primary scope of land-based testing as described in guideline G8 (IMO, 2008a) of the International Maritime Organization (IMO) is to evaluate the effectiveness of BWTS in removing organisms. Therefore these tests are conducted at full scale. This encompasses flow rates of 200 cubic meters per hour and a minimum holding time for as well treated as control water of five days. The framework for land-based testing is currently defined by guidelines G8 (IMO, 2008a) and G9 (IMO, 2008b) of IMO. Similar protocols are being developed or tested right now to suite national laws (e.g. the ETV protocols by the EPA and USCG in the US). However these guidelines are generic in nature and certainly at the time the first version of G8 was released in 2004/2005 there were no standard methods available. Test facilities had to find their own means of putting the intention of the guidelines into practice. Harmonisation efforts by the IMO via the GloBallast program and by the EU via the North Sea Ballast Water Opportunity project (NSBWO) show quite similar approaches to the problem by the different test facilities.

The ballast water tanks of ships are simulated by tanks in a size range of 200 to 500 cubic meters, with tanks of 200 to 300 cubic meters being the most common ones. Almost all test facilities use ambient, natural water. However the degree to which this water is altered to

meet certain criteria varies between the facilities. Test facilities that are located in biologically high productive and turbid areas need less manipulation. Others, who either do not have suitable water conditions or want to test independent of surrounding conditions use the water and add surrogate organisms and suspended matter. Between these approaches there is various degrees of manipulation and preparation of the test water. It is beyond the scope of this paper to discuss all of these options. However, it should be kept in mind, that water chemistry and preparation might have an influence on risk-assessment studies, e.g. the formation of by-products. Working with natural water makes the tests less predictable, while working with heavily modified waters increases the possibility of artefacts. Both approaches have pros and cons as well from a biological as from a chemical point of view and it is important to keep this in mind when analysing data from certification tests of BWTS.

Samples are generally taken on intake and on discharge. Samples are taken in-line from the pipes to avoid spatial and / or time bias. Analysis of the samples focuses on the biological parameters. Furthermore basic parameters characterizing the water body are measured. These are salinity, temperature, TSS, POC, DOC, pH and oxygen. Additional samples for, e.g. nutrients or chemicals can easily be taken. The taking of additional samples is facilitated by two factors. First the tests are conducted at full scale. Guideline G8 (IMO, 2008a) calls for a minimum volume of 200 cubic meters of treated water to be stored. Therefore the volumes involved do allow sufficient sampling, when considering the usual sample sizes of a few litres for most chemical analysis. Secondly, in order to take good and representative samples on intake and discharge, land-based test facilities are equipped with numerous sampling points at different locations.

Despite the comparable volume, the holding tanks used for land-based testing differ significantly from a ship's ballast water tanks. Tanks used for land-based testing usually have less internal structures than a ballast water tank. This is less trivial than it might appear at first glance. Structures do influence the movement of the water within the tank, while filling and discharging. Furthermore they can act as sediment traps. However, the role of sediment cannot be assessed during land-based certification, since the protocols unfortunately call for cleaning of the tanks between each test. In any case remains a tank of several hundred cubic meters a better representation of the real situation on board a vessel than any laboratory scale container. It is more complicated to keep stable conditions, e.g. temperature, in a laboratory scale set-up from a few hundred litres to maybe a few cubic meters as compared to a tank of at least 200 cubic meters. Furthermore the latter show spatial differentiation that can be tested for by sampling from the tank.

Tests that are conducted with natural water cover a range of different conditions. This is equally true for facilities that manipulate their intake water considerably as for those that do not. The variation in (chemical) water conditions is only lost if the test water itself is made artificially.

6.4 Linking land-based testing with G9 risk assessment

Based on the above, land-based test facilities can be used in a number of ways for risk-assessment. Examples include, but are in no way limited to:

- validation of laboratory findings on the chemical behaviour of active substances or the collection of such data when no or insufficient laboratory data is available,
- the same studies for by-products of treatments,
- identification and comparison of potential risks of different BWTS in a certain range of conditions, i.e. the environment of the test facility when working with natural water,
- safety of the BWTS in full-scale operation for the crew, e.g. noise levels, maintenance etc.,

- properties and fate of the treated water once discharged,
- validation of sampling and monitoring techniques,
- validation of models.

The advantage of designing such studies with and at land-based test facilities is the logistics. Test facilities are either having laboratories themselves or are in very close proximity to them due to the fact that the biological samples have to be analysed alive in most cases. Therefore it is possible to design studies that are logistical nearly impossible on board of a commercial vessel, while using an operational BWTS at full scale. Unfortunately not many formal connections are made between the physical testing of BWTS and the risk-assessment, so that such studies are not part of the validation and certification process of a BWTS.

Another aspect to be considered is, that the test facilities in turn can also profit from a closer cooperation with the various institutions involved in risk-assessment. An obvious example is, that there are no procedures on identifying health risks a BWTS might pose to testing personnel and subsequently a ship's crew at an early stage of the certification process. Less obvious maybe, but probably even more important is, that there is no cooperation on pilot studies. Test facilities and developers will of course gather and assess the relevant information on used active substances and environmental feasibility thereof. However an in-depth analysis of by-products and potential risks of these is usually beyond the means of both test facility and vendor. A more formalized cooperation between the two parties at an earlier stage of the process is desirable here.

6.5 References

- IMO 2008a. Guidelines for approval of ballast water management systems (G8). Annex3 Resolution MEPC.174(58) Annex: Parts 1,2,3 and 4
- IMO 2008b. Procedure for approval of ballast water management systems that make use of active substances (G9). Res MEPC.169(57)

References are available on the IMO website

[http://www.imo.org/KnowledgeCentre/HowAndWhereToFindIMOInformation/IndexofIMOResolutions/Pages/Marine-Environment-Protection-Committee-\(MEPC\).aspx](http://www.imo.org/KnowledgeCentre/HowAndWhereToFindIMOInformation/IndexofIMOResolutions/Pages/Marine-Environment-Protection-Committee-(MEPC).aspx)

7 Disinfection By-Product Formation During Ballast Water Treatment

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7.1 Abstract

For the reduction of aquatic species invasion, ballast water management systems (BWMS) will be installed on board ships in the near future. Many known systems make use of oxidising chemicals that are known to generate disinfection by-products (DBPs). Quantity and specification of these substances, several of which possess long-term hazardous properties, vary with the quality of treated water and have been only rarely investigated in marine surroundings. This paper presents an analysis of publicly available data on DBP formation during BWMS testing. The most commonly employed agent is chlorine, which generates trihalomethanes, halogenated acetic acids, and bromate in substantially larger quantities than reported from other water treatment areas. Levels differ considerably among systems, but are always highest in brackish water. An increase is also observed with increasing oxidant dose. For other parameters, such as natural organic matter or contact time, no clear correlation can be derived. Brominated species predominate, in particular bromoform and dibromoacetic acid. Ozonation, which is less frequently utilized, produces similar by-products, but in lower concentrations. Active carbon treatment of disinfected water prior to discharge effectively reduces DBP levels, while treatment with reducing agents, commonly applied to destroy excess oxidant, has no effect on organohalogens. The assessment of DBP formation during ballast water treatment is constrained by the lacking completeness and quality of available information. This concerns the extent, sensitivity and statistics of chemical analysis as well as the characterization of the test water, in particular with regard to natural organic matter, which is known to be a key parameter for disinfection by-product formation.

7.2 Introduction

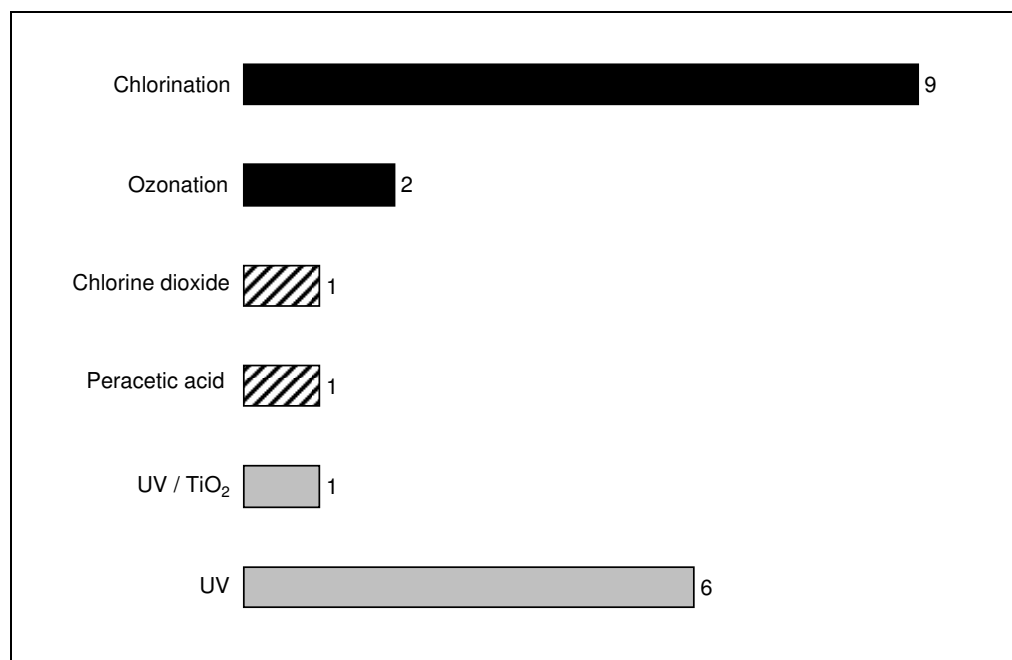
Many, if not most, ballast water management systems (BWMS) that have received approval by the International Maritime Organization (IMO) under the "Procedure for Approval of BWMS that make use of Active Substances (G9)" (IMO, 2008) rely on strong chemical oxidants, which react with components of the treated water under formation of disinfection by-products (DBPs). Based on the publicly available, non-confidential application dossiers of the BWMS in question, the BfR performed a desk study on the available data with respect to DBP formation, examining which substances are predominantly formed, in which quantities they are formed, and which parameters can be identified that influence their formation (Werschkun et al., 2012). Figure 9 shows an overview of approved systems at the time of writing. Only those based on chlorination and ozonation will be discussed in detail in the following.

7.3 Scope of reported data

Currently available information originates from testing of BWMS in laboratory or pilot scale experiments, land-based test facilities and prototypes installed on board ships. Such tests are primarily performed to demonstrate the efficacy of disinfection, but IMO procedure (G9)

also states the requirement to identify any “transformation or reaction products that are produced during or after employment of the ballast water management system”. With regard to DBPs, there is at present no mandatory list of substances to be included in the chemical analysis of treated water. Most applications take account of inorganic bromate, trihalomethanes, and halogenated acetic acids. Less frequently considered are halogenated acetonitriles, phenols, and hydrocarbons other than trihalomethanes. Quite remarkably, sum parameters of organically bound halogen, such as AOX or EOX, have only occasionally been measured.

Figure 9: Number of approved BWMS by treatment method



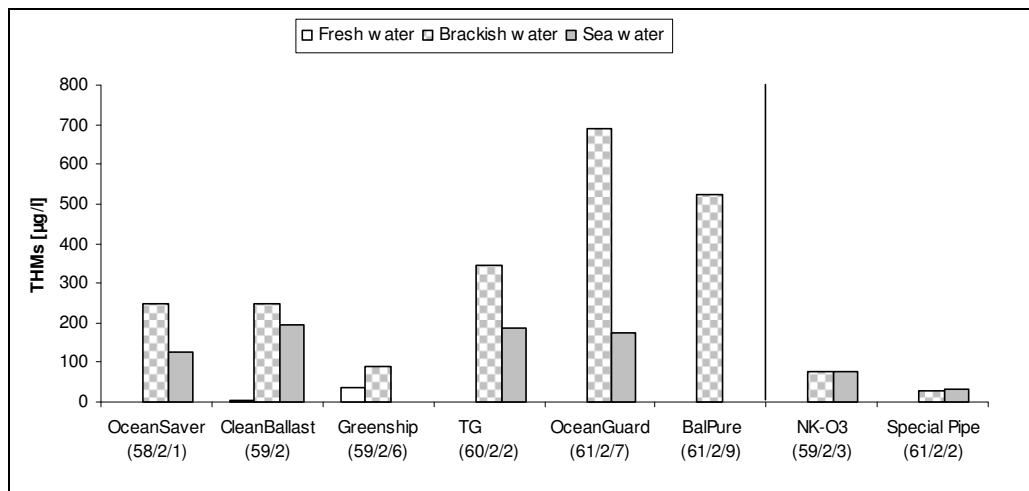
In addition to chemical analysis data, information on the characteristics of the test water and the applied disinfection process are also of relevance for an appraisal of DBP formation potential. The extent to which such specifications are reported is quite heterogeneous among the different dossiers. In most cases, but still not in all, salinity and organic matter content of the test water are specified, as is the holding time between initial disinfection and discharge or intermittent sampling. Other information is frequently missing, in particular the initially applied oxidant dose, which is a crucial parameter for DBP formation. Taken together, of the eleven systems considered, only eight had sufficient publicly available documentation to be included in further analyses.

7.4 DBP levels

Looking at DBP formation in test water of different salinities, and starting with trihalomethanes, figure 10 shows the maximum levels reported for six ballast water treatment systems based on chlorine and two systems based on ozone. At first sight, it is apparent that THM concentrations formed during ozonation of ballast water are lower than those formed during chlorination. Among themselves, the chlorination results differ considerably. The largest variation is seen for THM levels in brackish water (around 20 psu), ranging from 90 to almost 700 µg/l. At the same time, within a test series for the same chlorination system, brackish water always gave the highest levels. In full salinity seawater (around 32 psu), levels are lower and also more uniform among the different systems. This corresponds to model

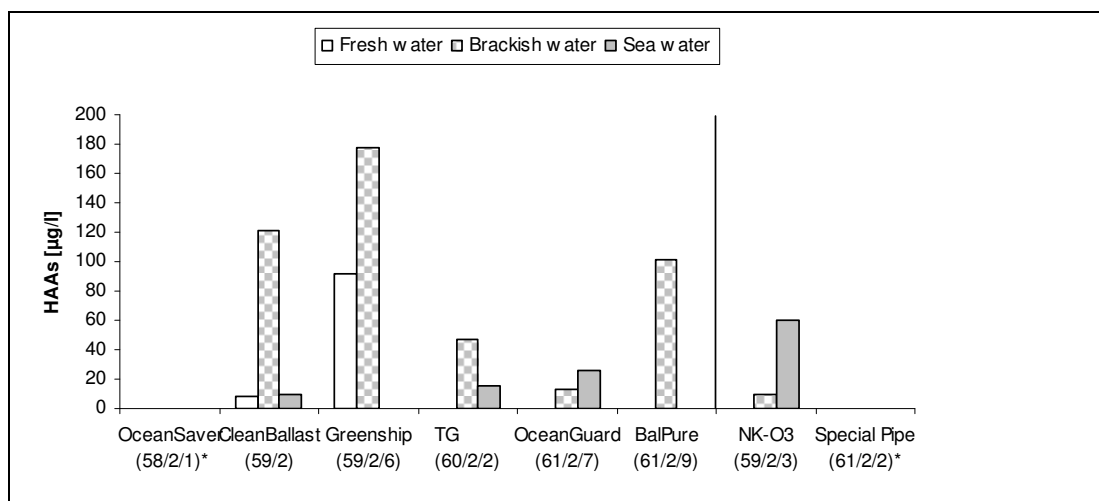
studies reported in the literature for chlorination of seawater from deep ocean areas as compared to coastal areas (Allonier et al., 1999; Fabbricino and Korshin, 2005). The observed higher DBP formation in coastal water has been alleged to the content of organic matter, which will be further explored below. In fresh water (salinity below 3 psu) performance of ballast water treatment systems has only occasionally been investigated. The observed levels vary from 6 to 40 $\mu\text{g/l}$, and, among other things, probably depend on the type of electrodes used.

Figure 10: Trihalomethane levels at different salinities (from Werschkun et al, 2012)



For the halogenated acetic acids, the available data base is smaller (figure 11). Not all studies included this substance class in the chemical analysis, and even those which did, did not in all cases include all nine chlorinated and brominated derivatives. In comparison to THM, HAA are generally formed in lower concentrations, up to 180 $\mu\text{g/l}$. With regard to the variation of values among and within the test series for different systems, a similar picture is obtained for HAA as the one shown for THM, before. The results shown for ozonation are probably not treatment related, since similar substance levels were detected in control and treated samples.

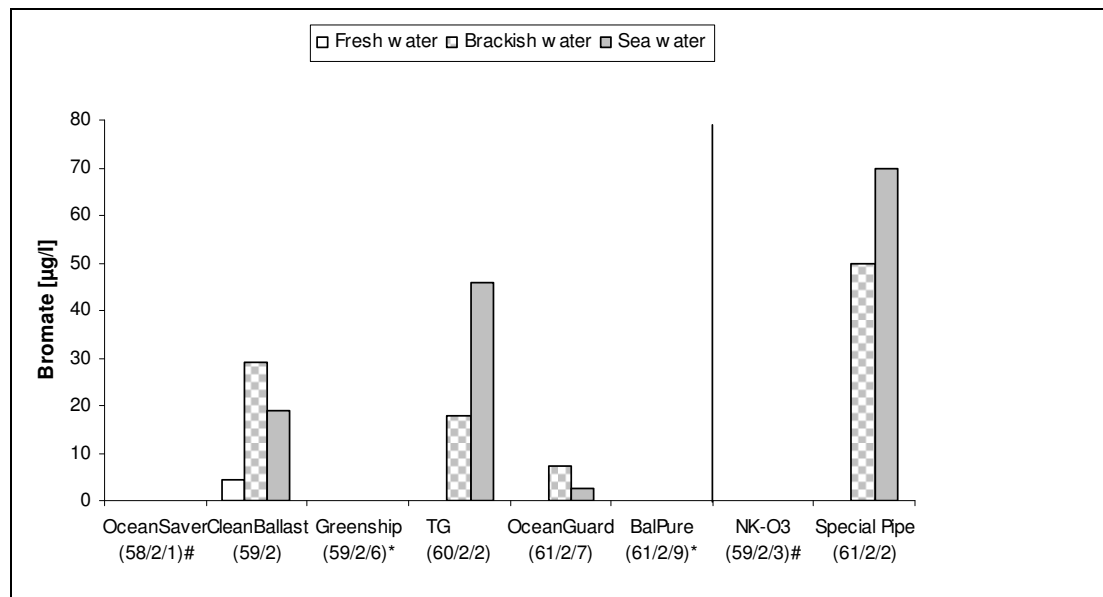
Figure 11: Haloacetic acid levels at different salinities (from Werschkun et al., 2012)



A further common by-product that is frequently included in the range of chemical analysis during ballast water treatment testing is the bromate ion (figure 12). While in some of the studies bromate was found in about the same order of magnitude with levels around 20 to 70

$\mu\text{g/l}$, in two other studies, one with a chlorine-based system and one with an ozone-based system, bromate was not detected under any of the tested conditions. In both cases, analysis was based on ion chromatography, a method of high sensitivity with a detection limit around 3 or 4 $\mu\text{g/l}$. A similar observation is reported in the literature, where it is discussed that bromate may initially be generated and then immediately consumed by components present in the water (Herwig et al., 2006). This still leaves the question open why such a phenomenon is not found in the studies performed with other systems.

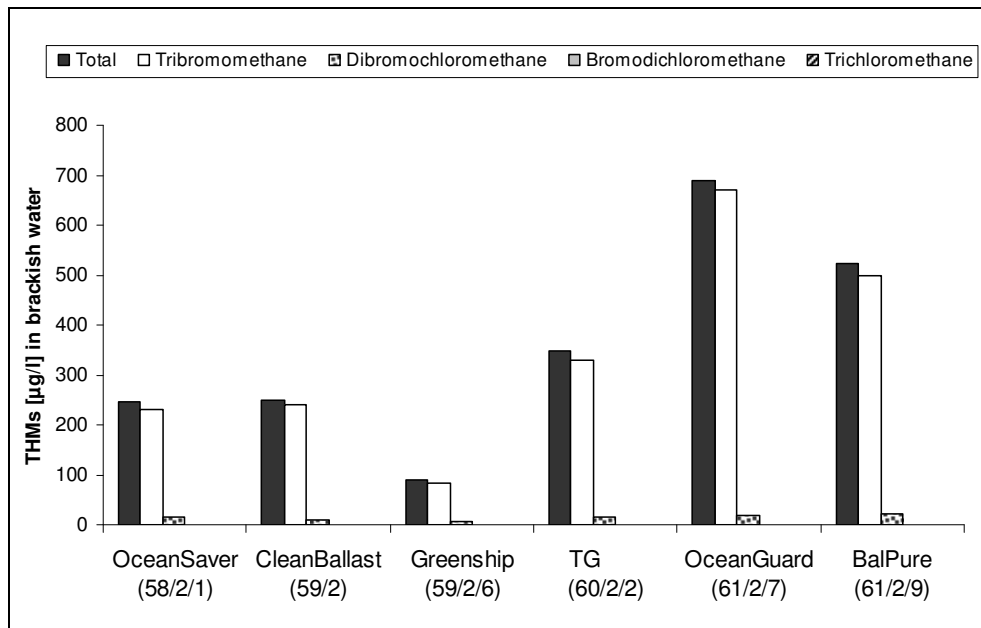
Figure 12: Bromate levels at different salinities (from Werschkun et al., 2012)



7.5 DBP composition

In terms of individual chemical species formed, figure 13 shows the composition of THM content from brackish water studies. These results confirm the expectation, based on chemical reactivity considerations (Ichihashi et al., 1999; Westerhoff et al., 2004), that in marine water brominated species are formed predominantly, if not almost exclusively. The total THM concentration almost entirely consists of bromoform. In addition, small amounts of mixed bromo-chloro derivatives are formed, but no chloroform.

Figure 13: THM species in brackish water (from Werschkun et al., 2012)

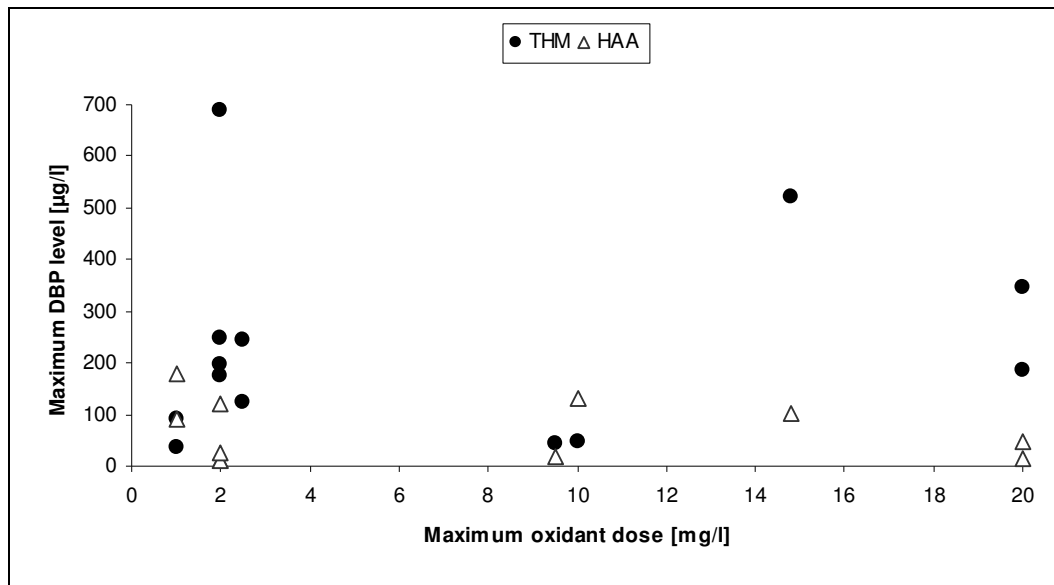


The results in full salinity seawater are quite similar, while in fresh water all possible bromo- and chlorospecies were found with no clear predominance (data not shown). For HAA the picture is a little different, in as far as not the highest brominated derivative predominates, which would be tribromoacetic acid, but rather dibromoacetic acid. Also found, to varying extent, are bromoacetic acid, tribromoacetic acid, mixed bromochloro- and even chloroderivatives. However, analysis of HAA data is complicated by the fact that only rarely the analyses included all nine possible brominated or chlorinated derivatives. Again, the distribution is similar in brackish water and full salinity sea water, while in fresh water comparatively more chlorocompounds were formed (data not shown).

7.6 Influencing factors

Next to a mere inventory of DBPs formed during ballast water treatment, the identification of parameters that influence the extent of their formation is of most interest. Commonly known factors influencing DBP formation are, for instance, oxidant dose, reaction time, and organic matter content of the test water (Liang and Singer, 2003).

Figure 14: Impact of oxidant dose on DBP formation (from Werschkun et al., 2012)



It is well established that DBP formation generally increases with increasing oxidant dose (Chowdhury et al., 2009). With regard to ballast water test results, the analysis suffers from the fact that the available documentation in most cases does not state which dose was actually applied during testing. Therefore, in figure 14 the maximum allowable oxidant dose of the system is plotted against the respective DBP levels reported. While a slight trend of a dose-related increase may be recognized for the THM data, this is not particularly pronounced, and for HAA levels, the data remain inconclusive. As can be expected, this analysis suffers from the fact that the included data are derived from the application of different systems to water of different origin and specification, and confounding factors thus abound.

