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Chlorination by-products in power station cooling waters

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Chlorination by-products in power station cooling water

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1 Introduction

Chlorine was first employed as a disinfectant at a drinking water treatment plant in Hamburg (Germany) in 1893. It is still extensively used as a powerful oxidising agent for bleaching and various water treatments including taste and odour control, disinfection of tap water and waste water, in the food industry and for biofouling control. Of all disinfectants it is the most extensively studied with regard to chemistry, toxicity and ecotoxicity (White, 1999; Jolley, 1976; Jolley *et al.*, 1978, 1980, 1983, 1985, 1990). Due to its well-tried technology, its long-term worldwide industrial use and its acceptable cost, chlorine remains the most common antifouling treatment throughout the world.

The chemistry of chlorine disinfection of natural waters is complex, particularly when applied to marine (saline) waters which are normally used for cooling at coastal power stations.

In solution, chlorine produces a mixture of hypochlorous acid and hypochlorite ion. In seawater this rapidly reacts with the bromide ion (present at 68 mg l^{-1} in full seawater) oxidising bromide to bromine and forming a mixture of hypobromous acid and hypobromite. With the exception of some low salinity estuarine and brackish waters most of the subsequent chemistry is bromine based. However, if ammonia levels are high there can be a competing reaction to form a variety of chloramines and bromamines. The disinfecting action in 'chlorinated' seawater will be expressed through a complex mixture of halogenated compounds comprising principally hypobromous acid and monobromamine (Khalanski and Jenner, 2011). To be effective a disinfectant must be highly reactive and efficient against a wide range of organic materials. Any residual oxidation capacity will be utilised in reaction with the dissolved (and particulate) organic matter present in all natural waters, e.g. humic and fulvic acids. The acute oxidants formed by chlorination are therefore (by definition) short-lived toxic compounds and are not persistent in natural waters. The major environmental concern of chlorination is the production of numerous more persistent compounds formed by complex reactions between chlorine (bromine) and mineral or organic constituents of natural waters collectively described as chlorination by-products (CBPs). Relatively little is known of the reaction kinetics, but there is a strong indication that CBP formation is not linearly related to initial hypochlorite and/or final total residual oxidant (TRO) concentrations. In seawater, CBPs will be mainly brominated compounds due to the abundance of bromide. Chlorinated by-products, at initial dosing concentrations of about 2 mg l^{-1} as chlorine, are not expected to be formed in appreciable amounts in seawater (Taylor, 2006). A summary of the main chemical pathways is given in Figure 1.

Many CBPs are persistent and have been proved or suspected to be toxic, mutagenic or carcinogenic for animals and humans when subject to long-term exposure. As a consequence, guidelines have been established by the World Health Organisation for CBPs in drinking water (WHO, 1993), and limit values for these substances have been implemented in national regulations. In contrast, there is no international consensus on the regulation of chlorine used to control biofouling in cooling water systems. There has been a plethora of local regulation (and in some cases outright prohibition), though implementation of the Water Framework Directive (2000/60/EC) is introducing a measure of consistency in Europe. Whilst the environmental aspects of the chlorination of freshwater are relatively well understood, it became evident during the mid-1970s that we lacked knowledge on the chemistry of the chlorination of seawater, and on the effects of the discharges of chlorinated seawater on marine biota (Block *et al.*, 1977). This led to many research initiatives during the 1980s and 1990s.

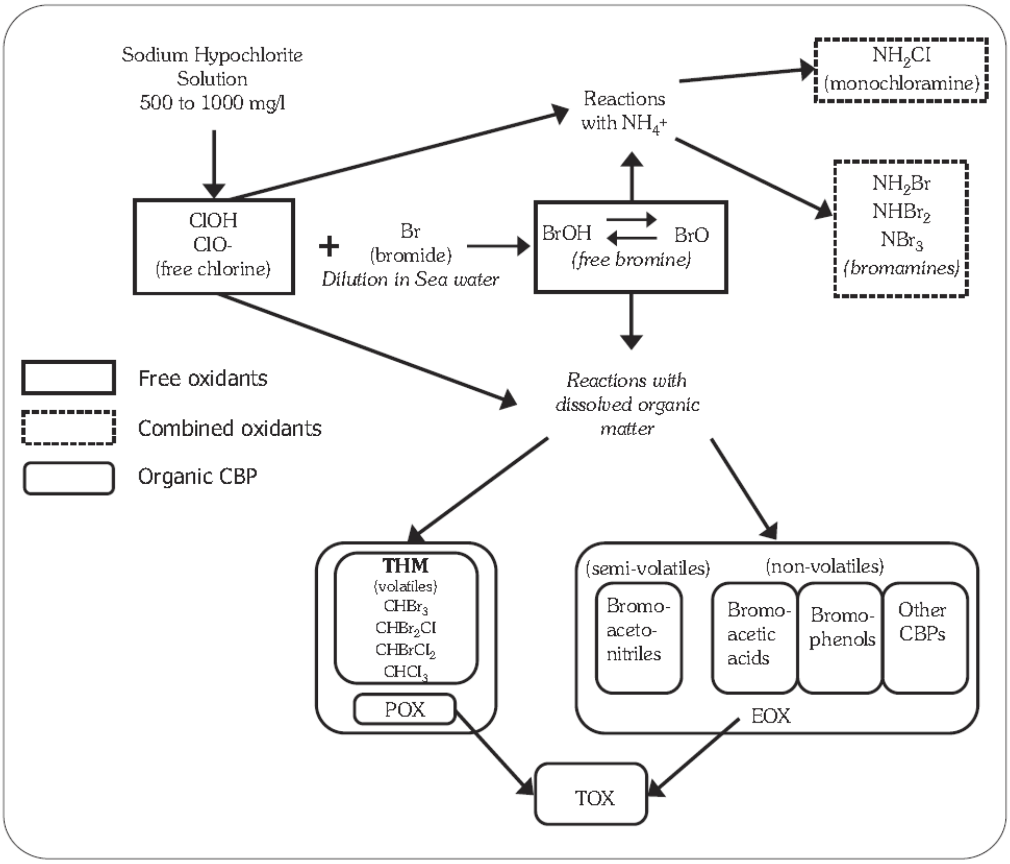

Figure 1 Outline of chlorine and bromine chemistry (from Khalanski, 2002)

