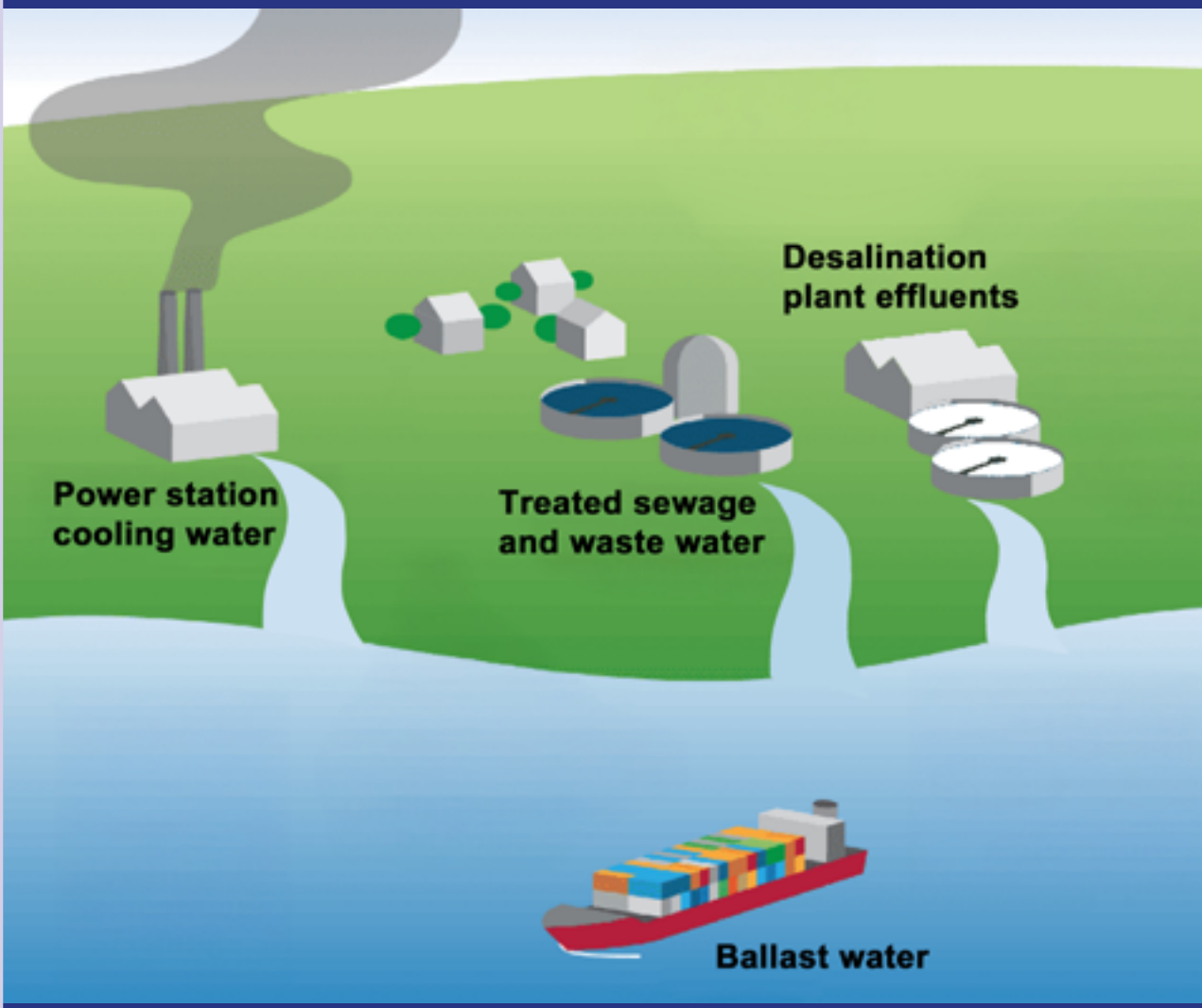
115

REPORTS AND STUDIES

GESAMP

Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

RELEVANCE OF INPUTS OF DISINFECTION BY-PRODUCTS INTO THE MARINE ENVIRONMENT



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SUMMARY

The anthropogenic and natural sources and pathways for the generation of halogenated in particular brominated hydrocarbons in marine waters are identified and explained. The basic chemistry for the generation of such products in marine waters is laid out together with the identification of these chemicals. Information is compiled and presented on the formation of disinfection by-products during disinfection processes in industrial cooling waters (in particular nuclear power plants), desalination plants, ballast water treatment, and wastewater treatment (including seawater toilets) is presented. The inputs of disinfection by-products from these different applications are estimated as far as possible; data gaps challenging such estimates are explained. The natural generation of brominated hydrocarbons in the marine environment is also discussed. Strategies for assessing the impact or risk for the marine environment, human health and the atmosphere (ozone layer) are evaluated. The report is the first of its kind for summarizing the generation of disinfection by-products in marine waters by sources, their generation pathways, their input into the marine environment and the exposure situation for marine life, humans and the atmosphere. Due to a lack of data, any reliable impact assessment is currently not possible. However, specific proposals for generating a better database through measurements and research are given.

EXECUTIVE SUMMARY

Oxidant treatment of seawater in coastal and sea-based installations (including ships) to reduce the number of organisms living therein has been increasing over the last decades. Some of these processes are applied to reduce fouling. Others are used to minimize the input of noxious or non-indigenous species into the marine environment. In some cases, disinfection processes are essential to protect human health against infectious diseases or to protect the biodiversity in the marine environment. In other cases, treatment is necessary for a safe and efficient operation of the technology. The chemical processes involved generate undesired organic compounds, so-called disinfection by-products (DBP), which are discharged into the marine environment. To date more than 700 disinfection by-products have been identified. Some of these compounds are suspected to exert long-term effects on human health or are potentially toxic to marine life. By evaporation from the ocean, some of these compounds may also have detrimental effects on the atmosphere (ozone layer).

During the last years, the situation has been assessed by GESAMP. Members of GESAMP were asked to assess the combined environmental impact of all kind of sources on the ocean. GESAMP noted that the technologies involved are falling under different United Nations areas of responsibilities, in particular the International Maritime Organization (IMO), the International Atomic Energy Agency (IAEA), the United Nations Environment Program (UNEP), and the United Nations Development Program (UNDP). A GESAMP scoping project co-funded by the German Federal Institute for Risk Assessment (BfR) started in 2017. During an international workshop in Berlin in late 2018, internationally renowned experts presented the current scientific state-of-the-art, discussed the available knowledge and identified the challenges involved in assessing the environmental impact. In the years following the workshop, this report on the actual state of knowledge and the challenges of this topic was compiled.

The main activities resulting in discharges of disinfection by-products into the marine environment in the order of treated volumes are:

1. Anti-fouling treatment of seawater used for cooling processes, in particular in electric power stations along the coasts,
2. Reduction of biofouling during desalination of seawater to produce drinking water and freshwater supply for agriculture in arid regions,
3. Treatment of ballast water according to an international convention to minimize the transfer of non-indigenous species by ships,
4. Disinfection of wastewater discharged into coastal areas to avoid hygienic risks (sewage treatment), including the use of seawater for toilets to reduce the need for freshwater.

The technical processes, the situation today and the future perspectives of these activities are presented. The chemistry behind the generation of disinfection by-products is well known and explained in detail. In contrast to chlorinated disinfection by-products identified in drinking water resulting from treatment of freshwater, brominated chemicals are dominating the by-products when disinfecting marine or brackish waters. Some of these disinfection by-products are also naturally produced by marine organisms in particular algae.

The quantification of global inputs of disinfection by-products and its analogues of natural origin is difficult due to heterogeneity in available data on different sources of such compounds. As bromoform is the most abundant disinfection by-product, it can be used as a proxy for the overall inputs of disinfection by-products from the different sectors.

The total estimated anthropogenic bromoform production and discharge adds up to 13.5 - 21.8 x 10^6 kg/a (kg per year) with contribution of 0.86 x 10^6 kg/a from ballast water; 11.8 to 20.1 x 10^6 kg/a from cooling water; 0.89 x 10^6 kg/a from desalination; 0.03 x 10^6 kg/a from saline sewage treatment (Hong Kong only). The natural bromoform production in marine water is estimated to be 76 to 870 x 10^6 kg/a. These figures are best estimates only not based on comprehensive and detailed studies in all cases. However, the dimension is well captured and should reflect the figures within an order of magnitude. On a global scale, the mass of naturally generated brominated hydrocarbons exceeds the anthropogenic production taking bromoform as a proxy. In specific coastal areas, man-made inputs can be the dominant source of brominated halocarbons in the marine environment compared to natural generation, depending on the discharge volumes from local industries, electricity power plants and ships.

The natural biotic and abiotic production and the identification of brominated, chlorinated and iodinated chemicals is complicated by the specific biosynthetic pathways in different marine species and the challenging chemical analyses. Specific data on the bio-generation of halogenated hydrocarbons in the oceans and coastal areas are often missing due to a lack of funding for basic marine research.

Ballast water management on ships has just started on a limited number of vessels and will thus increase significantly within the next decades. The load of disinfection by-products can only be estimated at this moment as different technologies are to be installed on ships, each leading to a specific generation of chemical by-products. Ballast water treatment could become a significant anthropogenic source for brominated hydrocarbons. However, there is a sophisticated regulatory procedure for approving ballast water management systems, thereby efficiently minimizing the impact on the marine environment and excluding significant toxic effects on humans and marine life.

Today, the knowledge on local and global inputs of disinfection by-products by cooling water treatment and the resulting environmental exposure is limited to specific regions and types of industrial plants. Most of the publicly available data are for the French and British nuclear power plants particularly along the English

Channel, at the Atlantic coast and the North Sea coast. Large volumes of water are treated against biofouling in power plants, although on a relatively low dosage, often with pulsed treatment and short exposure time in cooling waters. This results in significantly lower concentrations of brominated by-products compared to treated ballast water.

The desalination of marine water has become increasingly important during the last decades and is estimated to rapidly increase in the future due to population growth in coastal areas and climate change. Data from different plants show significant differences in active substance dosage, exposure time and generation of disinfection by-products. These variations result from the use of different technologies and the differing content of dispersed organic material in the coastal zones, e.g., brackish waters. However, the report estimates that this input represents the second largest part of the anthropogenic input of brominated hydrocarbons into the environment.

Disinfection of wastewater is to prevent the spread of pathogenic microorganisms. It is widely applied worldwide, although its use depends on regional situations and national legal requirements. In most cases, wastewater is not of marine origin thus not creating brominated but chlorinated disinfection by-products. The regulations in the USA and Europe often require a dechlorination technology before discharging the wastewater into coastal marine environments. Today, an extrapolation of the global and regional inputs of disinfection by-products is not possible due to the different and heterogeneous treatment regimes. However, detailed data exist for Hong Kong, where seawater is used for flushing toilets, resulting in nearly a quarter of the total water usage in this city. In this case, a strict regulatory system including monitoring of the brominated disinfection by-product concentrations is in place to minimize the impact on the coastal environment.

The report presents approaches for assessing the risks of disinfection by-products for humans and the environment. Up to now, the only globally accepted and most sophisticated procedure has been created for the approval of ballast water treatment systems. Risk assessments commonly evaluate specific (in general single) chemicals with their toxicity, including the determination of a no effect level, and the exposure concentrations. The application of such methods is complicated by the high number of disinfection by-products. Thus, a prioritization and selection of chemicals is needed. However, there are also field data available, mostly from French nuclear power stations and from Hong Kong, offering information about the exposure and potential impacts on marine life. When bromoform, the most abundant disinfection by-product is released into the atmosphere, it impacts the atmospheric chemistry and disturbs tropospheric ozone chemistry, thus leading to ozone depletion.

This report could not entirely clearly identify the strength of the impact on marine life, human health and the atmosphere created by the disinfection by-products. This is due to the limited knowledge on the generation of disinfection by-products. In particular, number, size and types of emitting industries are not fully identified. Future market shares of types of technologies installed on vessels responding to the recent implementation of ballast water management regulations are open to speculation. Based on assumptions and data quality, the estimates on the volume of natural generation of halogenated hydrocarbons in the marine environment vary. The very fragmentary measurements of halogenated hydrocarbons in the marine environment do not allow any confirmation of exposure assessment models. Thus, the exposure of marine life could not be quantified with strong scientific reliability. Although an impact on the marine environment, human health and the atmosphere is assumed, the strength of such impact remains unclear. At the moment, a specific risk assessment is not possible, mainly due to scarce exposure data.

In the report it is proposed to strengthen international efforts in marine science to build up a global data set on concentrations of halogenated hydrocarbons in the marine environment. Better scientific knowledge and thus more basic research on marine life is needed to identify the important biological pathways for the generation of halogenated hydrocarbons in various marine species and ocean regions. More Information is needed on the regional input of brominated hydrocarbons by desalination plants. Whereas scientific data on the input by nuclear power stations are existing in some regions, the global picture on power plants is still fuzzy. An overview on disinfected wastewater discharges from sewage plants as well as from industrial plants after disinfecting cooling water is missing. After the introduction of ballast water treatment on most vessels in the years to come, measurements should start in harbours and coastal zones to validate the exposure models and the scenarios used by the regulatory approval of such systems to protect from health and environmental hazards. Internationally harmonized projects for analyzing the discharges of disinfection by-products should be initiated. GESAMP could offer advice on such international projects and could support harmonization of approaches. A future report on the status of research could identify emerging data offering more substantiated impact assessments. Following research needs are identified:

1. More harmonized studies on the different industries are needed, i.e., analyzes of all major DBPs identified in at least one of the sectors should be added to the test plans in the different sectors in order to allow a more systematic overview on DBPs produced by different types of industrial applications.
2. A systematic understanding of the drivers for DBP formation and their relative abundance would be desirable.
3. Concerning the risk assessment for aquatic life and human health, an elaborated approach has been established for ballast water treatment. This approach could serve as a reference for assessment schemes in the other sectors.
4. A strengthening of international efforts in ocean science to build up a better database on concentrations of halogenated hydrocarbons in the marine environment

is advised. More scientific knowledge on marine life is needed to identify the important biological pathways for the generation of halogenated hydrocarbons in different marine species and regions.

5 The impact on the atmosphere needs further consideration.

GESAMP could offer advice on international projects and could support harmonization of approaches. A future report on the status of research could identify emerging data offering more substantiated impact assessments.

ACRONYMS

AOBr	Adsorbable organic bromine
AOC	Assimilable organic carbon
AOX	Adsorbable organic halogen
AS	Active substance (of a ballast water management system)
BA	Basic approval (of a ballast water management system by IMO)
BWMC	*International Convention for the Control and Management of Ships' Ballast Water and Sediments*
BWMS	Ballast water management system
BDCM	Bromodichloromethane
BP	Bromophenol
BWWG	Ballast Water Working Group; see GESAMP-BWWG
CDBMA	Chlorodibromomethylamine
CEC	Contaminant of emerging concern
CFC	Chlorofluorocarbon
CMR	Carcinogenic, mutagenic and reprotoxic properties
COP 21	United Nations Framework Convention on Climate Change, 21st Conference of the Parties
DBAA	Dibromoacetic acid
DBAcAm	Dibromonated acetamides
DBAN	Dibromoacetonitrile
DBM	Dibromomethane
DBCM	Dibromochloromethane
DBP	Disinfection by-product
2,4-DBP	2,4-Dibromophenol
2,6-DBP	2,6-Dibromophenol
DCAA	Dichloroacetic acid
DCBM	Dichlorobromomethane
DCP	Dichlorophenol
DHA	Dihalogenated acetaldehyde
DL	Detection limit
DMEL	Derived minimal effect level
DMF	Dual media filtration (as pre-treatment in a desalination plant)
DMS	Dimethylsulfide
DNEL	Derived no-effect level
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EfOM	Effluent organic matter
EOX	Extractable organic halogen
ERF	Environmental Risk Factor
ERA	Environmental risk assessment
EPR	European pressurized reactor
ESI-tqMS	Electrospray ionization triple quadrupole mass spectrometry
FA	Final approval (of a ballast water management system by IMO)
FAO	Food and Agriculture Organization of the United Nations
FO	Forward osmosis
FT-ICR MS	Fourier transform - ion cyclotron resonance mass spectrometry
GC-MS	Gas chromatography – mass spectrometry
GAC	Granular activated carbon

GCxGC-tqMS	Two-dimensional GC-quadrupole mass spectrometry
GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection
GESAMP-BWWG	Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) - Ballast Water Working Group
GISIS	Global Integrated Shipping Information System
HAA	Haloacetic acid
HAcAm	Haloacetamide
HalOcAt	Halocarbons in the ocean and atmosphere database project
HAN	Haloacetonitrile
HATS	Harbour area treatment scheme (Hong Kong)
JECFA	Joint FAO/WHO expert committee on food additives
HK	Hong Kong
HO_x	Hydrogen oxide radicals
HRAM	High resolution-accurate mass
IAEA	International Atomic Energy Agency of the United Nations
IARC	International Agency for the Research on Cancer (of the World Health Organization of the United Nations)
IMO	International Maritime Organization
IR	Inhalation rate
ISA	International Seabed Authority of the United Nations
LC	Lethal concentration (mostly LC50: lethal concentration for 50% of tested organisms)
LC ESI-tqMS	Ultraperformance triple quadrupole mass spectrometry
LC-MS	Liquid chromatography–mass spectrometry
LD	Lethal dose (mostly LD50: lethal dose for 50% of tested organisms)
LOAEL	Lowest observed adverse effect level
MADC	Maximum allowable discharge concentration
MBAA	Monobromoacetic acid
MIM	Monoiodomethane
MCAA	Monochloroacetic acid
MF	Microfiltration
NIS	Non-indigenous species
MSF	Multi-stage flash distillation (type of desalination plant)
NDMA	N-nitrosodimethylamine
NF	Nanofiltration
NGO	Non-governmental organization
NMOR	N-nitrosomorpholine
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration
NOM	Natural organic matter
NO_x	Nitrogen oxides
PAA	Peracetic acid
PAH	Polyaromatic hydrocarbon
PBDE	Polybrominated diphenyl ether
PBT	Persistent bioaccumulative and toxic properties
PCB	Polychlorinated biphenyl
PEC	Predicted environmental concentration
PMOC	Persistent mobile organic chemical
PNEC	Predicted no effect concentration
POP	Persistent organic pollutant

POX	Purgeable organic halogen
PPCP	Pharmaceutical and personal care product
PWR	Pressurized water reactor
(Q)SAR	(Quantitative) structure activity relationship
RCR	Risk characterization ratio (also called risk quotient, RQ)
RO	Reverse osmosis
RQ	Risk quotient (also called risk characterization ratio, RCR)
SAR	Structure activity relationship
SBS	Sodium bisulfite
STW	Sewage treatment works
TBAA	Tribromoacetic acid
TBM	Tribromomethane (Bromoform)
TCM	Trichloromethane (Chloroform)
TBP	Tribromophenol
TCAA	Trichloroacetic acid
TCP	Trichlorophenol
TGD	Technical Guidance Document on Risk Assessment
THA	Trihalogenated acetaldehyde
THM	Trihalomethane
TOBr	Total organic bromine
TOX	Total organic halogen
TRO	Total residual oxidants
TSS	Total suspended solids
TTL	Tropical tropopause layer
UF	Ultrafiltration
UN	United Nations
UNDP	United Nations Development Programme
UNEP	United Nations Environment Programme
IOC-UNESCO	Intergovernmental Oceanographic Commission of the United Nations Educational, Scientific and Cultural Organization
UNIDO	United Nations Industrial Development Organization
USEPA	United States Environment Protection Agency
USFDA	United States Food and Drug Administration
UV	Ultraviolet radiation
VOC	Volatile organic compound
VSLS	Very short-lived substances
WET	Whole effluent toxicity
WMO	World Meteorological Organization of the United Nations
WWTP	Wastewater treatment plant

1 INTRODUCTION

Marine water is subject to disinfection for several purposes. Ballast water management aims to prevent, minimize and ultimately eliminate the risks to the environment, human health, property and resources resulting from the discharge of harmful aquatic organisms and pathogens from ships. In cooling water circuits, disinfection strives to reduce biofouling and clogging in order to assure good thermal exchange rates and reduce maintenance needs. In desalination plants, disinfection seeks to limit biofouling, but also to control pathogens to assure a reliable and safe drinking water supply in arid regions. In wastewater treatment, the main function of the treatment is to limit the discharge of pathogens. This is also the case for seawater toilet systems, which are used in some coastal areas with limited freshwater supply, with the city of Hong Kong being the most relevant case worldwide. Furthermore, oxidative treatment is performed in miscellaneous sectors such as aquaculture and seawater aquaria to control animal diseases and improve water quality. However, these latter applications are less important sources of disinfection by-product (DBP) production in quantitative terms and are not further addressed in this report.

Different oxidizing chemicals can be used for disinfection purposes; they can either be added from storage tanks or be generated *in situ*. Some disinfection techniques (electro-chlorination, chlorination, ozonation) generate similar reactive intermediate oxidants and thus produce similar patterns of DBPs. Other oxidation techniques (e.g., chlorine dioxide, peracetic acid and hydrogen peroxide) typically produce different patterns of disinfection by-products (DBPs). However, relative composition and absolute concentrations of DBPs also depend on process parameters such as concentration of active substances, reaction time, as well as the chemical and physical characteristics of the treated water (salinity, organic matter, temperature, etc.). Therefore, DBP generation typically varies between different applications and sites even if similar or even identical techniques are applied.

More than 700 anthropogenic DBPs have been identified, mainly haloorganic compounds. However, haloorganic (also named organohalogen) compounds are generated not only during oxidative disinfection. The ubiquitous abundance of halides has resulted in the evolution of organohalogens in all regions of the earth. Haloorganic compounds are part of the spectrum of naturally generated compounds. More than 5000 organohalogen compounds have been described to be formed by marine organisms. Most of these compounds are distinct from disinfection by-products and are formed in small quantities by specialized organisms. However, some of the DBPs with the highest concentration in seawater disinfection are also produced as natural organohalogens, with bromoform being a major DBP and similarly a major natural halocarbon product in the marine environment. Sea grass and certain algal species are identified as main sources. In this report, anthropogenic production of DBPs is compared to naturally generation of these chemicals.

This report tries to assess the relevance of the input of disinfection by-products (DBPs) through anthropogenic activities such as industrial cooling units, desalination plants, ballast water treatment in ships and wastewater treatment/seawater toilets into the marine environment. Furthermore, as some of the DBPs are also produced naturally in the marine environment, the report also intends to give an overview on DBP-like compounds and quantities formed through natural processes. This is in particular to compare anthropogenic DBP production to the overall production. One important aim is the estimation of potentially harmful effects of anthropogenic DBPs to aquatic organisms in the marine environment, to human health and to the atmosphere compared to those from natural sources.

This report is the result of an international GESAMP workshop held in Berlin, Germany, 22-23 November 2018, at the German Federal Institute for Risk Assessment. At this event, the involved experts with different scientific backgrounds and work fields joined to exchange on the state of knowledge regarding DBP inputs into the marine waters. In the years following the workshop, this report on the actual state of knowledge and the challenges of this topic was compiled. It is a scoping exercise providing a basis to the organizations involved in GESAMP for the decision on future actions and research needs concerning potential risks of these compounds to marine life, human health and the atmosphere.

2 NATURAL PRODUCTION OF HALOCARBONS

Formation of organohalogens results from biogenic and abiotic processes in the terrestrial, aquatic marine and atmospheric environment, incorporating chlorine, bromine and iodine into organic compounds. While some organohalogen compounds can be formed photo-catalytically in the atmosphere and in water, the main source of most organohalogens in nature is their production as secondary metabolites by organisms. More than 5000 organohalogen compounds have been identified as natural products, most of which are of marine origin and contain bromine (Gribble 2010).

2.1 Sources and biological generation

The competition of marine organisms for limited resources has led to the emergence of many smaller and larger molecules, which contain halogens and are part of the natural defense mechanisms against attacks by micro-organisms, as chemical defense against overgrowth and as protection against predation. Sponges, sea squirts, salps, *appendiculariae*, corals, mosses, snails, molluscs, fungi, worms, micro-organisms associated with larger organisms, micro- and macroalgae, bacteria, cyanobacteria and other marine organism are capable of producing individual halogenated compounds. The physical and chemical conditions in the marine environment require specific biosynthetic pathways. Various halogen-peroxidases, as well as region-specific halogenases and methyl-transferases of marine and terrestrial organisms catalyze the halogenation reactions of organic compounds in the presence of chloride, bromide or iodide ions (Gribble 2010). Natural compounds from the metabolism of marine organisms can be accumulated to high concentrations in higher trophic organisms, which are not the producers of these compounds (e.g. Estrella *et al.* 2018).

2.2 Identified compounds

Most of the identified compounds are complex heterocyclic and aromatic molecules and are unique to individual organisms, thus not far spread in the environment (Gribble 2010 and references therein). Some of the structures are analogous to anthropogenic compounds and even complex brominated phenols, dioxins and dibenzofurans can be formed naturally by organisms. Several bromophenols, which are also formed during seawater disinfection, have been found in massive amounts in acorn worms and algae. Precursors of chlorinated, brominated and iodinated phenolic compounds can also be complex humic substances. Macroalgae, including brown, green and red algae and pelagic microalgae produce and release simple low molecular weight organohalogens such as halogenated alkanes, alkenes, alcohols, acids, aldehydes, ketones, amides, epoxides, esters, terpenes and phenols, but also retain more complex halogenated molecules. Especially red algae have unique biosynthetic pathways and can contain hundreds of different halogenated compounds, most of which are brominated. Two hundred different organohalogens have also been identified in one species of cyanobacteria (Gribble 2010). Microalgae essentially produce a mixture of halogenated methanes, with ratios of the different compounds varying from one study to the other. In quantitative terms, tribromomethane (bromoform) is always the dominant compound (Quack and Wallace 2003) and also occurs in large quantities as degradation products from more complex molecules (Gribble 2010; Paul and Pohnert 2011). Furthermore, it is the main compound produced in large amounts from biological processes, which overlap with the spectrum of DBP in oxidative water treatment. While several other bromoorganic compounds like bromophenols are produced from marine organisms, the subsequent analysis in this chapter focuses mainly on bromoform.

2.3 Quantification of bromoform production

Most of the natural organohalogen compounds produced are unique to individual marine organisms and are not widely dispersed in the marine environment (Gribble 2010). However, in a square kilometer of dense communities of marine fauna, e.g. worms (Higa and Sakemi 1983) and flora, e.g. macroalgae (Paul and Pohnert 2011), hundreds of tonnes of mainly brominated organics (including many different phenols) with contributions of iodinated and chlorinated compounds can be produced per year. Volatile haloalkanes from several marine sources represent a major part of the total quantity of organohalogens in the world's Oceans. As some of these compounds play an important role in the depletion of tropospheric and stratospheric ozone, their distribution has been relatively well studied in recent years. Bromoform is generally the major vector of natural organic bromine of marine origin to the atmosphere, while in the remote open ocean dibromomethane is often more significant (Ziska *et al.* 2013). Both are significant factors in the ozone depletion process. Ziska *et al.* (2013) provide an overview on existing measurements and model estimates for bromoform, dibromomethane and monoiodomethane concentrations in ocean surface waters based on different studies (Carpenter and Liss 2000; Liu *et al.* 2011; Quack and Wallace 2003; Yokouchi *et al.* 2005) and data extracted from the HalOcAt database (https://halocat.geomar.de/web/halocat/home) consisting of data from coastal stations, ship operations and aircraft campaigns.

In general, polar species appear to produce the least bromoorganic compounds, whereas subtropical and tropical species may be more efficient producers. Measured production rates for bromoform from marine algae range from 4 to 5,000 pmol bromoform per gram fresh weight per hour (as summarized by Quack and Wallace 2003; Leedham *et al.* 2013). Macroalgae have been estimated to produce 220,000 tonnes of bromoform annually with brown algae producing 60% of the total, due to their large biomass (Carpenter and Liss 2000). Some of these algae species are also cultured and thus have to be considered as anthropogenic sources.

The fate of the produced organohalogens in the marine environment is including uptake by organisms, biodegradation and -transformation, as well as abiotic trans-

formation and volatilization. The natural reactions and microbial respiration of halogenated organic molecules occur at significant rates, which are however much lower than other metabolic pathways such as sulfate reduction and methanogenesis. Volatilization into the atmosphere is a major pathway for low molecular compounds in the surface ocean, inter-tidal regions and shallow coastal areas.

While the metabolic processes are important parts of the oceanic bromine cycle, the main loss process of volatile compounds is their emission to the atmosphere. Hereby, bromoform is the major vector of organic bromine from the ocean to the atmosphere and together with dibromomethane, co-produced from micro- and macroalgae and as debromination product from bromoform, is a compound of concern. Both contribute to ozone depletion in the troposphere and the stratosphere with bromine, which has a sixty times higher ozone depletion potential than chlorine.

An overview on studies on estimated annual production rates of bromoform is provided in Table 2-1. Each of these studies targets different areas, such as the tropics, the open oceans excluding coastal areas or the global ocean. The most realistic range for natural bromoform production in global ocean water, which is the most relevant when aiming quantification of global budgets, is considered to be 385 to 870 x 10^6 kg/a (Wang *et al.*, 2019; Yokouchi *et al.*, 2005). As volatilization is assumed to be the main path of loss from the ocean for bromoform with an atmospheric lifetime of approximately 2 weeks and dibromomethane with an atmospheric lifetime of approximately 5 months, the annual production is assumed to be similar to the global flux to the atmosphere. However, these so-called "bottom-up" estimates based on the interpolation of surface atmospheric and oceanic measurements do not agree well with recent so-called "top-down" approaches based on atmospheric modelling. The latter generally result in higher emission estimates. This disagreement leaves room for significant missing sources in the global budget. Spatial and temporal events of high oceanic bromoform emissions are likely under-represented, which can be important for the transport of bromine into the troposphere and lower stratosphere (Ziska *et al.* 2013). Due to sparse measurements and limited process understanding, existing estimates of global air-sea flux distributions of bromoform and other halomethanes are still subject to large uncertainties. Coastal areas are underrepresented in observations and modelling.

Table 2-1: The annual natural marine production of bromoform (in 10^6 kg/a)

Amount[1]	**Area/Source**	**Published by**
220	macroalgae	Carpenter and Liss (2000)
840	global ocean	Quack and Wallace (2003)
870	global ocean	Yokouchi *et al.* (2005)
590	global ocean	Warwick *et al.* (2006)
840	global	Butler *et al.* (2007)
160	open ocean	Butler *et al.* (2007)
370	tropics	Palmer and Reason (2009)
530	global ocean	Ordóñez *et al.* (2012)
450	open ocean	Sousa Santos (2009)
300	global ocean	Liang *et al.* (2010)
270	open ocean	Liang *et al.* (2010)
76	open ocean	Stemmler *et al.* (2015)
385	global ocean	Wang *et al.* (2019)
210	global ocean	Ziska *et al.* (2013)

[1] Estimated amount of annual marine natural production or emissions

Table 2-2 provides an overview of marine surface concentrations of bromoform. Concentrations are higher in the equatorial region, upwelling areas, near coastal areas and in shelf regions. This is consistent with macroalgae and anthropogenic sources along the coastlines as well as biological sources in upwelling areas (Ziska *et al.* 2013). The data provided refer to mean values for larger regions. Local concentrations can be significantly higher. Nightingale *et al.* (1995) observed concentrations up to 0.47 μg/L in brown algae beds. Industrial areas can show concentrations in the several μg/L range, e.g. 0.5 to 2.2 μg/L in the Gulf of Fos (Boudjellaba *et al.* 2016) and more than 10 μg/L in the effluents of a power plant at the west coast of Korea (Yang 2001).

Table 2-2: Concentrations of bromoform in different sea regions

Area	**Bromoform [ng/L]**	**Published by**
North Atlantic	1.4 ± 0.85	Fogelqvist and Krysell (1991)
Northern North Sea	2.4 ± 1.4	Fogelqvist and Krysell (1991)

Whole North Sea	8.4 ± 7.7	Fogelqvist and Krysell (1991)
English Channel	10.1 ± 5.9	Fogelqvist and Krysell (1991)
Open ocean	0.03-0.15	Carpenter *et al.* (2009)
equatorial region	~1.5	Ziska *et al.* (2013)
upwelling areas (e.g., the Mauritanian upwelling region)	~5.3	Ziska *et al.* (2013)
near coastal areas	~4.3-10.6	Ziska *et al.* (2013)
shelf regions	~2-8	Ziska *et al.* (2013)
Tropics	0.9	Butler *et al.* (2007)

2.4 Conclusion

A highly diverse variety of halogenated metabolites are produced by terrestrial and marine organisms, as well as through photochemical and other natural abiotic processes. Brominated compounds dominate the molecules of marine origin. A variety of volatile halogenated compounds is emitted from the ocean and contributes to tropospheric chemistry, aerosol formation as well as to stratospheric ozone depletion. In quantitative terms, bromoform is the naturally produced haloorganic compound, which is produced by far in largest amounts in marine water. A realistic range of bromoform production in global ocean water is estimated to 385 to 870 x 10^6 kg/a. Natural biotransformation and respiration of halogenated organic molecules occur in many terrestrial and marine environments. Coastal areas are underrepresented in observations and modelling.

3 GENERATION OF DISINFECTION BY-PRODUCTS IN MARINE WATERS

Various chemical oxidants are used in water treatment for disinfection purposes, including chlorine (Cl_2), ozone (O_3), monochloramine (NH_2Cl), chlorine dioxide (ClO_2), peracetic acid (CH_3CO_3H) and hydrogen peroxide (H_2O_2). The lifetime of chemical oxidants during disinfection processes is mostly controlled by reactions with the dissolved organic matter (DOM), which is present in all kinds of natural waters. Typically, a large fraction of the applied oxidant dose reacts with DOM. This leads to a loss in efficiency of the disinfection process and to the formation of oxidant-specific disinfection by-products (DBPs) from the reactions of chemical oxidants with various DOM moieties such as phenolic functional groups. In addition, the reactions of chemical oxidants with natural or anthropogenic bromide and/or iodide may lead to a different speciation of the formed DBPs. This is of great importance for marine and brackish waters, where the oxidant chemistry is largely controlled by the high concentrations of bromide. After the first discoveries of formation of haloforms during chlorination of natural water in the 1970s (Rook 1974), research has been conducted to understand the processes of DBP formation, as well as their identification and quantification in different applications. To date, approximately 700 DBPs have been identified in various water matrices (Richardson and Ternes 2018) and with the diversity and complexity of precursors the total number of DBPs in drinking water alone will likely exceed 1,000 (Li and Mitch 2018).

3.1 Oxidant chemistry in marine water

Formation of hypobromous acid (HOBr)

The oxidant chemistry in marine and brackish waters is largely controlled by the high content of halide ions (Cl^-: 19,000 mg/L (542 mM), Br^-: 65 mg/L (0.81 mM), I^-: 0.05 mg/L (0.0004 mM)). Chemical oxidants cannot oxidize chloride, which, however, plays an indirect role in the speciation of the formed hypohalous acids. Bromide is by far the main reaction partner for the applied oxidants, because of a combination of the relatively high concentration and the second order rate constant for its reactions with chemical oxidants (Table 3-1). Iodide has the highest reactivity with chemical oxidants and depending on the primary oxidant may or may not lead to the formation of iodinated organic compounds (see below).

During oxidative water treatment of marine and brackish waters, bromide is oxidized to various bromine species with hypobromous acid/hypobromite (HOBr/OBr^-) being the most important ones (for kinetics see Table 3-1):

$HOCl + Br^- \rightarrow HOBr + Cl^-$
(equation 1)

$O_3 + Br^- \rightarrow BrO^- + O_2$
(equation 2)

$CH_3C(O)OOH + Br^- \rightarrow HOBr + CH_3COO^- + H_2O$
(equation 3)

$2NH_2Cl + H^+ + Br^- \rightarrow NHClBr + Cl^- + NH_4^+$
(equation 4)

Table 3-1: Kinetics of the reactions of selected oxidants with bromide and iodide. The half-life times for the oxidants in presence of 65 mg/L bromide and for iodide in presence of the selected oxidants are also shown.