Another generally established relationship in oxidative water treatment is the increase of disinfection by-products with increasing contact time of the treated water and the oxidant (Gallard and von Gunten, 2002). Figure 15 shows two exemplary data sets from testing of a chlorine-based ballast water system, measured over a total period of ten days, and an ozone-based system, measured over five days. Both were applied to two different test waters, the chlorination system covering both THM and HAA, the ozonation system only bromoform. In each case it can be seen, that the maximum concentration of DBPs is not reached immediately, but a rather fast increase in the initial phase of disinfection is followed by a phase that can be interpreted either as a very much reduced increase, or a plateau, or perhaps also a slow decline of DBP concentrations. In any case, it becomes clear that one single measurement immediately after initial disinfection cannot give a complete picture of DBP formation.

Figure 15: Impact of holding time on DBP formation

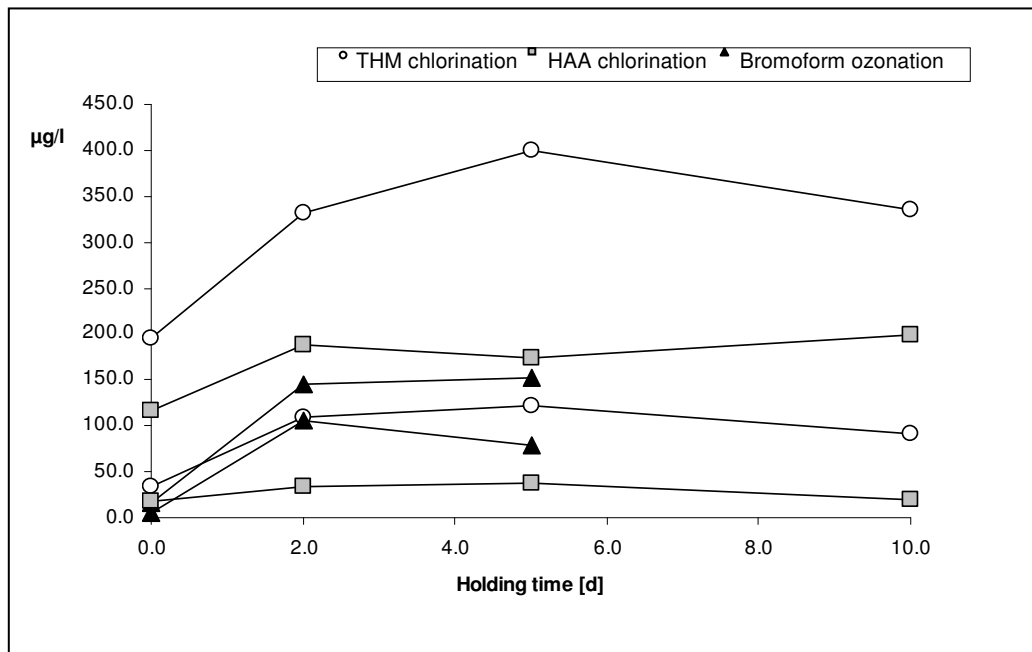
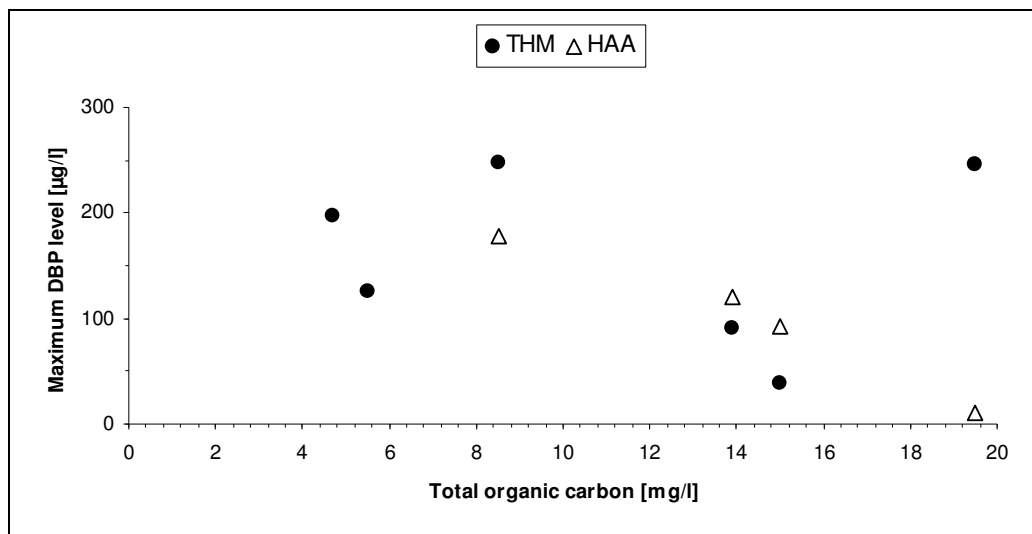


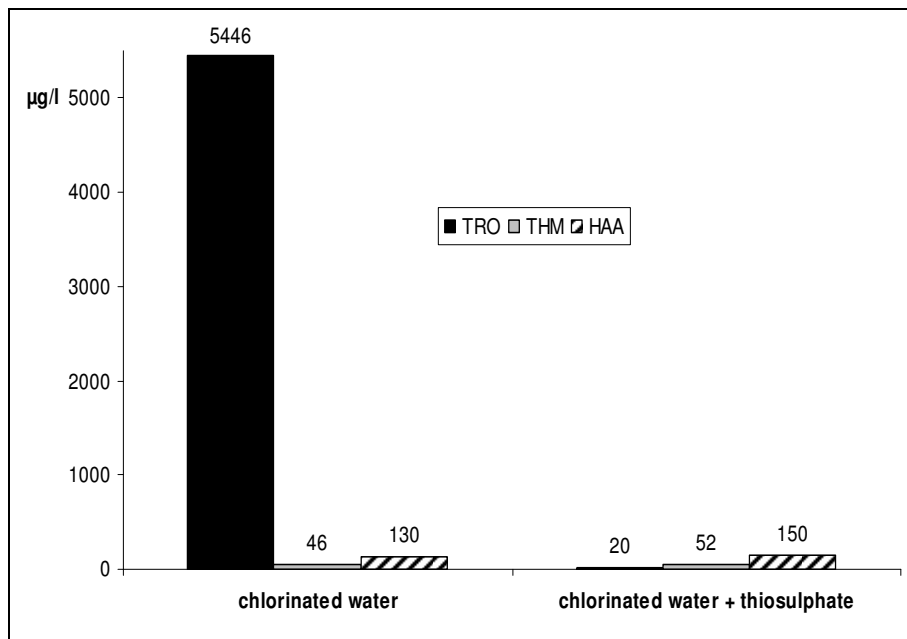
Figure 16: Impact of organic carbon content on DBP formation (from Werschkun et al., 2012)



According to observations from the literature, the commonly observed higher DBP levels in brackish water as compared to other test waters, might be attributed to the content of organic matter. Quantitative measurements of dissolved and suspended matter are often reported in the testing documentation, and in figure 16 DBP concentrations are plotted against total organic carbon content, with no correlation becoming apparent. Beside the mere quantity of organic matter present, its chemical structure also plays an important role for its susceptibility towards chlorination or bromination reactions. Electron-dense, unsaturated structures are known to give particularly high DBP yields. Regulations for BWMS testing set out minimum requirements with regard to the quantitative organic matter content of the test water. However, in order to meet these requirements, the test water is often enriched with artificial additives, which can be of a very different nature, e.g. natural algae extracts in one case and starch in another case. Such additives may therefore not give a representative picture of the extent of DBP formation in natural coastal or harbour water.

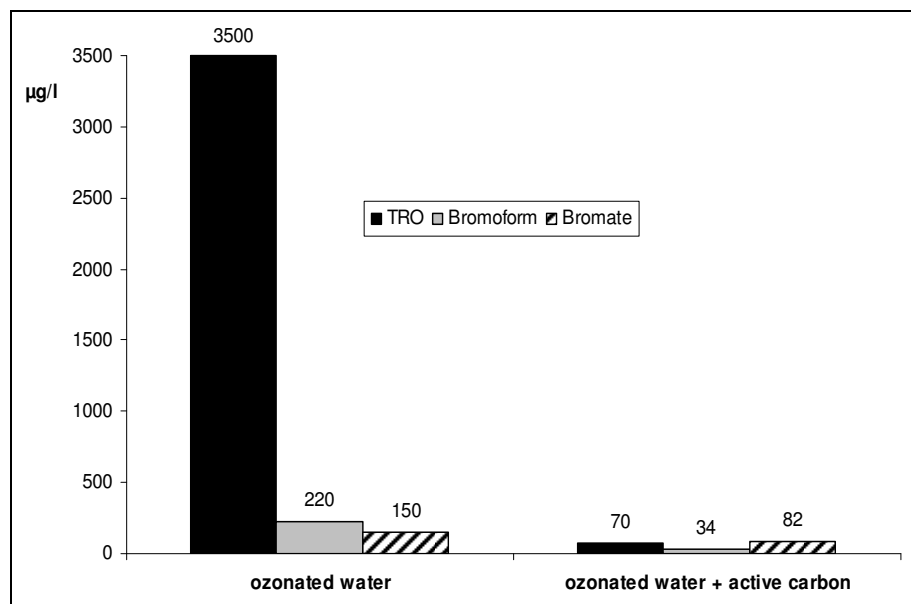
In ballast water treatment, chemical oxidants are mostly applied in excess quantities in order to prevent re-growth of organisms while the treated water is held in the ballast tanks during long voyages. Before this water is released into the environment, the excess oxidants must be destroyed. Most chlorination systems therefore incorporate a 'neutralization unit', which adds a solution of a reducing agent just prior to ballast water discharge. Figure 17 shows an example based on sodium thiosulphate. After initial chlorination, oxidative agents are present in a large excess of >5 mg/l. THM and HAA are formed as by-products. After addition of the thiosulphate, the oxidants are almost completely destroyed. However, the concentrations of DBPs remain practically unchanged, and in this form the treated water is then discharged.

Figure 17: Post-disinfection treatment with reducing agents



A far less frequently applied post-treatment method is the use of activated carbon. So far, this method has only been described for one BWMS based on ozone. Again, the treated water contains an excess of oxidant (figure 18). Bromoform and bromate are DBPs. After post-treatment in the active carbon unit of the system, chemical oxidants are destroyed, and also the concentrations of organic and inorganic by-products are considerably reduced before the water is discharged.

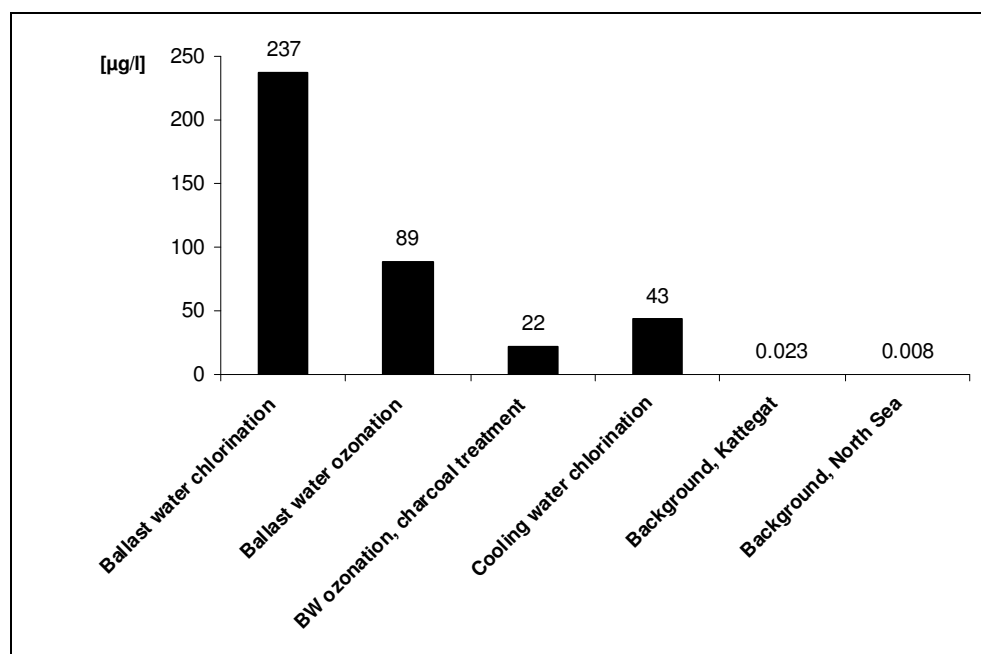
Figure 18: Post-disinfection treatment with active carbon



7.7 Putting DBP levels into perspective

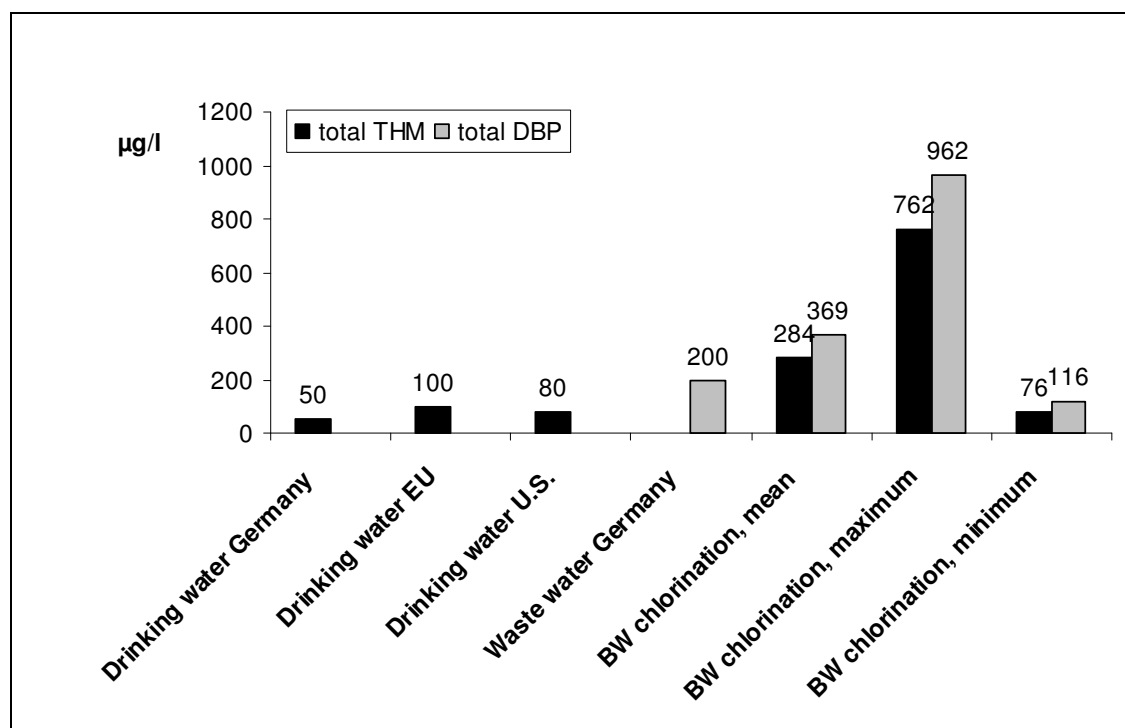
How do the substance levels in treated ballast water compare to levels produced in the marine environment from other sources? Using the example of bromoform, figure 19 summarizes the mean levels reported from testing of ballast water treatment systems, which range from >20 µg/l for ozonation with subsequent active carbon treatment to >200 µg/l for chlorination. Compared to this, a maximum level of 43 µg/l is reported for the chlorination of cooling water in coastal power stations (Taylor, 2006). With regard to background levels, the highest figure among different regions world wide is reported for the Kattegat region, which is 23 ng/l (Fogelqvist and Krysell, 1991). What this means with regard to the environment in regions where treated water is frequently discharged may worthy of further consideration.

Figure 19: Bromoform levels in marine waters



Secondly, how do DBP levels produced in ballast water treatment systems relate to regulatory limits for DBP concentrations in other areas of water treatment? Relevant values are summarised in figure 20. In drinking water, different limit values for total THM concentrations are established in Germany, the EU and the U.S., from 50 to 100 micrograms/litre. For the waste water of water treatment facilities, the German waste water regulation stipulates a maximum value of 200 µg/l for all absorbable organically bound halogen (AOX). It should be noted that the limit values mentioned do not relate to tolerable intake values derived from a toxicological risk assessment. In view of the carcinogenic properties of some DBPs, it is currently assumed that a toxicologically safe level cannot be defined. Instead, regulatory values reflect what can technically be achieved.

Figure 20: DBP limit values



The levels found in ballast water discharge after chlorination in the mean exceed these regulations. Maximum levels reported for some systems are distinctly higher. On the other hand, looking at the other end of the spectrum, this need not necessarily be the case. Even after chlorination of ballast water DBP levels may remain in a range that lies within the limits currently accepted for other areas of application. It may thus be worthwhile to investigate more closely why so much more DBPs were found in the testing of some BWMS compared to others. Ideally, something like best available technology standards for ballast water treatment might some day be defined.

7.8 Acknowledgements

I would like to thank my colleagues Sangeeta Banerji and Yasmin Sommer for their contributions to this evaluation. As part of the BfR work package in the North Sea Ballast Water Opportunity project it was supported by the EU Regional Development Fund.

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8 Human Exposure Scenario

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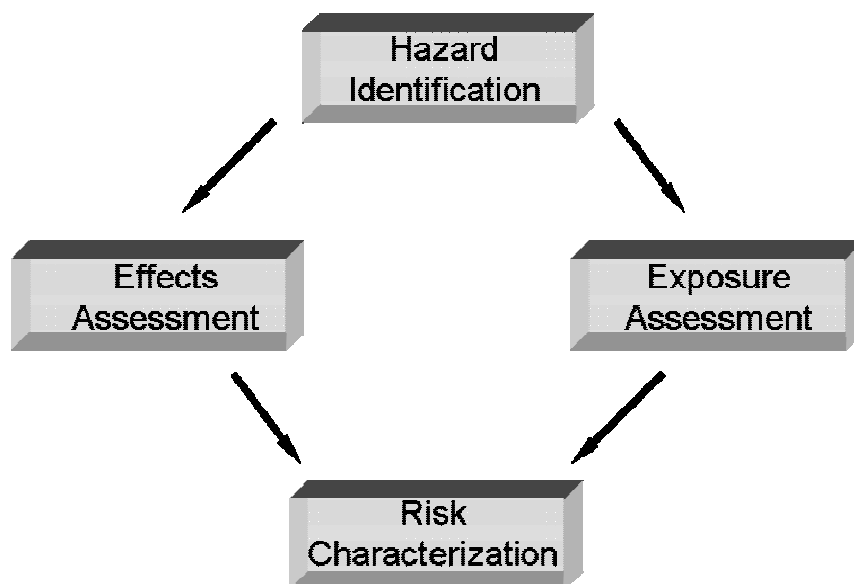
8.1 Abstract

Ships' ballast water is a major vector for the spread of invasive aquatic species, which have led to substantial ecological and economical damage in the past. In an effort to resolve this problem the International Maritime Organization (IMO) passed a convention for the management of ships' ballast water in 2004. This convention will eventually require ships' ballast water to be treated in order to eliminate harmful aquatic species and pathogens. Any ballast water management system using chemicals ('active substances') to eliminate organisms needs IMO approval. The approval is granted based on detailed application dossiers. Human health risk assessment is an important part of the approval procedure and requires identification of active substances and relevant chemicals as well as development of relevant exposure scenarios. This paper discusses human exposure scenarios in the setting of the overall health risk assessment procedure. It provides a comprehensive listing of occupational and non-occupational exposure situations. Important occupational exposure situations include dermal and inhalation exposure during ballasting, de-ballasting and maintenance. Relevant non-occupational exposure may occur via sea-food consumption as well as during bathing. Quantification of exposure is discussed as well.

8.2 Background

Any ballast water management system (BWMS) using active substances needs approval by the International Maritime Organization (IMO). The recommendation for approval is given by the 'Group of Experts on Scientific Aspects of Marine Environmental Protection' (GESAMP) based on detailed application dossiers. Human health risk assessment is an important part of the 'Procedure for Approval of Ballast Water Management Systems That Make Use of Active Substances (G9)' (IMO, 2008a). Appendix 2 of the 'GESAMP Methodology' identifies four stages of quantitative risk assessment, which are depicted in figure 21 (IMO, 2008b).

Figure 21: Risk assessment process (from Banerji et al., 2012)



The GESAMP Methodology provides basic information on how to perform these four steps. From 2006 to 2010 twenty-four different BWMS have received basic and/or final approval. From the twenty-four approved systems eighteen provided health risk assessment. Judged by the non-confidential dossiers, many of these assessments presented incomplete quantifications or were only qualitative in nature. Likely reasons were *inter alia* the limited toxicological information on many relevant chemicals (disinfection by-products) required for effects assessment as well as insufficient information on the work place conditions of the ship's crew required for assessing occupational exposure. This shows that the applicants for IMO approval may benefit from more detailed risk assessment guidance. GESAMP is currently working to update its Methodology in this respect (see also the paper by Linders in this volume). In the context of the European Union North Sea Ballast Water Opportunity Project (<http://www.NorthSeaBallast.eu>), which aims at regional harmonization and optimization of ballast water management, the BfR is investigating perspectives of human health risk assessment (Banerji et al., 2012).

8.3 Health hazard identification

IMO procedure G9 requires the identification of active substances and relevant chemicals. Applicants need to provide a specified dataset on their physical, chemical and toxicological properties (IMO, 2008a). Identification of the active substances is simple since these are by definition the substances responsible for disinfection. The more difficult point is to identify all relevant chemicals, predominantly disinfection by-products (DBPs), formed unintentionally.

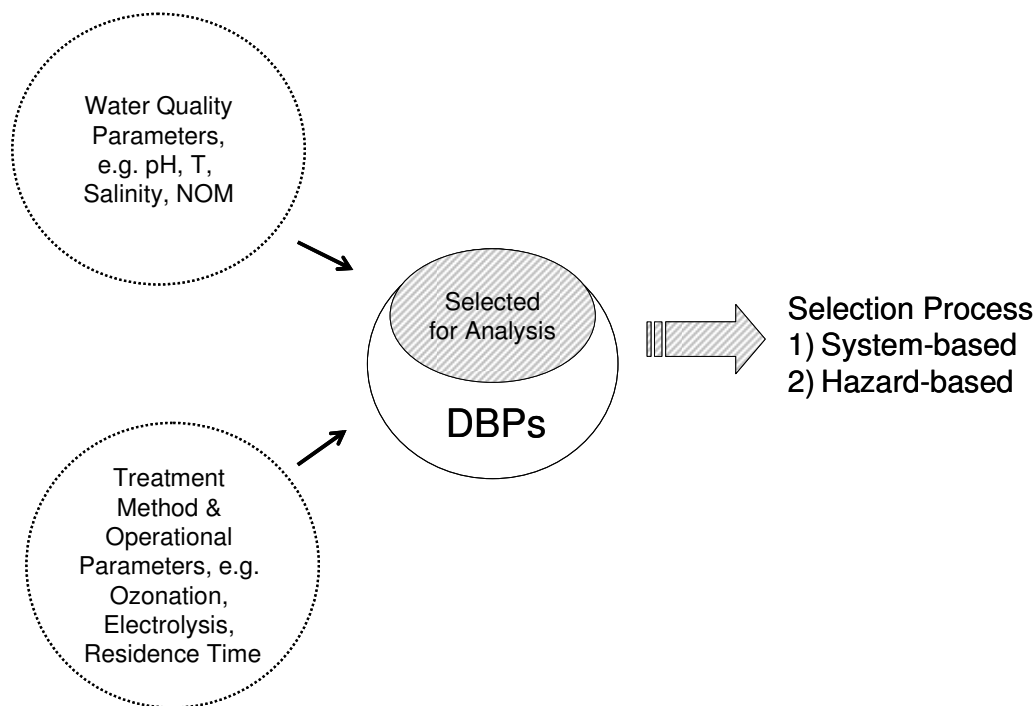
The majority of application dossiers only look at about 20 DBPs, most of them known from drinking water regulations, in particular trihalomethanes, haloacetic acids and bromate. In total, only about 40-60 different DBPs have been selected for analysis so far (Zipperle et al., 2011; Werschkun et al., 2012). In contrast, there are about 600–700 DBPs known from the drinking water setting (Richardson et al., 2007). Pool water disinfection revealed another 100 unique DBPs (Richardson et al., 2010). This shows that more comprehensive hazard identification is necessary for ballast water risk assessment. Information on the treatment of seawater is limited. Source water parameters like salinity, pH, temperature and structure of natural organic matter greatly influence by-product formation and need to be taken into consideration when analysing by-products of ballast water treatment (Werschkun et al., 2012, and references therein). We propose two complementary approaches for improved identification of by-products, a system-based approach and a hazard-based approach.

The system-based approach focuses on the disinfection methods used in ballast water treatment and identifies method-specific by-products. Currently known method-specific DBPs are, among others, (a) formaldehyde, bromate and bromoform for ozonation, (b) chlorate and dibromoacetic acid for chlorine dioxide treatment, and (c) trihalomethanes and haloacetic acids for electrolysis. Depending on the environmental parameters other DBPs are also formed. A critical aspect is that only a fraction of DBPs is actually known. A U.S. study, for example, found that in a chlorinated drinking water sample over 60% of the organic halide content was unknown (Richardson et al., 2002).