2 Natural brominated compounds in seawater

It is important to recognize that CBPs, including many brominated compounds, are not exclusively of anthropogenic origin. They may be formed photo-catalytically in the atmosphere, but the main source in nature is their production by organisms which use them as part of their natural defence mechanism against attack by micro-organisms and predators.

Marine and terrestrial organisms contain haloperoxidases that halogenate organic compounds in the presence of chloride, bromide or iodide ions (Gribble, 1994). In seawater, bromoform, other trihalomethanes (THMs) and non-volatile compounds such as bromophenols are produced by benthic and planktonic algae.

Typical levels for bromoform in seawater are given in Table 1.

Table 1 Mean concentrations of bromoform in the North Sea and North Atlantic (Fogelqvist and Krysell, 1991)

Location	Bromoform (ng l^{-1})	No. of samples
North Atlantic	1.4 ± 0.85	27
Northern North Sea	2.4 ± 1.4	7
Whole North Sea	8.4 ± 7.7	12
English Channel	10.1 ± 5.9	16

Somewhat higher concentrations have been reported by other studies. The concentration of bromoform reached 50 ng l^{-1} (0.05 µg l^{-1}) in February 1989 in the southern part of the North Sea (Nightingale, 1991). Such relatively high levels of bromoform from natural sources have also been measured in the English Channel: for example, 82.4 ng l^{-1} in a ‘non-polluted’ site (Connan *et al.*, 1996). Maximum concentrations in the coastal zone are found very close to macroalgae beds. On Great Cumbrae in the Firth of Clyde, Nightingale, Malin and Liss (1995) measured bromoform in the range of 170 to 460 ng l^{-1} (0.17–0.46 µg l^{-1}), though the relative proximity of the Hunterston power stations may have influenced this result.

A KEMA study reported that microalgae had natural production rates up to 500 ng g^{-1} dry wt, and a remarkable 50 µg l^{-1} was found at kelp beds in Norwegian fjords (Jenner and Mensink, 1993). From measurements of the biomass of benthic brown algae, the natural production of bromoform on the Brittany coast in France was estimated at about 371 tonnes yr^{-1} (Khalanski & Allonier, 1998; Allonier, 2000). On this basis, the natural production of bromoform in the English Channel is probably between a few hundred and several thousand tonnes per year.

To place this into context, a single EPR with a cooling water flow of 60 cumec, chlorinating for six months of the year and with 20 µg l^{-1} bromoform in the discharge, will release ~19 tonnes yr^{-1}.

KEMA has estimated that worldwide electricity generation could release up to 5.2 x 10^{4} tonnes yr^{-1}, which represents approximately 2.5–5% of the total natural (oceanic) bromoform production. (Unpublished data, 2011). Pathways for the natural formation of CBPs are summarized in Figure 2.

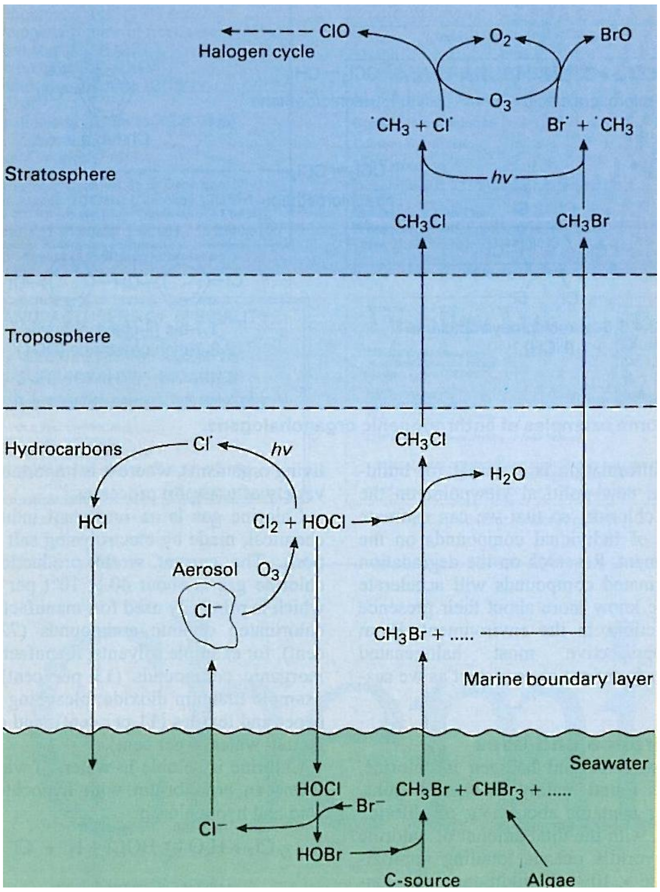

Figure 2 Halogen cycle in the marine environment (from Hoekstra and De Leer, 1995)

3 Chlorination by-products

The chemical action of all chlorine produced oxidants can be illustrated by considering the behaviour of chlorine. (Cotton and Wilkinson, 1972; White, 1999):

$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$

Depending on the pH value, perchloric acid partly dissociates to hypochlorite ions:
$Cl_2 + 2H_2O \leftrightarrow HOCl + H_3O + Cl^-$
$HOCl + H_2O \leftrightarrow H_3O^+ + OCl^-$

hypochlorite ions are themselves unstable
$OCl^- \rightarrow Cl^- + \text{'O'}$

Bromine, hypobromous acid, etc, will behave in a similar manner .