Equation[2]	Oxidant	Rate constant bromide-	t1/2 oxidant	Rate constant iodide-	t1/2 iodide (1 mg/L oxidant)
1	HOCl	1150 $M^{-1}s^{-1}$	0.74 s	4 x 10^8 $M^{-1}s^{-1}$	0.12 x 10^{-3} s
2	O_3	160-258 $M^{-1}s^{-1}$	3-5 s	2 x 10^9 $M^{-1}s^{-1}$	0.017 x 10^{-3} s
3	$CH_3C(O)OOH$	0.24 $M^{-1}s^{-1}$	1 h	4.2 x 10^2 $M^{-1}s^{-1}$	124 s
4	NH_2Cl	2.8 x 10^6 $M^{-2}s^{-1}$	50 min	2000 $M^{-1}s^{-1}$ (pH 7)	24 s
	ClO_2	$< 10^{-4}$ $M^{-1}s^{-1}$	> 2300 h	1870 $M^{-1}s^{-1}$	24 s

[2] Equation number according to the numbers given in text above in brackets.

Even though peracetic acid can oxidize bromide and iodide to the corresponding hypohalous acids, hydrogen peroxide, which is typically present in high concentrations in peracetic acid solutions, reduces HOBr and HOI back to the halide ions (Shah *et al.* 2015a; von Gunten and Oliveras 1997). Chlorine dioxide reacts very slowly with bromide (Hoigné and Bader 1994), and HOBr can only be formed indirectly via the production of HOCl from the reaction with phenolic moieties (Terhalle *et al.* 2018; Rougé *et al.* 2018). Hydrogen peroxide does not oxidize bromide to HOBr at circumneutral pH (von Gunten and Oliveras 1997).

HOBr undergoes an acid-base speciation with a *pKa* of 8.8 (equation 5) (Heeb *et al.* 2014).

$HOBr \leftrightarrows H^+ + OBr^-$ (equation 5)

Reaction kinetics are typically dominated by the protonated form (HOBr), because it is the stronger electrophile than hypobromite (von Gunten and Oliveras 1997).

Based on the kinetic data presented in Table 3-1 (half-life times) even though different primary oxidants might be used, in saline waters the active oxidant is mostly HOBr, which has consequences on the extent of DBP formation and speciation. Based on aqueous phase equilibria, partly other bromine species such as Br_2, BrCl, and Br_2O can be formed in saline waters (Heeb *et al.* 2014). A systematic and critical literature review on the reactivity of $HOBr/OBr^-$ and other bromine species with inorganic and organic compounds has been conducted previously (Heeb *et al.* 2014).

Fate of hypobromous acid

Hypobromous acid can be further oxidized to bromate or react with inorganic (e.g., hypoiodous acid (HOI)) and/or organic matrix (DOM moieties) constituents. Further oxidation of $HOBr/OBr^-$ is most relevant during ozonation where bromate is formed through a complicated mechanism including both ozone and OH-radical reactions (von Sonntag and von Gunten 2012). Bromate has also been observed in electrochlorination of seawater, but typically in lower concentrations (Jung *et al.* 2014). Furthermore, bromate can be formed by catalytic disproportionation of HOBr in presence of CuO, which is a corrosion product of copper in contact with chlorine/bromine (Liu *et al.* 2012).

Some moieties in the DOM (e.g., phenols) react readily with HOBr via electron transfer or electrophilic aromatic substitution reactions (Criquet *et al.* 2015). Electrophilic aromatic substitution by HOBr leads to the formation of brominated high- and low-molecular-weight organic DBPs. The sum of these high- and low-molecular-weight organic compounds constitutes the total organic bromine (TOBr) or adsorbable organic bromine (AOBr) (Kristiana *et al.* 2009; Hua and Reckhow 2006; Langsa *et al.* 2017).

Fate of hypoiodous acid

Table 3-1 shows that iodide is quickly oxidized to HOI by all chemical oxidants (I^- in the case of ClO_2). Similar to HOCl and HOBr, HOI can react with DOM moieties leading to the formation of iodinated DBPs (Allard *et al.* 2015). However, the lifetime of HOI is crucial, since HOI is oxidized by ozone quickly or by HOCl with moderate kinetics to iodate, a non-toxic sink for iodine (Bichsel and von Gunten 1999). Since HOBr is the major product of ozonation and chlorination of saline waters, the kinetics of the reaction of HOI with HOBr is crucial.

The apparent second order rate constant for this reaction at pH 7 is $k_{app}(HOBr/IO^-)$ = 740 M^{-1} s^{-1} (Criquet *et al.* 2012), which yields a half-life time of HOI of 65 s for a HOBr concentration of 14 μM, corresponding to a chlorine dose of 1 mg/L. Based on the relatively short half-life time and the slower reaction kinetics for the reaction of HOI with phenolic moieties compared to HOBr (Lee *et al.* 2005), the formation of iodinated DBPs is expected to be very low during ozonation or chlorination of saline waters (Criquet *et al.* 2012). In contrast, during chloramination or treatment with peracetic acid (absence of H_2O_2), a significant formation of iodinated DBPs is expected to take place since the half-life of HOI is long during chloramination processes (Zhao *et al.* 2016; Shah *et al.* 2015a).

3.2 Identity of DBPs in marine water

In the following sections, an overview of some of the typically observed and most prevalent DBPs is provided. As DBPs were first discovered in chlorinated drinking water, most DBP groups first detected were chlorinated (Rook 1974). Later on, when bromide-containing waters were investigated including marine waters, many bromo-analogues of Cl-containing DBPs were identified (Rook *et al.* 1978). Bromine-containing compounds represent the largest group of DBPs

detected in marine waters (Werschkun *et al.* 2012; Manasfi *et al.* 2019). Nitrogenous DBPs can be formed from oxidation reactions with relatively labile proteins and peptides or derived from algal organic matter present in uptake water as extracellular organic matter from algal cell exudates or intracellular organic matter released after cell lysis during oxidative treatment. The types and concentrations of the brominated DBPs depend strongly on the specific oxidizing conditions (oxidant, dose, reaction time, temperature, etc.) and on the characteristics of the organic matter present. In the following paragraphs, some important DBPs in saline waters are discussed. Some of the highlighted DBPs are found at higher concentrations, however, DBPs detected in lower concentrations may also play an important role as some DBPs have been found to be significantly more toxic than others (Wagner and Plewa 2017; Plewa *et al.* 2008).

3.2.1 *Trihalomethanes and other haloalkanes*

Trihalomethanes (THMs) are regulated in drinking water and quantitatively the most important group of DBPs generated during chlorination of both freshwater and marine water (WHO 2017). In freshwater containing low levels of bromide, chloroform ($CHCl_3$) is the major THM generated, whereas its brominated analogue, bromoform, predominates at high bromide levels (Richardson *et al.* 1999). All four chlorinated/brominated THMs ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) have been detected in chlorinated marine water, with chloroform ($CHCl_3$) being very minor and bromoform ($CHBr_3$) being by far the major THM (Shah *et al.* 2015b). Bromoform was estimated to represent 93 to 97% of all THMs formed in marine waters (Khalanski and Jenner 2012). The concentrations of iodinated THM are expected to be significantly lower than those of brominated THMs because the iodide concentration is much lower than the bromide concentration and the lifetime of HOI is relatively short except when NH_2Cl is used as the oxidant (Table 3-1) (Zhao *et al.* 2016).

Other haloalkanes including dihalomethanes, tetrahalomethanes, and dihalopropane have been identified in drinking water treated with ozone and chlorine/chloramine in very low concentrations. In the presence of bromide, the speciation of these haloalkanes was mostly brominated (Richardson *et al.* 1999).

3.2.2 *Haloacetic acids*

Haloacetic acids (HAAs) typically represent the second largest group within the whole DBP mixture. In marine water, dibromoacetic acid (DBAA) is observed as the compound with the second highest concentration after bromoform followed by tribromoacetic acid (Shah *et al.* 2015b). Other HAAs can be detected in considerably lower concentrations, including monobromoacetic acid, but also mono-, di- and trichloroacetic acid and bromochloro-, bromodichloro- and dibromochloroacetic acids (Fabbricino and Korshin 2005). HAAs are often summarized as the sum parameter HAA5 (sum of concentrations of monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA)) or HAA9, which include HAA5 and the sum of the concentrations of bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA). The relative contribution of HAAs to total DBPs has been reported to be 4 times higher in deep-ocean water (1500 m depth) compared to coastal seawater near the surface (Fabbricino and Korshin 2005). This highlights the influence of the characteristics of the DOM on the formation of DBPs

3.2.3 *Haloacetonitriles*

Haloacetonitriles (HANs) typically occur at higher concentrations in chlorinated and chloraminated drinking waters than many other nitrogen containing DBPs (N-DBPs) such as nitrosamines, halonitromethanes, and haloacetamides (Krasner *et al.* 2006). In chlorinated seawater, HANs constitute only a small portion of the formed halogenated DBPs with dibromoacetonitrile being the predominant HAN (Fabbricino and Korshin 2005). The formation of HANs is related to the presence of nitrogenous precursors in water. Natural organic matter (NOM) and other nitrogenous compounds such as amino acids contribute to the formation of N-DBPs (Li and Blatchley 2007). It seems that the characteristics and composition of nitrogen containing organic matter is more important than the overall DOM level in determining the formation of HANs (Chu *et al.* 2010; Xue *et al.* 2014).

3.2.4 *Bromate*

Bromate formation mainly occurs during ozonation. In freshwaters, the extent of bromate formation is roughly proportional to the bromide concentration. However, in saline waters bromate concentrations are much lower than expected from the high bromide levels. This is mainly due to the fast quenching of ozone and hydroxyl radicals by bromide, which does not allow any further oxidation of the intermediate HOBr by these two oxidants. It could be shown that bromate formation during ozonation of brackish and marine waters is rapid and complete within nearly 15 min (*Shah et al.* 2015a). Compared to typical bromate concentrations in drinking waters of a few μg/L, bromate formation during ozonation of brackish and marine waters with an ozone dose of 5 mg/L were in the order of 50-150 μg/L (*Shah et al.* 2015a). Chlorination typically does not lead to bromate formation, unless it is an electrochlorination or when the process is catalyzed by metal oxides such as copper oxide (Jung *et al.* 2014; Liu *et al.* 2012). During electrochlorination, the formed HOBr can be directly further oxidized to bromate at the electrode (Jung *et al.* 2014). Bromate is also formed during the treatment of saline waters with peracetic acid in the absence of hydrogen peroxide (Shah *et al.* 2015b). It is suspected that under these conditions bromate is formed by disproportionation of HOBr.

3.2.5 *Aromatic DBPs*

Aromatic DBPs such as 3,5-dibromo-4-hydroxybenzaldehyde, 3,5-dibromo-4-hydroxybenzoic acid, 3,5-dibromosalicylic acid, and 2,4,6-tribromophenol have been detected in bromide-rich water containing humic acid and treated with chlorine (Pan and Zhang 2013). However, some of these aromatic com-

pounds were only transient compounds which disappeared upon further reactions with bromine, leading to the formation of THMs and HAAs as final products (Pan and Zhang 2013). 2,4,6-tribromophenol has been detected in chlorinated seawater cooling effluents of power stations (Allonier *et al.* 1999b; Boudjellaba *et al.* 2016). This may be caused by lower chlorine doses, which leads to a higher stability of this product, which otherwise reacts further. Recent studies have also reported the occurrence of other aromatic DBPs in chlorinated saline wastewater, such as 2,6-dibromo-4-nitrophenol, 3,5-dibromo-4-hydroxybenzaldehyde, 3,5-dibromo-4-hydroxybenzoic acid, and 2,4,6-tribromophenol (Ding *et al.* (2013). There might be other unknown halogenated DBPs in chlorinated saline sewage effluents, which remain to be detected and quantified.

3.2.6 *Sum parameters for halogenated DBPs*

Since only a fraction of DBPs has been identified, global parameters such as adsorbable organic halide (AOX) or total organic halide (TOX) are used to quantify the total organohalogen content (Kristiana *et al.* 2009; Hua and Reckhow 2006; Langsa *et al.* 2017). The measured individual DBPs account for about 40-70% of TOX in chlorinated water (Krasner 2009; Chen *et al.* 2015). Hence, there is a need of sum parameters to evaluate the overall halogenated DBP content. Not all DBPs are identified or are amenable to extraction and chemical analysis techniques used routinely to determine DBPs. This results in a gap between quantified DBPs and the sum of organohalogens (e.g., TOX). Sum parameters are based on specified extraction procedures followed by an electro-chemical method such as microcoulometry. AOX designates organohalogens adsorbable on activated carbon and includes both polar and non-polar DBPs. This operationally defined parameter provides an estimate of the amount of halogens bound to organic structures (i.e. AOBr, AOCl, AOI), which in some way correlates to the total amount of DBPs. However, this parameter was established as a quality parameter for freshwater treatment. Without modification, the AOX measurement is not well suited for marine waters, since high amounts of inorganic halogens (e.g., chloride) disturb the absorption of organic chlorine and affect the measurement. This problem, however, could possibly be overcome with dialysis-based pretreatment to remove chloride (Liu, Ling, *et al.* 2018). Sum parameters adapted to marine waters are purgeable organic halide (POX) and extractable organic halide (EOX). THMs typically represent a significant portion of POX. EOX designates organohalogens extracted in an organic solvent and was specifically developed for measurements in solutions rich in chloride ions ($>$ 1 g/L). Although EOX is designated for organic halogens in sediments, it has been used for seawater (Jenner *et al.* 1998), but it is hampered by a significant loss of organic halogens during the extraction process (Han *et al.* 2017).

It is rarely possible to match the organohalogen concentration analyzed using these global parameters with the sum of the individually identified and quantified compounds, specifically for AOX and EOX. This "gap" suggests that not all DBPs have been identified and accounted for when adding up the individual DBP concentrations. Accordingly, a considerable portion of DBPs remains to be discovered by new analytical techniques. It is possible that macroscopic structures (i.e., partially halogenated but not completely fragmented organic macromolecules) represent a significant portion of these unknown organohalogens.

3.3 Identification and quantification of DBP by analytical methods

The detection and identification of DBPs formed during the oxidation of natural waters is complicated by the diversity of DBPs' physicochemical properties including volatility, polarity, speciation, and molecular weight. As a result of this diversity, there is no single method for the extraction/enrichment, separation, and detection of all DBPs present in a water sample. Early DBP research focused on the identification of volatile low-molecular-weight halogenated DBPs such as THMs identified using gas chromatography coupled to mass spectrometry (GC-MS) (Richardson 2002). Although GC-MS has played a key role in the identification of DBPs, its use is limited to the low-molecular-weight fraction since volatility and therefore amenability for GC analysis diminishes as the molecular weight increases. In addition, for ionic DBPs a derivatization step is often required to obtain adequate volatility and separation in GC. To overcome these limitations, liquid chromatography (LC)-MS techniques have been employed to analyze non-volatile and ionic compounds.

Table 3-2 lists some of the standard USEPA methods recommended for the analysis of DBPs in drinking water. These methods of DBP analysis are still employed for measuring most of the 18 DBPs that are typically regulated in drinking water including five haloacetic acids (HAA5), four THMs, chloral hydrate, dichloroacetonitrile, dibromoacetonitrile, trichloroacetonitrile, cyanogen chloride, formaldehyde and 2,4,6-trichlorophenol, bromate and chlorate (Table 3-2). Toxicological questions have led to interest in the discovery of not yet evaluated or unknown DBPs that may contribute to the overall toxicity of oxidant-treated waters. Furthermore, several studies highlighted a gap between global haloorganic content and identified DBP concentrations in water samples. As a consequence, some attention has shifted to the use of high and ultrahigh-resolution MS techniques to enhance the identification of unknown DBPs.

Table 3-2: List of analytes, with chemical groups and analytical methods.

Chemical Group	US EPA Method	Compounds
Halogenated methanes	524.2	trichloromethane, dichlorobromomethane, dibromochloromethane, tribromomethane (bromoform)
Halogenated hydrocarbon	524.2	1,2,3-Trichloropropane
Halogenated acetic acids	552.2	monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, bromochloroacetic acid, dibromochloroacetic acid, tribromoacetic acid, total HAAs (c.f. text above)
Halogenated acetonitriles	551.1	monobromoacetonitrile, dibromoacetonitrile, bromochloroacetonitrile, chloroacetonitrile, dichloroacetonitrile, tricloroacetonitrile
Inorganics	300.0	chlorate, bromate
Halogenated propionic acid	515.3	2,2-dichloropropionic acid (dalapon)
Halogenated nitroalkane	551.1	chloropicrin

US EPA documents referenced in the table:

300.0 Determination of inorganic anions by ion chromatography (revision 2.1; 1993)

515.3 Determination of chlorinated acids in drinking water by liquid-liquid extraction, derivatization, and gas chromatography with electron capture detection (revision 1; 1996)

551.1 Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection (revision 1;1995)

552.1 Determination of haloacetic acids and dalapon in drinking water by ion-exchange liquid-solid extraction and gas chromatography with an electron capture detector (revision 1; 1992)

524.2 Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry (revision 4.1; 1995)

The development of new analytical techniques including ultrahigh resolution Fourier-transform ion cyclotron resonance (FT-ICR MS), electrospray ionization triple quadrupole MS (ESI-TQ-MS), two-dimensional GC-quadrupole MS (GC x GC-qMS), GC Orbitrap MS, and LC Orbitrap MS has contributed to reducing the gap between identified DBPs and sum parameters of organic halogens (e.g., AOX, POX and EOX). These new techniques have identified DBPs commonly known as emerging DBPs, which include brominated and iodinated DBPs primarily found at elevated levels in treated natural brackish and seawater, as well as aromatic and higher molecular weight DBPs not identified in traditional GC- or LC-MS methods. New nitrogenous, iodinated and brominated DBPs take on added significance as research has shown that they are more toxic than routinely determined DBPs (Plewa *et al.* 2008). In addition, high-molecular-weight halogenated DBPs identified by some of these new techniques are not only more toxic but are also more stable than traditionally determined DBPs (Yang and Zhang 2013; Boudjellaba *et al.* 2016). In oxidant applications where no pretreatment of water is involved this is particularly significant as the primary precursor of DBPs are complex biopolymers (e.g., humic acid) in DOM leading to numerous high-molecular-weight DBPs that may be persistent.

The exploration of methods such as FT-ICR MS and UPLC/ESI-tqMS for identification of high-molecular-weight DBPs is an important step towards fully evaluating oxidant-treated waters. As discussed in other chapters, these high-molecular-weight DBPs tend to be large aromatic compounds that are more lipophilic and possess higher log P values. Consequently, they are more likely to bioaccumulate than the smaller traditionally determined DBPs. Furthermore, these large DBPs may also further hydrolyze to smaller DBPs over time so that the initial measurements of DBP concentrations may change after the water is discharged.

The development and use of analytical methods for the identification of unknown DBPs, structural elucidation and quantification is urgently needed. This may initially be accomplished with methods such FT-ICR MS to determine molecular formulas of new DBPs, but methods also need to be expanded to obtain structural information so that eventually, in conjunction with toxicity evaluation, quantitative structure activity relationships (QSARs) could be developed. This would provide a broader overview of the potential environmental impact of the discharge of water containing complex mixtures of DBPs into marine waters.

3.4 Conclusion

During oxidative water treatment of marine waters, bromide is oxidized to bromine, mainly in the form of hypobromous acid and hypobromite ions. Reactions of these bromine species with organic precursors, mostly natural but also anthropogenic, lead to the formation of predominantly brominated DBPs. The DBPs which have been reported in chlorinated seawater include THMs (predominantly bromoform), haloacetic acids (predominantly dibromoacetic acid), haloacetonitriles (predominantly dibromoacetonitriles) and halophenols

(predominantly 2,4,6-tribromophenol). The latter, as well as other aromatic DBPs, have been identified as intermediates during the reactions of humic acid with bromine. However, they tend to further react in the presence of excess bromine forming THMs and HAAs as stable final products. The release of DBPs by marine algae and other organisms also contributes to the natural occurrence of DBPs, in particular bromoalkanes, in seawater (Chapter 2). Similar to oxidative water treatment of marine and brackish waters, bromoform is by far the most important DBP that is produced by this biogenic production. Advances in mass spectrometry have allowed and continue to contribute to the identification of DBPs in water. Gas chromatography and liquid chromatography coupled with several mass spectrometry techniques are key to increasing the portion of identified DBPs. Combining chemical characterization and toxicity evaluation is important to enhancing our understanding of the environmental impact of the discharge of waters containing DBPs into the marine environment.

4 BALLAST WATER TREATMENT

4.1 Introduction

Ballast water is used to stabilize vessels at sea and is therefore essential for safe and efficient shipping operations. However, discharged ballast water can lead to the introduction of non-indigenous species (NIS), potentially becoming invasive and causing severe ecological, economic and human health impacts (Gollasch 2006; Ruiz *et al.* 2000). The ecosystem impacts of ballast water release arise from the survival of transferred species that then have the ability to establish a reproductive population and spread in the new environment. The introduced organisms are diverse and include species. Over 15 animal phyla are included (with especially common taxa being molluscs, crustaceans, worms, hydromedusae and flatworms) in addition to algae, seagrasses, viruses, bacteria, and other microorganisms (such as diatoms, dinoflagellates, and other protists. Many of the animals in ballast water are in planktonic stages (from larvae to adult), while those in ballast sediments may be adults as well as their diapause (resting) forms (NRC 2011). The effects of species invasions in many areas of the world have been devastating and are causing enormous damage to biodiversity and resources. Many species-specific traits and environmental factors can affect the ability of a species to survive and become invasive in the new environment, all of which can change depending on seasonal influences. The complicated matrix of abiotic factors (i.e., environmental), biotic interactions (e.g., competition, predation, parasitism and pathogens) and these traits makes the prediction of future bio-invasions implausible. However, quantitative data show the rate of bio-invasions is continuing to increase at an alarming rate and new areas are being invaded all the time, often resulting in irreversible damage to the environment (IMO 2018a). Some examples of aquatic bio-invasions causing major impacts can be found on the International Maritime Organization (IMO) website (IMO 2018d).

Shipping has been identified as a major pathway for the spread of species with ballast water and biofouling. As trade and traffic volume have continued to increase over the last few decades, the problem may not yet have reached its peak. Unfortunately, as previously mentioned, predicting future bio-invasions is not possible and the focus of invasive species control has shifted to specific vectors such as ballast water (Davidson *et al.* 2017). To address the spread of species induced by ballast water operations of ships, the IMO adopted the *International Convention for the Control and Management of Ships' Ballast Water and Sediments* (BWM Convention) in 2004, which entered into force on 8 September 2017. The Convention requires all ships in international traffic to carry out ballast water management procedures in order to achieve a given standard, assuming that there is a correlation between bio-invasion risk and density of organisms in discharged ballast water (Ruiz and Carlton 2003; Wonham *et al.* 2013). At the moment, there are two possibilities for a ship to comply with the Convention: 1) ballast water exchange with an efficiency of at least 95% volumetric exchange of the ballast water (D-1 standard) with the understanding that by the pumping-through method, pumping through three times the volume of each ballast water tank will be considered to meet the standard, and 2) discharge less than a certain amount of viable organisms per unit of volume depending on the size of the organism, whereby two classes of organisms are considered related to their minimum dimensions (i.e., organisms greater than or equal to 50 μm, typically considered as zooplankton, and organisms greater than 10 μm and less than 50 μm, typically considered as phytoplankton). In addition, discharge of certain indicator organisms shall not exceed specified concentrations. These limits are in detail described in the Regulation D-2 of the BWM Convention (BWMC 2004) and are presented in Table 4-1. This regulation is therefore called the D-2 standard. It should be noted that the D-1 standard will be phased out in the coming years, and the majority of ships will be expected to install a ballast water management system (BWMS) to treat ballast water before discharge. Ship owners may also develop so-called other methods.

Table 4-1: Ballast Water Performance Standard (D-2)

Parameter	Criterion
Organisms ≥ 50 μm in minimum dimension	< 10 viable organisms/m^3
Organisms < 50 μm and ≥ 10 μm in minimum dimension	< 10 viable organisms/mL
Concentrations of indicator microbes, as a human health standard	
— Toxigenic *Vibrio cholerae* (serotypes O1 and O139)	< 1 colony forming unit (cfu)/100 mL or < 1 cfu per 1 gram (wet weight) of zooplankton samples
— *Escherichia coli*	< 250 cfu/100 milliliters
— Intestinal Enterococci	< 100 cfu/100 milliliters

At the time of adoption of BWM Convention in 2004, it was unclear what kind of treatment processes would be proposed to meet the performance standards established. In order to assure that no unacceptable harm to the marine environment and human health is induced, the IMO rules require that systems using active substances (AS) have to be approved by the Marine Environment Protection Committee (MEPC) of the IMO taking into account the recommendations of the *UN Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection – Ballast Water Working Group* (GESAMP-BWWG) prior to being type-approved by the national authorities. Ballast water management systems (BWMS) are evaluated using a two tiered approach, called Basic Approval (BA) and Final Approval (FA), and is conducted by the GESAMP-BWWG (Bowmer and Linders 2010). This process deals only with the potentially negative side-effects of BWMS as these systems should not pose a risk to the environment, human health, ships and resources. The efficacy of the BWMS is described in the BWMS Code (IMO 2017a), which replaces the Guideline (G8) (IMO 2008a). The process of approval of a BWMS using active substances is described in the Procedure (G9) (IMO 2008b) and a more detailed description of the risk assessment process is presented in the *Methodology for information gathering and conduct of work of the GESAMP-BWWG* (GESAMP-BWWG Methodology (IMO 2017b)). Although not explicitly required by the BWMC (2004), - the Convention speaks of: "to prevent, minimize, and ultimately eliminate the transfer of Harmful Aquatic Organisms and Pathogens" - many BWMS make use of active substances to reach the reduction of viable organisms goals outlined in the BWMC (Table 4-1). Therefore, the formation of disinfection by-products (DBP) during ballast water treatment has been observed in many systems tested. In 2018, the GESAMP-BWWG has determined 39 chemicals as disinfection by-products that are commonly found in BWMS and for which applicants do not have to submit physico-chemical and toxicity/ecotoxicity data. The list of 39 chemicals and relevant characteristics of these chemicals are presented in an online database (BWWG-Database of chemicals most commonly associated with treated ballast water) found on the Global Integrated Ship Information System (GISIS) website at IMO (IMO 2018c). Potential risks resulting from generated DBPs have been analyzed and discussed (Werschkun *et al.* 2014; Werschkun, Sommer, *et al.* 2012; Werschkun *et al.* 2012).

4.2 Treatment process

Approved systems use physical and chemical methods to treat ballast water at uptake, during the voyage or, in selected systems, also at discharge in order to achieve the D-2 standard. Physical methods include filtration, hydrocyclone, ultraviolet radiation (UV) and ultrasound. Chemical methods typically employ oxidants such as chlorine (added in chemical form or generated *in situ* by electrolysis (electrochlorination)), ozone, hydrogen peroxide, chlorine dioxide and others. Almost all systems employ a combination of physical and chemical treatment methods and within this group the majority is using filtration and electrochlorination. An overview of treatment technologies is given in Table 4-2 whilst an overview of active substances applied is given in Table 4-3 based on David *et al.* (2018), where also the maximum allowable discharge concentration (MADC) is presented. The MADC is defined as the maximum concentration of the active substance in the discharged ballast water.

Table 4-2: Overview of technologies in ballast water management systems with Final Approval using active substances based on GESAMP-BWWG

Technology applied	Number of BMWS[3]	Remarks
Cavitation	4	No DBP formation
Chemical injection	18	DBP formation
Deoxygenation	2	No DBP formation
Electrochlorination	21	DBP formation
Filtration	28	No DBP formation
Flocculation	1	No DBP formation
Free radical formation	1	Some DBP formation

Technology applied	Number of BMWS[3]	Remarks
Heat	1	No DBP formation
Hydrocyclone	2	No DBP formation
In tank treatment with Active Substance	2	DBP formation
In tank treatment with inerts	0	-
Ultrasound	2	No DBP formation

[3] Several Ballast Water Management Systems use a combination of technologies listed in the left column. Numbers are representing the status at the Berlin Workshop (end of 2018).

It should be noted that the total number of technologies is greater than the number of FAs. The reason is that several BWMS use more than one technology. Even a combination of 3 technologies was observed.

Although some evidence for a generation of DBPs exists the quantity of DBP production is considered to be considerably low. In the beginning of the BWMS approval process at IMO, systems using UV radiation as the main treatment technology were considered as potentially generating DBPs and thus were assessed by the GESAMP-BWWG resulting in several final and basic approvals. However, based on the risk assessment process it became apparent that DBP generation is deemed to be almost negligible compared to Active Substances. The MEPC of IMO decided that UV-systems were not considered to form DBPs in relevant volumes and, therefore, should not be evaluated by the GESAMP-BWWG. However, it is possible that the formation of DBPs is related to the strength of the UV radiation (UV-C). It is unknown to what extend UV-systems on board ships produce DBPs as UV-A and UV-B radiation is also used. These latter systems are not considered to form DBPs.

Table 4-3: Active Substances used in ballast water management systems with maximum allowable discharge concentrations (MADC) (according to David *et al.* (2018)

Active Substance (AS)	Number of BWMS	MADC [mg/L]
Chlorine dioxide (ClO_2)	2	0.1
Hydrogen oxide radical /hydroxyl radical (OH•)	4	not applicable[4]
Hydrogen peroxide (H_2O_2)	2	0.5
Hydrogen peroxide / peracetic acid (H_2O_2/ $C_2H_4O_3$)	3	0.5 / 0.3
Hypochlorous acid (HOCl)	27	0.1
Ozone (O_3)	6	0.1
Polyaluminium chloride / polyamide sodium acrylate	1	not defined[5]
Sodium dichloroisocyanurate[6] (NaDCC)	2	0.1

[4] OH• has only a lifetime of milliseconds
[5] this is more a physical than a chemical process
[6] the BWWG considers that hypochlorous acid is the active substance.

The production of DBPs is only expected for systems that use active substances. The GESAMP-BWWG had up to 2019 recommended Final Approval for 45 systems using active substances, of which 36 systems have also been type-approved by the member states (IMO 2018b).

As the exact chemical speciation of fast reacting oxidants is difficult to establish, oxidant concentrations in water treatment are often quantified as total residual oxidants (TRO) providing a comparable measure. TRO is defined as all oxidants that can be measured by use of certain analytical methods, e.g. DPD (N, N-diethyl-p-phenylenediamine) colorimetric, amperometric. Some substances may act as oxidants but cannot be captured by these methods. A useful overview is given by Zimmer-Faust *et al.* (2014). Oxidant concentrations ranging from 2-20mg TRO/L (as Cl_2) are used in IMO-approved BWMS. Typically, the treatment is performed during uptake. The reaction in the ballast water tank continues as long as oxidants are available for consumption and can last up to the total holding time of the ballast water. Many systems aim to maintain a certain concentration of residual TRO over the total ballast water holding time in order to maintain the biocidal potential and prevent re-growth of organisms. In order to not release remaining oxidants into the environment, often a neutralization using chemical neutralizers such as sodium thiosulfate or sodium bisulfite is performed prior to or during discharge of treated ballast water. Based on the risk assessment by the GESAMP-BWWG, a TRO limit of 0.1 mg/L (as Cl_2) in discharged ballast water is considered to pose no unacceptable risks to the environment.

The composition and the concentration of DBPs depend on different factors. On the one hand, system dependent factors such as oxidant type and oxidant concentration are important, e.g., chlorine dioxide, although only used in one BWMS, has been described to produce lower concentrations and fewer DBPs compared to the most prominent oxidant treatments using chlorine, whereas ozone may produce bromate through further hypobromite (BrO^-) oxidation. On the

other hand, also water quality characteristics (salinity, DOC, TOC, TSS, pH, etc.) which depend on the place and time of uptake play an important role on the quantity and type of DBPs produced (see also Chapter 3). The relationship between the dose and the formation of DBP depending on other factors is currently not known. On the request of GESAMP-BWWG, a study is being carried out at the cooperating BWMS test facilities, Global TestNet, to find a statistical relationship between water characteristics and production of DBPs.

4.3 Quantification

In order to quantify the inputs of DBPs into the marine environment and the resulting environmental exposure, a number of aspects have to be considered:

- the total volume of treated ballast water,
- the ratio of systems using oxidants,
- the concentrations of DBPs in the treated ballast water,
- the locations where it is released, and
- how much dilution can be expected within the receiving environment?

4.3.1 *Amount of discharged ballast water*

In general, vessels discharge ballast water when loading cargo, and take up ballast water when unloading cargo. Therefore, a major part of ballast water operations is carried out in ports or during approach to ports (coastal areas, rivers, canals). The quantity of ballast water carried, however, primarily depends on the cargo handling operations carried out. Additional ballast operations may be needed depending on weather conditions or specific navigation needs (low water depth or pass under bridges). When expecting to sail through bad weather conditions and heavy seas, vessels would be in heavy ballast condition to improve the safety of navigation. The annual global ballast water discharges from vessels engaged in the international seaborne trade was estimated as 3.1 billion tonnes in 2013 (David 2015). Another estimate gives a value of 10 billion tonnes of ballast water per year (WHO 2011; IMO n.d.).

Today, informal communication suggests that UV treatment and electrochlorination has been installed on vessels as the dominating technologies with a market share of about one-third each. Use of oxidants and other disinfections might represent most of the rest. It is currently unclear, which market share the different techniques will attain by 2024, i.e., which part of the total ballast water discharged will actually be chemically treated compared to water treated with physical methods only, like UV treatment. Furthermore, it is not clear which oxidants will be used in what quantities. As a worst-case scenario, one could assume that 3.5 billion m^3 of ballast water will be treated generating DBPs.

4.3.2 *Identity and concentration of DBPs in ballast water*

An overview of the disinfection by-products detected during testing for approval of ballast water management systems is presented in Chapter 15 (annex of this report). The most detected DBPs with the highest concentrations are shown in Table 4-4, including some other statistical parameters. It should be noted that only substances contained in the GESAMP-BWWG Database are included in the table. Some DBPs are only rarely detected (e.g., aldehyde, see Chapter 15) and are therefore not included in the database. Some DBPs are always found in a concentration below the detection limit (DL). These substances are included in the Database because they would be analyzed without extra effort given the analysis technique used (e.g., trichloroethane). Applicants of BWMS have the obligation to search for all possible DBPs and if they detect a DBP not yet included in the Database a full risk assessment according the GESAMP-BWWG Methodology (IMO 2017b) has to be performed. For DBPs already included in the GESAMP-BWWG Database, no additional physico-chemical, toxicological and ecotoxicological information has to be submitted, because sufficient information is available in the Database.

Table 4-4: Most frequently identified disinfection by-products in BWMS[7]

DBP	Frequency[7]	Discharge concentration in [μg/L]				
		Min	Max	Median	Mean	SD
Bromate ion	20	6.85	920.00	33.48	119.74	245.81
Bromochloroacetic acid	27	0.10	246.70	5.60	15.11	46.59
Dibromoacetic acid	34	0.14	230.00	32.81	48.66	50.89
Dibromoacetonitrile	17	0.28	133.00	12.90	23.33	32.49
Dibromochloroacetic acid	18	1.50	32.70	8.67	10.77	8.23
Dibromochloromethane	33	0.03	120.00	16.00	22.11	28.15
Dibromomethane	10	0.06	9.62	1.62	2.82	3.41
Dichloroacetic acid	21	0.10	77.50	2.96	10.99	18.00
Dichloroacetonitrile	11	0.01	9.23	0.19	1.87	3.14
Dichlorobromoacetic acid	19	0.10	27.70	3.39	5.89	7.75
Dichlorobromomethane	27	0.04	70.50	4.36	9.52	14.49
Monobromoacetic acid	30	0.20	191.00	3.05	15.48	37.78

DBP	Frequency[7]	Discharge concentration in [µg/L]				
		Min	Max	Median	Mean	SD
Monochloroacetic acid	21	0.08	495.00	2.86	36.34	110.20
Tribromoacetic acid	26	0.10	970.00	19.30	103.43	197.78
Tribromomethane	36	0.08	890.00	229.00	247.14	213.67
2,4,6-Tribromophenol[8]	5	0.10	0.45	0.21	0.27	0.14
Trichloroacetic acid	18	0.50	150.00	9.74	26.25	40.98
Trichloromethane	21	0.10	257.00	3.87	29.80	61.14

[7] The selection of DBPs is limited to findings in Final Approval dossiers as the test conditions are relatively close to a realistic operational ballast water treatment. § Number of dossiers listing the respective disinfection by-product.
[8] 2,4,6-Tribromophenol is not frequently detected in treated ballas water, but was included for comparison to other treatment areas.

Most of the DBPs mentioned in Table 4-4 are mainly formed in systems that use electrochlorination whereas other systems are producing a specific selection of those. Some substances, e.g., the chlorinated substances are more likely to be formed when the BWMS had to be applied in freshwater. In seawater, more brominated substances are formed, while in brackish water a wider mixture of chlorinated and brominated substances is formed (see also chapter 3).