The hazard-based approach focuses on the toxicity of DBPs, especially long-term toxic effects like genotoxicity or carcinogenicity. Richardson et al. (2007) provide a comprehensive overview of currently known DBPs from drinking water disinfection of different source waters and their toxicity. Based on their review, the following DBPs may be of toxicological relevance, which are currently not selected for chemical analysis in the BWMS context: iodoacetic acid, iodoform, halo amides, aldehydes and halonitromethanes. These compounds have been found in sub to low microgram per liter levels in disinfected drinking water and are suspected to be genotoxic. Figure 22 illustrates the parameters influencing by-product formation and the two step-process for selecting by-products to be included for chemical analysis. Only

a combination of different selection processes can provide a thorough identification of by-products formed during the operation of BWMS.

Figure 22: Parameters influencing DBP formation and selection process (from Banerji et al., 2012)



8.4 Health effects assessment

Health effects assessment is basically evaluating the toxicity of chemicals based on animal experiments or validated non-animal testing methods. Regarding mammalian toxicity, the GESAMP Methodology recommends the assessment of acute toxicity, effects on skin and eye, repeated-dose toxicity (90 d), chronic toxicity (≥ 12 months), developmental and reproductive toxicity, carcinogenicity and mutagenicity/genotoxicity (IMO, 2008b). There should be a two-step effects assessment. The first step consists of identifying appropriate available studies, which address the above mentioned toxic endpoints. In the second step these studies are used to derive quantitative toxicological information, e.g. the dose at which no adverse effects occur, also known as NOAEL (no observed adverse effect level). These two steps have to be carried out individually for all active substances and relevant chemicals.

A different GESAMP group, responsible for evaluating the hazards of substances carried by ships (GESAMP-EHS) has compiled toxicological profiles of 18 DBPs and other relevant chemicals (IMO, 2010), which are generated or used by many BWMS. Out of the 18 substances more than 50% lack chronic toxicological data and have not been tested for carcinogenicity. For these compounds new toxicological studies need to be carried out. Whole effluent toxicity tests for genotoxic or carcinogenetic effects, e.g. Ames test, Comet assay, may be a feasible alternative.

For improved risk characterization, we propose that the compounds should be classified into different hazard categories based on the quantitative information derived in step two. We have extended the hazard evaluation procedure for chemical substances used by GESAMP-EHS (IMO, 2002; Banerji et al., 2012). This evaluation procedure can be used to assign substance-specific numerical ratings for each endpoint.

8.5 Human exposure assessment

The U.S. National Research Council (1991) defined exposure as 'contact over time and space between a person and one or more biological, chemical or physical agents'. Exposure assessment is the process of determining the full range of exposure situations (scenarios) that could occur due to the operation of a BWMS. It includes identification of the exposed population, exposure pathways, exposure routes and quantification of exposure. The scenarios are determined separately for occupational and non-occupational exposure because they differ in duration, frequency, type of population and possibility of exposure control.

8.5.1 Human exposure scenarios

Occupational exposure

The GESAMP Methodology recommends dividing the operational processes related to ballast water treatment into unit operations (IMO, 2008b). Work activities should be assigned to each of these unit operations. The exposure potential for each work activity should be determined in the last step. The purpose of this procedure is to ensure that no exposure situation is overlooked. However, the majority of the past dossiers did not follow such procedure. In most non-confidential dossiers, only two or three occupational exposure situations were identified and the full range of exposure scenarios was not assessed. Table 6 shows the unit operations and related work activities that can, in principle, be identified (Banerji et al., 2012). There are five unit operations: starting of the BWMS, ballasting, de-ballasting, cruising and maintenance. Additionally, malfunctions, accidents and emergency situations have to be considered, as they could create relevant exposures. Since the work activity related to starting the system differs from system to system we do not state specific activities within this unit operation. It is up to the manufacturer to identify these activities (regardless of their exposure potential). It should be noted that system-specific activities can occur during any unit operation and have to be stated in the dossier. Ballasting can lead to inhalation exposure when the air in the ballast tank, potentially containing toxic gases, is vented. De-ballasting may lead to dermal and inhalation exposure to spray drift. Ballast water treatment may lead to type-specific exposure as it depends on the treatment method and system. Sampling may lead to exposure to chemicals in the treated ballast water. During cruising the treated ballast water is stored. If gases from volatile substances escape the ballast tank inhalation exposure might occur. Maintenance involves sediment cleaning, tank inspection and type specific work activities, like chemical resupply. All these work activities can result in dermal contact and inhalation. Finally, malfunctions and accidents can occur during any of the previously identified work activities and can lead to exposure. The maritime emergency scenario is of relevance if the treated ballast water poses an additional risk during distress and salvage operations.

Non-occupational exposure

The non-occupational exposure relates to the risks for public health by the operation of BWMS. There are four worst case exposure scenarios:

- 1) Oral, dermal and inhalation exposure during bathing in the sea near de-ballasting ships
- 2) Oral exposure via contaminated seafood
- 3) Dermal and inhalation exposure of passengers during malfunctions, accidents or emergencies on ships
- 4) Dermal and inhalation exposure of harbour visitors due to spray drift from de-ballasting ships

Table 6: Unit operations and associated work activities for BWMS (from Banerji et al., 2012)

Unit Operation	Work Activity	Exposure Scenario	Exposure Route
Starting of BWMS	type specific activities to be documented, e.g. calibration	type-specific	dermal, inhalation
Ballasting	ballasting	potential exposure to volatile substances from exhaust air	inhalation
	treating of ballast water	type-specific	dermal, inhalation
	sampling	exposure to chemicals in treated ballast water	dermal, inhalation
De-ballasting	de-ballasting	potential exposure from spray drift	dermal, inhalation
	treating of ballast water	type-specific	dermal, inhalation
	sampling	exposure to chemicals in treated ballast water	dermal, inhalation
Cruising	storage of treated ballast water	potential exposure to volatile substances from exhaust air	inhalation
	sampling	exposure to chemicals in treated ballast water	dermal, inhalation
Maintenance	tank cleaning (sediment cleaning)	exposure to residual water, sediment and vapour of volatile substances in ballast tank	dermal, inhalation
	tank inspection	exposure to vapour of volatile substances in ballast tank	inhalation
	type specific: UV: change/cleaning of UV tubes ozone: filter change, electrode calibration chemicals: resupply, cleaning of storage tanks electrolysis: washing of filter cartridges, electrode calibration	type-specific	dermal, inhalation
Malfunctions	any of the listed work activities or independent thereof	leakage, ventilation breakdown	dermal, inhalation
Accidents	any of the listed work activities	e.g. splashing of chemicals during resupply	dermal, inhalation
Emergencies	distress and salvage operations	e.g. explosion, fire	dermal, inhalation

8.5.2 Exposure quantification

Quantification of exposure takes into account the properties of the chemical substance and the exposure scenario, which includes the exposure situation, the exposed population and the possible exposure routes. The European Chemicals Agency (ECHA) and the U.S. Environmental Protection Agency (US EPA), among others, provide guidance documents for exposure quantification (ECHA, 2008a; US EPA, 1992). Based on these guidance documents, five main equations can be used to quantify the exposure to a substance by the three possible exposure routes, i.e. inhalation, skin contact and ingestion. Exposure or uptake is normalized to body weight.

Quantification of inhalation exposure

Inhalation exposure is dependent on the contaminant concentration in the air (C_{air} = vapour concentration or particulate aerosol concentration), the event frequency, the event duration and the inhalation rate (ECHA, 2008a; US EPA, 1997).

$$\text{Exposure to vapours or aerosols (per day)} \quad (\text{Equation 1})$$

$$E_{\text{inhalation}} = C_{\text{air}} \times \text{frequency} \times \text{duration} \times \text{inhalation rate/body weight}$$

Quantification of dermal exposure

The ECHA and the US EPA use different dermal uptake models both of which can be used for determining dermal exposure from BWMS.

The ECHA approach assumes that 100 % of the substance is taken up by the skin independent of the exposure duration. Under these conditions, dermal uptake is dependent on the contaminant concentration in water C_{water} , the affected skin area, the thickness of the substance layer and the event frequency (ECHA, 2008a).

$$\text{A) ECHA Dermal Uptake Model (per day)} \quad (\text{Equation 2a})$$

$$E_{\text{dermal}} = C_{\text{water}} \times \text{skin area} \times \text{thickness of substance layer} \times \text{frequency/body weight}$$

The U.S. EPA approach takes into account that compounds have different dermal permeability described by the dermal permeation coefficient K_p . Assuming steady state, the dermal uptake is then dependent on the contaminant concentration in water C_{water} , the exposed skin area, the substance-specific dermal permeation coefficient K_p , the event frequency and duration (US EPA 1992; Xu et al. 2002). The dermal permeation coefficient K_p has to be determined experimentally.

$$\text{B) U.S. EPA Dermal Uptake Model (per day)} \quad (\text{Equation 2b})$$

$$E_{\text{dermal}} = C_{\text{water}} \times \text{skin area} \times K_p \times \text{frequency} \times \text{duration/body weight}$$

Quantification of oral exposure

Oral exposure is dependent on the contaminant concentration in source, the amount of ingested source, the event frequency and the bioavailability (set to 1 if unknown) (ECHA, 2008a).

$$\text{Oral exposure (per day)} \quad (\text{Equation 3})$$

$$E_{\text{oral}} = C_{\text{source}} \times \text{amount} \times \text{frequency} \times \text{bioavailability/body weight}$$

Total exposure for n situations per substance and population

The total exposure by all three routes is the sum of exposures for all routes and situations.

$$\text{Total daily exposure} \quad (\text{Equation 4})$$

$$E_{\text{tot}} = E_{\text{inh}} + E_{\text{derm}} + E_{\text{oral}}$$

Quantification of occupational exposure

Potential dermal and/or inhalation exposure could occur during any unit operation (see table 1). In order to quantify inhalation exposure to vapours (equation 1) the concentration of the substance in the air must be determined. Assuming equilibrium, the following equation can be used: $C_{\text{air}} = H^* C_{\text{water}}$

The Henry's Law constant H is an experimentally determined, temperature-dependent, compound-specific parameter, which describes its distribution between air and water. Inhalation rates and body weights can be obtained from statistical studies, e.g. compiled in the US EPA exposure factors handbook (US EPA, 1997). In order to quantify exposure to aerosols, e.g. from spray drift, the particulate DBP concentration needs to be determined experimentally. For quantification of dermal exposure two different equations can be applied: either equation 2a as a conservative approach if the permeation coefficient is unknown or equation 2b in cases where K_p values have been determined. Since oral exposure is very unlikely in an occupational exposure setting it is normally not quantitatively assessed. Thus, according to equation 4 the total occupational exposure if all tasks were performed by the same person would be (worst case):

$$E_{\text{tot}} = E_{\text{inh}}(\text{exhaust air}) + E_{\text{inh}}(\text{spray drift}) + E_{\text{derm}}(\text{spray drift}) + E_{\text{inh}}(\text{sampling}) + E_{\text{derm}}(\text{sampling}) + E_{\text{inh}}(\text{tank cleaning}) + E_{\text{derm}}(\text{tank cleaning}) + E_{\text{inh}}(\text{tank inspection}) + E_{\text{inh}}(\text{type specific}) + E_{\text{derm}}(\text{type specific})$$

Possible exposures from malfunctions, accidents and emergency situations should also be quantified based on statistical data, e.g. accident reports from marine insurance companies.

Quantification of non-occupational exposure

Potential oral exposure can occur from seafood consumption. In order to apply equation 3, the amount of consumed seafood needs to be determined. This information can be obtained from consumption studies, e.g. from the concise European food consumption database (<http://www.efsa.europa.eu/en/datex/datexfooddb.htm>). Seafood consumption greatly varies from county to country and among the population of a country. Therefore, as a worst case, data from seafood consumers should be used instead of the average consumption, whenever available, and the exposure of a child should be assessed as children tend to have proportionally higher risk. The contaminant concentration in seafood can be calculated from the bioconcentration factor as follows:

$$C = \text{bioconcentration factor (BCF)} * C_{\text{water}}$$

The bioconcentration factor is determined experimentally and represents the tendency of a chemical to accumulate in biological compartments. Bioaccumulation is dependent on lipophilicity and molecular weight. The lipophilicity is represented by the octanol/water partition coefficient $\log P_{\text{ow}}$, which often has a linear relationship with $\log \text{BCF}$. It is generally accepted that only substances with a $\log P_{\text{ow}}$ between 3 and 6 tend to bioaccumulate. Moreover, chemicals with a molecular weight above 500 kD do not display a tendency to bioaccumulate as they hardly penetrate biological membranes. All of the so far detected DBPs show a $\log P_{\text{ow}} < 3$ and are therefore unlikely to bioaccumulate. Nevertheless a study by Taylor (2006) in sea bass *Dicentrarchus labrax* found that bromoform easily accumulated in fat up to 1 mg/kg. One reason may be that many of the currently known DBPs are not readily biodegradable. Moreover, the majority of DBPs remains unidentified and their bioaccumulation characteristics are unknown.

A further non-occupational exposure scenario is sea bathing. Exposure can occur through swallowing of water, chronic dermal intake and exposure to vapours and aerosols. For most substances exposure to aerosols can be neglected if oral exposure occurs at the same time (Xu et al., 2003). The remaining two non-occupational exposures, i.e. passenger exposure during malfunction, accidents and emergencies on ships as well as spray drift on harbours resemble the occupational exposure of the crew in these situations and can be quantified

likewise. The total non-occupational exposure from seafood consumption, sea bathing and spray drift is:

$$E_{\text{tot}} = E_{\text{oral}} (\text{fish}) + E_{\text{oral}} (\text{bathing}) + E_{\text{dermal}} (\text{bathing}) + E_{\text{inh}} (\text{bathing}) + E_{\text{derm}} (\text{spray drift}) + E_{\text{inh}} (\text{spray drift})$$

8.6 Health risk characterization

The final step of the risk assessment process is risk characterization. This step combines data obtained from effects and exposure assessment to a statement of the level of risk. Risk characterization essentially means comparing the expected exposure level to the level of exposure deemed acceptable.

8.6.1 Regulatory values

For a lot of chemical substances regulatory values have been established. In the occupational exposure setting, occupational exposure levels (OEL) are defined, which should not be exceeded. They are based on an 8 hours/day and 5 days/week basis. This should be kept in mind when using OEL values for characterizing the occupational risk of the crew because a ship's work schedule tends to be very different from a normal work schedule. Regulatory values for the general population are mostly expressed as tolerable daily intake (TDI). For maritime accident assessment AEGL (acute exposure guideline level) values can be used (Rusch et al., 2002). Even though regulatory guideline values (OEL & TDI) can vary between countries they are convenient tools for risk characterization.

8.6.2 Determining risk without regulatory values

Most application dossiers focus on the regulated DBPs and the vast number of unregulated DBPs is often disregarded. This leads to a significant underestimation of risk.

When regulatory values are lacking, an established risk characterization scheme should be followed, e.g. the REACH approach (ECHA, 2008a), which is summarized in figure 23.

In the first step of the REACH approach, the most sensitive toxic effect is defined. Then the effect is classified as threshold or non-threshold. Threshold effects are those for which a safe level of exposure can be derived from the dose-response curve. Non-threshold effects are those where adverse effects are to be expected even at the lowest possible dose. If it is a threshold-effect an appropriate NOAEL or if not available, a LOAEL (lowest observed adverse effect level) is identified, which is used to calculate an endpoint -specific derived no-effect level (DNEL):

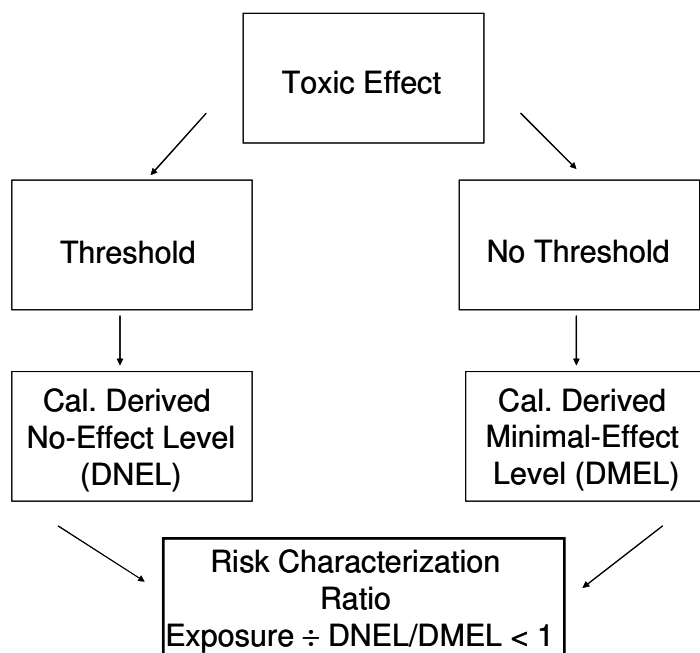
$$\text{DNEL} = \text{NOAEL} * (\text{AF}_1 * \text{AF}_2 * \text{AF}_n); \text{AF} = \text{assessment factor}$$

If it is a non-threshold-effect as is the case for many genotoxic carcinogens it is not possible to calculate a no-effect level since any non-zero dose may potentially lead to cancer. In this case, a semi-quantitative approach is chosen, which aims at defining a derived minimal effect level (DMEL). A minimal effect for a carcinogen can be a dose, which is expected to statistically cause cancer in one person per 10^5 . To determine a DMEL, a linear dose-response relationship is assumed. The T25 (dose creating tumours in 25% of the animals) is used as a starting point for linear extrapolation. After application of assessment factors, which results in

the human equivalent lifetime daily dose (HT25) the high to low dose extrapolation factor (HtLF) is applied, which for a cancer risk of 10^{-5} is set to 25000:

$$\text{DMEL} (10^{-5}) = \text{T25corr} * (\text{AF}_1 * \text{AF}_2 * \text{AF}_n) / \text{HtLF} = \text{HT25} / 25000$$

Figure 23: REACH approach for risk characterization



The assessment factors are used to adjust the study parameters to the exposure scenario at hand, e.g. extrapolation from animal to human, or for differences in exposure routes. The European Chemicals Agency gives an overview of the different assessment factors in Table R 8-19 of its guidance document (ECHA, 2008b). Depending on the exposure scenario, it may be necessary to calculate several endpoint-, route-, and population-specific DNELs and/or DMELs. In order to achieve a controlled risk the calculated exposure has to be lower than the DNEL or DMEL. In other words, the risk characterization ratio (RCR) has to be smaller than one:

$$\text{RCR} = \text{Exposure} / \text{DNEL} \text{ or } \text{Exposure} / \text{DMEL} < 1$$

8.7 Discussion and conclusions

We have introduced an approach for human health risk assessment with regard to BWMS, which comprises hazard identification, effects assessment, exposure assessment and risk characterization. Since experience with BWMS is limited each of these steps includes assumptions, which still need to be further investigated or validated. Health hazard identification for example relies on knowledge of the substances, generated by the various BWMS under different environmental conditions. Only about 10 % of all known DBPs are even considered for analysis during system testing. Moreover, it is to be expected that there are unique DBPs for ballast water disinfection. This shows that it is very likely that DBPs with adverse health effects are overlooked leading to incomplete risk assessment. Health effects assessment requires toxicological studies, which are at present only available for a small set of DBPs. Epidemiological studies have recently linked consumption of chlorinated drinking

water with bladder cancer (Cantor et al., 2010; Villanueva et al., 2007). Another study showed that swimming in a chlorinated pool for 40 min. produced DNA damage and mutagenic urine (Kogevinas et al., 2010). We therefore recommend to systematically explore whole effluent testing of treated ballast water with *in vitro* test systems for mammalian toxicity, e.g. mutagenicity, cytotoxicity. Human exposure assessment consists of assessing occupational exposure as well as exposure of the general public. With regard to crew exposure we have listed work activities for scenario building. Nonetheless, there may be the need for field studies to identify additional exposure sources, work patterns and the range of working hours. A study carried out on behalf of the U.S. Coast Guard observed that there could be peak work shifts during loading, discharging, and tank cleaning ranging from 13–30 h (Astleford et al., 1982). The study also noted that in spite of having closed recirculating ventilation systems deckhouses could be infiltrated by vapours through access doors during loading, tank cleaning and ballasting of cargo tanks. The final step of the health risk assessment process is risk characterization. This step combines the quantitative information derived from effects and exposure assessment. Since many DBPs have genotoxic and carcinogenic effects non-threshold effects may be of special concern and should be given special attention.

8.8 Acknowledgements

I would like to thank my colleagues Barbara Werschkun and Thomas Höfer for their contributions to this evaluation, which forms part of the BfR work package in the Ballast Water Opportunity project in the Interreg North Sea programme and was thus supported by the Regional Development Fund of the European Union.

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9 Determining the Environmental Risk – Proposal for an Emission Scenario Document (ESD) on Ballast Water Discharge Based on MAMPEC and the Consequences for the Risk Assessment

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9.1 Abstract

The treatment of ballast water with active substances for disinfection purposes may lead to the release of the active substances and disinfection-by-products (DBPs) into the environment. According to the “Procedure for approval of ballast water management systems (BWMS) that make use of active substances” (G9) it has to be shown by the applicant that for these systems no unacceptable adverse effects to environment, human health, property and resources are indicated. For the environment an environmental risk assessment (ERA) is done during the approval process by comparing the predicted environmental concentrations (PEC) and predicted no effect concentrations (PNEC). The PNEC is derived using ecotoxicological data and appropriate assessment factors, whereas the PEC is usually calculated with the software tool MAMPEC (Marine Antifoulant Model to Predict Environmental Concentrations). As this model was developed for the exposure calculation of leaching antifoulants it does not ideally fit the exposure due to ballast water treatment and discharge. The newest release, MAMPEC 3.0, however, is available in two different versions. One version was adapted to the specific requirements of ballast water risk assessment and takes into account results of a research project conducted on behalf of the German Federal Environment Agency (Umweltbundesamt, UBA). This project (“Guidance for a harmonized Emission Scenario Document (ESD) on Ballast Water discharge”, Zipperle et al., 2011) tried to harmonise the exposure assessment for the different BWMS to make the ERAs for different BWMS comparable. Therefore different parameters in MAMPEC were evaluated and discussed. These results were used for a new approach based on near-field analysis that was developed to assess the risks of rapidly reacting chemicals, taking into account the temporal and spatial heterogeneity of ballast water discharge as well as the fast decay of substances. To account for the fast decay of rapidly reacting chemicals on both sides of the environmental risk assessment (PEC and PNEC) it is proposed that the decay should not be considered at all during the risk assessment for oxidising substances. This means that the PNEC derivation should be based on the nominal or initial measured concentrations in the test system.

9.2 Definitions

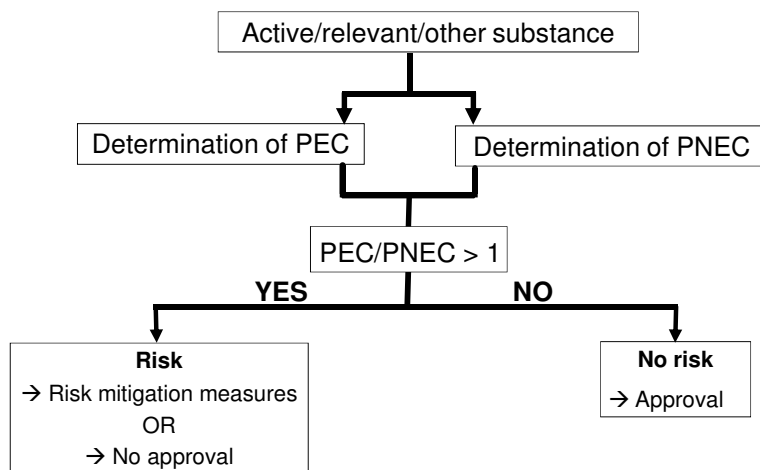
According to the “Methodology for information gathering and the conduct of work of GESAMP-BWWG” (MEPC, 2008) the following terms are defined as

- **Active Substances:** A substance or organism, including a virus or a fungus that has a general or specific action on or against harmful aquatic organisms and pathogens.
- **Other components** of a preparation: Any other substances in a preparation, other than the Active Substance(s) or Relevant Chemicals, produced during the treatment of ballast water.
- **Relevant Chemicals:** Transformation or reaction products that are produced during and after employment of the ballast water management system in the ballast water or in the receiving environment and that may be of concern to the ship’s safety, aquatic environment and/or human health.

9.3 Introduction to the environmental risk assessment

The treatment of ballast water with active substances for disinfection purposes may lead to the release of the active substances as well as disinfection-by-products (DBPs) into the environment. According to the “Procedure for approval of ballast water management systems (BWMS) that make use of active substances” (G9) it has to be shown by the applicant that for these systems no unacceptable adverse effects to environment, human health, property and resources are indicated. Generally speaking, the environmental risk assessment (ERA) for chemicals that are present in ballast water consists of two columns: the calculation of the predicted environmental concentration (PEC) and the predicted no effect concentration (PNEC) for all relevant environmental compartments. Usually the $PNEC_{\text{aqua}}$ and $PNEC_{\text{sediment}}$ are calculated for the aquatic compartment for substances used for or formed during the disinfection of ballast water. The ratio of the PEC and the PNEC indicates whether there is a risk or not (figure 24).