The disinfecting properties of chlorine in water are based on the oxidising power of the free oxygen atoms and on chlorine substitution reactions. The hypochlorite ion is a relatively poor disinfectant as its negative charge inhibits passage through the cell wall of organisms. A high proportion of the chlorine produced oxidant is used in oxidation of organic matter by the oxygen radicals, ultimately to CO_2 (carbonate, bicarbonate in aqueous systems). Intermediates such as aldehydes, carboxylic and aryl acids have been detected in freshwater systems, but the potential environmental risk comes from the production of chlorinated (or other halogenated) derivatives.

Chemical species generated by reactions of oxidation, addition and substitution with organic matters are called chlorination by-products. When applied to chlorination of saline waters, this term refers to a huge number of both chlorinated and brominated compounds. Among them several categories have been identified and quantitatively measured in low-level chlorinated cooling water from coastal power stations (Jenner *et al.*, 1997; Allonier *et al.*, 1999; Allonier, 2000; Taylor, 2006).

The chlorination of seawater, where brominated compounds predominate, probably represents a greater risk from by-product formation than chlorination in freshwater. The environmental properties and toxicity of brominated species is similar to their chlorinated equivalents, but the brominated oxidants are more reactive and have been observed to yield somewhat elevated levels of by-products, notably trihalomethanes, but also haloacetic acids (RAR, 2007).

Among the great number of brominated and chlorinated chemical species that could be formed in chlorinated seawater, the four major groups in terms of detection frequency and quantity are (Allonier, 2000):

- trihalomethanes
- haloacetic acids
- haloacetonitriles
- halophenols

Trihalomethanes: chlorine and bromine react with many organic substrates (phenolic compounds, aromatic acids, ketones) to produce chlorinated and brominated methane (Doré, 1989): chloroform, $CHCl_3$; bromodichloromethane (BDCM), $CHBrCl_2$; chlorodibromomethane (CDBM), $CHBr_2Cl$; and bromoform, $CHBr_3$. A significant consumer of TRO which goes to produce THMs will be the resorcinol structures that make up a large part of humic materials. All THMs are more or less volatile.

Haloacetic acids are, with the THMs, amongst the most frequently found CBPs in chlorinated waters (Miltner *et al.*, 1990). They are formed not only by reaction of TRO with organic compounds, but also by hydrolysis of haloacetonitriles. In chlorinated seawater two brominated acetic acids have been frequently identified: monobromoacetic acid (MBAA), $BrCH_2COOH$; and dibromoacetic acid (DBAA), $Br_2CHCOOH$. They are non-volatile.

Haloacetonitriles (HANs) are formed by oxidation of amino acids and the weak nitrogen bonds in protein chains (Doré, 1989). In chlorinated seawater, dibromoacetonitrile (DBAN), Br_2CHCN, is most commonly found (Jenner *et al.*, 1997). They are semi-volatile.

Halophenols: 2,4,6-tribromophenol (TBP) is the most commonly encountered, though dibromophenol (DBP) is occasionally reported. Halophenols are potentially unstable in cooling water plumes. Humic materials are broken down by chlorine to dihydroxyphenols which are then halogenated. In the presence of TRO halogenated phenols are further oxidised to quinones which will then be cleaved to CO_2 and haloforms. They are non-volatile

Bromate (BrO_3^-) may also be present, but it has often been ignored, probably because of the poor sensitivity of the classical analytical methods in the presence of high chloride matrix (detection limit = 5 mg l^{-1} as BrO_3^-) Recently IC-ICP-MS methods have been developed with detection limits of 2–3 µg l^{-1}, allowing detection of traces of bromate in seawater (Chen *et al.*, 2007). It is thought that bromate is formed mainly in the hypochlorite storage tanks.

A list of the CBPs most commonly analysed in seawater is given in Table 2.

Table 2 CBPs identified in chlorinated seawater (and in freshwaters at high bromide concentration) (Allonier, 2000)

Organohalogenated compounds	**Chemical formula**	**References**
Trihalomethanes		
Chloroform	$CHCl_3$	Heller-Grosmann *et al.* (1993)
Bromodichloromethane (BDCM)	$CHCl_2Br$	Heller-Grosmann *et al.* (1993)
Dibromochloromethane (DBCM)	$CHBr_2Cl$	Fayard and Iqbal (1987); Heller-Grosmann *et al.* (1993)
Bromoform	$CHBr_3$	Carpenter *et al.* (1981); Fayard and Iqbal (1987); Heller-Grosmann *et al.* (1993)
Haloacetonitriles		
Dibromoacetonitrile (DBAN)	Br_2CHCN	Jenner *et al.* (1997)
Haloacetic acids		
Monochloroacetic acid (MCAA)	$ClCH_2COOH$	Peters *et al.* (1991)
Dichloroacetic acid (DCAA)	$Cl_2CHCOOH$	Peters *et al.* (1991); Heller-Grosmann *et al.* (1993)
Trichloroacetic acid (TCAA)	Cl_3CCOOH	Peters *et al.* (1991); Heller-Grosmann *et al.* (1993); Kristiansen *et al.* (1996)
Monobromoacetic acid (MBAA)	$BrCH_2COOH$	Peters *et al.* (1991)
Dibromoacetic acid (DBAA)	$Br_2CHCOOH$	Peters *et al.* (1991); Heller-Grosmann *et al.* (1993); Kristiansen *et al.* (1996)
Bromochloroacetic acid (BCAA)	$BrClCHCOOH$	Peters *et al.* (1991); Heller-Grosmann *et al.* (1993)
Halophenols		
2,4,6-Tribromophenol (TBP)	2,4,6-$Br_3C_6H_2OH$	Bean *et al.* (1978, 1983); Jenner *et al.* (1997)
2,4-Dibromophenol (DBP)	2,4-$Br_2C_6H_3OH$	Bean *et al.* (1978, 1983); Jenner *et al.* (1997)
Bromophenol	BrC_6H_4OH	Bean *et al.* (1983)
Others		
2-Bromocyclohexanol	$BrC_6H_{10}OH$	Fayard & Iqbal (1987)
1,2-Dibromocyclohexanol	$Br_2C_6H_9OH$	Fayard & Iqbal (1987)
Bromate ion	BrO_3^-	Macalady *et al.* (1977)