4.3.3 *Estimated environmental concentrations*

Most of the ballast water discharge takes place in the in or close to ports where the ship loads cargo. The GESAMP-BWWG estimates the resulting concentrations in the harbour using the MAMPEC-BW model (version 3.1.0.3) (Deltares 2017). Originally, this model was designed to estimate the concentration of antifouling substances released from ships that are treated with antifouling paints and coatings. The model was adapted to fulfil the requirements of the risk assessment of DBPs from ballast water management systems (BWMS) and is currently used all around the world in the estimation of the DBP concentrations in the harbour and its surroundings after discharge of ballast water.

The model uses specific physico-chemical characteristics of the different DBPs and may also take into account degradation processes, like hydrolysis, photolysis and biodegradation, if such information is available. Generally, in the first instance (Tier 1), degradation is not taken into account. If the PEC/PNEC ratio for a specific DBP is exceeded at Tier 1, a Tier 2 calculation is performed where degradation is included.

Table 4-5 shows the modeled maximum concentrations in the harbour obtained using the standard GESAMP-BWWG harbour scenario, which assumes a ballast water discharge of 100,000 m^3/d and mean DBP concentration (as observed in BWMS test (Table 4-4)). Calculations in the harbour can be considered as the local concentration.

Table 4-5: Maximum concentrations of 17 most important DBPs in the harbour and in the surrounding waters in [µg/L].[9]

DBP	Measured mean concentration in ballast water [µg/L]	Calculated maximum concentration in the harbour MAMPEC-BW [µg/L]	Calculated maximum concentration in surrounding waters [µg/L]
Bromate ion	119.74	2.03	2.21×10^{-2}
Bromochloroacetic acid	15.11	2.56×10^{-1}	2.79×10^{-3}
Dibromoacetic acid	48.66	8.23×10^{-1}	9.00×10^{-3}
Dibromoacetonitrile	23.33	3.94×10^{-1}	4.31×10^{-3}
Dibromochloroacetic acid	10.77	1.82×10^{-1}	2.11×10^{-3}
Dibromochloromethane	22.11	2.44×10^{-1}	2.62×10^{-4}
Dibromomethane	2.82	3.07×10^{-2}	2.03×10^{-3}
Dichloroacetic acid	10.99	1.86×10^{-1}	3.39×10^{-4}
Dichloroacetonitrile	1.87	3.12×10^{-2}	1.09×10^{-3}
Dichlorobromoacetic acid	5.89	9.97×10^{-2}	9.08×10^{-4}
Dichlorobromomethane	9.52	1.05×10^{-1}	2.86×10^{-3}
Monobromoacetic acid	15.48	2.62×10^{-1}	6.72×10^{-3}
Monochloroacetic acid	36.34	6.15×10^{-1}	1.91×10^{-2}
Tribromoacetic acid	103.43	1.75	2.68×10^{-2}

[9] Calculations done with the MAMPEC-BW model using the standard harbour scenario (ballast water discharge of 100,000 m^3/d) and the mean measured concentration in tests as input (c.f. Table 4-4).

DBP	Measured mean concentration in ballast water [μg/L]	Calculated maximum concentration in the harbour MAMPEC-BW [μg/L]	Calculated maximum concentration in surrounding waters [μg/L]
Tribromomethane	247.14	2.95	4.85×10^{-3}
Trichloroacetic acid	26.25	4.44×10^{-1}	2.14×10^{-3}
Trichloromethane	29.80	2.81×10^{-1}	2.14×10^{-3}

The maximum concentration in the harbour and in the surrounding areas as shown in Table 4-5 are used as an estimation of the PEC for the risk assessment of Chapter 10 and 11. This is a worst-case assumption as potential disappearance of the substances due to several processes, like hydrolysis, evaporation and degradation is neglected. If these values do not affect the organisms in the aquatic environment, no further unacceptable effects may be expected.

The most relevant estimation seems to be the surrounding areas as these should not be classified e.g. as an economical area but more as an ecosystem that should be protected or as a recreational area. Both areas should be assumed to be of a good quality habitat that should not have any adverse effects on man and environment. For these areas no additional dilution should be considered as this is already been taken care of in the equations that are described in the MAMPEC-BW model. If another area being even more remote than the surrounding areas considered in MAMPEC-BW another dilution factor could be considered in the order of e.g., 10 or even 100. The current proposal is not to use an additional dilution factor but to accept the data from Table 4-5 as such.

On regional and intra-annual time scales, DBPs from ballast water can spread fast in the upper ocean (Maas *et al.* 2019). Concentrations are highly diluted with less than 3% of the initial DBP amount or a dilution factor >30. Tribromomethane (bromoform) is one major compound in treated ballast water. Since bromoform is a volatile organic compound, on longer time scales the atmosphere has to be considered as a sink. Around 80-100 % of the bromoform input is emitted into the atmosphere within several days (see Chapter 12). Thus, no long-term accumulation of volatile DBPs from ballast water is expected. Nevertheless, the input of DBPs into the environment is a continuous process. Therefore, in the ocean-atmosphere environment around ports there is always an immediate exposure to DBPs regardless of advective transport or sinks.

4.4 Conclusion

The amount of ballast water used on ships is estimated to be between 3 and 10 billion m^3 per year. A better estimate is not on hand and it is recommended to improve this figure as it would make risk assessments more reliable. Another rather uncertain estimate is the number of ships that will have a ballast water management system. For the assessment in this report, it is assumed that a total of 7 billion m^3 of ballast water is taken from the environment by ships each year of which 50% is subject to oxidant treatment, resulting in a total volume of treated ballast water of 3.5 billion m^3. Ballast water management systems that use active substances are generally using established technologies that are also used in other industrial land-based applications (see Chapters 5, 6, 7, and 8). The major technology used in ballast water management systems is electrochlorination (electrolysis) with the injection of chemicals as second largest technology applied. Filtration is often used as an initial technology to remove bigger particles with a mesh size of typically 50 μm. There is a tendency to lower this size to 40 μm. The dose of active substances applied varies between 2 and 20 mg AS/L depending also on the active substance (AS) used. As electrochlorination is used most often, and in addition to frequent use of injection of oxidants, where also hypochlorous acid is the active substance, the majority of systems produce disinfection by-products that will ultimately be discharged to the environment. The active substance may also be discharged but this is limited by the requirement of meeting the maximum allowable discharge concentration (MADC). This value is determined by the GESAMP-BWWG and national administrations have to check whether this value is met at all times. BWMS test facilities have determined over 100 DBPs of which 39 are included in the GESAMP-BWWG Database maintained at the IMO in London. Based on the data submitted in the dossiers of BWMS applicants, GESAMP-BWWG carries out a risk assessment for all relevant DBP determined for a specific system. The database contains physico-chemical, toxicological and ecotoxicological information for the 39 most common ballast water chemicals. Together with the measured discharge concentration, the predicted environmental concentration (PEC) and the predicted no-effect concentration (PNEC) are compared to determine the risk associated with a specific BWMS (see also Chapters 10 and 11). The measured discharge concentration of DBPs varies greatly with concentrations as high as the mg/L range until as low as in the low µg/L range (see Table 4-4).

In chapters 10, 11 and 12, a risk assessment is carried out for the environment, human health and the atmosphere. For that purpose, some assumptions are required. Based on the data mentioned in this chapter it is proposed to use the values in Table 4-6 as assumptions in the risk assessment. In addition, it is proposed to limit the risk assessment to the DBPs mentioned in Table 4-5.

Table 4-6: Assumptions for risk assessment

Parameter	
Amount of ballast water treated with active substances	3.5 x 10^9 [m^3/a]
Average dose applied	10 mg TRO/L (as Cl_2)
MADC	0.1 mg TRO/L (as Cl_2)
DBP concentrations in discharge	Mean value (Table 4-4) [mg/L]
Predicted environmental concentrations (PEC)	Calculated maximum concentration in the harbour and the surrounding water (Table 4-5)

5 COOLING WATERS

All cooling systems in industrial plants using seawater are affected by the excessive development of marine organisms that disrupt or even stop their operation. Fossil fuel and nuclear power stations at the seaside are particularly affected by this biofouling because of the large water volumes taken and the large size and complexity of the cooling systems.

The conditions for growth in cooling circuits are in particular favorable for sessile organisms such as mussels, barnacles and hydroids, with steady flow conditions providing an abundance of food while preventing the equivalent establishment of predatory assemblages. Such growth, termed macrofouling can be massive; it can restrict flow, partially or wholly block condensers and heat exchangers.

On the other hand, the surfaces of the cooling systems are covered by slime produced by marine bacteria. This thick film of a few μm to a few mm is composed of organic materials in which bacteria and other microorganisms develop. The excessive development of the biofilm leads to reduced heat exchange in the condenser and in the auxiliary heat exchangers. Bacterial corrosion of metals is also favored by biofilms (Jenner *et al.* 1997).

To maintain water flow and heat exchanges at the required level in the cooling system, it is necessary to implement anti-fouling techniques to control the excessive development of macrofouling and microfouling. As the aim of cooling water treatment is not disinfection, i.e., killing of organisms, but the reduction of settlement and growth, the term disinfection by-products may not be appropriate. Some authors use the term chlorination by-products instead in this context. For sake of consistency, we use DBP in this report also for products generated by cooling water treatment.

5.1 Purpose of oxidant treatment

Many techniques have been developed for the control of macro- and microfouling in cooling water circuits (Jenner *et al.* 1998). They focus on the design of circuits excluding areas of low water velocities, filtration of water to eliminate larvae, recirculation of heated water to avoid their fixation. Mechanical cleaning systems for condenser tubes reduce the growth of biofilms. The use of toxic or non-toxic paints and coatings reduces the fixation of macrofouling. Physical (UV light) or chemical treatments based on toxic or filming compounds have been applied to certain marine cooling systems. All these processes have not eliminated the use of oxidizing products and chlorination.

Due to its well-tried technology, its long-term worldwide uses and its reasonable cost, chlorine remains the most common antifouling treatment in industrial cooling water systems (Rajagopal 2012). The advantage of chlorination is also the rapid disappearance of the oxidants responsible for the acute toxicity in plumes of chlorinated water discharge. However, the chemical reactions of oxidants with organic materials present in seawater and with biofilms lead to the formation of mainly non-oxidant but persistent by-products (see Chapter 3). Because of their persistence in the marine environment, these by-products are transported over long distances and their long-term toxicity is subject to environmental and health assessments covered in other chapters of this report.

This chapter deals with the composition and concentration of these by-products in chlorinated cooling waters. The data used comes mainly from studies and monitoring programs carried out on cooling circuits of European thermal power stations located on the Channel and North Sea coastlines. The results may also be applicable in part to treatments with other oxidizing compounds (ozone and chlorine dioxide) as they oxidize seawater bromide ions and produce the same by-products at lower levels. It should, however, be noted that combination of ozone with bromides induces formation of bromates (see Chapter 3).

5.2 Treatment process

The fouling pressure and thus the need for chemical treatment depend on the site-specific water quality and the climatic conditions. For example, in highly turbid estuarine water, water flow in the system may induce an abrasive effect removing the biofilm in heat exchangers, limiting the settlement of macrofouling, and thus the need for disinfection.

In the majority of direct cooled coastal power stations, oxidant treatment is used for this purpose, typically low-level chlorination (Jenner *et al.* 1997). Low-level chlorination involves the addition of a chlorine-produced oxidant to the cooling water stream immediately at the intake to avoid settlements of fouling organisms on the trash racks.

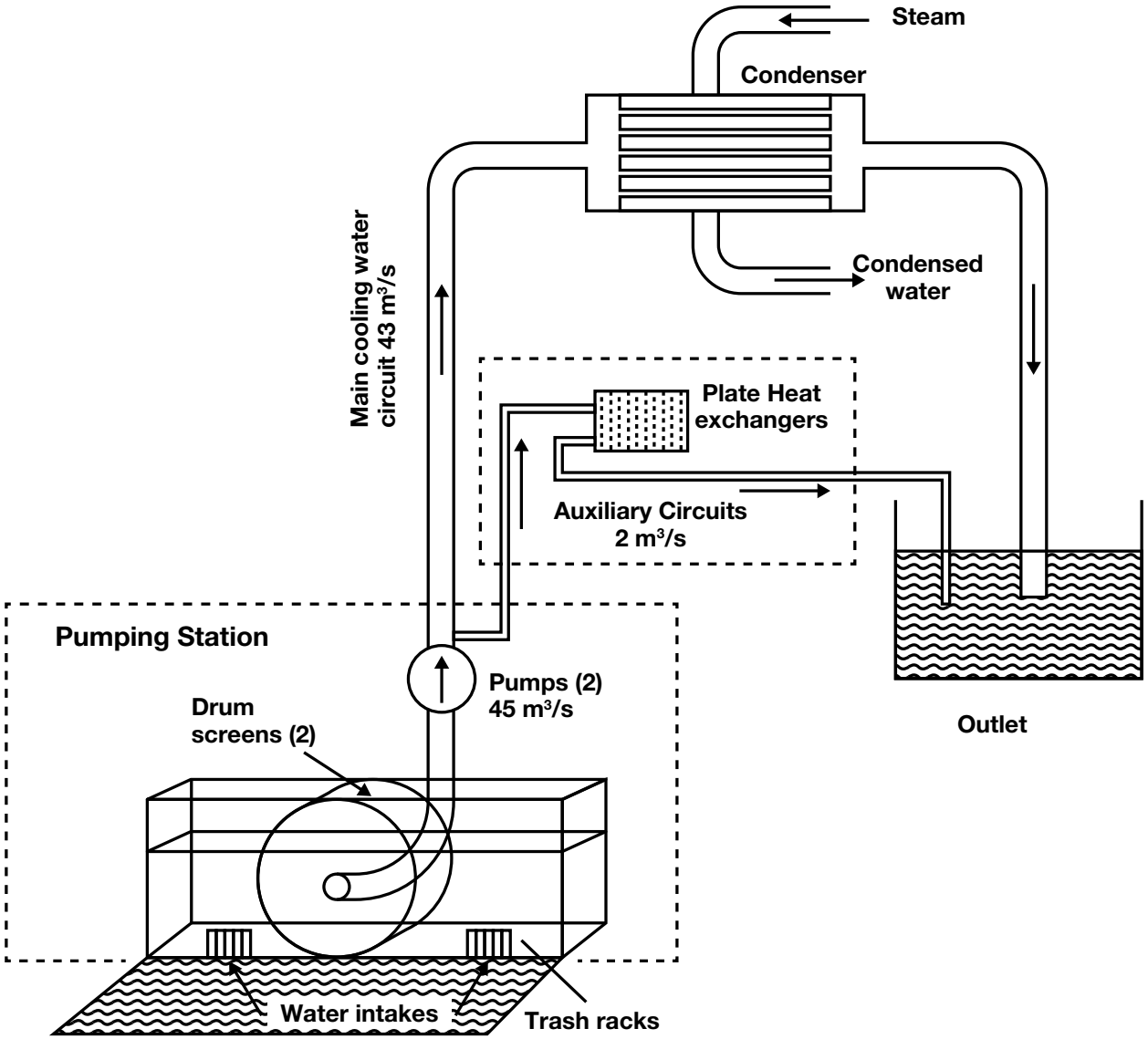

Figure 5-1: *Schematic view of direct cooling water circuits for a nuclear coastal power station. A tube heat exchanger (the condenser) is installed on the main circuit. Auxiliary circuits are equipped with plate heat exchangers that are more sensitive to blocking by biofouling (Jenner et al. 1998).*

The hypochlorite solution is either injected from a hypochlorite storage or produced on site by electrochlorination cells, which are generally used to treat large flows. In French nuclear power stations located on the Channel and the North Sea, each electrochlorination installation comprises:

- electrolysis cells in which the sodium hypochlorite (bleach) is produced from the sodium chloride according to the reaction: $NaCl + H_2O \rightarrow NaClO + H_2$
- a tank providing a short-term storage (a few minutes) of the concentrated hypochlorite at approximately 1 g Cl_2/ L in chlorine prior to injection,
- a device for injecting the solution into the circulating water (Figure 5-2).

In order to efficiently control microfouling and macrofouling, the low-level chlorination process requires to maintain a residual oxidant concentration equivalent to about 0.2 mg/L (expressed as Cl_2) at the outlet of all heat exchangers: condensers and auxiliary exchangers (Khalanski and Jenner 2012). The applied chlorine dose depends on the oxidant demand of the water and of the circuits; it is in the range of 0.5-1.5 mg/L. Figure 5-3 gives an example of the decay of residual oxidants during the transit of chlorinated water in a cooling circuit.

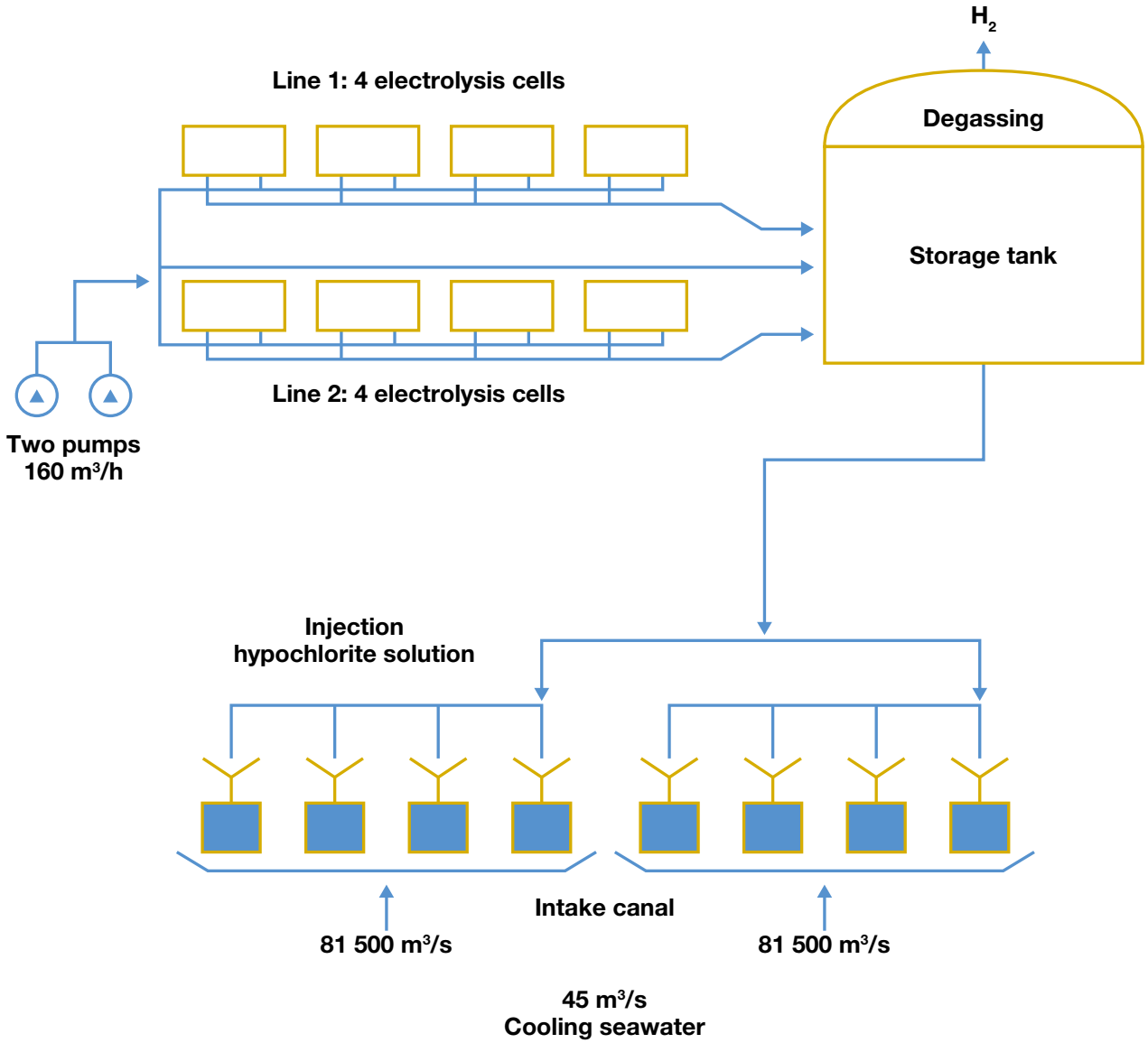

Figure 5-2: *Electrochlorination circuit at the Penly nuclear power station (Hartmann et al. 2011).*

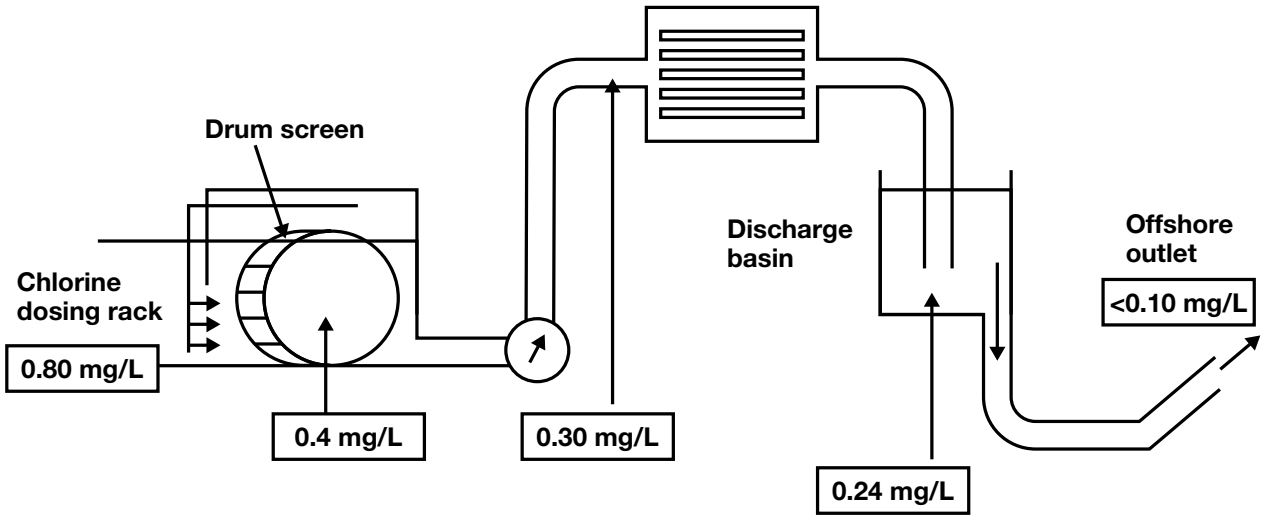

Figure 5-3: *Decay of Total Residual Oxidants at the Penly nuclear power station for a chlorine dosage of 0.8 mg/L (Jenner et al. 1998).*

When the growth of biofouling is moderate, it is possible to proceed to a semi-continuous chlorination. It is then necessary to perform high frequency injections called pulse-chlorination according to the sequence 30 minutes on - 30 minutes off. Intermittent chlorination, for example once a day for 8 hours can be efficient only at marine areas poor in food for filter-feeders (Jenner *et al.* 1998).

In the event of a very severe degradation of the thermal exchanges, the plant operator may apply a shock chlorination to clean up heat exchangers with chlorine concentrations greater than or equal to 2 mg Cl_2/L.

For macrofouling, the treatment procedure must be performed during the reproduction period in order to inhibit larval settlement and during the growth period in order to limit the growth rate of settled organisms. Typically, biofouling growth is more pronounced in warm water conditions, whereas in cold winter conditions when the growth rate is extremely low, oxidant treatment may not be required (Pacey *et al.* 2011).

In most of European countries, cooling water is treated for 6–9 months per year (from spring to fall) (Khalanski and Jenner 2012). At the French coastal power stations, chlorination is applied as long as the temperature of the water exceeds 10 °C (Hartmann *et al.* 2011).

In all cases, the optimization of antifouling methods requires to collect on site data on water quality, on the biological cycle of macrofouling organisms and on the development of bacterial slime.

5.3 Quantification

5.3.1 *Water use*

In thermal electricity production, different energy transformation processes are involved. Only one part of the energy contained in the combustible material can be transformed to electricity. The rest is dissipated as heat. The ratio of the electric power to the primary energy used is defined as the global efficiency. Typical values for overall efficiency or electricity production are 38 and 31 % for fossil fuel and nuclear power stations respectively (Table 5-1).

The majority of thermal electricity production relies on water for cooling purposes. In this context, the water use has to be differentiated: “withdrawal” is defined as the amount of water removed from the ground or diverted from a water source for use, while “consumption” refers to the amount of water that is evaporated or otherwise removed from the immediate water environment.

Once-through cooling systems achieve cooling by heating up the cooling water, whereas closed-loop systems achieve cooling mainly by evaporation of cooling water. Therefore, once-through cooling requires much higher water volumes than closed-loop systems. However, when using marine waters for cooling, the water consumption is not an issue. Therefore, once-through cooling is used in the majority of coastal power stations.

More than 100% of the produced electric power is transferred as dissipated heat to the cooling water for fossil fuel and nuclear power stations (Table 5-1). Due to differences in the production process, nuclear power production requires a higher amount of heat dissipation per produced electricity as compared to production relying on fossil fuel. The thermal power transferred to the cooling water is the product of the flow rate by heating (ΔT). The heating of the water and the volume of withdrawn water are therefore directly related. An overview on withdrawal of water and ΔT for fossil fuel and nuclear power stations is shown in Table 5-1.

Table 5-1: Requirements of cooling water for fossil fuels and nuclear power stations equipped with once-through cooling systems.

Thermodynamic data	**Fossil fuel**	**Nuclear**
Thermal power[10]	1.00	1.00
Electric power[10]	0.38	0.31
Cooling water[10]	0.45	0.65
Other losses[10]	0.17	0.04
Global efficiency (ratio of electric power to thermal power)	0.38	0.31
Ratio of dissipated heat into cooling water to electricity produced	1.2	2.1
Cooling water requirements		
Electric power	1000 MW	1000 MW
Transfer to Cooling water	1200 MW	2100 MW
Water flow for ΔT = 10 °C	30 m^3/s	50 m^3/s
Water flow for ΔT = 15 °C	20 m^3/s	33 m^3/s

[10] Thermal power is taken as 1 and electric power, cooling water, other losses are taken as parts thereof.

For nuclear power stations, with powers ranging from 900 MWe to 1650 MWe (i.e. for the new European Pressurised Reactor - EPR), water flows per unit varies from 40 to 60 m^3/s (Hartmann *et al.* 2011). The Gravelines nuclear power station, on the French North Sea coast, takes a total flow of 240 m^3/s when its six 900 MWe pressurized water reactors (PWR) units are in operation. The discharges of DBPs into the coastal environment obviously depend on the volumes of the cooling water flow.

5.3.2 *Coastal power stations on a global scale*

In 2016, approximately 25,000 TWh of electricity were produced worldwide (IEA 2018), the majority by fossil-fuel burning power plants with an increasing trend, see Figure 5-4. This trend mainly driven by Asia can be expected to continue, as new coal-fired power plants are currently in construction in China and India.

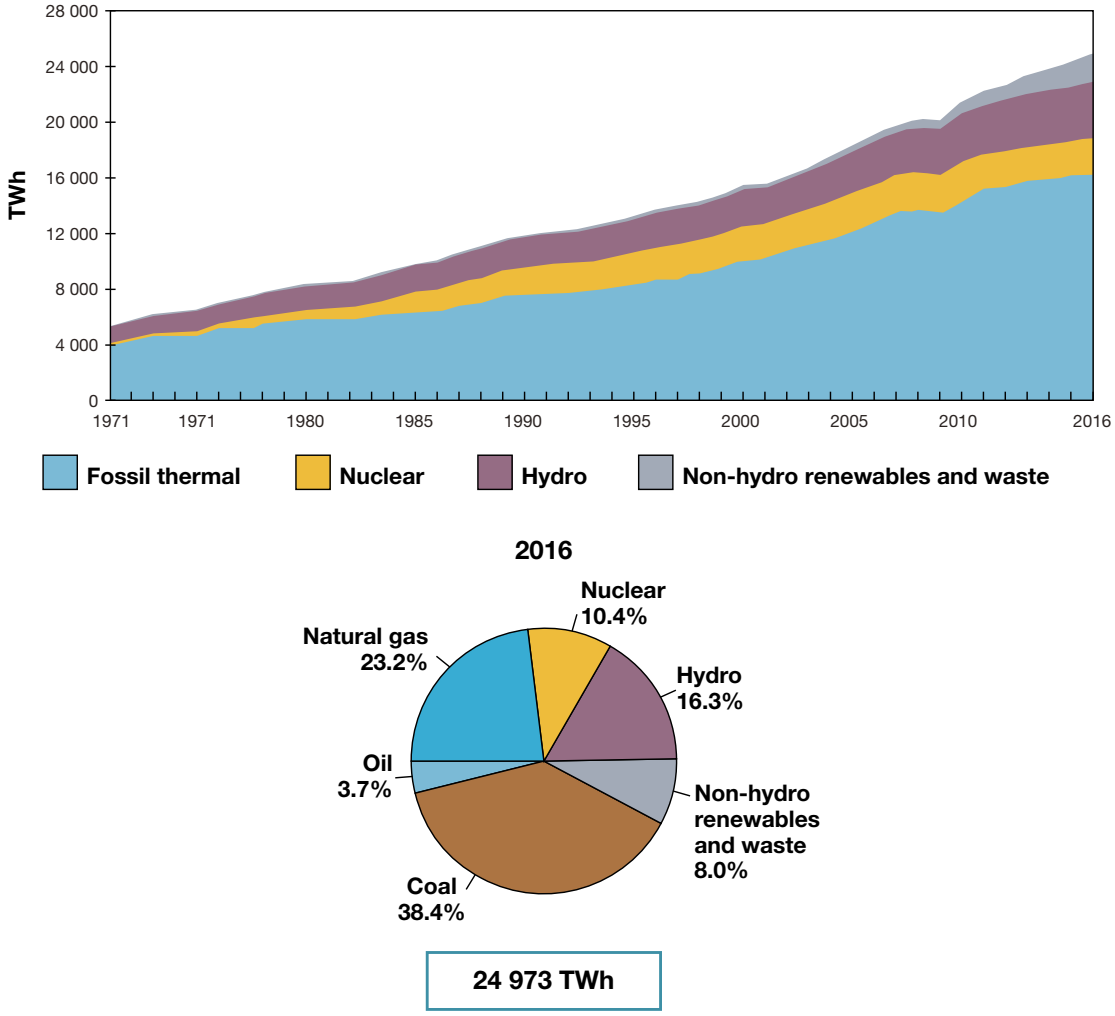

Figure 5-4: *World electricity generation [TWh] from 1971 to 2016 by fuel type IEA (2018)*

In total for 2016, the annual global thermal electricity production relying on cooling systems for heat dissipation amounts to 18,900 TWh. Based on an analysis of geographic information Maas *et al.* (2021) identified that about one fourth of power plant capacities are located at the coast. Assuming an equal distribution between fossil fuel and nuclear power production between coastal and inland production and an average heating of water by 12.5°C, an annual discharge of 4.7 x 10^{11} m^3 is estimated (Table 5-2). An alternative estimate of 8 x 10^{11} m^3/a has been proposed (Maas *et al.* 2021; Maas 2020) not differentiating between different cooling needs of the fuel types.

Table 5-2: Overview on global cooling water use in electricity production

	Production [TWh]	**Estimated discharge of Cooling ater in the sea at different water heating temperatures (m^3)**			
	Global	**Coastal PP**	**ΔT = 10 °C**	**ΔT = 12,5 °C**	**ΔT = 15°C**
Fossil Fuel	16,300	4 080	4.51 x 10^{11}	3.76 x 10^{11}	3.01 x 10^{11}
Nuclear	2 600	650	1.18 x 10^{11}	9.47 x 10^{10}	7.82 x 10^{10}
Total	18,900	4 730	5.69 x 10^{11}	4.70 x 10^{11}	3.79 x 10^{11}

For the next decades, the end of the coal/oil fired stations is a reasonable prospect, but gas and nuclear powers stations will probably remain a component of the energy mix that will be increasingly dominated by renewable energies.

5.3.3 *DBPs production in cooling water*

Although the chemistry of chlorine in marine water is similar, one can expect differences in DBP as water qualities and treatment processes vary between sites.

The production of DBPs in cooling circuits by chlorination of seawater is driven by different factors:

1 The abundance of bromides in seawater leads to the formation of predominantly brominated DBPs (see Chapter 3)

2 The water quality at the site (salinity, ammonia and organic compounds that may act as precursors for DBPs)

3 The treatment concentrations may influence the amount and composition of generated DBP.

4 Residence times inside the cooling water circuit typically vary between 2 and 15 min (Bruijs and Jenner 2012). When the cooling water is discharged through a long channel, the residence time can reach 30 minutes to 1 hour. The reaction times for oxidants with natural organic matter are thus considerably shorter compared to ballast water treatment.

Although chlorination is used all over the world, only few studies of DBP generation in cooling circuits are available. The most extensive study of DBPs in power plant cooling water was published by Jenner *et al.* (1997), covering 90 analyses of cooling water in 10 different coastal power stations in the United Kingdom (UK), France (F) and the Netherlands (NL). Since then, some additional data on this study were presented (Taylor 2006) and supplemental analyses were performed in the French power stations included in the above mentioned study (Allonier *et al.* 1999a). Additionally, studies on cooling waters of two Korean (KOR) and an Indian (IND) power station were published (Padhi *et al.* 2012; Yang 2001). An overview on selected DBPs detected in effluents of coastal nuclear power stations is presented in Table 5-3. This table is mainly intended as an overview of existing studies. Due to the heterogeneity of study design and quality, presented values are not comparable in quantitative terms. Anyway, it is shown that bromoform and dibromoacetonitrile can be detected in a large number of cooling waters.

Table 5-3: Overview on selected DBPs detected in power station effluents

Power station	Chlorine Dosage [mg/L as Cl_2]	Bromoform [μg/L]	DBAN [μg/L]	Tribromo phenol [μg/L]	DBAA [μg/L]	Reference
Heysham 2 (UK)	0.5-1.0	26.1	2.64			a
Dungeness (UK)	0.75-1.0	5.75	0.2			a
Wylfa (UK)	0.3-0.4	27.25	0.83			a
Bradwell (UK)	0.6-1.0	25	0.87			a
Hartlepool (UK)	0.5-1.0	3.5	$<$0.1			a
Sizewell A (UK)	0.6-1.0	14.5	$<$0.1			a
Paluel (FR)	0.37	3.1	0.1			a
	0.82	9.65	1.05			a
	0.2	26.8	2.83	0.14	10.19	b
Penly (FR)	0.62$\pm$0.1	13.37	NA			a
	0.5$\pm$0.08	15.01	NA			a
	0.57	7.37	0.94	0.1	7.25	b
Gravelines (FR)	0.64	6.37	NA			a
	0.8	18.63	NA			a
	0.77	26.75	3.61	0.37	9.5	b
Maasvlakte (NL)	0.8-1.5	11.54	0.83			a
	0.8-1.5	8.35	0.94			a
Madras (IND)	1.0	12-41				c
Youngkwang (KOR)	1	124				d
Ringhals (SWE)	1.5	100				e
Kori (KOR)				0.02		f

NA: not available; in order to increase readability, in some cases values were averaged and/or standard deviations omitted
Data extracted from: a Jenner *et al.* (1997), b Allonier *et al.* (1999a), c Padhi *et al.* (2012), d Yang (2001), e Fogelqvist *et al.* (1982), f Sim *et al.* (2009)

In the Indian power station of Madras, on the Tamil Nadu coast, different trihalomethanes were analyzed in the outlet of which bromoform was found to be the main constituent representing 96–98% of all THM. THM formation follows a seasonal cycle depending on the seawater chlorine demand. With a chlorine dosage of 1 mg/L, the maximum formation of bromoform was observed when the chlorine demand is maximum (41 μg/L in November 2010) and the minimum concentration (12 μg/L in February 2011) was measured when the chlorine demand is minimum (Padhi *et al.* 2012). Close to the cooling system outlet of the Korean Hanbit

Youngkwang nuclear power plant on the west coast of Korea, bromoform was measured at high concentration of 124 μg/L and decreased linearly in seawater with distance from the outlet (Yang 2001). In seawater at about 2 km near the Shin Kori nuclear power plant in Korea, traces of 2,4-dibromophenol and were detected at 0.53-32.7 ng/L and 2,4,6-tribromophenol was found in most of the marine area at 0.38-20.2 ng/L (Sim *et al.* 2009).

Table 5-4 provides a synthesis on ranges of DBP identified during the three year study on 10 European coastal power stations (Taylor 2006).

Table 5-4: Concentration ranges of DBPs detected in the effluents of coastal power stations in UK, France and the Netherlands (extracted from Taylor 2006)

DBP	**Concentration range [μg/L]**	
	Intake	**Outfall**
Chloroform	<0.1	<0.1–0.3
Bromoform	<0.1–1.0	1–43
Dibromochloromethane	<0.1	0.1–2.2
Dichlorobromomethane acetic acid	<0.1	0.1–1.0
Monochloroacetic acid	<1	<1
Dichloroacetic acid	<1	<1
Trichloroacetic acid	<1	<1
Monobromoacetic acid	<1	<1–5
Dibromoacetic acid	<2	<2–10
Dibromoacetonitrile	<0.1	0.1–5.0
2,4-Dichlorophenol	<0.4	<0.4
2,4,6-Trichlorophenol	<0.06	<0.06
2,4-Dibromophenol	<0.02	<0.02
2,6-Dibromophenol	<0.1	<0.1
2,4,6-Tribromophenol	<0.05	<0.05–0.3
Total organohalogens (extracted with petroleum ether acid/basic: EOX)	**0.3–2.4 μg Cl/L**	**1–13 μg Cl/L**
Total organohalogens (adsorbed through extraction of XAD resins with petroleum ether acid/basic: XADOX l)	**1–20 μg Cl/L**	**3–15 μg Cl/L**

Four major groups of DBPs have been identified in terms of detection frequency and quantity:

- Trihalomethanes (THMs): Chloroform, bromodichloromethane, chlorodibromomethane and bromoform. All THMs are volatile. THMs account for 46% to 65% of the total DBPs and are dominated by bromoform (more than 95%).
- Haloacetic acids (HAAs): Monobromoacetic acid and dibromoacetic acid. They are, partly formed by hydrolysis of haloacetonitriles and are non-volatile. Dibromoacetic acid comprises 25% to 45% of the total DBPs generated.
- Haloacetonitriles (HANs): Formed by oxidation of amino acids. Dibromoacetonitrile is most commonly found. They are semi-volatile. Dibromoacetonitrile represents 6% to 9% of the total DBPs generated.
- Halophenols: 2,4,6-Tribromophenol (TBP) is the most commonly encountered, though dibromophenol is occasionally reported. Halophenols are non-volatile. 2,4,6-TBP represents less than 1% of total DBP, but this compound is known to accumulate in water and because of its high log K_{ow} (4.13) could bioaccumulate in fish.

Other less frequently identified DBPs are reported in the review by Taylor (2006) as dibromoethane, chlorotoluenes, bromopropanes, chloropropanes and tribromobenzene.

Overall, these results show the same spectrum of DBPs. Although there is a qualitative homogeneity, we can observe a great variability of the measured concentrations at all power stations. It is attributable to the variability of the chemical quality of the water at each site, particularly the ammonia and dissolved organic matter content, but other factors inherent to the circuits themselves are involved. *In situ* data from analysis of chlorinated cooling water samples show large variations that are not only explained by differences in water quality but also by the inherent causes of circuits' complexity and variability of their operation.

The simple estimation of the chlorine dosage in a sample requires determination not only of the concentration of the hypochlorite solution but also of the actual dilution rate in the cooling water that is not constant, depending on the tidal cycle or the clogging of injection nozzles. It should be noted that the chlorine dosage is not often indicated in the publications or that it is supposed equal to the theoretical target value corresponding to the optimum operation of the installation as shown in Table 5-6.

The DBP formation depends on the transit time in the cooling circuits, the formation kinetics and the time required for the generation a specific DBP. Data from laboratory experiments with chlorinated seawater (Allonier *et al.* 1999a) show that 93% of bromoform generated in 24 hours is formed within 3 hours. 2,4,6-TBP and DBAA are formed more slowly: 30% in 6 hours for 2,4,6-TBP and 52% in 6 hours for DBAA (see Chapter 3). In the discharge plume, a few hours after the release, the cooling water is diluted and residual oxidants disappear. Data for DBAN indicate a slower process than for DBAA formation, probably due to the hydrolysis of DBAN. As the DBPs analysis are performed 1 to 4 days after sampling, the concentrations measured for bromophenol and DBAA overestimate the actual concentration at the outlet of the circuit and after dilution in the discharge plume.

Electricité de France (EDF) DBPs research program

From 1995 to 1998, EDF R&D carried out a program of measurements of the DBPs produced by chlorination at three nuclear power stations located at the Channel (Paluel and Penly) and at the North Sea coast (Gravelines).

During this study, attention was paid to reducing the uncertainty on DBPs analyses by carrying out an accurate estimation of the chlorine dosage in each sample taken from a circuit of which all the characteristics are known. An experimental study by addition of sodium hypochlorite to seawater collected at cooling water intakes made it possible to get rid of these difficulties, but it does not integrate the effect of biofilms on the walls of the circuits and in the condensers.

In accordance with the results of previous studies at European power stations, the four major groups of DBPs have been identified (Allonier *et al.* 1999a; Allonier 2000; Jenner and Whither 2011). In addition, bromate ions (BrO_3^-) have been detected in the hypochlorite solution produced at French power stations by electrochlorination. Bromide is oxidized by the active chlorine at high concentration in this solution (1 g Cl_2/L). According to the conclusion of a study conducted at EDF R&D, the formation kinetic of bromate is very slow and the retention time of the hypochlorite solution in the storage tank is too short (minutes) to produce high bromate concentrations in chlorinated cooling water.

Despite the variability of the results, the data collected at Penly, Paluel and Gravelines made it possible to specify the formation yields of the DBPs and to quantify the discharges at sea.

Relationships between the chlorine dosage and the DBP concentration were calculated from linear regressions. Bromoform is always present and measured above the threshold of quantification in chlorinated cooling waters, which is why linear relations between bromoform and the other DBPs were calculated when the amount of data allowed it. In case of a small number of values, the geometric mean of the ratios to the bromoform was retained. All these ratios are presented in Table 5-5.

Table 5-5: Weight ratios between DBPs and chlorine dosing or bromoform concentration in chlorinated cooling waters at three sites (according to Khalanski 2003).

	Ratio	**Paluel**	**Penly**	**Gravelines**
From data on chlorinated Cooling Waters	$CHBr_3$ [μg/L]/Ci[mg/L]	40.55 (LR)	25.11 (LR)	37.21 (LR)
	DBCM [μg/L]/ $CHBr_3$ [μg/L]	0.045 (LR)	0.016 (LR)	0.034 (LR)
	BDCM [μg/L]/$CHBr_3$ [μg/L]	0.003 (GM)	0.003 (GM)	0.0048 (GM)
	DBAA [μg/L] /$CHBr_3$ [μg/L]	0.380	0.984	0.355
	DBAN [μg/L]/$CHBr_3$ [μg/L]	0.106	0.128	0.135
	2,4,6-TBP [μg/L]/$CHBr_3$ [μg/L]	0.005	0.014	0.014
From Experimental Chlorination	$CHBr_3$ [μg/L]/Ci [mg/L]	24.84	19.39	21.05
	DBAA [μg/L] / Ci [mg/L]	ND	4.165	2.994
	DBAN [μg/L]/ Ci [mg/L]	ND	1.796	1.571
	2,4,6-TBP [μg/L]/ Ci [mg/L]	ND	ND	0.363
	DBCM + BDCM [μg/L]/ $CHBr_3$ [μg/L]	0.039	ND	ND
	$CHCl_3$ [μg/L]/$CHBr_3$ [μg/L]	0.004	ND	ND
	DBAA [μg/L] /$CHBr_3$ [μg/L]	0.168	ND	0.121
	DBAN [μg/L]/$CHBr_3$ [μg/L]	0.072	ND	0.063
	2,4,6-TBP [μg/L]/$CHBr_3$ [μg/L]	ND	ND	0.015

Ci: initial chlorine dosage; LR: linear regression; GM: ratio on geometric means; ND: no data.

The estimated DBP concentrations calculated from the ratios on Table 5-5 are shown in Table 5-6 for a chlorine dosage of 1.0 mg/L and are compared with the range of concentrations reported for European power stations by Taylor (2006).

Table 5-6: DBPs concentrations in chlorinated cooling water at three French power stations for an estimated chlorine dosage of 1.0 mg/L Cl_2 (according to Khalanski 2003).

	Power plant outlet concentrations Chlorine dosage 1 mg/L			Experimental chlorination on seawaters Chlorine dosage 1 mg/L			Concentration range in European power stations[11]
DBPs (μg/L)	**Penly**	**Paluel**	**Gravelines**	**Penly**	**Paluel**	**Gravelines**	
$CHBr_3$	25.11	40.55	37.21	19.39	24.84	2.05	1 to 43
DBCM	0.40	ND	1.27	ND	0.97[12]	ND	0.1 to 2.2
BDCM	0.08	0.12	0.18	ND	ND	ND	0.1 to 1.0
DBAA	20.10	15.41	13.21	4.16	ND	2.55	< 2 to 10
DBAN	3.21	4.30	5.02	1.8	ND	1.33	0.1 to 5.0
2,4,6-TBP	0.35	0.20	0.52	ND	ND	0.32	< 0.05 to 0.3
$CHCl_3$	0.75	0.36	0.16	ND	0.11	ND	< 0.1 to 0.3

[11] Concentration range recorded at European power stations (Taylor 2006, c.f. Table 5-4)
[12] DBCM+DCBM; ND: no data

At these three plants, the average level of continuous chlorination over the duration of the study was different and below the target concentrations: 0.31 mg/L, 0.52 mg/L and 0.79 mg/L instead of 1 mg/L at Penly, Paluel and Gravelines, respectively. However, there were relatively frequent interruptions of treatment and therefore reduced production of the hypochlorite solution. It has to be noted, that these interruptions in treatment are quite common. This illustrates the fact that the actual operating conditions are different from the optimal theoretical conditions. Estimated quantities of chlorine produced and DBPs released into the coastal marine environment based on these theoretical conditions are presented in Table 5-6.

Table 5-7: Estimated amount of DBPs in the chlorinated cooling water at the three French powers stations. Mean production estimated for the 2 to 6 units in operation with data collected on periods mentioned (according to Khalanski 2003).

	Penly Units 1-2 1995-2000	**Paluel Units 3-4 1996-1998**	**Gravelines Units 1 to 6 1991-2000**
Cooling water flow	90 m^3/s	180 m^3/s	252 m^3/s
Chlorine used [tonnes Cl_2/year]	468	1242	3148
$CHBr_3$ [t/a]	11.7	50.4	117.0
DBCM + BDCM [t/a]	0.2	2.5	4.6
DBAA [t/a]	11.6	19.1	41.6
DBAN [t/a]	1.5	5.3	15.8
2,4,6-TBP [t/a]	0.2	0.3	1.6

The mean yearly amount of bromoform produced in the period 2005-2017 at Gravelines is 62 t/a, but there is a great variability, in the range of 29 tonnes in 2012 to 106 tonnes in 2006 (as reported in EDF CNPE de Gravelines 2018). Thus, the estimate of bromoform discharges, assuming a continuous operation of chlorination at its optimum level (117 t/a) corresponding to the maximum chlorine production at this power station, is only reached in one year out of 13. The analytical data from environmental monitoring of DBP at Gravelines do not allow the validation of the relevance of the estimates of all DBP concentrations provided in Table 5-7 because the haloacetic acids and the haloacetonitriles are not measured and the other THMs than bromoform remain at levels generally below the threshold of quantification. However, in recent years, reports of environmental monitoring in Gravelines provide original results for the presence of bromophenols other than 2,4,6-TBP. Four bromophenols were analyzed at low concentrations: 2,6-DBP, 2,4-DBP, 3-BP, 2-BP. Between 2015 and 2017, the average concentrations for the two bromophenols more frequently recorded are 0.034 μg/L for 2,6-DBP and 0.016 μg/L for 2-BP (Antajan *et al.* 2017; Antajan *et al.* 2018).

DBPs study Rotterdam harbour 2016-2017

Between August 2016 and June 2017, four sampling sessions were carried out in the harbour of Rotterdam at a power station measuring THM with bromoform as target compound. This power station is using pulse chlorination and sampling was done during peak chlorination. At all sampling dates four duplicate samples were taken in the outlet area at different locations and three duplicate samples in the inlet area at different locations. The results are summarized in Table 5-8 for the four sampling periods.

Bromoform concentrations are differing between the seasons, showing lower ones in colder times. Probably, this is due to a variation in precursors the hypochlorite is reacting with.

Beginning in November 2016, an extra test sampling was done at high and low tide. Results show that there was no clear influence of the tidal cycle on the THM formation.

Table 5-8: Concentrations of THM at the outlet of a power station cooling circuit in the Rotterdam Harbour (according to Polman 2018).

	August 2016	November 2016	March 2017	June 2017
$CHBr_3$ [μg/L]	41 – 46	6.5 - 10.0	20	9.0 - 27.0
$CHClBr_2$ [μg/L]	1.8 - 1.9	ND	ND	0.6 - 1.4
Free oxidants [mg/L as Cl_2]	0.32	0.25	0.15	0.22

DBP study in Gulf of Fos

From 2014 to 2020, a research program funded by the French Agency of Research aims to identify nature and levels of DBPs generated by various industries using seawater for cooling or heating purposes in the Gulf of Fos (Marseille, Mediterranean Sea). This semi-enclosed bay gathers two large liquefied natural gas (LNG) terminals with maximum hourly regasification seawater flows of 30,000 m^3/h (electrochlorination) and 15,000 m^3/h (hypochlorite dosing), respectively.

There are also four power stations with very irregular operating levels according to seasonal and economical fluctuations with maximum cooling water flows up to 45,000 m^3/h. In addition, steel industry and oil refineries may also chlorinate seawater in volumes exceeding 10,000 m^3/h.

The mean levels found during the five measurement campaigns carried out during this period are presented in Table 5-9. This study shows that an important fraction of DBPs are still not known (ratio sum of identified DBP/EOX values) and research is thus still needed to identify their nature.

Table 5-9: Mean concentrations of DBPs at the outlet of various plants using chlorination in the Gulf of Fos on the French Mediterranean coast (according to Boudjellaba *et al.* 2016; Manasfi *et al.* 2019)

	Petrochemical plants [μg/L]	Thermal plants [μg/L]	Steel plant [μg/L]
Bromoform	4.4 - 9.8	0.57 - 0.64	0.3 - 1.8
Dibromochloromethane	0.03 - 0.13	0.01	0.05
Dibromoiodomethane	0.11	-	-
Bromal hydrate	2.5 - 5.3	0.06 - 0.07	0.6 - 1.4
Tribromonitromethane	0.1		0.1
Bromoacetonitrile	0.1	0.1	0.1
Bromochloroacetonitrile	0.17 - 0.26	0.04	0.05 - 0.07
Dibromoacetonitrile	0.7	0.2 - 0.7	0.01 - 0.30
Monobromoacetic acid	0.2	-	-
Bromochloroacetic acid	0.06	-	0.9
Dibromoacetic acid	3.8 - 4.2	0.42-3.5	0.04 - 0.21
Chlorodibromoacetic acid	0.32 - 0.37	-	0.23 - 0.30
Tribromoacetic acid	2.1 - 4.4	0.7	0.30 - 1.10
2,4,6-tribromophenol	0.3 - 0.4	-	0.1
Sum of identified DBPs	13.6 - 25.6	1.1	0.5 - 1.1
EOX	17.4 - 28.6	5.6	0.8 - 12.6

5.4 Estimated environmental concentrations

For releases of substances to natural areas PECs are needed to assess the resulting environmental risk. The European Commission (2003) has produced a methodological guide (Technical Guidance Document on Risk Assessment (TGD)) in which chemical discharges into the coastal marine environment are considered in particular. The procedure takes into account the evolution of substances into three compartments: water, suspended matters and sediments. This evolution depends on physico-chemical and biological processes (dilution, volatilization, hydrolysis, adsorption, sedimentation, biodegradation) that lead to the reduction of the concentration of substances in water from a point of discharge on the coast. This estimate is recommended on areas close to the release (local scale) and at a regional scale.

This method was applied to DBPs discharges by nuclear power stations on the French coast of the Channel and North Sea (Khalanski 2003). In this study, the PEC depends on three factors:

- The DBPs concentration at the outfall of power stations. The concentration of the major DBPs in the cooling water at EDF marine power stations is estimated from the formation ratios ($CHBr_3$/Chlorine and DBP/$CHBr_3$ (Table 5-7)) and the mean chlorine amount applied at each site (Table 5-6);
- The physical dilution into the volume of water in a theoretical marine area (local and regional scale);
- Two physical and chemical decaying processes reducing the DBPs concentration in water. It was assumed that DBPs do not interact with suspended solids and sediments. The only disappearance process from the liquid phase were volatilization of THMs according to a water depth-dependent model (Helz and Hsu 1978) and hydrolysis of dibromoacetonitrile to dibromoacetic acid (Bieber and Trehy 1983).

Close to the discharge point of the largest nuclear power station, at Gravelines, the dilution rate is 20, corresponding to a 5 % recirculation rate of the cooling water. This dilution factor was adopted as representative of the "near field" and representative of the local scale according to the TGD.

At the regional scale, a dilution factor of 100 was applied which is only five times higher than the dilution factor at the local scale. This choice is justified by the large flow of cooling water and the strong tidal currents in the Channel creating a kind of coastal river isolated from offshore water. In the regional box, the decay of DBPs is calculated over a period of 14 days on the basis of the general drift of coastal waters.

The results presented in Table 5-10 show that tribromomethane (bromoform) and dibromoacetic acid reach the highest concentrations. At the local scale, bromoform dominates with concentrations between 0.3 μg/L and 1.5 μg/L, while DBAA is the major DBP at the regional scale: 0.04 μg/L to 0.14 μg/L. This difference is due to the hydrolysis of dibromoacetonitrile to DBAA and the persistence of DBAA whose half-life of the decomposition process to oxoacetic acid is about 300 days (Exner *et al.* 1973).

Table 5-10: Calculated PECs of DBPs at the local and at the regional scales for cooling water discharged by three French nuclear power stations.

		Penly Units 1 – 2 90 m^3/s	**Gravelines Units 1 – 6 252 m^3/s**	**Paluel Units 1 – 4 180 m^3/s**
	DBP	**[μg/L]**	**[μg/L]**	**[μg/L]**
Local scale	CHBr3	3.95×10^{-1}	1.47	1.05
	DBCM	6.33×10^{-3}	5.00×10^{-2}	4.50×10^{-2}
	DCBM	1.20×10^{-3}	7.06×10^{-3}	2.93×10^{-3}
	CHCl3	1.19×10^{-2}	6.32×10^{-3}	9.49×10^{-3}
	DBAA	3.89×10^{-1}	5.22×10^{-1}	4.01×10^{-1}
	DBAN	5.06×10^{-2}	1.98×10^{-1}	1.12×10^{-1}
	2,4,6-tribromophenol	5.45×10^{-3}	2.06×10^{-2}	4.89×10^{-3}
Regional scale	CHBr3	1.99×10^{-2}	7.41×10^{-2}	5.32×10^{-2}
	DBCM	1.29×10^{-4}	1.02×10^{-3}	9.16×10^{-4}
	DCBM	1.21×10^{-5}	7.09×10^{-5}	2.95×10^{-5}
	CHCl3	5.15×10^{-5}	2.74×10^{-5}	4.12×10^{-5}
	DBAA[13]	8.82×10^{-2}	1.45×10^{-1}	1.03×10^{-1}
	DBAN[14]	6.33×10^{-4}	2.48×10^{-3}	1.40×10^{-3}
	2,4,6-tribromophenol	1.09×10^{-3}	4.12×10^{-3}	9.78×10^{-4}

[13] Including DBAA formed by hydrolysis of DBAN (half-life 85 hours)
[14] including the loss of DBAN by hydrolysis.

5.5 Conclusion

Treatment of cooling waters at coastal power stations is characterized by large volumes of treated water with relatively low oxidant concentrations. The reaction times are considerably shorter than in ballast water treatment (2 - 30 minutes) before discharge. The treated water is released at a well-defined outlet typically generating a plume around the outlet with DBP concentrations constantly above background levels.

Chlorination of cooling water from coastal power plants is widely used to prevent clogging of cooling water circuits by macrofouling and loss of thermal efficiency by bacterial slime. This chemical treatment is applied on large flows of seawater (tens to hundreds of m^3/s) with low chlorine concentration. Chlorine is added to the cooling water as a solution of sodium hypochlorite frequently produced *in situ* by electrochlorination cells.

It is possible to adapt the treatment periods, the chlorine concentrations and the frequency of treatments to the specific conditions to each plant. This optimization process results in minimizing the amount of hypochlorite used.

The oxidizing compounds responsible for macrofouling and microfouling toxicity disappear rapidly in the cooling water but their by-products (DBPs) are more stable, they persist in the marine environment and some can be transported over long distances.

Analyses carried out on chlorinated cooling water at European power stations showed the presence of four groups of DBPs with distinct chemical properties: trihalomethanes (THM), haloacetic acids, haloacetonitriles and halophenols. The formation of bromate ions is only effective at very high concentrations of chlorine but it is formed under very slow kinetics. As a result, bromate concentrations do not reach significant levels in the hypochlorite solutions produced by electrochlorination when the renewal time in the storage tanks does not exceed a few minutes.

Dominant DBPs are bromoform and dibromoacetic acid (DBAA). Both are found in all chlorinated effluents at concentrations significantly higher than the quantification limit. DBAA is formed by hydrolysis of dibromoacetonitrile (DBAN). Bromoform is the major DBP with an average concentration of 25.7 μg/L but peak concentrations of 124 μg/L have been reported.

In-situ data from analyzes of chlorinated cooling water samples show large variations that are not only explained by differences in water quality but also by the inherent causes of circuits´ complexity and variability of their operation.

For the assessment, estimates on average DBP concentration in discharges are based on data from three large power plants on the North Sea and North Sea coast (see Table 5-6) and an assumed average chlorine dosage of 0.75 mg/L (Cl_2). These data are used since they represent the most systematic analysis with a correlation of applied chlorine doses and produced DBP. As typical chlorine dosage range from 0.5 to 1 mg/l, and an average dosage of 0.75 mg/L is used for global estimation (Table 5-11).

Table 5-11: Estimated medium DBPs concentrations in chlorinated cooling water at nuclear power stations[15] for an estimated chlorine dosage[16] of 0.75 mg/L Cl_2

DBPs	Medium concentration based on data in Table 5-6 [μg/L]
$CHBr_3$	25
DBCM	0.6
BDCM	0.1
$CHCl_3$	0.3
DBAA	12.2
DBAN	3.1
2,4,6-TBP	0.3

[15] This estimation is based on European power stations data as outlined in the text and does not specifically include seasonal differences;
[16] As typical treatment concentration ranges from 0.5 to 1 mg/L, an average dose of 0.75 mg/L is assumed.

Apart from these four main groups of DBPs, other DBPs have been identified in recent research programs on chlorinated cooling circuits. New studies on these by-products are needed to complement the environmental and health impact assessments.

In chapters 10, 11 and 12, a risk assessment is carried out for the environment, human health and the atmosphere. Therefore, some assumptions are required. Due to the lack of data on industrial cooling, the assessment of global DBP production has to be restricted to existing data on coastal power plants. Based on the data mentioned in this chapter it is proposed to use the values in Table 5-12 as assumptions in the risk assessment.

Table 5-12: Assumptions for risk assessment

Parameter	
Amount of treated cooling water	4.7-8 x 10^{11} m^3/a
Average dose applied	0.75 mg TRO/L (as Cl_2)
Discharge of DBP	Mean value Table 5-11 [μg /L]
Predicted environmental concentrations	Calculated maximum concentration in the outlet and the surrounding water (Table 5-10)

6 DESALINATION

Rapid population growth and frequent droughts have accelerated the demand for freshwater supply around the world. For decades, desalination operations in many countries in the Middle East, the Mediterranean Basin, and South America as well as Australia, Japan, and the United States have provided drinking water to populations. The global capacity for water production through desalination has been estimated to be almost 100 million m^3/d in 2018 (Jones *et al.* 2019) but capacity and production is predicted to rapidly increase in the future (Hanasaki *et al.* 2016). The largest number of desalination plants is found in the Arabian Gulf. Around 60% of global desalination capacity treats seawater; the remainder treats brackish water (21%) and less saline water (Bennett 2013). The share of seawater has become larger according to the more recent data published by Jones *et al.* (2019). As a result, the impact of DBPs formed and released during desalination processes on the marine environment will also increase.

6.1 Treatment process

The treatment process can rely either on thermal desalination (i.e., distillation) or membrane-based desalination techniques (e.g., reverse osmosis (RO)). In total, reverse osmosis and distillation techniques represent 63% and 31% of the world treatment capacity, respectively (Gude 2016).

To prevent bacterial growth and biofouling in the intake structures and to improve the performance of filters, chemical disinfectants are used as a pre-treatment before multi-media filtration or membrane filtration. Free chlorine (i.e., HOCl/OCl^-) is the most commonly used disinfectant for pre-treatment as well as final disinfection. Chloramines, ozone, and chlorine dioxide are also used as alternative disinfectants. Disinfection of seawater and product water is essential in desalination plants (not always performed as pre-treatment in RO desalination plant) to prevent biofouling and contamination with pathogens, respectively.

Chlorination (continuous, intermittent, or shock) is generally used as pretreatment of seawater prior to desalination processes to control biofouling problems associated with heat exchangers in thermal processes and membranes in the RO process. DBP formation is strongly governed by three major factors: chlorine dose, contact time and the organic carbon content (i.e., TOC or DOC). Temperature and pH also play important roles in DBP formation. For RO desalination plants the chlorine dose and contact time vary with the chlorination mode (continuous, intermittent, shock; see also chapter 5), the location and the objectives (intake pipe can be used for other applications e.g., power plants). A dose in the range of 0.2 – 2 mg Cl_2/L is typically applied continuously to protect the intake pipe, although doses of up to 5 mg Cl_2/L are used in some installations (Kim et al 2015). The chlorine contact time can reach up to 45 min to 1 hour before injection of sodium bisulfite used to quench residual chlorine and RO filtration to avoid damage to membranes. Contact time should be shorter in RO plants using ultrafiltration as pre-treatment (UF/RO plant) than RO plants equipped with dual media filtration as pre-treatment (DMF/RO plant). For shock treatment the chlorine dose can be higher (i.e., 5 to 10 mg/L) with contact time ranging from 30 min to 1 hour, applied twice a day to once a week. Typically, the target is to maintain a residual concentration of 0.5 to 1 mg/L of free chlorine in the entire pre-treatment line. For thermal desalination plants (chlorine dose around 2 mg Cl_2/L) a residual chlorine concentration of 0.2-0.3 mg Cl_2 /L is targeted at the heat rejection section (Multi-stage flash distillation (MSF) plant) and no sodium bisulfite injection is required in the production line.

When regarding the DBPs, it is important to distinguish between the produced desalinated water, which might be dedicated to human consumption (notably when blended with fresh waters obtained from other sources) and the brine, which is rejected into the sea. Depending on the treatment process applied, different amounts of DBPs can accumulate in the different generated water fractions.

6.2 Quantification

Thermal desalination plants use higher quantities of the source water per freshwater quantities produced compared to reverse osmosis plants. Jones *et al.* (2019) estimate a global brine production and discharge of 142 million m^3/d taking into account specificities of combination of desalination technology and different feedwater qualities. 125 million m^3/d comes from seawater desalination plants situated close to the coastline. This equals a total estimated discharge of treated water from desalination plants into the marine environment of 4.6×10^{10} m^3/a.

Although thermal desalination plants use higher water volumes, the membrane desalination plants use large quantities of chemicals for pretreatment, control of membrane scaling and biofouling (Gude 2016). Higher DBP concentrations are typically observed in RO permeate than in thermal distillate (Kim *et al.* 2015). Table 6-1 shows DBP formation in chlorinated feed waters of desalination plants and their related conditions. THM and HAA concentrations reported in most chlorinated feed waters are well below 100 μg/L. However, oil spills near intakes, high chlorine doses or abundant precursors present in urban coastal areas characterized by high TOC may lead to enhanced THMs (mostly TBM) and HAAs (el Din *et al.* 1991; Agus *et al.* 2009). Relatively low levels of HANs (mostly dibromoacetonitrile (DBAN), dichloroacetonitrile (DCAN), and bromochloroacetonitrile (BCAN) among nine HAN species) and other DBPs such as bromophenols and iodinated THMs were also detected in chlorinated feed waters (Le Roux *et al.* 2015; Agus and Sedlak 2010). In both THMs and HAAs, brominated species are predominant in chlorinated seawater due to relatively high levels of bromide. Although THMs and HAAs are predominant DBPs in chlorinated seawater, haloacetamides (HAcAms) and haloacetaldehydes have also been detected from chlorination of saline groundwater affected by sea-level rise (Szczuka *et al.* 2017). A recent study revealed that hydrophobic neutrals and hydrophilic substances fractionated from seawater

DOM (<1 kDa MW) were the main sources of THMs and HANs, respectively (Yang *et al.* 2017). Shock (1 to 3 times a week) or intermittent chlorination (1 to 4 times a day) is considered to be better than continuous chlorination since long-term exposure to chlorine triggers the production of extra-cellular polysaccharides (Badruzzaman *et al.* 2019). However, pre-chlorination has become less common as a result of concerns of chlorinated DBPs but more importantly because of the production of AOC (assimilable organic carbon) that can promote biofouling.

Table 6-1: Overview on DBP occurrences in chlorinated feed water of desalination plants (extracted from Kim *et al.* (2015))

Locations and Reference[17]	DOC [mg/L]	Br- [mg/L]	THMs [μg/L]	HAAs [μg/L]	HANs [μg/L]	Other DBPs [μg/L]	Dose [mg/L] and contact time
Red Sea coast, Saudi Arabia[a]	0.98-1.62	60 0.05 (I^-)	6.18-18.41	5.35-6.86 HAA9	0.43-0.76 DBAN	1.90-2.57 I-THMs	0.25-0.5 (residual) or 0.7-1.0 (continuous)
Carlsbad, USA[b]	2.8		3.0-52	9.5-19 HAA9	0.5-1.9 DCAN, BCAN	0.3-0.6 Br-phenols	0.5-2.0 (initial) 2 hr
Tampa Bay, USA[c]	4.3-10.9[18]	49-56	490-860	69-175 HAA5			2.5-5.0
Ruwais, UAE[d]	5.3-9.0[17]		<25	<14.5 HAA5			
Al-Jubnail, Saudi Arabia[e]				7.0 HAA6			0.2-0.25 10-15 min
Okinawa, Japan[f]		68	35 (55 FP[19])				1.0 (residual) 24 hr
Ebara Corp, Japan[g]			15-25				0.3
Umm Al Nar, UAE[h]			78-95				0.2-0.3 (residual)
Jeddah, Saudi Arabia[i]	3.7[17]		3.3-24.0				0.5-2.0 (residual)
Eastern Coast, S. Arabia[j]	1.4-2.0[17]		3.1-27.9				
Shuwaikh, Shuaiba, Doha, Kuwait[k]	4.2-4.7		21.7-61.4				2.0 (residual)
Mean			95	32.8	2.4	0.45 (Br-phenols)	
Median			27.3	14.3	2.4	0.45	

[17] a. Le Roux *et al.* (2015), b Agus and Sedlak (2010), c. Agus *et al.* (2009), d. Elshorbagy and Abdulkarim (2006), e. Dalvi *et al.* (2000), f. Magara *et al.* (1996), g. Kojima *et al.* (1995), h. el Din *et al.* (1991), i. Mayankutty *et al.* (1991), j. Mayankutty *et al.* (1989), k. Ali and Riley (1989).
[18] TOC,
[19] Formation potential

Chloramines are widely used by drinking water utilities, particularly in the USA, as an alternative to chlorine to comply with stringent regulations for THMs and HAAs as chloramines form lesser amounts of these DBPs. In the presence of high bromide, however, bromamines which are more reactive oxidants and decay more rapidly can be produced from chloramines. Furthermore, chloramines lead to the formation of other types of DBPs including N-nitrosamines, HANs, HNMs, iodinated THMs, and iodinated HAAs. The formation of iodinated THMs can be enhanced during chloramination compared to chlorination (Jones *et al.* 2011; Jones *et al.* 2012), because the oxidation of hypoiodous acid (HOI), the principal oxidant involved in iodinated THM formation, to iodate (IO_3^-) is much slower for monochloramine (NH_2Cl) than for HOCl (Bichsel and von Gunten 1999, 2000; Hua and Reckhow 2007). Iodinated THMs have been known to be much more cytotoxic and genotoxic than the regular four THM species (Richardson *et al.* 2008). Although chloramines are used to control biofouling in desalination intake structures and RO membrane systems and to minimize the membrane damage associated with free chlorine, further studies on the DBP formation in chloraminated seawater at intakes of desalination plants are warranted. Comparison of chloramination and chlorination formation by-products was performed on algal bloom samples (main species was *Synecococcus* sp.) collected from seawater mesocosms operated in the Red Sea. Chlorination produced more HAcAms than chloramination from real algae (*Synecococcus* sp.), thus indicating that the nitrogen of HAcAms comes predominantly from DON through the decarboxylation of amino acids rather than from NH_2Cl. Dibrominated species of DBPs (i.e., DBAcAm, DBAA and DBAN) were the dominant species formed by both chlorination and chloramination of algal bloom samples (Nihemaiti *et al.* 2015).

Chlorine dioxide (ClO_2) does not form appreciable levels of chlorinated DBPs such as THMs and HAAs under typical water treatment conditions (Hua and Reckhow 2007). Even in the presence of high bromide, chlorine dioxide is a good disinfectant. Since chlorinated feed water can degrade RO membrane materials (in particular polyamide membrane), dechlorination with sulfite or activated carbon (typically contained in a filter) is required before the membrane train. Either development of chlorine-resistant membranes or the use of chlorine dioxide for pre-treatment can be applied to avoid the oxidation of membrane materials and to maintain the membrane performance. However, using of chlorine dioxide for disinfection produces inorganic DBPs such as chlorite (ClO_2^-) and chlorate (ClO_3^-). Some RO desalination plants in the USA and Spain use chlorine dioxide for pre-treatment and the United Arab Emirates (UAE) employs increasingly chlorine dioxide in thermal desalination plants as an alternative disinfectant (Agus *et al.* 2009). According to Yu *et al.* (2015), elevating the initial levels of organic substances and bromide ions not only enhanced the total content of HAAs formed, but also shifted the speciation of HAAs from the chlorinated to fully brominated forms at higher disinfectant doses and longer contact times of chlorine dioxide disinfection. Chlorine dioxide oxidation in the presence of bromide led to polyamide bromination and RO membrane deterioration (Mizuta 2014). On the contrary, Oh and Jang (2016) found that polyamide deformation was mitigated well with chlorine dioxide compared to chlorination. In experiments with simulated drinking water samples (3 mg/L of DOC, 200 μg/L of I^-), Pan *et al.* (2016) found that chlorine dioxide treatment (5 mg/L at pH 7.5 for 5 days) led to the formation of iodinated HAAs and phenolic iodinated DBPs with 42.3 μg/L (as I) of TOI, which is greater than chlorination, but less than chloramination. Therefore, further studies are warranted to investigate RO performance under initial and low concentration of chlorine oxide disinfectants as well as the applicability of chlorine dioxide as an alternative disinfectant to conventional chlorine.

Due to the formation of elevated bromate concentration, a probable human carcinogen, in the presence of high bromide, ozonation is generally not considered as a pre-treatment method at intakes of seawater desalination plants even though ozone (O_3), a strong oxidant, can effectively remove a variety of microorganisms resistant to other disinfectants (Westerhoff *et al.* 2005). Pre-ozonation of 5 mg/L successfully degraded precursors of halophenols during chlorination of seawater (Ding *et al.* 2018). Liu, Shah, *et al.* (2018) reported that less bromoform formed during ozonation (5 mg/L) than chlorination (7.4 mg/L) in natural and synthetic seawaters contacting various NOM extracts (2-5 mg/L of DOC).

Either brine or RO concentrate discharges may significantly affect the marine environment, notably in the vicinity of outfalls if not diluted sufficiently, because discharges may contain residues of pre-treatment and cleaning chemicals (e.g., disinfectants, coagulants and coagulant aids, anti-scalants, and anti-foaming agents), DBPs, and even heavy metals (released due to corrosion). Salinity and temperature altered by constant discharges can also influence the marine ecosystem (Miri and Chouikhi 2005; Lattemann and Höpner 2008). However, the impact of brine discharges from seawater desalination plants on aquatic organisms has not been well studied. DBP occurrences in brine produced from thermal and RO seawater desalination plants from several previous reports are listed in Table 6-2. In addition to THMs, HAAs, and HANs, low levels of iodinated THMs and brominated phenols were also reported in a few RO concentrates (Le Roux *et al.* 2015; Agus and Sedlak 2010). When taking into account the volume of brine produced from desalination processes, Le Roux *et al.* (2015) showed that a given plant can discharged several tonnes of halogenated organic compounds into the marine environment every year. In a recent study, however, very high levels of residual chlorine (i.e., up to 0.63 mg/L of total chlorine) and THMs (i.e., up to 620 μg/L of bromoform) were observed in seawater samples collected at the outfalls of a seawater RO desalination plant in Egypt (Hamed *et al.* 2017). Although extremely large volume of seawater can dilute brine discharges, the impact of continuous inflow of such high concentrations of residual chlorine and DBPs formed during pre-treatment on the marine environment may not be overlooked. A chronic exposure of high levels of organic halides may significantly affect the life cycle of sensitive benthic organisms and plankton near the outfalls of desalination plants. Due to the treatment process, DBP concentrations substantially differ between distillates and the rejected brine. The former is most relevant when assessing risks to human health whereas the latter is determining the potential risk to the marine environment. Furthermore, for the impact on the atmosphere the overall bromoform production is potentially relevant. As stated in Le Roux *et al.* (2015), 90% of THM4 were rejected as vent gases. Therefore, a separate assessment of the overall THM production (which will be sooner or later emitted to the atmosphere) and the DBP reject to marine waters may be warranted.

Table 6-2: Overview on DBP occurrences in thermal brines and RO concentrates of desalination plants (extracted and amended from Kim *et al.* 2015).

Location		THM [μg/L]	TBM [μg/L]	DBCM [μg/L]	DCBM [μg/L]	TCM [μg/L]	HAAs [μg/L]	MBAA [μg/L]	DBAA [μg/L]	TBAA [μg/L]	HANs [μg/L]	DBAN [μg/L]	BCAN [μg/L]	Other DBPs [μg/L]	R
Thermal Brine															
Red Sea coast, Saudi Arabia	Brine recycle	9.5	9.0	0.36	0.13	ND	5.5	0.2	4.4	0.88	1.46	1.03	0.43		a
	brine blowout	0.18	0.53	0.14	0.21	ND	4.5	ND	4.4	ND	0.50	0.50	ND		a
Ruwais, UAE	brine blowout	<1.0	<0.2 – 0.8	<0.2	<0.2	<0.2 – 0.23	<15.2	<1.0	<1.0 – 11.6	ND					b
Doha West and Al-Zor, Kuwait		1.0 – 2.0	1.8 0.7												c
Jeddah, Saudi Arabia		12.7 – 17.8	12.4 – 17.4	0.3 – 0.4											d
RO concentrate															
Red Sea coast, Saudi Arabia	1st pass conc. in plant 1	6.2	4.96	0.23	0.06	ND	0.78	0.17	0.61	ND	ND	ND	ND		a
	1st pass conc. in plant 2	22.6 – 52.9	51.3	1.48	0.06	ND	5.7 – 7.2	ND	2.52	3.67	0.6 – 1.2	1.17	0.04	1.6 – 2.0 (I-THMs)	a
Carlsbad, USA	fall	5.0 – 14	5 – 14			0.2 – 0.7	17 – 27				0.78 – 3.1			0.53 – 0.96 (Br-phenol)	e
	winter	29 – 61	10 – 20			20 – 41									e
Ebara Corp, Japan		24 – 39													f
Nuweibaa, Egypt		159	104	2.9	0.3	52									g
Mean[20]		**29.5**	**19.3**	**0.8**	**0.2**	**10.4**	**9.1**	**0.3**	**3.6**	**0.9**	**1.3**	**0.7**	**0.1**	**0.75 (Br-phenols)**	
Range		**0.2 – 159**	**0.2 – 104**	**0.23 – 2.9**	**0.06 – 0.3**	**ND – 52**	**0.78 – 27**	**ND – 0.17**	**0.6 – 11.6**	**ND – 3.67**	**0.5 – 3.1**	**ND – 1.2**	**ND – 0.4**	**0.53 – 0.96**	

a. Le Roux *et al.* (2015), b. Elshorbagy and Abdulkarim (2006), c. Saeed *et al.* (1999), d. Mayankutty *et al.* (1991), e. Agus and Sedlak (2010), f. Kojima *et al.* (1995), g. value on THM calculated mean THM concentration from three outlets from Hamed *et al.* (2017).

ND: not detected.

R: Reference.

[20] calculated from all values provided. If rages are given, the mean value was used for the calculation. ND was set to 0 for purpose of calculation.

6.3 Conclusion

The estimated total volume of water used for desalination of marine and brackish water is 4.6 x 10^{10} m^3/a, which is below the volumes used for cooling purposes. Oxidant concentrations are similar to concentrations used in cooling waters. The treated water is released at a well-defined outlet typically generating a plume around the outlet. Bromoform is the major DBP. Not only residual chlorine and DBPs, but also metals from corrosion and other additives such as anti-fouling, anti-foaming, and anti-scaling agents which can be released during desalination processes may pose direct and/or indirect threats to the marine environment. Moreover, very limited data on DBP occurrence are available. Therefore, systematic DBP studies in full-scale seawater desalination plants are warranted to provide profiles of THMs and HAAs as well as other emerging DBPs (e.g., HANs, HNMs, N-nitrosamines, iodinated THMs, haloacetamides, haloketones, chloropicrin, cyanogen halide, chloral hydrate, and halophenols, etc.) at each process and to articulate DBP formation and speciation during seawater disinfection with chlorine and alternative disinfectants. In addition, although about 600 DBP species have been identified, THMs and HAAs account for only about 50% of total organic halide (TOX), and a large fraction of DBPs is still unknown. TOX analysis (requires solid phase extraction using appropriate adsorbent prior to conventional TOX analysis method to avoid chloride interference) conducted on seawater samples collected from different stages of desalination plants may be a useful tool to be used for better understanding the impact of released DBPs on the marine environment as a result of chemical treatment during seawater desalination processes.

In chapters 10, 11 and 12, a risk assessment is carried out for the environment, human health and the atmosphere. Therefore, some assumptions are required. Based on the data mentioned in this chapter it is proposed to use the values in Table 6-3 as assumptions in the risk assessment.

Table 6-3: Assumptions for risk assessment

Parameter	
Amount of treated water for desalination	4.6 x 10^{10} m^3/a
Average dose applied	0.25 - 2 mg TRO/L (as Cl_2)
Discharge of DBP into marine water	Mean value given in Table 6-2 [μg/L]
Estimated bromoform discharge	19 μg/L
Predicted environmental concentrations	No information available

7 SEAWATER TOILETS

To mitigate the shortage of freshwater supply, seawater is used for toilet flushing in different coastal areas including Hong Kong, the city of Avalon (California), and several Pacific regions including the Marshall Islands and Kiribati (Boehm *et al.* 2009; Tang *et al.* 2007; Mirti and Davies 2005). Such a practice has been extensively implemented in Hong Kong since the 1950s, which plays an important role in Hong Kong's sustainable water management. In 2015, the Hong Kong Water Supplies Department (HK WSD) successfully expanded the seawater supply coverage to 85% of the population in Hong Kong. Seawater used for flushing toilets accounts for about 22.5% of total water usage in Hong Kong in 2008. Up to date, a total of 270 million cubic meters of seawater is supplied every year (i.e., 7.4 × 10^5 m^3/d), conserving an equivalent amount of local fresh water supply (HK WSD 2018). According to HK WSD (2018), the quality of treated seawater is only permitted for flushing toilets but not permitted for fresh water supply, as this seawater is not treated to the same standard as required for fresh water.

7.1 Treatment process

As shown in Figure 7-1 and Figure 7-2, the seawater is firstly screened by strainers to remove sizeable particles. It is then disinfected with chlorine or hypochlorite generated on-site before being pumped to service reservoirs and distributed to consumers. Typical treatment concentrations of chlorine are reported as 3-6 mg/L as Cl_2.

It should be noted that the seawater after toilet flushing is mixed with other domestic sewage and enters the sewerage systems in Hong Kong. Such a practice introduces very high levels of sea salts, in particular high levels of bromide and iodide (65 mg/L as Br^- and 60-120 mg/L as I^-+IO_3^- in seawater) into the sewage. According to the Hong Kong Drainage Service Department (HK DSD), the saline sewage is subjected to either enhanced primary or secondary sewage treatment in Hong Kong. Chlorination is the major cost-effective disinfection method that is used in the sewage treatment plants to prevent deterioration of the coastal water quality and protect swimmers from pathogenic infection. Stonecutters Island Sewage Treatment Works (SI STW) is a chemically enhanced primary sewage treatment plant with a treatment capacity of 2.0 × 10^6 m^3/d, which is one of the largest primary sewage treatment plants in the world.

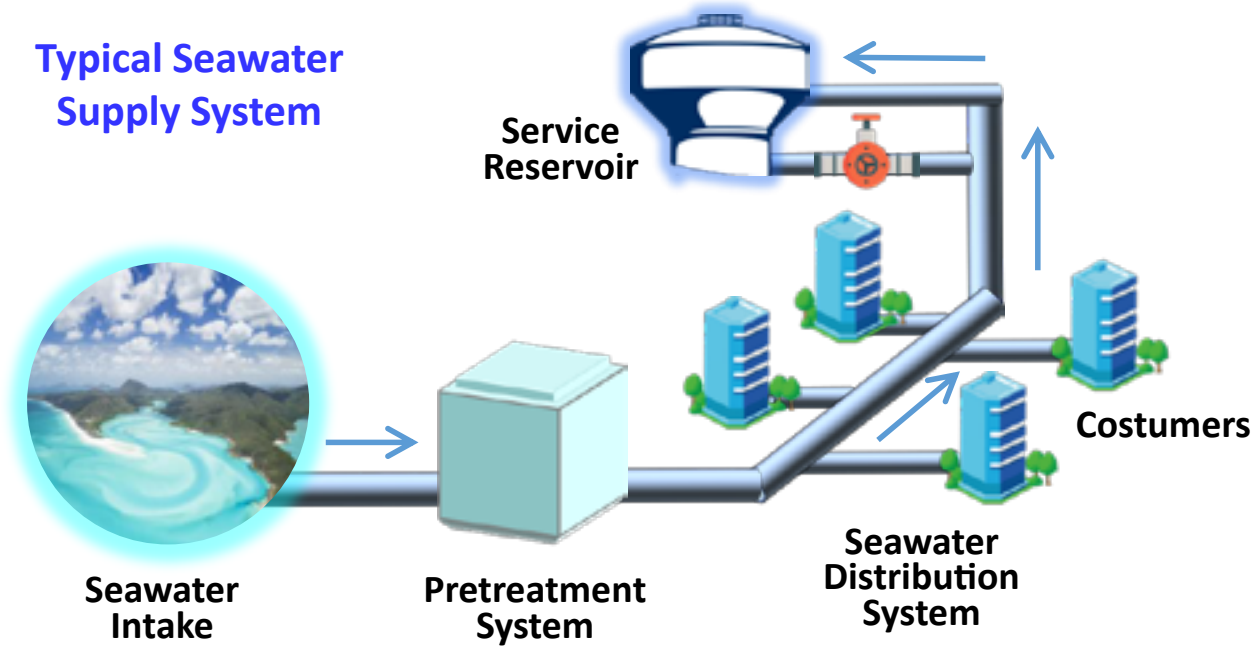

Figure 7-1: *Typical seawater supply system in Hong Kong (extracted from HK WSD 2018).*

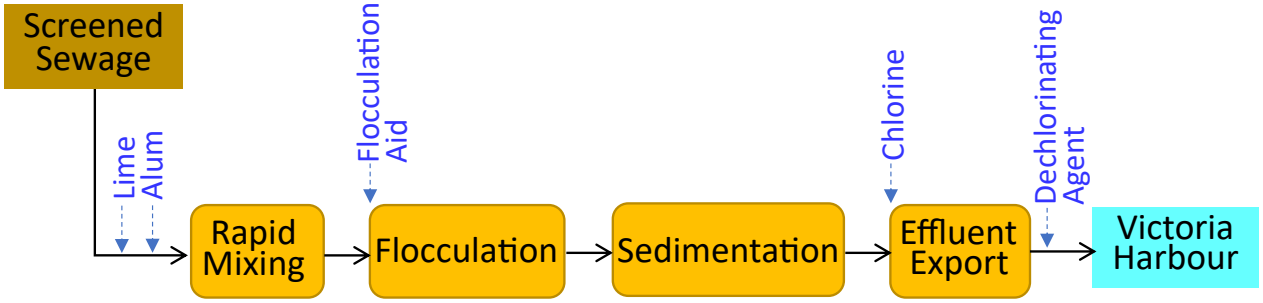

Figure 7-2: *The schematic treatment flow of SI STW (extracted from HK DSD 2009b).*

Figure 7-2 shows the treatment processes of the SI STW. The pre-screened saline sewage is dosed with ferric chloride in a mixing chamber and subjected to flocculation and sedimentation (i.e., primary treatment). The settled sewage is chlorinated at the inlet of a submarine outfall and dechlorinated by a sulfur-based dechlorinating agent prior to discharge. A high level of chlorine dose (i.e., 15 mg/L as Cl_2) and a contact time of 12 min are used in this sewage treatment plant for disinfection (Li *et al.* 2018). For the secondary sewage treatment in Hong Kong, the raw sewage is generally subjected to screening, degritting, primary sedimentation, biological treatment (mainly active sludge treatment), final sedimentation, and disinfection (Figure 7-3). Typical chlorine doses for disinfection are reported as 4-18 mg/L as Cl_2 and the contact times range from 15 to 30 min (Ding *et al.* 2013; Gong and Zhang 2015). The characteristics of the sewage effluent samples collected from the primary and secondary saline sewage treatment plants in Hong Kong are summarized in Table 7-1.

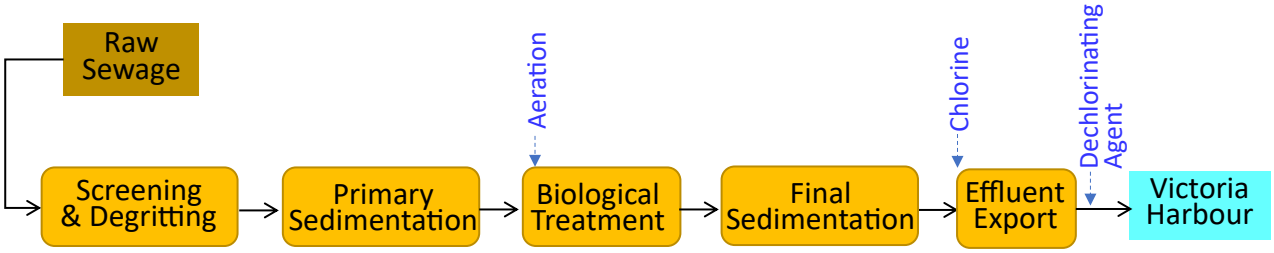

Figure 7-3: *The schematic treatment flow of a typical secondary treatment plant in Hong Kong (extracted from HK DSD 2009a).*

As shown in Table 7-1, the blend-in of seawater results in high levels of bromide, up to 31.5 mg/L as Br^- in the sewage effluent samples (Yang *et al.* 2005). During chlorine disinfection, the bromide ions in the saline sewage effluents are oxidized to HOBr, which can react with effluent organic matter (EfOM) to form brominated DBPs. Different from the DBP composition of chlorinated marine water, iodinated DBPs might be extensively produced in the chlorinated saline primary effluent. Due to the lack of nitrification (i.e., secondary treatment), high levels of ammonia, 21.2-24.3 mg/L, NH_4^+ as N (Yang *et al.* 2005; Ding *et al.* 2013; Li *et al.* 2018) are reported in the saline primary effluent samples, and a moderate level of iodide, 26.4 mg/L as I^-, was reported in one primary saline sewage effluent sample (Gong and Zhang 2015). After the chlorine addition to the saline primary sewage effluent, chloramine forms. As a weak oxidant, chloramine can oxidize iodide to HOI (but not further to IO_3^-), which then reacts with the EfOM in the sewage to form iodinated DBPs.

Table 7-1: Characteristics of sewage effluent samples collected from a primary and a secondary saline sewage treatment plant in Hong Kong (acc. to Yang *et al.* 2005).

Treatment scheme	Primary (enhanced coagulation, SI STW)	Secondary (active sludge process)[21]
Seawater blend-in ratio	≈25%	≈25%
NH_4^+ [mg/L as N]	21.2	2.8
DOC [mg/L as C]	47.2	7.2
UV254 [cm^{-1}]	0.174	0.112
SUVA [$L \cdot mg^{-1} \cdot m^{-1}$][22]	0.37	1.56
Br^- [mg/L]	31.5	22.0

[21] Shatin Sewage Treatment Work;
[22] Specific ultraviolet absorbance (SUVA) provides a general characterization of organic matter in a water sample and is typically performed for the purpose of determining DBP formation potential. SUVA is calculated by dividing the UV absorbance at 254 nm (cm^{-1}) by the dissolved organic carbon (mg/L) of a water sample, expressed in units of $L \cdot mg^{-1} \cdot m^{-1}$.

7.2 Quantification

The sewage is discharged to the marine environment directly after the treatment. About 93% of the population of Hong Kong is now served by the public sewerage system which treats 2.8×10^6 m^3/d of sewage from residential, commercial and industrial premises according to the data of the Hong Kong Drainage Service Department. As the saline sewage accounts for at least 70% of the total sewage, it should be considered as an important input of DBPs, in particular brominated/iodinated DBPs, to the marine water.

EfOM in the sewage consists of a variety of organic matter, including the organic compounds derived from micro-organism metabolization and human waste and the synthetic organic compounds such as industrial waste, detergents, and personal care products. A higher magnitude of complexity of brominated/iodinated DBPs can be formed in chlorinated saline sewage effluents than that in chlorinated marine water. Commonly known DBPs such as THMs and HAAs have been reported to form in chlorinated saline sewage effluents (Yang *et al.* 2005; Sun *et al.* 2009). According to Yang *et al.* (2005), all four chlorinated and brominated THMs were detected in the saline sewage effluents chlorinated at the breakpoint, with bromoform occupied 50-60% of the total THM molar concentrations. Seven chlorinated and brominated HAAs were also detected and the dominant species were trichloroacetic acid and dibromoacetic acid. With increasing the chlorine dose, the bromine incorporation ratio increased and the dominant HAA species were reported to be bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid. Beside THMs and HAAs, other polar/semi-polar brominated and iodinated DBPs have also been detected in chlorinated saline sewage effluents. These DBPs are aromatic halogenated DBPs, which are formed from the electrophilic chlorine substitution of the corresponding precursors in NOM and EfOM (Ding *et al.* 2013; Gong and Zhang 2015; Gong *et al.* 2016). An overview of the typical levels of DBPs reported in chlorinated saline sewage effluents in Hong Kong is shown in Table 7-2. There might be other unknown halogenated DBPs in chlorinated saline sewage effluents which remain to be detected and quantified.

Table 7-2: Concentrations of DBPs in chlorinated saline sewage effluents in Hong Kong.

	Primary effluent		Secondary effluent		Published by[23]
	Chlorine dose and contact time	**Levels [μg/L]**	**Chlorine dose and contact time**	**Levels [μg/L]**	
Chloroform	15 mg/L NaOCl as Cl_2 for 2 h	8.0	6 mg/L NaOCl as Cl_2 for 2 h	5.0	a
Dichlorobromomethane		11.6		4.9	a
Dibromochloromethane		15.6		2.5	a
Bromoform		26.5		31.8	a
Dichloroacetic acid		6.8		3.3	a
Trichloroacetic acid		5.0		5.7	a
Dibromoacetic acid		6.0		8.6	a
Tribromoacetic acid		8.0		2.8	a
Bromochloroacetic acid		4.2		1.4	a
Bromodichloroacetic acid		2.2		0.0	a
Dibromochloroacetic acid		0.0		0.0	a
Bromomaleic acid	15 mg/L NaOCl as Cl_2 for 30 min		6 mg/L NaOCl as Cl_2 for 30 min	2.36	b
5-Bromosalicylic acid		1.95			b
2,6-Dibromo-4-nitrophenol				4.33	b
3,5-Dibromo-4-hydroxybenzaldehyde				1.76	b
3,5-Dibromo-4-hydroxybenzoic acid				3.4 × 10–1	b
2,4,6-Tribromophenol				9.70 × 10–1	b
4-Bromophenol			6 mg/L NaOCl as Cl_2 for 30 min	1.62	c
2,4-Dibromophenol				5.80 × 10–1	c
2,4,6-Triiodophenol				4.00 × 10–4	c
2,6-Dichloro-4-nitrophenol				1.30 × 10–1	c
2,6-Diiodo-4-nitrophenol				1.13 × 10–3	c
3,5-Dichloro-4-hydroxybenzaldehyde				2.89 × 10–2	c
2,5-Dibromohydroquinone				2.0 × 10–1	c
Tetrabromopyrrole			6, 10, 15, 20 mg/L NaOCl as Cl_2 for 30 min	8.00 × 10–2 to 7.40 ×10–1	d
2,6-Diiodo-3,4,5-trihydroxybenzenesulfonic acid	18 mg/L NaOCl as Cl_2 for 30 min	9.10 × 10–1			e
2-Iodo-3,4,5-trihydroxybenzenesulfonic acid		5.70 × 10–1			e
2-Chloro-6-iodo-3,4,5-trihydroxybenzenesulfonic acid		4.30 × 10–1			e
2-Bromo-6-iodo-3,4,5-trihydroxybenzenesulfonic acid		1.07			e

	Primary effluent		Secondary effluent		Published by[23]
	Chlorine dose and contact time	Levels [μg/L]	Chlorine dose and contact time	Levels [μg/L]	
Total organic chlorine	0-18 mg/L NaOCl as Cl_2 for 30 min	14.9-84.8 (μg/L as Cl)	0-18 mg/L NaOCl as Cl_2 for 30 min	20.9-64.3 (μg/L as Cl)	b
Total organic bromine		8.0-110 (μg/L as Br)		8.8-402 (μg/L as Br)	b
Total organic iodine		7.2-13.6 (μg/L as I)			e

[23] Chlorination of the primary and secondary effluents was conducted in batch tests in the laboratory. Data extracted from a, Yang et al. (2005); b, Ding *et al.* (2013); c, Yang and Zhang (2013); d, Yang and Zhang (2014); and e, Gong and Zhang (2015).

7.3 Environmental concentrations

To date, limited coastal cities have adopted seawater toilets, which produce saline sewage effluents and generate numerous halogenated DBPs in chlorine disinfection, and eventually increase the DBP levels in receiving seawater nearby the discharge points. Maas *et al.* (2019) have estimated that the annual ballast water that is discharged to ports in the Pearl River Delta region (comprising three major ports, Hong Kong, Guangzhou and Shenzhen) has accounted for 8 % of global ballast water discharge (i.e., $2.71 \cdot 10^8$ m^3/a), which is less than half of the saline sewage discharge in Hong Kong (i.e., $7.30 \cdot 10^8$ m^3/a). Accordingly, the DBPs released from saline sewage effluents might be considered as a local hotspot in Hong Kong. Typical levels of the 30 halogenated DBPs (in particular low-level brominated and iodinated phenolic DBPs) in typical saline primary and secondary sewage effluent samples are shown in Table 7-2. After discharge, the DBPs in chlorinated sewage effluents will have different environmental behaviors due to their characteristics (e.g., volatility, polarity, and degradability). Volatile DBPs (such as bromoform) are expected to be outgassed and no longer accumulated in the receiving seawater. As for halo-aliphatic acids, dehalogenation and hydrolysis might occur in seawater. For halophenolic DBPs (including chloro-, bromo-, and iodo-DBPs), a recent study (Liu *et al.* 2017) has shown that some halogenated phenolic DBPs formed in chlorinated saline sewage effluents underwent photo-conversion in the seawater. Of note is that some halogenated DBPs in chlorinated saline wastewater effluents might not be photo-degradable in receiving seawater, but they can be biotransformed by aquatic species. A marine alga, *Tetraselmis marina*, has been reported to metabolize 2,6-dichloro-4-nitrophenol to less toxic products (Liu and Zhang 2014).

Concentrations of DBPs in the Mixed Sewage Effluent (prior to Discharge) and in the Receiving Seawater

The effect of sewage discharge to the receiving seawater in Hong Kong has been carefully monitored and evaluated by Hong Kong Drainage Service Department (HK DSD 2018). To improve the water quality in the Victoria Harbour, the saline sewage effluents together with urban runoffs and freshwater sewage effluents are collected from both sides of the Victoria Harbour (i.e., the mixed sewage effluent) and discharged to the harbour area through 23.6 km-long underground tunnels, which is also called "The Harbour Area Treatment Scheme" (HATS). The HATS comprises two stages. The HATS Stage 2A (hereinafter referred to as "the Project") has implemented advanced disinfection facilities, which consist of chlorination and dechlorination systems. The Project has been fully commissioned by the end of 2015. To comply with appropriate standards and requirement during operation of the Project, the levels of two major groups of regulated drinking water DBPs, trihalomethanes and haloacetic acids, in the mixed sewage effluent and receiving seawater have been monitored on a quarterly basis. The monitoring results are shown in Table 7-3 and Table 7-4.

Table 7-3: Concentrations of DBPs in the mixed sewage effluent (Monitoring from 25 October 2016 to 23 April 2018, data retrieved from HK DSD, 2018)

DBPs	Min. (μg/L)	Max. (μg/L)	Mean (μg/L)	Median (μg/L)	Estimated annual discharge (kg/a)
Trichloromethane	5.0	26.2	13.9	10.7	1.42×10^4
Bromodichloromethane	<1.0[24]	7.0	2.7	1.3	2.70×10^3
Dibromochloromethane	<1.0[24]	9.0	3.0	2.5	3.06×10^3
Bromoform	<1.0[24]	12.0	4.8	3.1	4.86×10^3
THM_4	**6.5**	**51**	**24.4**	**19.2**	**2.48×10^4**
Monochloroacetic acid	<2.0[24]	<5.0[24]	1.8	1.0	1.79×10^3
Dichloroacetic acid	10.0	28.0	16.7	15.0	1.71×10^4
Trichloroacetic acid	3.0	14.0	7.0	7.0	7.16×10^3

DBPs	Min. (μg/L)	Max. (μg/L)	Mean (μg/L)	Median (μg/L)	Estimated annual discharge (kg/a)
Monobromoacetic acid	<2.0[24]	3.0	1.5	1.0	1.53×10^3
Dibromoacetic acid	2.0	5.2	3.1	3.0	3.18×10^6
HAA_5	**20**	**47.2**	**30.1**	**28.5**	**3.07×10^7**

[24] For the DBPs in the sample with concentrations of "<1.0", "<2.0" and "<5.0" (i.e., quantitation limits), their concentrations were assumed to be the half of the corresponding quantitation limits, i.e., "0.5", "1.0" and "2.5", respectively, in calculating the mean concentrations.

Compared with the DBP levels in the chlorinated saline primary and secondary sewage effluent samples (Table 7-2), the DBP levels in the mixed sewage effluent were significantly lower, which might be due to dilution, evaporation, and degradation during the sewage transport. Although the levels of individual DBPs in the mixed sewage effluent varied with the collection dates, the median and mean DBP levels were similar. Then, the mean DBP levels were used to estimate the annual DBP inputs to the receiving seawater, i.e., Victoria Harbour. As the annual sewage discharge is 1.02×10^9 m^3/a, the corresponding DBP inputs are calculated and shown in Table 7-3. In summary, the annual THM4 and HAA5 inputs to the harbour area are 2.48×10^7 g/a and 3.07×10^7 g/a (i.e., 24.8 t/a and 30.7 t/a), respectively.

The DBP levels in the seawater samples collected in the harbour area were also monitored. The DBP levels in the receiving seawater were decreased by tens of times compared with those in the mixed sewage effluent, which might be similar to the diffusion pattern of DBPs released from ballast water to the surrounding waters (Table 4-5). Apart from trichloromethane and tribromomethane (bromoform), other trihalomethanes and haloacetic acids in the seawater near the effluent diffusers were at levels similar to those in the seawater 20-km away from the diffusers. The occurrence data for trichloromethane and bromoform in the seawater samples collected on different dates were summarized in Table 7-4. As bromoform is also a natural halogenated organic compound that can be produced through metabolism of marine species, the bromoform levels in the sampling spots (i.e., the seawater control) that were distant from the effluent diffusers were around 0.38 μg/L. The levels of trichloromethane and bromoform in seawater near the effluent diffusers were averagely 0.20 μg/L higher than those in the seawater control samples, indicating that the DBPs released from the saline sewage might have an immediate effect to the receiving seawater near the discharge points of the HATS project.

Table 7-4: Concentrations of DBPs in the receiving seawater in the Victoria Harbour (Monitoring from 24 July 2017 to 23 April 2018, data retrieved from HK DSD, 2018)

	Edges of the diffusers		Edges of mixing zone		Seawater control	
	P1	P2	P3	P4	P5	P6
Trichloromethane [μg/L]						
Min.	<0.1[25]	<0.1[25]	0.1	0.1	<0.1[25]	<0.1[25]
Max.	0.5	0.4	0.3	0.4	<0.1[25]	<0.1[25]
Mean	0.21		0.22		0.05	
Tribromomethane (bromoform) [μg/L]						
Min.	0.2	0.2	0.2	0.2	0.1	0.1
Max.	0.6	0.9	0.8	1.8	0.8	0.6
Mean	0.50		0.66		0.38	

[25] "<0.1" indicated that the concentration of trichloromethane was below the detection limit and it was assumed to be 0.05 μg/L in calculating the mean concentration. Six monitoring stations included two stations at the northwest and southeast edges of the effluent diffusers, P1 and P2; two stations at the edge of mixing zone (i.e., northwest and southeast edges of the effluent diffusion zone), P3 and P4; two control stations which were around 20-km away from the effluent diffuser, P5 and P6).

Besides the Victoria Harbour, other bays surrounding the Hong Kong Islands also receive the chlorinated saline sewage effluents. Feng *et al.* (2019) have reported the levels of two halophenols and four trihalomethanes in 11 seawater sampling spots that are 1-13 km distant from four major sewage discharge points in Hong Kong. The results are summarized in Table 7-5. In general, the levels of DBPs in the seawater decreased with increasing the distance from the discharge point. Trichloromethane and tribromomethane (bromoform) were the dominant DBP species and their maximum concentrations were at 0.53 and 0.55 μg/L, respectively. It should be noted that the levels of trihalomethanes in some samples were higher than those in the chlorinated sewage, indicating there might be other sources for them in seawater. The potential threat to the marine environment should be further evaluated and more factors that influence the DBP concentration, transport, and transformation, such as weather and current, should be considered.

Table 7-5: Halogenated DBPs in the Seawater around the Hong Kong Islands (data retrieved from Feng *et al.* 2019)

DBPs	Min. (ng/L)	Max. (ng/L)	Mean (ng/L)	Median (ng/L)
2,4,6-Trichlorophenol	1.3	9.4	4.0	2.8
2,4,6-Tribromophenol	3.1	18.0	7.7	5.9
Trichloromethane	129.6	528.5	294.1	339.5
Bromodichloromethane	<0.1[26]	29.4	7.4	5.9
Dibromochloromethane	3.9	30.7	14.0	15.5
Bromoform	86.5	551.2	315.8	350.2
THM4	284.6	1005.3	631.3	714.1

[26] "<0.1" indicated that the concentration of bromodichloromethane was below the detection limit and it was considered as 0.05 μg/L in calculating the mean value.

7.4 Conclusion

Due to the limited use of seawater toilets worldwide, Hong Kong was considered as a local hotspot and its DBP inputs to the marine environment were outlined and estimated in this chapter. The used flushing seawater is mixed with domestic freshwater sewage to generate saline sewage, which is treated via primary or secondary treatment, followed by chlorination and dechlorination. The total volume of the treated saline sewage effluent is 1.02 x 10^9 m^3/a. The discharge of treated sewage effluent may increase the concentrations of halogenated DBPs in the surrounding seawater which is 0-13 km distant from the discharge points. Trichloromethane and tribromomethane (bromoform) are the major DBPs detected at levels up to 0.5 and 1.8 μg/L, respectively, in the receiving seawater.

Because saline sewage effluents contain high levels of bromide and iodide, a variety of brominated and iodinated DBPs are detected and identified in chlorinated saline sewage effluents. Many of the identified DBPs are brominated and iodinated phenolic DBPs.

A study (Liu *et al.* 2017) has shown that some halogenated phenolic DBPs formed in chlorinated saline sewage effluents underwent photo-conversion in the seawater, which was overall a dehalogenation and detoxification process. The results indicate that the emerging brominated/iodinated phenolic DBPs in chlorinated saline sewage effluents might not be too severe a threat to the marine organisms in receiving seawater. Of note is that some halogenated DBPs in chlorinated saline wastewater effluents might be persistent in receiving seawater, and further studies are needed to identify them and control their formation.

In chapters 10, 11 and 12, a risk assessment is carried out for the environment, human health and the atmosphere. Therefore, some assumptions are required. Based on the data mentioned in this chapter it is proposed to use the values in Table 7-6 as assumptions in the risk assessment.

Table 7-6: Assumptions for risk assessment

Parameter	
Amount of treated saline sewage	1.0 x 10^9 · m^3/a
Average dose applied	4-18 mg TRO/L (as Cl_2)
Discharge of DBP into marine water	Values given in Table 7-2 [μg/L]
Environmental concentrations	Measured maximum concentration in the surrounding seawater in Table 7-5 [ng/L]

8 WASTEWATER TREATMENT

8.1 Introduction

Disinfection of wastewater prior to effluent discharge into the sea is used as disinfecting treatment to preserve the health of the coastal marine environment, in particular in those areas used for recreation and mariculture (Yang *et al.* 2000). To comply with European Urban Wastewater Treatment (Directive 91/271/EC), the Marine Strategy Framework Directive, the Shellfish Directive (Directive 79/923/EEC) and the Bathing Water Directive (Directive 2006/7/EC), European Member States have had to recommend *appropriate treatments*[27] to achieve the following:

- Prevent the spread of human pathogenic micro-organisms coming from wastewater effluents to the aquatic environments (Monarca *et al.* 2000) ;
- Provide protection to humans against exposure to waterborne pathogenic microorganisms, notably from fecal contamination (Mansilha *et al.* 2009).

These more stringent (advanced) treatments shall be left to the discretion of the competent authorities of each European Member State and employed to comply with quality objectives of community directives.

Disinfection, as a « quaternary » treatment, is widely used around the world, and in Europe continually where there is a need to protect bathing waters or shellfish-growing areas.

Figure 8-1 identifies the locations where disinfection is used in European wastewater treatment plants before discharge into sensitive areas (coastal areas included) (European Environment Agency 2015).

In an international report, Jacangelo and Trussell (2002) have identified the modes of disinfection most used for wastewater treatments based on data issued from 22 countries. These treatments could be divided into two kinds: chemical and physical ones. According to this data, the most commonly used agents/treatments include chlorine gas, UV irradiation, sodium hypochlorite, ozone, and membranes (as shown in Figure 8-2).

Besides disinfection, concerns about the ecological adverse effects of introducing wastewater-carried micropollutants into water streams are driving towards increased interest in upgrading wastewater treatment to ensure micropollutant abatement (von Gunten 2018).

8.2 Chemical disinfection

The chemical disinfectants are chlorine or chlorine-based disinfectants (gaseous chlorine, sodium hypochlorite, chlorine dioxide, electro-generated chlorine from brine or seawater, chloramine, trichloroisocyanuric acid), ozone, lime, peracetic acid and in a lesser extent bromine chloride, and formic acid.

Chlorination is still the most widely used method for disinfecting the effluents from wastewater treatment plants both in Europe (Collivignarelli *et al.* 2017) and the USA where approximately 65% of total municipal wastewater is chlorinated (Drinking Water Inspectorate 1988). Krasner *et al.* (2009) report that wastewater treatment plants apply median chlorine doses of 2.4 - 2.7 mg Cl_2 /L, for good and poor nitrification conditions respectively.

In the USA, wastewater chlorination is commonly followed by a step of dechlorination before the release of effluents into receiving waters. The USEPA has proposed stringent discharge requirements for total residual chlorine (mean 7.4 μg/L for saltwater). In Italy, the legislation states that active chlorine concentration should be reduced below 0.2 mg/L, before discharge into the sea. The two most common dechlorination processes use sulphur dioxide or granular activated carbon (GAC), though sodium bisulphite, sodium sulphite, sodium thiosulphate, sodium metabisulphite or ascorbic acid may also be used. Although dechlorination eliminates residual chlorine, preventing further formation of DBPs in the sea, it does not eliminate DBPs that were already formed during chlorination (Watson *et al.* 2012).

Ozone is being increasingly used for wastewater disinfection and removal of micropollutants in the USA and in Europe (Gottschalk *et al.* 2010; Nasuhoglu *et al.* 2018). This use has the potential to form bromate in seawater (Dong *et al.* 2018) and *N*-nitrosodimethylamine (Zimmermann *et al.* 2011) or nitrates in presence of ammonium (Graham and Paraskeva 2001).

Ozone is both an efficient bactericide and virucide, characterized by its rapidity and the low concentrations required. Typical ozone doses in practice for secondary effluents are 10 to 15 mg/L for a contact time of 10 min (Martínez *et al.* 2011). In addition to its disinfecting properties, ozone is known to efficiently abate many micropollutants (Bourgin *et al.* 2017).

Peracetic acid (PAA) is used as an alternative chemical method for disinfecting urban wastewater. PAA-based disinfection has long been considered without adverse effects on the receiving environment because of its rapid evolution into innocuous and easily biodegradable by-products such as acetic acid and active oxygen in the marine environment (Sánchez-Ruiz *et al.* 1995; Dell'Erba *et al.* 2007). Indeed, several works showed that initial PAA concentrations from 1 to 15 mg/L and contact times from 15 to 60 min can result in proper disinfection of primary, secondary and tertiary effluents. The rate of decomposition of PAA decomposes into acetic acid and oxygen is highly dependent on the water matrix composition (Domínguez Henao *et al.* 2018).

[27] Treatment of urban wastewater by any process and/or disposal system which after discharge allows the receiving waters to meet the relevant quality objectives and the relevant provisions of this and other Community Directives

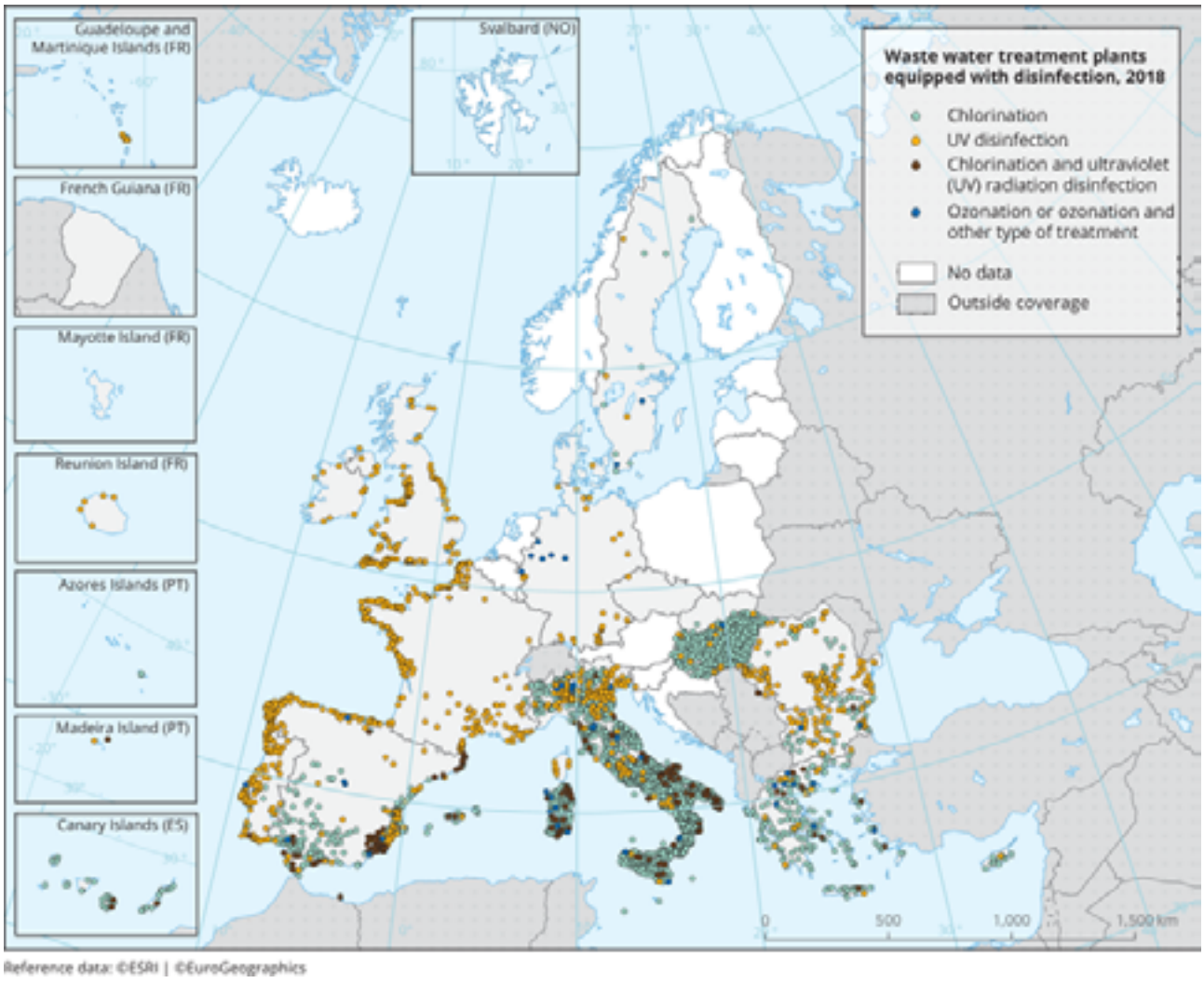

Figure 8-1: *Map showing Urban Wastewater Treatment Plants (UWWTs) equipped with disinfection in the EU-28 countries , based on data from 2018 (reproduced from European Environment Agency; 2020)*

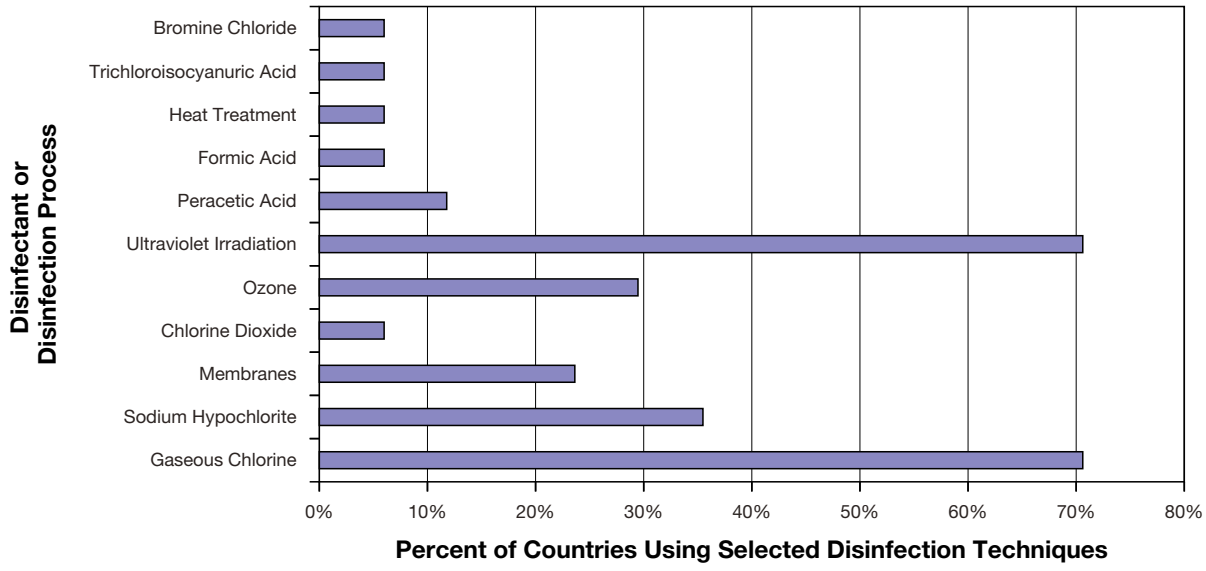

Figure 8-2: *Types of water disinfectants or disinfection processes employed by countries providing national reports (adopted from Jacangelo and Trussell 2002).*

8.3 Physical disinfection

The two main physical processes used for wastewater disinfection are UV treatment (mostly UV-C) and membrane filtration.

Ultra-violet (UV) disinfection is an established and increasingly popular alternative to chemical disinfection of wastewater. UV-based facilities operate successfully on secondary effluents with flow capacities from 2.7 m^3/d - 2.2 m^3/s. Wastewater quality is a major limiting factor because high concentrations of solids can absorb UV and protect microorganisms by encapsulation. Secondary treatment is necessary for UV to be both technically and economically feasible. Factors governing the efficiency of disinfection are UV dose (the product of lamp intensity and contact time) and wastewater quality. Typical operational dosages for secondary effluents range from 30 to 50 mJ/cm^2 (millijoule per square centimeter). Inactivation of viruses requires 3-4 times the dose for bacteria, whilst bacterial spores and cysts are up to 9 and 15 times more resistant. Comparison of UV dose with chemical dosages is difficult, but the range of UV doses for different pathogens appears narrower than that of chlorine. It is a more efficient virucide than chlorine.

UV radiation applied for disinfection is usually $>$200 mJ/cm^2 and therefore exceed UV-dose requirements for a 10,000 fold reduction (a so-called 4-log inactivation) of most pathogens including UV-resistant organisms (e.g. adenovirus). UV irradiation sources usually consist of either low- or medium-pressure mercury lamps with mono- or polychromatic emission spectra, respectively (Miklos *et al.* 2018).

Membrane filtration processes (or pressure-driven membrane processes) have been widely applied in water and wastewater treatment for many decades. These processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), forward osmosis (FO), and reverse osmosis (RO).

An important aspect to consider with pressure-driven membrane treatment is the potential environmental implication of the waste stream. Membrane treatment results in the generation of retentates (brines) which are highly enriched in contaminants of emerging concern (CECs), salts, and natural organic matter. Brines are often discharged into water bodies without additional treatment, which is a non-sustainable practice for obvious reasons. Furthermore, oxidative cleaning (chlorination) of membranes to oppose membrane fouling may well result in the formation of toxic DBPs originating from the reaction of reactive chlorine species with biofilm-coated compounds. Due to high CEC concentrations, the safe discharge of brine would require a post treatment for pollutant removal.

8.4 DBPs generated as a function of disinfection process

Chlorine and chloramine can react easily with organic matter present in wastewater to produce various DBPs. The wide array of formed DBPs include halogenated carbonaceous DBPs such as trihalomethanes (THMs) and haloacetic acid (HAAs), halogenated nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HANs), halonitromethanes (HNMs), and haloacetamides, and non-halogenated DBPs such as N-nitrosodimethylamine (NDMA) (Sgroi *et al.* 2018).

In wastewater, dissolved organic matter (DOM) with polyhydroxyaromatic moieties, esters and ketones are thought to be the primary DBP precursors. Chlorine and chloramine can react with these compounds through halogenation reactions (oxidation, substitution and addition) to produce halogenated intermediates. These intermediates will further generate small molecular DBPs such as THMs through hydrolysis or decarboxylation reactions (Ma *et al.* 2016). The presence of iodide and bromide in chlorinated wastewater leads to the formation of iodinated and brominated DBPs, respectively. The formation of iodinated and brominated DBPs is of considerable health concern, as they typically exhibit a highly enhanced mammalian cell cytotoxicity and genotoxicity as compared to their chlorinated analogues. Furthermore, the presence of iodide and bromide can influence the degradation kinetics of CECs (Prasse *et al.* 2015).

Data about the levels of DBPs in chlorinated wastewater effluents are scarce. The available data based on studies conducted in the USA have reported the levels of several classes of DBPs including THMs, HAAs, HANs, and HNMs (Table 8-1). In a study by Krasner *et al.* (2009), wastewater effluents were found to contain low concentrations of THMs and HAAs prior to chlorination treatment. Chlorination resulted in different DBP formation patterns depending on whether or not the WWTP achieved good nitrification. Chlorine addition to poorly nitrified effluents (formation of chloramines as main disinfectants) formed low levels of halogenated DBPs but substantial amounts of NDMA. Chlorination of well-nitrified effluent (free chlorine is the main disinfectant) typically resulted in substantial formation of halogenated DBPs but much less NDMA (Table 8-1).

Table 8-1: Concentrations of DBPs reported in wastewater effluents

Disinfectant	DBP	Level in wastewater effluent	Published by
None (background level, before disinfection)	THMs	ND to 7.9 μg/L; median = 1.3 μg/L	Krasner *et al.* (2009)
	HAAs	ND to 35 μg/L; median = 6.2 μg/L	Krasner *et al.* (2009)
	Chloropicrin	ND	Krasner *et al.* (2009)
	HANs	ND	Krasner *et al.* (2009)
	NDMA	2.7 ng/L	Krasner *et al.* (2009)

Disinfectant	DBP	Level in wastewater effluent	Published by
Chloramines (chlorine was added to poorly nitrified wastewater)	THMs	Median = 2 μg/L	Krasner *et al.* (2009)
	HAAs	Median = 8.9 μg/L	Krasner *et al.* (2009)
	HANs	ND to 12 μg/L (median and 75th percentile levels of 0.3 and 0.8 μg/L, respectively)	Krasner *et al.* (2009)
	Chloropicrin	ND to 0.6 μg/L	Krasner *et al.* (2009)
	Dihalogenated acetaldehydes (DHAs)	ND to 6.4 μg/L	Krasner *et al.* (2009)
	Trihalogenated acetaldehydes (THAs)	ND to 2.0 μg/L	Krasner *et al.* (2009)
	NMDA	11 ng/L	Krasner *et al.* (2009)
Chlorine (chlorine was added to well nitrified wastewater)	THMs	11 to 92 μg/L (median = 57 μg/L)	Krasner *et al.* (2009)
	HAAs	13 to 136 μg/L (median = 70 μg/L	Krasner *et al.* (2009)
	HANs	0.9 to 30 μg/L (median = 16 μg/L)	Krasner *et al.* (2009)
	Chloropicrin	ND to 0.7 μg/L	Krasner *et al.* (2009)
	Dihalogenated acetaldehydes (DHAs)	2.1 to 12 μg/ (median = 7.2 μg/L)	Krasner *et al.* (2009)
	Trihalogenated acetaldehydes (THAs)	3.8 to 49 μg/L (median = 16 μg/L)	Krasner *et al.* (2009)
	NMDA	3 ng/L	Krasner *et al.* (2009)
Chlorine	THMs	0.14 to 11.16 μg/L[28]	Hladik *et al.* (2014)
	HANs	0.04 to 0.89 μg/L[28]	Hladik *et al.* (2014)
	HNMs	ND to 3.1 μg/L[28]	Hladik *et al.* (2014)
Chlorine	HNMs	ND to 1.5 μg/L[28]	Song *et al.* (2010)

[28] the presented levels have been found in effluents of wastewater treatment plants which did not receive brines co-produced with oil and gas production (produced waters).

During ozonation, two reactive species are involved, i.e., ozone and hydroxyl radicals formed during the decomposition of ozone in water. Ozonation could lead to the formation of bromate in bromide-rich water, N-nitrosodimethylamine (NDMA), and N-nitrosomorpholine (when amino compounds are present). Moreover, other by-products could be formed during ozonation due to the oxidative breakdown of complex dissolved organic matter present in wastewaters, which are usually readily biodegradable and can be measured as e.g., assimilable organic carbon (AOC). The kinetics of formation of these organic by-products during wastewater ozonation is still largely unknown, but the global parameter AOC has been proven to be higher after ozonation, with up to a six-fold increase reported by Zimmermann *et al.* (2011) and Wert *et al.* (2007). Besides the increase of AOC, the levels of total carboxylic acids (including formic, acetic and oxalic acids) and total aldehydes (including glyoxal, formaldehyde and acetaldehyde) were found to be also higher after ozonation (Table 8-2). In line with the formation of such products, it has been observed that the toxicity to certain aquatic organisms increases after wastewater ozonation, with mostly an improvement after a biological treatment step. Since these oxygen-rich by-products are often easily biodegradable, a biological post-treatment step is routinely implemented after oxidation treatment in drinking water and wastewater effluents (von Gunten 2018).

Table 8-2: Examples of DBPs generated during ozonation of wastewaters

DBPs	Level (ozone rate)	Published by
bromate	7.5 μg/L (0.74 O_3/g DOC) - 60 μg/L (11 mg/L O_3)	Zimmermann *et al.* (2011); Wert *et al.* (2007)
NDMA	15 – 537 ng/L	Zimmermann *et al.* (2011); Sgroi *et al.* (2018)
NMOR	3 ng/L	Zimmermann *et al.* (2011)
Acetaldehyde	45 μg/L (7 mg/L O_3)	Wert *et al.* (2007)
Formaldehyde	95 μg/L (7 mg/L O_3)	
Formic acid	526 μg/L (7 mg/L O_3)	
Oxalic acid	274 μg/L (7mg/L O_3)	

UV irradiation is associated with very little formation of DBPs compared to the chemical disinfection processes (Krasner *et al.* 2009). However, the potential of mutagenic organic by-product formation during application of medium-pressure UV irradiation to nitrate-containing water has been recently argued (Hofman-Caris *et al.* 2015; Kolkman *et al.* 2015). The photolysis products of nitrate (mainly peroxynitrite) react with dissolved organic matter by hydroxylation, nitration and nitrosation reactions forming organic by-products (Martijn *et al.* 2014). While potential reaction mechanisms have been proposed (Reckhow *et al.* 2010; Shah *et al.* 2011), a comprehensive understanding has not yet been achieved. However, nitrated aromatic compounds are expected to be the most toxic DBPs formed in this process (Martijn *et al.* 2014).

Peracetic acid exists as an equilibrium mixture with hydrogen peroxide, acetic acid and water (12% w/w PAA). The highly oxidative nature of PAA makes it capable of reacting with organic compounds in wastewater; there is concern over the possible formation of epoxides and (through free chlorine formation by peroxide radicals) chlorinated organic compounds. However, a recent paper has demonstrated that peracetic acid could result in the formation of substantial amounts of bromamines that may in turn react with organic matter to form brominated DBPs (Heeb *et al.* 2017).

8.5 Conclusion

The compliance with European directives regarding the appropriate treatment of wastewaters before their discharge into the aquatic environment to prevent the spread of infectious diseases to humans, along with increasingly developing concerns about micropollutant discharges in wastewater, are prompting the use of disinfection/oxidation processes in wastewater treatment. The available well-established methods include chlorination, UV irradiation, and ozonation. The nature of DBPs and extent of their formation using these methods strongly depend on the quality of water to be disinfected. Chlorination of wastewater is associated with the formation of a wide array of halogenated and non-halogenated DBPs, while ozonation is associated with the formation of oxidation by-products including bromate, aldehydes, ketones, and carboxylic acids. Although UV irradiation forms least DBPs compared to chemical oxidation processes, its formation of toxic DBPs can be enhanced in the presence of certain matrix components. Since the significance of the impact of these discharges on the marine and human health remains unclear, further research in this direction is warranted.

In chapters 10, 11 and 12, a risk assessment is carried out for the environment, human health and the atmosphere. Therefore, some assumptions are required. Based on the data mentioned in this chapter it is proposed to use the values in Table 8-3 as assumptions in the risk assessment.

Table 8-3: Assumptions for risk assessment

Parameter	
Amount of treated wastewater	No information available
Average dose applied	2.4-2.7 mg TRO/L (as Cl_2)
Discharge of DBP into marine water	Median values given in Table 8-1 for chlorination [µg/L]
Predicted environmental concentrations	No information available

9 ENVIRONMENTAL INPUTS AND CONCENTRATIONS

This chapter aims to provide an overview on the DBP production, their inputs into the marine environment and resulting environmental concentrations resulting from different anthropogenic activities. For this purpose, information provided in the Chapters 4 to 8 for the different industrial sectors is summarized. It is intended as basis for the risk assessments carried out in the Chapters 10 to 12.

9.1 Inputs from different sources

Table 9-1 provides an overview on oxidant treatment conditions and estimated volumes of water treated in the different applications.

Table 9-1: Treatment concentrations, reaction times and total treated volumes for the different sectors as outlined in chapters 4-8

Input (Chapter)	Oxidant dose [mg Cl_2/L]	Reaction times	Estimated volumes [m^3/a]
Ballast water (4)	10 (2-20)	1-21 days	3.5×10^9 [29]
Cooling water (5)	0.75 (0.5-1)	2-30 minutes	$470 – 800 \times 10^9$
Desalination (6)	0.25 - 2	10 minutes-few hours	46×10^9
Seawater toilets (7): Saline sewage treatment	4-18	12-30 minutes	1.0×10^9
Wastewater treatment (8)	2.4-2.7	no information	no information

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

In Table 9-2, an overview is given on mean concentrations of major DBPs detected in the treated or discharged water of the different industries. The data show that DBP concentrations are generally higher in ballast water compared to other sectors, e.g., for bromoform, the major DBP, a mean concentration of 247 μg/L was detected whereas only 10% of this value are typically observed in power plant cooling water, desalination brine and wastewater effluent from seawater toilets. No consistent data is available for wastewater treatment due to the heterogenic nature of treated waters and different methods used. The relatively high concentration in ballast water is coherent with the high oxidant doses and long reaction times used for treatment. Furthermore, DBPs containing chlorine appear to be present in relatively low concentrations in power plant cooling water compared to discharge from other sectors, possibly reflecting the more constant quality of marine water treated. Ballast water and wastewater may be characterized by varying water qualities and thus also varying bromide concentrations, which might shift the spectrum of generated DBPs to chlorinated species.

Table 9-2: Mean concentrations in the treated water (discharge concentrations) in μg/L

DBP	Ballast water	Cooling water	Desalination	Seawater toilets (1st/2nd)	Wastewater treatment
THM					
Bromoform	247.14	25.7 21 [b] 9.8 [d1] 0.64 [d2] 1.8 [d3]	19	26.5/31.8	No Information (NI)
Trichloromethane	29.80	0.3 0.24 [b]	10.4	8.0/5.0	NI
Dibromochloromethane	22.11	0.6 1.0 [b] 0.13 [d1] 0.01 [d2] 0.05 [d3]	0.8	15.6/2.5	?
Dibromomethane	2.82	-	-	NA/NA	NI
Dichlorobromomethane	9.52	0.1 0.14 [b]	0.2	11.6/4.9	NI
HAA					
Bromochloroacetic acid	15.11	0.9 [d3]	-	4.2/1.4	NI
Dibromoacetic acid	48.66	12.2 10.4 [b] 4.2 [d1] 3.5 [d2] 0.21 [d3]	3.6	6.0/8.6	NI
Dibromochloroacetic acid	10.77	0.37 [d3]	-	BDL/BDL	NI
Dichloroacetic acid	10.99	< 1 [c]	-	6.8/3.3	NI
Dichlorobromoacetic acid	5.89	-	-	2.2/BDL	NI
Monobromoacetic acid	15.48	5 [c]	0.3	BDL/BDL	NI

DBP	Ballast water	Cooling water	Desalination	Seawater toilets (1st/2nd)	Wastewater treatment
Monochloroacetic acid	36.34	< 1 [c]	-	BDL/BDL	NI
Tribromoacetic acid	103.43	4.4 [d1] 0.7 [d2] 1.1 [d3]	0.9	BDL/2.8	NI
Trichloroacetic acid	26.25	< 1 [c]	-	5.0/5.7	NI
HAN					
Dibromoacetonitrile	23.33	3.1 4.0 [b] 0.7 [d2] 0.3 [d3]	0.7	NA/NA	NI
Dichloroacetonitrile	1.87	-	-	NA/NA	NI
Others					
Bromal hydrate	-	5.3 [d1] 0.07 [d2] 1.4 [d3]		NA/NA	
Bromate ion	119.7	5 [a]	-	NA/NA	NI
2,4,6-Tribromophenol	0.27	0.3 0.41 [b] 0.4 [d1] 0.1 [d3]	0.75	NA/1.0	

[a] Power stations - electrochlorination with short residence time (minutes) in storage tanks
[b] Range of averages at nuclear power stations on the English Channel and North Sea (Khalanski 2003)
[c] Concentration ranges at coastal power stations in UK, France and The Netherlands (Taylor 2006)
[d] Concentration ranges in cooling water of plants on the Gulf of Fos, Mediterranean coast (Boudjellaba *et al.* 2016; Manasfi *et al.* 2019). d1: petrochemical plants, d2: thermal stations, d3: steel plants.

9.2 Estimated global DBP production

Water treatment is performed globally in the sectors mentioned in Chapters 4 to 8. Along the coast where water resources are unlimited, billions of m^3 of seawater are used, mostly for cooling of power plants and desalination (Table 9-1).

The global cooling water discharge to marine water is estimated to be between 470 x 10^9 m^3/a and 800 x 10^9 m^3/a. Due to the lack of data on industrial cooling, the assessment of global DBP production has to be restricted to existing data on coastal power plants.

Desalination plants treat high amounts of marine water, mostly in arid regions. The global amount of concentrate water (brine) discharged is estimated to be 46 x 10^9 m^3/a. Over 50% of discharge originates from desalination plants located on the Arabian Peninsula. Thus, other regions have relatively less impact from desalination. Nevertheless, the environmental impact of discharges from desalination plants can be locally significant in cities where such plants are located. The rising demand for fresh water in the future will result in an increase of this sector.

Future input of treated ballast water can add locally to the DBP concentrations around large ports (Maas *et al.* 2019). However, this source is much less in volume, so that large-scale effects might not be relevant. All applications are expected to increase through increasing demand from economic growth and population rise.

Based on the volumes of treated water in the different sectors (Table 9-1) and observed mean DBP concentrations in the treated water or discharge (Table 9-2) the global production of DBPs can be estimated. Table 9-3 provides estimated global production volumes for bromoform. It is assumed that the major part of the produced DBP represent direct inputs into the marine environment and that the volatile compounds enter the atmosphere either directly (e.g. by outgassing from produced water) or via evaporation after discharge into marine water. Since bromoform is the most prominent DBP it can serve as a proxy to compare the input from different sectors. The total estimated anthropogenic bromoform production and discharge adds up to 13.5 x 10^6 kg/a to 21.8 x 10^6 kg/a with contribution of 0.86 x 10^6 kg/a from ballast water; 11.8 x 10^6 kg/a to 20.1 x 10^6 kg/a from cooling water; 0.89 x 10^6 kg/a from desalination; 0.03 x 10^6 kg/a from saline sewage treatment (Hong Kong only). Most of the estimates are based on realistic assumptions for discharged water volumes and mean values for observed or estimated DBP concentrations. Therefore, this assessment does not represent a worst-case scenario. Furthermore, this assessment does not take into account potential additional bromoform generation resulting from the degradation of other DBP, which could contribute to the total bromoform flux to the atmosphere. The natural bromoform production in marine water has been estimated to be 76 x 10^6 kg/a to 870 x 10^6 kg/a (Table 2-1). Anthropogenic bromoform production thus equals approximately 2–6% of global marine bromoform emissions depending on whether higher or lower boundaries are used. However, this relative contribution of the anthropogenic DBP production to the overall inputs depends not only on the uncertainty of the estimated anthropogenic inputs but also on the uncertainties in the quantification of the natural production.

Table 9-3: Estimated global anthropogenic bromoform production by applications (as outlined in chapters 4 to 8)

	Bromoform [10^6 kg/a]
Ballast water (4)	0.86
Cooling water (5)	11.8 – 20.1
Desalination (6)	0.89
Seawater toilets (7): Saline sewage treatment	0.03
Wastewater treatment (8)	no information
Total anthropogenic production	13.5 – 21.8

9.3 Environmental concentrations

Environmental concentrations of DBPs depend on the emitted quantities but also on the characteristics of the receiving environment. Furthermore, the fate of the individual DBPs in the surface water depends on the lifetime, solubility and volatility of the compound and the background abundance in ocean and atmosphere. The major compound, tribromomethane (bromoform), is highly volatile and expected to be outgassed relatively quickly and no long-term accumulation in the ocean is expected.

Environmental concentrations can be assessed by measurements of DBP in receiving environments or by prediction of estimated dilution of the effluent. Examples for measured environmental DBP concentrations have been reported for surrounding water of power plants (chapter 5) and in receiving seawater for treated sewage effluents (chapter 7). Environmental concentrations can also be estimated based on the knowledge about effluent concentration and on assumptions of specific or generic dilutions. Predicted Environmental Concentrations (PEC) have been established for cooling water on the local and regional scale assuming a dilution rate of the effluent of 20 and 100 respectively (Chapter 5) and ballast water based on model dilution in a generic harbour (Chapter 4). An overview on concentrations in the local environment for selected DBPs is provided in Table 9-4.

Table 9-4: Measured or predicted environmental DBP concentrations in different sectors

DBP [μg/L]	**Cooling water**	**Ballast water**	**Seawater toilet sewage effluent**
	predicted local environment (Table 5-10)	predicted maximum concentration in surrounding water (Table 4-5)	measured (edge of mixing zone Table 7-4)
$CHBr_3$	0.395	2.95	0.22
DBCM	0.006	0.244	
DCBM	0.0012	0.105	
$CHCl_3$	0.012		0.66
DBAA	0.389	0.823	
DBAN	0.05	0.394	
2,4,6-tribromophenol	0.005		

Ports can be local hot spots of bromoform air-sea flux (emission) to the atmosphere. This is highly dependent on wind conditions and latitude. Wind strength drives the air-sea gas exchange while deep convection in tropical regions allows gases to be quickly transported. The global bromoform input from water treatment can be calculated using the values given in Table 9-1 and Table 9-2.

Non-volatile compounds such as dibromoacetic acid (DBAA) with a half-life of about 300 days (Exner *et al.* 1973) can accumulate in coastal zones and can be transported by currents and tides over large distances.

On local and short-time scales of a few days, all DBPs contribute to the predicted environmental concentration (PEC) in the aquatic environment. Hence, at large industrial sites where ports, power plants or desalination plants are located all the treated water discharges together can significantly increase DBP concentrations in the coastal ocean. This is important for metropolitan areas in temperate zones like Europe and North America or tropical and subtropical regions, like East and Southeast Asia. For toxicological assessment and PEC calculation of DBPs along the coast, all concentrations from the different sectors have to be taken into account. In coastal regions, natural concentrations and sources of organohalogens can be outweighed by their anthropogenic analogues.

For regional and long-term analysis, the lifetime and the volatility of a compound play crucial roles. DBPs will spread along the sea surface and can be advected by current systems into the open ocean or accumulate in marginal seas (Maas *et al.* 2019). For volatile compounds such as tribromomethane (bromoform), the initial concentration is important in order to assess whether these compounds can spread in the ocean

or will be outgassed. Bromoform was usually considered to be almost entirely of natural origin (Quack and Wallace 2003; Ziska *et al.* 2013). With the large water volumes from cooling water, bromoform can provide an extra input permanently into the ocean (Maas *et al.* 2021). This input has been shown to provide a significant contribution along the coast in East Asia which might close a gap in the estimation of bromoform sea-air flux (Maas *et al.* 2019; Maas *et al.* 2021).

10 IMPACT ON AQUATIC ORGANISMS

10.1 Introduction

In this chapter, the impact of DBPs or the risk of these substances to marine life are investigated. In this report, the words "impact" and "risk" are considered the same and will be used here in both forms. If these two terms are to be distinguished then the term "impact" should be reserved in the widest sense (Verhoeven *et al.* 2012), and may include risk assessment, qualitatively and quantitatively, as well as risk management options like socio-economic assessment, cost-benefit analysis and remediation. The term risk assessment should then be reserved for the quantitative analysis of the risks, in this case to aquatic organisms. The first attempt, therefore, should be the establishment of an Environmental Risk Assessment for aquatic organisms exposed to DBPs in marine ecosystems.

This report is directly related to the DBPs. Other types of stressors like biocides and micro-pollutants, although they may be precursors for DBPs, are not taken into account.

The approach taken here has to be "pragmatic". For an in-depth risk assessment available data may be insufficient for a scientifically solid conclusion on the risk to aquatic organisms. In the earlier chapters, the various inputs of DBPs have been identified with some quantification of the amount and concentration of several DBPs. Here, the results of the Chapter 4 to 8 and the resulting environmental concentrations defined in Chapter 9 will be used for the exposure estimation of the aquatic environment to relevant levels of DBPs. As part of the "pragmatic" approach, the ecotoxicological data for the main disinfection by-products determined in ballast water will be used for the risk assessment (see further below). Generally, the risk to aquatic (marine) life can be estimated in several ways:

- the classical risk quotient PEC/PNEC approach, which means the comparison of two concentrations, the Predicted Environmental Concentration (PEC) and the Predicted No-effect Concentration (PNEC). The PEC is the concentration to which the organisms are exposed while the PNEC is derived from available ecotoxicological laboratory tests performed with the substance under consideration.
- comprehensive water testing, which means the water, including all chemical substances present, is tested in an ecotoxicological test to identify potential effects of the water considered. In this investigation the potential effects of all substances present are included. For ballast water this type of study is carried out with the treated ballast water and the results are used for the final risk assessment of BWMS. This type of tests is called Whole Effluent Toxicity (WET) test.

In principle, the classical PEC/PNEC approach will be applied for the risk assessment but also mixtures can be integrated by applying risk indices, the sum of PEC/PNEC of individual components. This approach can only cover known chemical hazards and will therefore be complemented by using direct ecotoxicological testing on produced water to capture known and unknown chemicals contributing to mixture effects.

10.2 Hazards

The vast majority of ecotoxicity test data on all types of chemicals including DBPs, biocides and micro-pollutant stem from freshwater organisms. The processes governing the expression of toxicity in freshwater and marine organisms are generally similar. For example, baseline toxicity upon exposure to non-polar organic substances, i.e., the accumulation of substances in the phospho-lipid layer of membranes and disturbance of its function, is common in freshwater and marine organisms. In critical review on the use of species sensitivity distributions for the ecological risk assessment. Del Signore *et al.* (2016) concluded that available studies do not indicate systematic or consistent differences in the sensitivity of marine versus freshwater taxa. On the other hand, in some cases differences for specific modes of action have been observed. For example, reactive substances show lower toxicity in seawater (GESAMP 2002).

The GESAMP-BWWG also evaluated the persistent, bioaccumulative and toxic (PBT) properties of the DBPs involved. A substance having a classification as PBT has never occurred in the evaluations of any BWMS. Therefore, substances with PBT properties are not excluded, but are unlikely to be formed during the treatment processes relevant to ballast water in relevant quantities so that they do not contribute to the risk quotient due to low exposure together with sufficient dilution in the receiving waters. In addition to this, neither endocrine disruption nor adsorption to the sediment have been identified as relevant for the DBPs found.

A risk assessment procedure is a strictly defined process that takes into account all the available data that are analyzed according to the scheme in Figure 10-1.

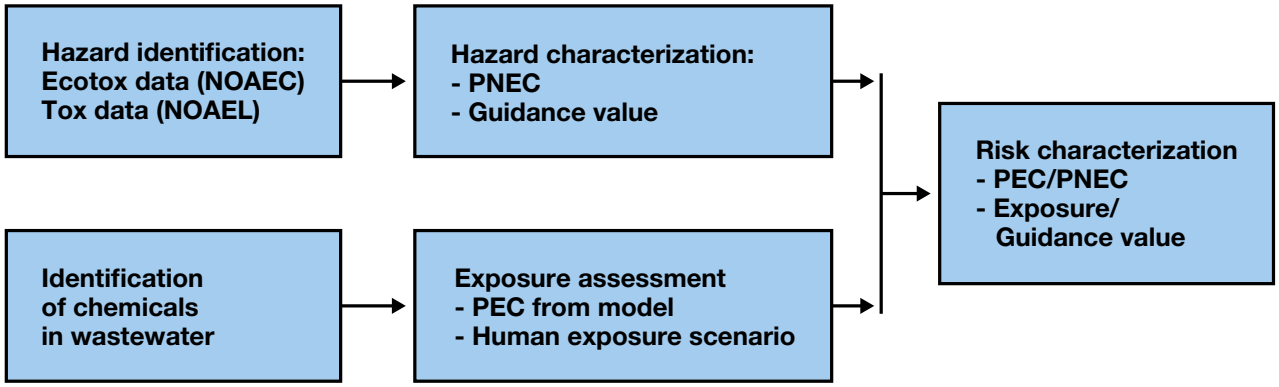

Figure 10-1: *Steps in the risk assessment approach (modified from GESAMP, 2019)*

It should be noted that Figure 10-1 also includes human health risk assessment. In the hazard identification, the toxicological or ecotoxicological information on no observed adverse effect concentrations (NOAEC) or no observed adverse effect levels (NOAEL) is used to establish a concentration or exposure level that will not cause effects to aquatic organisms or to human health (the PNEC or the guidance value). For the exposure assessment, the physico-chemical information (molecular weight, solubility, vapour pressure, octanol-water partition coefficient, Henry's law constant, etc.), the emission data (load of the chemical) are transferred into an environmental distribution model (in the case of BWMS, the MAMPEC model) to estimate the predicted environmental concentration (PEC). Comparison of the hazard assessment and the exposure assessment will lead to a PEC/PNEC ratio for the aquatic organisms and the risk characterization ratio (RCR) for the human health assessment. A ratio above 1 will indicate that a risk cannot be excluded and that further research, including higher tier assessments may be required. If the ratio is less than 1 it is assumed that no toxic effect of the current exposure is expected.

10.2.1 *Disinfectants*

The exposure to the disinfectants applied is considered an acute hazard as their concentration will be quickly attenuated during the disinfection process. Therefore, disinfectants themselves are considered more of a acute hazard to target organisms in the ballast water tank than in the marine environment (Anasco *et al.* 2008). For ballast water management systems there are regulatory limits: the oxidants should not exceed the maximum allowable discharge concentration (MADC) determined by GESAMP-BWWG based on the evaluation of the BWMS. In chapter 4, the MADC for the common disinfectants used in BWMS are indicated. For example, the MADC for TRO has been established at 0.1 mg/L expressed as Cl_2.

10.2.2 *Disinfection by-products*

The development of an environmental hazard assessment for DBPs is hindered by the absolute number of DBPs formed by the oxidation of natural waters, the number of unidentified DBPs, and the lack of effect data for the individual DBPs that have been identified (Li and Mitch 2018; Krasner 2009; Richardson 2008). Some effect data are available for those main DBPs regularly detected in drinking water and ballast water. There are almost no effect data available for the higher molecular weight DBPs, many of which are only identified by molecular formulas using emerging techniques such as FT-ICR MS. The experience with ballast water disinfection has shown that the most frequently occurring DBPs are the low molecular-weight DBPs. In exceptional cases a higher molecular weight DBP has been found, like bromobenzene, chlorobenzene or some phenols. But for the general evaluation of BWMS this rarity made these substances irrelevant for further risk assessment. The DBP with the highest molecular weight in the working group´s database is 2,4,6-tribromophenol. It must be noted, however, that in general, toxicity increases with hydrophobicity, which often increases with molecular weight, and brominated DBPs are typically more toxic than chlorinated DBPs (Plewa *et al.* 2008).

Higher molecular weight DBPs are likely to be more bioaccumulative and more toxic than the common DBPs like trihalomethanes and haloacetic acids. Many smaller and low molecular weight DBPs such as trihalomethanes are volatile and will partition to air due to their high Henry's law constant. They have a low bioaccumulation potential.

10.2.3 *PNEC values for DBPs*

For the DBPs mentioned in Chapter 4 (Table 44) the GESAMP-BWWG derived PNEC values based on information in the scientific literature or used by internationally recognized bodies like USEPA, USFDA, WHO, JECFA, OECD and EU. Based on the number and quality of the ecotoxicity tests available for three trophic levels of aquatic organisms, generally algae, crustaceans and fish, an assessment factor was determined. If the dataset was complete, which means a good quality chronic test for the three trophic levels, an assessment factor (AF) of 10 was applied to the lowest available NOEC to estimate the PNEC. If only acute data were available, an assessment factor of 10^3 was applied. If the dataset was very incomplete, e.g. only one acute ecotoxicity study of good quality, an assessment factor of 10^4 may be applied to estimate the PNEC. The assessment strategy of GESAMP-BWWG is described in more detail in the Methodology (IMO 2017b). Table 10-1 gives an overview of the lowest chronic NOEC, the assessment factor and the final PNEC for the substances covered by Table 4-4.

Limited toxicity data are available for marine organisms in the literature towards individual brominated DBPs because ecotoxicity tests are commonly conducted on real (or reconstituted) samples that contain not only DBPs but also residual oxidant. When toxicity data were not available for the brominated compounds, the toxicity information for the closest resembling chlorinated compound was commonly used. In addition to this, it should be noted that the GESAMP-BWWG preferred to use the assessment factor approach instead of a (quantitative) structure-activity relationship ((Q)SAR) approach. The resulting PNECs for the DBPs under consideration are presented in Table 10-1.

Table 10-1: NOEC, assessment factor (AF) and PNEC used in the evaluation of BWMS

Disinfection by-product	NOEC [mg/L]	AF general	PNEC general [μg/L]
Bromate ion	1.4×10^{1}	1.0×10^{2}	1.4×10^{2}
Bromochloroacetic acid	1.6	1.0×10^{2}	1.6×10^{1}
Dibromoacetic acid	6.9×10^{1}	1.0×10^{1}	6.9×10^{3}
Dibromoacetonitrile	5.5×10^{-1}	1.0×10^{4}	5.5×10^{-2}
Dibromochloroacetic acid	3.0	1.0×10^{1}	3.0×10^{2}
Dibromochloromethane	6.3×10^{-2}	1.0×10^{1}	6.0
Dibromomethane	4.5×10^{1}	1.0×10^{2}	4.5×10^{2}
Dichloroacetic acid	2.3×10^{1}	1.0×10^{3}	2.3×10^{1}
Dichloroacetonitrile	2.4×10^{1}	1.0×10^{3}	2.4×10^{1}
Dichlorobromoacetic acid	3.0	5.0×10^{1}	6.0×10^{1}
Dichlorobromomethane	7.8×10^{-1}	1.0×10^{1}	7.8×10^{1}
Monobromoacetic acid	1.6	1.0×10^{2}	1.6×10^{1}
Monochloroacetic acid	5.8×10^{-3}	1.0×10^{1}	5.8×10^{-1}
Tribromoacetic acid	1.4×10^{2}	1.0×10^{1}	1.4×10^{4}
Bromoform	4.8	5.0×10^{1}	9.6×10^{1}
Trichloroacetic acid	3.0	1.0×10^{1}	3.0×10^{2}
Trichloromethane	1.5	1.0×10^{1}	1.5×10^{2}

The background data of the NOECs, AFs and PNECs, as presented in Table 10-1 are available in the database GISIS at IMO (IMO, 2019).

10.2.4 *Direct Toxicity Assessment*

In the introduction to this Chapter (Section 10.1), two approaches were presented for the toxicity testing. This paragraph deals with the comprehensive toxicity testing with water samples taken from the system or the environment. The comprehensive toxicity testing may also be called direct toxicity assessment or, as it is usual in ballast water testing, Whole Effluent Toxicity (WET) testing. In this case, the effluent refers to the discharged ballast water after treatment by the BWMS, which includes the disinfection process and in most cases neutralization. In the majority of cases, information on toxicity testing of the water near discharge points of the potential emission of DBPs will not be available. In the framework of the Ballast Water Management Convention (BWMC, 2004) with the Procedure G9 (IMO 2008b), the applicant is required to perform WET testing for at least three organisms from different trophic levels, e.g. algae, crustaceans and fish and at three salinities, freshwater (<1 PSU), brackish water (10 – 20 PSU) and seawater (28 – 36 PSU). The applicant is required to send full chemical analyses of the discharge water at day 0, day 1 (or 2), and day 5 after treatment. Algae testing results reflect a population growth endpoint, and therefore can be considered a chronic toxicity test. Generally, the test facility collects sufficient water from the mostly land-based tests to perform the required WET tests at three salinity levels. The test facility prepares a dilution series with the collected water, typically 100%, 50%, 25%, 12.5% and 6.25%. In most cases, no toxicity was seen in the fish and crustacean tests but for algae most effects were determined varying between less than 6.25% until above 50% dilutions of treated ballast water. This information is contained in the published reports of GESAMP-BWWG. In principle, the WET tests have to be carried out at basic approval and at final approval. However, at basic approval a laboratory set-up may be used with simulated ballast water while at final approval the water has to be taken from the full-scale BWMS in operation. However, the toxicity observed was generally quite low as a dilution factor of five was mostly sufficient to neutralize the toxicity to below the NOEC of the effluent. This dilution factor of five is used by GESAMP-BWWG in its near ship scenario for the risk assessment.

Research has also shown algal toxicity of water treated with strong oxidants, even after neutralization of TRO to below the detection limit. In some cases, Dissolved Organic Carbon (DOC) addition before chlorination changed toxicity test results (Lee *et al.* 2015; Lee *et al.* 2017; Park *et al.* 2017). Lee *et al.* (2017). It was observed that algal toxicity of oxidant-treated water increased with the addition of starch before sodium hypochlorite treatment causing a reduction in population growth despite neutralization with sodium bisulfite.

It should be noted, however, that several proposed tests have not been evaluated and are not (yet) implemented in the evaluation methodology of GESAMP (IMO 2017b). In the future, more tools may be available. The GESAMP-BWWG is of the opinion that WET tests for the Final Approval carry more weight than the laboratory results at Basic Approval. However, in a few cases, the GESAMP-BWWG had to decide that the effects determined in the WET test results at Final Approval were too strong for the BWMS under consideration to receive a recommendation for Final Approval. It also happened that the source water used by the applicant or the test facility was already too contaminated with anthropogenic substances that the quality of the test was questioned.

Although the results of the WET tests play an important role at Final Approval of BWMS, uncertainties concerning their use for risk assessment remain which result from differences in the quality and the questioned acceptance of different bioassays. Furthermore, thresholds of acceptable biological effects are currently not defined in a consistent way. Therefore, research and improvement of the quality control of these bioassays is needed prior to any general recommendation concerning the use of WET results for risk assessment and management decisions in other areas. However, it is recommended that these tests, if improved, should play a more important role in the future.

With respect to potential bioaccumulation, the GESAMP-BWWG concluded that none of the DBP most commonly associated with ballast water discharges is bioaccumulative as their octanol / water coefficient K_{ow} and their bioconcentration factor BCF, estimated from this K_{ow}, are too low to cause unacceptable bioaccumulation. Only the log K_{ow} of 3.9 for 2,4,6-tribromophenol is somewhat elevated and points to potential bioaccumulation. The highest experimental BCF for 2,4,6-tribromophenol is 513 with the range being 20 to 513. Generally, it is assumed that substances with a BCF lower than 2000 are not considered as bioaccumulative (PBT and vPvB criteria according to Annex XIII of REACH). However, an investigation of DBPs in conger eel muscle (Boudjellaba *et al.* 2016) identified 2,4,6-TBP in muscle samples (10 out of 15 samples), which was consistent with 2,4,6-TBP having the highest BCF of 513 for fish (Saçan *et al.* 2004; OECD 2003).

Industrial Cooling Waters (Chapter 5)

Calculation of PEC and PNEC

An environmental risk assessment for the input of DBPs by discharges of chlorinated cooling waters of four nuclear power stations located on the French coast of the English Channel (Khalanski 2003) was based on the method advocated by the European Commission (2003). This method consists in determining the PEC, concentration of a given substance in a marine area by using measured concentrations of the DBPs and applying a dilution factor of 20. This dilution factor is based on specific data to characterize the local area, in particular the rate of recirculation of chlorinated seawater. For the regional scale a dilution factor of 100 is used. The PNEC is the concentration that does not cause a biological effect on marine organisms by applying an assessment factor (AF) to the minimum NOEC. The Risk Quotients (RQs) are calculated as the ratio PEC / PNEC or PEC / (NOEC/AF).

The PECs calculated in this study are reported in Table 5-10. In this study, the PEC depends on three factors:

- the DBP concentration at the outfall of the power stations,
- the physical dilution into the volume of water in a theoretical marine area,
- the physical and chemical decaying processes reducing the DBP concentration in water.

Two marine zones of different extension are defined according to the physical dilution factor of the DBPs. Close to the discharge point of the largest power station, at Gravelines, the dilution rate of DBPs is only 20, corresponding to the 5 % recirculation rate of the cooling water. This dilution factor was adopted as representative of the “near field” in the vicinity of the point of discharge and representative of the local scale.

At the regional scale, a dilution factor of 100 was applied for all the nuclear power stations; it is only five times the dilution rate in the near field of discharge. This choice is justified by the large flow of chlorinated cooling water and the strong tidal currents in the Channel creating a kind of coastal river isolated from offshore water, it can overestimate DBP concentrations at the regional scale

It is assumed that the DBPs do not interact with suspended solids and sediments. The only causes of decay in DBP concentration are THM volatility and DBAN hydrolysis to DBAA.

NOECs are derived from five toxicity tests performed on marine organisms of different trophic levels (Table 10-2). The NOECs show a wide variability, from 50 μg/L (DBAN on sea urchin) to 18,000 μg/L (DBAN on algae and DBAA on oyster). For the purpose of this study, the lowest NOEC obtained in these five bioassays was used as a PNEC. Calculated Environmental Risk Factors (ERF) are shown in Table 10-3 for the local scale and in Table 10-4 for the regional scale using two AF: 10 and 100. At the local scale (near field) and AF=100, the calculated Environmental Risk Factor (ERF) remained below 1 for all DBPs, and its maximum value was observed for the DBAN (0.1 – 0.4). At the regional scale, maximum ERFs were observed at Gravelines for DBAA (0.029) and tribromomethane (bromoform) (0.015). The lowest ERFs were found for 2,4,6-TBP and trichloromethane (chloroform).

Table 10-2: No effect observed concentration (NOEC) in bioassays on marine organisms (Khalanski 2003): (1) Cytotoxicity on cell culture of marine clam's gill (2) Embryo-larval toxicity on sea urchin (3) Embryo-larval toxicity on oyster (4) Marine algae culture, growth inhibition (5) Microtox© Bioassay 15 min.

	Clam gill (1)	**Urchin (2)**	**Oyster (3)**	**Algae (4)**	**Bacteria (5)**
Compound	NOEC [μg/L]	NOEC [μg/L]	NOEC [μg/L]	NOEC [μg/L]	NOEC [μg/L]
Bromoform	500	1000	1000		3410
Dibromochloromethane (DBCM)		2500			3160
Dichlorobromomethane (CDBM)		2500			> 250
Monobromoacetic acid	500				6850
Dibromoacetic acid (DBAA)	500	2500	18,000		
Dibromoacetonitrile (DBAN)		50		18,100	1006
2,4,6-Tribromophenol (TBP)		1000			< 2250

Table 10-3: Environmental risk factors (ERF = PEC/PNEC) for DBPs in chlorinated cooling water of four French nuclear power stations at the local scale using AF 10 and AF 100.

Local scale (near field)	**NOEC [μg/L]**	**Penly 2 units**		**Gravelines 6 units**		**Paluel 4 units**	
		PEC/PNEC		**PEC/PNEC**		**PEC/PNEC**	
		AF 10	**AF 100**	**AF 10**	**AF 100**	**AF 10**	**AF 100**
Bromoform	500	7.91×10^{-3}	7.91×10^{-2}	2.94×10^{-2}	2.94×10^{-1}	2.11×10^{-2}	2.11×10^{-1}
DBCM	2500	2.53×10^{-4}	2.53×10^{-3}	2.00×10^{-4}	2.00×10^{-3}	1.80×10^{-4}	1.80×10^{-3}
DCBM	2500	4.80×10^{-6}	4.80×10^{-5}	2.82×10^{-5}	2.82×10^{-4}	1.17×10^{-5}	1.17×10^{-4}
Chloroform	500	2.37×10^{-4}	2.37×10^{-3}	1.26×10^{-4}	1.26×10^{-3}	1.90×10^{-4}	1.90×10^{-3}
DBAA	500	7.78×10^{-3}	7.78×10^{-3}	1.04×10^{-2}	1.04×10^{-1}	8.01×10^{-3}	8.01×10^{-2}
DBAN	50	1.01×10^{-2}	1.01×10^{-1}	3.97×10^{-2}	3.97×10^{-1}	2.24×10^{-2}	2.24×10^{-1}
2,4,6-TBP	1000	5.45×10^{-5}	5.45×10^{-4}	2.06×10^{-4}	2.06×10^{-3}	4.89×10^{-5}	4.89×10^{-4}

Table 10-4: Environmental risk factors (ERF = PEC/PNEC) for DBPs in chlorinated cooling water of four French nuclear power stations at the regional scale using AF 10 and 100

Regional Scale	**NOEC [μg/L]**	**Penly 2 units**		**Gravelines 6 units**		**Paluel 4 units**	
		PEC/PNEC		**PEC/PNEC**		**PEC/PNEC**	
		AF 10	**AF 100**	**AF 10**	**AF 100**	**AF 10**	**AF 100**
Bromoform	500	3.99×10^{-4}	3.99×10^{-3}	1.48×10^{-3}	1.48×10^{-2}	1.06×10^{-3}	1.06×10^{-2}
DBCM	2500	5.15×10^{-7}	5.15×10^{-6}	4.07×10^{-6}	4.07×10^{-5}	3.66×10^{-6}	3.66×10^{-5}
DCBM	2500	4.83×10^{-8}	4.83×10^{-7}	2.84×10^{-7}	2.84×10^{-6}	1.18×10^{-7}	1.18×10^{-6}
Chloroform	500	1.03×10^{-6}	1.03×10^{-5}	5.49×10^{-7}	5.49×10^{-6}	8.24×10^{-7}	8.24×10^{-6}
DBAA	500	1.76×10^{-3}	1.76×10^{-2}	2.90×10^{-3}	2.90×10^{-2}	2.06×10^{-3}	2.06×10^{-2}
DBAN	50	1.27×10^{-4}	1.27×10^{-3}	4.96×10^{-4}	4.96×10^{-3}	2.79×10^{-4}	2.79×10^{-3}
2,4,6-TBP	1000	1.09×10^{-5}	1.09×10^{-4}	4.12×10^{-5}	4.12×10^{-4}	9.78×10^{-6}	9.78×10^{-5}

Bioaccumulation of DBPs in marine biota

In aquatic organisms, the bioaccumulation of organic compounds and their biomagnification in food chains depends on their ability to accumulate in fat (lipophilicity). The lipophilicity of a substance is inversely proportional to its solubility in water. As a result, the octanol: water partition coefficient (K_{ow}) is best suited to evaluate the bioaccumulation potential. For ionizable chemicals such as the haloacetic acids, which are fully deprotonated (and anionic) in the water and the halogenated phenols, which are partially deprotonated, the K_{ow} overestimates the bioaccumulation potential but can be used as a worst-case scenario as the K_{ow} refers to neutral species.

The application of this method results in an estimation of the potential bioconcentration factors for the major DBPs (Table 10-5). The water-soluble haloacetic compounds are the least likely bioconcentrating: BCFs of 3 to 4. The three brominated THMs are relatively water soluble with BCFs between 18 and 55. Tribromophenol

is distinguished by its low water solubility which induces a significant potential bioconcentration: the BCF is ranging from 490 to 600 (Table 10-5). The highest experimental BCF was 513 (Saçan *et al.* 2004).

Table 10-5: Half-life estimation in seawater and determination of the potential bioconcentration factor (BCF) for DBPs (according to Jenner and Whither 2011).

	Volatility	Half life (d)	Log K_{ow}	Water solubility (g/L)	Bioconcentration BCF
Bromoform	volatile	3.5[30]	2.27 – 2.67	0.86 – 5.0	30.2 – 37.2
Dibromochloromethane	volatile	2.12[30]	2.23 – 2.24	2.26 – 4.4	22.9 – 55.0
Bromodichloromethane	volatile	1.62[30]	1.88 – 2.10	2.9 – 4.7	17.8 – 29.5
Dibromoacetic acid (DBAA)	non-volatile	300	1.22	25.7	3.7
Dibromoacetonitrile (DBAN)	semi-volatile	3.5[31]	1.06	59.2	2.8
Tribromophenol (2,4,6-TBP)	non-volatile	Few days	3.92 – 4.02	0.01 – 0.07	489.8 – 602.6

[30] half-life for the top 5 m of water column.
[31] Hydrolysis of DBAN producing DBAA.

Experimental data on bromoform (Table 10-6) show BCF $<$ 1 to 8 at the most, lower than the QSAR estimates but in agreement with the BCF of 1.4 for the 2,4,6-tribromophenol reported by (Grove *et al.* 1985) "in the edible portions of all aquatic organisms consumed".

Table 10-6: Bioconcentration factors (BCF) of bromoform reported after exposure of marine biotas for 28 days (according to Gibson *et al.* 1979).

Organism	Water concentration (mg/L)	Body burden after 28 days (mg/kg wet weight)	BCF
Bivalve molluscs			
Crassostrea virginica	0.03 0.09 0.86	0.00 0.0 – 0.18 0.22 – 0.48	 0 – 2 0.26 – 0.56
Mercenaria mercenaria	0.03 0.09 0.99	0.00 – 0.03 0.23 – 0.25 0.00 – 0.21	0 – 1 2.6 – 2.8 0.1 – 0.21
Prototaca staminea	2 19	1.08 14.25	0.54 0.75
Shrimp			
Penaeus aztecus	0.03 0.05 0.29	0.26 0.00 0.37	8.67 0 1.28
Fish			
Brevoortia tyrannus	0.03 0.04 0.21	0.00 0.15 0.67	0 3.75 3.20

The differences between BCFs estimated by QSAR and the experimental or field data are due to the variability in the fat content of the tissues on which the DBPs are performed. The data reported in Table 10-7 and Table 10-8 indicate that BCFs measured on the flesh of low-fat molluscs and muscle tissue of fish are much lower (1-3) than the BCFs of 139 measured on the abundant abdominal fat in the sea bass from an aquaculture farm using chlorinated seawater.

It also appears that the bromoform content of the mussels decreases very rapidly (48 hours) after stopping the chlorination (Table 10-7).

Table 10-7: Bromoform concentration in molluscs collected at the Gravelines power station in chlorinated effluents (according to Jenner and Whither 2011).

	Black mussel *Mytilus edulis* Discharge canal	**Black mussel *Mytilus edulis* Discharge plume**	**Periwinkle *Littorina littorea* Discharge canal**
Date	µg/kg wet weight	µg/kg wet weight	µg/kg wet weight
23/04/81[32]	19.8	0.0	
06/08/01[32 33]	36.5	7.5	41.0
19/10/81[32]	5.4	4.5	6.2
13/11/81[32]	14.7		
19/11/81[34]	6.5	0.70	
20/11/81[34]	1.0		
21/11/81[34]	0.0		
22/11/81[34]	0.0		
Bromoform in water (mean concentration)	17.5 µg/L[32]	4 µg/L[32]	17.5 µg/L[32]
Bioconcentration factor	1 – 2	1 – 2	1 – 3

[32] chlorination on.
[33] Although in the original paper also this date is given more probable is 06/08/81.
[34] chlorination off.

Table 10-8: Bromoform concentration in fish muscle and abdominal fat collected at the Gravelines power station in chlorinated effluents and fish of the fish farm using this water (modified according to Jenner and Whither 2011).

Discharge canal *Mugil cephalus* (Sea mullet)			**Fish farm *Dicentrarchus labrax* (Sea bass)**		
bioconcentration [µg/kg wet weight]	water [µg/L]	Bioconcentration Factor	bioconcentration [µg/kg wet weight]	Water [µg/L]	Bioconcentration Factor
Muscle 10/09/1981 30	17.5	1.7	Fat 22/04/1981 600	6	100
Muscle 10/09/1981 27	17.5	1.5	Fat 21/05/1981 1767	13	136
Muscle 10/09/1981 18	17.5	1.0	Fat 19/11/1981 1050	7.25	145
			Fat 12/12/1981 187.5	3	62
			Fat sept. 1995 894	6	149
			Muscle 04/04/1996 7	3	2.3
			Muscle 12/12/1996 32	13	2.5

Fish farms using marine chlorinated waters

A study on long-term exposure of sea bass (*Dicentrachus labrax*) cultured in fish farms has been summarized by Jenner *et al.* (1997) and Taylor (2006). In addition to THM, measurements of dibromoacetonitrile, dichloroacetonitrile and total organohalogens (TOX) have been done. The study compared the liver pathologies characterized by morphological abnormalities, necrosis and pre-neoplastic lesions on three groups of fish:

- cultured fish from a fish farm using the chlorinated seawater from the cooling water of Gravelines power station on the French North Sea coast,
- cultured fish from other fish farms in France and Spain,
- wild fish from the Atlantic of Spain and fish collected in the discharge plume of the Gravelines power station, close to the outfall of the outfall canal.

Histopathological results did not show any liver tissue damage that could be attributed to DBPs exposure. However, fish farming produces a clear increase of fat in the liver and development of fat masses in the abdominal cavity. TOX levels in wild fish muscle from non-chlorinated waters were not different to those in fish from chlorinated water. Based on these data, exposure of sea bass to DBPs in chlorinated seawater containing 3 to 13 μg/L bromoform does not affect fish growth and does not induce liver pathology other than fat accumulation caused by nutrition practice in aquaculture.

Ecological monitoring at local scale

Ecological monitoring programs are implemented at all French nuclear power stations in order to compare the environmental impact of plant operation to predicted impact assessment. Such programs produce long-term series of data (up to now 29 to 38 years) on the chemical, microbiological and biological components of the marine coastal ecosystem. A specific survey of local and regional fisheries is also made.

The Survey program includes monitoring of:

- pelagic system (hydrology, chlorination data (TRO, haloforms) microbiology, phytoplankton, and zooplankton),
- fish populations (larvae and eggs of Sole and Sprat) or crustaceans (shrimps),
- benthic macrofauna (intertidal and subtidal).

The marine research institute IFREMER (Institut Français de Recherche pour l'Exploitation de la Mer) is in charge of these monitoring programs. Annual reports are published (Antajan *et al.* 2017); they produced conclusions about the impact of discharges by comparing data collected on measuring stations located in a dilution gradient of the discharge plume. This program also tracks the long-term evolution of the coastal ecosystem in a reference station outside the discharge plume.

Oxidant compounds are responsible for the impact of cooling water chlorination, producing decrease of bacteria and phytoplankton biomass in the cooling water system and in a part of the discharge plume. The rapid disappearance of oxidants in the plume leads to recovery of plankton productivity (Khalanski *et al.* 1985). No adverse effects on the plankton populations are detected by the ecological monitoring in the local area when oxidant concentration remains below 0.02 mg/L. The monitoring programmes also did not show any impact caused by DBPs or other chemical discharges in the local area.

Several other DBP monitoring studies have been conducted. Sim *et al.* (2009) conducted a study of halophenols (HPs) in the area surrounding a chlorinated cooling water discharge and found two bromophenols in both water and sediment samples. Another recent study assessed the formation of a wide range of DBPs (i.e. THMs, HAAs, HANs acetaldehydes, HPs) when seawater is chlorinated for the control of biofouling such as for cooling water and other industrial applications (Manasfi *et al.* 2019). However, neither paper describes ecotoxicological experiments with only a recommendation to perform toxicity experiments and do risk assessments.

Desalination Plants (Chapter 6)

Very few studies on brine discharge from desalination plants have been performed, focusing mainly on the impact of salinity (Yoon and Park 2011; Voorhees *et al.* 2013; Benaissa *et al.* 2017; Chang 2015; Cortes *et al.* 2018). None of these studies provide insight on the DBP concentrations used in these effluent tests.

Seawater Toilets (Chapter 7)

Toilet flushing with seawater results in saline wastewater, which may contain approximately 33–50% seawater. Halogenated disinfection by-products (DBPs), in particular brominated and iodinated DBPs, have recently been found in chlorinated saline wastewater effluents. The brominated and iodinated DBPs in chlorinated saline wastewater effluents might cause adverse effects to marine ecology. Recent studies have shown that brominated and iodinated DBPs are generally significantly more developmentally toxic and growth inhibitory than their chlorinated analogues, and halophenolic DBPs are generally significantly more toxic than trihalomethanes and haloacetic acids (Yang and Zhang 2013; Liu and Zhang 2014). The adverse effects of halogenated DBPs in concentrated chlorinated wastewater effluents were distinctly noted in the acute toxicity tests with the marine species (Yang *et al.* 2015).

Wastewater treatment (Chapter 8)

GESAMP hazard evaluations include a reprotoxic endpoint, which includes adverse effects on development as well as reproductive effects of adults. While reproductive effects entail lengthy and expensive tests, there are developmental tests that can be employed that are relatively short, inexpensive and have internationally accepted guidelines. Hutchinson *et al.* (1998) assessed the developmental, genotoxic and cytotoxic effects of disinfected municipal sewage effluents using a marine polychaete worm assay and observed a reduction in development of embryo-larvae as well increase in

cytotoxicity. Yang *et al.* (2015) applied this test to halogenated DBPs and chlorinated saline sewage effluent. Two- and three-step chlorination of sewage effluent (i.e. dosing chlorine in separate steps with a lower dose) was also demonstrated to reduce formation and toxicity of DBPs (Li, Yang, *et al.* 2017; Li, Zhang, *et al.* 2017).

10.3 Exposure Assessment

In chapters 4 to 8 the potential input of DPB into the aquatic environment is presented. Depending on the characteristics of the receiving environment (e.g., water volume, mixing) and assumptions on the fate of the considered DBP, the concentrations of DBPs in the marine ecosystem can be estimated. These so-called predicted environmental concentrations (PEC) serve as a reference for the exposure concentrations. Unlike PNEC values, which are intended to represent a generic predicted chemical concentration which is unlikely to show unacceptable effects in the aquatic environment, PEC values are specific for the assessed scenario.

For example, the discharge concentrations of DBP determined in ballast water presented in chapter 4 were used for the PEC calculation in a standard commercial harbor using the MAMPEC model (as presented in chapter 4.3.3). This mathematical model was originally developed for antifouling paint biocides and has been adapted for a use under ballast water discharge situations (Van Hattum *et al.* 2016). For the PEC estimation it is assumed that all ships will use a specific BWMS (Zipperle *et al.* 2011). The MAMPEC BW model has been used extensively by the BWWG in a standard GESAMP-BWWG harbour scenario and has also been used to calculate PECs in other scenarios (David *et al.* 2018). Resulting from the application of the MAMPEC BW model are environmental concentrations given as a statistical distribution with values for the maximum concentration, the 95% concentration, the average concentration, the median concentration, and the minimum concentration for the harbour and the surrounding areas.

PECs have been calculated for the surrounding water at three French nuclear power stations on the local and regional scale by an application of dilution factors 20 and 100 on DBP concentrations in the discharged cooling water (as presented in chapter 5.4). Similar approaches could be adapted for other industrial fields. However, due to lacking data and because of non-standardised dilution regimes, they have not been used for the purpose of this report.

10.4 Risk Assessment

The two approaches for assessing risks (see Section 10.1) are differentiated as follows. The conventional component-based approach to risk assessment is the risk quotient approach (PEC/PNEC), where the measured or predicted environmental concentrations are related to predicted no effect concentrations. A calculated ratio of PEC/PNEC $>$ 1 indicates a potential risk in the environment (Delacroix *et al.* 2013). In this approach, one can only include known DBPs with existing effect data. (The establishment of PNEC values is presented and discussed in Section 10.2.3.) The alternative to such approach is a direct toxicity assessment at different water samples. This approach (discussed in chapter 10.2.4.) goes beyond the known and quantifiable chemicals and also includes potential synergistic effects of chemicals, but typically refers to single test results and therefore the observed effects cannot be quantitatively related to exposure concentration. Furthermore, this approach is limited to comparative assessments. Such more holistic approach is also prone to artifacts when the toxicity tests also respond to other stressors that act together with the DBPs in mixtures.

For the risk assessment in the authorization process of ballast water management systems, a detailed scheme for risk assessment has been established where modelled DBP concentrations resulting from discharge are compared to predicted no effect concentrations. Generally, the GESAMP-BWWG chooses to use the maximum concentration as a worst case. Typically, using this approach, risks resulting from local peak concentration of some DBP near a ship cannot be excluded. However, such elevated concentrations will be diluted below critical concentration within typical harbour water volumes.

A local risk assessment based on the PEC/PNEC approach was performed by Zhang *et al.* (2014) for ballast water treated with hydroxyl radicals in a Chinese harbour, which demonstrated that the highest risk resulted from the disinfectant NaOCl. Of the DBPs, only monochloroacetic acid (MCAA) posed a risk due to its high occurrence and low PNEC derived from algal toxicity (Zhang *et al.* 2014).

Other local risk assessments have been performed for other industrial installations discharging DBP containing water, such as cooling water from power plants. The overall outcome of the assessment shows that local effects on aquatic organisms in the direct surroundings of the installation cannot be excluded. However, as outside of this area dilution in sea water is important, a rapid decrease of concentrations can be expected. Therefore, there is no toxicity risk from anthropogenic DBP inputs for marine life on the global scale based on these assessments for the surrounding area to the discharge outlet.

11 IMPACT ON HUMAN HEALTH

The impact of disinfection by-products (DBPs) on human health has been extensively studied in the context of drinking water since the 1970s (WHO 2000; Richardson *et al.* 2007). In many industrialized countries, the identified health risks have led to the establishment of limit values and monitoring requirements for the most frequently occurring DBPs in drinking water (WHO 2017). The impact of DBPs from marine water on human health differs from the drinking water situation in two ways. First, the pattern and quantities of DBPs formed in marine applications are different in that the predominant species are brominated DBPs, which have different toxicological properties than their chlorinated counterparts. Second, human exposure to DBPs is different. While DBPs in drinking water are consumed on a daily basis in fairly predictable quantities through oral intake, exposure to DBPs in marine water is assumed to happen less frequently, following scenarios that are associated with a considerable degree of uncertainty.

11.1 General principles of human health risk assessment

The assessment of risks to human health from chemical substances is a stepwise procedure that combines the identification and characterization of potential hazards, i.e., toxicological effects, of the chemicals and the estimation of likely human exposure through contact with them (Figure 11-1).

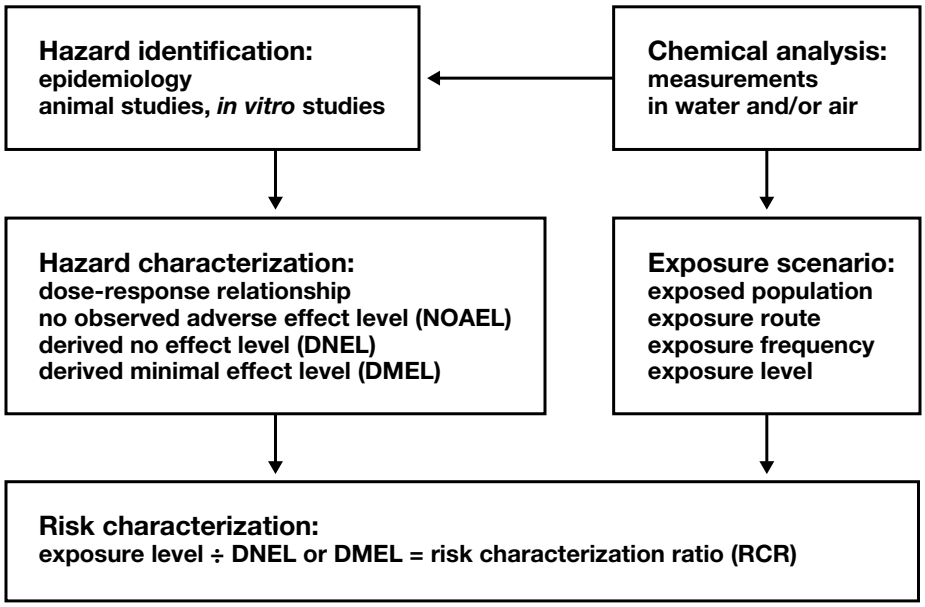

Figure 11-1: *Different steps of human health risk assessment.*

Information regarding potential hazards can in principle be derived from observation in humans, animals or experimental models in vitro. Most commonly, toxicological studies in laboratory animals are used. They provide insights regarding what type of adverse effect a chemical may cause as well as the dose-response relationship. Ideally, the study data include a dose level at which no adverse effect was observed, i.e., the no observed adverse effect level (NOAEL). The NOAEL observed in animals serves as starting point for the calculation of the derived no effect level (DNEL) in humans, using appropriate assessment factors that account for physiological differences between the tested animal species and humans, the variability within the human population, differences in the duration of the laboratory study and the expected human exposure, the quality of the experimental data etc. If a chemical can cause cancer through a genotoxic mechanism of action, a DNEL cannot be defined because theoretically a single molecule could trigger carcinogenesis. Instead, a derived minimal effect level (DMEL) is used that represents a certain probability of cancer formation (e.g., 1 in 10^5 or 1 in 10^6). Information regarding human exposure to chemical substances can be obtained by biomonitoring, i.e., the analysis of materials such as urine, blood, hair etc., or by measurements in the environment and the definition of certain exposure scenarios that make assumptions regarding the exposed population group, the exposure route (i.e., ingestion, skin contact or inhalation) and the frequency and duration of exposure. These parameters allow the calculation of estimated exposure levels. The final step of risk assessment is risk characterization: Division of the exposure level by the DNEL or DMEL gives the risk characterization ratio (RCR). If the exposure level exceeds the DNEL or DMEL, i.e. the RCR is greater than 1, risks to human health cannot be excluded.

11.2 Hazards (mammalian toxicity)

With regard to potential health hazards of DBPs, numerous studies are available, including both laboratory and epidemiological data. For instance, the consumption of chlorinated drinking water has been associated with increased incidence of bladder cancer and adverse reproductive outcomes (Nieuwenhuijsen *et al.* 2000; Villanueva *et al.* 2004). So far, it has not been possible to link the observed health effects to any

specific DBP present in drinking water, by statistical analysis nor based on mechanism of action. Therefore, the relevance of the epidemiological findings for DBPs in drinking water to the assessment of potential health effects of DBPs in marine water is uncertain, since the DBP mixtures generated in both settings differ substantially. The presentation of experimental toxicity data in this chapter focusses on those chemical classes of DBPs that have been most frequently reported from marine applications: bromate ion, trihalogenmethanes, halogenated acetic acids, and some halogenated acetonitriles (Table 1-11).

Table 11-1: Toxicity data of DBPs relevant for the marine environment[35].

	LD_{50}[36] [mg/kg bw]	LC_{50}[37] [mg/L]	NOAEL [mg/kg bw]	LOAEL[38] [mg/kg bw]	DNEL [µg/kg bw/d]	Carcinogenicity Classification	DMEL [µg/kg bw/d]
Bromate	160	n.d.[39]	1.1 (rat, 2 y)	n.a.[40]	11	IARC 2B[41] (1999); USEPA B2[42] (2001)	0.1
Trichloromethane	450	9.2 (6 h)	n.d.	15 (dog, 7.5 y)	120	EU cat. 2[43] (2010)	n. a.
Bromodichloro methane	450	n.d.	n.d.	6 (rat, 2 y)	20	IARC 2B (1999)	2.4
Dibromochloro methane	800	n.d.	30 (rat, 13 wk)	n.a.	110	USEPA C[44] (2004)	1.5
Bromoform	1,100	3.0 (4 h)	25 (rat, 13 wk)	n.a.	89	USEPA B2 (2004)	7.7
Chloroacetic acid	55	0.3 (1 h)	3.5 (rat, 2 y)	n.a.	35	no (EU 2005)	n.a.
Dichloroacetic acid	800	n.d.	n.d.	13 (dog, 90 d)	60	IARC 2B (2014)	1.7
Trichloroacetic acid	1,600	32 (4 h)	30 (dog, 90 d)	n.a.	430	IARC 2B (2014)	n.d.
Bromochloro acetic acid	n.d.	n.d.	75 (rat, 90d)	n.a.	380	IARC 2B (2012)	0.1
Bromodichloro acetic acid	500	1.5 (4 h)	250 (rat, 2 y)	n.a.	2,500	clear evidence in animals (NTP 2015)	1.7
Dibromochloro acetic acid	n.d.	n.d.	89 (rat, 14 d)	n.a.	150	n.d.	n.a.
Bromoacetic acid	50	3.0 (4 h)	3.5 (rat, 2 y)	n.a.	35	n.d.	n.a.
Dibromoacetic acid	1,700	n.d.	38 (mice, 4 w)	n.a.	36	IARC 2B (2012)	0.1
Tribromoacetic acid	n.d.	n.d.	30 (dog, 90 d)	n.a.	430	n.d.	n.a.
Dichloroacetonitrile	330	n.d.	8 (rat, 90 d)	n.a.	29	IARC 3[45] (1999)	n.a.
Dibromoacetonitrile	250	n.d.	23 (rat, 90 d)	n.a.	82	IARC 2B (2012)	n.d.

[35] Unless otherwise noted, data are from the GISIS database of ballast water chemicals (IMO 2018c);
[36] LD50: lethal dose for 50% of tested population after oral or dermal administration;
[37] LC50: lethal concentration for 50% of tested population after inhalation;
[38] LOAEL: lowest observed adverse effect level;
[39] n.d.: no data identified;
[40] n.a.: not applicable;
[41] possibly carcinogenic to humans based on sufficient evidence in animals;
[42] probably carcinogenic to humans based on sufficient evidence in animals;
[43] suspected human carcinogen based on limited evidence;
[44] possibly carcinogenic to humans based on limited evidence in animals;
[45] not classifiable as to its carcinogenicity to humans.

Trihalomethanes are volatile substances of limited solubility in water. In contact with skin or eyes, they act as irritants. Otherwise, their acute toxicity is moderate to low. Their chronic toxicity is mainly characterized by their carcinogenic potential. All four trihalomethanes have been classified as possibly or probably carcinogenic to humans by competent expert groups (European Commission 2010; IARC 1999). While it is assumed that chloroform causes tumor formation as a consequence of chronic inflammation, genotoxic

mechanisms cannot be ruled out for the other trihalomethanes (ATSDR 2005; IARC 1999). Bromate has also been found to be carcinogenic in animals, with some evidence of genetic toxicity due to the metabolic generation of bromine radical intermediates (NTP 2007). Halogenated acetic acids are present in water in their acid and acetate forms to varying degrees and are thus generally more water soluble and less volatile. Due to their acidic nature, they can all exhibit corrosive effects on skin and cause serious eye damage in high concentration. Data on systemic acute toxicity is missing for some substances. The lethal dose after oral application ranges from around 50 mg/kg body weight (bw) for monochloro- and monobromoacetic acid to more than 1,500 mg/kg bw for trichloro- and dibromoacetic acid. Chronic toxicity data is also incomplete in some cases and of varying quality. Generally, those substances that are known from drinking water treatment have been investigated in more detail. While monochloroacetic acid has been determined not to cause carcinogenicity in animals in an extensive EU risk assessment (European Commission 2005), clear evidence of carcinogenicity in animals has been observed for five other substances (IARC 2012, 2014; NTP 2015). Trichloroacetic acid is assumed to act through multiple non-genotoxic mechanisms. For dichloroacetic acid, bromochloroacetic acid, bromodichloroacetic acid and dibromoacetic acid, both non-genotoxic and genotoxic mechanisms of tumor generation are under discussion (IARC 2012, 2014; NTP 2015). No carcinogenicity data are available for dibromochloroacetic acid, monobromoacetic acid, and tribromoacetic acid. Only very few toxicity data are available for halogenated acetonitriles. Locally, irritant and even corrosive effects on skin and eyes have been reported. The acute systemic toxicity is moderate. Available data on long-term toxicity are of mixed quality, with some of the study durations being in the sub-chronic rather than in the chronic ranges. Dibromoacetonitrile has been classified as possibly carcinogenic to humans (IARC 2012), with evidence for a genotoxic mechanism of action. For the other halogenated acetonitrile, insufficient data is available to evaluate their carcinogenic potential.

11.3 Exposure assessment

Human exposure to DBPs in marine water generally occurs through oral ingestion of or dermal contact with treated water, through inhalation of DBP vapors released from treated waters to the atmosphere, or through the consumption of fish or seafood containing DBPs taken up from treated water. In order to quantify exposure, scenarios are developed that define specific exposure situations in terms of exposure route (ingestion, dermal uptake, inhalation), exposure time (frequency and duration), the quantity of the medium to which exposure occurs (water, air, seafood) and the concentration of DBPs in this medium (Banerji *et al.* 2012; IMO 2017b). For risk assessment purposes, it is common practice to distinguish between occupational exposure scenarios concerning only a limited group of employees in certain industries and exposure scenarios concerning the general public. Occupational exposure will not be covered in this chapter. One reason is that the activities and scenarios involved are very specific for the respective industry and even for each individual workplace, and it would exceed the scope of this text to describe them all. Another reason is that occupational exposure to chemicals, as part of occupational safety, is subject to national legislation and a number of regulations and mitigations are in place that differ from country to country.

Exposure of the general public to DBPs in marine water can occur during swimming in polluted water and through the consumption of seafood that is contaminated with DBPs taken up from polluted water. Swimming can lead to oral, dermal and inhalation uptake (U) at the same time: $U_{swim} = U_{inhal} + U_{dermal} + U_{oral}$. The respective quantities are estimated separately by the following equations:

$U_{inhal} = C_{air} \times InhR \times ET \times Bio \times bw^{-1}$, with	$C_{air} = C_{water} \times H$ [mg/m^3] C_{water} = measured or calculated concentration ÷ dilution factor 100 H = Henry's Law Constant InhR = inhalation rate, set as 1.25 m^3/h ET = exposure time, set as 2.5 h/d Bio = bioavailability, set as 1 bw = body weight, set as 60 kg
$U_{dermal} = C_{water} \times A_{skin} \times TH \times n \times Bio \times bw^{-1}$, with	C_{water} = measured or calculated concentration ÷ dilution factor 100 A_{skin} = area of skin exposed, set as 1.94 m^2 TH = thickness of layer on skin, set as 0.0001 m n = number of events, set as 5 d^{-1} Bio = bioavailability, set as 1 bw = body weight, set as 60 kg
$U_{oral} = C_{water} \times IngR \times ET \times Bio \times bw^{-1}$, with	C_{water} = measured or calculated concentration ÷ dilution factor 100 IngR = ingestion rate, set as 2.5 x 10^{-5} m^3/h ET = exposure time, set as 2.5 h/d Bio = bioavailability, set as 1 bw = body weight, set as 60 kg

The assumptions included in these equations regarding physiological parameters, exposure frequency and duration are based on guidelines and manuals provided by recognized organizations such as the World Health Organization, the European Chemicals Agency, or the U.S. Environmental Protection Agency. The concentration in water needs to be determined specifically for each DBP and each situation under consideration. In the case of ballast water management, the concentrations in the harbour or in the surrounding waters are calculated with the software MAMPEC based on the concentrations measured in ballast water discharge during land-based testing (see also chapter 4).

The potential oral uptake of DBPs through the consumption of seafood can be calculated from the quantity of seafood consumed and the concentrations of DBPs it contains, which is directly correlated to the DBP concentrations in water:

U_{food} = Cfood x Qfood x Bio x bw^{-1}, with	C_{food} = concentration of DBP in food = C_{water} x BCF C_{water} = measured or calculated concentration [e.g. μg/L] BCF = bioconcentration factor (L/kg) Q_{food} = quantity of food consumed, set as 188 g/d Bio = bioavailability, set as 1 bw = body weight, set as 60 kg

As the bioconcentration factor is not known for many DBPs, their octanol-water partition coefficient (log K_{ow}) is generally used instead.

The exposure through swimming and the consumption of seafood can also be combined to a figure representing the total exposure to DBPs from marine water: $U_{total} = U_{food} + U_{swim}$.

11.4 Human health risk

Table 11-2 summarizes the human exposure levels and risk characterization ratios (RCR) resulting from DBPs generated by ballast water management. The calculations are based on the maximum concentrations observed in ballast water discharge during the testing of ballast water management systems and represent a worst-case scenario (see also chapter 4). Even then, the RCR values remain below 1, i.e., no risk human health is expected for all substances except bromate. As can be seen, the largest contribution to the total exposure to bromate originates from swimming in contaminated water. As it seems unlikely that people swim directly in the harbour, the calculation can be refined by modifying the initial assumptions: using the concentration in the surrounding waters instead of the harbour itself leads to a much lower RCR value. This example illustrates the importance of the initial assumptions regarding exposure for the overall outcome of the risk assessment. Another source of uncertainty is the lack of toxicological data for some DBPs. In particular, information regarding potential carcinogenicity is missing for several of the halogenated acetic acids and acetonitriles. In the case of trichloroacetic acid and dibromoacetonitrile, possible carcinogenicity has been recognized (IARC 2012, 2014) but the available data are insufficient for the derivation of a DMEL value. Therefore, the risk assessment at this stage can be only preliminary.

Table 11-2: Human exposure to DBPs from ballast water management and resulting health risks.

	Concentration[46] [μg/L]		Human exposure[47] [μg/kg bw x d]			RCR[48]
	Discharge	**Harbour**	**Swimming**	**Seafood**	**Total**	
Bromate	920	16	0.27	0.01	0.28	2.5 (0.03[49])
Trichloromethane	260	2.4	0.24	0.03	0.27	0.002
Bromodichloro methane	71	0.7	0.05	0.01	0.06	0.02
Dibromochloro methane	120	1.3	0.05	0.03	0.08	0.05
Bromoform	890	11	0.31	0.40	0.71	0.09
Chloroacetic acid	500	8.4	0.14	0.003	0.15	0.004
Dichloroacetic acid	78	1.3	0.02	0.002	0.02	0.01
Trichloroacetic acid	150	2.5	0.04	0.008	0.05	0.0001

[46] Highest reported concentrations of DBPs in ballast water discharge and the resulting concentrations in harbour water as calculated with the software MAMPEC (cf. chapter 4);
[47] internal concentrations of DBPs in humans that might result from activities in sea water of the highest reported concentrations of DBPs (column to the left), calculated with the formulae described in the text above;
[48] risk characterization factor: calculated by dividing the total human exposure (column to the left) by the derived no effect level (DNEL) or the derived minimal effect level (DMEL) in case of potential carcinogens (cf. Table 11-1) – an RCR value above 1 indicates a potential health risk;
[49] using the predicted concentration in surrounding waters instead of the harbour, since swimming directly in the harbour seems rather unlikely.

	Concentration[46] [μg/L]		Human exposure[47] [μg/kg bw x d]			RCR[48]
	Discharge	Harbour	Swimming	Seafood	Total	
Bromochloroacetic acid	250	4.2	0.07	0.04	0.11	0.9
Bromodichloroacetic acid	28	0.5	0.008	0.005	0.01	0.008
Dibromochloroacetic acid	33	0.6	0.009	0.006	0.02	0.0001
Bromoacetic acid	190	3.2	0.06	0.001	0.06	0.002
Dibromoacetic acid	230	3.9	0.07	0.002	0.07	0.5
Tribromoacetic acid	970	16	0.29	0.13	0.41	0.001
Dichloroacetonitrile	9.2	0.2	0.003	0.001	0.004	0.0001
Dibromoacetonitrile	130	2.2	0.04	0.001	0.04	0.0005

For applications other than ballast water treatment the available data about environmental concentrations of DBPs are not sufficient to perform the same systematic assessment of potential human exposure. Most information is available for the impact of cooling water chlorination in coastal power stations (see also chapter 5). Measurements in the effluent at different locations in the UK and France gave concentrations of 1-43 μg/L for tribromomethane (bromoform), 0.1-2.2 μg/L for dibromochloromethane, 2-10 μg/L for dibromoacetic acid, and 0.1-5 μg/L for dibromoacetonitrile, respectively (Khalanski 2003; Taylor 2006). While these values are considerably lower than those reported for ballast water, the cooling water discharge is continuous, and it is not easy to predict what kind of steady-state environmental concentrations will eventual be generated. Khalanski reported measurements of bromoform in marine biota close to cooling water outlets. The maximum values of 30 μg/kg in fish and 36.5 μg/L in mussels would result in human exposure levels around 0.1 μg/kg bw x d, which is lower than the 0.4 μg/kg bw x d that are calculated as the worst-case exposure level from consumption of seafood exposed to treated ballast water.

Although the risk assessment at this stage can be only preliminary, any significant human health risk is highly unlikely. Toxicological and chemical information that would replace the still missing data will not impact the result significantly. The human risk assessment presented above for the human exposure near to the ship and via harbour waters is based on the discharge concentrations from ballast water treatment. Such discharge concentrations from vessels are the highest observed from the disinfection processes outlined in chapters 4 to 8 of this report. Likewise, the concentrations resulting from natural biosynthesis by marine organisms (as outlined in chapter 2) are far below the exposure resulting from discharge of treated ballast water. None of the concentrations measured in other sectors is higher than the concentrations taken for the human risk assessment outlined above. Therefore, it can be concluded that based on today´s knowledge no significant human risk is expected to result from any of the processes leading to human exposure via the marine environment.

12 IMPACT ON THE ATMOSPHERE

A large amount of the DBPs generated during the chlorination of freshwater and marine water belongs to the group of trihalomethanes (THMs). In freshwater, chloroform is the major compound generated, while bromoform predominates at high bromide levels in marine waters. These THMs are released into the atmosphere where they can impact atmospheric chemistry by disturbing local tropospheric ozone chemistry, air quality and stratospheric ozone depletion. In this chapter, we will describe the overall role of THMs such as chloroform and bromoform in the atmosphere. The contributions of anthropogenic THMs from water disinfection in comparison to THMs from natural sources will be discussed and a synthesis is given.

12.1 The role of Very Short-Lived Substances in the atmosphere

Halogenated short-chained hydrocarbons (in short halocarbons) from water disinfection mix with natural sources of the compounds in freshwater, coastal, shelf or open ocean waters depending on the release location. The halocarbons are emitted into the atmosphere through the air-sea interface as soon as the water concentration is above the equilibrium state with the atmosphere. On regional and global scales, the air-sea gas exchange is the most important sink mechanisms for halocarbons from the oceanic mixed layer.

Bromoform and dibromomethane are the major carriers of bromine from the ocean to the atmosphere (Penkett *et al.* 1985). There is a large spatiotemporal variability of the air-sea exchange (Liu *et al.* 2013; Butler *et al.* 2007), as observed emissions from the water phase can vary by an order of magnitude or more – even during one cruise for measurements. Many factors contribute to this variability, including subsurface biogeochemical processes, proximity to coastal sources, wind speed, and sea surface temperature (e.g., Stemmler *et al.* 2015). Uncertainties of global halocarbon emission estimates are large, with bottom-up bromoform emissions being a factor of two lower than top-down estimates, most likely due to poor temporal and spatial data coverage (e.g. Ziska *et al.* 2013).

Natural sources of chloroform are dominated by microbial production in the ocean and soil, while anthropogenic sources include chlorodifluoromethane (HCFC-22) and fluoropolymer production, paper manufacturing, and water chlorination. The largest source was at first identified to be the marine production in offshore seawater contributing about 50% (McCulloch 2003), however, recently increasing emissions turned the attention to industrial sources (Fang *et al.* 2019). Similar to the brominated halocarbons, large spatial gradients can cause significant representation uncertainties in the emission estimates.

Once released into the atmosphere, halocarbons will contribute to the halogenated very short-lived substances (VSLS). They are quickly oxidized or photodissociated to reactive halogen species which play an important role for tropospheric chemistry (Saiz-Lopez and von Glasow 2012). Reactive halogens participate in the depletion of ozone by catalytic cycles and thus have a large impact on the tropospheric ozone (10% annual mean depletion) which contributes approximately -0.10 $W \cdot m^{-2}$ to the radiative flux at the tropical tropopause. Furthermore, reactive halogen species act directly as oxidants (e.g., for dimethylsulfide (DMS) and mercury) and alter tropospheric HO_x and NO_x ratios which in turn impacts the global lifetimes of many trace gases, most importantly methane. Thus, VSLS emissions strongly impact the atmospheric oxidizing or self-cleaning capacity, i.e., the capacity of the atmosphere to oxidize and thus remove a large variety of organic and inorganic species.

VSLSs are not only important for tropospheric chemistry, but also impact stratospheric composition. In contrast to the long-lived ozone-depleting substances, a substantial fraction of VSLS can be oxidized and washed out in the troposphere. However, in regions of rapid transport by deep convective events, VSLS can be carried from their oceanic source directly into the stratosphere before being oxidized (Aschmann *et al.* 2011; Tegtmeier *et al.* 2012). Reactive halogens originating from VSLS oxidation can also be entrained into the stratosphere if not removed from the atmosphere by falling rain or ice. The impact of heterogeneous chemistry (releasing halogens back to the gas phase) on the efficiency of wet deposition as a sink for total bromine and iodine is currently under discussion (Aschmann *et al.* 2011; Dix *et al.* 2013).

On a global scale, increasing evidence from observational and modelling studies suggest that brominated VSLS provide a significant contribution of ~5 (3–7) ppt to stratospheric bromine, which was about 25% of total stratospheric bromine in 2016 (Engel and Rigby 2018). Atmospheric chloroform concentrations were relatively stable during 1990–2010, but increased after 2010 (Fang *et al.* 2019). If the emissions continue to grow at the current rate, the recovery of the ozone layer could be delayed by several years. Due to their short lifetimes and their atmospheric variability the quantification of their contribution is much more difficult and has much larger uncertainties than for long-lived compounds. Overall, the full impact of oceanic halogen compounds on middle atmosphere composition, chemistry and climate is highly uncertain related to the uncertainties in surface emissions, convective transport processes and microphysical properties. Once brominated VSLS have reached the stratosphere in the form of source gas or product gas, they participate in ozone depletion at middle and high latitudes (Braesicke *et al.* 2013; Sinnhuber and Meul 2015; Yang *et al.* 2014).

12.2 Impact anthropogenic Very Short-Lived Substances

The contribution of bromoform from ballast water treatment to atmospheric halogen budgets has been analyzed in detail for two exemplary harbour regions, Singapore and the Pearl River Delta (Maas *et al.* 2019). Ballast water treatment around Singapore can locally double oceanic bromoform emissions into the atmosphere. In both regions, all bromoform is directly outgassed leading to an additional bromine input into the atmosphere of around 495 and 312 kmol $CHBr_3$/a (per year) for the Pearl River Delta and Singapore, respectively. Analyses by Maas (2020) show that the anthropogenic bromoform input from ballast water treatment in the near future will only have a minor contribution to the global atmospheric bromine budget with 3–13 Mmol Br/a compared to a global climatological bromine flux of 1.7 Gmol Br/a. Current ballast water discharge volumes of about 3.4 billion m^3/a are too small to produce globally significant amounts of anthropogenic bromoform. This corresponds to 0.1 % of global bromoform emissions from all sources and is thus not relevant for stratospheric ozone depletion (Maas *et al.* 2019).

Anthropogenic bromine from industrial cooling water can be expected to be more important, as the total amount of water used is larger than used for ballast water management. Recent model-based estimates show that for South-East Asia alone, the emissions are on average 24 Gg Br per year (Maas *et al.*, 2020), which is 30% more than the measurement-based estimate of total emission derived for the same region (18 Gg Br per year (Fiehn *et al.* 2018)). About 90 % of this anthropogenic bromoform is discharged north of 20° N, while in the tropics natural sources dominate. In the marine boundary layer of East Asia, anthropogenic bromoform in coastal regions amounts up to 0.5–1.6 ppt during boreal summer and is thus 2–7 times larger compared to existing estimates. As most of the power plants are situated in the northern subtropics, the anthropogenic bromoform is confined to the northern hemisphere subtropics during boreal summer. However, during boreal winter, some part of the anthropogenic bromo-

form is transported by the north-easterly winter monsoon towards the tropical regions. Here, convective events lead to an additional entrainment of 0.03 ppt bromoform from industrial sources into the upper troposphere/lower stratosphere. In summary, the high anthropogenic bromoform emissions in the East China, Yellow and Japan Seas do not efficiently reach the stratosphere, unless the anthropogenic bromoform is advected with the Asian winter monsoon into the tropics, in which case it can lead to an increased entrainment of 14–19 % over this area.

12.3 Conclusion

Bromoform from treated ballast water can be expected to have no effect on the stratospheric ozone layer, as the overall amount of bromoform produced in ballast water is small compared to the global production. The case is different for bromoform from treated cooling water, where larger water amounts lead to a larger input of bromoform into the atmospheric boundary layer. However, as most of the industrial sources are located in the northern hemisphere subtropics, a large fraction of the bromoform emitted with treated cooling water stays confined to the troposphere and is not contributing to stratospheric ozone depletion.

It is so far not completely clear what the impact of anthropogenic VSLS emitted in form of disinfection by-products on the atmosphere will be. The challenge for such an assessment results from the fact that measurements in the marine and atmospheric environment show the combined amount of VSLS originating from natural and anthropogenic sources. In order to estimate the input of anthropogenically produced halocarbons into the environment, a bottom-up approach is needed. Such an approach should rely on representative halocarbon concentrations in treated water and information on the amount, timing and location of the release of the water into the environment. Such estimates, however, are subject to large variations, e.g., concentrations of bromoform found in treated water depend strongly on the study region, time of analyses and methodology. Future bottom-up studies and measurement campaigns close to large water treatment sites are required.

13 CONCLUSIONS

Disinfection by-products (DBPs) are produced during oxidant treatment of natural water performed for disinfection purposes or fouling control. The spectrum of these DBPs generated in marine waters differs significantly from DBP in fresh water such as drinking water. Whereas in fresh water chlorinated DBP are predominant, brominated DBP are most abundant in marine water. This is related to the relatively high concentration of bromides in marine waters, which can be oxidized to hypobromous acid playing a key role in the oxidation process and DBP formation.

Bromoform has been identified as the major DBP in all technical applications using oxidants in seawater. Furthermore, other DBP, e.g., halomethanes, haloacetic acids, haloacetonitriles and halophenols have been observed, with dibromoacetic acid, tribromoacetic acid, dibromoacetonitrile, 2,4,6-tribromophenol and bromate being often detected. However, the absolute concentration and the relative abundance of the different compounds vary between different applications reflecting variable process parameters (e.g., oxidant concentration, reaction time) and water quality parameters (e.g., characteristics and concentration of organic matter).

Some compounds identified as DBP are also of natural origin. Bromoform is synthesized by different algae and kelp species making it the organohalogen produced in highest amounts in the marine environment. Furthermore, bromophenols (with 2,4,6-tribromophenol most often detected) are part of the natural bromine containing compounds of marine origin. For most other DBP, no or only very limited natural production volumes have been described. Therefore, most DBP have to be considered as mainly anthropogenic compounds with little overlap with natural compounds except bromoform and bromophenols.

The quantification of global inputs of DBPs and its analogues of natural origin is difficult due to heterogeneity in available data on different sources of these compounds. Since bromoform is the most abundant DBP, it can serve as a proxy to compare the input from different sectors. The total estimated anthropogenic bromoform production and discharge adds up to 13.5 x 10^6 kg/a to 21.8 x 10^6 kg/a with contribution of 0.86 x 10^6 kg/a from ballast water; 11.8 x 10^6 kg/a to 20.1 x 10^6 kg/a from cooling water; 0.89 x 10^6 kg/a from desalination; 0.03 x 10^6 kg/a from saline sewage treatment (Hong Kong only). Most of the estimates are based on realistic assumptions for discharged water volumes and mean values for observed or estimated DBP concentrations. Potentially, the inputs could be higher in case the conducted studies on DBP concentrations in cooling water are not representative for other regions and other anthropogenic inputs may also be quantitatively relevant, e.g., emission from wastewater treatment, which could not be quantified due to missing data. Therefore, this assessment does not represent a worst-case scenario. Furthermore, this assessment does not take into account potential additional bromoform generation resulting from the degradation of other DBP, which could contribute to the total bromoform flux to the atmosphere. The natural bromoform production in marine water has been estimated to be 76 x 10^6 kg/a to 870·x 10^6 kg/a (Table 2-1). Anthropogenic bromoform production thus equals approximately 2–6% of global marine bromoform emissions depending on whether higher or lower boundaries are used. This range not only reflects the uncertainty of the estimated anthropogenic inputs but also the uncertainties in the quantification of the natural production.

The overall risk to global marine life (aquatic organisms) is estimated to be low. However, regional hotspots close to points of discharge may exist where risks for aquatic organisms may be present.

For the assessment of ballast water management systems, a detailed scheme for risk assessment has been established where modelled DBP concentrations resulting from discharge are compared to predicted no effect concentrations. Typically, risks resulting from local peak concentration "near ship" cannot be excluded. However, such elevated concentrations will be diluted below critical concentration within typical harbour water volumes. Due to their low lipophilicity, most DBP are not bioaccumulative and are thus not bioconcentrated in aquatic organisms entering the food chain. However, in the future these model-based calculations should be validated in local environments near or in ports by periodic monitoring and observation of biological parameters.

Risks to human health resulting from swimming and sea food consumption have been estimated to be very low, at least for the studied exposure scenario for ballast water treatment. Even in an unrealistic worst-case exposure scenario, e.g., swimming near a ship during ballast water discharge, no significant health effect has to be expected. Similar assessments are not available for discharges from other technical applications. However, it is estimated that exposure will never be higher than in this direct near ship environment. It can therefore be assumed that risks to human health resulting from disinfection process discharges would not be significant or would be low.

As bromoform is a highly volatile compound, it contributes to the transport of halogens into the atmosphere and therefore contributes to the reduction of tropospheric and stratospheric ozone. For the assessment of the contribution of industrial emissions to this process, not only bromoform emissions via effluents but also direct emissions to the atmosphere would have to be considered. It is so far not completely clear what the impact of anthropogenic bromoform emitted in form of disinfection by-products on the atmosphere will be.

The overall outcome of the assessment shows that globally there is no risk from anthropogenic DBP inputs for marine life and human health, even though local effects on aquatic organisms cannot be excluded. The impact on the atmosphere is difficult to quantify at the current stage.

It has to be stated there is a lack of data allowing for a more comprehensive analysis and risk/impact assessment. Although there are high quality studies on individual sites, e.g., cooling circuits of some nuclear power plants and rather abundant information of DBP generation in ballast water treatment resulting from data requirements for the authorization process, the overall picture is still very patchy as different compounds are typically analyzed. Whereas for ballast water 39 compounds are analyzed, many studies on cooling water provide data only on bromoform. Furthermore, uncertainties arise from the unavailable information, e.g., how much marine water is used for cooling purposes worldwide, and from unknown future developments, e.g., the increased installation of desalination plants or the relative amount of ballast water management systems using oxidants to be installed.

A future stronger impact on the marine environment is possible with the expected increase in the number of desalination plants, with additional wastewater management systems and further anti-fouling strategies. These developments should be followed and approvals like those for ballast water management systems should be introduced to control the risk in particular for the local marine environment when different sources of DBPs could add up.

Following research needs are identified:

1. More harmonized studies on the different industries are needed, i.e., analyses of all major DBPs identified in a least one of the sectors should be added to the test plans in the different sectors in order to allow a more systematic overview on DBP spectra in the different industries.
2. A systematic understanding of the drivers for DBP formation and their relative abundance would be desirable.
3. Concerning the risk assessment for aquatic organisms and human health, an elaborated approach has been established for ballast water treatment. This approach could serve as a reference for assessment schemes in the other industries.
4. A strengthening of international efforts in ocean science to build up a better database on concentrations of halogenated hydrocarbons in the marine environment is advised. More basic science on marine life is needed to identify the important biological pathways for the generation of halogenated hydrocarbons in different marine species and regions.
5. The impact on the atmosphere needs further consideration.

GESAMP could offer advice on international projects and could support harmonization of approaches. A future report on the status of research could identify emerging data offering more substantiated impact assessments.

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15 ANNEX – LIST OF DBP FOUND IN BWMS

Maximum concentrations, frequency and presence in GISIS of BWMS in μg/L

Substances	maximum	Count	GISIS	Comment
acetaldehyde	890	10	+	
aldehyde	4380	1	-	
benzoic acid	180	2	-	
bromate	2900	50	+	
bromide	1800	2	-	
bromoacetonitrile	16	3	-	
bromobenzene	89.6	5	-	
bromochloroacetic acid	510	66	+	
bromochloroacetonitrile	25	22	+	
bromochloromethane	28	5	-	
bromodichloroacetic acid	100	20	-	
bromodichloromethane	15	17	-	
chloral hydrate	79	17	+	
chloramine	20	1	-	
chlorate	8400	8	+	
chlorine dioxide	200	1	-	
chlorite	3600	1	-	
chloroacetonitrile	0.03	1	-	
chlorobenzene	3.1	4	-	
chlorodibromoacetic acid	5	3	-	
chlorodibromomethane	157	1	-	
chlorophenol (2)	0.016	2	-	
chlorophenol (3)	0.02	2	-	
chlorophenol (4)	0.03	3	-	
chloropicrin	18	24	+	
chlorotoluene (2)	0.34	1	-	
chlorotoluene (4)	0.28	1	-	
dalapon	101	14	+	
dibromoacetic acid	640	88	+	
dibromoacetonitrile	670	51	+	
dibromochloroacetic acid	52.5	42	+	
dibromochloromethane	410	83	+	

Substances	maximum	Count	GISIS	Comment
dibromo-3-chloropropane (1,2)	0	0	+	always < DL
dibromoethane (1,2)	3	1	-	
dibromomethane (1)	72	17	+	
dibromophenol (2,4)	0.06	2	-	
dibromophenol (2,6)	0.01	2	-	
dichloroacetic acid	300	48	+	
dichloroacetonitrile	12	27	+	
dichlorobromoacetic acid	36	22	+	
dichlorobromomethane	290	48	+	
dichloroethane (1,1)	0.34	2	+	
dichloroethane (1,2)	250	10	+	
dichloroethene (1,1)	0.2	2	-	
dichloroethene (cis-1,2)	0.2	1	-	
dichloroethene (cis-1,2)	0.26	1	-	
dichloroethene (trans-1,2)	1.9	3	-	
dichloromethane	15.8	10	+	
dichlorophenol (2,3)	0.02	2	-	
dichlorophenol (2,4)	0.13	1	-	
dichlorophenol (2,5)	1.94	2	-	
dichlorophenol (2,6)	0.03	2	-	
dichlorophenol (3,4)	0.07	1	-	
dichlorophenol (3,5)	0.03	1	-	
dichloropropane (1,2)	29.5	3	+	
dichloropropionic acid (2,2)	0.1	1	-	
diethylamine	110	2	-	
diethylaminobenzoic acid (p-N,N)	280	2	-	
fluoride	40	2	-	
formaldehyde	85	13	+	
isocyanuric acid	17000	6	+	
monobromoacetic acid	393	71	+	
monobromoacetonitrile	24	16	+	
monochloramine	490	6	+	
monochloroacetic acid	513	44	+	
monochloroacetonitrile	7	4	+	
naphthalene	0.21	1	-	
pentachlorophenol	4.68	2	-	
perchlorate	3.5	2	-	
sodium bisulfite	5000	1	-	
sodium hypochlorite			+	Active Substance
sodium sulfite	720	1	-	
sodium thiosulphate	5840	8	+	
Sulfate	310000	1	-	
Sulfite	280000	1	-	
tetrachloroethene	0.28	1	-	
tetrachloromethane	0.36	3	+	
tetrachlorophenol (2,3,4,5)	0.06	1	-	
tetrachlorophenol (2,3,4,6)	0.01	1	-	

Substances	maximum	Count	GISIS	Comment
tetrachlorophenol (2,3,5,6)	0.01	1	-	
thiosulfate	250000	2	-	
toluene	3.12	1	-	
tribromoacetic acid	970	61	+	
tribromoacetonitrile	11	3	-	
tribromobenzene (1,2,4)	1.05	1	-	
tribromoethane	1.4	1	-	
bromoform	1700	96	+	
tribromophenol (2,4,6)	6.3	12	+	
trichloroacetic acid	350	42	+	
trichloroacetonitrile	1.53	4	+	
trichlorobenzene (1,2,3)	9	3	-	
trichlorobenzene (1,2,4)	12	3	-	
trichloroethane (1,1,1)	0	0	+	always $<$ DL
trichloroethane (1,1,2)	0	0	+	always $<$ DL
trichloroethene	0	0	+	always $<$ DL
trichloromethane	440	51	+	
trichlorophenol (2,3,4)	0.418	2	-	
trichlorophenol (2,3,5)	0.03	1	-	
trichlorophenol (2,3,6)	0.03	2	-	
trichlorophenol (2,4,5)	0.03	1	-	
trichlorophenol (2,4,6)	0.503	2	-	
trichlorophenol (2,4,6)	0.1	1	-	
trichlorophenol (3,4,5)	0.09	1	-	
trichloropropane (1,2,3)	4.1	3	+	

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