Figure 24: Environmental risk assessment



For the calculation of the $PNEC_{\text{aqua}}$ data concerning possible short-term and long-term effects for at least three different taxonomic groups, i.e. algae, invertebrates and fish, is needed and has to be provided by the applicant. To reduce the degree of uncertainty data on two additional taxonomic groups, e.g. molluscs and echinoderms, should be provided if possible (MEPC, 2008). Depending on the completeness and the reliability of the data an assessment factor is chosen (MEPC, 2008). Then the $PNEC_{\text{aqua}}$ is calculated by dividing the lowest available aquatic effect concentration with the chosen assessment factor. Additionally the treated ballast water is tested in whole effluent tests (WET). These tests should provide information on whether the mixture of all substances present in the ballast water, i.e. active substances, relevant chemicals and other chemicals, might have an enhanced or reduced toxicity compared to the toxicity of the single substances.

The PEC is calculated with the software tool MAMPEC (Marine Antifoulant Model to Predict Environmental Concentrations) for most of the BWMS. As older releases of the software were developed for the exposure calculation of leaching antifoulants, it did not ideally fit the exposure due to ballast water treatment and discharge. The newest release, MAMPEC 3.0, however, is available in two different versions. One version was adapted to the specific requirements of ballast water risk assessment and takes into account some recommendations of a research project conducted on behalf of UBA (Zipperle et al., 2011). 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 BW emissions and of the fate of the substances. The data on the environmental fate of the substances should be provided by the applicant as these parameter are specific for each substance that is used for BW treatment. However, MAMPEC 3.0 included a data set for substances that are often detected as DBPs during the ballast water treatment.

After the derivation of the PEC and the PNEC for the aquatic compartment the ratio of the two parameters is calculated. A PEC/PNEC ratio above 1 is defined as an unacceptable risk because it means that the concentration of the substance in the environment will be higher than the concentration that is likely to cause no effect in organisms. If this is the case the system cannot be approved. An approval is only possible, if the configuration of the BWMS is changed, e.g. lower dosing of the active substance (while still remaining effective) or a neutralisation unit (if scientifically justified) and the afterwards performed refined risk assessment shows that no risks for the environment remain.

In the following the derivation of the PEC for the aquatic compartment is discussed.

9.4 The research project

In this chapter the results of the research project “Guidance for a harmonized Emission Scenario Document (ESD) on Ballast Water discharge” are discussed, which was conducted on behalf of the UBA by Andreas Zipperle, BIS, Hamburg; Jos van Gils, DELTARES, Delft; Dr. Bert van Hattum, Institute for Environmental Studies, University of Amsterdam; Prof. Dr. Susanne Heise, BIS, Hamburg; Hamburg University of Applied Sciences. The aim of the research project was the development of a possible way to calculate comparable realistic worst case PECs for ballast water discharges. The report for this project can be found under <http://www.umweltbundesamt.de/uba-info-medien/4114>.

9.4.1 Sensitivity analysis

As MAMPEC is already used in many applications the project started with a sensitivity analysis of MAMPEC to find its strengths and weaknesses.

Methods

The sensitivity analysis of MAMPEC included:

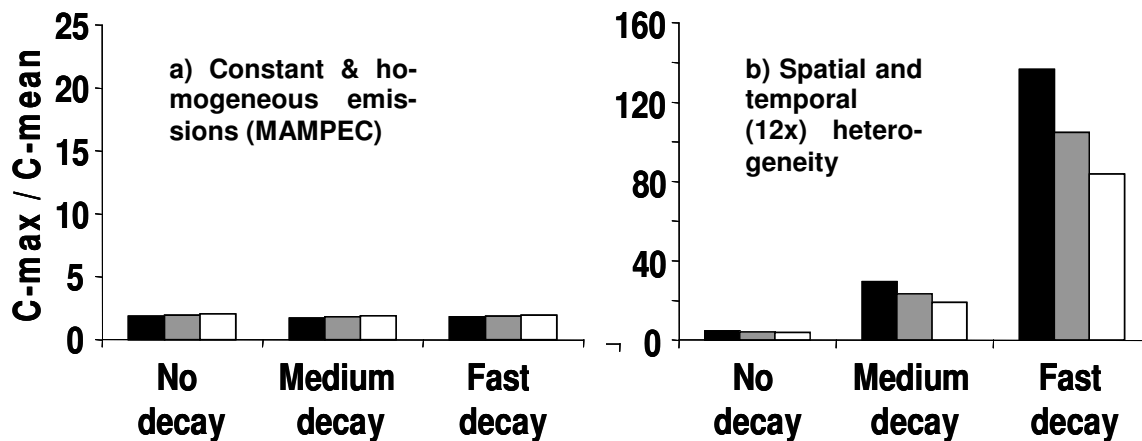
- the heterogeneity of the BW discharges, both in space and time (maximum discharge rate is 12x the average discharge rate, with randomly distributed individual discharges with a duration of 2 hours),
- the variable degradation of relevant substances (“no decay”, “medium decay”, “fast decay”),
- the variability of the flushing characteristics

Results

In figure 25a the results of the sensitivity analysis with the original MAMPEC calculations are shown, whereas figure 2b shows the results of the sensitivity analysis with modified calculations (maximum discharge rate is 12x the average discharge rate, with randomly distributed individual discharges with duration of 2 hours). The shade of grey of the columns shows the flushing characteristics: the lighter the grey, the faster the flushing of the harbour. As it can

be seen in figure 25a the calculations of MAMPEC, based on constant and homogeneous emissions, show only small differences between the calculated maximum (C_{\max}) and average (C_{mean}) concentration for all parameters while the modified simulations that take into account the characteristics of ballast water discharge – i.e. spatial and temporal heterogeneity, variable persistence and variable flushing characteristics – indicate strong variations between C_{\max} and C_{mean} (please note the different scale on the Y-axis).

Figure 25: Results of the sensitivity analysis with a) original calculations and b) modified calculations (Zipperle et al., 2011, p 43)



A conclusion that can be drawn from the results is that the faster the decay the higher the difference between maximum and average concentration will be and that the maximum concentration cannot be properly assessed with the traditional MAMPEC approach, so that the environmental risks from fast decaying substances as they are often used for ballast water treatment might be underestimated. During the simulation for “no decay” a rate constant of 0 d^{-1} , for “medium decay” a rate constant of 0.693 d^{-1} (half-life of 1 d) and for “fast decay” a rate constant of 4.16 d^{-1} (half-life of 4 h) was assumed. This leads to the conclusion that the maximum concentration of substances that have a shorter half-life than 1 d should be assessed in another way.

To summarize, the following conclusions were drawn (Zipperle et al., 2011):

- The average concentration (C_{mean}) from treated BW discharges can very well be estimated by MAMPEC (or other suitable steady state models).
- The spatial and temporal heterogeneity of the BW discharges will result in substantial differences between average and maximum concentrations. Such differences are most relevant for rapidly decaying substances (half-life shorter than 1 d) and cannot be evaluated by MAMPEC as it may underestimate the C_{\max} .
- Flushing rate into the environment and substance decay rate have the highest impact on PEC estimation. Hence, implementation of standardized substance property data is a very important step.

9.4.2 Near-field-analysis

As a result from the sensitivity analysis a new approach for the calculation of the maximum concentrations (C_{\max}) was developed. This approach is especially valid for the calculation of the maximum exposure to substances with half-life shorter than 1 d whose acute risk potential might be underestimated by the MAMPEC approach and should be used during the ERA.

Methods

For the calculation of the C_{\max} the near-field approach was proposed. The “near-field” is defined as the zone where discharge characteristics control the mixing behaviour (Doneker, 2002) and addresses an individual discharge and ship rather than a whole harbour. This approach is often used in water quality regulations to calculate the mixing at the end of e.g. wastewater pipes. At this point the mixing is source-induced, due to the momentum and/or the buoyancy of the plume. The formula for the calculation of C_{\max} is shown in figure 26.

Figure 26: Calculation of C_{\max}

$$C_{\max} = \frac{C_{BW} + (S - 1) \cdot C_{Mean}}{S}$$

C_{BW} = concentration of chemicals in the BW
 S = dilution factor at the end of the near field zone
 C_{mean} = average concentration as calculated from the scenarios
 C_{\max} = maximum concentration (“realistic worst case”)

The relevant factors for the near-field behaviour of the discharge are (Zipperle et al., 2011):

- the discharge characteristics:
 - discharge rate (m^3/s)
 - duration of an individual discharge (s)
 - location of the discharge (m above or below water level)
 - initial velocity of the discharges (m/s)
 - temperature ($^{\circ}\text{C}$) and salinity (ppt) of the discharge (kg/m^3)
- the environmental characteristics:
 - ambient velocity (m/s)
 - water depth (m)
 - ambient temperature ($^{\circ}\text{C}$) and salinity (ppt), optionally as a function of depth.

Based on these relevant factors and environmental data from a GloBallast inventory (Clarke et al., 2003, appendix 6) two different case studies were modelled with the CorMix expert system to derive a realistic worst case dilution factor S . The parameters were chosen in a way to model two extreme cases. In case A, a negatively buoyant plume (i.e. sinking) was assumed, in case B a positively buoyant plume (i.e. rising). The parameters are summarized in table 7.

Table 7: Modelling conditions for the dilution/dispersion

Conditions	Case A	Case B
Harbour salinity	estuarine or riverine environment (0 ppt)	high natural salinity (40 ppt)
BW salinity	35 ppt	35 ppt
Temperature	5–25 °C	20–30 °C

Case A is based on the consideration that many harbours are situated in an estuarine or riverine environment and have a salinity which is significantly lower than that of the open ocean. For Case A, it is assumed that a ship is taking in BW in open sea (salinity 35 ppt) and discharging BW in a low salinity environment (0 ppt), a situation which occurs in a number of places all around the world. In this case the BW discharge is heavier than the ambient water. This salinity difference was evaluated over a range of temperatures. A range of 5–25 °C was selected (Zipperle et al., 2011).

Case B is based on the consideration that many harbours are situated in an environment with a high natural salinity, which is significantly higher than that of the open ocean, for example in the Red Sea, Arabian Gulf or Mediterranean. For Case B, a ship taking in BW in open sea (salinity 35 ppt) and discharging BW in a high salinity environment (40 ppt) is assumed, a situation which occurs in a considerable number of ports. In this case the BW discharge is lighter than the ambient water. This salinity difference was evaluated over a range of temperatures. A range of 20–30 °C was selected (Zipperle et al., 2011).

Results

The modelling has shown that the dilution factor increases with increasing ambient current velocities, smaller BW discharges and larger discharge depths. The temperature has no effect on the factor. The results ranged from a dilution factor of above 1000 at high ambient current velocities to below 5 at stagnant conditions. For this reason a dilution factor of $S=5$ for the harbour and $S=50$ for the shipping lane was chosen. During their third Stocktaking Workshop the GESAMP-Ballast Water Working Group concluded that “a dilution factor of 5 could be used to calculate the maximum concentration for a near-field assessment in a harbour environment and decided to test this factor $S=5$ on practical situations” (MEPC, 2011).

9.4.3 Input parameters

In the research project the relevance of the current input parameters of MAMPEC were evaluated as well (Zipperle et al., 2011):

Ballast water volume

Based on the data of the port of Rotterdam (van Niekerk, 2008) the use of a BW discharge volume of 100.000 m³/d was proposed to include the relevance of the BW discharge (e.g. already used in MEPC, 2010, final approval granted). This discharge is supposed to be a realistic worst case approach for a basin in the port of Rotterdam in relation to the water volume of the basin.

Structure

The use of a simplified river basin-like structure with reduced mixing (already applied in MAMPEC 2.0) was found to be sufficiently realistic in matters of the water exchange with the surrounding waters. However it should be kept in mind that this might underestimate the risks for the surrounding waters as it is assumed during the calculations that only little amounts of the ballast water might enter the surrounding environment.

Temperature

To be able to judge the use of 15°C as the average temperature the average winter temperatures of 357 ports worldwide were evaluated. The source of the temperatures was the aforementioned GloBallast study, containing environmental parameters of 357 ports (Clarke, et al., 2003). After assessing the temperatures it seemed reasonable to use 6°C for a realistic worst case to be able to detect risks resulting from slower degradation in cold water. Nevertheless the GESAMP decided in their 3rd Stocktaking Meeting to keep the set 15°C as a default value in MAMPEC (MEPC, 2011). In terms of harmonization this is acceptable if all approvals use this value. But if there is a suspicion that a substance might degrade slower in colder environments the use of 6°C in MAMPEC might give an indication whether there might be an unacceptable risk in this case.

Other parameters

Preferably other water quality parameters like DOC, chlorophyll or the salinity should be evaluated and harmonized as well, unfortunately no data was available to do so. Regarding the pH the GESAMP set 8.0 as default for MAMPEC 3.0 “in order to reflect the average value in natural seawater” (MEPC, 2011).

9.5 Discussion

The sensitivity analysis showed that the PEC is, amongst other things, highly dependent on the degradation rate of the respective substances. As the formula used for the near-field approach includes the results of MAMPEC, it may include the degradation rate as well (if information is entered in the software tool). The next question to be answered is which PNEC_{aqua} for rapidly degrading chemicals should be compared to a PEC derived by a near-field analysis (see figure 26). Rapidly reacting chemicals like oxidising substances often have very short half-lives and can therefore be considered as rapidly degrading. It is important that the degradation rate is equally considered on both sides of the risk assessment, i.e. PEC and PNEC. During the derivation of the C_{mean} with MAMPEC for the derivation of the PEC, it is possible to include the degradation rate into the calculation. This would lower the PEC considerably for rapidly degrading substances. A PNEC for rapidly degrading chemicals (e.g. oxidising chemicals) that is derived with nominal or initially measured test concentrations would be considerably higher than the PNEC based on measured concentrations at the end of the test as then most of the substance would already have degraded. This would lead to an underestimation of the resulting risk.

For the European Directive 98/8/EC concerning the placing of biocidal products on the market a guidance document was developed to address this problem. The proposal is based on the OECD Guidance Document No. 23 on aquatic toxicity testing of difficult substances and mixtures (OECD, 2000) but takes into account the special exposure patterns for biocidal products (European Commission, 2011). It gives guidance on how to treat continuous or semi-continuous long-term exposure for rapidly reacting chemicals. This exposure path is also relevant for the substances released during the ballast water discharges of several ships anchoring in the same harbour. The paper gives an idea on how to balance the derivation of PEC and PNEC for oxidising substances like the ones that are often used for ballast water treatment: “(...) If for a special substance there is information on the mode of action from which it can be concluded that effects are only expected to be acute (e.g. oxidising substances), the initial concentrations can be used for the effects assessment and compared with the initial PEC for the risk characterisation. Examples for such substances are hydrogenperoxide or hypochlorite (...)”.

This would lead to the conclusion that for rapidly degrading chemicals used for ballast water treatment like oxidising substances the PNEC should not be based on the measured results at the end of the test but on the initially measured or nominal concentration as long as the

PEC does not take degradation into account as well. This option was already considered in the Methodology for the risk assessment under G9 as it states that "...for situations where only short-term exposures are expected, an additional PNEC for short-term exposure may be useful" (MEPC, 2008). For chemicals whose mode of action is not known measured concentrations at the end of the tests or the time weight average approach described in the EU guidance document should be used (European Commission, 2011). This presumes that a valid detection method with a sufficient level of quantification is available for the respective substance. For these substances the degradation should also be considered at the derivation of the PEC.

9.6 Conclusions

As it was shown in the sensitivity analysis the average concentration (C_{mean}) can be calculated with the existing MAMPEC software for all chemicals. For the calculation of maximum concentrations (C_{max}) of rapidly degrading chemicals with half-life shorter than 1 d the near-field approach should be used. For rapidly degrading substances the consideration of the degradation is crucial during the derivation of the PNEC as well. A neglect of this might lead to an underestimation of the environmental risk. A solution might be to assume no degradation during the exposure assessment and compare this PEC with a PNEC based on initially measured or nominal concentrations for the before mentioned substances.

9.7 Acknowledgement

We would like to thank our contractors Andreas Zipperle, Jos van Gils, Bert van Hattum and Susanne Heise for the excellent work they have done for the research project.

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10 Monitoring Strategies and Challenges – Disinfection By-Products from Ballast Water Treatment

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10.1 Abstract

Most ballast water treatment plants use highly toxic chemical agents in order to effectively prevent the spreading of alien species. Therefore, it is necessary to control the presence, concentration, and effects of such chemical agents in the environment. Depending on the purpose of monitoring and on the chemical properties of the agents, sampling strategies have to be designed in order to cope both with acute and chronic burdens or effects. Because of the wide variety of chemical compounds under evaluation, the development of monitoring strategies is quite a challenging task. The active agents and possible transformation products exhibit a broad range of chemical and physical-chemical properties such as reactivity, volatility and polarity, which strongly influence environmental reaction and distribution processes. In order to analyse this variety of different compounds, several different procedures have to be used: the methods of choice for volatile and lipophilic compounds are GC and GC-MS, while non-volatile and polar compounds may require use of ion chromatography and HPLC-MS techniques. Additional, special procedures may be required for selected constituents. Analytical procedures must be specific, sensitive (trace level), and robust; further, they should be fast and cost-effective. In addition to chemical analysis of specific compounds, it is necessary to apply screening techniques to evaluate the toxic effects of effluents on the receiving water body.

10.2 Introduction

Chemical agents for ballast water treatment (BWT) must have highly toxic properties in order to be effective in preventing the spreading of alien species. Therefore, it is of high importance to control their occurrence, concentrations, and effects in the marine environment. In addition, transformation products of the active substances may also be harmful to the marine environment and may have to be observed as well.

Environmental monitoring is quite a complex task with many aspects to be considered (Figure 27). Before setting up a monitoring strategy, its purpose must be clearly defined: There are two general approaches – emission control or immission observation and evaluation:

Monitoring emissions at the ballast water outlet would aim to

- control threshold values,
- control processes or
- quantify emissions.

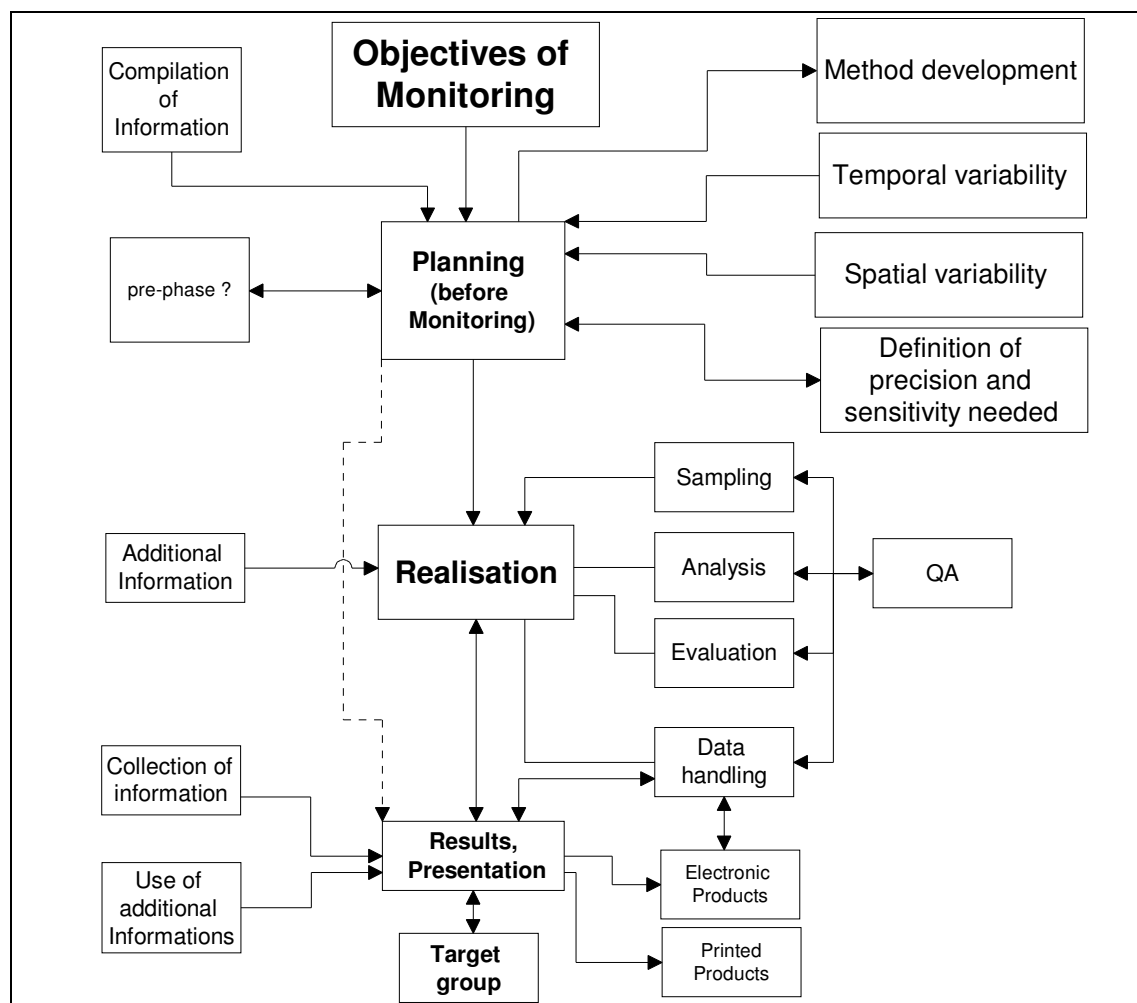
In contrast, monitoring of the environment focuses on the determination of concentrations in the receiving and adjacent water bodies (harbours, shipping lanes, ocean) in order to evaluate the

- input of hazardous substances
- distribution and level of pollutants
- time trends
- assessment of effects (toxicological data (NOEC), background values)

The two general objectives – control of thresholds or observation of concentrations and effects in the environment – determine in particular sampling and analysis parameters such as:

- Temporal resolution (observation of single events, maximum or average concentrations)
- Spatial resolution (observation of additional sources or of particularly sensitive areas)
- Concentration range
- Analytical quality
- Speed of response

Figure 27: Aspects of monitoring planning and implementation



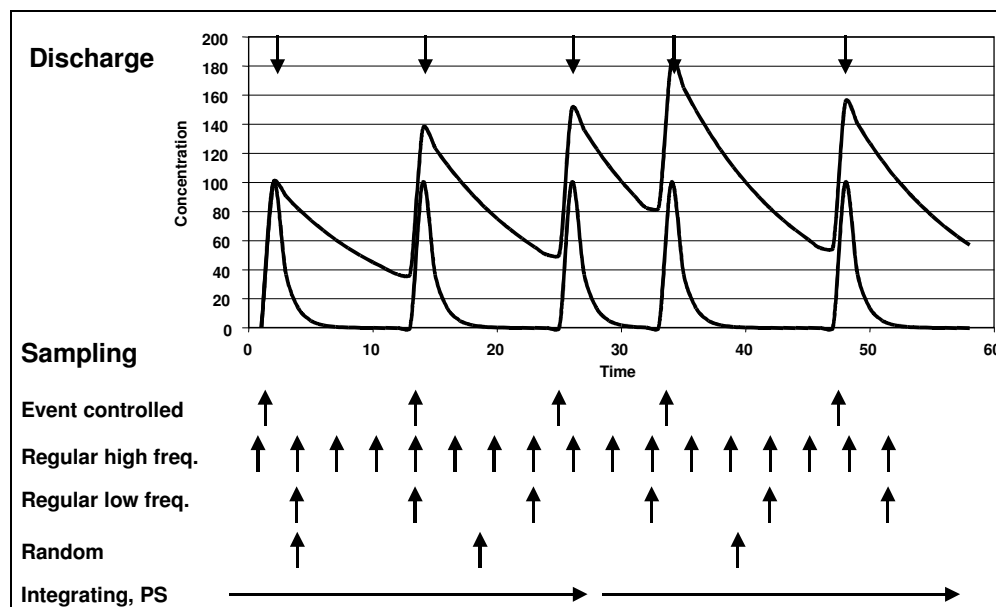
10.3 Sampling and monitoring strategies

10.3.1 Temporal aspects

Monitoring of hazardous substances within existing national and international monitoring programmes focuses on long-term investigations of chronic pollution. Important programmes covering Northern European waters are COMBINE (Cooperative Monitoring in the Baltic Marine Environment) of HELCOM (Helsinki Commission: Baltic Marine Environment Protection Commission), CEMP (Coordinated Environmental Monitoring Programme) of OSPAR (Convention for the Protection of the Marine Environment of the North-East Atlantic), and the German BLMP (Bund-Länder-Messprogramm). Their objectives are the observation and as-

assessment of input, distribution, fate and temporal trends of hazardous substance concentrations. These general monitoring programmes are not well suited to meet the special purposes and requirements for monitoring contaminants originating from BWT. The reasons for this are mainly different spatial and temporal aspects.

Figure 28: Temporal variability of two model compounds with different decay or dilution rates and the effect on observations using different sampling strategies



Monitoring of ballast water treatment emissions focuses mainly on local emissions and their spreading and effects at local or regional scales. These emissions are specifically coupled to distinct emission events within a limited area. As is shown in Figure 2, the resulting concentrations of disinfection by-products (DBPs) are highly dependent on the time passing between discharge and sampling. Further, the observed concentrations are strongly influenced by the kinetics of degradation, evaporation and/or dispersion processes. Examples given in Figure 28 show the changes over time in the concentration of two chemicals having different decay rates which are discharged at irregular intervals by several ships. Five different sampling strategies (I to V) have been investigated; they yield quite different concentrations for the scenarios shown.