The bulk of the CBPs detected in cooling water are represented by this subset of compounds (Jenner *et al.*, 1997, Khalanski, 2002):

- bromoform
- bromodichloromethane (BDCM)
- chlorodibromomethane (CDBM)
- monobromoacetic acid (MBAA)
- dibromoacetic acid (DBAA)
- dibromoacetonitrile (DBAN)
- 2,4,6-tribromophenol (2,4,6-TBP)

4 Formation of CBPs in power station cooling water

The majority of the oxidant added to cooling water is ultimately used in the formation of CO_2. The different CBPs are produced in the following quantitative sequence, as expressed in Table 3:

Haloforms > other THMs > haloacetic acids > halonitriles > halophenols.

Table 3 Utilization of chlorine by marine cooling water (Bean *et al.*, 1978)

Reaction	**% of TRO consumed**
Organic antifouling oxidation to CO_2	50–80
Non-haloform organic halogens (THM precursors)	1–6
Haloforms	0.5–5
Haloacetonitriles	0–5
Halophenols	~0.1

In a long-term study by EDF on three coastal nuclear power stations, chloroform was intermittently detected. There was no correlation with either chlorine dosage or bromoform concentration, and it is surmised that the origin of the chloroform is the hypochlorite solution or natural production, rather than formation in the cooling water.

The formation of CBPs is influenced by the chlorine dose, water quality and local environmental conditions. Levels of the dominant CBPs, bromoform and DBAN, for a range of power stations with differing dose rates and at different seasons are shown in Table 4. The overall bromoform formation is c.16 $\mu g\ l^{-1}$ and is c.1.5 $\mu g\ l^{-1}$ for DBAN.

Table 4 Bromoform and DBAN at the power station outfalls

Power station	**Period/ date**	**No. of samples**	**NaOCl dosage (mg l^{-1} as Cl_2)**	**Bromoform (µg l^{-1})**	**DBAN (µg l^{-1})**
Heysham (UK)	11/08/92–15/12/92	5	0.5–1.0	29.20 ± 24.25	3.15 ± 3.59 (4 samples)
	12/01/93–07/09/93	4	0.5–1.0	23.00 ± 8.24	2.12 ± 1.08
	22/11/93–23/11/93	9	9.4	0.72	
Dungeness (UK)	03/08/93	1	0.75–1.0	5.75	0.20
Wylfa (UK)	21/09/93	1 1	0.3–0.4	27.50 27.00	0.87 0.79
Bradwell (UK)	19/10/93	1	0.6–1.0	25.00	0.87
Hartlepool (UK)	17/08/93	1	0.5–1.0	3.50	<0.1
Sizewell (UK)	23/08/93	1	0.6–1.0	14.50	<0.1
Paluel (FR)	14/10/92	1 1	0.37 0.82	3.10 9.65	0.10 1.05
Penly (FR)	27/05/93–18/08/93	11	0.62 ± 0.10	13.37 ± 4.17	NA
	21/06/94–27/07/94	18	0.50 ± 0.08	15.01 ± 3.22	NA
Gravelines (FR)	13/04/93–18/04/93	3	0.64	6.37 ± 4.62	NA
	03/05/93–25/10/93	26	0.80	18.63 ± 3.70	NA
Maasvlakte (NL)	02/07/92–22/10/92	16	0.8–1.5	11.54 ± 5.40 10 samples	0.83 ± 0.56 6 samples
	16/05/93–10/08/93	10	0.8–1.5	8.35 ± 12.35 7 samples	0.94 ± 1.22 3 samples
AVERAGE				**16.32 ± 2.10**	**1.48 ± 0.56**

All data are averages of duplicate samples. NA = not available.

5 Occurrence and distribution of CBPs

During the early 1990s the production of CBPs and comparison of the range of compounds produced under conditions of chlorination was examined during several studies at power stations in France, the Netherlands and the United Kingdom. The key study was undertaken by KEMA, in co-operation with Akzo Nobel, EDF, British Energy and the Dutch power generation companies, at Gravelines, Maasvlakte, and Heysham II power stations. Both EDF and British Energy performed separate studies at, respectively, Gravelines, Paluel and Penly power stations and Wylfa, Heysham and Sizewell power stations. This section provides an overview of the key results obtained, with results from the different studies combined in the tables (Jenner *et al*., 1997; Taylor, 2006).

5.1 Trihalomethanes

The field data confirmed that the THM produced in the largest quantity was bromoform, with mean concentrations of 25.16 µg l^{-1} at Heysham (UK), 11.4 µg l^{-1} at Maasvlakte (NL) and 18.6 µg l^{-1} at Gravelines (NL). To compensate for differing chlorine dose rates the yield of CBPs was expressed as a ratio to bromoform. The ratio (BDCM+DBCM):bromoform, calculated on mean values, is about 3% at Heysham and Gravelines and 7% at Maasvlakte (Table 5). Bromoform represents 93–97% of the total THMs. Chloroform was below the detection limit (0.1 µg l^{-1}) at all marine power stations during this study.

Table 5 Mean concentration of THMs measured on the chlorinated cooling water at three European marine power stations and ratio to bromoform (Jenner *et al.*, 1997)

	µg l^{-1}	**µg l^{-1}**		**(BDCM+DBCM):bromoform**	
Power station	**Samples (n)**	**Bromoform**	**BDCM+DBCM**	**Ratio**	**%**
Heysham 2	14	25.16	0.7	0.03	2.78
Maasvlakte	17	11.4	0.8	0.07	7.02
Gravelines	26	18.23	0.6	0.03	3.29

5.2 Haloacetonitriles

In this group, the only HAN measured above the detection limit was dibromoacetonitrile. The ratio DBAN:bromoform, calculated on the mean values, is in the range of 9-11% at Heysham II and 7-11% at Maasvlakte (Table 6). The ratio calculated on the mean values of all the samples is 8.57%

Table 6 Mean concentration of DBAN measured on chlorinated cooling water at three European marine power stations and ratio to bromoform (Jenner *et al.*, 1997)

		µg l^{-1}	**µg l^{-1}**	**DBAN:bromoform**	
Power station	**Samples (n)**	**Bromoform**	**DBAN µg l^{-1}**	**Ratio**	**%**
Heysham 2 (UK)	5	29.20	3.15	0.11	10.79
	9	23.00	2.12	0.09	9.22
Maasvlakte (NL)	10	11.54	0.83	0.07	7.19
	7	8.35	0.94	0.11	11.26
Other studies					
Dungeness (UK)	1	5.75	0.20	0.03	3.48
Wylfa (UK)	2	27.25	0.83	0.03	3.04
Bradwell (UK)	1	25.00	0.87	0.03	3.48
Paluel (F)	1	3.1	0.10	0.03	3.23
	1	9.65	1.05	0.11	10.88

5.3 Halophenols

The most common halophenol measured above the detection limit (46% of all samples) was 2,4,6-tribromophenol. The mean concentration was 0.26 µg l^{-1} at Heysham and 0.29 µg l^{-1} at Maasvlakte (Table 7) (2,4-dibromophenol was also detected infrequently with a maximum concentration of 0.055 µg l^{-1}, at Dungeness).

Table 7 Mean concentration of TBP measured on the chlorinated cooling water at three European marine power stations and ratio to bromoform (Jenner *et al.*, 1997)

	µg l^{-1}	**µg l^{-1}**	**TBP:bromoform**	
Power station	**Bromoform**	**2,4,6-TBP**	**Ratio**	**%**
Heysham 2 (UK)	25.16 (n=14)	0.26 (n=9)	0.01	1.03
Maasvlakte (NL)	11.4 (n=17)	0.29 (n=9)	0.03	2.54
Other study				
Paluel (F)	9.65 (n=1)	0.12 (n=1)	0.01	1.24

n = number of samples

5.4 Summary

The results from these surveys showed that at the point of discharge bromoform concentrations varied from 53.45 µg l^{-1} (Heysham) to 3.1 µg l^{-1} (Paluel) and dibromoacetonitrile concentrations from 11.39 µg l^{-1} (Heysham) to 0.1 µg l^{-1} (Paluel). Other compounds detected in the discharge were bromodichloromethane and dibromochloromethane, with concentrations of 0.8 and 0.7 µg l^{-1}, respectively, at Maasvlakte and Heysham; 2,4,6-tribromophenol at 0.26µg l^{-1} (Heysham) and 0.29 µg l^{-1} (Maasvlakte); and 2,4-dibromophenol at 0.055 µg l^{-1} (Dungeness). The variations in CBP concentrations among the different stations is believed to be caused mainly by differences in the water quality of the intake.

6 Seasonality and impacts of temperature

In the United Kingdom, chlorination is normally only undertaken when the risk of fouling is greatest, typically during late spring through to autumn. Even during this restricted period, water temperatures can vary significantly and this may be expected to influence the kinetics of CBP formation and survival.

Little information has been found on seasonal variation in temperate climates. Some limited data are presented in Table 11 of this report that may indicate higher levels of accumulation in mussels and periwinkles in summer.

7 Environmental decay of CBPs

Bromoform is persistent in natural waters, with anaerobic degradation the probable degradation pathway. The main process for elimination from water is volatilisation. A simple model for estimating volatilisation of bromoform (and other THMs) from seawater is that of Helz and Hsu (1978):

$C_t = C_0 * \exp(-k_1 * t/L)$ half life (hrs) = $\ln(0.5) * (L/-k)$

where C_t = concentration at time t; C_0 = initial concentration; L = water depth in centimetres; k = transfer coefficient in centimetres per hour; t = time in hours.

Taylor (2006) has given decay constants and half lives for bromoform, DBCM, DCBM and DBAN (see Table 8).

Table 8 Decay constants and half lives for bromoform, DBCM, DCBM and DBAN (Taylor, 2006)

		Bromoform	**DBCM**	**DCBM**	**DBAN**
Total loss	1st order rate constant hr^{-1}	0.027	0.040	0.08	0.05
	half life (hr)	26	17	9	14
Net volatalisation loss	first order rate constant hr^{-1}	0.024	0.031		
	half life (hr)	28	22		

Measurements in the discharge plume from Heysham Power Station showed reasonable agreement between measured concentrations of bromoform and concentrations calculated according to the dilution rate of the cooling water based on water temperature (ie, using temperature as a conservative tracer).