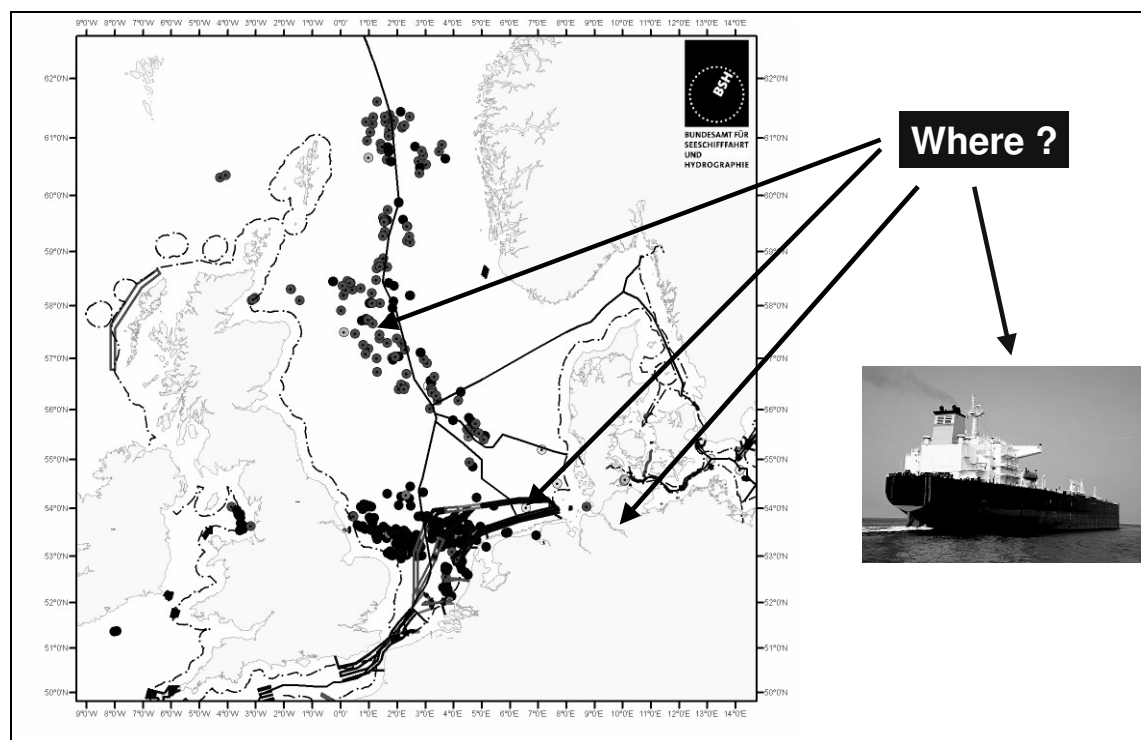
- I Event-controlled sampling would yield reliable maximum concentrations because discharges and sampling are taking place synchronously. However, this requires precise timing and a high logistical effort.
- II Regular sampling at fixed times and high frequencies (e.g. every day at 9:00 am and 9:00 pm) would yield a good and representative time coverage; but the frequency of sampling and analysis would be higher than under I.
- III Reducing the sampling frequency would yield much less representative results.
- IV The same would happen with random sampling. By reducing the number of samples, time coverage would decrease further.
- V To cope with the high variability of discharges, time-integrating sampling and monitoring is an interesting approach. In principle, such a technique is available in the form of passive samplers (PS), which consist of adsorbing devices deployed in the water for a certain pe-

riod of time (days to weeks). This sampling strategy would allow a mean contamination level to be determined with a reduced sampling and analysis effort.

10.3.2 Spatial aspects

The effort needed to carry out the different sampling strategies depends on the particular sampling location. As shown in Figure 29, discharges of treated ballast water may occur in harbours, roadsteads, shipping lanes or near offshore oil production platforms. Samples thus are taken either on board ships, in harbours, or in offshore waters. The farther the sampling sites are away from land bases the more difficult and expensive sampling becomes. Therefore, sampling strategies I to II with high sampling frequencies are only possible in harbours or on board ships, whereas strategies III to V will be the methods of choice at offshore locations.

Figure 29: Locations of possible emissions and sampling strategies (dots: offshore oil and gas production platforms, blue lines: shipping routes)



10.3.3 Analytical aspects

The type and amount of hazardous substances produced during ballast water treatment depend mainly on the treatment technique and special active compounds (Cl_2 , ClO_2 , O_3) used and on the properties of the ballast water itself. Most active compounds are oxidising agents, and the majority of approved BWT plants are currently using chlorine as active agent. Owing to the fact that seawater has a high natural amount of bromine (as bromide), a large number of chlorinated and brominated DBPs will be produced in the disinfection process. Table 8 shows a list of the most important DBPs currently known.

The spectrum of compounds is fairly broad, ranging from inorganic salts through polar halogenated acids and phenols to volatile halogenated methanes, hydrocarbons and acetonitriles. In addition, it can be assumed that more compounds can be produced which are not

yet known currently. The formation of DBP depends on many environmental parameters such as salinity, bromide concentration, oxygen content, suspended matter and dissolved organic carbon content, temperature, and light. Many of the compounds formed are persistent and toxic. Therefore, it is necessary to know their concentrations in ballast water and in the receiving water body. Some of the compounds formed may occur naturally, which complicates the evaluation. 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 (SPM) or sediments and exhibit little bioaccumulation potential. Thus, they can be transported by currents over large distances if they are persistent.

Table 8: Disinfection by-products observed in BWT effluents

Relevant chemicals (Disinfection by-products)	Molecular Formula	Relevant chemicals (Disinfection by-products)	Molecular Formula
Halogenated Methanes		Halogenated Phenols	
Trichloromethane	CHCl ₃	2,4-Dibromophenol	C ₆ H ₄ Br ₂ O
Tetrachloromethane	CCl ₄	2,6-Dibromophenol	C ₆ H ₄ Br ₂ O
Tribromomethane	CHBr ₃	2,4,6-Tribromophenol	C ₆ H ₃ Br ₃ O
Dibromochloromethane	CHBr ₂ Cl		
Dichlorobromomethane	CHBrCl ₂	Halogenated Acetic Acids	
Halogenated Hydrocarbons		Monochloroacetic acid	CH ₂ ClCOOH
1,2-Dibromoethane	C ₂ H ₄ Br ₂	Dichloroacetic acid	CHCl ₂ COOH
1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	Trichloroacetic acid	CCl ₃ COOH
Tetrachloroethene	C ₂ Cl ₄	Monobromoacetic acid	CH ₂ BrCOOH
1,2,3-Trichloropropane	C ₃ H ₄ Cl ₃	Dibromoacetic acid	CHBr ₂ COOH
1,2-Dibromo-3-chloropropane	C ₃ H ₄ Br ₂ Cl	Tribromoacetic acid	CBr ₃ COOH
2-Chlorotoluene	C ₇ H ₇ Cl	Bromochloroacetic acid	CHClBrCOOH
4-Chlorotoluene	C ₇ H ₇ Cl	Dibromochloroacetic acid	CBr ₂ ClCOOH
1,2,3-Tribromobenzene	C ₆ H ₃ Br ₃	Bromodichloroacetic acid	CBrCl ₂ COOH
Halogenated Acetonitriles		Inorganics	
Chloroacetonitrile	CH ₂ ClCN	Chlorite Ion	ClO ₂ -
Dichloroacetonitrile	CHCl ₂ CN	Chlorate Ion	ClO ₃ -
Trichloroacetonitrile	CCl ₃ CN	Nitrite Ion	NO ₂ -
Monobromoacetonitrile	CH ₂ BrCN	Nitrate Ion	NO ₃ -
Dibromoacetonitrile	CHBr ₂ CN		
Tribromoacetonitrile	CBr ₃ CN	Neutralization	
Bromochloroacetonitrile	CHBrClCN	Sodium Bisulfate	NaHSO ₄
Halogenated Amines		Sodium Sulfite	Na ₂ SO ₃
Monochloramine	NH ₂ Cl	Sodium Thiosulfate	Na ₂ S ₂ O ₃
Dichloramine	NHCl ₂	Sodium Sulfate	Na ₂ SO ₄

Classical POPs show a different environmental behaviour. Most of them are semi-volatile to non-volatile and evaporate slowly in air. Nevertheless, they can be transported over long distances by air (grasshopper effect). As they are predominantly non-polar they show a high bioaccumulation tendency and are concentrated at solid phases of SPM or sediments. Therefore, they are eliminated quite rapidly from the water phase by sedimentation.

The different chemical and environmental characteristics of classical POPs and BWT chemicals have significant effects on monitoring parameters such as the monitoring matrix, concentration ranges, and spatial objectives. As a consequence, the monitoring of BWT chemicals will concentrate on the water phase, with medium to low concentrations, and on local and regional scales (Table 9). In contrast, 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.

Table 9: Environmental characteristics for the monitoring of BWT chemicals and classical POPs

	BWT chemicals	Classical POPs
Monitoring matrix	water (air)	sediment biota water (air)
Bioaccumulation	low	medium to high
Safety margin	no	yes
Monitoring concentrations	medium to low	very low (ultra-trace)
Area of interest	local, regional, (global?)	local, regional, global

Sampling and analytical procedures are chosen in dependence on the compounds to be analysed and on their concentrations. Typical concentrations of DBP chemicals produced in BWT are listed in Table 10 (Zipperle et al., UBA, 2011), allowing expected levels to be estimated. Expected levels in the vicinity of the pipe outlet are calculated for dilution factors of 5 and 100. These concentrations are about 2 to 4 orders of magnitude higher than those of classical POPs in the marine environment.

Table 10: Concentrations of DBP chemicals observed in a BWT plant # (adapted from Zipperle et al., 2011)

Substance	Untreated control water [µg/L]	Treated water [µg/L]	Treated water, after neutralization [µg/L]	5-times dilution [µg/L]	100-times dilution [µg/L]
TRO as Cl2 [mg/L]	0; 0	8.78; 2.54	0; 0.1		
AOX	0.42; 0.36	0.78; 0.96	0.82; 1.02		
1,1-Dichloroethane	N.D.	0.13; N.D.	N.D.		
1,2-Dichloroethane	0.23; N.D.	0.4; N.D.	0.39; N.D.		
Trichloromethane	3.17; N.D.	6.64; N.D.	5.71; N.D.	1.3	0.06
Dibromomethane	N.D.	N.D.; 4.13	N.D.; 3.17		
1,2-Dichloropropane	N.D.	N.D.; 0.04	N.D.		
Dichlorobromomethane	3.5; N.D.	6.34; 0.34	5.92; 0.27		
Dibromochloromethane	2.55; N.D.	15.2; 13.5	14.4; 12.9		
Tribromomethane	1.96; N.D.	290; 592	280; 585	58; 118	2.9; 5.9
Dichloroacetonitrile	0.62; N.D.	3.98; N.D.	1.04; N.D.		
Chloropicrin	0.1; N.D.	1.94; 0.49	1.74; 0.4		
Dibromoacetonitrile	N.D.	19.5; 16.8	17.4; 16.5		
Monochloroacetic acid	46.8; 3.23	292; 513	289; 430	58; 103	2.9; 5.1
Monobromoacetic acid	N.D.	N.D.; 18.6	N.D.; 16.2		
Dalapon	N.D.	22.4; 9.51	18.2; 4.2		
Trichloroacetic acid	N.D.; 4.86	3.41; 8.36	1.85; 2.61		
Bromochloroacetic acid	N.D.; 12.5	205; 409	184; 390	41; 82	2.1; 4.1
Dibromoacetic acid	N.D.	2.63; 160	2.11; 45.8		
Tribromoacetic acid	N.D.	192; 166	174; 140	38; 33	1.9; 1.7

BWT system Smart Pipe: row of filter compartments 30 - 50 µm; seawater electrolysis; neutralization (Na₂S₂O₃). Treatment upon uptake.

The techniques and procedures needed to analyse the different concentration ranges are described in Table 11. For monitoring undiluted ballast water (tank, outlet) the analysis is easiest and can be done by direct analysis in most cases, e.g. GC-MS and HPLC-MS/MS, without a time- and labour-consuming pre-concentration step. Within the dense plume from the emitting ship (about 5-fold dilution) this will be possible for major constituents as well. However, with increasing distance and increasing dilution, the analysis will become more and more difficult and labour-intensive and thus more expensive because additional enrichment and pre-concentration steps will be necessary. In addition, sampling will become more expensive because of higher logistics requirements.

Table 11: Analytical techniques needed for the determination of DBPs at various concentration levels

Sampling object	Concentration range [µg/L]	Analytical technique	Pre-treatment
Ballast water	0.1–500	GC-MS (direct, headspace) LC-MS/MS (direct)	none
Discharge plume (5 time dilution)	0.02–100	GC-MS (direct, headspace) LC-MS/MS (direct)	none for major compounds
Distance (100 time dilution)	0.01–5	GC-MS/MS (purge and trap) LC-MS/MS	purge and trap (GC) SPE (GC,LC) passive sampling

10.4 Monitoring Strategies

Against this background, the following three monitoring strategies were investigated to assess their pros and cons:

10.4.1 Monitoring of Ship Emission

In this scenario, samples are taken at the pipe of the ship; environmental concentrations can be obtained by mathematical modelling

Characteristics

- Easy sampling (outsourcing, cheap)
- Easy analysis (direct analysis, cheap)
- Applicable everywhere
- Use for emission control and environmental monitoring

Challenges

- Legal or logistic problems?
- Optimisation of sampling and analysis
- Validation and control of modelling

10.4.2 Monitoring in Harbours

In this approach, discrete samples are taken at specified stations and times in the harbour, more or less close to the emitting ships. Monitoring in large harbours with high and regular shipping frequencies is more effective than in small harbours. Alternatively, instead of sampling at specified times, time-integrating sampling using passive samplers is possible without major logistic problems.

Characteristics

- Moderate sampling effort
- Moderate analysis effort (possibly direct analysis)
- Environmental monitoring only

Challenges

- Optimisation of sampling and analysis procedures
- Statistical optimisation of sampling times and frequencies
- More samples are needed
- Assessment (drinking water regulation?)

10.4.3 Monitoring of shipping routes or open sea areas

Also in this scenario, discrete samples are taken at specified stations and times. However, due to the larger distance from the source and the need to cover large distances to remote areas, sampling logistics are much more difficult. Both sampling and analysis are much more expensive. Integrating sampling using passive samplers can help to reduce the sampling effort, although even PS require higher logistic efforts with increasing distance from land.

Characteristics

- Expensive sampling
- Expensive analysis (extraction/enrichment necessary)
- Environmental monitoring only
- Persistent compounds only

Challenges

- Optimisation of sampling and analysis procedures
- Statistical optimisation of sampling times and frequencies
- Can probably not be optimised for specific purpose but has to be integrated into “normal” monitoring sampling
- Finding proxies (persistent and high concentration compounds)
- Differentiation towards “natural” background or other sources
- Assessment criteria for environmental quality standards and evaluation of low level toxicity of mixtures

It should be added that these considerations are valid not only for chemical analysis but for the investigation of biological and toxic effects as well and that both are needed for a holistic evaluation of the effects of BWT on the environment.

10.5 Conclusion

- The purposes of monitoring must be clearly specified.
- The monitoring objectives determine important parameters such as temporal and spatial resolution and, consequently, effort and costs.
- Chemical analysis of active chemicals and DBPs is complex because of the wide variety of compounds with their different properties; it is not easy but feasible (matter of price).
- Sampling is a most challenging problem because of the variability of emissions (temporal and spatial coverage).
- Passive sampling might be a promising approach because of its time-integrating characteristic; however, it is not yet an established method.
- Emission monitoring coupled with dispersion modelling might be a good option for improving the cost/benefit relation.
- Assessment and evaluation of the effects of multi-component mixtures of the BWT effluents is a challenging problem still to be solved.

10.6 References

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11 Ballast Water Treatment: Implications for Genetic Damage to the Natural Biota

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11.1 Abstract

There is a growing scientific and regulatory concern over the presence of genotoxic and carcinogenic contaminants in the environment. While presence of such contaminants could be a risk to human health *via* the food chain, in ecotoxicological terms, damage to the genetic material could have significant implications for the short- and long-term survival of the natural biota. In human health arena, determination of sub-lethal biological responses or biomarkers following exposure to environmental contaminants contributes to assess exposure, estimate internal and biological effective doses to elucidate underlying basis of diseases, identify susceptible groups and to take preventive action to avoid detrimental outcomes. Despite the fact that in common with humans, similar biological responses could be observed in natural biota, until recently relatively little importance has been given to applications of biomarkers in environmental risk assessment (ERA). This review aims to highlight the significance of induction of genetic damage in the natural biota and role of biomarkers in ERA and, associated regulatory developments. The review also endeavours to update the existing information pertaining to ecotoxicity and genotoxicity of currently used disinfectants while elucidating the mechanisms of induction of potential detrimental biological responses following production of disinfection by-products (DBP).

11.2 Significance of genotoxicity in the natural biota

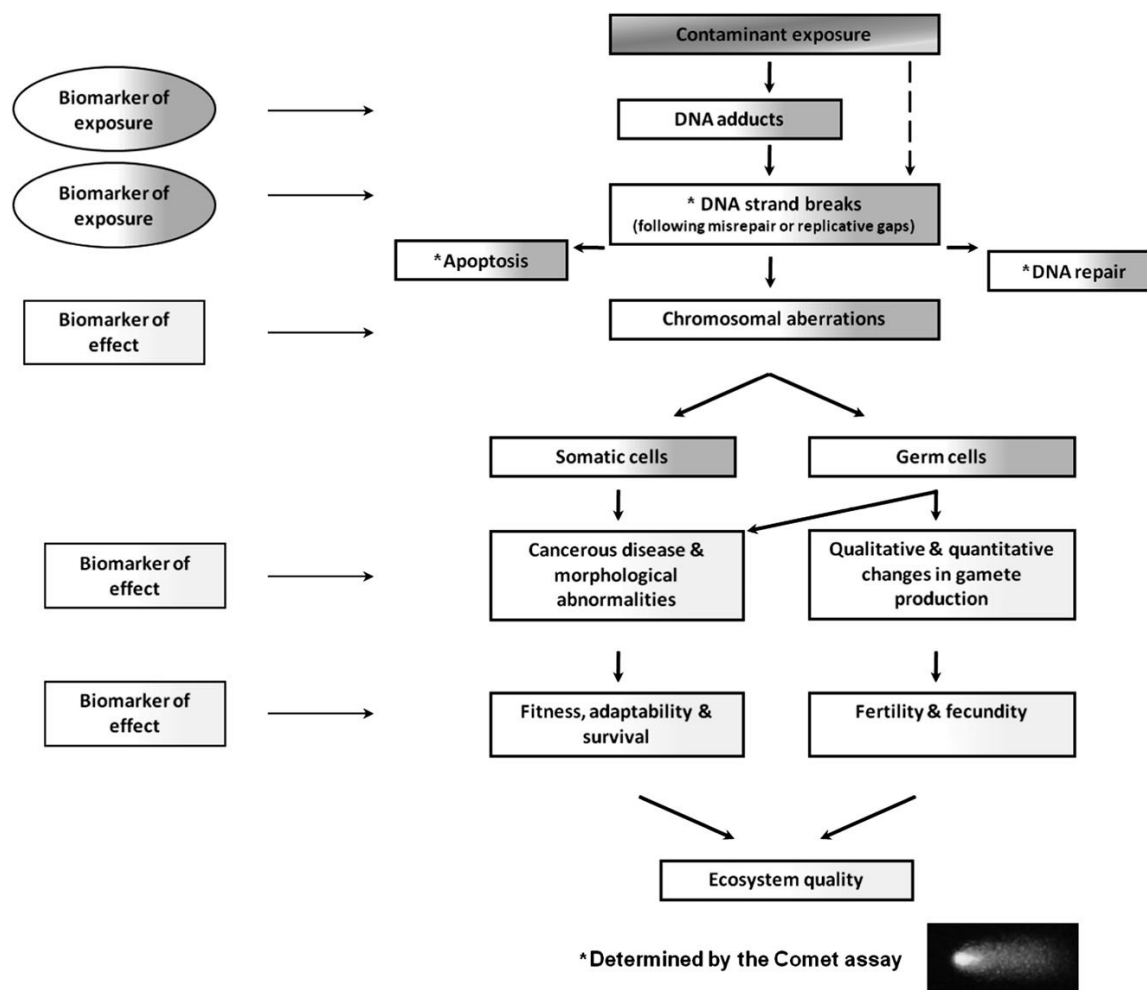
Given the universal make-up and functionality of DNA, it is generally accepted that qualitatively, the induction of genetic damage following exposure to environmental contaminants across phylogenetically disparate groups of organisms is the same (Dixon et al., 2002; Jha, 2004). Historically however, in contrast to the human health arena, where the impact of environmental contaminants is evaluated at individual level, the health of the natural biota or wild species has been traditionally appreciated at the population level. In this context, whilst the genotoxic effects are considered to be important for the initiation and promotion of carcinogenesis, one of the major health concerns in the human health arena, this disease has not been considered important for natural biota. This is despite the fact that under the microscope neoplasia whether in humans or in natural biota (e.g. fish or mussels) have similar mechanisms of production and pathological features. The rationale for this conception being that occurrence of neoplasia in the natural biota with enormous reproductive surplus is not an ecologically relevant endpoint to assess the health of the environment. This old paradigm is however being challenged scientifically for two reasons (a) induction of genetic damage in aquatic or natural biota could serve as a surrogate or sentinel for human health and (b) induction of genetic damage (whether in somatic or germ cells) could indicate a potential threat to biodiversity (Jha, 2004, 2008; Bickham et al., 2000). Whilst there have been several studies pertaining to risk to human health via the food chain (Urban et al., 2009; Tomasallo et al., 2010; Chen et al., 2009) there have been some inherent difficulties in correlating the impact of environmental contaminants simultaneously on humans and the natural biota, especially for diseases with long latency period (e.g. malignancy). There has however been some information in the literature suggesting that human health is inexorably linked with the health and long-term survival of the biota (Jha, 2004; 2008). In parallel with the human health arena

(DeMarini, 2012), there is also growing concern about potential transmissions of genetic damage to the offspring. Furthermore, 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). It is therefore important to study the impact of genotoxic agents on natural biota to protect both human and environmental health.

11.3 Role of biomarkers in environmental risk assessment (ERA) and regulatory developments

Whilst there have been inherent difficulties in linking human health with the health of natural biota, several studies have shown the induction of pre-neoplastic and neoplastic lesions (i.e. histopathological biomarkers) in fish and invertebrates following exposure to a range of contaminants in the natural environment. Such lesions have also been linked with genotoxic effects using a range of biomarkers or biological responses (e.g. DNA adducts, DNA strand breaks, induction of micronuclei) and with specific contaminants (Myers et al., 1998; Lyons et al., 2004; Frenzilli et al., 2004; Vogelbeinet al., 1990; Hesselman et al., 1988; Gardner et al., 1991; Bolognesi and Hayashi, 2011; Theodorakis et al., 2012). Whilst the application of these biomarker responses in the human health arena is well established for regulatory and epidemiological studies, there have until recently not been any substantial regulatory developments with respect to the use of biomarkers in the management of natural biota or the aquatic environment. As a result, incorporation of these biomarkers into legislations for environmental risk assessment (ERA) has been lacking and the focus continued to be on chemical measurements in the context of environmental quality standards (EQS), although some of the international initiatives (e.g. the Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR) had recommended the use of biomarkers for environmental monitoring programmes (Hagger et al., 2006).

Figure 30: Significance of DNA damage (from Jha, 2008)



In this context, looking at the list of biomarkers recommended or considered promising for biological effects monitoring programmes of the International Council for the Exploration of the Sea (ICES), a large number of them are intended to determine the genotoxic effects of contaminants (ICES, 2004; Hagger et al., 2006). Furthermore, the water framework directive of the European Union (EU WFD; Directive 2000/60/EC) emphasizes the need for biological elements as well as physicochemical and hydromorphological components for the determination of good ecological status. Because of the inclusion of 'biological elements', bioassays (i.e. mortality, growth or reproduction), well established in some European programmes (e.g. OSPAR), may have a place within the ERAs. From the regulatory perspective, therefore, there has been some emphasis to complement our traditional reliance on analytical techniques for environmental monitoring with a measurement of biological responses in natural biota. In particular, the EU WFD, while emphasising the need for ecological quality of the hydrosphere, particularly focuses on those contaminants which are carcinogenic, mutagenic or show reproductive toxicity (Borja et al., 2004; Fuerhacker, 2009). It is however to be pointed out that toxicity of environmental contaminants could be manifested in a varieties of way and the same toxicants, whether organics, metals or organometalics, could simultaneously act as genotoxicants, repro-toxicants, neurotoxicants or immunotoxicants (Jha, 2008). These sub-lethal effects inadvertently affect the Darwinian fitness, including reproductive success of the organisms (Jha, 2008). There is therefore 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. This will however

require proper optimisation and validation of a range of biomarkers in ecologically relevant biota in order to meet the growing concern (Jha et al., 1996; Atienzar et al., 2000).