The following equation was derived:

$CHBr_3 = 12.30e^{-0.002D}$

where D is the distance from the outfall in metres (R^2 of 0.87).

This implies that bromoform is relatively stable in the environment. Similar behaviour can be expected for many other CBPs, though halophenols appear to be unstable in the presence of excess TRO and will decay to haloforms.

8 Toxicity of CBPs to fish and other biota

Eco-toxicity will be dependent on a number of independent factors including abundance, stability, volatility and their hydrophilic or lyophilic properties. Ecotoxicity should be divided between acute toxicity (eg, chlorine produced oxidants) and chronic toxicity (eg, certain CBPs).

Bioaccumulation in aquatic organisms and biomagnification in food chains both affect chronic toxicity, and depend on the ability of an organic substance to accumulate in fats. Water solubility and the octanol:water partition coefficient (K_{ow}) are the basic chemical characteristics most appropriate when evaluating bioaccumulation potential. (See Table 9.)

Table 9 Physico-chemical properties associated with bioaccumulation processes of the major CBPs

	Half life† (days)	**Volatility**	**Log K_{ow}**	**Water solubility (g l^{-1})**	**Log BCF**
Bromoform	3.5	volatile	2.27–2.67	0.86–5.0	1.48–1.57
DBCM	2.12	volatile	2.23–2.24	2.26–4.4	1.74–1.36
BDCM	1.62	volatile	1.88–2.10	2.9–4.7	1.25–1.47
DBAA	300	non-volatile	1.22	25.7	0.57
DBAN	3.5	semi-volatile	1.06	59.2	0.45
TBP	few days*	non-volatile	3.92–4.02	0.01–0.07	2.69–2.78

†Half lives are for the top 5 m of water column; K_{ow} = octanol:water partition coefficient;
BCF = bioconcentration factor, based on the quantitative structure activity relationship (QSAR); *More rapid in the presence of excess TRO.

Haloacetic compounds (DBAA and DBAN) are water soluble, with low octanol:water partition coefficients. THMs are relatively water soluble and their log K_{ow} remain low. For these compounds, the bioconcentration factor should be in the range of 2 to 50. TBP appears more susceptible for bioaccumulation, but the QSAR evaluation leads to a BCF of only 600. A bioconcentration factor as low as 1.4 in ‘edible portions of all aquatic organisms consumed by Americans’ is reported for 2,4,6-TBP (Grove *et al.*, 1985).

Experimental work by Gibson *et al.* (1980) indicated a BCF of between 1 and 4 except for shrimps, where the BCF was >8. (Table 10).

Table 10 Bioconcentration of bromoform after exposure of marine invertebrates and fish for 28 days (Gibson *et al.*, 1980)

	Water concentration (mg l^{-1})	**Body burden after 28 days (µg g^{-1} wet wt)**	**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 0.09–0.21	0–1 2.6–2.8 0.1–0.21
Prothotaca 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

BCF = *bioconcen*tration factor

Field data collected on mussels, periwinkle and mullet at Gavelines Power Station in 1981 showed a BCF for bromoform between 1 and 3 (Table 11). This fits well with the results of Gibson (Table 10).

The depuration of bromoform from mussels was complete in two days after the cessation of chlorination, confirming the low BCF of bromoform in marine invertebrates and fish.

Table 11 Measurements of bromoform in molluscs and fish flesh collected during the chlorination period at Gravelines Power Station

	Sampling site			
	Outlet canal		**Dyke**	
Date	**Mussels** **_Mytilus edulis_** **(µg kg^{-1} wet wt)**	**Periwinkle** **_Littorina littorea_** **(µg kg^{-1} wet wt)**	**Fish (Mullet)** **_Mugil cephalus_** **(µg kg^{-1} wet wt.)**	**Mussels** **_Mytilus edulis_** **(µg kg^{-1} wet wt)**
23/04/81	19.80			0.00
06/08/01	36.50	41.00		7.50
10/09/81			27.00	
10/09/81			18.00	
10/09/81			30.00	
19/10/81	5.40	6.20		4.50
13/11/81	14.70			
19/11/81	6.50			0.70
20/11/81	1.00			
21/11/81	0.00			
22/11/81	0.00			
Bromoform in water		15–20 µg l^{-1}		4 µg l^{-1}
BCF		2–3		1–2

There are limited data on the toxicity of THMs to marine biota. Table 12 summarises available aquatic toxicity data. The results in Table 12 show clearly that toxicity within 96 hours is three orders of magnitude above levels encountered in power station discharges.

The biological effects of long-term exposure of sea bass, *Dicentrarchus labrax*, to CBPs were studied in relation to power station cooling water chlorination (Jenner *et al.*, 1997; Taylor, 2006). Parameters considered of interest were bioconcentrations of CBPs in fat and muscles and liver histology. CBPs measured were THMs, dibromoacetonitrile, dichloroacetonitrile and total organohalogens (TOX as Cl kg^{-1} fat). Liver pathology was performed with light microscopy for abnormalities, necrosis and signs of pre-neoplastic lesions. Commercially cultured fish in the chlorinated effluent of Gravelines Power Station were used as the exposed group. Comparable cultured fish from farms on the Spanish and French coast were used as controls. Wild sea bass from sites considered uncontaminated on the Atlantic coast of Spain and wild fish from the cooling water plume of Gravelines Power Station were used as reference.

Table 12 Published data on the THM toxicity (EC50 = effect concentration 50%, and LC50 = lethal concentration 50%) to aquatic biota (Allonier, 2000)

Species, biological stage	**Compound**	**Toxicity (mg l^{-1})**	**Reference**
Vibrio fisheri Marine bacteria	Chloroform	5 min EC50 = 2,464	Kaiser & Devillers (1994)
Skeletonema costatum Marine diatom alga	Bromoform	96-hr EC50 = 11.5–12.3	EPA (1980)
Selenastrum capricornutum Freshwater alga	Bromoform	96-hr EC50 = 112–116	EPA (1980)
Daphnia magna	Chloroform	48-hr LC50 = 29	Le Blanc (1980)
Freshwater crustacean	Bromoform	48-hr LC50 = 46	
	Bromoform	48-hr LC50 = 46.5	EPA (1980)
Daphnia pulex Freshwater crustacean	Bromoform	96-hr LC50 = 44	Trabalka *et al.* (1980)
Mysidopsis bahia Marine Mysid shrimp	Bromoform	96-hr LC50 = 24.4	EPA (1980)
Micropterus salmoides	Chloroform	96-hr LC50= 45–56	Anderson & Lusty (1980)
Salmo gairdneri		96-hr LC50= 15–22	
Ictalurus punctatus		96-hr LC50= 75	
Lepomis macrochirus		96-hr LC50= 13–22	
Lepomis macrochirus Freshwater fish	Bromoform	96-hr LC50 = 29	Buccafusco *et al*. (1981)
Cyprinus carpio	Chloroform	96-hr LC50 = 161	Trabalka *et al*. (1980)
Carp embryos	BDCM	96-hr LC50 = 119	
	DBCM	96-hr LC50 = 53	
	Bromoform	96-hr LC50 = 76	
	Chloroform	96-hr LC50 = 97	Mattice *et al*. (1981)
	BDCM	96-hr LC50 = 67	
	DBCM	96-hr LC50 = 34	
	Bromoform	96-hr LC50 = 52	
Cyprinodon variegatus Saltwater fish	Bromoform	96-hr LC50 = 17.9 Embryo-larval: Chronic value = 6.4	EPA (1980)
Crassostrea virginica Oyster larvae	Bromoform	24-hr LC50 = 1	Stewart *et al*. (1979)

Results of this study indicate that long-term exposure to CBPs does not impose an ecotoxicological risk on sea bass in chlorinated water within the concentration range used for anti-fouling control. Extensive histopathological study did not show any signs of liver tissue damage that could be attributed to CBP exposure. The THM bromoform was found in relatively high concentrations in cultured sea bass fat, up to 1.7 mg kg^{-1} (ie, a *bioconcen*tration factor of 70 to 160). Bromoform rapidly disappeared from the fat after chlorination was stopped, with concentrations below detection level (<3 µg kg^{-1} fat). Muscle tissue did not show any bioconcentration of bromoform. Other CBPs found frequently in the fat were dibromo- and dichloroacetonitrile. TOX levels in fish fat were not positively correlated with CBP exposure. On the contrary, when CBP levels were high (summer), TOX levels were relatively low. TOX levels in wild fish from uncontaminated water were comparable to those in fish from chlorinated water. It can be concluded that for sea bass, and probably for most fish species, survival rates of all fish live stages are comparable in chlorinated and non-chlorinated water. Long-term exposure to CBPs produced by low-level chlorination (1–2 mg l^{-1} TRO) did not impose ecotoxicological stress. Also, it is reported that fish can detect low levels of chlorine and may actively avoid areas with higher chlorine concentrations (Gammon, 1971). Such behaviour would help limit the exposure of fish to CBPs. Several researchers have noted that fish can live in areas where the total residual chlorine concentrations are supposedly lethal to fish. Minnows exposed to 0.12 mg l^{-1} chlorine were able to tolerate a ‘lethal’ dose three to four times longer than fish from chlorine-free water (Stewart *et al.*, 1996; Lotts and Stewart, 1995). However, these findings have not always been confirmed in later studies. Cook and Schreer (2001) conclude that the combination of chlorine residuals and temperature up to the thermal maximum of a given freshwater fish species will enhance the toxic effect by chlorine.

Published data show a much lower toxicity on aquatic biota for THMs than for oxidizing compounds However, results of Stewart *et al.* (1979) show a relatively high sensitivity of oyster larvae to bromoform.

An EDF R&D programme on CBPs used the common Microtox© toxicity test on a marine bacteria – an inhibition bioassay on marine algae and the most sensitive ecotoxicological bioassay – to compare the toxicity of the major CBPs (Table 13):

- cytotoxicity test on cultured bivalve cells (gill of the marine clam *Ruditapes decussatus*); bivalve cell viability is assessed by using the MTT reduction method (Allonier, 2000)
- embryo-larval bioassay on sea urchin *Paracentrotus lividus* (His *et al.*, 1999)
- embryo-larval bioassay on oyster larvae *C. gigas* (His *et al.*, 1999)

Table 13 LOEC and NOEC (mg l^{-1}) data for CBP toxicity on marine organisms

Compound	**Clam gill (1)**	**Urchin (2)**	**Oyster (3)**	**Algae (4)**	**Bacteria (5)**
Bromoform	LOEC: 1.00 NOEC: 0.50	LOEC: 2.50 NOEC: 1.00	LOEC: 1.80 NOEC: 1.00		LOEC: 5.12 NOEC: 3.41
DBCM		LOEC: 5.00 NOEC: 2.50			LOEC: 47.41 NOEC: 31.60
CDBM		LOEC: 5.00 NOEC: 2.50			LOEC:> 250 NOEC:> 250
Monobromo-acetic acid					LOEC: 10.28 NOEC: 6.85
DBAA	LOEC: 1.00 NOEC: 0.50	LOEC: 5.00 NOEC: 2.50	LOEC: 24.0 NOEC: 18.0	LOEC: 26.2 NOEC: 18.1	
DBAN	LOEC: 1.00 NOEC: 0.50	LOEC: 0.10 NOEC: 0.05			LOEC: 2.39 NOEC:1.00
2,4,6-tribromo-phenol		LOEC: 2.50 NOEC: 1.00			LOEC: 2.25 NOEC:< 2.25
Sodium bromate			LOEC: > 7.5 NOEC: 7.5	LOEC: >80 NOEC: 80	
Chloroform		LOEC:>10 NOEC:>10			

(1) Cytotoxicity on gill cells of the marine clam *R. decussatus*; (2) Embryo-larval toxicity on sea urchin *P. lividus*; (3) Embryo-larval toxicity on oyster *C. gigas*; (4) Growth inhibition of the marine diatom *Pheodactylum tricornutum*; (5) Microtox© Bioassay 15 min (Khalanski, 2002). LOEC: lowest observable effect concentration; NOEC: no observed effect concentration.