11.4 Ecotoxicity and genotoxicity of disinfectants in natural biota

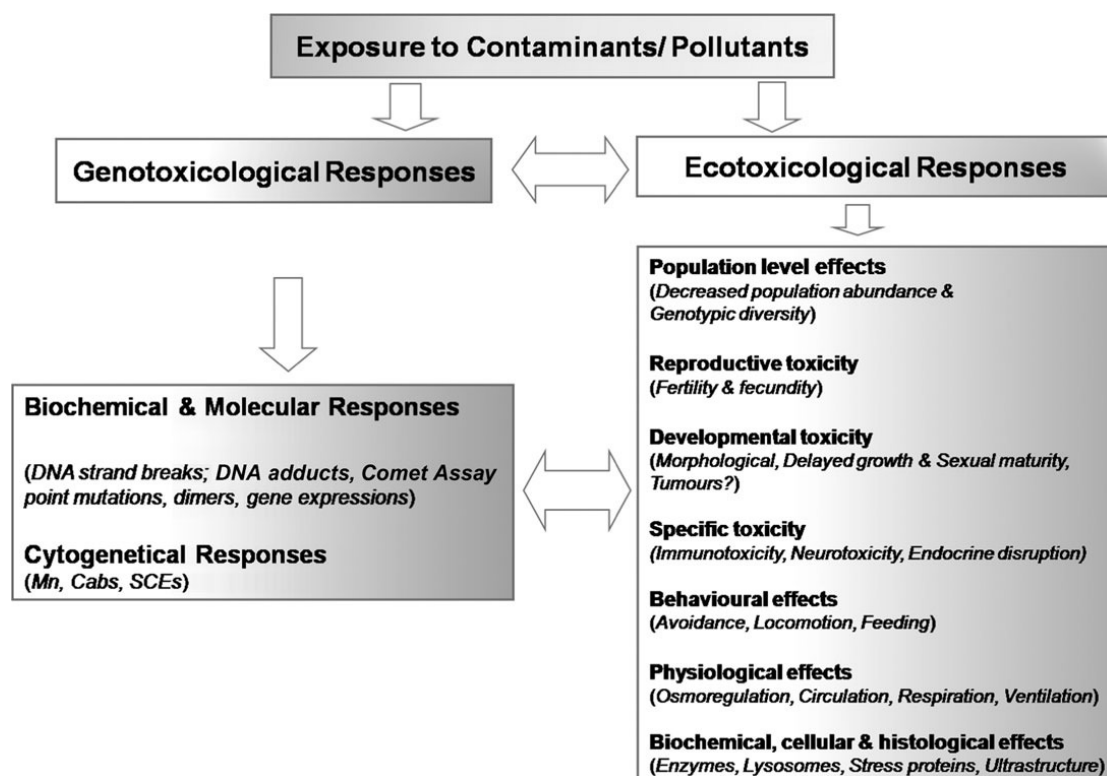
Diminishing quality of estuarine and coastal waters in different parts of the world has resulted in different measures to meet the regulatory demands set in place to for the protection of environmental quality. These processes involve, for instance, the treatment of wastewater with different chemical or physical agents (i.e. ultraviolet radiation, ozone, peracetic acid and chlorine) to kill pathogenic organisms in order to maintain a set standard of water quality parameters. Given the ease of treatment with these agents and to benefit from already existing technology for wastewater management, it is not surprising that ballast water treatment strategies have been broadly developed adopting similar approaches. In many cases, treatment of power station cooling waters discharged into coastal environments also adopt this approach, especially using chlorine based products (e.g. sodium hypochlorite) to control bio-fouling. In parallel with the human health arena, however, these treatment strategies have raised concerns for their mutagenic or genotoxic potential to the aquatic biota, both in freshwater and marine environment. Despite these emerging concerns, there have been limited studies where the potential ecotoxic (e.g. bioassays) and genotoxic effects of different treatment processes have been evaluated in the native or natural biota. In this context it should be pointed out that 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 disinfection by-products, there have indeed been very limited studies where *in vivo* tests using natural biota have been carried out to determine expressed genotoxic effects which take into account the environmentally realistic routes of exposure, metabolism, excretion and DNA repair capabilities of the organisms. The limited available studies have evaluated the effects treating either normal (or clean) water or waste water with different disinfecting agents. Whilst most of these studies have been carried out with respect to evaluating the ecotoxic and genotoxic potential of chlorine disinfection by-products, some studies also used other disinfectants. Only a few studies have however been carried out to compare the relative ecotoxicity or genotoxicity of these treatments.

In order to assess the risk posed by chlorate on aquatic organisms, available data from different studies was critically reviewed (van Wijk and Hutchinson, 1995). Based on the geometric mean $E(L)C_{50}$ values, in general it was concluded that chlorate is non-toxic to most of the freshwater and marine species examined but highly toxic to certain macro brown algal species. It is noteworthy that in the marine food chain algal species play a very important role and any damage to algal populations will eventually have knock-on effects on the entire ecosystem leading eventually to loss of biodiversity. The actual mode of action of chlorate in sensitive species is however far from clear. It is therefore important to enhance our understanding of the actual mechanism of chlorate toxicity in sensitive species, especially expression of enzymes (e.g. nitrate reductase) involved in activation and detoxification processes. It should also be pointed out that although genotoxicity, a sub-lethal effect, could be tied to a range of other toxicity parameters (Jha et al., 2000b), a direct correlation with EC_{50} or LC_{50} values commonly used for ecotoxicity might not be appropriate.

In order to compare the influence of disinfectants alternative to chlorine (e.g. chlorine dioxide, ozone, peracetic acid and UV) on the formation of mutagenic and toxic compounds in wastewater, samples were collected before and after disinfection in summer and winter seasons and then absorbed using silica C18 cartridges. Concentrates were then used for studies of mutagenicity (i.e. Ames test) and generic toxicity (i.e. bioluminescence assay using *Vibrio fischeri* photobacteria). In addition, two plant assays (*viz.* *Allium* and *Tradescantia*) were used for the potential induction of micronuclei (Monorca et al., 2000). The study suggested that all disinfectant treatments produced bacterial mutagenicity, particularly treatment with

ClO_2^- or ozone. The *Allium cepa* test gave positive results only for peracetic acid (PAA)-treated wastewater sampled in winter and the *Tradescantia* test was found to be negative for all the treatments. The marine bacterial test for toxicity showed positive response for raw wastewater, ClO_2^- and PAA-disinfected waters. An approach involving different tiers of assessment is important in assessing the biological impact as well as to assess effectiveness of different treatment strategies. In this context, wastewater disinfection processes (e.g. halogenation, ultraviolet irradiation, ozonation) are known to induce chemical changes among non-microbial aqueous constituents of the wastewater. These chemical changes could lead to altered toxic behaviour on the biota and could be equally important for the ballast water treatment strategies. A study using undiluted effluent samples from seven different wastewater treatment facilities exposed to commonly applied disinfectants was carried out. The study suggested that when un-disinfected effluent did not display toxicity, as determined by *Ceriodaphnia dubia* (water flea) survival and reproduction, no toxicity was observed following any of the disinfection procedures, either. However, when toxicity was displayed in the un-disinfected effluent, all disinfectants demonstrated the ability to enhance the toxicity with a trend: chlorination/dechlorination > ozonation > UV irradiation, individual samples showing substantial variation (Blatchley III et al., 1997).

Figure 31: Linking Genotoxicity with other toxicological responses (from Jha, 2008)



Using a test system based on marine polychaete, *Platynereis dumerilii*, ecotoxicity and genotoxicity of sodium hypochlorite treated (disinfected) primary (settled) effluent from a municipal sewage treatment work was evaluated in terms of embryo-larval development, cytotoxicity (as determined by proliferation rate index of the embryo-larval cells) and genotoxicity. Whilst exposure to dilutions of disinfected sewage in seawater led to a marked reduction in normal embryo-larval development, with a simultaneous increase in cytotoxicity (which was used to determine maximum tolerated dose or MTD), no genotoxicity (as determined by chromosomal aberrations) was observed (Hutchinson et al., 1998). Interestingly, these observations were in line with the previous study by the group where polychaetes exposed to non-disinfected sewage showed developmental toxicity and cytotoxicity but did not exhibit

any cytogenetic damage (Jha et al., 1997). This is in contrast to other studies where enhanced cytogenetic damage in the embryo-larval stages of this species was reported following exposure to environmentally relevant contaminants (i.e. tributyltin) and the species was found to be more sensitive compared to bivalve molluscs, a target species for this anti-fouling paint (Jha et al., 2000a). Given the enhanced sensitivity of embryo-larval stages for toxicological injuries (Jha et al., 2000b), lack of genotoxic effects following sodium hypochlorite (NaOCl) in polychaetes is in contrast to some of the studies using freshwater species described later (e.g. Gauthier et al., 1989) and perhaps indicate loss of highly damaged cells through programmed cell death or apoptosis in these early stages of development. Molecular approaches are required to elucidate the mechanisms of toxicity at different levels of biological organisation. Eventually, if the genotoxicity of these compounds or disinfection by-products (DBP) are established in the mammalian system, carcinogenic activities of these chemicals would be considered. Such exposures have therefore implications for both human and environmental health.

Several acute ecotoxicity studies have been carried out on representative marine biota to determine their relative sensitivity towards toxic effects in different life stages. To assess impact of residual chlorine from NaOCl-treated seawater to non-target marine organisms, bioassays were carried out on marine amphipod, *Hyale barbicornis* and estuarine fish, *Oryzias javanicus*. For ballast water treatment, these species could be considered non-target species. Although NaOCl was acutely toxic to both the organisms, long-term exposure to residual chlorine from NaOCl-treated waters caused no major adverse effects since chlorine in the treated water was reduced to about 10% by 23h-holding and 1h-aeration (Anasco et al., 2008). While interpreting the results of such studies, it is therefore important that environmentally relevant exposure scenarios are included in the experimental plan to avoid uncertainty and minimise the confounding factors influencing the toxicity measurements. While there have been many acute toxicity studies on mature adult organisms, resting eggs from invertebrates represent a challenge to ballast water treatment technologies due to morphological and biochemical adaptations to stress that also protect eggs from anthropogenic stressors. When evaluating the potential efficacy of disinfectants for ballast tank treatment, the toxicity of glutaraldehyde and NaOCl was investigated in resting eggs of the freshwater flea, *Daphnia mendotae*, and marine brine shrimp (*Artemia* sp.). In contrast to *D. mendotae*, which displayed inconsistent responses, glutaraldehyde was found to be toxic to resting eggs of *Artemia* sp., (LC_{90} : $226 \pm 10 \text{ mg L}^{-1}$). NaOCl was however similarly toxic to resting eggs of *Artemia* sp. and *D. mendotae* (LC_{90} : 86 ± 3.0 and $78 \pm 1.6 \text{ mg l}^{-1}$). The study suggested that resting eggs are less sensitive than other life stages. Furthermore, the biocide concentrations effective against other life stages may be ineffective against resting stages (Raikow et al., 2007). It is therefore important to consider the life stages of different target and non-target species when designing the treatment strategies.

The main concern of genotoxic effects in aquatic or natural biota originates from the human health arena and in order to determine the potential genotoxic impact of disinfection processes, a few studies have also been carried out on freshwater species. For example, in the freshwater environment, erythrocytes from the larvae of urodele amphibian (newt), *Pleurodeles waltl*, suggested that chlorine levels of 0.125 and 0.25 ppm (following use of sodium hypochlorite) led to significant elevations in micronuclei (Mn). The level of Mn also increased with 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 (viz. sodium hypochlorite and chlorine dioxide) and an alternative disinfectant (viz. peracetic acid), induction of DNA damage (using the comet assay) and micronuclei (Mn) 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). Whilst there have been some studies pertaining to ecotoxicity and genotoxicity evaluation of different disinfectants or their by-products, there has been virtually no work related to genotoxicity of these processes or products on plant species. In this context, using *Tradescantia* micronucleus (Mn) assay, two by-products of water chlorination (viz. 3-chloro-4-(dichloromethyl)-5-hydroxy-2[5H]-furanone: MX and 3,4-dichloro-5-hydroxy-2[5H]-furanone: MA) were evaluated. The study suggested that MX and MA induced a dose-dependent increase of Mn in pollen mother cells when doses up to 100 µg MX and 500 µg MA were applied directly to the inflorescences. In contrast, exposure of the stems in aqueous solutions containing up to 1 mg l⁻¹ MX and 10 mg l⁻¹ MA did not cause a positive response (Helma et al., 1995). The limited number of studies clearly needs to be further extended to determine the relative sensitivity of different biota under different exposure scenarios.

11.5 Mechanistic aspects and conclusions

Whatever the methods or procedures for the disinfection of the ballast water (e.g. chlorine, ozone or UV radiation), they can directly or indirectly react with naturally occurring organic matter, pollutants, or anions (e.g. bromide, iodide). DBPs formed in these reactions (e.g. halo-methanes, haloacetic acids) are considered to be responsible for mutagenicity of drinking water and have been linked with the incidence of certain cancer in human populations (Gomez-Bombarelli et al., 2012). Whilst many of these products and by-products are under regulation, some of them are yet under the radar of regulatory authorities. For example, halofuranones (e.g. MXA), formed as a result of chlorination of organic matter (e.g. humic acids) are known genotoxic and carcinogenic agents (McDonald et al., 2005; IARC, 2004). In addition to the generation of free radicals, their genotoxicity appears to be through alkylation of purine and pyrimidine bases, especially of the amino groups (Gomez-Bombarelli et al., 2012). Whilst some work has been carried out to elucidate the kinetics of the formation of DBPs and their alkylation potential under in vitro conditions, such mechanistic studies are lacking with ecologically relevant aquatic biota under in vivo conditions. Examination of kinetics, tissue specific concentrations and effects on enzyme systems have been elucidated for dichloroacetic acid (DCA), a product of chlorine disinfection in rainbow trout showing differential tissue specific responses (Fitzsimmons et al., 2009) but more work is required to further elucidate these mechanistic aspects.

Whilst there have been a large number of studies pertaining to potential health implications of DBPs in the human health arena, their negative impact on health outcome in natural biota at sub-lethal concentrations are yet to be firmly established in an environmentally realistic set-up. This is going to be a very challenging task due to various inherent limitations not only for setting-up an experimental design but also for the selection of relevant organisms from a large number of taxa from different habitats. Apart from physiology and life span, these organisms have different life or reproductive strategies and would show differential sensitivity for different life stages (e.g. embryo-larval, reproductive). As mentioned earlier, in the human health arena the main concern about DBPs is due to their potential carcinogenic effects. Even if we consider that carcinogenic effects are not relevant to aquatic biota, especially for those species which have reproductive surplus, it has to be remembered that toxicity of any environmental contaminants could be manifested in a variety of ways (Jha, 2008). It is therefore not surprising that in addition to potential carcinogenic and mutagenic impact, DBPs have been associated with a range of adverse biological effects including respiratory defects, teratogenic effects and reproductive impairment in humans (Bove et al., 2002; Cedergren et al., 2002; Shaw et al., 2003; Toledano et al., 2005; Windham et al., 2003). In line with observations in human populations, fitness of natural organisms in terms of reproductive success could be affected following exposure to disinfectants or their by-products which will ultimately impact short- and long-term survival of the exposed species and hence environmental sustainability. It is also to be remembered that contaminants in the natural environment occur in

all probable combinations and various physico-chemical characteristics such as oxygen and pH levels could also influence the biological responses, including induction of genetic damage (Mustafa et al., 2011, 2012; Hansen et al., 2012). These factors need to be taken into account when evaluating the potential genotoxic and ecotoxic risk of different treatments. Furthermore, in line with the human health arena (DeMarini, 2012), impacts on the germ cells of natural biota are also of vital importance. More work is required to fill the gaps in our existing knowledge.

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12 Risk Assessment of Ballast Water Treatment Systems under Procedure (G9)

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12.1 Abstract

Under the responsibility of the International Maritime Organization, risk assessment of Ballast Water Management Systems (BWMS) takes place in a tiered system with two tiers, the first tier is the Basic Approval evaluation and the second tier is the Final Approval. Before a BWMS can finally be put on the market the administration of the applying country has to issue a Type Approval, indicating that all requirements have been met. The risk assessment evaluates the risks for the environment as well as for humans – workers (the crew) and general public –, and the ship itself.

A technical working group, the GESAMP⁴ Ballast Water Working Group (BWWG), is in charge of the evaluation of the BWMS and the Marine Environmental Protection Committee (MEPC) takes the decision on the approval of the BWMS. The BWWG further developed its own methodology to evaluate the BWMS. The methodology is considered to be a living document that will be updated if necessary and will be based on developments of the submission of BWMS within the framework of the Ballast Water Management Convention. This paper deals with the latest proposals on the methodology.

The model MAMPEC-BW version 3.0 has been developed for the estimation of the Predicted Environmental Concentrations (PEC) in the marine environment after discharge of ballast water in a standardized model harbor. The new model will be used for the estimation of potential effects on humans and the environment. The paper will focus on the risk assessment on humans, the workers in BWMS and the general public. Some remarks will be made on the uncertainties that normally go along with risk assessments. The purpose is the protection of the world's oceans and coastal areas from bio-invasion ensuring at the same time that ballast water management practices used to comply with the Convention do not cause greater harm than they prevent.

12.2 Introduction

In 2004 the Ballast Water Management Convention (BWMC) has been adopted that will oblige ships to treat the ballast water preventing the discharge of ballast water containing harmful organisms that could cause bio-invasion in the area of discharge. The treatment of ballast water can be carried out using certain chemicals. Therefore, a guideline (G9) is included in the BWMC, regulating that the discharge of treated ballast water using chemicals should occur without any harmful effects to the ship, its crew, humans and the environment. To provide advice on the effects of ballast water management systems (BWMS) using active substances to these areas at risk, a technical group, the GESAMP-BWWG, was established. After about five years of experience, this working group has finalized major updates and additions to its methodology on the conduct of work to advise the Marine Environmental Protection Committee (MEPC), taking in account the knowledge gained evaluating ca. 60 BWMS. The proposed updated methodology is dealt with in this document.

⁴GESAMP stands for „IMO/FAO/UNESCO-IOC/WMO/UNIDO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection”.

12.3 Evaluation of BWMS

The GESAMP-BWWG evaluates the BWMS with respect to several topics: 1) the risk of discharge of ballast water to the receiving environment (aquatic organisms); 2) the risk to the people that get in contact with BWMS because of their profession (crew and port state control); 3) the risk to the public at large that may recreate in waters where ships discharge ballast water or eat contaminated seafood; and 4) the ship itself (corrosion). The process of risk assessment for chemicals in general is well developed. Many countries have to make decisions on the registration of chemicals intended for the control of harmful pests and diseases, e.g. pesticides and biocides. Also in putting industrial chemicals on the market the management tool of risk assessment is used. The basic principles of this process are also adopted by the GESAMP-BWWG to evaluate the risks of discharge ballast water.

The applicant provides a dossier to the regulating authorities, in this case to IMO and MEPC, containing information on the substance and the use, including data on the identity (physico-chemical properties), the fate and behavior in the environment (sorption and degradation) and potential toxic effects (human toxicology and ecotoxicology). First the data are evaluated on the quality, whether the data are generated using generally accepted methods, e.g. OECD test guidelines. Only scientifically justified data are accepted for further use in the risk assessment. Some data are used for the estimation of potential concentrations in the environment, the environmental exposure assessment. The final result of this evaluation are the predicted environmental concentrations (PEC). Often use is made of mathematical models to describe the behavior of the substance in the environment based on typical information, such as the octanol/water partition coefficient, the sorption capacity to soil or sediment, and the abiotic or biotic degradation potential of the substance, e.g. half-life in water or soil. In the hazard assessment the effect data are used for the estimation of safe levels of the substance in the environment or for humans. The (eco)toxicity data include acute and chronic endpoints. Using safety factors, to account for required safety and uncertainty in the data, a safe level is estimated resulting in a predicted no-effect concentration (PNEC) for the environment or a derived no-effect level (DNEL) for human exposure. Finally, the results of the exposure assessment and the hazard assessment are compared to each other using a risk characterization ratio (RCR). The value of the RCR defines whether or not a potential risk may be expected for the topic under consideration. In case risk cannot be excluded a further in-depth assessment may be needed.

12.4 Risk assessment tools for BWMS

In order to perform the approach outlined in section 2, the GESAMP-BWWG has developed its methodology on the conduct of work. A proposed revision of the methodology has recently been forwarded to MEPC for comments, suggestions and adoption. The focus of the revision has been on

- 1) the development of a data base for the most occurring disinfection by-products (DBPs) generated during the BWMS operation,
- 2) the model development and scenario description to calculate the PEC in a standardized harbor environment, and
- 3) the definition and analysis of the unit operations for crew and port state control in the handling of BWMS.

Especially if electrolysis of seawater is the main disinfection process, which is the case in the majority of the BWMS currently evaluated, a huge number of DPBs may be formed, of which trihalomethanes (THMs) and haloacetic acids (HAAs) are the most important. A list of 18 DBPs has been prepared, containing those DBPs that occur most frequently and also in the

highest amount. The physico-chemical properties, the fate and effect data have been incorporated in the data base for further use in the risk assessment.

As the model to be used for the calculation of the PEC the GESAMP-BWWG adopted the MAMPEC⁵-model as the most suitable model currently available. The MAMPEC-BW, version 3.0, has been specifically developed for the GESAMP-BWWG. In the model a specific scenario has been defined describing the harbor environment and an emission scenario for the discharge of ballast water. In the harbor scenario the most relevant parameters are defined as pH, temperature, particulate organic matter, dimensions of the port, and exchange volume with the surroundings. The emission scenario defines the amount of ballast water discharged each day. The result of the MAMPEC calculation is the yearly average and median concentration of the substance under consideration, its maximum and minimum and its 95-percentile. As a worst-case situation the maximum value is currently used for the evaluation. As an example, the discharge of ballast water in the model harbor was estimated at E+5 m³/d. The Group considered that also for the area around the ship where the actual discharge takes place a situation of higher risk may occur. Therefore, a near sea scenario has been defined as well taking an additional dilution factor of 5 into account for the short term exposure of aquatic species.

For the human exposure scenario the MAMPEC results may be used for the estimation of the exposure of the general public. The general public may be exposed by oral intake, dermal uptake and inhalation of discharged ballast water during swimming in contaminated areas. Also, oral exposure may arise from the consumption of fish caught in these contaminated areas. However, for the estimation of the risk to the crew and port state control MAMPEC is not suited as exposure may take place during handling of the chemicals used in the BWMS or during operation of the BWMS. The possibilities of exposure are defined in the unit operations involved in the BWMS. These unit operations have to be defined for each individual BWMS as the specific circumstances may change from one system to the other. The number of exposure events and the amount occurring have been estimated for a worst-case and a realistic case. As an example for human exposure, sampling of ballast water tanks may result in dermal and inhalatory exposure at a frequency of 2 hours per day and 5 days a week for acute exposure, and an additional assumption of 45 weeks a year would lead to chronic exposure.

12.5 Data base

As outlined above, the GESAMP-BWWG developed a data base with information on the most relevant DBPs generated during ballast water treatment. The current list contains the substances shown in Table 13.

Table 13: DBPs in the GESAMP BWWG data base

#	Substance	#	Substance
1	Sodium bromate	10	Dibromoacetic acid
2	Potassium bromate	11	Tribromoacetic acid
3	Bromoform	12	Monochloroacetic acid
4	Chloroform	13	Dichloroacetic acid
5	Dibromochloromethane	14	Trichloroacetic acid
6	Dichlorobromomethane	15	Bromochloroacetic acid
7	Sodium hypochlorite	16	Monochloroamine
8	Sodium thiosulphate	17	Trichloropropane
9	Monobromoacetic acid	18	Dibromoacetoneitrile

⁵MAMPEC stands for Marine Antifoulant Model to Predict Environmental Concentrations.

The data base serves two main purposes: First, to ensure that for all substances included in the data base the same physico-chemical data and effect data are used in the risk assessment for these substances independent of the BWMS in which they occur. This provides consistency over the substances and systems evaluated. Second, the main DBPs currently identified in BWMS happen to be quite well-known, rather simple organic compounds. For many of them risk assessments have been carried out by institutions in the USA or EU but also by non-governmental bodies like the World Health Organization (WHO). Therefore, the GESAMP-BWWG and IMO face the submission of data in manifold as each applicant will provide the data available in public literature, for instance on the substance bromoform. Once a substance has been included in the data base no public available data have to be submitted anymore with the dossier for Basic and Final Approval. The waiving of data on these substances is restricted to information that may be found in scientific literature and in risk assessment documents carried out by national or international bodies that generally also have carried out an evaluation of the quality of the data based on established criteria like standard test guidelines (OECD), GLP, etc. It should be recognized that data required for the functioning of the BWMS, like the whole effluent toxicity (WET) test and the chemical analysis of the treated ballast water can never be waived and are exempted from this waiving process.

12.6 Risk assessment for crew and port state control

Humans that may most be affected by a BWMS are the people that work with the BWMS during its operation in all aspects, the crew, and the people that have to inspect the working of the BWMS during operation and during stand-by. The GESAMP-BWWG made an analysis of activities, the unit operations, during which crew and/or port state control could be affected by the BWMS. A unit operation takes into account the amount of treated ballast water and the time duration a crew member may be exposed to the chemicals used or generated in the BWMS. The exposure to these compounds is expressed as a dose in milligram per kilogram bodyweight per day (mg/kg bw/d). Based on the toxicological information on the compounds a hazard dose is calculated using the most relevant toxicological endpoint and an appropriate assessment factor. The assessment factor takes into consideration the quality and origin of the establishment of the most relevant endpoint, the most relevant route of exposure and the most appropriate duration of exposure. The resulting final endpoint is the Derived No-Effect Level (DNEL), also expressed as mg/kg bw/d. The ratio of exposure and DNEL determines whether to expect a risk or a safe situation. In the following section more detail will be given on this approach.

12.6.1 Crew

The activities carried out by the crew potentially causing exposure to chemical compounds when handling BWMS are summarized in Table 14.

Table 14: Activities of crew causing exposure to chemicals from BWMS

Activity (Unit Operation)	Exposure	Frequency/Duration/Quantity
Delivery, loading, mixing or adding chemicals to the BWMS	Potential dermal and inhalation for leakage and spills. For closed or automated systems the exposure is assumed to be minimal	Solids:100mg/container handled Liquids: 0.1mL/container handled
Periodic cleaning of ballast tanks	Inhalation of air in the ballast water tank	8 hours/day for 5 days/week; 1 event/year (acute/short term exposure)
Periodic cleaning of ballast tanks	Dermal exposure to the whole body	8 hours/day for 5 days/week; 1 event/year (acute/short term exposure)
Carrying out ballast water treatment activities	Case by case	
Maintenance work on the BWMS	Case by case	
Normal work on deck unrelated to any of the above	Inhalation of air released from vents	1 hour/day for 6 months (short-term exposure)

For each of the unit operations, except the case-by-case situations, an exposure equation has been defined describing the exposure related to the depending variables. In case of the dermal exposure, for example, due to delivery, loading, mixing or adding chemicals to the BWMS the following equation is used:

$$Dose_{derm} = \frac{C_{form} \cdot N \cdot E_{hand} \cdot \rho \cdot f_{derm}}{V_{form} \cdot BW}$$

where:

$Dose_{derm}$	=	skin exposure (mg/kg bw/d)
C_{form}	=	concentration of active substance in formulation (%w/w)
N	=	number of containers handled (10)
E_{Hand}	=	contamination to concentrated formulation during 1 event (0.1 mL)
ρ	=	density (1 g/mL)
f_{derm}	=	dermal absorption factor (1)
V_{form}	=	volume of preparation handled (L)
BW	=	body weight (default = 60 kg)

Finally, all the exposure routes are added together to estimate the total exposure dose for crew to chemicals used in that BWMS.

12.6.2 Port State Control

In an analogous way the exposure possibilities for Port State Control personnel is estimated using the exposure assumptions given in Table 15. Addition of the exposure routes gives an estimation of the total dose to which PSC personnel may be exposed when dealing with activities of a specific BWMS.

Table 15: Activities of Port State Control causing exposure to chemicals from BWMS

Activity (Unit Operation)	Exposure	Frequency/Duration/Quantity
Ballast Water Sampling	Inhalation of air in the tank headspace	2 hours/day for 5 days/week (acute exposure); 45 weeks/year (chronic exposure)
Ballast Water Sampling	Dermal exposure to primarily hands	2 hours/day for 5 days/week (acute exposure); 45 weeks/year (chronic exposure)
Ballast tank inspections	Inhalation of air in the ballast water tank	3 hours/day for 1 day/month (acute exposure)

12.7 Risk assessment for the general public

For the estimation of the exposure of the general public two potential routes are distinguished: 1) recreational activities in the sea, swimming in areas contaminated with ballast water and 2) consumption of seafood from such contaminated areas.

Table 16: Exposure routes for the general public

Situation	Exposure	Frequency/Duration/Quantity
Recreational activities in the sea	Inhalation of chemicals partitioning into the air above the sea	5 hours/day for 14 days of the year
Recreational activities in the sea	Dermal exposure to chemicals whilst swimming in the sea	5 hours/day for 14 days of the year
Recreational activities in the sea	Swallowing of sea water contaminated with treated ballast water	5 hours/day for 14 days of the year
Consumption of seafood exposed to treated ballast water	Oral consumption	Once or twice/day equivalent to 0.188 kg/d (Japan)

Again, as an example, the concentration of chemicals in seafood that consumed is calculated according to the following equation:

$$C_{fish} = BCF \cdot PEC_{mampec}$$

and

$$U_{fish} = \frac{QFC \cdot C_{fish} \cdot BIO_{oral}}{BW}$$

where:

C_{fish}	=	concentration in fish ($\mu\text{g}/\text{kg}$)
BCF	=	bioconcentration factor (L/kg)
PEC_{mampec}	=	concentration of chemical in water derived from MAMPEC ($\mu\text{g}/\text{L}$)
U_{fish}	=	uptake of chemical from eating fish
QFC	=	quantity of fish consumed per day (= 0.188 kg/d (Japan))
BIO_{oral}	=	bioavailability for oral intake (default = 1)
BW	=	body weight (default = 60 kg)

Finally, all exposure routes from Table 16 are added for the estimation of the total exposure. For the derivation of the hazard dose, based on the DNEL, reference is made to the description in the methodology of GESAMP-BWWG.

12.8 Conclusions

The methodology of GESAMP-BWWG has been further developed during a series of three stock taking workshops to which additional experts have been invited on specific topics like the MAMPEC model development and the human exposure scenario development. The group considered the current methodology quite complete and more or less in place. Therefore, the time is there to request parties for suggestions and criticism on the proposals. The methodology should be considered a living document to which new information may be added or items be changed if scientific developments indicate the need. In addition, the methodology has to be tested in practice. Changes have been performed taking into account current experience and knowledge, which is based on the major use of disinfection by electrolysis of seawater and the associated production of DBPs. If other substances will be proposed as active substances, changes have to be made or other concepts have to be developed and used to perform an acceptable risk assessment for those cases. Nevertheless, the main principles of risk assessment – exposure assessment, hazard assessment and risk characterization – will be kept as the basic keystones.

Potential areas of further development of the methodology can be the evaluation of key model parameters, like the tidal exchange volume of water in the harbor, the temperature in the harbor in relation to the temperature at which degradation of the substance has been determined, a correction factor may be needed to account for the temperature difference. An important area of research could be the necessity of a second or higher tier assessment situation in case the worst-case situation leads to unacceptable risk. Also the occurrence of many other possible DBPs should be further assessed. Literature sources have shown that over 600 different substances have been analyzed in all kind of disinfection processes. It remains to be seen whether applicants have to search more thoroughly for more DBPs. Finally, the potential exposure to substances showing carcinogenicity, mutagenicity and reproductive toxicity, so-called CMR-substances, should be further analyzed as some of the DBPs have such classifications.

To answer the questions posed in these potential areas of concern, stock taking workshops will be held on a yearly basis and successively the group will discuss with invited experts in the field the possible solutions. The final aim of controlling the world-wide spread of invasive aquatic species may require still scientific input to gain more insight in the area of ballast water management to advance the protection of the world's oceans and coastal areas from bio-invasion ensuring at the same time that ballast water management practices used to comply with the Convention do not cause greater harm than they prevent.

12.9 Acknowledgement

The author wishes to acknowledge the input of the GESAMP-BWWG and of all the invited experts who contributed to the current status of the methodology on the evaluation of the environmental and human risk assessment of ballast water discharges.

12.10 References

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References are available on the IMO website

[http://www.imo.org/KnowledgeCentre/HowAndWhereToFindIMOInformation/IndexofIMOResolutions/Pages/Marine-Environment-Protection-Committee-\(MEPC\).aspx](http://www.imo.org/KnowledgeCentre/HowAndWhereToFindIMOInformation/IndexofIMOResolutions/Pages/Marine-Environment-Protection-Committee-(MEPC).aspx)

13 Assessment of Hazardous Substances in Marine Environmental Monitoring Programmes. Approaches and Developments

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13.1 Abstract

In 2010, assessments of hazardous substances in the marine environment have been published by the international conventions for the protection of the marine environment of the North Atlantic Ocean (OSPAR) and the Baltic Sea (HELCOM). Besides only a small number of substances which have been reported by most of the countries, time gaps in data records and insufficient spatial coverage of sampling stations in the marine area, a main problem was to select, and where not available, to develop appropriate assessment tools. This includes particularly the general methodical approach, a classification system, the selection of appropriate indicators with regard to the aims of the program, the derivation of threshold values, the degree of aggregation and finally to be simple enough to present the results in an understandable way without loss of important details. One example is HELCOMs approach in 2010 to assess the state of the Baltic Sea with respect to the aims of the Baltic Sea Action Plan (BSAP) for hazardous substances, trying to combine concentrations of hazardous substances and their effects in an integrative way. Also in 2010, OSPAR published a "Quality Status Report", in which the status of hazardous substances was assessed in relation to cessation targets, their temporal development (trends), and the contamination level, based on effects and background concentrations. The actual task will be to derive acceptable threshold values and to harmonize, in the course of the implementation of the EU Marine Framework Directive (MSFD), the different systems for the marine environment as far as appropriate with the regulation of inland and coastal waters under the EU Water Framework Directive (WFD).

13.2 Monitoring of hazardous substances

Monitoring of hazardous substances in the marine environment is performed mainly in the framework of international and regional conventions. For Northern Europe, the conventions for the protection of the Northeast Atlantic Ocean, the OSPAR Convention, and for the Baltic Sea, the Helsinki Convention (HELCOM), were signed in the 1970s. Since then, monitoring programs were performed and assessments of the data were published, assisted by guidelines produced by working groups consisting of experts from the member countries. The Mediterranean and the Black Sea are covered by the Barcelona and the Bucharest Convention, respectively, which are part of the UN Environment Programme. Since 2000 for the coastal areas and since 2008 for the open sea, monitoring under the EU Water Framework Directive (WFD) and the Marine Strategy Framework Directive (MSFD) has become obligatory for EU member states. Nevertheless, the regional conventions will continue to play an important role, particularly within the MSFD, due to their experience in monitoring from planning marine monitoring programs up to the status assessment and to assist the regional cooperation and harmonization. Besides this, regional conventions also involve non-EU countries like Iceland and Norway in the Northeast Atlantic Ocean and Russia in the Baltic Sea. Scientific support is supplied by the International Council for the Exploration of the Sea (ICES), which covers the areas of both OSPAR and HELCOM.

13.3 Planning and performance

Planning and performance of monitoring programs include typically the determination of the following subjects:

- Aim, strategy, and indicators;
- parameters and compartments for the measurement;
- within the sampling strategy the station grid, frequency, period (season), duration, the use of fixed stations (buoys, automatic sampling devices) or a survey by ship;
- sample treatment and analysis;
- data calculation, storage, distribution, and quality assurance;
- and finally the assessment, presentation and publication of the results, which may include also recommendations for measures to improve the status of the marine environment.

13.4 Descriptors, indicators and parameters

The MSFD defines eleven qualitative descriptors for a good environmental status (MSFD Annex I). Two of them are relevant for hazardous substances:

*“(8) Concentrations of contaminants are at levels not giving rise to pollution effects.
(9) Contaminants in fish and other seafood for human consumption do not exceed levels established by Community legislation or other relevant standards.”*

The descriptors are linked to characteristics, pressures and impacts (MSFD Annex III), for hazardous substances defined as *“A description of the situation with regard to chemicals, including chemicals giving rise to concern, sediment contamination, hotspots, health issues and contamination of biota (especially biota meant for human consumption)”* and the related impact of *“Contamination by hazardous substances”* including *“pesticides, antifoulants, pharmaceuticals, resulting, for example, from losses from diffuse sources, pollution by ships, atmospheric deposition and biologically active substances, introduction of non-synthetic substances and compounds (e.g. heavy metals, hydrocarbons, resulting, for example, from pollution by ships and oil, gas and mineral exploration and exploitation, atmospheric deposition, riverine inputs), introduction of radionuclides.”*

Certain organic compounds, trace metals and radionuclides serve as indicators or parameters, the selection depending on their properties (persistent, bio-accumulative, toxic, endocrine), but also on their occurrence or their potential to occur in the marine environment and the analytical possibilities to detect them in biota, sediment or seawater. Typical parameters are

- trace metals: Hg, Cd, Pb, Cu, Zn;
- organometallic compounds: tributyltin (TBT);
- organic compounds:
 - chlorinated: organochlorine pesticides (hexachlorobenzene, hexachlorocyclohexanes, DDTs), polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins/dibenzofurans, chlorinated paraffins;
 - brominated: polybrominated diphenyl ethers, polybrominated biphenyls, hexabromocyclododecane;
 - fluorinated: perfluorinated compounds (perfluorooctane sulfonate, perfluorooctanoic acid); and
- radionuclides : Pu-239, Pu-240, Pu-238, Am-241, Sr-90, Cs-137, Po-210.

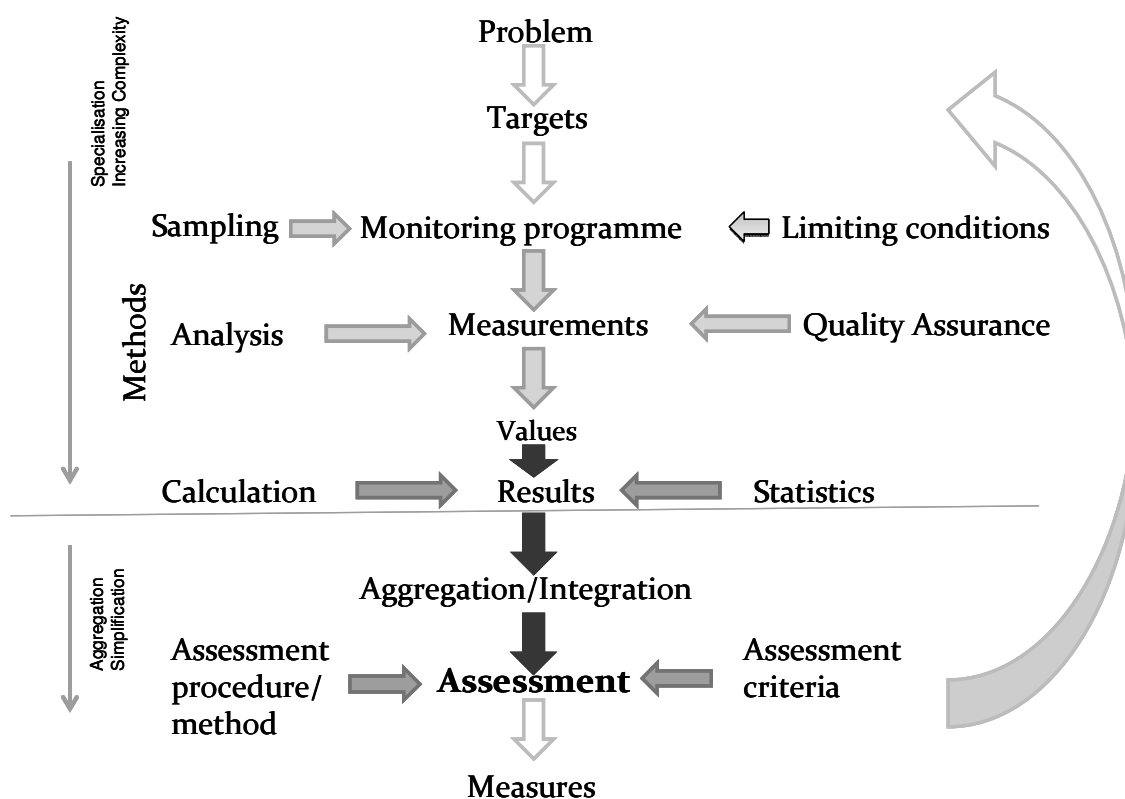
13.5 Assessment

The objectives of an assessment are

- (i) spatial distribution (identification of main sources of inputs, hot spots, gradients),
- (ii) temporal changes (trends: direction, significance, turning points) and
- (iii) status in relation to
 - (a) established assessment criteria: from unacceptable to excellent
 - (b) effectiveness of measures taken for improvement.

Assessments can describe the status therefore on the basis of a single parameter at different stations, a single parameter at one station over time, or integrated by parameters, time and area or combinations of these. For example, the fitted values of the trend curves can be used for a spatial assessment of different areas for a certain year.

Figure 32: Overview of environmental assessment processes



To determine the status in relation to a reference situation, e.g. undisturbed by human impacts, reference values are needed. For chemical elements and substances typical thresholds are

- (i) the background concentration (BC) for natural occurring substances like metals, where the geochemical background represents this status, or the background assessment concentration (BAC) in those cases where it is impossible to derive the BC due to the lack of possibilities to determine the "real" background. The BC/BAC represents the transition point from a high quality status to a good status and can be used to detect whether the aim of the precautionary principle is fulfilled.

- (ii) the environmental assessment concentration (EAC), which describes the concentration value below which a negative impact on the marine environment is not to be expected. The Environmental Quality Standard (EQS) from the EU-WFD characterizes also the border between effect and non-effect concentration. Besides measurement of chemical concentrations, biological effect methods will serve as indicators for this purpose.

Neither the regional conventions nor the relevant EU directives for the protection of the marine environment use concepts like maximum allowable inputs for hazardous substances. This would be contrary to the precautionary principle as well as to the aim of maintaining a good environmental status or, where this is not the case, to restore this status when possible.

The number of classes in an assessment scheme and the transitions points or threshold values, respectively, differ between the different monitoring programs and may cause unacceptable inconsistencies, e.g. when comparable and neighboring areas are covered by two different regulatory programs (EU-WFD and MSFD) or national territories, e.g. in the Wadden Sea between the Netherlands and Germany. On the other hand, a unique threshold for a large area may not be suitable due to different conditions, e.g. a different geochemical background, perhaps associated with assimilation of the used test organism. The first step should be to harmonize the EACs for OSPAR and HELCOM and the EQS for the MSFD, as the underlying criteria are identical.

A larger task will be the (further) development of methods to derive the EAC/EQS-values for the amendment of existing values, where necessary, and the establishment for new substances. The weakness of some existing thresholds is caused by the method applied for their derivation, i.e. the use of test systems consisting of freshwater organisms exposed to a single compound under laboratory conditions and the transfer of the obtained test results to organisms of a higher trophic level in marine waters impacted by a mixture of many substances under natural conditions. How to deal with mixture toxicity is one unsolved problem. But as it is obviously impossible to get all the information from field or mesocosm experiments, new approaches to calculate conversion factors from test system to the natural environment are needed, e.g. how to shift a dose-response relation adjusting by measuring and modeling comparable parameters/properties in test and monitored organism.

Decision makers like to attain a simple answer for a complex context. This requires the aggregation of assessments on single indicators: Instead of many single results for single chemicals a statement for all chemicals, biological effects, biodiversity and eutrophication as one status for a certain area is preferred. The aggregation and integration can be performed e.g. on

- (i) data of a certain parameter (e.g. statistical median, mean)
- (ii) Integration of different indicators (e.g. hazardous substances and their effects).

The methods and procedures may include

- (iii) weighing results from parameters within one group with respect to e.g. their toxicity
- (iv) the application of the „one-out-all-out principle“.

How far an aggregation is meaningful depends on the purpose, for which the status information shall be used. The right balance between the reduction of data and the achievement of still meaningful results to assist the deduction of measures is essential.

The examples of the recent assessments performed by OSPAR and HELCOM in 2010 reflect the difficulty to produce graphs presenting information in a condensed manner without losing essential details. The integration of hazardous substances and other impacts has been done in an “additive” way and does not result in a single number or color code. HEL-

COM expresses the overall status by the magnitude of ten pressure indicators for a certain area. OSPAR presented a pilot impacts assessment against pressures of four species groups and four habitat types against five groups of pressures for three regions and also a qualitative summary of the regional status, kind of pressure and status, pictured by a colored symbol, completed by arrows or question marks for the trend.

These two assessments have given valuable examples how to proceed on the way from single compound assessments to an ecosystem assessment. The national initial assessments for the Marine Strategy Framework Directive, which have to be finalized by mid 2012, are mainly based on results from assessments performed in the last years. The next assessment will hopefully benefit from the experiences made in the last regional assessments and the research which is initiated in national and international projects and in the framework of the regional conventions, e.g. HELCOM Coreset and OSPAR MIME.

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*OSPAR publications on hazardous substances are available under
http://www.ospar.org/v_publications/browse.asp?menu=01080304580000_000000_000000*

14 A Holistic View on Ballast Water Management Systems

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14.1 Abstract

The main priority of any ballast water management systems (BWMS) is to comply with the Ballast Water Convention. The Regulation D-5 of the Convention states that the International Maritime Organization (IMO) is required to review the 'Ballast Water Performance Standard' considering a number of criteria including safety consideration, environmental acceptability, and cost-effectiveness, in addition to the biological effectiveness of removing or rendering inactive harmful aquatic organisms in ballast water. Nevertheless, the Convention makes no mention about the means by which to achieve this. Consequently, the approach, the variables and the assessments considered may depend upon the criteria of the person responsible. Hence, several factors may get unattended in the type-approval process. This paper goes beyond the provisions of the Convention and shows ways to achieve a complete and holistic assessment of BWMS to make sure that the approved technologies are sustainable. That is, to guarantee that they are environment-friendly, cost-effective and safe to humans and the environment.

14.2 Introduction

The International Convention for the Control and Management of Ship's Ballast Water and Sediments ('the Convention') aims to reduce the transportation of species across the globe in ballast water by eliminating viable organisms before its discharge. To achieve this, regulation D-5 for example states that any ballast water management system (BWMS) must guarantee that ballast water management practices do not cause greater harm than they solve. Furthermore, the IMO is required to review the 'Ballast Water Performance Standard' considering a number of criteria including: (1) compatibility with ship designs and operations; (2) safety consideration; (3) environmental acceptability; (4) cost-effectiveness; and (5) the biological effectiveness of removing or rendering inactive harmful aquatic organisms in ballast water. The Convention, therefore, adopts an integrated approach in solving the problems associated to the introduction of species through ballast water. The criteria can be classified in the following groups:

Environmental aspects

- Environmental acceptability
 - Degradability of active substances
 - Impact of biocides on marine ecosystems
- Biological effectiveness

Social aspects

- BWMS is safe for the ship, personnel, environment, society

Economic aspects

- Cost-effective

A sustainable BWMS maybe defined, therefore, as a system which is technically feasible (meets regulation standards), cost-effective, and with an acceptable environmental and social impact.

Including environmental, social and economic criteria holistically in the design of a product is not new in industry (Klöpffer, 2003). The Life Cycle Thinking is the most common example. Life Cycle Thinking is defined as the approach that incorporates these criteria along the product chain, including the consumption and end of use phase (Hauschild et al., 2005). Experience can be found in literature where life cycle methods, i.e. Life Cycle Assessment, Life Cycle Costing and Social Life Cycle Assessment, are applied to improve the sustainability footprint of a product (Frischknecht, 1998; Fet et al. 2000). Both, the life cycle thinking and the Convention, seek the same goals for a new BWMS, i.e. to include environmental, social and economic aspects in the design. Hence life cycle methods could be used to design sustainable BWMS that meet the IMO criteria.

Despite the similarities, the variables analysed in both approaches are not necessarily the same ones. For example, while the Convention focuses mainly on impacts derived from the creation and management of active substances and many other variables relevant because of their toxicity within the ballast water, a sustainable BWMS would focus on the origin/toxicity/amount of the materials used for building the BWMS, the energy required to power the BWMS and related air pollution, the consumables required to run the systems, for a same functional unit⁶.

The Convention is in a very good position to develop sustainable BWMS and adopt an integrated approach to ballast water management. This paper describes the essence of a holistic approach to ballast water management. The aim is to show designers/manufacturers of technologies the tools available to improve the sustainability level of BWMS. Likewise, the most common variables in the sustainability assessment are described as well as the common methods to assess the sustainability of technologies. The paper finishes with a short discussion about the position of IMO guidelines G8 and G9 in relation to a holistic view on ballast water management.

14.3 The Holistic Approach

According to Charter and Tischner (2001) the design for sustainability involves a change in behaviour and purpose; guarantees a reduction of environmental impacts by reducing the consumption of materials and energy or otherwise selecting lower impact materials or energy options; incorporates socioeconomic dimensions of sustainability into the design, thereby producing a positive impact on the health and productivity of workers. The assessment of sustainability of a product design or a new alternative design is, therefore, the core element to optimise the design from the sustainability point of view.

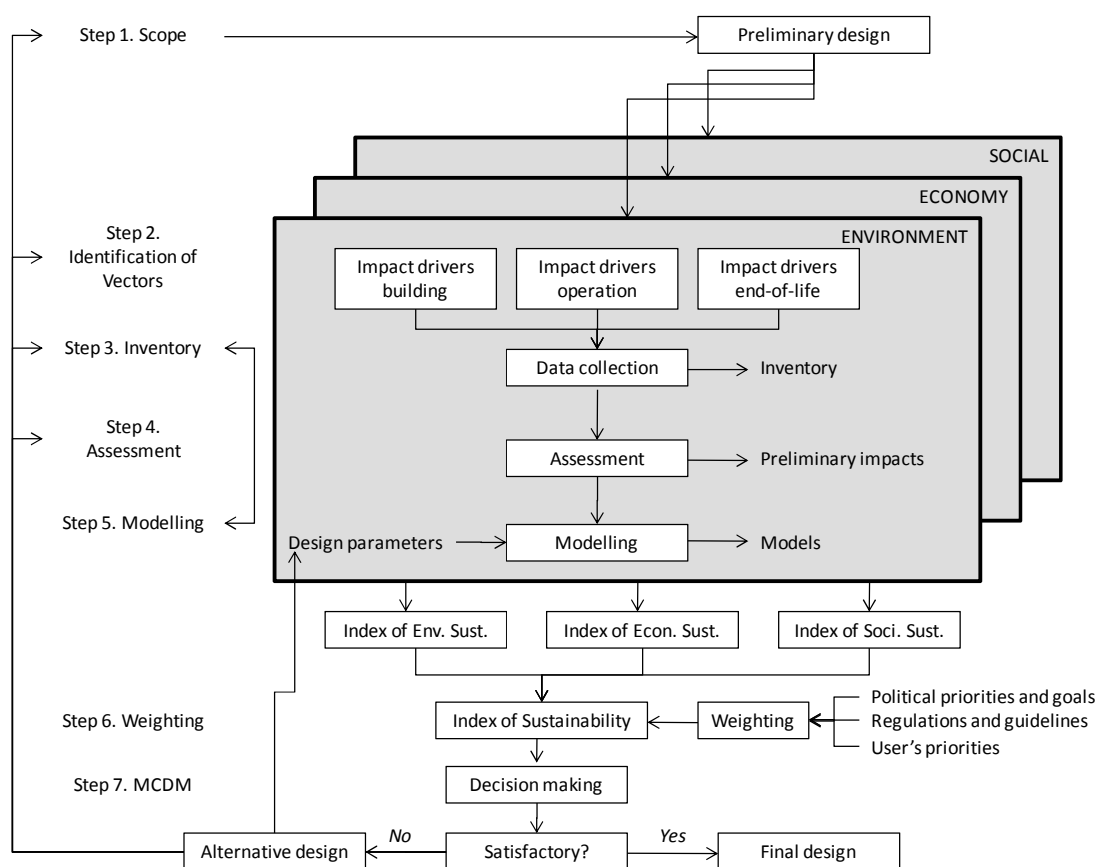
The limitation of the available methodologies to assess sustainability of marine technologies (including BWMS) has led to the development of a specific sustainability assessment methodology for the maritime context, focused on mainly onboard technologies (Figure 33). The methodology is based on life cycle methodologies: Life Cycle Assessment for the environmental sustainability, Life Cycle Costing for the economic sustainability and the Social Life Cycle Assessment for the social aspects (Klöpffer, 2003; UNEP, 2009; Dreyer *et al.*, 2006). Briefly explained, the methodology is divided into seven steps: Step 1: *Scope*; Step 2: *Identification of vectors*; Step 3: *Data inventory*; Step 4: *Assessment*; Step 5: *Modelling and indices*; Step 6: *Weighting*; and Step 7: *Decision-making*. The first five steps may be independ-

⁶Functional unit is a quantified performance of a technology for use as a reference unit in the comparison of different alternatives.

ently applied to every sustainability dimension (i.e. environmental sustainability, economic sustainability, social sustainability) and to each targeted system. Three independent sustainability indices are obtained at the end of Step 5 as the outcome of the previous steps, each representing a relative sustainability performance of the targeted BWMS. Then these indices may be weighted in Step 6, following current policies which create a global sustainability numerical indexing. In Step 7, these outcomes are compared to the requirements and goals set by the user in Step 1, and decisions will be made so as to select the most sustainable alternative for the sought-after goals (Basurko and Mesbahi, 2012).

In order to facilitate the process of the sustainability assessment, a computing tool has been developed in LabVIEW incorporating the modelling of the BWMS attributes. Figures 34-37 show the appearance of the user-interface. The following sections capture the essence of the variables and assessment considered in the sustainability assessment without going into details. More detailed information on the methodology and sustainability assessment of marine technologies can be found in Cabezas-Basurko (2010) and Basurko and Mesbahi (2012).

Figure 33: Flowchart of the methodology to holistically assess sustainability of marine technologies (Basurko and Mesbahi, 2012)



14.3.1 Environmental aspects

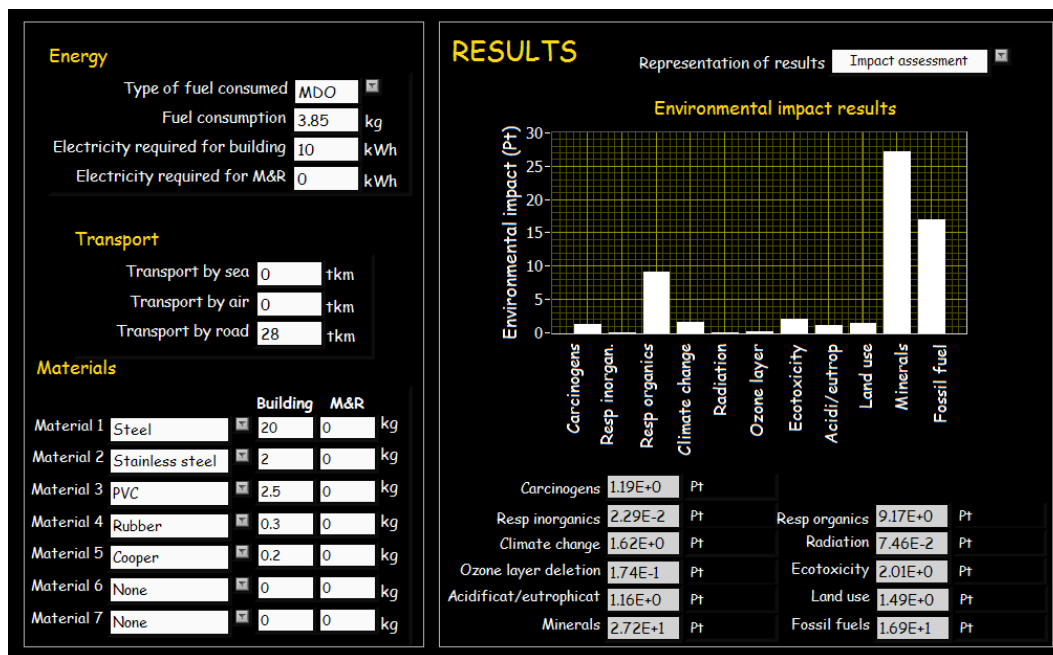
The BWMS related variables that can induce impact need to be clearly identified, described, and quantified in order to estimate the environmental impact. These variables are usually identified for manufacturing, operation and maintenance and end-of-life stages. The most common variables can be classified as: the use of materials (including quantity, origin and nature of the construction materials), energy consumption (including amount and source of

energy), consumables (such as active substances, by-products or replacements), maintenance of the BWMS and related variables, waste generation and management, transportation of BWMS to the user, and emissions to air, soil and land derived from the manufacturing and use of the BWMS.

In order to estimate environmental impacts, BWMS attributes and environmental impacts were modelled in LabVIEW. As a result, a user-interface was developed. The screenshot is shown in Figure 34. The environmental impacts were based in the databases of SimaPro7. To operate it, data referring to technology attributes are introduced on the left side of the interface. After running it, the tool predicts the associated environmental impacts. Results are both graphically and numerically presented.

The IMO regulations and guidelines, such as D-2, D-5, G2, G8 and G9 of the Convention, are mainly centred on the conditioning of treated water prior to discharge. Furthermore, the environmental acceptability is focused on the degradability of active substances and the impact of biocides on marine ecosystems. In contrast, the methods used to undertake Life Cycle Assessments do not currently consider ecological effects. Hence, noticing the missing approaches of both assessments, it may seem natural to include these two approaches in one, making them complementary, in order to have a holistic environmental assessment of BWMS.

Figure 34: Appearance of the environmental impact assessment tool (with random values)



14.3.2 Social Aspects

Ensuring the human equity and wellbeing at different societal levels is the key priority of Social Sustainability. This requirement matches with the intentions acknowledged by the Convention, i.e. 'the BWMS must be safe for the environment, crew and the ship'. Researchers have adopted a wide range of approaches to assess social impacts. Many are based on qualitative assumptions making the assessment biased depending on the criteria of the practitioner. Sustainable metrics are essential to have a holistic assessment of sustainability of BWMS (i.e. including environmental and social impacts, and costs); hence, the quantitative assessment of social impacts is preferred.

The most widely accepted method to assess social impacts in life cycle engineering is the Social Life Cycle Assessment (SLCA). SLCA classifies social impacts in five susceptible areas to be affected by the impact, i.e. 'areas of protection', as a result of the creation and use of a specific technology. These areas of protection are *workers, users, local community, society, and value chain actors* (Benoit *et al.*, 2010). SLCA are usually time-consuming, social data are often collected through questionnaires and interviews, and answers are given in qualitative, semi-quantitative and quantitative manner. The work has been limited to evaluate the impact on the *User* area of protection. The variables studied have been those, which can affect the wellbeing of a seafarer and which are commonly related to the risk assessment of marine technologies (Cabezas-Basurko, 2010). The variables considered are shown in Table 17.

Table 17: Input variables

Input Variables		Qualitative Descriptor
Noise	Level of noise	"None", "Low", "Medium", "High"
	Time exposed to noise	
Vibration	Level of vibration	
	Time exposed to vibration	
Mechanical hazard	Magnitude of mechanical hazard	
	Time of exposed to mechanical hazards	
Electrical hazard	Magnitude of electrical hazard	
	Time of exposed to electrical hazards	
Thermal hazard	Thermal (hot/cold) hazard	
	Time exposed to thermal hazard	
Optical hazard	Magnitude of optical hazard	
	Time of exposed to optical hazards	
Radioactive hazard	Magnitude of radioactive hazard	
	Time of exposed to radioactive hazards	
Odour	Amount of odour emitted by technology	
	Time of exposed to odour	
Skin	Toxicity of product if in contact with skin	
	Time the skin is exposed to that product	
Eye	Toxicity of product if in contact with eye	
	Time the eye is exposed to that product	
Ingestion	Toxicity of product if ingested	
	Amount ingested	
Inhalation	Toxicity of product if inhaled	
	Amount inhaled	
Job	Level of maintenance required	"Low", "Medium", "High"
	Is the job repetitive or variable?	"Yes" or "No"
	Is the job manual or automatic?	"Yes" or "No"
	Is the job exiting or boring?	"Yes" or "No"
Environment	Does operator use any personal protection equipment?	"Yes" or "No"
	Are there any pollution protection measures available on the workplace such as ventilators?	

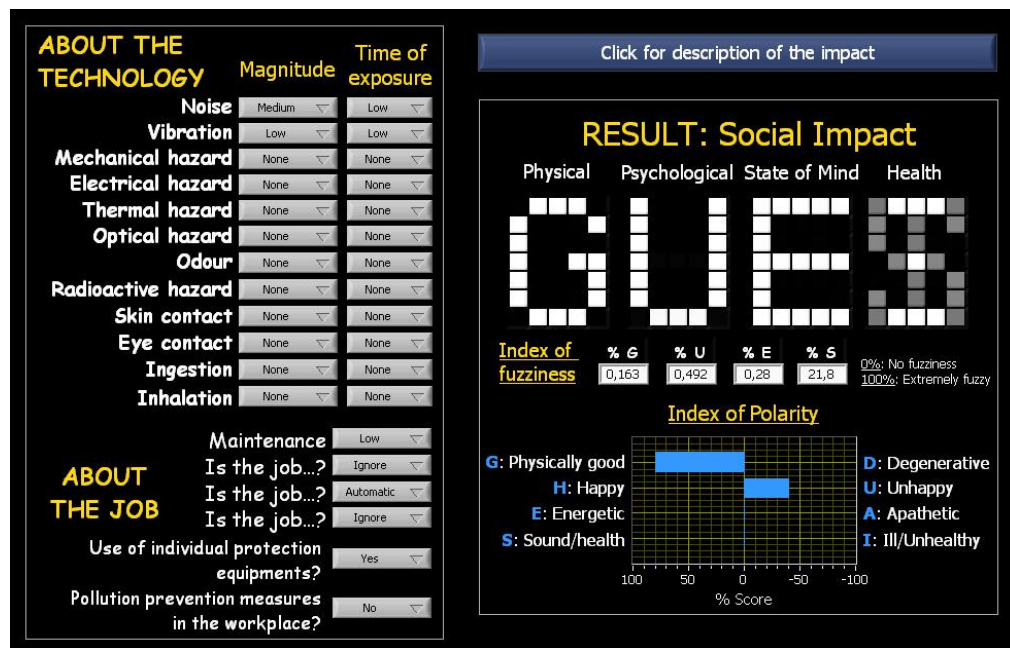
A new methodology has been developed to present a more objective approach towards the assessment of social impacts of BWMS. This methodology was inspired by the Myers-Briggs Type Indicator (MBTI) psychometric personality tests (Briggs-Myers *et al.*, 1998) which classifies the way people act, live and communicate in society in 16 personality types which come described in a four-letter code each.

According to the World Health Organisation (WHO) health is "a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity" (WHO,

1946). Based on this definition, health has been divided into four streams. It entails a physical condition, a mental stability, the well-being of the person, and the absence of disease. Following the WHO definition of health, social impact has been similarly defined by four streams which indicate consequences of the effect the direct contact with the BWMS exerts on the health of the user or seafarer. The four social impact streams are: (1) the impact on the musculoskeletal system i.e. “physical impact”; (2) generation of mental disorder, i.e. “psychological impact”; (3) the effect on the cognitive state, i.e. “impact on the state of mind”; and (4) the impact on the biological health, focusing only on the disease or illness, i.e. “impact on health”.

Each input and output entries were converted from qualitative to quantitative data by allocating a numerical score to each option. The Artificial Neural Network technique was used to model the data. The outcome of the methodology provides a user-friendly computing tool, which predicts the social impacts of a given technology and its job characteristics in a quantitative manner (Figure 35). More information about the development of this methodology can be found in Cabezas-Basurko (2010).

Figure 35: Appearance of the tool developed for assessing social impacts of marine technologies (with random values)



14.3.3 Economic Aspects

Life Cycle Costing (LCC) is one of the most successful tools utilised in life cycle engineering when dealing with the economic dimension of sustainability (Hutchins and Sutherland, 2006; Hunkeler and Rebitzer, 2005; Huppel et al., 2004). According to Hunkeler and Rebitzer (2005) LCC is “an assessment of all costs associated with the life cycle of a product that are directly covered by any one or more of the actors in the product life cycle (suppliers, producers, user/consumer, end-of-life actors), with complementary inclusion of externalities that are anticipated to be internalised in the decision-relevant future”. Hence direct and indirect costs are equally analysed.

The cost elements commonly included in LCC are capital costs, taxes and insurance, manning costs, cost of consumables, energy costs, training costs, maintenance costs, environmental costs (e.g. polluting fines and awards due to good environmental performance), social

costs (safety measures, compensations, etc.), and decommissioning costs. The costs have been also modelled in a LabVIEW. The appearance of the LCC assessment tool is shown in Figure 36. The model is a user-interface in which values can be introduced for LCC variables. The model calculates in return the life cycle cost for that specific scenario in € per year. In order to complement the model and additional model has been also written in LabVIEW which allows the user to compare several scenarios in relation to their life cycle costs (Figure 37).

Figure 36: Appearance of the tool developed for assessing life cycle costs of marine technologies (with random values)

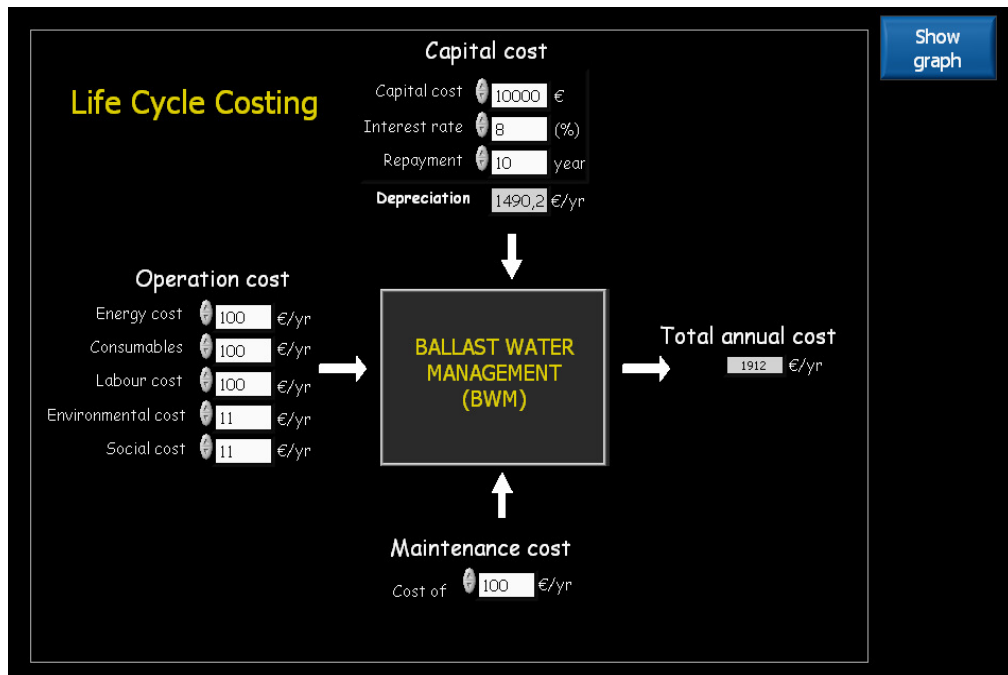
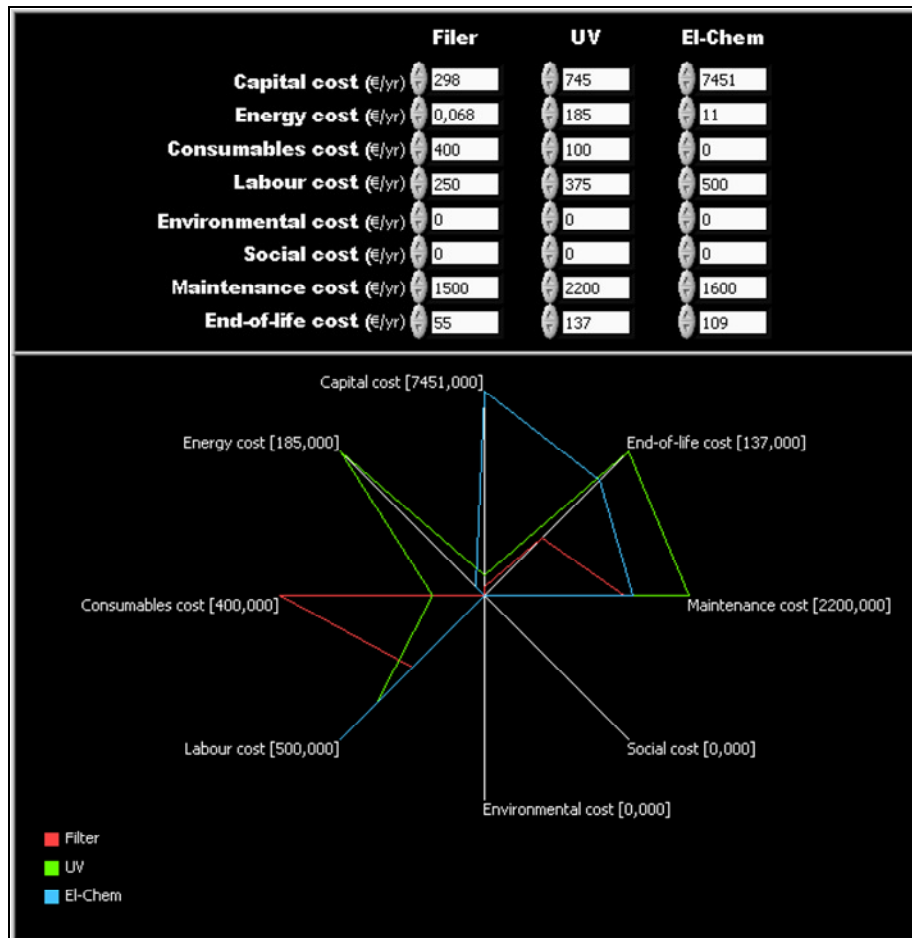


Figure 37: Example of a representation of main life cycle costs for three hypothetical different scenarios or alternatives

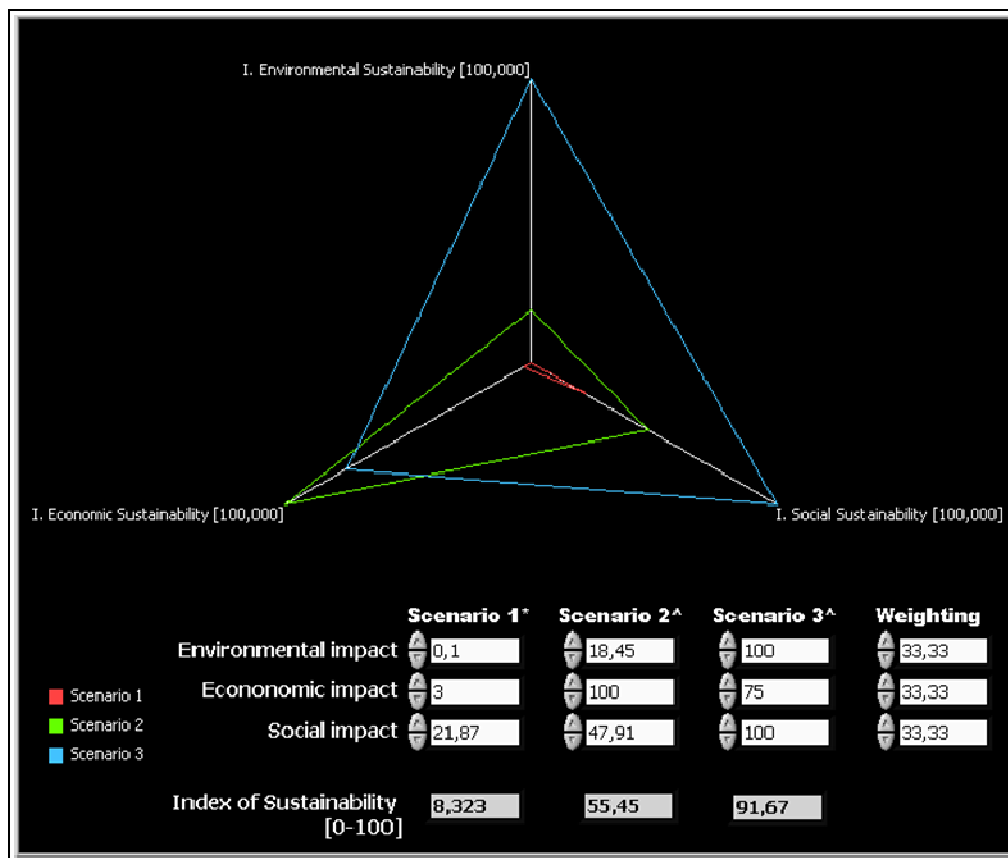


14.3.4 Integration

The integration of environmental, social and economic assessments can only be achieved by ensuring a common functional unit (Hunkeler and Rebitzer, 2005). A good functional unit for ballast water management is the function of “treating one tonne of ballast water” with different ballast water treatment systems. The analysis for this functional unit predicts which technology produces larger environmental impact, which costs the most, and which is the most harmful for the crew to operate. The application of the holistic approach together with the functional unit ultimately allows the calculation of the sustainability indices of each technology, and subsequently comparison amongst different scenarios.

All models explained above have been designed in an interconnected manner. Thus, when the user introduces, for example, the fuel consumption, this value is incorporated into the programme and transferred to their respective sustainability dimension assessment page and incorporated into their assessment models. In order to calculate the sustainability, the user needs to introduce manufacturing and operational data in the computing tool. The tool, consequently, computes the results in three separate windows, one per each dimension (shown by Figures 34-37), showing the numerical details of the BWMS assessments. There is also a fourth window (Figure 38), in which the scores calculated in each sustainability dimension are shown and the four sustainability indices' results are calculated.

Figure 38: Representation of the holistic assessment of sustainability for three random scenarios applying equal weighting to sustainability dimensions



Overall results of the assessment are shown as Scenario 1*. Furthermore, the tool allows comparing the results of an additional two scenarios or alternatives. To do so, results of previously calculated scenarios may be introduced by hand by the user in Scenarios 2 and 3. The tool subsequently computes the Index of Sustainability and presents the results in a 0–100 range, with 100 being the dimension with a major impact, and 0 the one with the least impact. Similarly, there is an option of weighting each sustainability dimension in order to reflect the importance the user gives to each dimension of sustainability. As default, an equal weighting is applied.

14.4 Discussion: Do IMO guidelines G8 and G9 cover all aspects?

The Convention watches over the wellbeing of the crew, ship, environment, and society. But it makes no mention about the means by which to achieve this. The sustainability assessment of BWMS can be the answer to bridge this gap since it can assess the environmental, economic and social performances of any BWMS.

Nevertheless, the methods and databases used in sustainability assessments (i.e. LCA, LCC and SLCA) have been originally designed for land-based industries. Furthermore, experiences in the marine field are scarce. Consequently, marine impacts are currently not fully assessed. Therefore, it will take some effort and experience to specifically adapt them for marine applications to become a real representation of marine impacts. This would mean, for example, including marine ecological models or biocides effects on marine life within the assessment methods.

It is envisaged that a holistic assessment of ballast water management is needed. And the Convention and the sustainability assessment are complementary. Both together ensure that all aspects affecting the wellbeing of the environment, crew, ship and society are considered under the same umbrella and are consequently assessed. In the long run, it may be interesting to consider a wider range of variables in the design and optimisation stage of BWMS in order to help shipping industry march towards a more sustainable future.

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