9 Summary and Conclusions

- There is no published European quality standard for bromoform or for any of the other commonly encountered CBPs. The only relevant statutory environmental quality standard (EQS) appears to be that for chloroform. Under the Water Framework Directive chloroform is characterized as a priority substance with an EQS of 2.5 µg l^{-1} expressed as an annual average (Defra, 2009). In the Netherlands an interim bromoform standard is applied in the Rotterdam area of 16 µg l^{-1} expressed as a 24-hr average over the full water column at 1,000 m from a discharge.
- The evidence available up to 1995 suggests that the concentrations of THM in the discharges from a wide variety of power stations and industries in Europe are of the order of 10^{-3} of the EC50 and LC50 data from published results. This implies that in the marine environment there is no acute toxic effect expected from these compounds.
- Dominant CBPs: Only bromoform and dibromoacetonitrile were found in all chlorinated cooling water effluents at concentrations significantly higher than the detection limits
- Range in effluent bromoform concentrations: Highest at Heysham, with mean of 25.16 µg l^{-1}. Lowest at Dungeness and Hartlepool: 5.75 µg l^{-1} and 3.5 µg l^{-1}, respectively. Mean at Maasvlakte was 11.4 µg l^{-1}, and at Penly and Gravelines 14.2 µg l^{-1} and 16.7 µg l^{-1}, respectively.
- Seasonal variance: Higher concentrations of bromoform were found in the Heysham effluent over the summer; a similar pattern was apparent at Maasvlakte. Progressive formation of bromoform occurred downstream: at all stations the average concentration of bromoform in the final cooling water effluent was marginally higher than that directly in front of the main condensers.
- Bromoform and DBAN production rates: averaging across all sites, a chlorine dose of c.1 mg l^{-1} TRO (as Cl_2) resulted in a mean cooling water effluent bromoform concentration of 16.32 ± 2.10 µg l^{-1}. The equivalent mean DBAN concentration was 1.48 ± 0.56 µg l^{-1}
- Dichlorobromomethane and dibromochloromethane: both consistently present in the cooling water effluents but at relatively low levels. Mean effluent concentrations of both compounds at Maasvlakte, Heysham and Gravelines were 0.8, 0.7 and 0.6 µg l^{-1}, respectively, whilst concentrations in the effluents of other stations were all <0.3 µg l^{-1}.
- Chloroform: Below the detection limit of <0.1 µg l^{-1} in the effluents of all but Hartlepool on the heavily industrialised Tees Estuary where a single spot sample was found to contain 1.5 µg l^{-1}.
- 2,4,6-Tribromophenol: Rarely observed, with means of 0.26 µg l^{-1} at Heysham; 0.29 µg l^{-1} at Maasvlakte; and 0.12 g l^{-1} at Paluel.

The disinfectant properties of chlorinated seawater are expressed by a mixture of (mainly brominated) oxidizing compounds of which hypobromous acid (HOBr) is the most important. These oxidising compounds are of necessity acutely toxic, but are reactive, unstable and short lived, so present little threat to the ecosystem of the receiving water. The non-oxidizing secondary products, CBPs, are relatively stable and have the potential to express chronic toxicity to marine biota. Fortunately they have only a limited tendency to bio-accumulate and, outside the immediate vicinity of a cooling water discharge, are found at concentrations two to three orders of magnitude below their acute toxic levels. This indicates that although their *potential* for causing environmental impact exists, in practical terms it is very limited.

Good practice requires adoption of a precautionary approach. The presence of CBPs, even at low concentrations, must not be ignored, and levels around a power station outfall need to be monitored. Bromoform is universally found to be the dominant CBP in saline systems, and once an area is characterised, routine monitoring for bromoform should prove an effective sentinel for CBP distributions.

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Appendix A Acronyms

BDCM	Bromodichloromethane ($CHBrCl_2$)
BCF	Bioconcentration Factor
CBP	Chlorination By-Product
DBCM	Dibromochloromethane ($CHBr_2Cl$)
DBAA	Dibromoacetic acid ($Br_2CHCOOH$)
DBAN	Dibromoacetonitrile (Br_2CHCN)
DBCM	Dibromochloromethane
DBP	Dibromophenol
EPR	European Pressurized Reactor
IC-ICP-MS	Anion-exchange chromatography and inductively coupled plasma mass-spectrometry
HAN	Haloacetonitrile
LOEC	Lowest Observable Effect Concentration
MBAA	Monobromoacetic acid
MTT	tetrazolium salt technique (MTT is actively ingested by cells and subsequently converted enzymatically from a yellow, soluble form to a reddish purple crystal)
NOEC	No Observed Effect Concentration
NNB	New Nuclear Build
POX	Purgeable organohalogens
QSAR	Quantitative Structure Activity Relationship
THM	Trihalomethane
TBP	Tribromophenol
TOX	Total Organohalogens
TRO	Total Residual Oxidants
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration