

Assessment of Regulated and Emerging Disinfection By-Products in South East Queensland Drinking Water

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The Urban Water Security Research Alliance (UWSRA) is a \$50 million partnership over five years between the Queensland Government, CSIRO's Water for a Healthy Country Flagship, Griffith University and The University of Queensland. The Alliance has been formed to address South East Queensland's emerging urban water issues with a focus on water security and recycling. The program will bring new research capacity to South East Queensland tailored to tackling existing and anticipated future issues to inform the implementation of the Water Strategy.

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FOREWORD

Water is fundamental to our quality of life, to economic growth and to the environment. With its booming economy and growing population, Australia's South East Queensland (SEQ) region faces increasing pressure on its water resources. These pressures are compounded by the impact of climate variability and accelerating climate change.

The Urban Water Security Research Alliance, through targeted, multidisciplinary research initiatives, has been formed to address the region's emerging urban water issues.

As the largest regionally focused urban water research program in Australia, the Alliance is focused on water security and recycling, but will align research where appropriate with other water research programs such as those of other SEQ water agencies, CSIRO's Water for a Healthy Country National Research Flagship, Water Quality Research Australia, eWater CRC and the Water Services Association of Australia (WSAA).

The Alliance is a partnership between the Queensland Government, CSIRO's Water for a Healthy Country National Research Flagship, The University of Queensland and Griffith University. It brings new research capacity to SEQ, tailored to tackling existing and anticipated future risks, assumptions and uncertainties facing water supply strategy. It is a \$50 million partnership over five years.

Alliance research is examining fundamental issues necessary to deliver the region's water needs, including:

- ensuring the reliability and safety of recycled water systems.
- advising on infrastructure and technology for the recycling of wastewater and stormwater.
- building scientific knowledge into the management of health and safety risks in the water supply system.
- increasing community confidence in the future of water supply.

This report is part of a series summarising the output from the Urban Water Security Research Alliance. All reports and additional information about the Alliance can be found at <http://www.urbanwateralliance.org.au/about.html>.



Chris Davis

Chair, Urban Water Security Research Alliance

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EXECUTIVE SUMMARY

Naturally occurring organic matter, which is present in raw waters, reacts with disinfectants to form disinfection by products (DBPs). Their presence in drinking water is of concern as some have been linked to potential health effects.

As described in the South East Queensland Regional Plan 2009-2031, the purpose of the South East Queensland Water Strategy is to ensure water in the region is managed on a sustainable and integrated basis to provide secure and reliable supplies of acceptable quality for all uses for the long term. Public health and safety will not be compromised and the highest water quality standards appropriate to use will always be maintained. Investigating the presence of emerging and regulated DBPs in South East Queensland (SEQ) drinking water is a key component to guaranteeing that these goals can be achieved. The impact of DBPs on drinking water quality in SEQ was also identified as a medium research priority by Queensland Government officers. Simultaneously, utilities in SEQ recognised the lack of information and understanding about the occurrence and fate of regulated and emerging DBPs in the SEQ drinking water system treatment plants (bulk supply), bulk transport infrastructure and the distribution system.

Generally in Australia, and in particular in SEQ, water is transported over long distances via the water distribution system and chloramines are often used as disinfecting agents due to their high stability relative to chlorine. It has been shown that alternative disinfectants such as chloramines, ozone or even UV light can generate different DBPs compared to those generated by chlorine [1]. The SEQ Water Grid is a network of treatment facilities and pipes that moves treated drinking water across a region of 22,420 square kilometres. Pipelines can be operated in either direction to enable alleviation of localised water needs in a flexible way, drawing upon the region's supplies. Disinfectants are added to ensure that the water is safe to drink from a microbiological perspective, preventing acute human health effects.

The SEQ Water Grid covers a number of regions which use different disinfection regimes - chlorination and chloramination - and, therefore, amending disinfectants during distribution is necessary and dependent on the local demand. Addition of ammonia is required to transform chlorine to chloramines while addition of chlorine to reach the breakpoint is necessary to transform chloramines to chlorine. However, the effects of transforming disinfectants and mixing waters of different nature on the formation of DBPs are poorly understood. Consequently, an assessment of emerging and regulated DBPs formed during the production and distribution of drinking water in SEQ was required. At the same time, a better understanding of the mechanism of formation and transformation of those DBPs within the drinking water system was also required to better establish strategies for their reduction without compromising disinfection. Moreover, Australian source waters used for drinking water can contain high concentrations of bromide and iodide, and this may increase the formation of brominated and iodinated DBPs depending on the disinfection strategy [2, 3]. Brominated DBPs have been found to be more toxic than their chlorinated analogues and the iodinated DBPs have greater toxicity still [4]. This is of potential concern, particularly for desalinated water and other salinity impacted waters, which are common in Australia.

DBPs are formed by the oxidation of naturally occurring organic matter, halides, and anthropogenic contaminants present in source waters. Although coagulation, designed to remove suspended organic material from water, is undertaken as a standard aspect of water treatment, previous research at the Smart Water Research Centre, Griffith University, indicated there was no reduction in DBP formation potential of *N*-nitrosodimethylamine (NDMA) and the sum of the four regulated THMs (total THMs, or tTHMs) by performing coagulation on the source water studied. This revealed two points: the inability to remove halides from raw waters using conventional coagulation techniques, and the difficulty in removing the low molecular weight (more reactive) organic matter fraction by conventional coagulation. Both dissolved organic carbon and dissolved organic nitrogen were reduced

by this treatment strategy. However, formation potential of the DBPs studied was not reduced. By understanding the specific chemical nature of the components of natural organic matter responsible for DBP formation, a more targeted approach to the removal of these DBP precursors becomes possible.

The key research questions of this project were:

- What are the effects in terms of DBP formation of blending drinking water (of different qualities from different sources) within the SEQ Water Grid? What are the effects in terms of DBP formation of the transformation of disinfectants in the Water Grid?
- Which emerging and regulated DBPs are of concern in the SEQ context, considering it has two separate disinfection regimes being utilised in different areas?
- What components of natural organic matter are not removed by enhanced coagulation strategies employed in the SEQ context? Can strategies to remove natural organic matter or halides be successfully applied to minimise the formation of DBPs?

In order to answer these research questions, the project was split in two main parts, each being carried out at a different university. The University of Queensland was in charge of investigating the effect on DBP formation of blending drinking water and converting disinfectants, while the main goal of Griffith University was to investigate the removal of organic matter and halides from water as well as to better characterise the organic matter in SEQ source waters. Finally, a survey of DBP occurrence was conducted at the Capalaba Water Treatment Plant (WTP) and at nineteen sampling points of the distribution system, for six months through spring-summer 2011 as well as in the LinkWater conversion (WQMF) stations. This work was done by The University of Queensland with assistance from Griffith University.

The key findings of this research can be summarised as follows:

- Capalaba WTP, Molendinar WTP, Mt Crosby East WTP and Tugun desalination plant were investigated for the potential of DBP formation as an example of different source waters found in SEQ. From these results, it was shown that Capalaba is the source water with highest potential for DBP formation as a result of high dissolved organic carbon concentration. Tugun desalination water has negligible potential for DBP formation. Mt Crosby East WTP was characterised by a higher concentration of bromide that shifted the formation of DBPs to those containing bromine atoms, which are suspected to be more toxic than the chlorinated compounds.
- Compared to chlorine, monochloramine generally resulted in lower concentrations of DBPs with the exception of 1,1-dichloropropanone and iodinated trihalomethanes. However, the formation of some DBPs such as haloacetonitriles (HANs), chloral hydrate (CH) and halonitromethanes was increased when chloramines were used before chlorine disinfection in comparison to the use of chlorine alone. Therefore the conversion of chloramines to chlorine via breakpoint chlorination is not recommended for waters with high risk of DBP formation.
- In collaboration with the National Research Centre for Environmental Toxicology (Entox), we investigated the toxic effects of the non-volatile fraction of the disinfected waters in laboratory experiments. Results obtained from bioassays testing cytotoxicity and several reactive endpoints showed similar trends to the chemical analysis of quantified DBPs. This demonstrates the potential of bioassays to be employed as assessment tools for DBPs in drinking water samples.
- An increase of DBP formation was observed in laboratory experiments blending waters containing residual chlorine and chloramines without prior conversion to homogenise residual disinfectants. However, the final level of DBPs was, in all instances, below the Australian Drinking Water Guidelines (ADWG).

- During the survey study around Capalaba, it was observed that different DBP speciation occurred as a result of different dissolved organic carbon/bromide (DOC:Br) ratios. Haloacetonitriles were measured at relatively high concentrations for locations serviced primarily by Capalaba WTP. Even though they were measured below WHO limits, we recommend investigating possibilities to control the formation of haloacetonitriles at the drinking WTP as they are suspected to be more toxic than carbon-based regulated DBPs. NDMA was not detected above the limit of detection (5 ng/L). NDMA formation potential of source water at the Capalaba WTP was 11.4 ± 3.4 ng/L, which is also well below the ADWG value (i.e., 100 ng/L).
- The study at the LinkWater conversion stations showed that all regulated DBPs were within the ADWG for all sampling events at the two tested conversion stations, even during the breakpoint trials. No additional DBPs are formed during the conversion of chlorine to chloramine, even after long contact times. However, after chlorine breakpoint the formation of specific DBPs such as HAN and CH increased, which is in agreement with the observation presented in point 2 above.
- A number of adsorptive treatment strategies were used on a synthetic water matrix of variable alkalinity, DOC and halide concentration to assess DBP precursor removal and formation potential. This study showed that, when bromide was present in the source water, enhanced coagulation (EC) and EC combined with powered activated carbon (PAC) treatment led to increases in the formation of specific, highly brominated DBPs upon chlorination. This was due to the increased Br:DOC ratio of the treated waters relative to untreated samples. However, these treatments were effective in controlling chlorinated DBP formation upon chlorination.
- MIEX® resin and granular activated carbon (GAC) beds were able to adsorb bromide and iodide to some extent, as well as adsorbing DOC. This was not always sufficient to stop the increased formation of some highly-brominated DBPs upon chlorination, however they offered improved outcomes for DBP formation compared to EC and combined EC/PAC treatment.
- EC combined with silver-impregnated activated carbon (SIAC) treatment offered excellent removal of both DOC and halide, and overall lower DBP formation than any other treatment upon chlorination. EC/GAC and EC/SIAC were the most superior treatments studied for chlorinated DBP removal.
- Applying the above adsorptive treatments (followed by chlorination) to raw waters sourced from Capalaba WTP, Molendinar WTP and Mt Crosby WTP demonstrated the same principles. Capalaba raw water formed the highest concentrations of chlorinated DBPs (which were well-controlled by all treatments), Mt Crosby raw water formed high concentrations of brominated DBPs due to the high Br:DOC ratio of that source water (which was optimally controlled by EC/SIAC) and Molendinar formed the lowest concentrations of DBPs generally, due to the naturally low natural organic matter, low halide nature of the water source.

1. INTRODUCTION

1.1. Disinfection By-Products in Drinking Water

The disinfection of drinking water is important to ensure that water is safe to drink. Water disinfection is one of the most significant public health moves forward of the last century; its introduction reduced cholera incidence by 90%, typhoid by 80%, and amoebic dysentery by 50% in the United States [5]. There are two types of disinfection: primary disinfection which achieves the desired level of pathogen kill or inactivation, while secondary disinfection maintains a disinfectant residual in the water that prevents its regrowth. However, although chemical water disinfection is necessary, it has also raised a public health issue: the potential for cancer and reproductive/development effects associated with chemical DBPs [1]. Bladder and colorectal cancers have been associated with exposure to chlorination by-products in drinking water [6, 7], and experimental evidence suggests that exposure also occurs through inhalation and dermal absorption [8].

Disinfectants are powerful oxidants that oxidise natural organic matter, anthropogenic contaminants and bromide/iodide naturally present in most source waters (rivers, lakes and many groundwaters) and meanwhile generate DBPs. It is well known that DBPs are currently present in most drinking water supplies that have been subject to disinfection. Many hundreds of DBPs exist in treated drinking water and while the exact figure is not known, at least 600 have been identified [1]. The low levels of many of these DBPs, coupled with the analytical costs in testing water samples for them, means that in practice only a handful of DBPs are actually monitored.

The formation of different DBPs depends on the chemical disinfectant used, the quality of raw water, the disinfectant dose, the pH, the temperature and the time available for reaction (Ct or contact time). Figure 1 shows a schematic diagram of the reaction of organic and inorganic DBP precursors with disinfectants to form regulated and emerging DBPs [9].

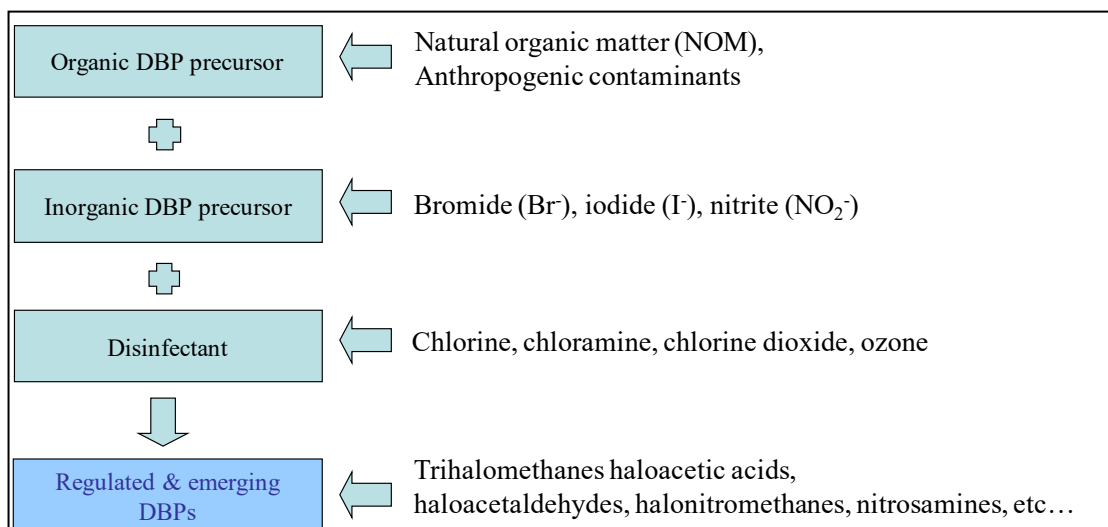


Figure 1: Schematic diagram of the reaction of organic and inorganic DBP precursors with disinfectants to form regulated and emerging DBPs adapted from Krasner [9].

Regulated DBPs only capture a fraction of all by-products and may miss many others often referred to as emerging DBPs. Moreover, although the use of chlorine may produce high concentrations of chlorination by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs), many other DBPs can be formed at lower concentrations (i.e., <0.01 mg/L and often <0.001 mg/L). Among these low concentration DBPs, brominated and iodinated DBPs may be found. However, the low concentration of those DBPs should not be directly related to the toxicological effects as it has been found that brominated DBPs are both more genotoxic and carcinogenic than are chlorinated compounds and recent studies show that iodinated DBPs have even greater toxicity than their

brominated analogues [4]. There are no iodinated DBPs that are currently regulated. In addition, DBPs that have a nitrogen atom incorporated into the structure are far more toxic and genotoxic, and some even carcinogenic, than those DBPs that do not contain nitrogen [10].

A nationwide study of emerging DBPs at different drinking water treatment plants showed that the highest formation of one subgroup, iodo-THMs, was in a plant where chlorine and ammonia were simultaneously added to form monochloramine [11]. Moreover, iodoacetic acids (among the most cyto- and genotoxic of all DBPs) were prevalent in waters treated under these conditions [12]. Iodine-containing DBPs also cause a medicinal odour and taste at concentrations as low as 0.02 µg/L. In the same nationwide study, many bromine-containing DBPs were identified in finished waters that contained bromide in their source waters. At bromide concentrations in excess of 0.2 mg/L, the concentration of these DBPs was of concern from a toxicity perspective both in terms of reproductive and developmental effects as well as cancer. Such bromide concentrations may be present in coastal areas, where tidal ingress into the public sewer system can occur as it is the case in most regions of Australia. Also desalinated water may be a potential source of these DBPs due to the higher concentrations of bromide and iodide in comparison to conventional water sources.

The acute health risk to humans of pathogenic micro-organisms in drinking water is estimated to be about 10,000 to 1,000,000 times higher than the risk of developing cancer through long-term exposure to DBPs [13]. However, because of the potential human health effects associated with chlorinated drinking water, regulations for selected halogenated DBPs have been introduced in some countries even though they represent only a fraction of all by-products. These regulations have driven some utilities to switch from free chlorine to chloramine for terminal disinfection even though a higher proportion of the by-products associated with chloramination are unidentified compared to those associated with chlorine and their impacts on human health are unknown.

1.2. Strategies of Disinfection

In order to better control DBP formation when disinfecting drinking water it is important to understand the DBP formation and speciation depending on the disinfection strategy. In general, the formation of DBPs is caused by the reaction between natural organic matter, including humic and fulvic substances, and disinfectants. Inorganic ions such as bromide and iodide will also influence the speciation of DBP formation. This section aims to review the DBPs that may be generated depending on the disinfection strategy.

For decades, chlorine has played an important role in water treatment. Chlorine is the most widely applied disinfectant. The advantage of chlorine is that it can be produced easily and that it is relatively cheap. Chlorination can be achieved by addition of hypochlorite as a solution (i.e., sodium hypochlorite) or in solid form (i.e., calcium hypochlorite). In both cases, the addition process involves injecting the disinfectant into the water supply pipe at a controlled rate. When calcium hypochlorite is used it must be first dissolved in a mixing/holding tank. Sodium hypochlorite can also be generated onsite by electrolysis of sodium chloride solution using specialised equipment. If chlorination is used, the presence of a free chlorine residual in the distribution systems provides evidence of initial disinfection and protection against recontamination from backflow, pipeline breaks or other causes.

Chlorine reacts with naturally occurring organic matter and/or anthropogenic compounds to produce a mixture of DBPs such as THMs and HAAs. Other DBPs that may be generated at lower concentrations are halogenated acetonitriles, trichloroacetaldehyde, chlorinated phenols, chlorinated furanones, halonitromethanes, cyanogen halides, haloketones and haloaldehydes. However, the total organic halogen content (TOX) identified so far accounts for only around 50% of the total DBPs formed [14]. Also, chlorate may be present as a contaminant from chlorination (when solutions of sodium hypochlorite are used). Since the discovery of chlorination by-products (mainly THMs), the use of alternative disinfectants has increased. Common alternative methods of disinfection are chloramination, ozone, chlorine dioxide or ultraviolet light.

Figure 2 presents a summary of the percentages of DBP classes of the water treatment facilities surveyed in the U.S. EPA Nationwide Occurrence Study [11].

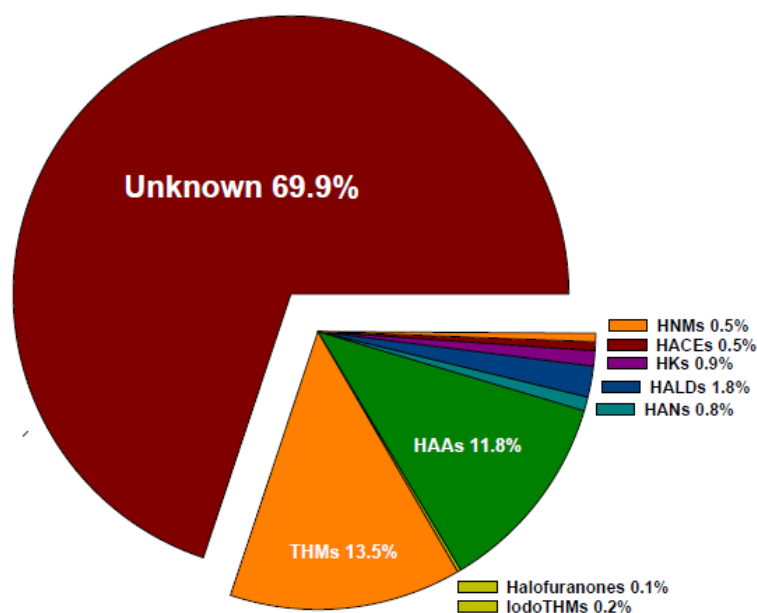


Figure 2: Summary of the distribution of the median values of the DBP chemical classes in water analysed in the U.S. EPA Nationwide Occurrence Study as a component of TOX [11].

Chloramines are formed when water containing ammonia is chlorinated or when ammonia is added to a water containing chlorine. Also pre-formed monochloramine can be directly injected into the water. This is an effective bactericide that produces fewer regulated DBPs than chlorination. However, little is known about other DBPs generated when chloramines are used. Hua and Reckhow [15] found that chloramines produced a higher percentage of unknown TOX than free chlorine. They also formed more iodoform and total organic iodine (TOI) than free chlorine in the presence of iodide. Moreover, the disinfection properties of monochloramines are weaker. In general, it is much less effective against viruses or protozoa than free chlorine. Therefore, chloramine is most appropriate for use as a secondary disinfectant to prevent bacterial regrowth in a distribution system. A crucial parameter to control when disinfecting water with chloramines is the chlorine-to-ammonia ratio. When water is disinfected by means of chloramination, monochloramine (NH_2Cl), dichloramine (NHCl_2) or trichloramine (NCl_3) can be formed at different proportions with a maximum of two inorganic chloramines coexisting at specific conditions. The proportion of the species present in solution is dependent on the ratio of chlorine to ammonia and on the pH used. At pH levels usually present in drinking waters (i.e., pH=6-8), the predominant chloramine species are monochloramine and dichloramine. Since the Cl:N molar ratio employed in water disinfection is below 1, monochloramine can be considered as the main species present in solution [16, 17]. Chloramine DBPs include cyanogen halides formed at much higher concentration than formed by chlorine, halonitromethanes, *N*-nitrosamines such as *N*-nitrosodimethylamine (NDMA), dihaloacetonitriles, dihalogenated acetic acids, dihalogenated acetaldehydes among others [11, 18]. Most of those DBPs are not included in the drinking water regulations.

Figure 3 schematically shows a generalisation of the formation of DBPs depending on the disinfectant employed.

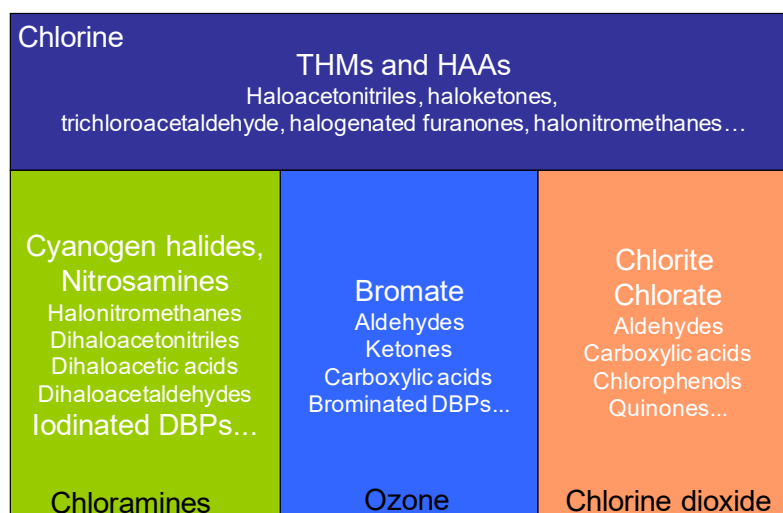


Figure 3: Schematic generalisation on the formation of DBPs depending on the disinfectant employed.

1.3. Regulation of Disinfection By-Products in Drinking Water

Since the discovery of chloroform as a DBP in drinking water in the early 1970s, significant research efforts have been made to improve our understanding of DBP formation and control. To date, more than 600 DBPs have been identified in drinking waters [19]. To minimise consumer exposure to hazardous DBPs while maintaining an adequate disinfection and control of targeted pathogens, the World Health Organisation (WHO) and the authorities in most developed countries have introduced drinking water guidelines and standards [20, 21].

However, despite the daunting number of identified DBPs, only 12 DBPs (4 THMs, 3 HAAs, trichloroacetaldehyde, cyanogen chloride, 2,4,6-trichlorophenol, formaldehyde, bromate, chlorite and *N*-nitrosodimethylamine) are currently regulated in Australia under the Australian Drinking Water Guidelines (ADWG) [22]. Additional DBP regulations may be proposed and implemented as potential health risks of many unregulated DBPs are determined [1]. Moreover, known DBPs are considered individually or as family group in the current regulations. However, it is possible that when these compounds are ingested together, their combined effects on health may be different from their individual effects. Epidemiological studies examine DBPs as a generic group and can be useful in determining overall effects [8].

DBPs are regulated in drinking water by the US EPA at 80 µg/L for the sum of four THMs (tTHM), 60 µg/L for the sum of five HAA (HAA5), 10 µg/L for bromate and 1 mg/L for chlorite [23]. The Stage 2 Disinfectants and Disinfection By-Products Rule did not change the guideline values for these DBPs, however, the Stage 2 rule changed the method for computing DBP levels, which now use locational running annual averages for THM4 and HAA5 compliance. The USEPA regulates tTHMs, corresponding to the sum of chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (TBM), at 80 µg/L [24], while the value for the ADWG is 250 µg/L [22]. There are 15 HAAs which can be formed in the presence of chlorine, bromide and iodide. The most common are dichloroacetic acid (Cl₂AA) and trichloroacetic acid (Cl₃AA). Other species, found generally at lower levels, are bromochloroacetic acid (BrClAA), dibromoacetic acid (Br₂AA), monochloroacetic acid (ClAA) and monobromoacetic acid (BrAA) as well as additional iodine-containing counterparts. In the USA, the sum of Cl₂AA, Cl₃AA, Br₂AA, ClAA and BrAA is commonly denoted as HAA5 and is currently regulated at 60 µg/L [24].

In Australia, only ClAA, Cl₂AA and Cl₃AA are regulated, at 150, 100 and 100 µg/L, respectively [22]. In the case of HAAs, Australia is only regulating three chlorinated species and none of the bromine containing HAAs. It has been shown that bromine containing HAAs may be present at higher

concentration in coastal waters due to the higher concentration of bromide ion [25]. This would be of special concern in Australia and the need to include those in the regulations must be stressed. In fact, this observation was made in one of the few papers reporting DBPs concentration in Australia. In 1998, Simpson and co-authors published a survey on DBPs concentration in different states of Australia and they found important differences in the DBPs speciation based on the different concentrations of bromide [26].

Table 1 shows the comparison between DBPs regulated in drinking water for Australia, USA and Europe in comparison to the World Health Organisation (WHO) recommendations [21-23, 27].

Table 1: DBPs regulated in drinking water [21-23, 27].

DBPs	USEPA (µg/L)	WHO (µg/L)	European Union Standards (µg/L)	2011 Australian DW Guideline (µg/L)
Bromate	10	10	10	20
Bromoacetic acid	60 as HAA5			
Bromodichloromethane	80 as tTHMs	60	100 as tTHMs	250 as tTHMs
Bromoform	80 as tTHMs	100	100 as tTHMs	250 as tTHMs
Chlorate		700		
Chloroform	80 as tTHMs	300	100 as tTHMs	250 as tTHMs
Chlorite	1000	700		800
Chloroacetic acid	60 as HAA5	20		150
Dibromochloromethane	80 as tTHMs	100	100 as tTHMs	250 as tTHMs
Dichloroacetic acid	60 as HAA5	50		100
Trichloroacetic acid	60 as HAA5			100
Dichloroacetonitrile		20		
Dibromoacetic acid	60 as HAA5			
Dibromoacetonitrile		70		
N-nitrosodimethylamine		0.1		0.1
Trichloroacetaldehyde (chloral hydrate)				20
Cyanogen chloride (as cyanide)		70		80

1.4. Disinfection By-Products

1.4.4 Regulated versus Emerging DBPs

This section gives an overview of the regulated versus unregulated emerging DBPs and their mechanisms of formation related to specific disinfection strategies. Richardson published an excellent review covering the genotoxicity and carcinogenicity of regulated and emerging DBPs [1]. This overview is not included in this document. More recently, an innovative method for prioritising emerging DBPs in drinking water on the basis of potential impact on public health has been published by Hebert and collaborators [28]. The emerging DBPs identified as posing the greatest potential risk using the method were as follows: NDMA and other nitrosamines, halofuranones, chlorate, formaldehyde and acetaldehyde and 2,4,6-trichlorophenol.

Regulated DBPs

There are four regulated THMs: chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (TBM). Trichloromethane, or chloroform, was the first DBP identified in drinking water. The formation of THMs in chlorinated waters is due to a complex reaction between chlorine and natural organic matter (NOM), including humic or fulvic substances. In addition to four bromo- and chloro-THMs, iodo-THMs have also been identified in chlorinated water containing iodide, especially in sea water. The presence of iodide significantly increases the number of THMs potentially formed, that are not currently regulated. Together, the

THMs and the HAAs are the two most prevalent classes of DBPs formed in chlorinated drinking waters, accounting for approximately 25% of the halogenated DBPs [11]. Reported tTHM concentrations range from a minimum of 3.1 µg/L to a maximum of 1280 µg/L [29]. The USEPA Information Collection Rule (ICR), which involved 500 large drinking water plants in the USA, reported mean levels in the distribution system of 38 µg/L and 90th percentage levels in the distribution system of 78 µg/L for tTHMs. TCM was by far the most prevalent of THMs measured, and it had the highest mean concentration of 23 µg/L [30]. THMs are formed at significantly lower levels in chloraminated drinking waters, and TBM can be formed in high-bromide source waters treated with ozone [31]. Disinfection with chlorine dioxide does not form THMs; however low THMs levels can be present due to chlorine impurities in chlorine dioxide [1].

Haloacetic acids are another major group of DBPs formed in drinking water disinfected with chlorine. There are nine common HAAs although only three of them are currently regulated in Australia. These are: monochloroacetic acid, dichloroacetic acid and trichloroacetic acid. HAAs can also be formed by disinfection with chloramines, chlorine dioxide and ozone but normally they are formed at higher concentrations with chlorine [1]. The mean concentration of HAAs found in the ICR was 23 µg/L and a 90th percentile of 47.5 µg/L [30]. Chloramines form substantially lower levels of HAAs, which is one of the reasons why it has become a popular alternative disinfectant for public water systems that cannot meet the regulations with chlorination. Chlorine dioxide may also form HAAs, primarily dichloroacetic acid [11, 19]. Ozone is also well known for reducing the levels of HAAs relative to chlorine. However, when source waters contain elevated levels of natural bromide, dibromoacetic acid (non regulated in Australia) has been observed [32].

Chloral hydrate (CH) may be formed as a by-product during chlorination. Even though its concentration is significantly lower than for THMs and HAAs, CH and its brominated analogues (non-regulated) are the third largest group of organic DBPs found in chlorinated water [33]. Although CH is primarily a chlorination DBP, either ozone or dichloramines can produce acetaldehyde, which can react with additional chlorine to form CH [34]. Reported concentrations of CH range from 1.7 µg/L to 3.0 µg/L [29]. This DBP has been found at higher concentration levels in distributions than in finished drinking waters [30].

Cyanogen chloride (CNCl) is regulated in Australia as cyanide at 80 µg/L. This is a specific DBP generated when water is disinfected with chloramines. CNCl has been found in finished water supplies, usually at concentrations below 10 µg/L. The concentration in water when chlorination was used for disinfection was reported to be 0.4 µg/L. The level was higher (1.6 µg/L) in chloraminated water [35]. Its brominated analogue, cyanogen bromide, is commonly detected in chloraminated water that contains bromide.

NDMA is a DBP of water disinfected with chloramines. Main parameters related to the NDMA formation are the contact time and the disinfectant dose. Since it is not possible to compromise the contact time for disinfection during the treatment of drinking water, research must focus on reducing NDMA precursors before adding the disinfectant. Apart from precursor compounds such as dimethylamine, tertiary amines or other dissolved organic nitrogen, polyelectrolytes and ion-exchange resins used as coagulants such as PolyDADMAC have also been related to NDMA formation in several water treatment plants when disinfecting water with chlorine and chloramines [36]. NDMA was included in the ADWG at 100 ng/L in 2011 [22]. In the US and Ontario it has been reported that NDMA is found at concentrations above 2 ng/L in 1 of every 10 samples, primarily in systems using chloramines. Other nitrosamines are rarely detected [37].

Bromate is a common inorganic DBP found in ozonated water containing naturally occurring bromide (> 50 µg/L). The formation of bromate in water involves many complex reactions. Many models have been developed to illustrate the bromate formation pathways or mechanisms. They are different depending on; whether ozone or the hydroxyl radical attack, the water pH, and the presence of ammonia [33]. In general a higher pH leads to a higher formation of bromate because of the presence of OBr⁻ as the predominant species at pH > 8.7 that reacts quickly with O₃ generating OBr₃⁻. Also, the concentration of hydroxyl radicals is higher at a higher pH. The increase of these radicals increases the generation of bromate. In the ICR, bromate was detected in ozonated drinking water at levels ranging

from <0.2 to 25.1 µg/L, and in 11% of the chlorine dioxide-treated drinking water samples, at levels ranging from below detection to 2.4 µg/L [30]. In ozonated drinking waters treated with hypochlorite as a secondary disinfection method, bromate levels increased on average by 0.84 µg/L (from bromate contamination in the hypochlorite) over the level formed by ozone only. Apart from ozonation, other studies have shown that bromate can be formed with chlorine dioxide disinfection [19] particularly when this practice is conducted in the presence of sunlight.

Chlorine dioxide is used as a disinfectant for drinking water supplies too. When added to water, it dissociates into chlorite and, to a lesser extent, chlorate. It is usually generated on site due to handling and transportation difficulties. Chlorite was included in the ADWG at 800 µg/L in 2011 [22]. The richest data on chlorite concentrations comes from the ICR, which included 28 water-treatment plants using chlorine dioxide. The median level of chlorite was 0.29 mg/L at these facilities [30].

Emerging DBPs

As already stated, more than 600 DBPs have been identified in disinfected drinking water [19] although only a small fraction of them are currently regulated by the ADWG [22]. Those DBPs that are not included in the present regulations are known as emerging DBPs. This section aims to summarise the families of emerging DBPs and their mechanisms of formation depending on the specific disinfection strategies employed.

There are nine halonitromethanes (HNMs) that can be formed during disinfection. Those are chloronitromethane, bromonitromethane, dichloronitromethane, dibromonitromethane, bromochloronitromethane, trichloronitromethane (chloropicrin/TCNM), tribromonitromethane (bromopicrin), bromodichloronitromethane, and dibromochloronitromethane. TCNM has been the most commonly measured example of this class although more recently other halonitromethanes have been identified in disinfected water [38]. Also, research indicates that halonitromethanes may be increased in formation when pre-ozonation is used before chlorine or chloramine treatment [11, 12]. Concentrations of halonitromethanes reported have been found to be between 0.1 and 15 µg/L [11, 12]. Recent research indicates that chloropicrin may be formed during subsequent chlorination of medium-pressure UV disinfected water [39, 40]. This increase is explained by the formation of reactive nitrogen species from photolysis of nitrate by medium-pressure UV at wavelengths lower than 240 nm. This effect has not been observed for low-pressure UV lamps since they emit monochromatic light at 254 nm. This may be of concern for those plants that receive water with significant nitrate concentrations.

As already stated, only three HAAs are regulated in Australia in comparison to the USEPA guidelines, that regulate five [23]. Non-regulated HAAs in Australia include bromoacetic acid and dibromoacetic acid. Apart from that, there are four other HAAs currently not regulated in the U.S. either. Those are bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid. The sum of the 9 bromo-chloro-haloacetic acids is known as THAA9. A study of Singer and co-authors emphasises the importance of measuring all 9 HAA since determining only the five regulated ones (three in Australia) can significantly underestimate the total exposure, especially for water systems that contain appreciable levels of bromide in their source waters [41]. Moreover, as already stated, bromine-containing DBPs are generally more toxic than chlorine-containing DBPs [1].

Five iodo-acids have been identified in finished drinking water: iodoacetic acid, bromiodoacetic acid, (Z)-3-bromo-3-iodopropenoic acid, (E)-3-bromo-3-iodopropenoic acid, and (E)-2-iodo-methylbutenedioic acid [4]. These iodo-acids are of concern not only for their potential health effect, but also because recent research indicates that they may be formed at increased levels (along with iodo-THMs) in waters treated with chloramines. In aqueous oxidative processes with ozone, chlorine, or chloramine, naturally occurring iodide can easily be oxidised to hypoiodous acid (HOI) which can react with natural organic matter or be further oxidised to iodate. While iodate is the desired sink for iodine in drinking waters, iodo-DBPs are problematic. The probability of the formation of iodo-DBPs during drinking water disinfection increases in the order ozone < chlorine < monochloramine [42].

Iodo-THMs include dichloriodomethane, bromochloriodomethane, dibromiodomethane, chloriodomethane, bromodiodomethane, and iodoform. The first studies on iodo-THMs were conducted mainly because of the taste and odour problems since there is a low threshold for detection of medicinal tastes and odours in drinking water. However, toxicological studies showed that this family may be more toxic than brominated and chlorinated compounds [1]. Reported values for I-THMs are around 15 µg/L [1]

Iodo-THMs can form in drinking water treated with chlorine or chloramines when natural iodide is present in the source waters, and they have been found as DBPs in drinking water in many countries.

Controlled laboratory studies carried out by Bichsel and von Gunten [42] showed that chloramination with ammonia addition before chlorine addition increased the formation of iodo-THMs, whereas pre-chlorination favoured the formation of bromochloro-THMs. Chlorination produced both iodate and iodo-THMs; addition of increased amounts of chlorine lowered iodo-THMs concentrations and raised iodate concentrations. In contrast, no iodo-THMs were formed by ozonation. However, other studies observed iodo-THMs after ozonation and chloramination as a result of a lower ratio of ozone to natural organic matter that implies less conversion of iodide to iodate [12]

Although they are not included in the regulations in the U.S., haloacetoneitriles (HANs) have been measured in several occurrence studies [12, 35]. Chloro-, bromochloro-, dibromo-, and trichloroacetoneitrile (HAN4) are the most common measured HAN species. These HAN have been identified in plants that disinfect water with chlorine, chloramine, chlorine dioxide, and ozone. Reported values for HAN ranges between <0.5 to 41 µg/L [1]. Plants using chloramines had the highest levels in their finished drinking waters. High HANs have also been identified in distribution system waters treated with post-chloramination as compared to free chlorine. HANs have been found to be significantly more toxic than the regulated DBPs [43]

Halopropanones are also known as haloketones (HKs). There exist six HKs, and these are: dichloropropanone, bromochloropropanone, dibromopropanone, trichloropropanone, bromodichloropropanone, chlorodibromopropanone, and tribromopropanone. In addition to dihalopropanones and trihalopropanones, tetrahalopropanones, pentahalopropanones and hexahalopropanones may be formed in drinking water. The latter are not stable under high pH conditions and undergo degradation. They may be formed by reaction between existing HKs and chlorine. The reaction between propanone, an ozonation DBP, and chlorine is one of the main mechanisms for the formation of high levels of dichloropropanone and trichloropropanone in ozonated water [33].

Haloacetamides (HAMs) have been identified as DBPs from drinking water treatment plants and from laboratory studies. Haloacetamides include trichloroacetamide, dichloroacetamide, chloroacetamide, bromochloroacetamide, dibromoacetamide, bromodichloroacetamide, chloriodoacetamide, dibromochloroacetamide, bromiodoacetamide, tribromoacetamide, bromoacetamide, iodoacetamide and diiodoacetamide. Haloacetamides have been found to be cyto- and genotoxic [44]. There is preliminary evidence that chloramination and ozone without biofiltration may increase the formation of haloacetamides. Because nitriles can hydrolyse to form haloacetamides, it is known that the haloacetamides are hydrolysis products of the corresponding HANs, which are commonly found as DBPs. Typical reported values range from 7 to 10 µg/L [1].

In addition to CH (regulated DBP in Australia), there are mono- and dihalogenated acetaldehydes, as well as bromine-containing analogues of CH. Dihalogenated aldehydes have been related to disinfection with chloramines and ozone (when used without further biofiltration). Values reported using this disinfection strategy range from 8 to 12 µg/L [9]. On the other hand, trihalogenated aldehydes occur at higher concentrations at plants that use chlorine than at those that use chloramines when similar types of water quality are being treated. If ozonation is used without biofiltration, there should be increased formation of trihalogenated acetaldehydes during post-chlorination.

Halofuranones are potent mutagens and have been found in chlorinated waters at concentrations as high as 850 ng/L [12]. Not much is known about halofuranones because of the difficulties encountered

in the analytical techniques. However, it is known that those compounds are generally stable in the simulated distribution system test [1].

Chlorate, like chlorite, is a DBP from chlorine dioxide treatment. However, it can be also present as a contaminant from chlorination (when solutions of hypochlorite are used). Data from the ICR, which represents the most extensive data currently available for chlorate, showed a median concentration of 0.12 mg/L [30].

Due to the limitation of current technologies, many halogenated DBPs are not yet identified in disinfected waters. TOX is a measurement of the total halide-containing DBPs formed in water, including chlorine, bromine and iodine. Similar to the total organic carbon (TOC) or chemical oxygen demand (COD), TOX does not yield information on the chemical structure of the organic compounds. However, TOX measurement can be further separated into total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI).

In chlorinated samples, 50% of TOX can reportedly be assigned to known, individual species. The percentage of unknown DBPs is even greater in chloraminated drinking water (i.e., 80%) [19]. Generally chloramination produces less TOX than chlorination but, as already stated, less information is available on the specific DBPs generated. Moreover, TOI, which is of great health concern, is generated in higher concentrations by chloramines than by chlorine. However, it must also be emphasised that not all the DBPs are halogenated species. Therefore, TOX cannot be a comprehensive measure of all DBPs generated but only a partial source of information.

1.5. Strategies to Minimise DBPs Formation

The best strategy to minimise DBP formation is to minimise the presence of DBP precursors (primarily NOM and halides) prior to disinfection. Good removal of NOM can be achieved through a number of approaches:

- 1) Membrane filtration such as reverse osmosis or nanofiltration.
- 2) Enhanced coagulation (coagulation/flocculation conducted under conditions of optimal coagulant dose and pH).
- 3) Adsorption onto activated carbons.
- 4) Oxidant addition such as ozonation.
- 5) Anion exchange, such as MIEX® resin.
- 6) Biological treatment/biofiltration.
- 7) Advanced oxidation processes.

Membrane techniques can be employed as an effective barrier for DBP precursors, especially nanofiltration. Membranes may offer a new approach to DBP control in drinking water, especially where other approaches are either not feasible (e.g. ozonation generating bromate) or unattainable by conventional processes (e.g. final disinfectant dose required to meet CT objective will engage the inorganic precursor to produce a high level of halogen incorporation in DBPs). However, due to their high capital and operation costs, membrane technologies are rarely implemented for this purpose.

Both enhanced coagulation and carbon adsorption have been identified as Best Available Technologies (BAT) by the USEPA [23], for organics removal from drinking water sources. Enhanced coagulation is a coagulation process optimised for TOC removal. However many water quality conditions affect TOC removal. Those parameters include alkalinity, pH, turbidity, TOC concentration, nature of NOM and temperature. The design and operation conditions include coagulant dose and type, pH, pre-oxidation, coagulation aids, mixing and mixing time, sedimentation process, and sludge handling.

The use of alternative disinfectants or combinations of disinfectants can effectively reduce the formation of regulated DBPs. However, as already stated, each disinfectant generates its own suite of DBPs and has its own limitations. The regulated DBPs have been historically selected as indicators of

total DBPs formed when disinfecting water with chlorine [1] but these only capture a fraction of all by-products and miss many others including those associated with alternative disinfectants.

Anion exchange resins such as MIEX® have been successfully employed in recent years for NOM removal, often prior to a coagulation step (e.g. Wanneroo GWTP, WA)[45]. Anionic NOM is exchanged for chloride ions at the exchange sites of the resin, which can be easily regenerated once exhausted. Studies have reported improved removal of NOM using MIEX® than traditional coagulation methods [46]. A recent 2 year study found that pre-treatment with MIEX® before either traditional coagulation or microfiltration produced water with a consistently lower DOC and SUVA than water without MIEX® pre-treatment [47]. The inclusion of MIEX® into the treatment train allowed a more consistent water quality that was less affected by changes in the raw water DOC, over the 2 years of the study.

Carbon adsorption is a process that can remove both DBPs and DBP precursors. Both GAC and PAC are commonly used in the water industry. Biological treatment such as use of biologically activated carbon can remove NOM from water sources by enzyme-controlled microbial degradation as well as adsorption. Importantly, DBP precursor removal by biological treatment is dependent on the biodegradability of the NOM present. A water with a highly biodegradable NOM content will be most suitable for biological treatment [46].

Advanced oxidation processes are those in which hydroxyl radical is produced *in situ*. Examples of these are O₃/UV, UV/H₂O₂, O₃/H₂O₂ and Fenton's reactions [46]. All of these processes produce hydroxyl radical, which indiscriminately and quickly reacts with organic compounds, thereby degrading NOM. Advanced oxidation processes can in principle completely mineralise NOM to carbon dioxide. However, in practice, partial oxidation is the more economically feasible mode of treatment. Although NOM is degraded by these processes, specific DBPs can still be increased, due to their precursors being formed by the degradation process.

1.6. Strategies for the Removal of Halides from Drinking Water Sources, and their Applicability in Disinfection By-Product Minimisation

The presence of bromide (Br⁻) and iodide (I⁻) in source waters can result in the formation of brominated and/or iodinated DBPs upon exposure to NOM and disinfectant, which are often more toxic than their chlorinated analogues [1, 2, 4, 48, 49]. Both natural processes, including seawater intrusion and dissolution of geologic sources, and anthropogenic activities, such as seawater desalination, generation of mining tailings, chemical production, production of sewage and industrial effluents, may contribute to bromide concentrations in drinking water sources [1, 2, 48, 50]. Similarly, seawater intrusion, seawater desalination and dissolution of geologic sources contribute to iodide concentrations in drinking water sources [2, 51, 52], although biological activity of microorganisms and marine algae can contribute to iodide removal from water sources through specific metabolic processes [53]. Table 2 shows typical bromide and iodide concentration in different source waters.

Table 2: Examples of levels of bromide and iodide in different source waters.

	Bromide (µg/L)	Iodide (µg/L)
Seawater	65000 [54]	35.8 – 51.1 [55]
Desalinated seawater	650 [56, 57]	<4 [55]
US rivers (median)	35 [58]	0.5-212 [60]
US ground water	16 [59]	30 [61]

Current drinking water treatment schemes are challenged to effectively remove ambient bromide and iodide before final disinfection, in order to produce acceptable levels of the suspected carcinogen bromate [62], when using ozone or advanced oxidation processes [63], and brominated/iodinated DBPs when disinfecting with chlorine or chloramines [15, 52].

It is well known that bromide and iodide present in water may react differently with different disinfectants [64-67]. The kinetic rate constants of bromide and iodide with chlorine and chloramine in the formation of HOBr and HOI, respectively, are shown in Table 3.

Table 3: Rate constants for bromide and iodide oxidation by common disinfectants.

	Chlorine	Monochloramine
$\text{Br}^- \rightleftharpoons \text{HOBr}$	$1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [65]	$0.014 \text{ M}^{-1}\text{s}^{-1}$ [67]
$\text{I}^- \rightleftharpoons \text{HOI}$	$4.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [66]	$2.4 \times 10^{10} \times [\text{H}^+] \text{ M}^2\text{s}^{-1}$ [64]

The reaction of bromide with free chlorine is five orders of magnitude faster than with chloramine [67]. On the other hand, both disinfectants react relatively quickly with iodide ion [64, 66]. HOBr, formed from bromide, may then react with NOM and generate bromine-containing DBPs. In the presence of excess free chlorine, HOI is largely oxidized to iodate (IO_3^-), the desired sink for iodide, but in the presence of chloramines it is relatively stable, as shown by the relevant rate constants [42]. Therefore, in the presence of chloramines, HOI will react with certain organic precursors producing iodine substitution and the generation of iodinated analogues of many of the chlorine- and bromine-containing DBPs.

Table 4: Rate constants of HOI and HOBr reaction with common disinfectants.

	Chlorine	Monochloramine
HOBr	$2.95 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ [68]	$2.86 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ [69]
HOI	$52 \text{ M}^{-1}\text{s}^{-1}$ [42]	$<2.0 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ [42]

Although some brominated DBPs are regulated in the ADWG [22] (in particular; bromate, bromodichloromethane, dibromochloromethane and bromoform) the highly variable nature of NOM and its reactivity with different disinfectants means that there may be many other brominated and/or iodinated DBPs species formed in any given treated water in which these halides are present. Strategies for DBP minimisation vary, but can be broadly classified into three categories; DBPs precursor removal (halides and NOM), optimising disinfection to minimise DBPs formation, and DBPs removal prior to water distribution (for example, air-stripping of volatile DBPs such as THMs) [70]. One advantage that DBPs precursor removal has over other DBPs minimisation strategies is that it is not specific to removing/lowering a particular suite of DBPs, it can broadly minimise all DBPs, both known and unknown, potentially creating greater trust in the quality of the water produced. All disinfection methods produce their own suite of DBPs, however, minimising the precursors available for this to occur is applicable regardless of disinfection method employed. As water regulation becomes increasingly stringent and salinity impacted water sources are increasingly utilised, there may be a need for effective bromide and iodide removal to control the formation of emerging DBPs.

1.7. Techniques for Halide Removal from Water

The objective of bromide and iodide removal is to control the formation of brominated and/or iodinated DBPs (both organic and inorganic). Bromide and iodide removal techniques can be broadly classified into three categories, namely; membrane, electrochemical and adsorptive techniques.

1.7.1 Membrane Techniques

Over the past 50 years, membrane technologies have become a distinguished separation technology with significant commercial applications in the water industry. With increasing water demands and diminishing water supplies due to escalating populations, environmental degradation and climate change, membrane technologies are being employed to produce high quality potable water from impaired and alternative water supplies. Membrane techniques comprising reverse osmosis (RO),

nanofiltration (NF), ion exchange membranes, electrodialysis (ED) and electrodialysis reversal (EDR) are discussed in the following sections.

Reverse Osmosis

RO is a process whereby water is forced through a semi-permeable membrane under pressure to remove organic contaminants and salts, producing purified water (Figure 4). There are 2 main types of RO membranes; cellulose acetate and more recently thin-film composite membranes, each with differing water flux, rejection and physiochemical characteristics [71]. Most commercially successful RO membranes are thin-film composites with a top ultra-thin active filtration layer that consists most commonly of cross-linked polyamide (50-200 nm) but other polymers such as piperazine and others are employed as well. This thin layer is backed by an intermediate porous polysulfone support and a grid of polyester fibres to provide the desired mechanical stability [72]. Some membranes also have a surface coating that yields a more hydrophilic, neutral and fouling-resistant surface [73-76]. The active layer of RO membranes is the main barrier against the permeation of salt and contaminants which results from a combination of equilibrium partitioning at the water/active layer interfaces, and diffusive and advective transport [73, 76-80].

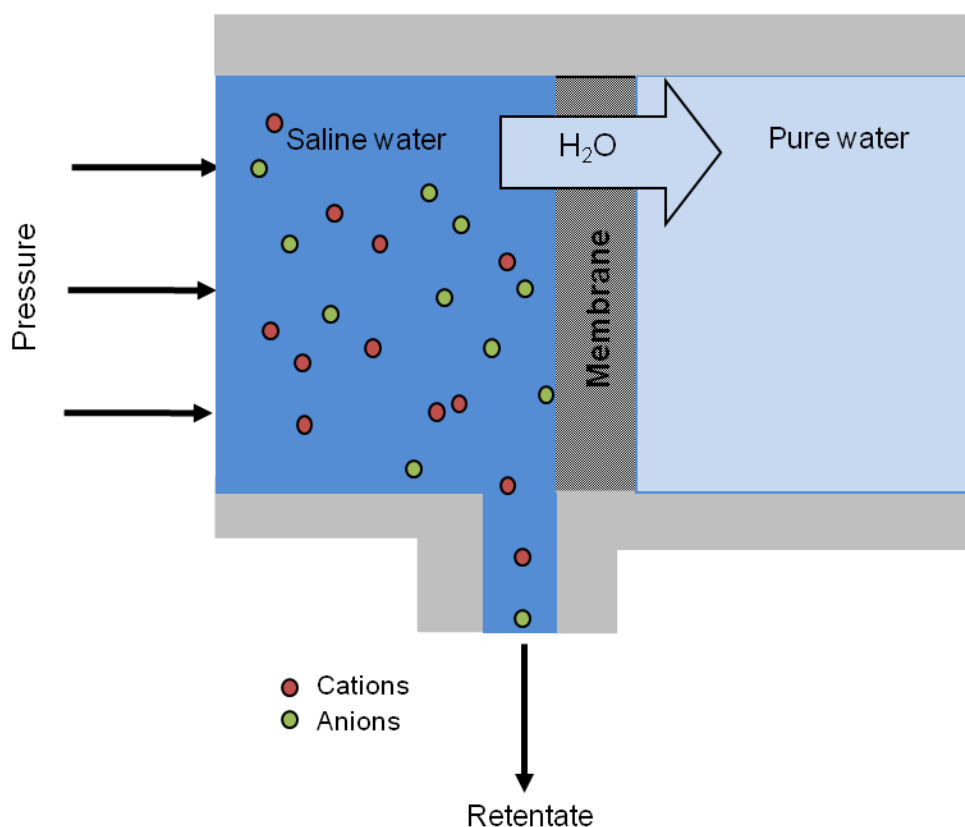


Figure 4: Schematic of the RO process. Note that while this illustrates the desalination process, other contaminants present in water including NOM and small organic molecules can also be rejected by RO membranes.

The broad spectrum of solute rejection of RO membranes allows the utilisation of seawater, brackish water and reclaimed water as alternative potable water sources [81, 82]. A comprehensive review of the early history of RO membrane development is available [83]. Recent developments in drinking water treatment applications of RO have been discussed by many including Greenlee *et al.* [84], Fritzmann *et al.*, [85], Pearce *et al.* [85], Veza *et al.* [86], Antrim *et al.* [87], Koutsakos and Moxey [88], Redondo and Lomax [89, 90], Wolf *et al.* [91], Vial *et al.* [92] and Laborde *et al.* [93].

RO membranes typically have a salt rejection of 98-99%, although several recently developed membranes can achieve 99.7-99.8% salt rejection under standard conditions [82, 94-101]. The current body of literature indicates that RO membranes reject monovalent halide ions to differing degrees. The rejection of ionic solutes by RO membranes has been observed to follow the Hofmeister series, that is, rejection increases with increasing hydrated radius. Ions with high hydration energy (determined by its hydrated radius and charge density) are superiorly rejected due to their low partition coefficient with the hydrophilic membrane [102, 103]. The halide rejection occurs in the following sequence: $F > Cl > Br > I$. This is identical to the order of decreasing hydration energy and decreasing hydrated radius of the ions.

A study by Magara *et al.* [57] investigating bromide removal from seawater using RO with spiral modules of aromatic polyamide, achieved over 99% bromide rejection. Similarly, several other studies of RO have found high bromide rejection, ranging from 93-99.3%, depending on the membrane used, and operating conditions [104-107]. Khan *et al.* found that RO membranes display a high rejection of iodide ions (71-90%) [106]. RO can reject over 89% of the total iodide from seawater [55]. The viability of several RO membranes in treating oilfield-produced brackish water for water reuse and iodide recovery has been investigated [108, 109]. The aromatic polyamide membranes were ranked according to the rejection of iodide as: Koch TFC-HR (92%) > Toray TMG-10 (87%) > Koch TFC-ULP (82%) > Dow/Filmtec XLE (80%). Furthermore, Koch TFC-HR, Koch TFC-ULP and Toray TMG-10 membranes rejected between 98 and 100% of both chloride and bromide ions [108]. Dow/Filmtec FT-30 membranes achieved 99.55% rejection of bromide at 2 MPa and 99.50% rejection of iodide at 5 MPa [110].

Table 5: Bromide and iodide rejection capacity for a number of RO membrane types.

Membrane	Type	Initial Anion Concentration		Competing Anions Present	Water Type*	Rejection Capacity		Pressure (kPa)	Flow Rate (L/min)	pH	Temp (°C)	Reference
		Br ⁻ (mg/L)	I ⁻ (mg/L)			Br ⁻ (%)	I ⁻ (%)					
SWC4+	Composite Polyamide	71	-	Y	N, SW	99.8	-	6480	63.2	7.9	20	[104]
SWC5	Composite Polyamide	64.4	-	Y	N, SW	99.34	-	5065	11933	8.0	25.1	[104]
SWC6	Composite Polyamide	64.4	-	Y	N, SW	99.34	-	5065	11933	8.0	25.1	[104]
SWC4+b	Composite Polyamide	71	-	Y	N, SW	99.8	-	6480	63.2	7.9	20	[104]
SWC6	Composite Polyamide	64.4	-	Y	N, SW	NS	-	5065	11933	8.0	25.1	[104]
Trisep X-20®	Composite Polyamide	>0.160	-	Y	N, WW	~ 90%	-	-	60–90	-	-	[106]
Multiple Tested	NS	-	0.0358 - 0.0511	Y	N, SW	-	89	-	-	7.1-7.6	26.1-38.5	[55]
TFC-HR	TFC® Polyamide	51.3	49.9	Y	N, OB	90.7	92	558.8	0.5	6	11±1	[108]
TMG-10	Cross Linked Fully Aromatic Polyamide Composite	51.3	49.9	Y	N, OB	100	87	558.8	0.5	6	11±1	[108]
TFC-ULP	Proprietary TFC® polyamide	51.3	49.9	Y	N, OB	100	82	558.8	0.5	6	11±1	[108]
XLE	Polyamide Thin-Film Composite (TFC)	51.3	49.9	Y	N, OB	-	80	558.8	0.5	6	11±1	[108]
FT30	Polyamide Membrane	3995	6345	N	SW	99.6	99.4	2000	-	6.8	25	[110]

*Water type – N = Natural water, SW = seawater, WW = waste water, OB = oilfield brines. '-' = data not available.

Table 6: Physical characteristics of the halide ions.

Halide	Atomic Weight	Electronegativity (Pauling Scale)	Molar Hydration Enthalpies (kcal/mol) [111]	Non-Hydrated Radius (Å) [112]	Hydrated Radius (Å) [112]
F ⁻	18.99	3.98	-98	1.16	3.52
Cl ⁻	35.45	3.16	-79	1.81	3.32
Br ⁻	79.90	2.96	-71	1.95	3.30
I ⁻	126.90	2.66	-62	2.16	3.31

RO is a proven technology for the removal of an extensive range of contaminants, and this was the most effective bromide and iodide removal technique of all investigated. Importantly, this technique can remove both organic and inorganic DBP precursors simultaneously making it invaluable in DBP minimisation. However, RO remains relatively expensive, requires extensive pre-treatment, has high energy consumption due to high operating pressures, and is susceptible to scaling, as well as brine disposal difficulties. The capital and operational expenses of RO as well as the disposal of the generated concentrate currently restricts the widespread application of this technique in drinking water treatment plants.

Nanofiltration

NF is a pressure driven membrane process, which is an intermediate between RO (non-porous diffusion) and ultrafiltration (porous-sieving) membrane processes, and exhibits features of both [113]. Compared to RO, NF generally runs at somewhat lower pressures, thereby reducing energy costs. It also has less resistance to the flow of both solvents and solutes [114-116]. Although there are many types of membranes, most applications of NF use polyamide thin-film composite membranes in a spiral wound configuration [82]. Like RO membranes, most NF membranes are charged, thus electrostatic interactions also influence the transport and selective rejection behaviour of NF membranes [113]. Consequently, depending on the molecular weight cut-off of the membrane, many NF membranes can effectively separate both NOM, small organic molecules (such as pesticides, pharmaceuticals and endocrine disrupting compounds) [117-125] and salts from water. Salts rejected include bromide and iodide ions, although in general, polyvalent ions may be more easily retained than monovalent ions [126-130].

Harrison *et al.* [131] investigated the ion rejection of two commercial NF membranes (NF-90 and NE-90) in a seawater desalination application (Table 7). The NF-90 membrane achieved 94-96% bromide rejection and 84-91% iodide rejection. Similarly, NE-90 membrane accomplished 94-97% bromide rejection and nearly 90% iodide rejection. The authors found that salt rejection generally increased with pressure, until their maximum rejection threshold was reached, beyond which the rejection started to decline with increasing pressure. This is to be expected and holds for all RO and NF membranes. A maximum rejection threshold for bromide was observed at 3.4 MPa. Anion rejection was not significantly affected by water temperature under the conditions tested.

Table 7: Bromide and iodide rejection capacity for a number of NF membrane types.

Membrane	Type	Initial Anion Concentration		Competing Anions Present	Water Type*	Rejection Capacity						Reference
		Br ⁻ (mg/L)	I ⁻ (mg/L)			Br ⁻ (%)	I ⁻ (%)	Pressure (kPa)	Flow Rate (L/min)	pH	Temp °C	
NF-90 (200 Da)	Polyamide TFC	1030	1	Yes	S	94-96	84-91	4000	1	7.8 - 9.8	20	[131]
NE-90 (200 Da)	Polyamide TFC	1030	1	Yes	S	94-97	~90	4000	1	7.8 - 9.8	20	[131]
NF70-2540 (180 Da)	Polyamide TFC	-	719.5	No	S	-	80	1200	-	-	-	[132]
NF45- 2540 (200 Da)	Polyamide	-	2538	No	S	-	56.785	NS	1.16	-	20	[103]
NF45-2540 (200 Da)	Polyamide	-	2538	No	S	-	56.785	NS	1.16	6	20	[133]
NF-70 (200 Da)	TFC polyamide film active surface	79.9	-	No	S	>93	-	2000	1.16	6.8	25	[110]
NF-90 (200 Da)	Polyamide TFC	51.3	49.9	Yes	N	80	78.3	1241 - 1275	0.5	6	25	[108]
TFC-S (200 Da)	Polyamide TFC	51.3	49.9	Yes	N	-	69.5	1241 - 1275	0.5	6	25	[108]
ESNA (200 Da)	Polyamide TFC	51.3	49.9	Yes	N	-	55.6	1241 - 1275	0.5	6	25	[108]

*Water type – N = Natural water, S= synthetic. '-' = data not available.

Lhassani *et al.* [132] investigated the selective demineralisation of water by NF with particular emphasis on monovalent anions. The study achieved a maximum rejection of iodide (80%) with NF70 membrane at a pressure of 1200 kPa. Although the membrane selectivity favoured chloride over iodide ion, it was demonstrated that this can be reversed at pressures over 800 kPa, thus showing that operating conditions can be adjusted to selectively remove individual ions of the same valence. Pontie *et al.* [103] and Diawara *et al.* [133] demonstrated that tight NF membrane NF-45 can selectively separate monovalent halides, following the Hofmeister series of halide ions: $F > Cl > I$. The membrane reflection coefficient and solute permeability were observed to be correlated with the hydration energy of halide ions. Tight NF-45 membrane was shown to have mass transfer properties similar to RO membranes.

NF membranes with a molecular weight cut off of 150-300 Da have been observed to reject up to 50% of bromide and bromate from low-turbidity source waters [58]. Prados-Ramirez *et al.* [134] saw a 63% rejection of bromide upon conducting NF on bromide-spiked river water. Pontié *et al.* [110] found NF-70 membranes reject approximately 94% of bromide at a pressure of 1.5 MPa. The study demonstrated that halide ions are transferred across NF membranes by two mechanisms; convective and solubilisation-diffusion. Pontié *et al.* [110] also demonstrated that under low pressure, retention of halide ions follow the Hofmeister series, however under high pressure, chloride and bromide order is inverted. Drewes *et al.* [108] investigated the salt and iodide rejection from oilfield-produced brackish water utilising three NF membranes: NF-90 (Dow/Filmtec), TFC-S (Koch) and ESNA (Hydranautics). The membranes were ranked according to the rejection of iodide, as: NF-90 (78%) > TFC-S (69%) > ESNA (55%). The NF-90 membrane rejected over 80% of both chloride and bromide [108]. In contrast, Listiarini *et al.* [135] and Chellam and Krasner [136, 137] found that NF was inefficient for bromide removal, however, the operating conditions investigated, including pressure, permeate flux, anion concentrations and water type, varied significantly from those used for successful applications of NF for bromide removal.

When compared to RO, NF has slightly lower capital costs, significantly lower operational costs due to lower operating pressures, can be operated at a higher water recovery, which means a smaller waste concentrate stream, while achieving comparable bromide and iodide removals [131]. Due to these advantages, the application of NF has increased, especially in industrial applications and drinking water treatment. This membrane technique still experiences (although to a lesser extent) the same limitations as RO. NF requires extensive pre-treatment, has medium to high energy consumption, and is susceptible to scaling and brine disposal difficulties. Again, like RO, NF has the advantage of having capacity to remove both organic (NOM) and inorganic (halide) DBP precursors simultaneously.

Electrodialysis and electrodialysis reversal

The ED process uses a driving force of direct current (DC) to transfer ionic species through cell pairs of oppositely charged membranes, allowing their separation from the source water (Figure 5) [50, 138]. The degree of salt removal is directly proportional to the current and inversely proportional to the flow rate through each cell pair [139]. Thus, hydraulic and electrical staging are used to achieve the desired salt removal. The hydraulic and electrical staging in the membrane stack array configuration used in ED water treatment systems is determined by the source water quality and the level of water quality required [50]. Membranes are composed of a polymer matrix with charged groups attached, with pores that allow ions to permeate. EDR is a modification of the ED process, where electrode polarity is periodically reversed during the treatment process to reduce scaling and clean membrane surfaces [50, 138]. EDR has been successfully used for desalination, waste treatment, treatment of boiler feed and process water, and hardness removal, providing a reliable and economical alternative to RO of brackish waters [140, 141]. The EDR process is used as a 'finishing' treatment for desalting brackish water with TDS concentrations of up to 4000 mg/L. After 4000 mg/L the energy costs dramatically increase, reducing its competitiveness with other membrane techniques such as RO [142]. The halide rejection of ED and EDR has been summarised (Table 8).

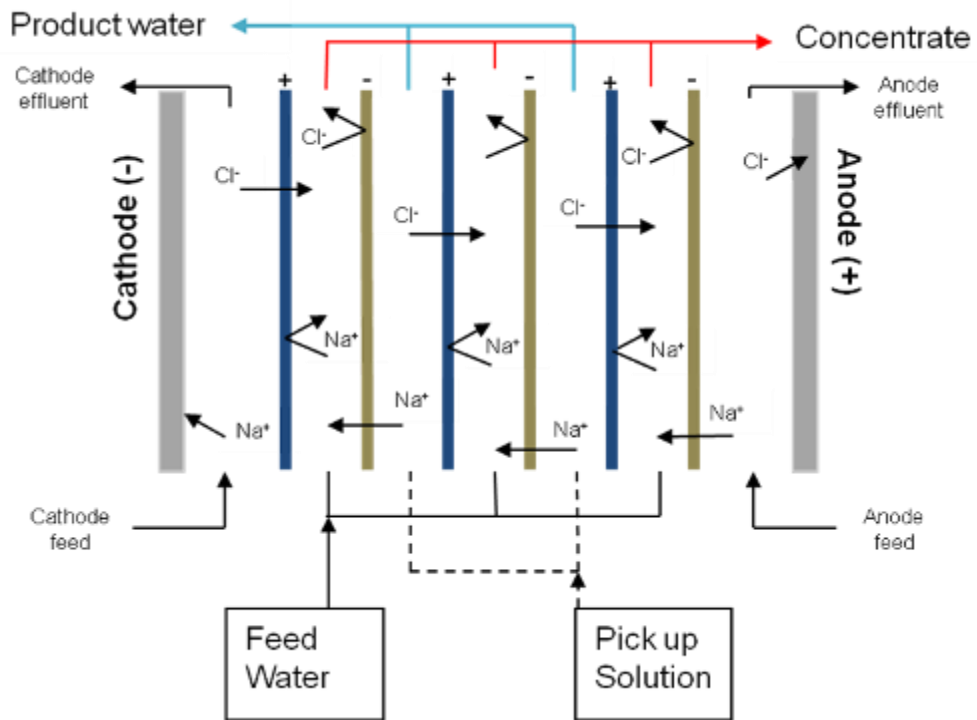


Figure 5: Schematic of the ED process (example using NaCl solution).

Table 8: Parameters and halide rejection capacity for ED/EDR techniques.

Exposure Time (h)	No. of Cell Pairs	Membrane Type	Initial Anion Concentration		Competing Anions Present	Water Type*	Halide Rejection Capacity		Current (V)	Flow Rate (L/min)	Water Recovery (%)	pH	Temp (°C)	Reference
			Br ⁻ (mg/L)	I ⁻ (g/L)			Br ⁻ (%)	I ⁻ (%)						
0.5-1	600	Mark III to Mark IV type	0.5-1.2	-	Yes	N	75-80	-	-	138000	90-94	6.5-7.3	25	[143]
-	250	AR204-SZRA and CR67-HMR	0.185	-	Yes	N	72	-	180-190	233.3	92-93	7.6	25	[140]
12	2	DE81	-	1.2 -12.7	No	S	-	92-97	-	-	-	-	25	[144]

*Water type – N = Natural water, S= synthetic. '-' = data not available.

Recently, Valero and Arbós [143] conducted a 28 month pilot plant study of EDR, as well as a study of the implementation of EDR in Llobregat's desalination drinking water treatment plant (DWTP) in Barcelona, Spain. The pilot plant study utilised the same source water as is treated at Llobregat's DWTP. Anthropogenic activities severely impact the quality of this source water, which consequently has substantial concentrations of salts, NOM and micropollutants, causing elevated concentrations of DBPs during the drinking water treatment process ($160 \pm 40 \mu\text{g/L}$ THMs). EDR was incorporated into the water treatment system after GAC treatment, in both pilot and full-scale studies. On average the pilot study achieved over 75% bromide, 60% chloride, 65% electrical conductivity (EC), 58% total alkalinity (TAC), 30% TOC, 75% NO_3^- , 70% SO_4^{2-} , 80% Ca^{2+} , 70% K^+ and 80% Mg^{2+} reduction, while maintaining over 90% water recovery. The improved chemical quality of the water resulted in a decrease in tTHMs formation potential (THM-FP) to $64 \pm 60 \mu\text{g/L}$, which was below the regulated concentration of $100 \mu\text{g/L}$. During the trial the systems' performance was highly robust and reliable with no operational problems experienced [143]. Llobregat's DWTP (with full-scale application of EDR) has the capacity to produce an average of $200,000 \text{ m}^3/\text{day}$, making it the world's largest desalination plant using this technology. The plant obtained water quality parameters and THM-FP consistent with the pilot study values. Optimisation of the plant achieved a maximum of 80% bromide and 80% EC reduction, while maintaining over 94% water recovery. Furthermore, Valero and Arbós showed EDR treatment allows the control of THM speciation as a result of Br^- removal, resulting in a reduction of brominated species in favour of chlorinated species.

Van der Hoek *et al.* [140] investigated the possibilities of applying EDR as an alternative for RO filtration in three integrated membrane systems (IMS) that use ozone for disinfection. The IMS-1 system used pre-treated (coagulation/sedimentation/filtration) Rhine River water and further treated sequentially with ozonation, biologically activated carbon filtration, slow sand filtration and RO; IMS-2 treatment was the same as IMS-1, however the RO step was replaced with an EDR step; IMS-3 took pre-treated Rhine River water then treated sequentially with EDR, ozonation, biologically activated carbon filtration and slow sand filtration. IMS-1 and IMS-3 were able to achieve compliance with bromate regulation, however, IMS-2 could not. IMS-3 reduced bromide concentrations by 72% (prior to the disinfection step), thus reducing bromate formation to $5 \mu\text{g/L}$ after ozonation [140], in compliance with the European Union drinking water standard [145]. The authors found IMS-3 (using EDR) had lower energy and chemical consumption and thus lower operational costs when compared to IMS-1 (using RO) however, RO provided a dual barrier for disinfection and removal of organic compounds such as NOM and pesticides, which is an advantage over the EDR process [140]. EDR membranes AR204-SZRA (anion) and CR67-HMR (cation) both manufactured by Ionics were used in this study.

Permselectivity of ions is determined by ion exchange selectivity and mobility selectivity (steric and membrane density effects) with a membrane [146]. Generally, ions with higher valence and a smaller hydrated radius have a higher permeability in an ion exchange membrane than ions with lower valence and larger hydrated radius. Hann *et al.* [147] found the permselectivity counterion exchange sequence of an anion-exchange membrane containing quaternary ammonium groups as fixed charges was: $\text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$. Sata and colleagues have also conducted several studies on the effect of hydrophilicity of anion-exchange membranes on the permselectivity of specific anions in ED [148-151]. The group showed that permselectivity of specific anions is mainly dependent on the balance between hydration energy of anions with hydrophilicity of the membranes. Specifically, the more hydrophobic membranes have a higher permselectivity for less hydrated (higher hydration energy) ions. In keeping with this, increasing hydrophobicity of the strongly basic anion-exchange membrane enhanced the permeation of bromide and iodide, while decreasing the permeation of fluoride ions. As expected, increasing the hydrophilicity of the membranes reversed this trend.

Inoue *et al.* has carried out several investigations into the removal of radioactive iodide ion (^{125}I) from wastes using ED with anion-exchange paper membranes [144, 152-156]. These membranes were found to be electroconductively more permeable to iodide than to chloride ions, allowing iodide to be concentrated from the feed stream [144]. In a further project, covalent linking of glucose and urea to membranes was reported to increase the membrane/solution distribution of iodide, however the diffusion process of iodide within the membrane was not significantly altered, relative to the

unmodified membrane [153]. Inoue *et al.* also worked on membrane separation control using three different anion-exchange groups bound to a pulp/cellulose fibre matrix: trimethylhydroxypropylamino, diethylaminoethyl and 50% saturated quaternary diethylaminoethyl [154]. It was observed that the membrane permeability for iodide was higher than chloride in all three cases. Notably, trimethylhydroxypropylamino groups improved the iodide diffusion process, whereas 50% quaternary diethylaminoethyl groups improved the iodide solution/membrane distribution process. High iodide permselectivity was achieved in membranes with the trimethylhydroxypropylamino quaternary amine anion-exchange group, due to electrostatic effects [155, 156].

Relative Advantages and Disadvantages of the Membrane Techniques

The ED/EDR processes are not commonly used in drinking water treatment plants although examples of successful implementation do exist [143, 157]. The main advantages of ED compared to other membrane techniques are; minimal pre-treatment of feed water is required, higher water recovery can be achieved than for RO, although process recoveries for EDR should be similar to NF [50]. EDR membrane life would be expected to be higher than RO membrane life (7-10 years for EDR membranes versus 5-7 years for RO membranes) [50]. EDR has several technical and economic limitations, including high energy consumption and high capital cost [158]. ED/EDR has the potential to be widely applied to brackish and anthropogenically-impacted waters to enable the utilisation of alternative sources of water, however, more research is needed in the membrane development and in the optimisation of ED/EDR for large scale drinking water treatment plants. A limitation of ED/EDR processes is that unlike RO and NF, they do not remove neutral, organic DBP precursors, they exclusively remove ionic species, i.e., hardness, halides, and other salts. Therefore, the use of this technology without an additional organic matter removal step may decrease the level of bromination/iodination of organic DBP precursors during disinfection, but may not decrease the total concentration of DBPs formed. Furthermore, ED and EDR do not provide any disinfection, unlike NF and RO, however, these techniques can be used in the presence of a chlorine residual, thereby enabling disinfection and reducing biological fouling of membranes.

1.7.2 Electrochemical Techniques

Electrochemical techniques have been successfully used to remove contaminants from various industrial wastewaters and environmental waters [159, 160]. Electrochemical techniques comprising electrolysis and capacitive deionisation (CDI) are briefly discussed in the following sections.

Electrolysis

Electrolysis is a process that uses the passage of an electric current through a solution to induce chemical decomposition [161]. Historically, electrolysis processes have been used to produce bromine from brines containing bromide [162-164]. Kimbrough and Suffet [162] examined the feasibility of using electrolysis to remove bromide from drinking water sources (Table 9). Carbon rod cathodes and dimensionally stable anodes (DSA) were used in the electrolysis cell. Electrolysis of raw water oxidised bromide to a mixture of hypobromite, hypobromous acid and bromine gas. Degassing this solution with carbon dioxide caused a decrease in the solution pH, driving the conversion of hypobromite to hypobromous acid, which was then volatilised, along with bromine gas, leading to a decrease in the solution concentration of bromide. The rate of bromide removal is dependent on the applied current and effectiveness of air stripping. Upon chlorination the electrolysed water produced lower THMs concentrations and decreased the proportion of brominated THMs formed. The authors suggest that the removal of bromide should also reduce the formation of other brominated DBPs.

Table 9: Parameters and bromide oxidation capacity of electrolysis methods.

Br ⁻ (mg/L)	Competing Anions Present	Water Type*	Br ⁻ Oxidation Capacity (%)	Flow Rate (L/min)	Contact Time (s)	Current	pH	Temp (°C)	Reference
0.200	Yes	N	>99	0.420	240	700 mA	-	-	[162]
0.461	Yes	S	79	-	39	14 mA/in ²	~7.5	-	[165]

Note: iodide was not included in these studies.

*Water type – N = Natural water, S= synthetic. '-' = data not available.

An electrolytic process that combines disinfection with the removal of bromide from raw water was patented by Bo [165]. Electrolysis cells used silver cathodes and DSA arranged in parallel fashion. During electrolysis chloride was oxidised to chlorine gas, providing disinfection, while bromide ions were oxidised to bromine gas which volatilised without requiring stripping. High bromide removal efficiency is achieved due to the high silver conductivity and large electrode surface contact area coupled with several passes of the solution through the electrolysis cell. The effectiveness of this process is dependent upon the chloride:bromide ratio, the magnitude of the electrical current, ionic strength of the water, distance between electrodes, water residence time in the cell and electrode material. Bromide removal efficiency decreased with lower influent bromide concentrations. At low bromide concentrations (<125 µg/L) the process achieved between 48%-62% removal, but at high bromide (>200 µg/L) concentrations bromide removal increases to between 47%-79%. Brominated THMs concentrations (generated by THM-FP) were reduced by 27% after the initial bromide concentration was reduced from 461 µg/L to 48 µg/L during the treatment. This reduction in Br-THMs may be expected to be greater, given the excellent bromide removal reported, however, the authors report losing chlorine residual during the THM FP of the high bromide sample, so they may not have formed a maximum of Br-THMs during the experiment. Additionally, several electrolysis processes that remove bromide by producing bromine gas from different aqueous sources, including brines, bittern and waste effluents have been patented [166-175].

Although electrolysis has been shown to remove bromide reasonably on a small scale the feasibility of large scale application to drinking water treatment has not been assessed. Further development of electrodes would be required as part of working toward larger scale treatment.

Capacitive Deionisation

CDI is a recently developed electrolysis technology for removing ionic species from aqueous solutions using porous activated or aerogel carbon electrodes (Figure 6) [176, 177]. The deionisation process occurs by an induced electrical potential difference across an aqueous solution, which flows in between oppositely charged porous electrodes. As a result of the applied electrical potential, ions are adsorbed in the electrodes, deionising the product stream [178]. Although CDI technology is in its infancy, it has the potential to develop into a feasible low-cost alternative to membrane and thermal desalination of brackish waters (Table 10) [179-181]. The CDI process operates at ambient conditions of temperature and pressure, requires minimum pre-treatment, does not require chemicals for scaling control or chemical cleaning, has low voltage requirements and a low fouling/scaling potential [179]. The adsorption capacity of carbon aerogels is dependent upon the surface characteristics of the electrodes, including; surface area, size and microstructure of pores, electrical conductivity, chemical composition and electrical double-layer capacity [176, 177, 182]. Halides are usually removed from solution by electrostatic attraction within the electrode, whereas large polyvalent oxyanions, heavy metals, and colloidal impurities can be removed by means of chemi/physorption, electrodeposition, electrophoresis, double-layer charging and possibly faradaic reactions, as well as simple electrostatic interactions [182, 183]. Electrode polarity is reversed after saturation to regenerate carbon aerogel electrodes [180, 181, 184].

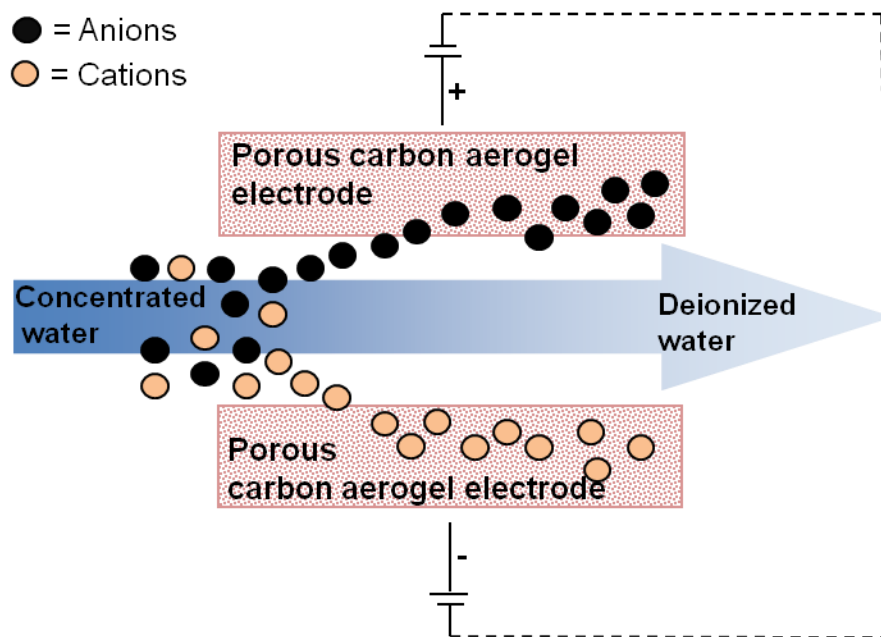


Figure 6: Schematic showing the capacitive deionisation (CDI) process.

Table 10: Parameters and halide removal capacity from CDI studies.

Initial Anion Concentration				Halide Removal Capacity						
Br ⁻ (mg/L)	I ⁻ (mg/L)	Competing Anions Present	Water Type*	Br ⁻	I ⁻	Flow Rate (mL/min)	Current (V)	pH	Temp (°C)	Reference
399.5	-	No	S	0.13 and 0.18 mmol/g [#]	-	100	1.4	7	-	[176]
79.9	126.9	No	S	0.059 mmol/g [#]	0.063 mmol/g [#]	10	1.2	-	25	[177]
191.8	304.56	No	S	0.108 mmol/g [#]	0.154 mmol/g [#]	10	1.2	-	25	[177]
50.3	49.5	No	S	50%	69.7%	250	1.3		23	[179]
~75	~30	Yes	N	62.5%	77%	560	1.3	7.5-9.1	23	[179]
0.36	-	Yes	S	86.11%	-	50	1.3	-	-	[180]

*Water type – N = Natural water, S= synthetic. ‘-’ = data not available.# Percent removals not available.

Gabelich *et al.* [176] and Ying *et al.* [177] report that an ion's hydrated radius may regulate the ionic species' sorption capacity into carbon aerogel electrodes. Monovalent ions with smaller hydrated radii were preferentially removed from solution over multivalent ions. Additionally, counterion valency appears to have a strong influence on an individual ion's sorption capacity [176]. Experiments conducted with natural waters showed the sorption capacity of carbon aerogels was significantly lower when a high concentration of NOM was present. The authors suggest pre-treatment for NOM removal would increase effectiveness of CDI in treating natural waters [176]. CDI was found to increase in total capacity for anion removal in the order of $\text{Cl}^- < \text{Br}^- < \text{I}^-$, thus this technique could be used most effectively to selectively recover iodide from solutions [177]. Ying *et al.* [177] theorised this effect was due to iodide ions having a partial charge-transfer coefficient larger than bromide and chloride ions. The adsorption capacity of the carbon aerogel electrodes was shown to increase with increasing solution concentration of ionic species, voltage, and surface area of the electrodes. Due to its selectivity, this technique has the potential (with further development) to be applied in the removal of halides from drinking water sources.

Welgemoed and Schutte [180] developed an industrial CDI bench scale prototype (MK-8A) and evaluated the module's performance for coal-bed methane brackish water desalination. The module achieved high ionic species reduction in artificial brackish water, reducing the feed stream conductivity from 1000 $\mu\text{S}/\text{cm}$ to 23.4 $\mu\text{S}/\text{cm}$ at a flow rate of 50 mL/min. Interestingly, in the artificial system bromide had the highest reduction percent of all ions monitored (86.11%). The prototype was then tested on naturally occurring brackish water from the natural gas industry in Wyoming, USA. It reduced the feed stream conductivity from 2095 $\mu\text{S}/\text{cm}$ to <1000 $\mu\text{S}/\text{cm}$ at approximately 70% water recovery rate. Rinse brine was recycled, reducing the volume of waste brine produced. Furthermore, the authors compared the costs of RO, EDR and CDI for brackish water desalination to a potable water standard. CDI could be significantly cost effective compared to RO for brackish water applications (CDI: US\$0.11/1000 L, RO: US\$0.35/1000 L). CDI could also reduce brackish water desalination costs by 70% when compared to existing EDR technologies. A water recovery rate of 70% while still retaining quite a high conductivity (2095 $\mu\text{S}/\text{cm}$ to <1000 $\mu\text{S}/\text{cm}$) is, however, quite inferior to what could be achieved with RO, i.e. organic precursor removal and disinfection, as well as halide removal.

The viability and ion selectivity of CDI technology in treating brackish water generated during natural gas mining for water reuse and iodide recovery has been investigated [179]. CDI testing units used in this study were provided by CDT Systems, Inc. The anion sorption capacity of the carbon aerogel (in mol/g aerogel) was dependent upon initial ion concentrations in the feed water. That is, the ions present in the greatest concentration were adsorbed to a greater extent, following the order $\text{Cl}^- \geq \text{Br}^- > \text{I}^-$. However, the maximum percentage of removal for these anions followed the opposite trend; $\text{I}^- > \text{Br}^- > \text{Cl}^-$, which the author's attributed to iodide's higher partial charge-transfer coefficient compared to the other anions, and intermolecular interactions with the carbon-aerogel electrodes, resulting in a higher sorption capacity. In concurrence with the findings of Ying *et al.* [177], bench scale tests showed preferential sorption of iodide from brackish water even in the presence of dominant coexisting ions. The removal of iodide reached 69% and removal of bromide reached 50% in artificial water [179]. During the regeneration phase, 77-107% of sorbed iodide was recovered from the carbon aerogels (a recovery >100% was attributed to the desorption of iodide from the previous run). The authors found bench scale and pilot scale CDI cells exhibited similar sorption capacities. During the pilot study the maximum removals observed were 83% of UV_{254} , 77% of I^- , 62% of Br^- , 40% of Ca^{2+} , 40% of alkalinity (as CaCO_3), 34% of Mg^{2+} , 18% of Na^+ and 16% of Cl^- . However, field experiments employing a three stage CDI treatment could not meet the water quality standards for reuse due to high total dissolved solids (TDS) concentrations. To resolve this issue additional CDI stages were applied to simulate a multi-stage desalination treatment. Ten CDI stages were needed to reduce TDS to an acceptable level for reuse.

Shiue *et al.* [185] have enhanced the efficiency of CDI by using spiral wound electrodes (activated carbon coated on titanium foil) in combination with online electrolytic ozonation. This allows the reduction of uncharged constituents and disinfection of water by ozone, in addition to the removal of charged species by CDI. Ozone was produced by low-voltage electrolysis of water. The electricity

retrieved at the discharging of CDI operation could be harnessed for use in producing ozone, thus increasing energy efficiency.

CDI technology is a promising alternative for brackish water desalination, although the operational performance and sorption capacity of the electrodes may need further development before the technology becomes economically feasible [179].

Membrane Capacitive Deionisation

Membrane Capacitive Deionisation (MCDI) is a modification of the CDI process, in which ion-exchange membranes are added onto a CDI system (Figure 7) [186, 187]. Ion-exchange membranes are positioned in front of their corresponding charged electrodes. MCDI has several advantages over CDI namely; the membranes inhibit ions from leaving the electrode region, thereby increasing the salt removal efficiency of the process, and ion release from the electrode region (during electrode regeneration) is more efficient [186]. Both Lee *et al.* and Li found that MCDI had a higher salt removal rate than traditional CDI systems, with 19% and 49% higher rejection found, respectively [187, 188]. Although no specific studies on bromide and iodide removal were found using this process, MCDI would be expected to produce improved halide removal efficiency to that experienced with CDI, and is thus an area of potential future research.

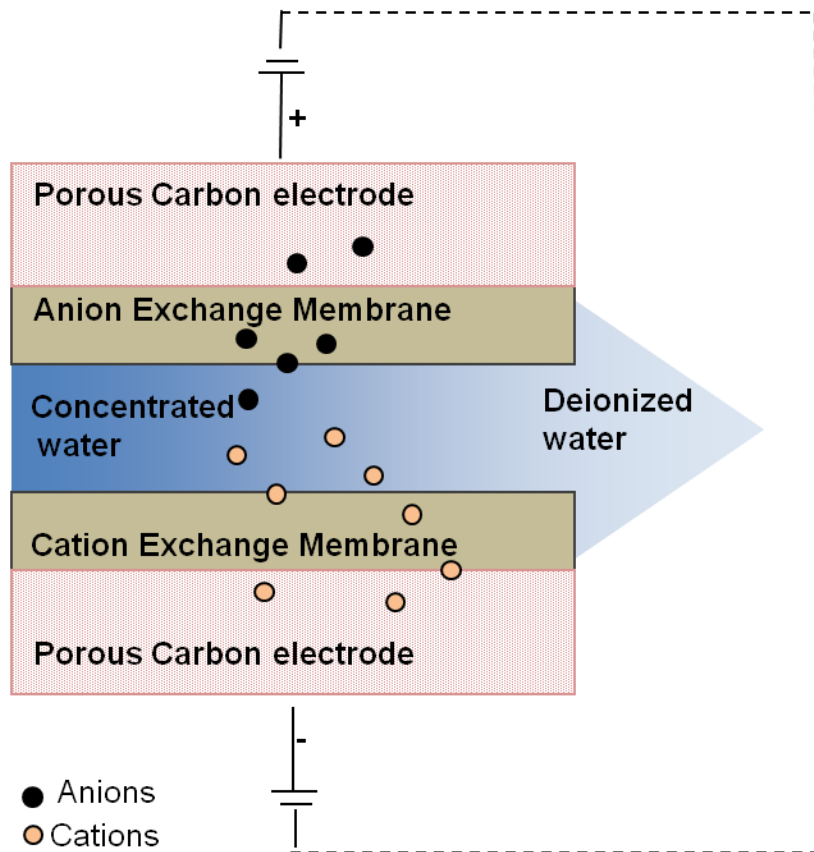


Figure 7: Schematic showing the membrane capacitive deionisation (MCDI) process.

Relative Advantages and Disadvantages of the Electrochemical Techniques

The CDI and MCDI processes are not currently used in the treatment of drinking water. The CDI process is both robust and energy efficient, although MCDI may be expected to be able to remove halides with greater efficiency than CDI. With further development CDI has the potential to be applied to drinking water, wastewater, boiler water and coal seam gas water deionisation, as well as brackish water desalination [178]. Conversely, the potential for large-scale application of electrolysis to halide removal during water treatment may be limited, due to difficulties in scaling up the process, although this has not yet been explored. Areas in which further development would be expected prior to widespread use of CDI technology are related to the optimisation of deionisation, commercial development of aerogels, full scale application and commercialisation of the technique.

1.7.3 Adsorption Techniques

Although membrane techniques can successfully reduce bromide and iodide concentrations in water, surface sorption methods form a major component of halide reduction research and application because of their ease of application and low cost. Recent research has continued to explore the development of low cost, effective, bromide and iodide adsorbents. Sorption techniques comprising; hydrous oxides, activated carbons, silver-doped activated carbons and carbon aerogels, ion-exchange resins, aluminium based adsorbents and soils, are briefly discussed in the following sections.

1.7.3.1 Hydrous Oxides

Layered Double Hydroxides

Layered double hydroxides (LDHs) (also called hydrotalcite-like compounds (HTCs)) are attracting considerable attention for their ability to selectively remove contaminants in aqueous systems [189-200]. LDHs consist of positivity charged metal hydroxide layers, with interstitially located anions and water molecules [197, 201, 202]. They have large surface areas and numerous sites for anion exchange, making them ideal ion-exchangers and adsorbents. Additionally, LHDs are produced from low-cost precursors that can be easily regenerated [190, 197, 198]. A summary of studies investigating halide removal using LDH's is reported (Table 11).

Curtius and Kattilparampil [210] studied the application of Mg-Al-Cl LDH for ^{135}I removal from radioactive wastes. It was found that the adsorption of iodide was independent of pH between 3.5 and 8.5. In the test parameters studied the sorption capacity for iodide decreased with increasing chloride concentrations. A Kentjono *et al.* [203] study using Mg-Al-(NO₃) LHD found that the optimum pH for iodide removal was 9.0–9.2. The maximum iodide adsorption capacity achieved was 10.1 mg/g at a LDH dose of 20 g/L and pH of 9.2. The optimum pH for iodide adsorption coincides with that of boron adsorption, however they do not compete with each other's adsorption, indicating that this LDH could be used to simultaneously remove both boron and iodide. The iodide removal capacity of thiosulfate intercalated Zn-Al LDH has been reported by Thomas and Rajamathi [204]. Approximately 60% of iodide ions were intercalated in the interstitial layer of the LDH, making it a potentially useful treatment for the removal of iodide from drinking waters.

Table 11: Summary of parameters for halide adsorption studies using LDHs.

LDH Type	Initial Anion Concentration		Water Type*	Competing Anions Present	Halide Removal Capacity						Reference
	Br ⁻ (mg/L)	I ⁻ (mg/L)			Br (%)	I ⁻ (%)	Adsorbent Dose (g/L)	Time (h)	pH	Temp °C	
Mg-Al-(NO ₃)	-	342	N, WW	Yes	-	59	20	4	9.2	25	[203]
Zn-Al	-	330	S	No	-	60	-	-	7	-	[204]
Mg-Al	100	-	S	No	27.5	-	1	24	-	30	[205, 206]
Mg-Al (molar ratio of 2)	-	100	S	No	-	35	1	-	-	30	[205, 206]
Mg-Al (molar ratio of 3)	-	100	S	No	-	88.4	1	-	-	30	[205, 206]
Mg-Al (molar ratio of 4, calcined at 500°C)	100	100	S	No	94	96.1	1	24	-	30	[205, 206]
Cu ₆ Al ₂ (OH) ₁₈	-	1	S	Yes	-	9600 mL/g [#]	10	24	-	25	[207]
Cu ₆ Cr ₂ (OH) ₁₈	-	1	S	Yes	-	4,200 mL/g [#]	10	24	-	25	[207]
Cu ₆ Ga ₂ (OH) ₁₈	-	1	S	Yes	-	1,700 mL/g [#]	10	24	-	25	[207]
Mg-Fe	0.2	-	N	Yes	60	-	10	0.16	~7-8	-	[208]
Mg-Al-Fe	0.2	-	N	Yes	60	-	10	0.16	~6.5-7.5	-	[208]
Zn-Al	-	1269	S	Yes	-	14	10	48	6	-	[209]

*Water type – N = Natural water, S= synthetic, WW = waste water. ‘-’ = data not available. #Adsorption coefficient (Kd) reported, percent removals not available.

The Lv group investigated the influence of LDH calcination temperatures and the Mg:Al molar ratio on the adsorption of bromide from water by Mg-Al LDHs [205, 206]. The bromide and iodide adsorption capacity of calcined LDHs is higher than that of uncalcined LDHs. Adsorption capacity of bromide and iodide increased with increasing calcination temperature between 200 °C and 500 °C, however it drastically decreased with calcination temperatures from 500 °C to 800 °C. A maximum bromide and iodide adsorption capacity of 94.0 mg/g and 96.1 mg/g, respectively, was achieved with LHD calcination at 500 °C. It was found that a Mg:Al molar ratio of 4 had the highest capacity to remove bromide and iodide from aqueous solution. Additionally, the group found that increasing adsorbent concentrations from 0.2 g/L to 1.0 g/L significantly increased bromide removal from 73.4% to 91.6%, after which the removal plateaus off to a maximum of 94% using 5 g/L [205]. Similarly, adsorbent concentrations from 0.2 g/L to 1.0 g/L significantly increased iodide removal from 39.4% to 96.5%, after which the removal plateaus with a maximum of 97.6% using 4 g/L [206]. LHDs maintained similar bromide removal capacities after five regeneration cycles [205, 206].

A preliminary study on the effect of layered hydroxides metal composition on iodide sorption was conducted by Pless *et al.* [207]. Uncalcined layered hydroxides containing Cu^{2+} exhibited the highest sorption for iodide, followed by Ni^{2+} and Co^{2+} . The authors found calcination decreased the sorption of iodide, however calcination temperatures were only 550°C for 1 or 24 hours and only a limited number of layered hydroxides were tested.

Echigo's group investigated the removal of bromide from a real water matrix by LDH's to control the formation of brominated DBPs in the drinking water treatment process [208]. Two LDH's, Mg-Fe-LDH (ratio 4:1) and Mg-Al-Fe-LDH (ratio 8:1:1) were compared to a commercially available gel-type polystyrene-divinylbenzene quaternary amine anion-exchange resin; Diaion SA10A. An approximately 60% reduction in bromide using a real water matrix was achieved using both LDH's, whereas an approximately 73% reduction in bromide was achieved with the Dianion resin. The LDH's selectivity sequence was shown to be $\text{HCO}_3^- \gg \text{NO}_3^- > \text{Br}^- > \text{SO}_4^{2-}$ and hence LDH's were found to be better for bromide removal in a water matrix with high sulfate ion and low bicarbonate and nitrate concentrations due to their selectivity for bromide under these conditions and faster ion exchange reactions in comparison to Diaion SA10A. However, in the presence of bicarbonate, bromide removal was impaired due to the LDH's preferential adsorption of this anion rather than bromide. This may limit the extent to which these LDH's could be used in bromide removal from drinking water sources, since they would not be expected to be useful under high bicarbonate conditions. Organic carbon (measured as TOC) was not removed by either LDH, indicating it was rejected by the ion-sieve effect of the LDH's. This is important since organic carbon comprises many DBP precursors, so although bromide may be efficiently removed (in low alkalinity conditions), the organic DBP precursors would be expected to remain. The performance of LDH's was found to be comparable to Diaion SA10A in terms of the treatment volume and the bromide uptake before breakthrough for low alkalinity waters. The authors conclude that the application of LDH in the drinking water treatment process would provide similar performance to organic resins such as Dianon SA10A without the potential for secondary contamination.

A Zn-Al LDH adsorbed approximately 14% of iodide from a deionised solution but almost none from a mineralised solution containing 1 mM Cl^- , 15 mM SO_4^{2-} , and 5 mM HCO_3^- at an initial KI concentration of 0.01M at both pH 7 and 10 [209]. Thus, in a multi-ion solution LDH exhibited preferential selectivity of bicarbonate and sulfate over iodide, in agreement with several other studies [209, 211, 212]. The usefulness of LDHs for halide removal from water is therefore dependent on the nature of the other anionic species present in solution.

Despite this limitation, LDHs have been shown to effectively remove bromide and iodide from real water matrices. Several LDHs' anion sorption performance was comparable to commercially available resins in terms of the treatment volume and anion adsorption before breakthrough. Additionally, ion exchange reactions were shown to be faster using LDH's than commercial ion-exchange resins, and no concerns about secondary contamination when using LDH's have been raised, unlike many commercial ion-exchange resins. The preferential adsorption of bicarbonate over bromide ions, and both sulfate and bicarbonate over iodide ions, for particular LDH's is an important limitation,

however, further investigation into the large scale application of promising LDH's is warranted, given they are a prospective low-cost treatment technology, which has the potential for widespread application in drinking water treatment.

Sol-Gel Double Hydrous Oxide

In a recent development, the sol-gel method was used to synthesise an inorganic ion exchanger based on a double hydrous oxide ($\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) [213]. Adsorption behaviour of fluoride, chloride, bromide, and bromate ions was investigated by varying experimental parameters including time, pH and adsorbant concentrations. The ion exchanger exhibited both cation and anion-exchange capacity, which reached values of 1.38 and 1.8 mEq/g, respectively. Adsorption of selected anions was observed over the pH range 3 - 8.5, with maximum bromide adsorption occurring at $\text{pH} < 5$. Kinetic data on bromide sorption fit a pseudo-second-order model, with a rate coefficient of 0.16 min^{-1} . Within the first 10 min of treatment 50% of the bromide ions were adsorbed. The maximum bromide sorption capacity achieved was 80 mg/g at bromide concentrations of 200 mg/L (Table 12). Investigation into competitive adsorption of Br^- and BrO_3^- at equal concentrations found that at concentrations over 40 mg/L bromide and bromate, competition for adsorption sites favoured bromide, whereas for lower concentrations of bromide and bromate, bromate dominated adsorption. A number of other novel sol-gel double hydrous oxides have recently been developed, and have been shown to have bromide removal capability [214].

Further investigation into the ion-exchange interactions with organic matter and complex water matrices under field conditions is needed before the suitability of these adsorbents for drinking water treatment can be more thoroughly evaluated. Further research should also include the development and study of new types of sol-gel double hydrous oxides.

Table 12: Summary of halide adsorption studies using sol-gel double hydroxides.

Type	Initial Anion Concentration		Competing Anions Present	Halide Removal Capacity		Time (h)	pH	Temp (°C)	Reference
	Br ⁻ (mg/L)	Water Type*		Br ⁻ (%)	Adsorbent Dose (g/L)				
Fe ₂ O ₃ ·Al ₂ O ₃ ·xH ₂ O	120	S	Yes	80	2	48	-	<u>22</u>	[213]
Mg–Al-(3a-1)–NaC	198.2	S	Yes	75.7	2	-	4.5	<u>22</u>	[214]
	198.2	S	Yes	13.1	2	-	8.5	22	
Mg–Al-(3a-1)–N	198.2	S	Yes	66.6	2	-	4.5	<u>22</u>	[214]
	198.2	S	Yes	77.7	2	-	8.5	22	
Mg–Al-(3a-1)–KC	198.2	S	Yes	78.7	2	-	4.5	<u>22</u>	[214]
	198.2	S	Yes	-	2	-	8.5	22	
Mg–Al-(3b)–NaC	198.2	S	Yes	13.1	2	-	4.5	<u>22</u>	[214]
	198.2	S	Yes	12.1	2	-	8.5	22	
Mg–Al-(3b)–N	198.2	S	Yes	14.1	2	-	4.5	<u>22</u>	[214]
	198.2	S	Yes	15.1	2	-	8.5	22	
Mg–Al-(3b)–KC	198.2	S	Yes	13.1	2	-	4.5	<u>22</u>	[214]
	198.2	S	Yes	12.1	2	-	8.5	22	
Mg–Al-(3d-120)–NaC	198.2	S	Yes	12.1	2	-	4.5	<u>22</u>	[214]
	198.2	S	Yes	11.1	2	-	8.5	22	
Mg–Al-(3d-160)–N	198.2	S	Yes	9	2	-	4.5	<u>22</u>	[214]
				13.1	2	-	8.5	22	

Note: literature on iodide adsorption was not available.

*Water type –S= synthetic. ‘-’ = data not available.

1.7.3.2 Carbon

Porous carbon materials have been widely used in water treatment to remove various contaminants because of their large surface area and high adsorption capacity.

Coal and Activated Carbon

Balsley *et al.* [215] studied the iodide adsorption capacity of lignite and sub-bituminous coal. Adsorption of iodide onto coal was found to be highly pH-dependent. Lignite achieved a maximum sorption of 34% at pH 3.9, and above that pH iodide adsorption capacity rapidly decreased. In contrast, sub-bituminous coal exhibited higher adsorption capacity over a wider pH range, with a maximum iodide sorption of 46% at pH 6.2. However, further investigation showed the adsorption capacity of coal decreases over time. Kaufhold *et al.* reported a 13-21% sorption capacity of a Merck activated carbon for the removal of iodide [209]. Sorption capacity was slightly higher at pH 7 than pH 10. Interestingly, investigation into competitive adsorption showed iodide sorption was not affected by competing anions. Maes' group also investigated adsorption of iodide on activated carbon under aerobic and anaerobic conditions [216]. Results showed the dissociation constant (K_d) values decreased from 2000 mL/g under aerobic conditions to 70 mL/g under anaerobic conditions. Due to the well-documented high affinity of iodine towards activated carbon [217-219], the authors concluded that iodide removal is facilitated by the oxidation of iodide to iodine by dissolved oxygen, which is subsequently adsorbed by the activated carbon. Hence, the effectiveness of activated carbon in iodide removal is dependent on dissolved oxygen concentrations [216]. Some studies on halide adsorption using coal and activated carbon have been summarised (Table 13).

Use of activated carbons in the water industry has been increasing due to increasing environmental regulations and its ability to adsorb a wide range of contaminants. Price varies depending on demand, quality and cost of production. Although activated carbon is widely used in the water industry (primarily for organics removal) this technique is not generally utilised for bromide/iodide removal, due to limited efficiency in this context.

Table 13: Iodide adsorption capacity of coal and activated carbon.

Type	Initial Iodide Concentration		Iodide Removal Capacity						
	I ⁻ (mg/L)	Water Type*	Competing Anions Present	I ⁻ (%)	Adsorbent Dose (g/L)	Time (h)	pH	Temp °C	Reference
Lignite	1.3	S	Yes	34	1-20	24	3.9	25	[215]
Sub-bituminous coal	1.3	S	Yes	46	1-20	24	6.2	25	[215]
Merck activated carbon	1269	S	No	15	10	48	7	-	[209]
	1269	S	No	13	10	48	10	-	
	1269	S	Yes	21	10	48	7	-	[209]
	1269	S	Yes	15	10	48	10	-	

Note: studies on bromide adsorption were not available.

*Water type –S= synthetic. ‘-’ = data not available.

Silver Impregnated Activated Carbon

Hoskins *et al.* [220] investigated two bituminous coal-based silver-impregnated granular activated carbons (AgAC) (0.05 and 1.05 wt% Ag) and their unimpregnated counterparts (GAC) in their ability to remove iodide from aqueous solutions by a series of batch sorption and leaching experiments. Silver impregnation did not significantly alter the texture and pore structure of unimpregnated GAC. Interestingly, iodide sorption onto AgAC was independent of pH until silver became saturated with iodide, after which iodide sorption increased with decreasing pH indicating a more positively charged surface and less competition from hydroxide ions at lower pH values. The authors concluded iodide sorption is initially controlled by precipitation of silver iodide, and subsequent removal occurs as a result of adsorption onto the GAC, which is a pH-dependent phenomenon. The 0.05% AgAC sorption behaviour closely resembled its unimpregnated GAC, due to the small silver concentration relative to total iodide concentration. In contrast, the 1.05% AgAC exhibited noticeably greater iodide sorption than its unimpregnated GAC at pH values of 7 and 8, while their performances were comparable at a pH of 5 (Table 14). At a dose of 1 g/L sorbent, at pH 8 with an initial iodide concentration of 425 μM , approximately 390 $\mu\text{mole/g}$ of I⁻ was sorbed onto the AgAC. Several silver impregnated activated carbon treatment processes that remove iodide from drinking water have been patented [221-223].

Table 14: Summary of studies investigating silver impregnated activated carbons' halide adsorption capacity.

AgAC Type	Initial Iodide Concentration		Iodide Removal Capacity							Reference
	I ⁻ (mg/L)	Water Type*	Competing Anions Present	I ⁻ (µmol/g)	Adsorbent Dose (g/L)	Time (days)	pH	Temp		
AgAC	1.0 – 200.5	S	No	153.7–143.6	1	7	5	-	[220]	
(1.05 wt % of Ag)	1.0 – 200.5	S	No	120.4–103.9	1	7	7	-		
	1.0 – 200.5	S	No	93.4–83.0	1	7	8	-		
	1.0 – 200.5	S	No	50.0–30.7	1	7	5	-	[220]	
AgAC (0.05 wt % of Ag)	1.0 – 200.5	S	No	8.98–3.82	1	7	7	-		
	1.0 – 200.5	S	No	3.93-3.10	1	7	8	-		
	0.127	S	Yes	98 %^	-	-	-	20	[224]	
(20 wt % of Ag)										

Note: studies specifically on bromide adsorption were not available.

*Water type –S = synthetic. '-' = data not available. ^Adsorption in µmol/g was not reported, therefore a percent removal shown.

Silver Chloride Impregnated Activated Carbon

Ho and Kraus demonstrated pre-treatment of activated carbon with silver (20 wt% Ag) and chloride, to form a silver chloride impregnated activated carbon (AgClAC), caused a large increase in the uptake of iodide, relative to unimpregnated activated carbon [224]. The iodide-chloride concentration ratio did not significantly affect the efficiency of iodide adsorption. Long term experiments with tracer iodide solutions (10^{-7} M) passed over small columns (<0.5 cm³) achieved over 98% iodide removal after several thousand column volumes of treatment. The authors hypothesised that ion exchange of chloride for iodide is due to the differences in solubility between silver chloride and silver iodide (K_{sp} 10^{-10} and 10^{-17} , respectively). More recently, Karanfil *et al.* [225] demonstrated that in streams of low iodide concentrations AgClAC could be used instead of AgAC to reduce silver leaching. Both AgClAC and AgAC (1.05 wt% Ag) exhibited relatively similar iodide sorption, independent of pH, however, under acidic conditions silver leaching from AgClAC was significantly lower than from AgAC (6% and 50%, respectively). Experiments conducted using a groundwater contaminated with ¹²⁹I showed similar iodide sorption using both AgAC and AgClAC as adsorbants.

Silver impregnated activated carbons have widespread applications in domestic drinking water, beverage and food industry, mineral water bottling, and laboratories [226]. They provide a means for water purification without a large infrastructure burden and are also a safe and effective method of controlling/preventing bacterial growth. This technique has the potential for widespread application in the drinking water industry, since both NOM and halides may be lowered using this method, thereby lowering DBPs formation. However, further development is required in the areas related to; effects of competing anions, efficiency in complex water matrices, and the optimisation of the technique for large scale water treatment plants. Leaching of silver from these materials can be controlled by a dedicated silver-impregnation process, therefore ensuring the safety of the product for drinking water use. For example, Norit 18x40 AG 1 has a silver content of 0.1% by mass, and a water-extractable silver concentration of 0.01 mg/L [227]. Individual commercially available silver-impregnated activated carbons will vary in the extent of silver leaching, and information on this is available in the specifications for the individual materials.

Silver Doped Carbon Aerogels

Sánchez-Polo and colleagues have conducted several studies into the effectiveness of silver doped activated carbon aerogels for bromide and iodide removal from drinking water [228-231] (Table 15). Halide adsorption onto silver-doped carbon aerogels was significantly higher than for activated carbon [231]. The maximum adsorption capacity for chloride, bromide, and iodide were 7.32, 3.01, and 1.98 $\mu\text{mol/g}$, respectively, using a silver-doped carbon aerogel with a surface area of 428 ± 30 (m²/g), characterised by an elevated surface acidity (pH = 4.5 ± 0.1), high concentration of surface oxygen (O = $21 \pm 1\%$), and a wide dispersal of Ag⁺ covering $10 \pm 1\%$ of the aerogel surface. The initial study showed that an increase in the silver concentration reduced the surface area of the aerogel and increased mesopore and macropore volumes. However, halide adsorption capacity increased with silver concentrations on the aerogel surface. The adsorption capacity of the adsorbent increased with decreasing radius size of the halide ion (adsorption capacity and halide affinity decreased in the order; Cl⁻ > Br⁻ > I⁻), indicating steric hindrance in the sorption of larger ionic radius halides on silver-doped aerogels. The presence of chloride and NOM reduces the efficiency of silver-doped aerogels in removing bromide and iodide from aqueous solution. High concentrations of chloride (40 mg/L) reduced the adsorption capacity of bromide and iodide to 36% and 33%, respectively, from 3.01 and 1.98 $\mu\text{mol/g}$ in the absence of chloride to 1.91 and 1.33 $\mu\text{mol/g}$ in the presence of chloride.

Table 15: Halide adsorption by silver doped carbon aerogels under specific conditions.

Type	Initial Anion Concentration		Water Type*	Competing Anions Present	Halide Removal Capacity		Adsorbent Dose (g/L)	pH	Flow Rate (mL/min)	Temp (°C)	Reference
	Br ⁻ (mg/L)	I ⁻ (mg/L)			Br ⁻ (μmol/g)	I ⁻ (μmol/g)					
Silver-doped aerogels	0.15	0.15	S	Yes	3.01	1.98	3	6.5- 7	1.5	25	[228-231]
Carbonised silver-doped aerogels	0.15	0.15	S	No	4.68	3.71	3	7	1.5	25	[228-231]
Activated silver-doped aerogels	0.15	0.15	S	No	5.78	5.03	3	7	1.5	25	[228-231]

*Water type –S= synthetic

The effects of carbonisation and activation of silver-doped aerogels on bromide and iodide removal has also been studied [229]. Carbonisation and activation of silver-doped aerogels increased the surface area, and mesopores and macropores volumes slightly decreased. Carbonisation and activation treatments significantly increased the aerogel's adsorption capacity of bromide and iodide, due to increased microporosity as well as electrostatic interactions. Activation treated aerogels increased bromide and iodide sorption capacity by 92% and 154%, respectively, compared to the untreated silver aerogel. Although carbonisation and activation treated aerogels exhibited higher adsorption capacity than the untreated silver-aerogel, all adsorption capacities were considerably lower in natural waters. The authors conclude the reduced sorption capacity is a result of organic matter blocking pores and the presence of competing anions. The anion affinity for silver-doped aerogels is quite high in comparison to aerogels that do not include silver, indicating that in addition to chemisorption, electrostatic interactions contribute to halide adsorption in silver-doped aerogels. Additional research examined the adsorption of bromide and iodide under dynamic conditions chosen to simulate a water treatment plant using Lake Zurich water [230]. This study also examined the regeneration of exhausted aerogels. Results showed aerogel columns have a high removal efficiency of iodide and bromide from synthetic water (60 - 71%), however, these values decreased to 31 - 56% when natural waters were tested. This agrees with the reports discussed above and may be a consequence of the presence of NOM and competing anions. Regeneration with NH_4OH results in the replacement of the halide ions with ammonia to form a silver-ammonia complex, which transforms adsorption sites from Ag^+ to $\text{Ag}(\text{NH}_3)_x^+$ according to equation (1) [228, 230].



Regeneration of the columns enabled the recovery of approximately 100% of the initial adsorptive capacity of the aerogel, with no significant changes in the adsorption characteristics after three adsorption/regeneration cycles. Investigation into the possible leaching of organic polymer precursors from the aerogels found that these are not released in high concentrations ($>0.1 \text{ mg/L}$). The number of surface silver adsorption sites is not significantly altered after regeneration. Silver-doped aerogels have also been shown to exhibit strong, long-term antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* [232].

Silver-doped activated carbon aerogels are a promising technique to remove bromide and iodide from drinking water, thereby lowering DBPs formation. Metal-doped carbon aerogels may also find application in the treatment of wastewater. The high cost of production at this time has been the main limitation of this technology. Additionally, research has been limited to lab-scale studies. Further research and development to lower the cost of aerogel production will be integral to the expansion of carbon aerogel technology into large-scale treatment processes.

1.7.3.3 Ion Exchange Resins

MIEX®

Orica Watercare's MIEX® (Magnetic Ion EXchange) resin was developed specifically for the removal of NOM from natural waters [233-236]. MIEX® is a strong base anion-exchange resin with iron oxide integrated into a macroporous polyacrylic matrix, which provides the resin with magnetic characteristics, aiding the agglomeration and settling of the resin. MIEX® resin beads are 2-5 times smaller than traditional resins ($\phi \approx 180 \mu\text{m}$), resulting in an increased surface area to volume ratio that allows rapid ion exchange kinetics [237, 238]. A review of the literature reveals that in addition to NOM removal it is capable of removing bromide [233-241]. Several studies have shown MIEX® efficiently reduces NOM concentrations, consequently reducing THMs precursors and oxygen demand [233-236, 240, 242, 243]. The charge density of NOM isolates have been shown to have the most significant effect on NOM affinity with MIEX® [241, 243]. Removal of bromide by MIEX® resin is highly dependent on the alkalinity of the water and competing ion concentrations [233-236, 240, 243]. Under optimal conditions MIEX® was able to reduce bromide concentrations by approximately 93%, however under less favourable conditions reductions in the order of 60% were typically achieved [240]. Boyer's study showed that the ion-exchange capacity of regenerated MIEX® resin was

significantly lower than virgin MIEX® (20-28%) [244]. In high alkalinity waters, bromide is unable to compete effectively against bicarbonate ions for the exchange sites on the strong base anion-exchange resin [234, 240, 243]. Therefore, in high alkalinity waters where bromide removal is less efficient, subsequent chlorination of MIEX® treated water can still cause significant concentrations of brominated THMs and HAAs to be formed [235, 245].

MIEX® resin is a proven and highly successful NOM removal technology. However, the simultaneous removal of bromide in addition to NOM is often not efficient when treating a raw drinking water matrix. There is potential to apply MIEX® for bromide removal in low alkalinity waters, however, further research is required to understand the conditions under which this will provide an efficient bromide-reduction treatment, as well as to understand the affinity of MIEX® with iodide.

Table 16: The bromide adsorption capacity of MIEX® resin is shown.

Adsorbent/Coagulant Used	Initial Bromide Concentration		Competing Anions Present	Bromide Removal Capacity						
	Br ⁻ (mg/L)	Water Type*		Br ⁻ (%)	MIEX® Dose (mL/L)	Alum dose (mg/L)	Time (h)	pH	Temp. (°C)	Reference
MIEX®	0.100	S	Yes (NaCl and DOC)	35	1	-	1	8	22	[233]
MIEX®	0.100	S	Yes (NaCl and CaCO ₃)	29	1	-	1	8	22	[233]
MIEX®	0.900	N	Yes	64	8	-	1	8.1	15	[234]
Alum	0.076	N	Yes	4	-	60	1	8	20	[235]
MIEX®	0.076	N	Yes	28	5	-	1	8	20	[235]
MIEX® + Alum	0.076	N	Yes	26	5	16	1	8	20	[235]
Alum	0.083	N	Yes	-2	-	60	1	8	20	[235]
MIEX®	0.083	N	Yes	45	2	-	1	8	20	[235]
MIEX® + Alum	0.083	N	Yes	49	2	5	1	8	20	[235]
Alum	0.240	N	Yes	0	-	60	1	8	20	[235]
MIEX®	0.240	N	Yes	17	2	-	1	8	20	[235]
MIEX® + Alum	0.240	N	Yes	21	2	4	1	8	20	[235]
Alum	0.540	N	Yes	2	-	60	1	8	20	[235]
MIEX®	0.540	N	Yes	15	4	-	1	8	20	[235]
MIEX® + Alum	0.540	N	Yes	13	4	20	1	8	20	[235]
MIEX®	0.167-0.218	N	Yes	20-28	0.224	-	1	6.6-6.9	17-26	[236]
MIEX® + Alum	0.0381	N	Yes (155 mg/L CaCO ₃)	-0.7	6	12	1	8.2	25	[240]
MIEX® + Alum	0.0945	N	Yes (91 mg/L CaCO ₃)	43	8	45	1	7.3	25	[240]
MIEX® + Alum	0.163	N	Yes (20 mg/L CaCO ₃)	94	8	10	1	7.2	25	[240]
MIEX® + Alum	0.0137	N	Yes (4 mg/L CaCO ₃)	BDL	2	10	1	6.1	25	[240]
MIEX®	0.150	N	Yes	83	8	-	0.5	7	26	[246]

Note: studies of iodide adsorption using MIEX are not yet available.

*Water type – N = Natural water, S= synthetic. BDL = below detection limit. '-' = data not available.

Other Anion-Exchange Resins

Any strong anion-exchange resin could be expected to display some bromide and iodide adsorption capacity under favourable conditions. Hsu and Singer [233] compared Ionac A-641 and Amberlite IRA910 polystyrene resins to MIEX® and found that the polystyrene resins were more efficient for bromide removal while MIEX® was more effective at NOM removal. A number of commercially available resins have been compared (Tables 16, 17 and 18).

Ion-exchange resins have been used widely in many applications of drinking and wastewater treatment. Ion-exchange is a moderately expensive water treatment. Strong anion-exchange resins that are capable of adsorbing both bromide and iodide are commercially available. However, their application to drinking water treatment is limited due to cost and reduced removal efficiency in complex matrices. Generally, as concentrations of competing anions and NOM increase in the water matrix, the adsorption of bromide and iodide decreases. There is potential to apply strong anion-exchange resins for bromide and iodide removal after pre-treatment to remove NOM and/or competing anions. Many patented resins are modified with metals, which increases cost and the potential for leaching, therefore lowering suitability for potable water treatment. Most have not been applied on a large scale, however, with more research they have the potential for specific wastewater applications. Further research investigating the affinity of strong anion-exchange resins for iodide would be beneficial, since most studies reviewed focussed on bromide adsorption [233, 246-248]. Further investigation into the risk of leaching from various resin types as well as improved cost-effectiveness would also be beneficial.

Table 17: Commercially available water treatment resins – parameters for use and subsequent halide adsorption efficiency.

Resin Type	Initial Anion Concentration		Water Type*	Competing Anions Present	Halide Removal Capacity		Adsorbent Dose (g/L)^	Contact Time (h)	pH	Temp (°C)	Reference
	Br ⁻ (mg/L)	I ⁻ (g/L)			Br ⁻ (%)	I ⁻ (%)					
Ionac A-641	0.300	-	S	Yes	76	-	2 mL/L	5	8	22	[233]
Amberlite IRA910	0.300	-	S	Yes	73	-	2 mL/L	5	8	22	[233]
Duolite A-161	159.8	-	S	No	56	-	4	3	-	27	[249, 250]
Duolite A-162	7990	-	S	No	**Log K _d 5.48	-	4	3	-	25	[250]
Amberlite IRA-400	7990	12.7	S	No	**Log K _d 3.80	**Log K _d 4.50	4	3	-	32.0	[248]
Indion-850	2876.4	5.1	S	Yes	66.6	57.5	10	4	-	25	[251]
Duolite A-116	-	0.51	S	No	-	50	5	3	-	25	[252]
Duolite A 101D	399.5	-	S	No	89	-	2.5	3	-	25	[253] [253]
	399.5	-	S	No	96	-	2.5	3	-	45	
Duolite A 102D	399.5	-	S	No	86	-	2.5	3	-	25	[253] [253]
	399.5	-	S	No	89	-	2.5	3	-	45	
Duolite A-113	3403.7	5.3	S	No	54	45.3	2.5	4	-	25	[247]
DOWEX- MARATHON 11s	0.110	-	N	Yes	87	-	8 mL/L	0.5	7	-	[246]
DOWEX- MARATHON MSA	0.110	-	N	Yes	90	-	8 mL/L	0.5	7	-	[246]
Amberlite IRA-938	0.150	-	N	Yes	87	-	8 mL/L	0.5	7	-	[246]
Diaion SA10A	0.204	-	N	Yes	73.5	-	-	10	6.5-7.5	-	[208]

*Water type – N = Natural water, S= synthetic. **Percent removals were not reported, therefore K_d's have been included here. ^Units are g/L unless otherwise specified. '-' = data not available.

Table 18: Commercially available water treatment resins and their halide removal efficiencies.

Resin	Uses	Type	Matrix	Functional Groups	Br ⁻ (%)	I ⁻ (%)	Reference
Amberlite IRA-400	Demineralisation, electroplating	Type 1 strong base anion exchange resin	Cross linked polystyrene	Quaternary amine	87	-	[248]
Amberlite IRA910	Treatment of highly saline solutions, sugar industry use in mixed bed polisher	Type 2 strong base macroreticular anion exchange resin	Macroreticular crosslinked polystyrene	Dimethyl ethanol amine	73	-	[233]
Amberlite IRA-938	Deionisation of water and removal of organics	Strong base macroporous anion exchange resin	Styrene	Quaternary amine	87	-	[246]
Diaion SA10A	Desalination	Strong base anion exchange resin	Gel, porous styrenic polymer	Quaternary amine	73.5	-	[208]
DOWEX™ 1	Removal of uranium, perchlorate, hexavalent chromium and iodide. Purification of radiochemicals.	Type 1 strong base anion exchange resin	Styrene-divinylbenzene copolymer, gel	Quaternary amine	-	>90	[254]
DOWEX-MARATHON 11s	Multi-bed demineraliser - recommended for treating waters that contain naturally occurring organic matter	Type 1 strong base anion exchange resin	Styrene-divinylbenzene copolymer	Acrylic	87	-	[246]
DOWEX-MARATHON MSA	Demineralisation of high organic matter waters, catalysis, and the extraction of heavy metals in the form of complex anions	Type 1 macroporous strong base anion exchange resin	Styrene-divinylbenzene copolymer	Quaternary amine	90	-	[246]
Duolite A-113	Water demineralisation	Type 1 strong base anion exchange resin	Crosslinked polystyrene	Quaternary amine (-N(CH ₃) ₃ ⁺)	54	45.3	[247]
Duolite A-161	Production of ultrapure water	Type 1 macroporous strong base anion exchange resin	Styrene-divinylbenzene copolymer	Quaternary amine (-N(CH ₃) ₃ ⁺)	56.3	-	[249, 250]
Ionac A-641	Demineralising high organic matter waters and catalysis, extraction of heavy metals.	Strong base anion exchange resin	Polystyrene	Quaternary amine	76	-	[233]
Indion-850	Two stage deionisation	Macroporous weak base anion exchange resin	Styrene-divinylbenzene copolymer	Tertiary and quaternary amine groups	66.6	57.5	[251]

Table 19: Patented anion exchange resins with halide removal capacity.

Patent Number	Resin Type	Unmodified Resin*	Functional group of final (patented) resin	Uses	Reference
7588690	Macroporous resin-	Purolite® CT275, Purolite® CT276	Ag	Concentrating iodide from solvent	[255]
5624567	Strong-base anion exchange resin	-	Trialkyl amine	Iodide removal from aqueous solutions	[256]
6379556	Strong-base anion exchange resin	Amberlite IRA-400 Amberlyst A-21.	Quaternary amine	Recovery of iodide from chemical process wastewater	[257]
5366636	Chelating resin (gel)	Chelex 100 Chelex 20	Ag	Disinfection and halide removal	[258]
3050369	Strong-base anion exchange resin	Dowex 1 Dowex 2 Dowexx 11 Dowex 21A	Quaternary amine	Recovery of iodide from brines	[259]
2261021	Anion exchange resin	-	Aryl/methylene	Recovery of halogens from fluids	[260]
3352641	Strong-base anion exchange resin	-	-	Iodide removal from brines and natural gas well waters	[261]
5220058	Macroreticular resin	Mesoporous or macroporous	Ag, Pd, Hg	Removal of iodide impurities from acidic aqueous solutions	[262]
2945746	Strong-base anion exchange resin	-	Quaternary amine	Removal of iodide from natural brines	[263]
4451375	Strong-base anion exchange resin	Resins bearing picolylamine functionality (DOW XFS-43084 and xfs-4195)	Picolylamine ion	Iodide adsorption from acidic aqueous solutions	[264]

*Resin from which patented (modified) resin was made.

1.7.3.4 Aluminium Coagulation

Ge and Zhu [265] reported that bromide sorption by aluminium coagulation can occur via three possible pathways (equations 2-4):

- (1) $(\text{H}_2\text{O})_6\text{Al}^{3+} + \text{Br}^- \rightleftharpoons (\text{H}_2\text{O})_5\text{AlBr}^{2+}$,
- (2) $(\text{H}_2\text{O})_5\text{AlOH}^{2+} + \text{Br}^- \rightleftharpoons (\text{H}_2\text{O})_4\text{AlOHBr}^+$, or
- (3) $(\text{H}_2\text{O})_4\text{Al}(\text{OH})_2^+ + \text{Br}^- \rightleftharpoons (\text{H}_2\text{O})_3\text{Al}(\text{OH})_2\text{Br}$

Ge *et al.* [266] showed that in synthetic water, 93.3–99.2% removal efficiency of bromide was achieved by coagulation with aluminium chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) in the absence of humic acids. In the presence of humic acids, bromide removal was decreased by approximately 20% to 73.2% at a dose of 3 mg/L aluminium chloride (Table 20). In natural water, 87.0% of bromide was removed using a significantly higher coagulant dose (15 mg/L). Bromide removal efficiency was relatively stable from pH 4–8, however at pH 9 removal efficiency drastically decreased to 44.2%. The effects of coexisting ions on removal of bromide by aluminium coagulation was also investigated [265]. It was observed that bromide removal decreased from 82.8–99.2% in deionised water to 62.1–87.0% in raw water, indicating bromide removal was significantly affected by coexisting ions and humic acids, present in natural water [265]. Humic acid was also found to be adsorbed by aluminium coagulation, and the efficiency of this was diminished in the presence of 0.2 mg/L bromide in raw water (92.3% as compared to 97.0% in deionised water). Both experiments were conducted with 15 mg/L coagulant at pH 6. The addition of NO_3^- (10 mg/L), HCO_3^- (250 mg/L), Cl^- (250 mg/L), SO_4^{2-} (250 mg/L) and H_2PO_4^- (250 mg/L) to deionised water decreased bromide removal efficiency by 8.0%, 11.5%, 14.6%, 21.2% and 40.8% respectively. The authors did not investigate the compounding effects a mixture of competing anions would have on bromide removal.

The aluminium coagulation of bromide is inhibited by the presence of organic matter and anions in natural source waters. Although the authors show reasonable bromide reductions with small volumes of natural waters, this required large coagulant doses, in order to compensate for the inhibitory effects from competing anions and NOM. Further investigation into halide adsorption optimisation and potential to be used in conjunction with other techniques to improve halide removal would be of interest.

Table 20: Summary of data on bromide adsorption during aluminium coagulation.

Initial Bromide Concentration		Bromide Removal Capacity					
Br ⁻ (mg/L)	Water Type*	Competing Anions Present	Br ⁻ (%)	Adsorbent Dose (mg/L)	Time (h)	pH	Reference
2.0	S	No	30.4	7	2 ½	6	[265, 266]
0.2	S	No	98.8	7	2 ½		
0.2	S	Yes	98.4	15	2 ½	6	[265, 266]
0.2	S	(6 mg/L humic acid)	73.2	3	2 ½	6	[265, 266]
0.2	N	Yes	87.0	15	2 ½	6	[265, 266]
0.2	N	Yes	74.5	15	2 ½	7	[265, 266]
0.2	N	Yes	62.1	15	2 ½	8	[265, 266]
0.2	N	Yes	62.3	7	2 ½	6	[265, 266]
0.2	N	Yes	55.9	7	2 ½	7	[265, 266]
0.2	N	Yes	43.5	7	2 ½	8	[265, 266]
0.2	S	Yes	94.5	15	2 ½	7	[265, 266]
0.2	S	Yes (250 mg/L HCO ₃ ⁻)	83.8	15	2 ½	7	[265, 266]
0.2	S	Yes (250 mg/L SO ₄ ²⁻)	74.5	15	2 ½	7	[265, 266]
0.2	S	Yes (250 mg/L Cl ⁻)	80.7	15	2 ½	7	[265, 266]
0.2	S	Yes (10 mg/L NO ₃ ⁻)	87.0	15	2 ½	7	[265, 266]

Note, data on iodide adsorption using this technique was not available.

*Water type – N = Natural water, S= synthetic.

1.7.3.5 Soils

Several research groups have studied the adsorption of iodide on soil, with particular emphasis on radioactive iodide [267-275] (Table 21). Dai *et al.* [268] studied iodide adsorption using soil from China. It was shown that iodide sorption exhibited a linear relationship with soil organic matter concentration, a polynomial relationship with free iron oxide content and a logarithmic relationship with cation exchange capacity. K_d for iodide sorption onto these soil samples ranged from 0.78 to 6.59 mg/kg. Dai *et al.* (2009) deduced that higher sorption capacity was due to the higher proportion of ferric oxides and aluminum oxides in soils. Similarly, Whitehead [276,277], Sheppard *et al.* [275] and Gu and Schulz [270] observed that iodide adsorption by soil was dependent on ferric oxides, aluminium oxides and soil organic matter. Common soil components (Kaolinite, bentonite, quartz sand, Fe_2O_3 , Al_2O_3 and humic acids) iodide sorption capacities from water were investigated by Muramatsu *et al.* [272]. Quartz sand, Al_2O_3 , kaolinite and bentonite had limited or no sorption capacity. Humic acid was shown to sorb approximately 70% of iodide out of a synthetic water solution. Sorption of iodide by Fe_2O_3 was very high (~80%) from deionised synthetic water, however, in a complex system with competing molecules Fe_2O_3 would not be expected to contribute significantly to iodide adsorption. Couture and Seitz reported that 30% of iodide was sorbed from water by hermatite (Fe_2O_3) and less than 5% was sorbed by Kaolinite ($Al_2Si_2O_5(OH)_4$) [278]. Sheppard *et al.* [267] found iodide adsorption significantly decreased in the presence of competing anions.

Table 21: The iodide adsorption capacity of soils.

Type	Initial Iodide Concentration		Iodide Removal Capacity							Reference
	I ⁻ (mg/L)	Water Type*	Competing Anions Present	I ⁻ (%)	Adsorbent Dose (g/L)	Time (h)	pH	Temp (°C)		
Udic Ferrisols	4	S	No	57.5	100	40	5.05	25	[268]	
Perudic Ferrisols	4	S	No	13.2	100	40	5.45	25	[268]	
Udic Isohumisols	4	S	No	12.8	100	40	7.95	25	[268]	
Udic Luvisols	4	S	No	11	100	40	7.85	25	[268]	
Orthic Aridisols	4	S	No	10.9	100	40	8.51	25	[268]	
Field soil	-	S	No	>90	100	24	5.4	23	[272]	
Paddy soil	-	S	No	>90	100	24	5.7	23	[272]	
Sandy soil	-	S	No	>70	100	24	5.5	23	[272]	
Japanese Andosols	-	S	No	>99	100	48	4	23	[274]	
Japanese Kanuma	-	S	No	>55	100	48	4	23	[274]	

Note: data on bromide adsorption onto soils was not available.

*Water type – S= synthetic. ‘-’ = data not available.

The investigation of Kaplan *et al.* [271] into soil isolates found illite had a significant iodide adsorption capacity ($K_d = 15.14 \pm 2.84$ mL/g), which was pH dependent. Desorption experiments showed that F^- , Cl^- , Br^- , and $^{127}I^-$ displaced $^{125}I^-$ that was sorbed onto illite, by $43 \pm 3\%$, $45 \pm 0\%$, $52 \pm 3\%$, and $83 \pm 1\%$ respectively. Desorption was shown to increase from 43% to 83% with increasing size of the competing anion, indicating I^- is weakly associated by anion or ligand exchange with the illite structure. Yoshida *et al.* [274] studied the adsorption of iodide from deionised water by Japanese Andosols and Kanuma soils. Approximately 99% and 55% of iodide was adsorbed from aqueous solution at pH 4 by Andosols and Kanuma soils respectively. Anion sorption can occur on positive charges on either free hydroxides of iron and aluminium or on the edges of aluminosilicate clay mineral lattices [277]. Yoshida *et al.* [274] reported that the sorption of iodide on Kanuma soil increased with decreasing pH and was described by Henry isotherms, suggesting that iodide was electrostatically adsorbed on the described positive charges. The observed relationship between I^- and pH on Kanuma soil was in agreement with Whitehead's [277] and Musicic's [279] studies on iodide sorption onto ferric hydroxide and aluminium hydroxide. Balsley *et al.* [215] showed imogolite-bearing soil had significant iodide sorption between pH 4 and 5.5.

The potential application of soils appears to be an economical and efficient method for halide removal for potable water treatment, assuming organic matter concentration of water was not increased by the process. Further research to evaluate the practical applications of different soils and their components on DBPs precursor removal is warranted.

1.7.3.6 Relative Advantages and Disadvantages of Adsorptive Techniques

Adsorptive techniques for halide removal are generally cheaper and more easily implemented than membrane or electrochemical techniques, however, their adsorption efficiency is often adversely impacted by the presence of competing anions and NOM in natural waters. Although activated carbons and MIEX® are used in drinking water treatment, they are employed for organic matter adsorption, rather than for halide removal. Development of adsorptive techniques that effectively removed NOM and halides in the presence of competing anions would represent an important step forward in DBPs precursor removal.

1.7.4 Comparison of the Three Classes of Halide Removal Techniques

The specific experimental conditions of the reviewed research varied greatly, making quantitative comparisons of bromide and iodide removal difficult. Discussion of each removal technique's potential for commercial application in drinking water treatment is intended to guide further research, rather than to conclusively indicate which technology is preferable, due to the lab-scale nature of much of the research reviewed.

Evaluating bromide and/or iodide removal efficiency of each technique requires the consideration of all experimental conditions, including water type, flow rate, pressure, current, adsorbent load, adsorption capacity, initial anion concentration, pH, contact time, system regeneration, effects of competing anions, ease of application and overall cost. Not all authors report these experimental conditions, making comparison between different removal technologies challenging. The overall bromide and iodide removal capacity of the three removal technique categories, taking these many parameters into account to the extent that it is possible, is discussed herein (Table 22).

In general, membrane techniques have the highest bromide and iodide removal for natural drinking water matrices, and offer the additional benefits of NOM removal and disinfection. Electrochemical techniques were found to be preferable over adsorption techniques because their halide removal efficiencies were higher in natural drinking water matrices. Despite several lab-scale studies finding that adsorbents achieved high bromide and iodide removals, generally their adsorption capacity was greatly diminished in the presence of competing anions and NOM in natural drinking waters, thus, adsorption techniques are likely to be the least applicable to halide removal in drinking water treatment at this stage in the development of the technology. With this in mind, however, the cost-effectiveness and ease of applicability of adsorbent techniques suggest that this will continue to be an

important area of research, and with further development to circumvent the current limitations, surface sorption methods still may have the greatest potential in widespread DBP management.

In terms of efficiency of halide removal, RO is the optimal membrane technique of those discussed here. NF is also excellent in achieving halide removal, however, the performance of this technique is lower than that of RO. ED and EDR are not as well-developed in accomplishing optimal halide removal as RO and NF, although excellent removals can still be attained.

Membrane technologies have the highest bromide and iodide removal capacity of all the techniques discussed here, but they are also the most expensive. Despite this, with increasingly stringent regulations on water quality and a movement to increased utilisation of alternative water sources, membrane filtration is emerging as an economically viable alternative to conventional methods for removal of a wide array of microbial and chemical contaminants, including halides.

In natural drinking water matrices, the electrochemical techniques discussed here have shown high bromide and iodide removal capacity. Although CDI is at an early stage of its development, it has a greater likelihood of applicability to the drinking water treatment industry for halide removal than electrolysis, due to the difficulty of increasing electrolysis to a water treatment plant scale. With further development and research CDI could be widely applied to the water industry, rivalling membrane techniques.

Adsorption processes are promising methods for the removal of bromide and iodide for DBPs minimisation in terms of cost effectiveness and simplicity of design and operation. However, for use in environmental water matrices, further development of these techniques is required in order to overcome the detrimental effect of competing anions and NOM present in potable water sources on halide adsorption.

Table 22: Qualitative comparison of bromide and iodide removal techniques for use in drinking water treatment.

Technology Class	Treatment Method	Applicability to Full-Scale Drinking Water Treatment	Br ⁻ Removal (%)	I ⁻ Removal (%)	Halide Removal in Drinking Water Matrix	Cost	Available on Commercial Scale for Water Treatment
Membrane	RO	H	90-99.8	80-92	H	H	P
	NF	H	93-97	55-91	H	H	P
	ED/EDR	H	72-80	92-97	H	H	P
Electrochemical	Electrolysis	L	79-99	-	M	H	N/A
	CDI	ML	50-86.1	69.7-77	M	H	FD
Adsorption	LDH	MH	27-94	14-96	M	L	FD
	Sol-gel double hydrous oxide	MH	9-80	-	M	ML	FD
	Coal and Activated Carbon	M	-	13-46	L	L	P*
	AgAC	U	-	-	U	M	FD
	Silver doped carbon aerogels		3.01-5.78 $\mu\text{mol/g}$ adsorbent [#]	1.98-5.03 $\mu\text{mol/g}$ adsorbent [#]	U	MH	FD
	MIEX	M	2-83	-	L	MH	P*
	Other resins	M			M	MH	P*
	Aluminium coagulation	M	34-98	-	L	L	FD
Soils	M	-	11-99	U	L	FD	

H- High, MH- medium/high, M-Moderate, ML- medium/low, L-Low, N/A- Not applicable, FD- further development needed for bromide and iodide reduction application, P- proven technology in drinking water treatment, U- unknown. *Not used specifically for halide removal, in practice they are used for NOM removal during drinking water treatment. #Percent removals were not available.

1.8. Research Directions

Several areas in which additional research is needed to assess the bromide and iodide reduction capacity of treatment technologies have been identified. The main areas relevant to DBPs management in drinking water by removing halide precursors are: optimisation of technologies such as EDR, electrolysis, LDHs, silver-doped aerogels and resins for the water treatment plant scale; adaptation for commercial production/application of resins, soils and aerogels; minimising the effects of competing anions and NOM on adsorptive techniques for halide removal; improving energy efficiency of membrane techniques and development of improved membranes for EDR; studying bromide and iodide removals by MCDI and optimising the deionisation achievable by CDI; decreasing production costs of resins and silver-doped aerogels; developing understanding of optimal silver-doping for best cost/benefit in silver-doped activated carbons.

There is a general need for further development of halide removal techniques able to be used in commercial water treatment applications. Most halide removal studies have investigated removals of specific anions in isolation from other halides and other potentially competing anions. There is a need to assess halide reduction methods with respect to both bromide and iodide, as well as competing anions. Removal of both halides and NOM simultaneously represents the ideal solution for DBP control by precursor removal, however, in general the membrane techniques are the only processes of those reviewed here that are efficient in doing this. Further potential is in the development of hybrid techniques from the combination of less efficient/limited techniques, to achieve this ultimate goal, of efficient NOM and halide removal for DBP minimisation.

2. MATERIALS AND METHODS

2.1. Chemicals

All DBP analytical standards were purchased from Sigma-Aldrich (Castle Hill, Australia) except dichloriodomethane (DCIM), chlorodiodomethane (CDIM), bromochloriodomethane (BCDIM), dibromiodomethane (DBIM) and bromodiodomethane (BDIM) which were purchased as pure compounds from Orchid Cellmark (New Westminster, Canada). The standards provided by Sigma-Aldrich are chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (TBM) as THMs calibration mix of 100 µg/mL of each analyte in methanol. Dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), 1,1-dichloropropanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), and trichloronitromethane (TCNM) were purchased as EPA 551B Halogenated Volatiles Mix at 2000 µg/mL each in acetone. CH standard was 1000 µg/mL in acetonitrile. 1,2-dibromopropane (97%) was also purchased from Sigma-Aldrich (Castle Hill, Australia) and used as internal standard during DBP analysis. NDMA and other nitrosamines had a purity of >99.9 % and were obtained from Supelco. Deuterated d_6 -NDMA and d_{14} -NDPA (*N*-nitrosodipropylamine) were used as surrogate and internal standard, respectively (>98.9 %, Accustandard and Ultra Scientific, respectively).

Analytical grade 99.9% methyl *tert*-butyl ether (MtBE) was purchased from Sigma-Aldrich as Chromasolv® quality and used as extraction solvent. Sodium sulfate anhydrous (10-60 mesh) was purchased from Mallinckrodt chemicals (Phillipsburg, USA). Ammonium chloride (TraceSELECT®, ≥99.9% purity), sodium hydroxide (SigmaUltra, ≥98%, pellets) and sodium hypochlorite solution (reagent grade, available chlorine ≥4%) were used to disinfect the waters and were purchased from Sigma-Aldrich (Castle Hill, Australia) as well as potassium dihydrogen phosphate (KH₂PO₄, Fluka, puriss. p.a., ≥99.5% and Acros 99%) and disodium hydrogenphosphate (Na₂HPO₄·2H₂O, Fluka, puriss. p.a., ≥99.5% and Acros 99%) were used to prepare pH buffer solutions. Commercial N,N diethyl-1,4 phenylenediamine sulfate (DPD) test kits (Hach, Notting Hill, Australia) were used for the analysis of free and total chlorine. Ascorbic acid (Sigma-Aldrich Castle Hill, Australia, ACS reagent 99%) was used to quench the residual disinfectant prior to analysis. All solutions were prepared using analytical grade reagents and HPLC grade water (Honeywell Burdick & Jackson, Taren Point, Australia).

Aluminium sulfate (Al₂(SO₄)₃·18H₂O (98%)), magnesium sulfate (MgSO₄) (≥99.5%), and calcium sulfate (CaSO₄·2H₂O (98%)) were purchased from Sigma-Aldrich. Individual 1000 mg/L TraceCert bromide and iodide aqueous standards were obtained from Fluka Analytical. Suwanee river NOM isolate was purchased from the International Humic Substances Society (batch number 1R101N). Used, regenerated, MIEX® resin was obtained from a South Australian water treatment plant (WTP). Norit W35 PAC was purchased from Sigma-Aldrich, and samples of Norit GCN1840 and Norit 18×40AG1 were donated by Norit Nederland BV.

2.2. Site Description and Sample Collection

For the study on the effect of disinfection strategy on the formation of DBPs and the effect of mixing different water qualities, source waters for bench-scale tests were collected after coagulation and before disinfection at three different water treatment plants in South East Queensland showcasing an array of different water characteristics. Samples were taken from January 2011 to June 2011. Samples were collected in acid washed amber bottles and were shipped on ice to the laboratory where they were immediately filtered. The formation potential tests were initiated within 24 hours of sampling.

For the sampling survey across Capalaba region samples were taken at Capalaba WTP and from the distribution system (Figure 8) during five sampling events during spring-summer 2011. The sampling dates were 5/9/2011, 3/10/2011, 7/11/2011, 21/11/2011 and 6/12/2011.

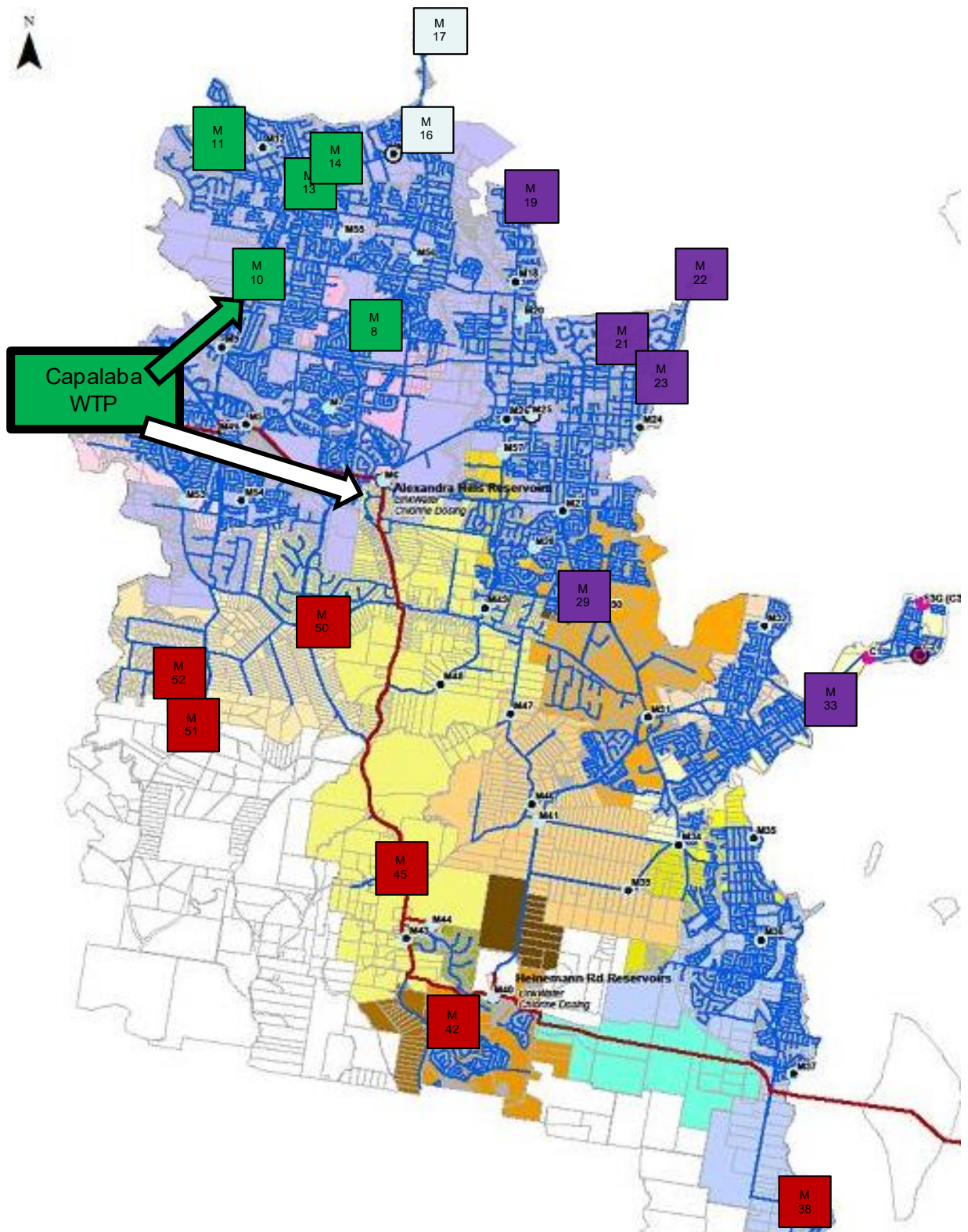


Figure 8: Sampling points selected for the study. NSI= North Stradbroke Island. Green=Capalaba WTP source water, red=NSI WTP source water, purple=Alexandra Hill Reservoir (Capalaba + NSI), blue=Capalaba + Alexandra Hill Reservoir (Courtesy of Allconnex Water) White arrow represents water from Capalaba to Alexandra Hill Reservoir.

For the study of DBP formation in SEQ waters before and after EC or EC combined with PAC, MIEX®, GAC, or SIAC (Section 1) treatments, raw water samples were taken from Capalaba WTP, Mt Crosby WTP and Molendinar WTP, on two separate sampling dates (17/5/2012 and 18/6/2012). Samples were collected in 20 L HDPE drums that had been detergent and acid-washed. Samples were transported immediately to the laboratory at which they were stored at 4°C until use for bench-scale DBP precursor removal treatments followed by DBP formation potential test (experiments initiated within 24 h).

2.3. DBP Analyses

DBP analysis used a liquid-liquid salted microextraction and gas chromatography (GC) with electron capture detector (ECD) [11]. Sample pH was adjusted to pH 3.5 with 0.2 N sulfuric acid and extracted using 3 mL of MtBE containing 200 µg/L of 1,2-dibromopropane as an internal standard. After the addition of ~10 g pre-baked (at 500°C) sodium sulfate, the samples were vortexed for 1 minute and left to settle for 5 min. Finally, ~1.5 ml of MtBE extract was transferred into 2 ml vials for injection. The analysis was carried out using an Agilent 7890A GC-ECD (Forest Hill, Australia), with the chromatographic separation performed on a dual column system using a DB-5 Agilent column (30 m length × 0.25 mm inner diameter × 1.0 µm film thickness) and a DB-1 Agilent (30 m length × 0.25 mm inner diameter × 1.0 µm film thickness). Pulsed splitless injection was used at a temperature of 200°C. The oven temperature program was as follows: 40°C for 25 min, ramp to 145°C at 5°C/min and held for 2 min and then ramp to 260°C at 20°C/min and held for 10 min. The ECD temperature was set at 290°C. The relative percent differences (RPD) for the duplicate samples were in all instances lower than 10%. The reporting limit for all the DBPs was 0.1 µg/L and the recovery was between 80% and 120%.

The method used for *N*-nitrosamines analysis is based on EPA Method 251 (Munch and Bassett, 2004). In that analysis, water is passed through a carbon solid phase extraction (SPE) cartridge and the *N*-nitrosamines are eluted off with dichloromethane. The extracts are concentrated by evaporation under nitrogen to 1 mL and analysed by capillary gas chromatograph-mass spectrometer (GC-MS) in Positive Chemical Ionisation (PCI) mode with anhydrous ammonia as the chemical ionisation gas (Finnigan Trace G.C. Ultra and Finnigan Trace DSQ Mass Spectrometer with Ammonia Chemical Ionisation). Fifty microlitres of a 0.5 mg/L deuterated NDMA stock solution in methanol solvent was added as a surrogate to each 1 L sample to evaluate the percentage of recovery of the extraction (25 ng/L). For SPE, commercial EPA coconut carbon cartridges for NDMA analysis (Restek) were used. Methanol, dichloromethane (HPLC grade) and MilliQ water were used as solvents. Glass fibre filters were obtained from Whatman. Teflon 1/8" tubing, weights, tubes, tube adaptors, and a 12-port vacuum manifold for performing SPE were purchased from Supelco. The charcoal cartridge was conditioned with 8 mL of dichloromethane, followed by 15 mL of methanol and 25 mL of HPLC water. The cartridge was allowed to dry during dichloromethane and methanol cleaning but not during the last cleaning with HPLC water. The flow rate for sample loading was adjusted to < 10 mL/min. After finishing the loading, cartridges were cleaned with 10 mL of HPLC water and dried under vacuum for 10 minutes. For elution, 30 mL of dichloromethane was passed first through the charcoal cartridge and then through a 6 mL tube packed with previously dried sodium sulfate. A final 1 mL was collected for analysis. Fifty nanograms per litre of internal standard were added to the final 1 mL. Every batch was accompanied by a standard spiked solution and a blank to determine the performance of the extraction and the possible NDMA contamination in the water. Two microlitre samples were splitless injected into the gas chromatograph at 250 °C. The column used was ZB-5MS (30 × 0.25 × 1.0). The initial temperature of the oven was 40 °C for 1 min. Then a ramp was programmed at 40 °C/min to 265 °C. Final temperature was held for 5.4 minutes. Helium gas at 1 mL/min was used as carrier. Anhydrous ammonia gas, 99.99 % pure, was used in the mass spectrometer to facilitate positive chemical ionisation. The reagent gas flow for CI was 3.5 mL/min. The NDMA detection limit for the technique was 5 ng/L.

2.4. Anion Analysis

All anion analysis was conducted using a Dionex ICS-5000 ion chromatography system. For fluoride, chloride, bromide, nitrite, nitrate, sulfate, and phosphate analysis the system was run in one-dimensional mode with an IonPac AS19 analytical column (4 mm internal diameter × 250 mm length) with flow rate of 1 mL/min and injection volume of 250 µL. The gradient employed was as follows: the first 10 minutes held KOH concentration at 10 mM, then a gradient was applied which ramped to 58 mM KOH over 30 minutes. This concentration was held for 5 minutes before returning the KOH concentration to 10 mM over 3 minutes. Iodide analysis employed an IonPac AS19 analytical column in the first dimension and an IonPac AS19 capillary column in the second dimension. Matrix elimination was achieved by trapping the iodide peak on a MAC200 monolith anion concentrator (0.75 × 80 mm) then injecting onto the second, capillary, column. The gradient employed was as follows: in the first dimension, 10 mM KOH was used as the eluent for the first ten minutes, after which a ramp was applied that reached 58 mM KOH at minute 40. This was held for 5 minutes then a gradient was applied to decrease KOH concentration back to 10 mM KOH over 14 minutes. Concurrently, in the second dimension, eluent concentration (KOH) was held at 4 mM for 27.6 minutes, then a ramp was applied until minute 30 to give a KOH concentration of 35 mM, that was then ramped slowly to reach 70 mM at 55 minutes. The flow rate was 1 mL/min for the analytical column and 0.01 mL/min for the capillary column, and injection volume was 500 µL. Calibration standards, blank-matrix and spiked-matrix standards were run with each batch as quality controls. Bromide and iodide analyses reported in chapter 6 were analysed by the following methods: bromide ions were analysed by ion chromatography (Metrohm 861, Herisau, Switzerland) with a conductivity detector, and the samples were chemically and CO₂ suppressed to lower the baseline. Iodide was quantified by ion chromatography with ultraviolet (UV) detector (Dionex ICS-2000, Scoresby, Australia). The limits of reporting for these methods were 20 and 10 µg/L for bromide and iodide ions, respectively.

2.5. Excitation-Emission Matrix Spectroscopy

Fluorescence measurements of NOM were performed using a PerkinElmer LS-55 luminescence spectrometer (PerkinElmer, Australia) in a quartz cuvette. The spectrometer displayed a maximum emission intensity of 1000 arbitrary units (AU). Excitation wavelengths were monitored from 200 nm to 400 nm at steps of 5 nm, and emission wavelengths were monitored from 280 nm to 500 nm with a 0.5 nm step. A 290 nm cutoff was used to limit the second-order Raleigh scattering. Excitation and emission scan slits were set at 7 nm and the scan speed was set at 1200 nm/min. Samples were allowed to equilibrate to room temperature prior to analysis in order to minimise the temperature effect. All samples were diluted to give an absorbance of maximum 0.05 at 220 nm and for all fluorescence data, MilliQ water blank was subtracted.

2.6. Other Analyses

Dissolved organic carbon (DOC) was measured using a JENA multi N/C 3100 instrument (Jena, Germany) and in a Shimadzu TOC-VCSH TOC analyser using a high temperature catalytic oxidation method (Standard Method 5310A) [280]. UV₂₅₄ was measured using a Bio-Rad SmartSpec Plus spectrophotometer. All samples were filtered through 0.45 µm syringe filters prior to analysis. Dissolved organic nitrogen (DON) was calculated to be the difference between Total Kjeldahl Nitrogen (TKN) and NH₄-N nitrogen. TKN was measured using a Lachat QuickChem (Loveland, US). Ammonium nitrogen and nitrate were measured on a Lachat flow injection analyser as per the Lachat QuickChem (Loveland, US).

2.7. DBP Formation Potential Test

All glassware used during these experiments was soaked in detergent for at least 8 hours, and then in a 10% nitric acid solution for at least 8 hours, then rinsed with methanol and milliQ water. To evaluate the formation potential of DBPs, first the specific chlorine demand was determined using Standard

Method 5710 (Clesceri *et al.*, 1998). Chlorine and chloramine dose for the DBP formation potential tests were calculated to obtain a residual chlorine concentration similar to what would be found in a real application of drinking water disinfection (i.e, around 2 mg/L as Cl₂).

Two aliquots of 240 or 225 mL for each sample were buffered at pH=7 with phosphate buffer (20 mM). Free chlorine (as sodium hypochlorite, NaOCl) or preformed monochloramine was dosed to equal the chlorine demand (calculated according to Method 5710, Standard Methods for the Examination of Water and Wastewater [280]), plus 2 mg/L chlorine (as Cl₂), to ensure a final residual in the range 2 ± 1.5 mg/L after the 72 h contact time. Monochloramine stock solutions were prepared daily by slowly adding NaOCl into a rapidly stirred NH₄Cl solution adjusted to pH=8 with NaOH, and using a Cl:N molar ratio of at least 1:1.2 to avoid breakpoint chlorination resulting from local excess of hypochlorite (Mitch and Sedlak, 2002). Samples were kept headspace free in contact with the disinfectants for three days in the dark and at constant temperature (23±1 °C). After this time, the samples were quenched using ascorbic acid and stored headspace free at 4 °C until extraction within 24 hours. Three days of contact time was employed in these experiments according to Koch and co-authors (1991). Another batch of samples was used for the disinfectant conversion experiments. To this aim, ammonia was added to the chlorine samples adding monochloramine if necessary to obtain the final required residual concentration. Chlorine was added to the samples containing monochloramine to obtain the final desired chlorine residual via breakpoint chlorination. After three days of contact time, the samples were quenched using ascorbic acid and stored headspace free at 4 °C until extraction within 24 hours. The breakpoint was experimentally determined in every sample.

A concentration of 2 mM (140 mg/L Cl₂) was used to determine the NDMA FP of the selected waters. The test was performed at pH 6.8 which was achieved by adding 700 mg/L KH₂PO₄ and 880 mg/L Na₂HPO₄·2H₂O to the water sample (10 mM phosphate buffer). To evaluate the NDMA FP test, dimethylamine (DMA) was added to the solution as a known NDMA precursor as described previously in the literature (Gerecke and Sedlak, 2003; Mitch *et al.*, 2003a). All experiments were performed in 2 L amber glass bottles, which were stored at room temperature (23±2 °C) in the dark for seven days. The total chlorine was measured daily. On the seventh day, the residual chloramine concentration was quenched with 2.5 g/L sodium sulfite (added as a solid to the sample) to prevent further NDMA formation. The samples were then analysed for NDMA. Data obtained from these experiments was compared with the results reported in the literature (Gerecke and Sedlak, 2003; Mitch *et al.*, 2003a).

2.8. Solid Phase Extraction for Bioassays

SPE using 1 cc Oasis HLB (Waters, Rydalmere, Australia) cartridges was done as described [281]. The relative enrichment factor (REF) of the sample in the bioassays corresponds to the product of the enrichment by SPE (factor of 2000) and the dilution in the bioassay (typically 15 to 20000 times diluted) and can also be computed as water volume equivalent transferred to the bioassay divided by the total volume of the bioassay (equation 5). The REF in the experiments ranged from 0.1 to 150.

$$(5) \quad \text{REF} = \frac{\text{water volume equivalent transferred to bioassay}}{\text{total volume of bioassay}}$$

Aliquots of the MtBE extracts prepared for chemical analysis as described in section 2.3 were also submitted to the bioassays with a maximum REF of 3 but the MtBE dominated the overall toxicity. For example, the EC₅₀ was equivalent to 5% MtBE in the Microtox assay. Due to the volatility of some of the DBPs, the MtBE extract could not be evaporated for enrichment. Thus further toxicity experiments were only conducted with SPE extracts.

2.9. Bioassays

The solid phase sample extracts were submitted to the bioassays listed in Table 23 performed according to the protocols in the cited literature references. Effect concentrations (EC) were derived from full log-logistic (cytotoxicity and protein damage) or linear (genotoxicity and oxidative stress) concentration-effect curves and the ECs (EC_{50} , concentration at which 50% of cytotoxicity was observed, and $EC_{IR1.5}$, concentration that caused an induction ratio of 1.5 in the stress response assays) were converted to toxic equivalent concentrations (TEQ) using equation 6. The EC(reference chemical) refers to the effect concentration (EC) of a potent and selective reference chemical for the respective bioassay.

$$(6) \quad TEQ = \frac{EC(\text{reference chemical})}{EC(\text{sample})}$$

The reported results are the average of two or three independently replicated samples, with the exception of the bioassay for oxidative stress response, where all experimental data were evaluated as a common concentration effect curve and the error bars correspond to the propagated standard deviations of the linear regression.

Table 23: Bioassays for non-specific and reactive toxicity applied in the present study.

Mode of Action	Assay	Targeted Chemicals (reference for method)	Effect Concentration EC	Reference Chemical/ Toxic Equivalent Concentration (TEQ)	Reference of Original Method	Reference of Protocol Used in the Present Study
Cytotoxicity	Bioluminescence inhibition assay with <i>Vibrio fischeri</i>	All chemicals	EC ₅₀ : effect concentration causing 50% inhibition of bioluminescence	Virtual baseline toxicant/ Baseline-TEQ	[282]	[283]
Cytotoxicity	AREc32 cell viability w/ MTS	All chemicals	EC ₅₀ : effect concentration causing 50% reduction of cell viability	Not defined	[284]	[285]
Genotoxicity	<i>umuC</i> (genotox)	Hard electrophiles (e.g., methyl methanesulfonate)	EC _{IR1.5} : effect concentration causing an induction ratio of 1.5	4-Nitroquinoline-N-oxide/ 4NQO-EQ	[286]	[283]
		Aromatic amines, polycyclic aromatic hydrocarbons)	EC _{IR1.5} : effect concentration causing an induction ratio of 1.5	2-Aminoanthracene/ 2AA-EQ	[286]	[283]
Protein damage	<i>E.coli</i> GSH±	Soft electrophiles (e.g., Seanine)	EC ₅₀ : effect concentration causing 50% reduction of growth rate	No TEQ defined, measure of the specific effect is the TR _{GSH} , the ratio between EC ₅₀ (GSH+) to EC ₅₀ (GSH-)	[287]	[288]
Oxidative stress	Induction of Nrf2 in AREc32	Quinones, reactive oxygen species	EC _{IR1.5} : effect concentration causing an induction ratio of 1.5	t-Butyl hydroquinone/ tBHQ-EQ	[289]	[285]

2.10. Synthetic Water Matrix

A matrix of 18 synthetic waters (17 plus blank) of differing characteristics were utilised for all DBP formation potential and DBP precursor removal experiments described in chapters 0 through to 1. The experimental matrix was developed based on a face-centered central composite design, with 3 variables, namely, NOM concentration (measured as mg/L DOC), halide concentration (combined Cl⁻, Br⁻ and I⁻) and alkalinity. Synthetic waters were made by dosing 1L samples of laboratory purified water with bromide standard (to give final concentrations of 100 µg/L, 450 µg/L, or 800 µg/L as Br⁻), iodide standard (to give final concentrations of 4 µg/L, 18 µg/L, or 32 µg/L as I⁻) and Suwanee river NOM isolate to give final DOC concentrations of approximately 3 mg/L, 7.5 mg/L, and 12 mg/L. Alkalinity concentrations were 38 mg/L, 138 mg/L, or 238 mg/L as CaCO₃. Sodium chloride was added to give a Br⁻/Cl⁻ ratio of 1:300 by weight, to mimic a natural water [48]. Calcium sulfate and magnesium sulfate were also added, in proportion to alkalinity, as described [280]. After making the waters, the pH was adjusted to 7 with dilute HCl. Each 1L sample was stored in an amber glass bottle at 4°C until use (within 24 hrs). These three water quality parameters were investigated in terms of their impact on DBP formation and speciation upon chlorination or chloramination, both with and without EC and EC combined with a secondary, adsorptive treatment. The data generated from these samples was subjected to Response Surface Modelling (RSM) using MODDE version 5 software, in order to determine the relationships between the starting water quality parameters and the DBPs formed.

2.11. Enhanced Coagulation

Bench-scale EC jar tests were performed in accordance to US EPA's Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual [290], using a Platypus Jar Tester, equipped with 4 overhead stirrers and 1L jars. The synthetic waters were treated using individual coagulant doses optimised to give greatest NOM removal and a final pH in the range 5.5 – 6.5 for each sample (from 30 to 120 mg/L Alum (as Al₂(SO₄)₃•18H₂O) depending on the sample alkalinity and starting NOM concentration). Following the addition of the coagulant, the samples were subjected to rapid mixing for 1.5 min at 200 rpm, flocculation for 13.5 min at 30 rpm, then settled for 60 min before vacuum filtering through Whatman No. 1 filter papers to simulate sand filtration at the WTP [291].

2.12. MIEX® Treatment

After EC, samples were dosed with 10 ml/L regenerated, settled MIEX® resin, then jar tested for 30 min at 100 rpm, settled for 5 minutes, then vacuum filtered through Whatman No. 1 filter papers. The MIEX® used was sourced from a South Australian WTP and was therefore a used resin that was regenerated by stirring (with an overhead stirrer) with a 10% NaCl solution prior to use.

2.13. Powdered Activated Carbon Treatment

All samples were dosed with 60 mg/L of Norit W35 PAC, then jar tested for 30 min at 100 rpm, before being allowed to settle for 5 min. Samples were then vacuum filtered through Whatman No. 1 filter papers.

2.14. Granular Activated Carbon Treatment

GAC (Norit GCN1840 and Norit 18×40AG1) were soaked overnight in laboratory purified water and rinsed prior to use to remove fines. Aqueous activated carbon slurries were then loaded into columns with a total volume of 6.36 cm³ (10 cm height × 0.9 cm diameter, aspect ratio of 8.1) with a final weight of 6 g of GAC loaded into each column. Care was taken to avoid the inclusion of air bubbles in the column beds. Approximately 125 bed volumes of sample were passed over each GAC column, at a flow rate that allowed an empty bed contact time (EBCT) of 10 minutes (0.6 mL/minute). Each column took approximately 24 h to treat the whole sample.

3. EFFECT ON DBP FORMATION OF TRANSFORMATION OF DISINFECTANTS – LABORATORY SCALE EXPERIMENTS

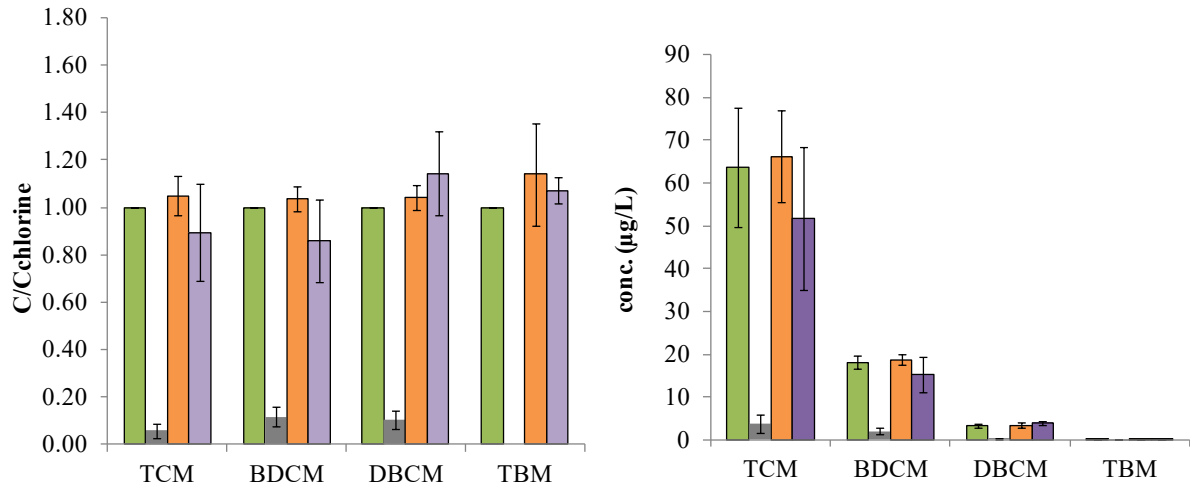
The aim of this part of the study was to investigate the effect on DBP formation of transforming disinfectants. To this aim source water from Molendinar WTP, Capalaba WTP and Mt Crosby WTP was taken after coagulation and before disinfection in acid washed amber glass bottles and was kept cool until shipped to the laboratory. The water samples were filtered (Whatman 1, pore diameter 11 µm) to simulate sand filtration at the WTP. Combined reverse osmosis permeate was taken before final disinfection at Tugun desalination plant. Table 24 shows the average water characteristics for the waters after filtration in the lab including their chlorine and monochloramine demand. The formation of DBPs from the Tugun desalination plant was negligible in all occasions and hence has not been included in this report (tTHMs < 2 µg/L, 4HANs < 1.0 µg/L, I-tTHMs < 0.2 µg/L, HKs < 0.1 µg/L and CH<0.5µg/L).

Table 24: Average properties of the source waters selected for the study. Intervals correspond to the standard deviation between the values obtained from four independent sampling events. na=not analysed.

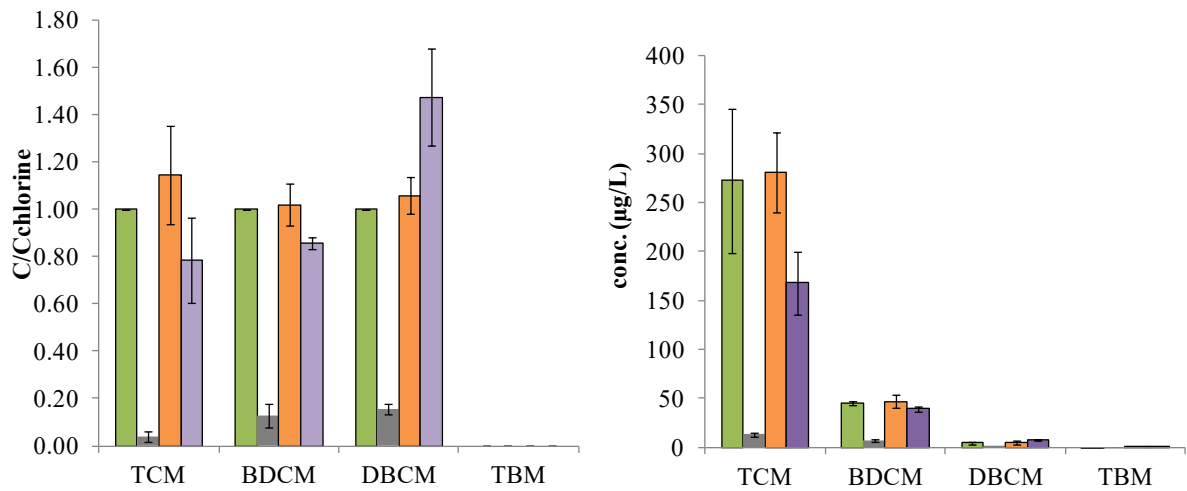
	DOC (mg/L)	NO ₃ ⁻ (mg/L)	DON (mg/L)	Conductivity (µS.cm)	pH	SUVA (L/mg.m)	HOCl Demand (mg/L)
Molendinar	2.7 ± 1.6	0.04 ± 0.03	0.29 ± 0.09	131 ± 41	6.8 ± 0.3	2.2 ± 1.0	3 ± 1
Capalaba	10.3 ± 5.7	0.38 ± 0.41	0.41 ± 0.22	175 ± 54	6.3 ± 0.2	2.4 ± 1.5	9 ± 2
Mt Crosby	2.8 ± 0.8	0.33 ± 0.05	0.21 ± 0.14	349 ± 83	6.6 ± 0.4	2.5 ± 0.5	4 ± 2
Tugun desalination (n=2)	<1.00	0.01 ± 0.01	n.a	55 ± 20	8	n.a	0

DBP formation was measured after three and six days of contact time between source water and disinfectant to estimate the effect of this parameter. From this data it was seen that most of the DBPs were already formed after three days. Therefore, we compared herein the DBPs generated after four specific scenarios (i) three days contact time with chlorine, (ii) three days contact time with monochloramine, (iii) three days contact time with chlorine followed by three days contact time with monochloramine, and finally (iv) three days contact time with monochloramine followed by three days contact time with chlorine.

Molendinar



Capalaba



Mt Crosby

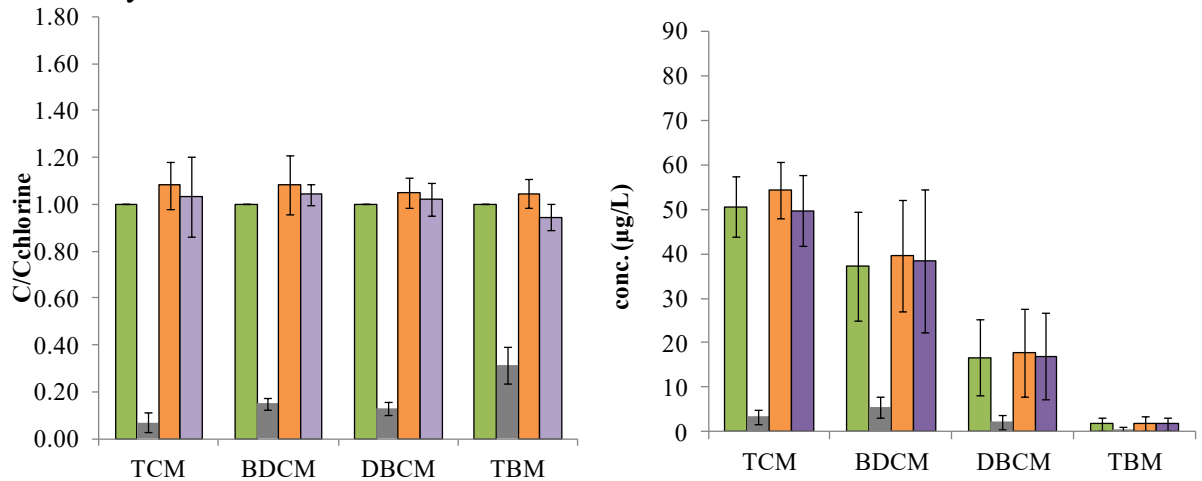


Figure 9: Trihalomethane formation potential of Molendinar, Capalaba and Mt Crosby waters after coagulation and filtration. pH=7, T=23±2°C. Disinfectant dose=disinfectant demand + 2 mg/L (chlorine) and/or 3.5mg/L (monochloramine). n=4. Left= relative formation of DBPs in comparison to chlorine (green). Right= average concentration of DBPs measured. Error bars correspond to the standard deviation of four sampling events. Green= chlorination, grey=chloramination, orange=chlorine converted to chloramine and purple=chloramine converted to chlorine.

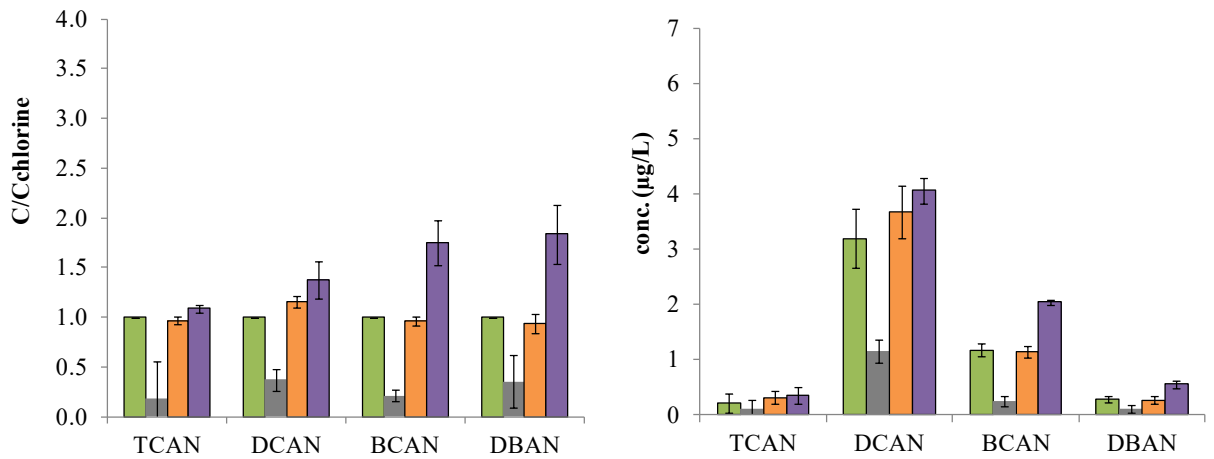
THMs in conjunction with HAAs are the most prevalent DBPs in drinking water, formed as a result of the reaction between chlorine and natural organic matter. Figure 9 left shows the relative formation of TCM, BDCM, DBCM and TBM following disinfection strategies i-iv for the four source waters selected for this study. A value higher than one indicates an increase in the formation of the specific THM when compared to sole chlorination. Figure 9 right shows the individual values measured. The formation of DBPs during chloramination followed by chlorination was not investigated during sampling campaign 1, hence only three values are used to evaluate the effect of this conversion on the formation of DBPs.

In general the highest concentration of THMs was observed when disinfecting source water from Capalaba WTP with chlorine. Molendinar and Mt Crosby source waters generated lower and similar concentration of DBPs, though Mt Crosby showed an increased concentration of bromine containing DBPs, which are in many cases more toxic than their chlorinated analogues. From Figure 9 left, we can also see that monochloramine generates significantly less THMs than chlorine, as expected [9]. Hua and Reckhow [15] found that chloramines produced a higher percentage of unknown TOX than free chlorine. This means that because chloramines are much weaker oxidants than free chlorine, organic matter may be halogenated but organic molecules may not be broken down to the extent required to generate THMs or other small DBPs. No differences were observed between the DBPs generated after disinfecting the waters with chlorine (i) and with chlorine followed by monochloramine (iii) or viceversa. Figure 10 shows the average formation of HANs following disinfection strategies i-iv for the four source waters selected for this study presented as described in Figure 9. There is no guideline value in the ADWG for any of the HANs included in the study however the WHO recommended values for DCAN and DBAN are 20 and 70 $\mu\text{g/L}$, respectively [292].

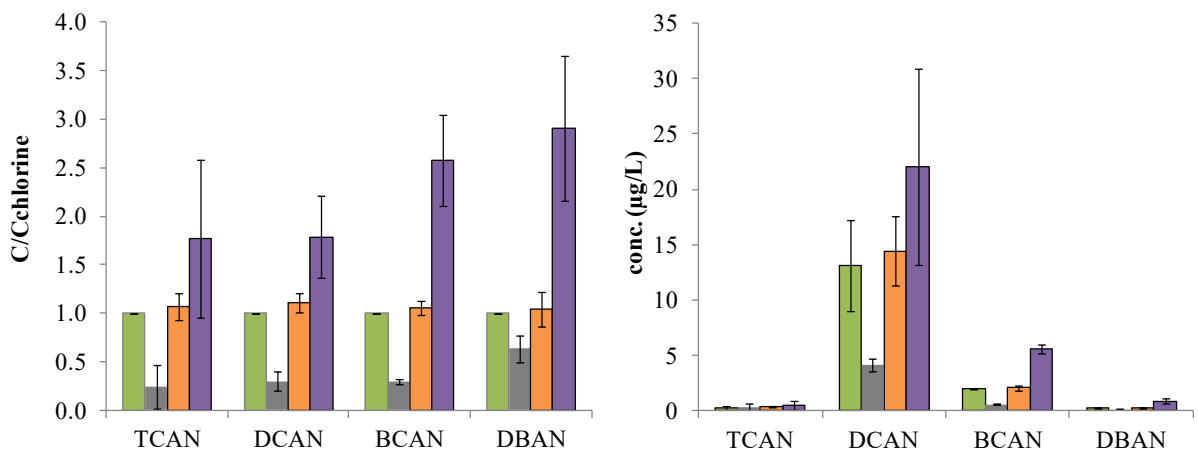
Total HAN concentrations in Molendinar and Mt Crosby were in line with the findings of Bougeard *et al.* [293], who reported levels of HANs between approximately 0.023 and 5.5 $\mu\text{g/L}$ when using formation potential tests. However, concentrations measured from Capalaba WTP source water were extremely high, in particular, results obtained for DCAN, though this specific DBP has previously been the major HAN observed [293]. Dihalogenated HANs are reported to be more stable than the trihalogenated HANs [294]. In addition, TCAN can undergo base-catalysed hydrolysis at pH higher than 5.5 (here, the pH was 7.0) which is the likely explanation as to why it was rarely detected in this study [295].

Disinfecting with monochloramine rather than chlorine (ii), decreased the concentration of HANs by at least a factor of three. Hua and Reckhow [15] also found that concentrations of HAN were reduced when using monochloramine and low concentrations of dihalogenated HANs ($<1 \mu\text{g/L}$) were formed. No significant differences were observed when comparing the DBPs generated after disinfecting the waters with chlorine and with chlorine followed by monochloramine. A common trend of HAN increase could be seen for the disinfection strategy iv (monochloramine followed by chlorine) in comparison to disinfection strategy i (chlorine) and iii (chlorine followed by monochloramine). Yang and co-authors investigated the origin of nitrogen in nitrogen containing DBPs (N-DBPs) such as HAN during chloramination with Labelled ^{15}N -monochloramine. They found that nitrogen in N-DBPs originates from both NH_2Cl and organic-N compounds [296]. We could then suggest that the increase observed in HAN formation when disinfecting water with chloramines prior to chlorine could be due to nitrogen addition to NOM that is further oxidised when adding the chlorine to generate HAN. Therefore, the final concentration of HAN generated may have been increased because there is more nitrogenated organic matter.

Molendinar



Capalaba



Mt Crosby

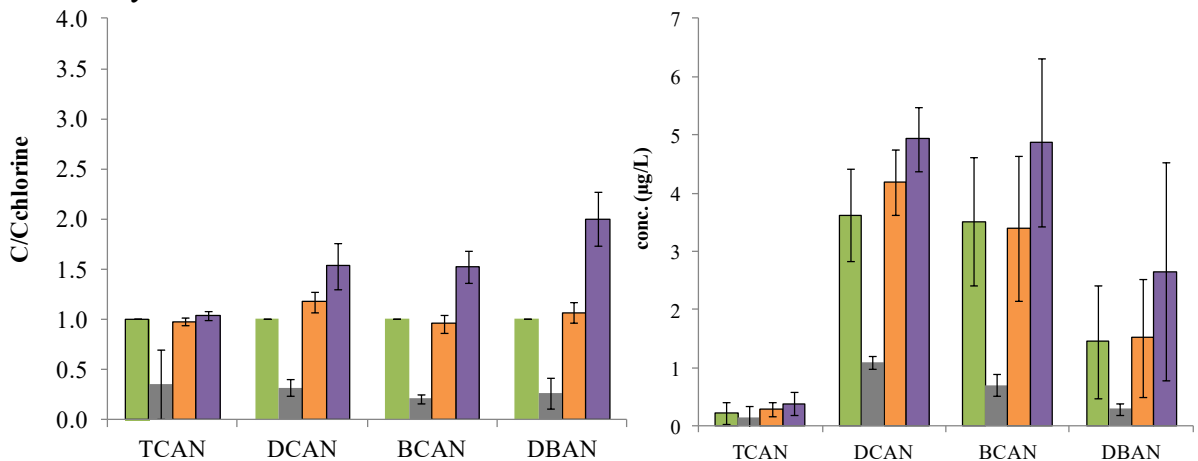


Figure 10: Haloacetonitrile formation potential of Molendinar, Capalaba and Mt Crosby waters after coagulation and filtration. pH=7, T=23±2°C. Disinfectant dose=disinfectant demand + 2 mg/L (chlorine) and/or 3.5mg/L (monochloramine). n=4. Left= relative formation of DBPs in comparison to chlorine (green). Right= average concentration of DBPs measured. Bars correspond to the standard deviation of four sampling events. Green= chlorination, grey=chloramination, orange=chlorine converted to chloramine and purple=chloramine converted to chlorine.

Figure 11 shows the average formation of HKs following disinfection strategies i-iv for the four source waters selected for this study. Bars represent the inter-day standard deviation of four sampling events.

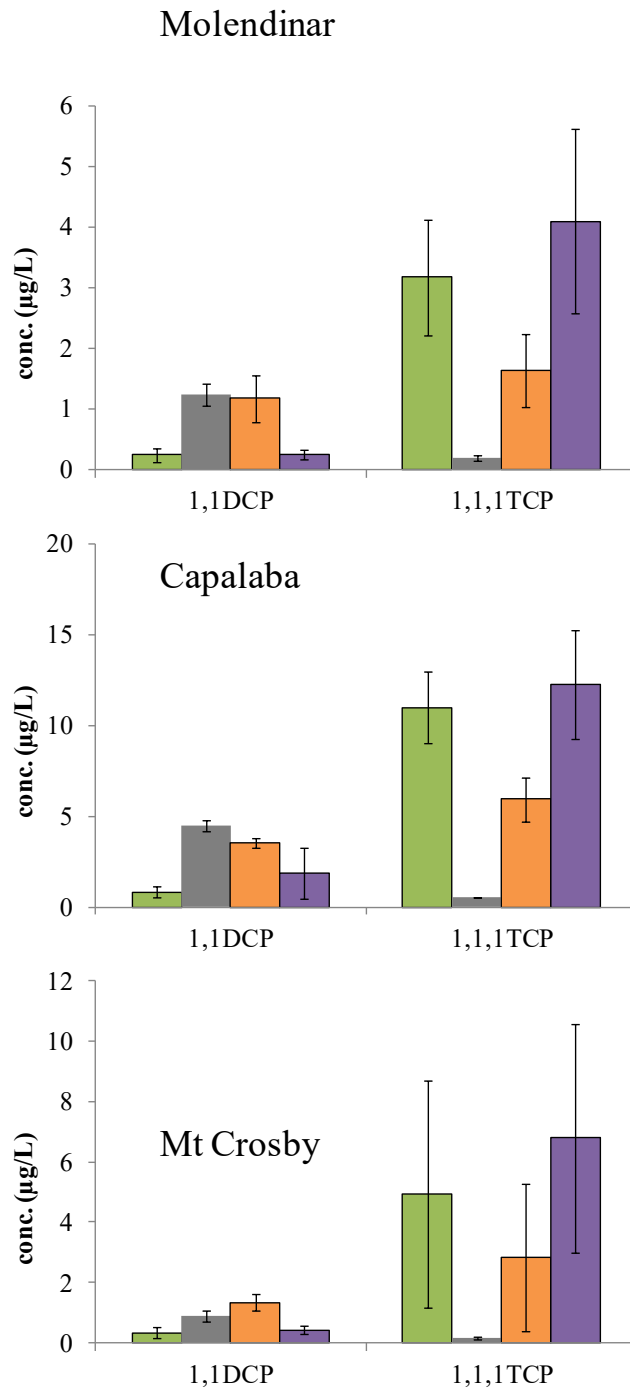


Figure 11: Haloketone formation potential of Molendinar, Capalaba and Mt Crosby waters after coagulation and filtration. pH=7, T=23±2°C. Disinfectant dose=disinfectant demand + 2 mg/L (chlorine) and/or 3.5mg/L (monochloramine). n=4. Bars correspond to the standard deviation of four sampling events. Green= chlorination, grey=chloramination, orange=chlorine converted to chloramine and purple=chloramine converted to chlorine.

There is no guideline value in the ADWG for any of the HKs included in the study. However, 1,1,1-TCP is of particular interest for distribution systems since, even though it is not regulated, the hydrolysis of 1,1,1-TCP ($k=1.82 \times 10^{-1} \text{ h}^{-1}$ at pH 7 [297]) can generate the same molar concentration of TCM and augment TCM concentration during transport. Hydrolysis may explain the lower

concentration of 1,1,1-TCP in strategy iii (chlorine → monochloramine) compared to chlorine alone (i) and also explain the slight increases of TCM in Figure 9 in strategy iii compared to i. 1,1-DCP is the only DBP that is generated at higher concentration in the presence of monochloramine. These differences in the formation of 1,1-DCP and 1,1,1-TCP with chlorination and chloramination can be partially explained by a simplified model developed by Reckhow and Singer [14]. In this model, chlorination of fulvic acid solutions leads to the formation of intermediate by-products, such as 1,1-DCP ($\text{CHCl}_2\text{-CO-CH}_3$). 1,1-DCP can be further oxidised by chlorine and form 1,1,1-TCP ($\text{CCl}_3\text{-CO-CH}_3$). This model reveals that further chlorine attack and hydrolysis are essential for the formation of 1,1,1-TCP. However, monochloramine is not able to provide further chlorine substitution and hydrolysis, as 1,1-DCP is found to be very stable in the presence of monochloramine. Similarly, it is expected that other intermediate by-products ($\text{CHCl}_2\text{-CO-R}$, $\text{R}\neq\text{-OH}$) may not easily be substituted by chlorine to form $\text{CCl}_3\text{-CO-R}$ in monochloramination. Thus, in a chloraminated solution, the concentration of 1,1-DCP is high but almost no 1,1,1-TCP is detected. However, from our experiments we observed that further 1,1-DCP could be formed even after prior chlorination (strategy iii). This could mean that maybe different precursors are involved in the generation of the two HKs. We are currently investigating this hypothesis.

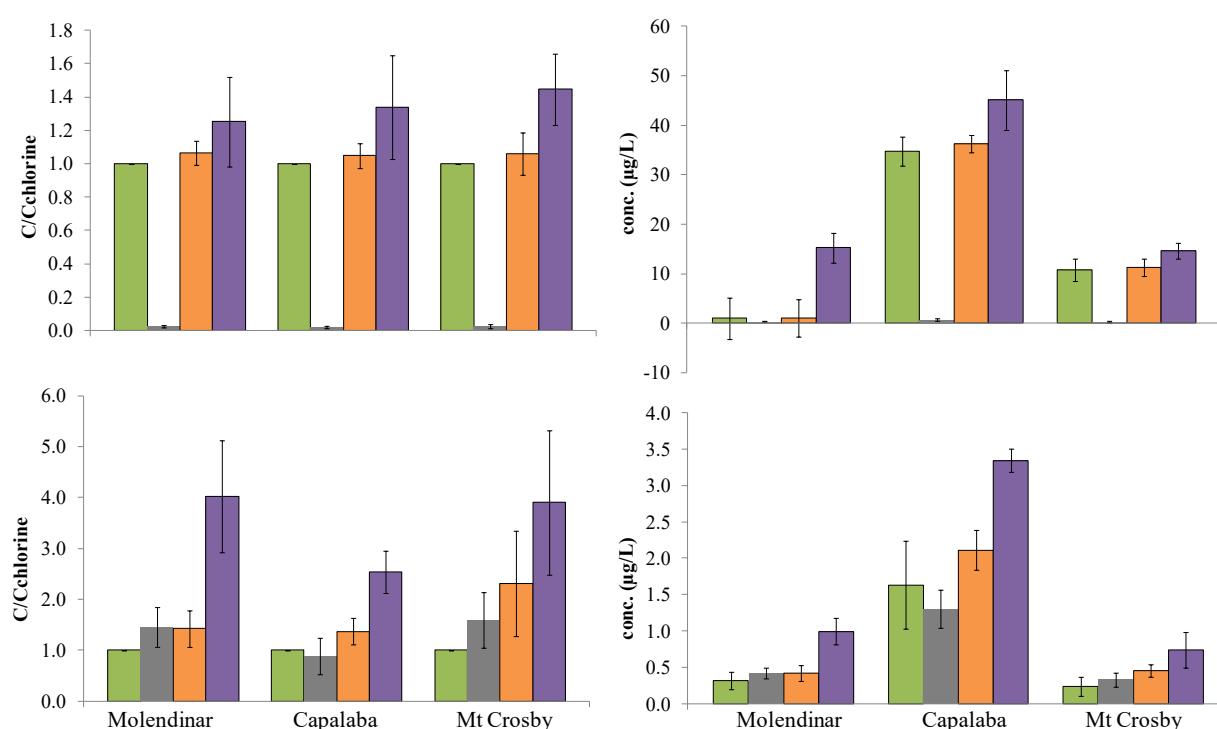


Figure 12: Chloral hydrate (top) and trichloromethane (bottom) formation potential of Molendinar, Capalaba and Mt Crosby waters after coagulation and filtration. pH=7, T=23±2°C. Disinfectant dose=disinfectant demand + 2 mg/L (chlorine) and/or 3.5mg/L (monochloramine). n=4. Left= relative formation of DBPs in comparison to chlorine (green). Right= average concentration of DBPs measured. Bars correspond to the standard deviation of four sampling events. Green= chlorination, grey=chloramination, orange=chlorine converted to chloramine and purple=chloramine converted to chlorine.

CH is included in the ADWG and its guideline value is 20 µg/L [22]. Beside THMs and HAAs, CH is the next most prevalent DBP in chlorinated drinking water, formed as a result of the reaction between chlorine and NOM. Figure 12 shows the formation of CH and trichloronitromethane (TCNM) following disinfection strategies i-iv for the four source waters selected for this study.

As seen in Figure 12, monochloramine did not generate CH, while concentrations formed during chlorine disinfection, chlorine followed by monochloramine or monochloramine followed by chlorine were relatively high. Dabrowska and Nawrocki [298] studied the effect of contact time on the

formation of CH. They observed that the reaction of chlorine with organic matter takes place as long as chlorine is available in the water. The concentration of CH may continuously increase in the water supply system. However, Koudjonou and co-authors [299] observed upon conducting the controlled laboratory chlorination of acetaldehyde under typical drinking water conditions (pH 6.7, 7.6 and 8.8, and temperature 4 °C and 21 °C) the formation of CH, the most common halogenated acetaldehyde, increased with contact time (0–10 days). However, at increased pH and temperature, CH reached maximum levels and subsequently broke down partially to chloroform and other unidentified compounds. TCNM seems to be the DBP that is most affected by the transformation of disinfectants since chlorination followed by chlorine disinfection increased its formation by at least a factor of two in all instances. The increase observed for TCNM and other DBP formation could be explained by the alteration of NOM by chloramination into a more reactive form.

Finally, the formation of I-THMs was also included in this study. I-THMs may be formed when disinfecting water with chloramines in the presence of iodine and these DBPs have been reported to be much more toxic than their brominated or chlorinated counterparts [300]. Formation of DCIM was observed when disinfecting with monochloramine in Capalaba and Mt Crosby source waters at an average concentration of 0.61 ± 0.14 and 0.41 ± 0.06 µg/L, respectively. These concentrations remained constant when transforming monochloramine to chlorine. Disinfection of Mt Crosby source water with monochloramine also generated BCIM and DBIM at 0.72 ± 0.54 µg/L and 0.17 ± 0.04 µg/L, respectively, showing a shift to brominated species in that WTP.

3.1. Conclusions

- In general the highest concentration of DBPs formed was observed when disinfecting source water from Capalaba WTP with chlorine. Molendinar and Mt Crosby WTPs generated lower and similar concentration of DBPs, though Mt Crosby showed higher concentrations of bromine containing DBPs. The Tugun desalinated water generated extremely low concentrations of DBPs as a result of the low TOC present in the water.
- Compared to chlorine, monochloramine generally resulted in lower concentrations of DBPs with the exception of 1,1DCP and I-THMs.
- Chloramines used after chlorine do not generate additional DBPs to the ones previously generated during chlorination, with the exception of 1,1DCP.
- Chloramines used before chlorine alter NOM and affect the final DBPs formed compared to application of chlorine alone. Some DBPs such as THMs seem to be reduced when employing this strategy at Capalaba and Molendinar, while the final concentration of HAN, CH and TCNM is increased in comparison to the use of chlorine alone.

4. BIOANALYTICAL ASSESSMENT OF THE FORMATION POTENTIAL OF DISINFECTION BY-PRODUCTS – LABORATORY SCALE EXPERIMENTS

This part of the study was carried out at the National Research Centre for Environmental Toxicology (Entox) in order to investigate the level of cytotoxicity, reactive modes of toxic action and stress response pathways in the source water taken from the drinking water plants discussed in section 3. The bioanalytical results were compared with chemical analytical data for twelve regulated and emerging DBPs. Only chlorinated and chloraminated waters were employed for this study.

In vitro cell-based bioassays are adequate monitoring tools for that purpose [301]. They give an account of the mixture effects and, if distinct modes of toxic action are targeted, also an idea about the characteristics of the toxic chemicals in water samples. Most *in vitro* bioassays of individual DBPs and disinfected water samples have targeted genotoxicity and mutagenicity [302-307], which is evident given the link to cancer development [308] but more recently, indicators of oxidative stress have also been assessed [309].

DBPs are primarily formed by oxidative processes involving chlorine, chloramine or alternative disinfectants like ozone and chlorine dioxide [1]. Since many DBPs are reactive chemicals with a wide range of electrophilic properties, we cannot expect that their reactive toxicity is limited to DNA damage but rather that a suite of reactive mechanisms towards all nucleophilic biomolecules such as DNA, proteins and lipid is relevant [287, 310, 311]. If bioassays are to be used as a monitoring tool, effects that are based on the ultimate manifestation of effect (such as DNA damage and formation of reactive oxygen species [309]) can be complemented with more sensitive early warning signs such as the onset of repair and defence mechanisms in cells. The cellular stress responses are especially suitable for this task [312]. They are activated before actual harm occurs, but they prove the presence of associated stressors. The DNA damage repair mechanisms and the oxidative stress response are particularly relevant for DBPs. In response to reactive oxygen species and chemicals such as many DBPs that have electrophilic properties, cells can trigger the production of a large variety of antioxidant and detoxifying enzymes. These pathways can be intercepted and visualised by linking the target gene on a plasmid to a reporter gene that encodes for a fluorescence protein or an enzyme that can be quantified by a colour reaction [301]. These so-called reporter gene assays are simple bioanalytical tools potentially capable of quantifying DBPs at very low concentrations.

Disinfected water contained considerable amounts of DBPs, while all source waters had concentrations of DBPs below or around the limit of reporting (LOR 0.1 µg/L). Concentrations of DBPs generated from disinfecting desalinated water were negligible as already presented in section 3.

A summary of the results obtained in this part of the study is detailed in Table 25.

Table 25: Summary of chemical analytics and bioassay results (SW = source water, HOCl = chlorination, NH₂Cl = chloramination). Chemical concentrations are the average of two samples for the disinfected samples (relative percent difference between the samples was typically less than 10%) and a single experiment for the source water [313].

	Capalaba Source Water			Molendinar Source Water			Mt Crosby Source Water			Desalination Plant			Blanks	
	SW	HOCl	NH ₂ Cl	SW	HOCl	NH ₂ Cl	SW	HOCl	NH ₂ Cl	SW	HOCl	NH ₂ Cl	Lab Blank	Field Blank
Microtox														
EC ₅₀	8.16	2.40	4.33	13.48	6.04	9.44	11.80	6.09	7.00	24.78	20.72	18.94	51.29	18.06
±	1.59	0.59	0.80	2.37	1.69	2.35	1.42	1.46	1.31	1.19	2.64	0.87	0.92	0.84
Baseline-TEQ (mg/L)	1.52	5.22	2.86	0.92	2.10	1.33	1.04	2.06	1.77	0.49	0.59	0.64	0.24	0.67
±	0.30	1.29	0.53	0.16	0.59	0.33	0.13	0.49	0.33	0.02	0.08	0.03	0.00	0.03
umuC														
EC _{IR1.5} -S9	134.41	14.23	37.08	107.02	49.10	73.89	>150	31.40	66.58	>150	>150	>150	>150	>150
±	100.12	0.86	10.60	76.76	21.07	27.01		1.12	4.99					
EC _{IR1.5} +S9	144.60	26.61	>150	>150	124.31	>150	>150	>150	>150	>150	>150	>150	>150	>150
±	14.14	4.00			54.72									
4NQO-EQ -S9 (µg/L)	0.14	0.87	0.33	0.14	0.25	0.17	<0.06	0.39	0.18	<0.06	<0.06	<0.06	<0.06	<0.06
±	0.14	0.34	0.02	0.06	0.03	0.01		0.12	0.05					
2AA-EQ +S9 (µg/L)	0.74	4.05	<0.71	<0.71	0.95	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71
±	0.07	0.61			0.42									
E. coli														
EC ₅₀ GSH+	>500	324	828	>500	>500	>500	>500	584	499	>500	>500	>500	>500	>500
EC ₅₀ GSH-	>500	47	269	363	121	437	>500	134	722	>500	>500	>500	>500	>500
Toxic Ratio	-	6.9	3.1	-	-	-	-	4.4	0.7	-	-	-	-	-
AREc32														
EC _{IR1.5}	8.6	1.8	2.9	9.9	4.8	5.6	7.8	2.8	4.5	40.9	32.0	37.4	50.0	37.1
±	0.4	0.1	0.1	0.7	0.1	0.1	0.3	0.1	0.1	1.8	1.6	2.0	1.9	1.1
tBHQ-EQ (µg/L)	25	123	76	22	45	40	28	78	49	5.4	6.9	5.9	<5	5.9
±	7	36	22	6	13	11	8	23	14	1.6	2.0	1.7		1.7

Overall, the results of the bioassays were in qualitative agreement with chemical analysis with higher DBP formation by the source water with higher DOC despite the fact that, at this stage, the bioassays are limited to non-volatile DBPs and none of the quantified DBPs are actually present in the SPE extracts. Figure 13 illustrates this direct comparison. Capalaba after chlorination had the highest levels of baseline-TEQ and at the same instance also the highest concentrations of DBPs, expressed as sum of the individual species analysed. For each sample NH₂Cl produced lower DBP levels and lower baseline-TEQ levels but it is also interesting to compare Capalaba NH₂Cl with Molendinar HOCl to see that overall DBP levels can differ by more than a factor of two while baseline-TEQ is not significantly different. Another particularly interesting example is Mt Crosby WTP, the only plant where Br-DBPs are equally high or higher than Cl-DBPs and the baseline-TEQ is higher than of Molendinar WTP where Cl-DBPs dominate. Thus, the chemical analysis and bioanalysis provide the same trends despite different chemicals being assessed by the two methods: volatile DBPs in chemical analysis and non-volatile DBPs in the bioassays.

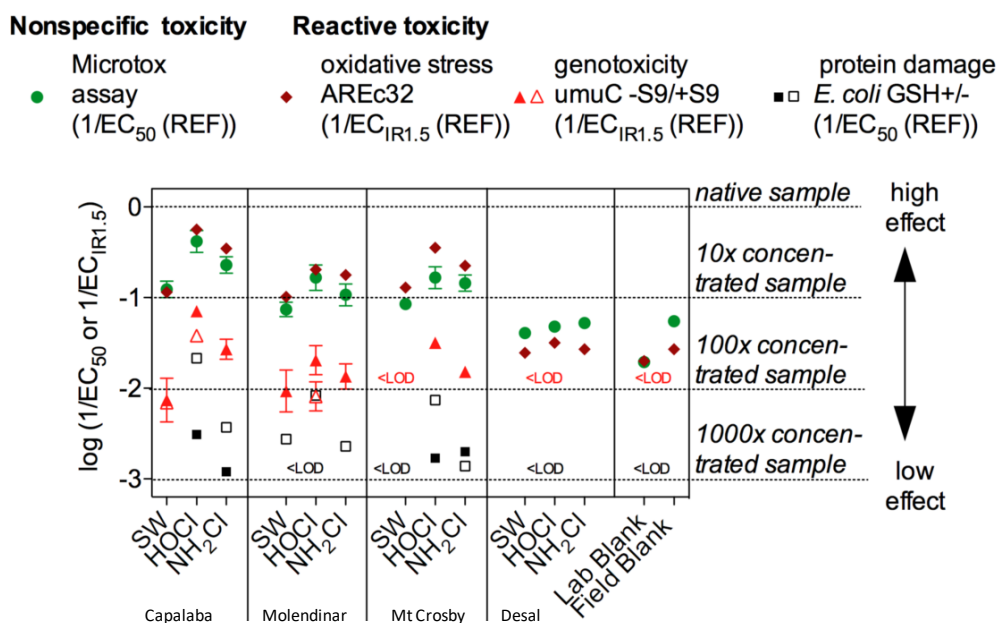


Figure 13: Summary of the bioassay results for the four different source waters (SW) disinfected each with chlorine (HOCl) or chloramines (NH₂Cl) [313].

We attempted unsuccessfully to submit the MtBE extracts to the bioassays and the effect of MtBE dominated the overall effect. We also injected the SPE extracts for bioanalysis into the GC and could not identify any of the target chemicals. The SPE is prone to loss of volatile chemicals in two phases during the extraction process: (a) during drying of the SPE cartridge prior to elution by solvent and (b) during evaporative reduction of the solvent volume. Also the HLB solid phase that was used in the present study might be suboptimal for DBPs. Coconut charcoal is one of the common sorbents for DBPs like NDMA and at present we are trying to optimise the SPE extraction process by combining a series of different solid phases to increase the extraction yield and we are working on an air-stripping based method to capture the volatile chemicals. For a valid direct comparison between chemical analysis and bioassays it will be important to use a common sample preparation and sample enrichment method. As a minimum, the measurement of absorbable organic halogens can be used for mass balancing but again this approach is limited as it is only applicable for halogen containing DBPs and will be blind to nitrosamines and other N-DBPs. Despite these shortcomings it is still remarkable how consistent the results of chemical and bioanalysis are.

4.1. Conclusions

- This is a preliminary study which was limited to non-volatile DBPs and demonstrates the toxicological significance of the formed DBPs and the ability of bioassays to assess this effect.
- Source water with higher organic matter and/or bromide formed more DBPs and showed higher effects.

5. EFFECT ON DBP FORMATION OF BLENDING DIFFERENT SOURCE WATERS – LABORATORY SCALE EXPERIMENTS

The aim of this part of the project was to understand if there was a risk of DBP formation as a result of blending different waters with different residual disinfectants without prior conversion to homogenise residual disinfectants during the mixing. This is important as the SEQ water Grid is composed of different networks employing chlorine or chloramines that are transformed according to the final disinfectant employed.

To this aim we mixed all the waters used in chapter 3 after being exposed to three days of contact time with chlorine or chloramines. We did not mix different waters containing the same residual disinfectant. Table 26 show the matrix of waters mixed and left for three more days of contact time to measure the final formation of DBPs as a result of the blending. As the Tugun desalination plant was only sampled two times it was not included in this experiment.

Table 26: Matrix of waters being mixed in the experiment.

Water A	Water B
Molendinar HOCl	Capalaba NH ₂ Cl
Molendinar HOCl	Mt Crosby NH ₂ Cl
Capalaba HOCl	Molendinar NH ₂ Cl
Capalaba HOCl	Mt Crosby NH ₂ Cl
Mt Crosby HOCl	Molendinar NH ₂ Cl
Mt Crosby HOCl	Capalaba NH ₂ Cl

After mixing the waters we did not adjust the final concentration of chlorine to overcome the breakpoint, in order to investigate the formation of DBPs in the event that the two different waters are mixed in the grid. Figure 14 shows the region where the formation of DBPs was explored in this experiment.

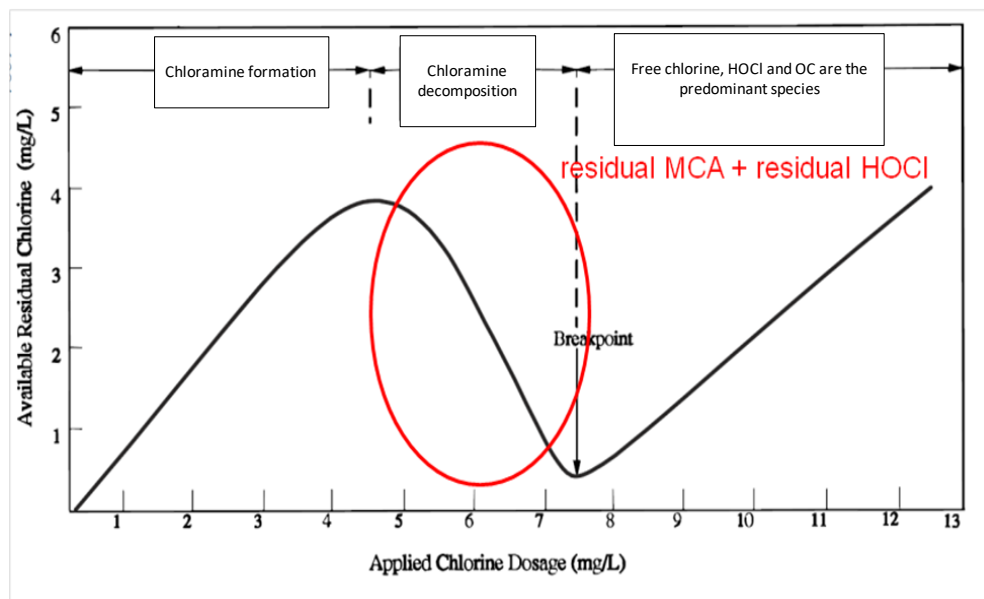


Figure 14: Theoretical equilibrium breakpoint chlorination scheme (1.0 mg/L ammonia-N; pH 7; temperature 25°C; contact time 2 hours) [314]. The section where this experiment took place is highlighted in red.

In order to investigate the risks of DBP formation in these specific conditions we calculated the predicted concentration by measuring the DBP concentration present in each fraction and comparing it to the final DBP concentration measured. Figure 15-18 show this comparison at three levels of concentration range.

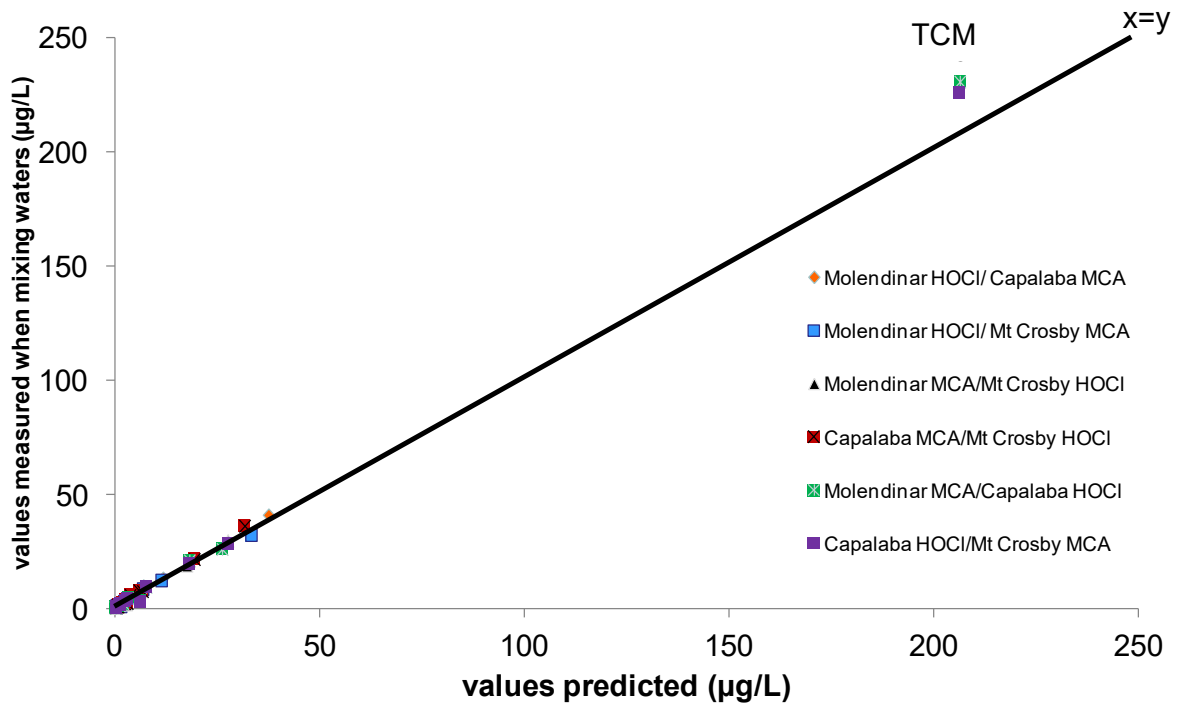


Figure 15: Comparison of DBPs formed after three days of contact time at pH=7 and 23°C and predicted when mixing different disinfected waters with residual concentration equal to HOCl=2±1.5 Cl₂ mg/L and NH₂Cl=2±3.5 Cl₂.

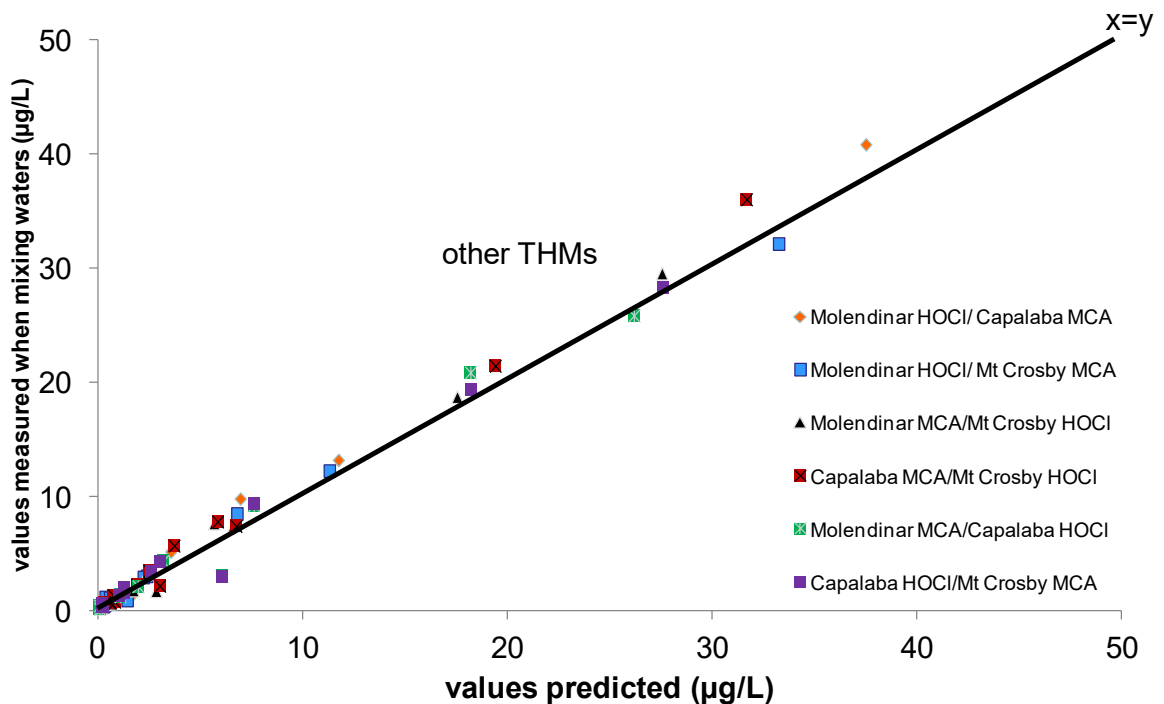


Figure 16: Zoomed graph of Figure 15 comparing the DBPs formed after three days of contact time at pH=7 and 23°C and predicted when mixing different disinfected waters with residual concentration equal to HOCl=2±1.5 Cl₂ mg/L and NH₂Cl=2±3.5 Cl₂.

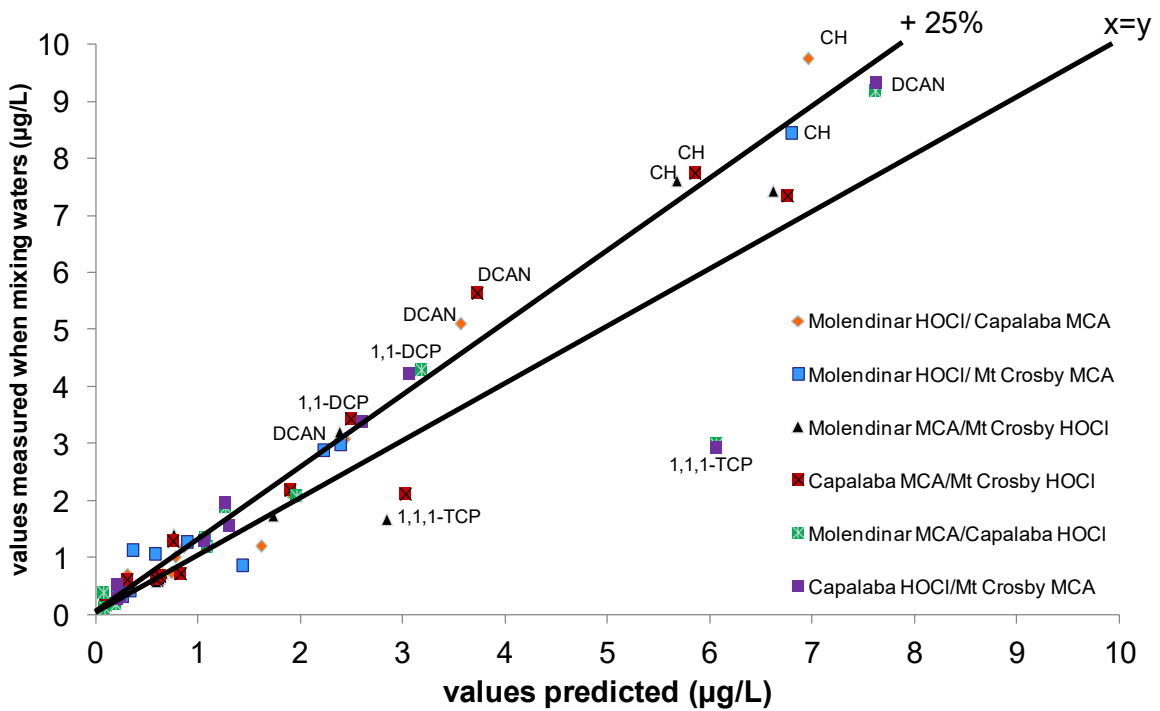


Figure 17: Zoomed graph of Figure 17 comparing the DBPs formed after three days of contact time at pH=7 and 23°C and predicted when mixing different disinfected waters with residual concentration equal to HOCl=2±1.5 Cl₂ mg/L and NH₂Cl=2±3.5 Cl₂.

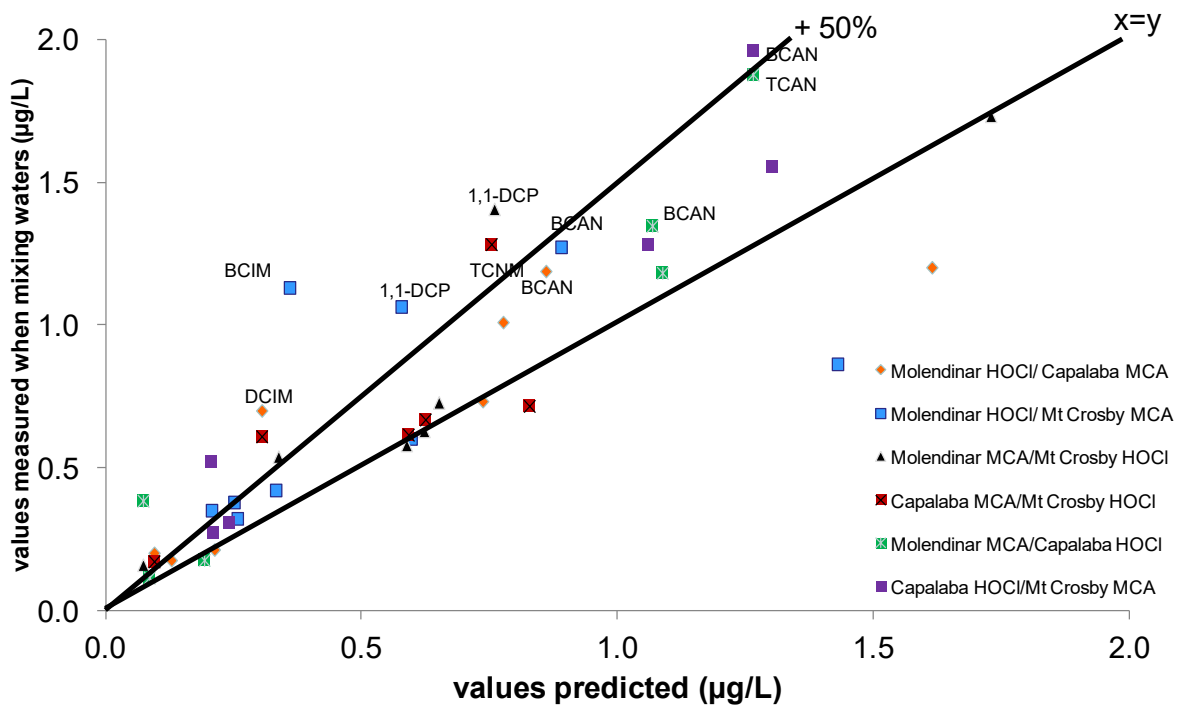


Figure 18: Zoomed graph of Figure 17 comparing the DBPs formed after three days of contact time at pH=7 and 23°C and predicted when mixing different disinfected waters with residual concentration equal to HOCl=2±1.5 Cl₂ mg/L and NH₂Cl=2±3.5 Cl₂.

As it can be seen, HANs, CH and TCNM were generated at a concentration between 25-50% of that predicted by the individual concentrations measured in the different waters. This is in agreement with the findings presented in Chapter 3 that showed that a higher formation of N-DBPs and CH could be possible if chloraminated waters were exposed to chlorination. However, it needs to be noted that the increase on DBP formation remained below the ADWG [22].

5.1. Conclusions

- The blending of different disinfected waters did not generate DBP above the ADWG.
- An increase of DBP formation was observed when blending waters with different disinfectants, in comparison to the predicted value. The predicted value was calculated by adding the concentration of DBPs present in the specific waters before being mixed.

6. CASE STUDY - OCCURRENCE OF NON-REGULATED DISINFECTION BY-PRODUCTS FROM THE CAPALABA REGION'S DISTRIBUTION SYSTEM

Table 27 shows TOC, bromide, DON values and the standard deviation for the sampling points selected for this study and Capalaba WTP. Samples have been divided according to the source water used. Samples M16 and M17 provide water from Capalaba WTP and Alexandra Hill Reservoir, which is a mix of Capalaba and NSI, hence a higher proportion of Capalaba water is expected for these waters in comparison to sites M19-M33, which supply water from Alexandra Hill Reservoir without further blending. As seen, maximum average TOC values were around 5-6 mg/L and were found in sampling points with a higher percentage of water from Capalaba WTP, while lower values were found in sampling points providing water from NSI. Bromide concentration ranged between 0.025 and 0.07 mg/L across the samples. DON was clearly higher in Capalaba water in comparison to NSI.

Table 27: TOC=total organic carbon, DON=dissolved organic nitrogen, SUVA=specific UV absorbance. Cap= Capalaba WTP, NSI=North Stradbroke Island WTP.

Sampling Point	n	Source water	TOC mg/L	St dev	Br- mg/L	St dev	DON mg/L	St dev
M8	5	Cap	3.83	0.79	0.025	0.004	0.29	0.29
M10	5	Cap	2.31	2.07	0.036	0.007	0.21	0.08
M11	4	Cap	4.93	0.72	0.051	0.006	0.29	0.15
M13	5	Cap	4.49	1.18	0.038	0.006	0.36	0.04
M14	4	Cap	4.07	1.42	0.040	0.005	0.29	0.08
M16	5	Cap + NSI (via Alexandra Hills res)	4.92	2.25	0.041	0.007	0.33	0.26
M17	4	Cap + NSI (via Alexandra Hills res)	2.93	0.64	0.060	0.008	0.27	0.13
M19	5	Alexandra Hills res (Cap + NSI)	1.67	0.63	0.030	0.005	0.15	0.12
M21	4	Alexandra Hills res (Cap + NSI)	2.46	1.81	0.030	0.005	0.11	0.10
M22	2	Alexandra Hills res (Cap + NSI)	1.07	0.34	0.027	0.005	0.14	0.07
M23	4	Alexandra Hills res (Cap + NSI)	2.10	2.48	0.043	0.007	0.20	0.18
M29	4	Alexandra Hills res (Cap + NSI)	1.00	1.07	0.066	0.003	0.11	0.04
M33	2	Alexandra Hills res (Cap + NSI)	0.55	0.34	0.060	0.002	0.11	0.01
M38	3	NSI	1.97	2.18	0.065	0.009	0.10	0.03
M42	3	NSI	1.89	2.56	0.070	0.003	0.09	0.12
M45	3	NSI	0.64	0.50	0.066	0.001	0.14	0.11
M50	4	NSI	0.46	0.42	0.064	0.004	0.08	0.10
M51	5	NSI	0.75	0.47	0.059	0.006	0.15	0.09
M52	3	NSI	1.21	0.34	0.061	0.002	0.13	0.11
Cap	4		5.99	0.97	0.053	0.007	0.32	0.11

THMs in conjunction with HAAs are the most prevalent DBPs in drinking water and are formed as a result of the reaction between chlorine and NOM. Figure 19 shows the mean concentrations of tTHMs found in Capalaba WTP and the distribution system.

In all instances, tTHMs values were lower than the ADWG value of 250 µg/L. Elevated values were found in M8-M17 which correspond to sampling points providing water from Capalaba WTP. On the other hand, the remaining sampling points provided water with a high contribution of NSI treated water. Average concentrations of tTHMs at Capalaba WTP were lower than at M8, M11, M13, M14 and M16, which evidenced the ability of THMs to increase during distribution systems, mainly as a result of hydrolysis of other DBPs [297]. Sampling points providing water from Capalaba showed a distribution of concentrations in the order: TCM>BDCM>DBCM>TBM, which is common speciation

in drinking water with high concentration of organic carbon and low concentration of bromide. However, the speciation of THMs measured in sampling points providing water from NSI was DBCM>BCDM>TBM>TCM as a result of the presence of bromide in low organic carbon waters (< 2 mg/L). The rate constant of bromide with HOCl to generate HOBr is 1.5×10^3 1/M·s [65] and the rate constant of THMs formation is in the range of 0.01 and 0.03 1/M·s [315]. It is known that once formed, hypobromous acid reacts about 10 times faster than chlorine with NOM since the activities of electrophilic substitution for electron release to stabilise a carbocation are more favourable for the Br atom due to its higher electron density and smaller bond strength relative to the Cl atom [316]. Hence, the formation of Br-DBPs is limited by the initial Br concentration whereas the Cl-DBPs would be limited by the organic matter concentration. To illustrate this effect, the inset in Figure 19 shows the average concentration of THMs in the waters with high contribution of NSI WTP.

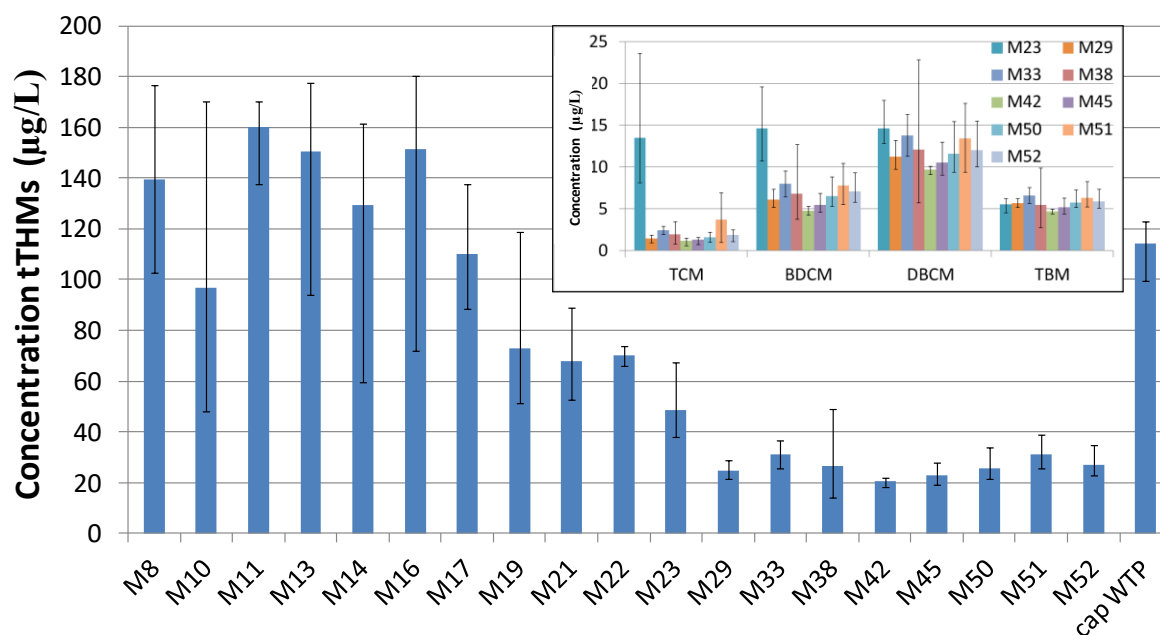


Figure 19: Average concentration and range of tTHMs in Capalaba WTP and distribution system. Inset shows the THMs speciation in waters from NSI.

Figure 20 shows the average concentration of the four analysed HANs. In agreement with Bougeard and co-authors [293], all four analysed HANs were detected in all waters and their concentrations were typically an order of magnitude lower than the concentration of THMs. Also the bromine/chlorine speciation was different between the sampling points providing water mainly from Capalaba WTP or NSI WTP as a result of the different concentration of TOC. Maximum concentrations measured corresponded to DCAN. Dihalogenated HANs are reported to be more stable than the trihalogenated HANs [294]. In addition, TCAN can undergo base-catalysed hydrolysis at pH higher than 5.5, which is the likely explanation as to why it was rarely detected in this sampling campaign, as the pH of all the samples was 7 ± 0.4 [295]. Although HANs are not included in the ADWG, the WHO has recommended the concentration of DCAN and DBAN to be 20 and 70 µg/L, respectively [292].

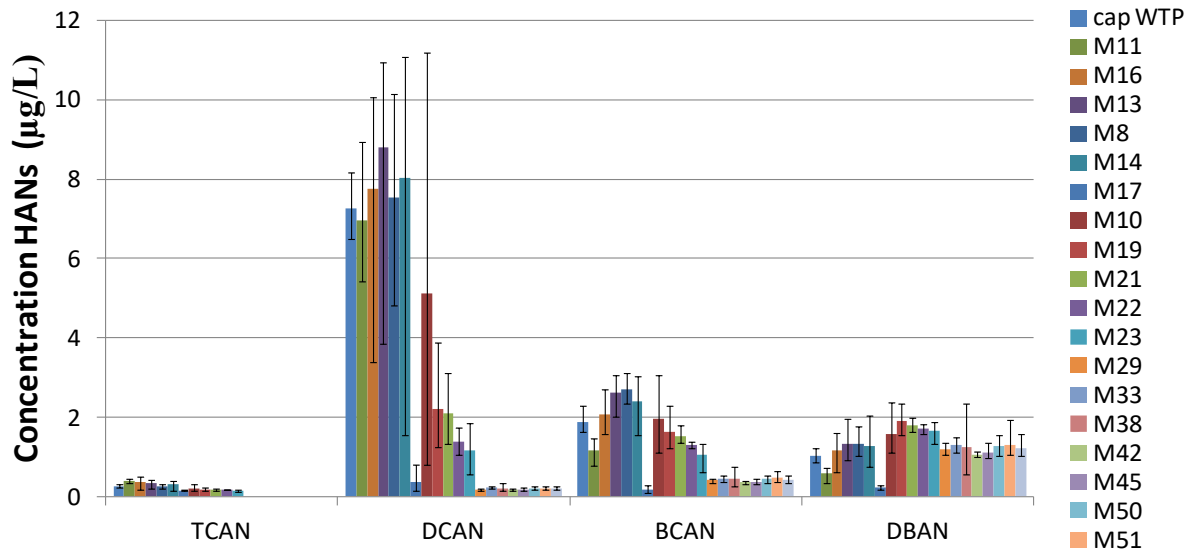


Figure 20: Average concentration and range of HANs in Capalaba WTP and distribution system.

Besides THMs and HAAs, CH is the next most prevalent DBP in chlorinated drinking water. Figure 21 shows the average concentration of CH also in conjunction with TCNM and two HKs.

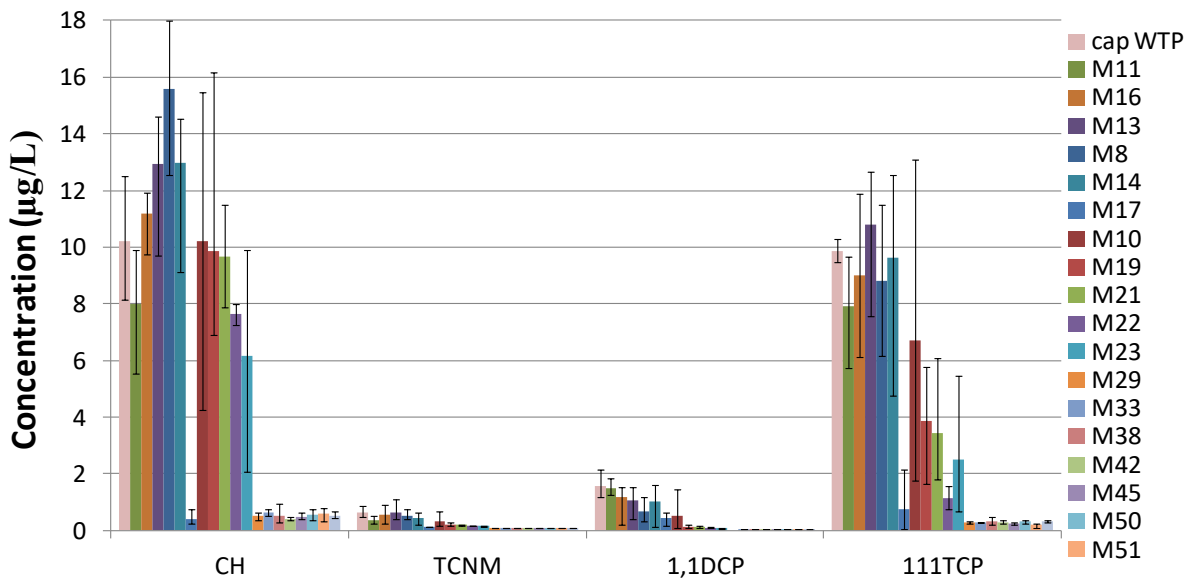


Figure 21: Average concentration and range of CH, TCNM, 1,1-DCP and 1,1,1-TCP in Capalaba WTP and distribution system.

At almost all the sampling points providing water from Capalaba WTP, concentration of CH was measured above 10 µg/L. Dabrowska and Nawrocki [317] studied the effect of contact time on the formation of CH. They observed that the reaction of chlorine with organic matter takes place as long as chlorine is available in the water due to the different precursors involved in these reactions. Thus, the concentration of CH may continuously increase in the water supply system. CH has been previously studied, but the appearance of CH in drinking water is not well understood and causes many controversies [317]. Trehy *et al.* [34], reported that amino acids are potential precursors of CH and suggested that the precursors for TCM and CH are different. According to Ueno *et al.* [318], nitrogen compounds and amino acids produced CH in the chlorination process.

TCNM and 1,1-DCP concentrations were low in all instances, while 1,1,1-TCP was found at concentrations up to 12 µg/L in the waters coming from Capalaba WTP. The differences in the formation of 1,1-DCP and 1,1,1-TCP can be partially explained by a simplified model developed by Reckhow and Singer [14]. In their model, chlorination of fulvic acid solutions led to the formation of intermediate by-products, such as 1,1-DCP, that could be further oxidised by chlorine to 1,1,1-TCP. This model reveals that further chlorine attack and hydrolysis are essential for the formation of 1,1,1-TCP.

Five iodinated-THMs were also measured in this study. We did not find I-THMs above 3.5 µg/L which concurs with the measurements of iodide in the samples that were in all instances below the limit of 0.01 mg/L detection (LOD). Similarly, NDMA was not detected above the 5 ng/L LOD across the distribution system. NDMA formation potential of source water at the Capalaba WTP was 11.4 ± 3.4 ng/L (n=3) which is below the ADWG (i.e., 100 ng/L).

Finally, NDMA and four other nitrosamines (i.e., nitrosodiethylamine, nitrosopiperidine, nitrosodibutylamine, nitrosomorpholine) were measured at Capalaba WTP and distribution system. Any nitrosamines was detected above the limit of detection (NDMA = 5 ng/L, nitrosodiethylamine and nitrosomorpholine = 10 ng/L and nitrosopiperidine, nitrosodibutylamine = 20 ng/L). NDMA formation potential of source water at the Capalaba WTP was 11.4 ± 3.4 ng/L, which is also well below the ADWG value (i.e., 100 ng/L).

6.1. Conclusions

All regulated DBPs were measured below ADWG values in all analysed samples across the Capalaba region.

- THM concentration followed the order TCM>BDCM>DBCM>TBM in sampling points providing water from Capalaba and DBCM>BCDM>TBM>TCM in waters blended with NSI water as a result of different DOC:Br ratios.
- HANs were measured at relatively high concentrations for locations serviced primarily by Capalaba WTP. Even though they were measured below WHO limits we recommend investigating possibilities to control the formation of HANs at the drinking WTP as they are suspected to be more toxic than carbon-based regulated DBPs.
- NDMA was not detected above the limit of detection (5ng/L). NDMA formation potential of source water at the Capalaba WTP was 11.4 ± 3.4 ng/L, which is also well below the ADWG value (i.e., 100 ng/L).

7. CASE STUDY - OCCURRENCE OF NON-REGULATED DISINFECTION BY-PRODUCTS AT LINKWATER CONVERSION STATIONS

This part of the study aimed to investigate the formation of DBPs at two conversion stations located in the Gold Coast region: a) Gramzow Road conversion station; and b) Chambers Flat conversion stations.

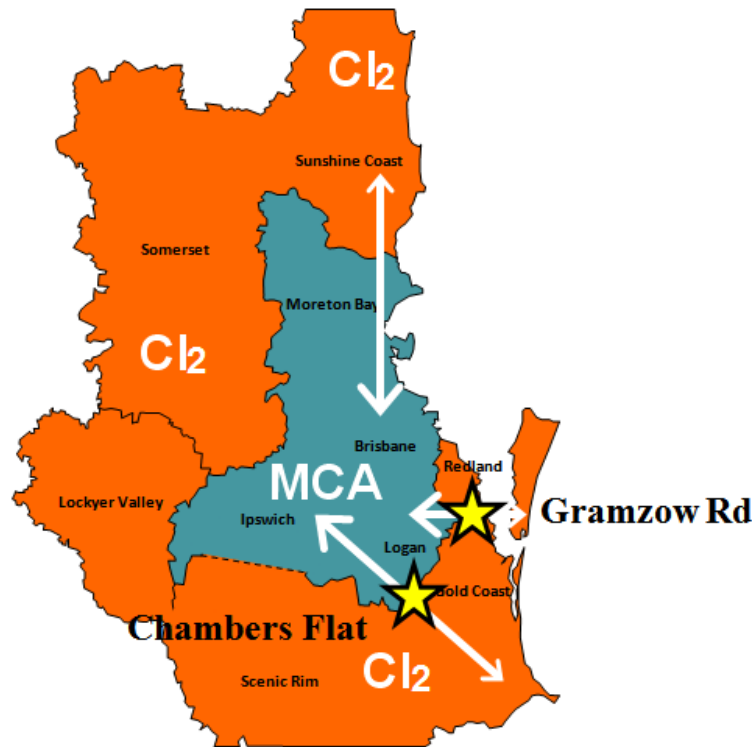


Figure 22: Approximated location of the two investigated conversion stations in SEQ.

We monitored the formation of DBPs during chloramination operation (i.e., ammonia is added to water containing residual chlorine to generate chloramines) and the results are plotted in Figure 24. As seen in that figure, DBPs generated were in all instances below the ADWG. Moreover, there was no additional formation of DBPs during the conversion process. This result is predictable as the sample was taken and quenched immediately after chloramination and hence there was not enough time to further generate DBPs. In order to investigate the potential to generate DBPs after this conversion of disinfectants, we left three samples taken after chloramination in contact with the disinfectant without quenching for 1, 2 and 4 days at 23 °C in the dark. The results of the conducted experiments are plotted in Figure 24.

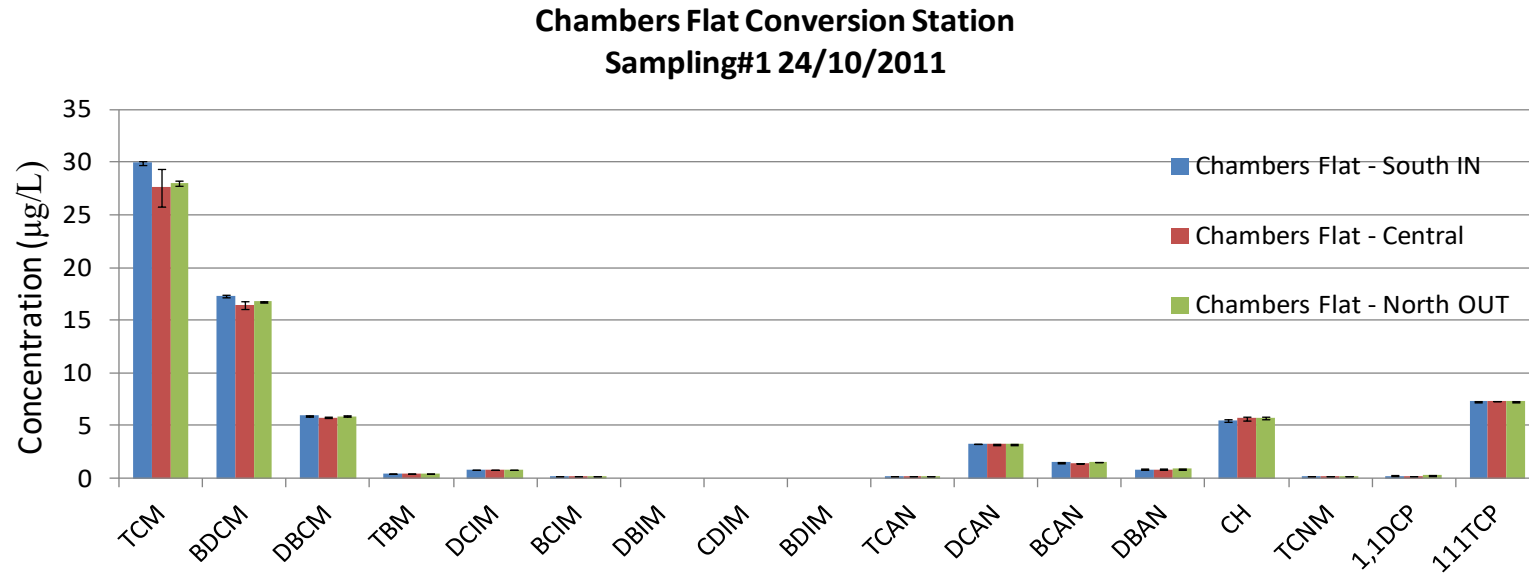
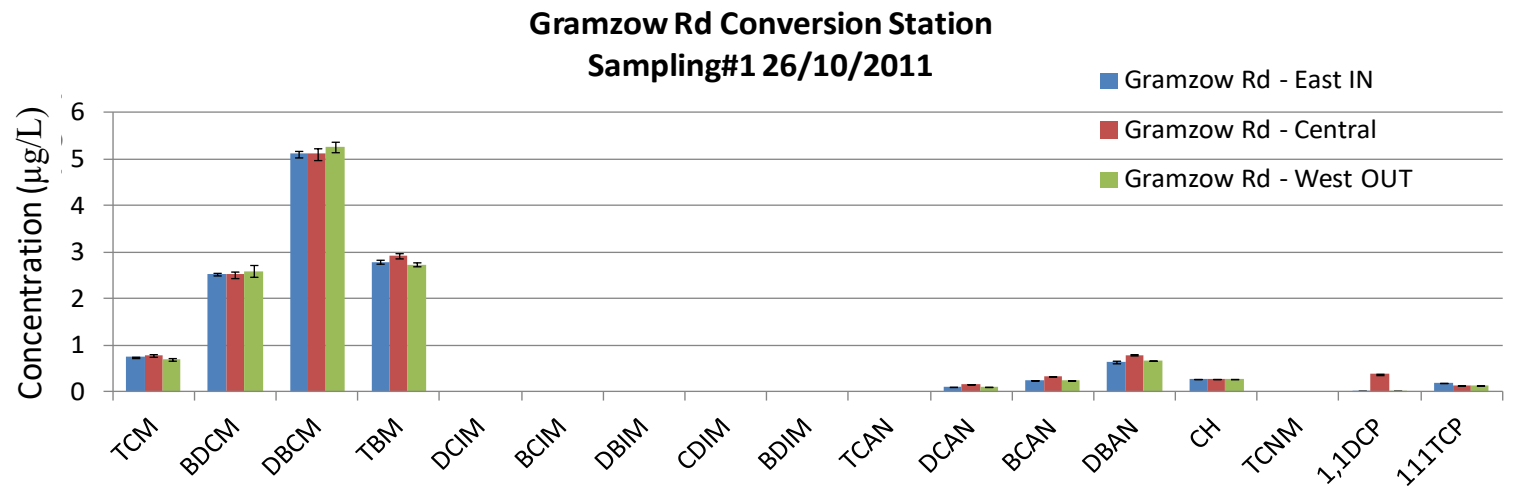


Figure 23: Formation of DBPs at Chamber Flat Conversion Station and Gramzow Road Conversion Station.

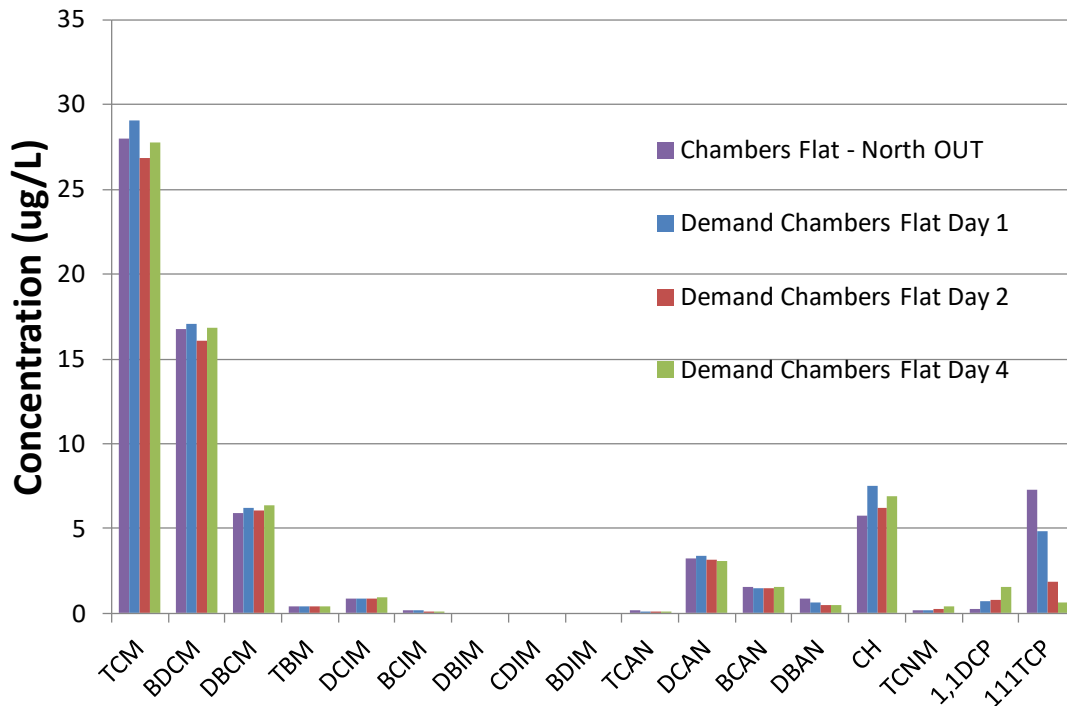


Figure 24: DBPs generated at Chambers Flat during the conversion of chlorine to monochloramine and left for 1, 2 and 4 days of contact time at 23°C.

As seen, the formation of DBPs remained stable except for 1,1-DCP, which is a typical DBP of chloramines, and for 1,1,1-TCP that underwent hydrolysis after this contact time and was not generated further in the presence of chloramines.

We also had the opportunity to measure the formation of DBPs at Gramzow Road Conversion Station during a breakpoint chlorination event (i.e., when chloramines is converted to chlorine by further addition of chlorine overcoming the breakpoint). The results for THMs of this sampling are shown in Figure 25. The light blue lines plotted correspond to the THM measured during the conversion of chlorine to chloramines while the dark blue correspond to the formation of THMs when converting chloramine to chlorine via break point chlorination. The figure also shows the formation of DBPs after 24 hours of contact time during both conversions. Figure 276 shows the results for HANs, CH, TCNM and I-THMs formation. This results show that, although there was no extra formation of DBPs during chloramines formation (light blue bars in Figures 25 and 26), the formation of all DBPs, except THMs and 1,1-DCP, increased after 24 hours after breakpoint chlorination. This increase was particularly significant for HAN and CH, which is in agreement with our observations presented in Chapter 3 (i.e., use of chloramines prior to chlorine increases the formation of nitrogen containing DBPs and CH).

7.1. Conclusions

- All regulated DBPs are within ADWG for all sampling events at the two tested LinkWater conversion stations, even during the breakpoint trials.
- No additional DBPs are formed during the conversion of chlorine to chloramine even after long contact times. However, after chlorine breakpoint the formation of HANs and CH increased (more research is required).

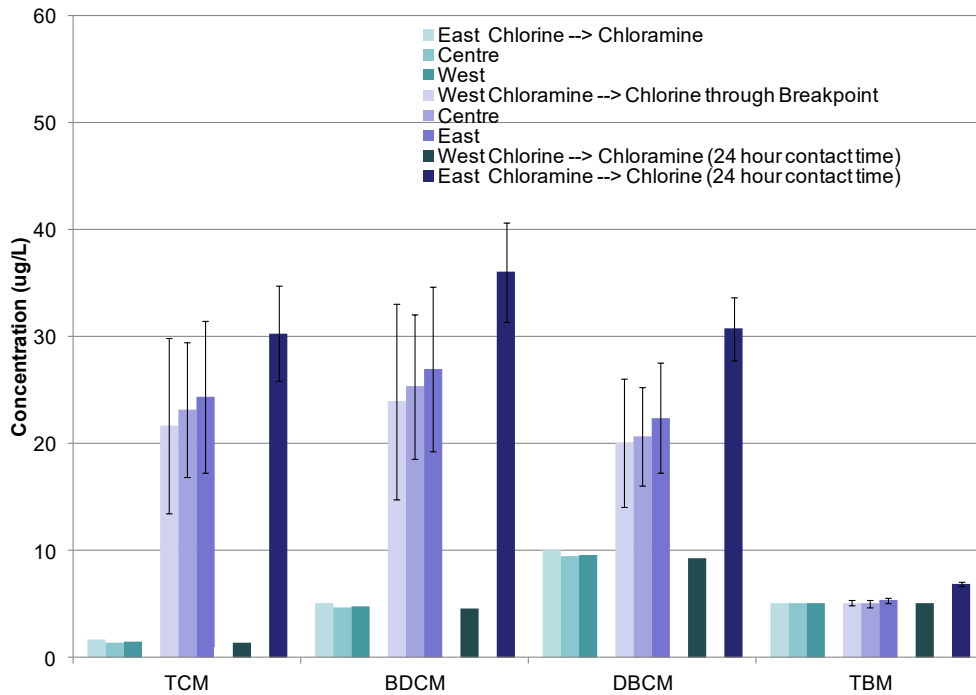
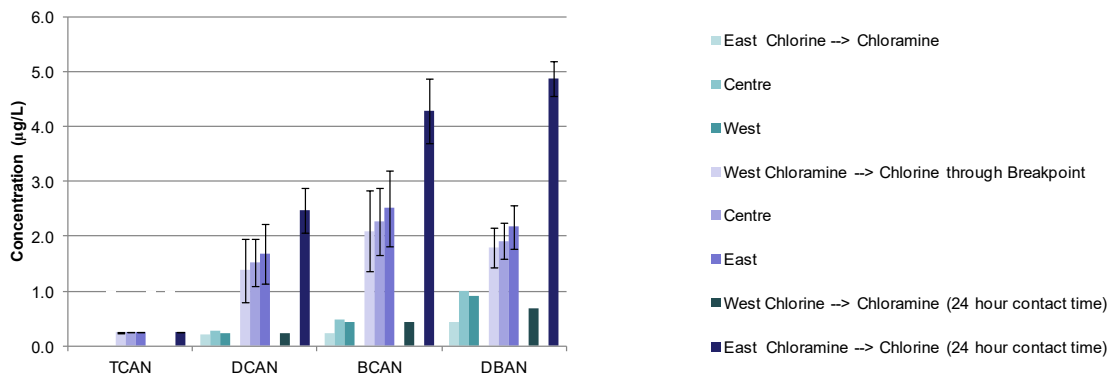
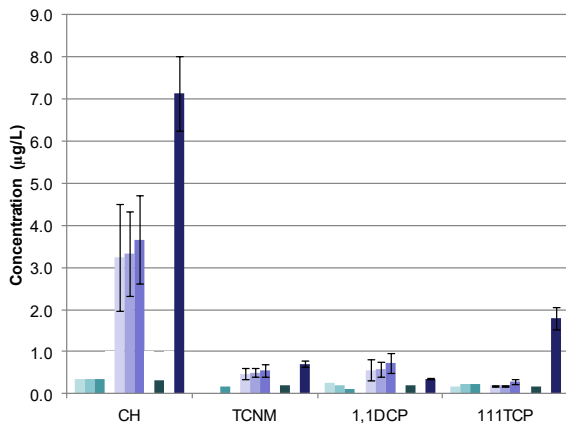


Figure 25: THMs generated at Gramzow Road Station during the conversion of chlorine to chloramine and vice versa and as well as the results after 24 hours of contact time at 23°C.

Haloacetonitriles



Chloral Hydrate, Trichloronitromethane and Haloketones



Iodinated DBPs

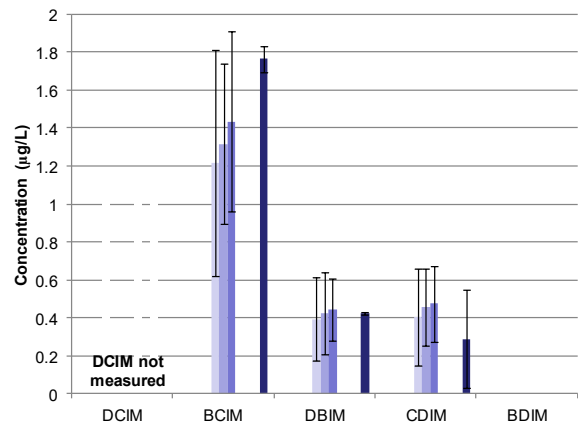


Figure 26: DBPs generated at Gramzow Road Station during the conversion of chlorine to chloramine and vice versa and as well as the results after 24 hours of contact time at 23°C.

8. RESPONSE SURFACE MODELLING OF DBP FORMATION AND SPECIATION

This part of the study investigated the formation of DBPs in synthetic waters to understand the parameters affecting their speciation. Alkalinity, bromide concentration and NOM were the parameters investigated.

Chloramination of the matrix of synthetic waters led to low levels of TCM ($<1.5 \mu\text{g/L}$), DCAN ($<0.2 \mu\text{g/L}$) and 1,1-DCP ($<3.0 \mu\text{g/L}$) being formed, however, all other DBPs in the suite investigated were not formed by chloramination irrespective of halide concentration, NOM concentration or alkalinity. Chlorination of the samples of same starting water quality parameters as used in the chloramination experiments led to formation of all the DBPs in the suite studied apart from the iodinated-THMs. These were not formed in any case throughout the study described in chapters 7-12. All DBP results discussed herein are as derived from chlorination formation potential experiments, unless otherwise specified.

8.1. Alkalinity

In general, increasing alkalinity was associated with an increase in the level of bromination of THMs and HANs. Although individual, highly brominated THMs (DBCM and TBM) increased in concentration with increasing alkalinity (Figure 27), total THMs concentration (tTHM) was negatively correlated with alkalinity. While DBAN was clearly favoured under high alkalinity conditions and TCAN clearly decreased in concentration, a simple relationship between alkalinity and tHAN could not be determined. Chlorinated DBPs such as CH, TCAN and TCM were negatively correlated with alkalinity (Figure 28). This agrees with a recent report [319] that found a statistically significant positive relationship between alkalinity and DBCM and bromochloroacetic acid concentration, but a negative relationship with fully chlorinated species. They suggest an immobilisation of hydrophobic NOM under the high ionic strength/hardness conditions of high alkalinity waters, leading to enrichment of hydrophilic NOM, which have fewer DBP precursor sites available for reaction, therefore for a given bromide and NOM concentration there will be a higher bromide:organic precursor ratio under high alkalinity conditions. A later study [320] found that alkalinity at the first point of chlorine addition was positively correlated with bromine substitution factor (BSF) and that this was most strongly correlated with the THM and dihaloacetic acid classes, and slightly less strongly correlated with dihaloacetonitriles and trihaloacetic acids. Both of these previous studies use data from the Information Collection Rule Database to generate their models, whereas our study uses laboratory-generated data. Our data found that BSF was strongly linked to alkalinity for the THM4 compounds (standardised coefficient (SC) = 0.041) and the HAN4 compounds (SC = 0.077).

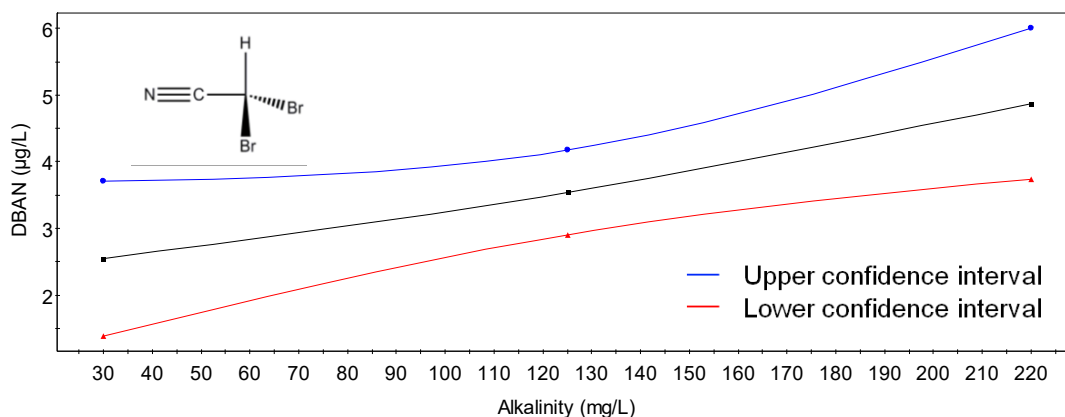


Figure 27: Change in DBAN concentration with alkalinity. Confidence level is 0.95, $R^2 = 0.961$.

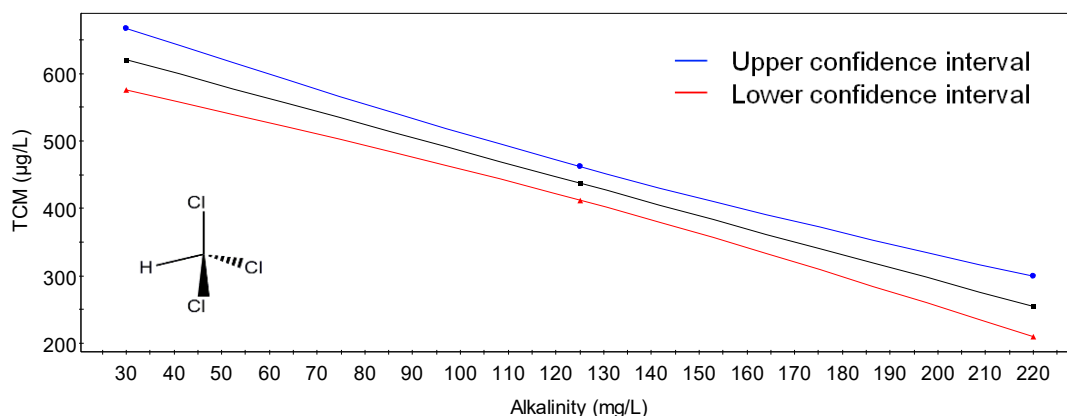


Figure 28: Change in TCM concentration with alkalinity. Confidence level is 0.95, $R^2 = 0.993$.

8.2. Bromide Concentration

Bromide concentration was strongly correlated to bromide substitution into both THMs and HANs (Figure 29), and inversely correlated to the fully chlorinated DBPs; TCM, TCAN, DCAN, and 1,1,1-TCP (Figure 30). Changes in CH, TCNM, and 1,1-DCP were not significant, thus a relationship with bromide concentration was not identified for these chlorinated DBPs. More importantly, our study found that THM4 and HAN4 occurred at higher concentrations with increasing bromide concentration at the point of disinfection (Figure 31). The effect of bromide concentration on DBP formation and speciation has been previously studied [52]. Under chlorination conditions, the oxidation of bromide by chlorine will occur to form HOBr, which is highly reactive with NOM and thus forms Br-DBPs. While HOCl is known to be a stronger oxidant than HOBr, it is a less efficient substitution agent. Therefore, once bromide is oxidised by chlorine to form HOBr, bromine substitution into NOM is favoured. In agreement with our report, the authors found that bromide concentration at the point of disinfection was correlated to higher total THM4 and HAN4 concentration, as well as a higher level of bromination of these compounds. This observed increase in THM4 concentration with bromide concentration has also been reported more recently [321].

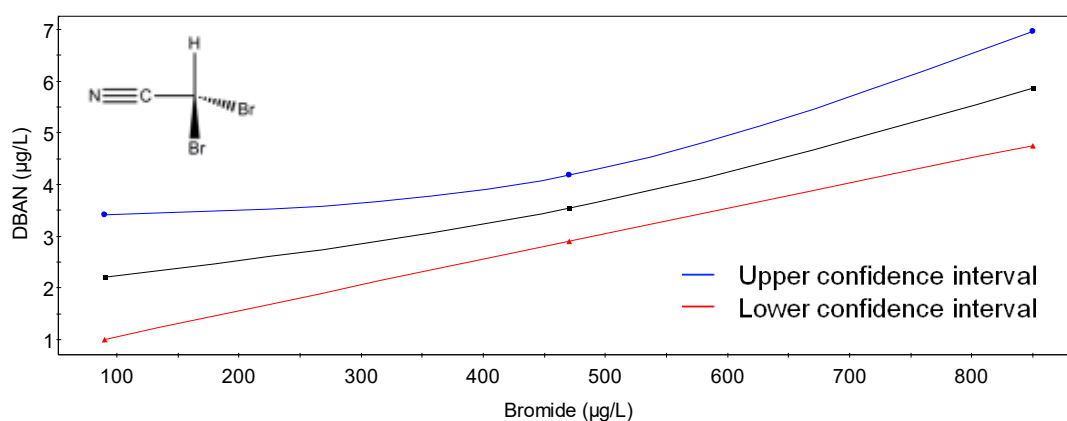


Figure 29: Change in DBAN concentration with increasing bromide concentration. Confidence level is 0.95, $R^2 = 0.910$.

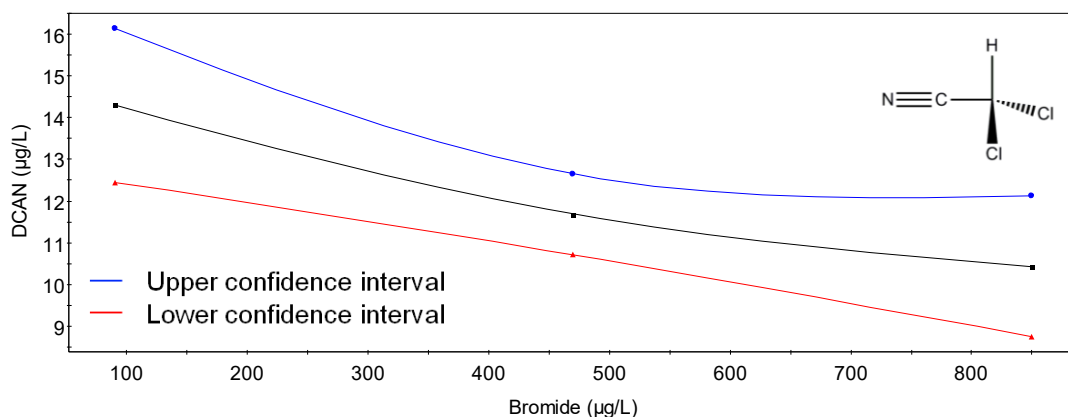


Figure 30: Change in DCAN concentration with increasing bromide concentration. Confidence level is 0.95, $R^2 = 0.992$.

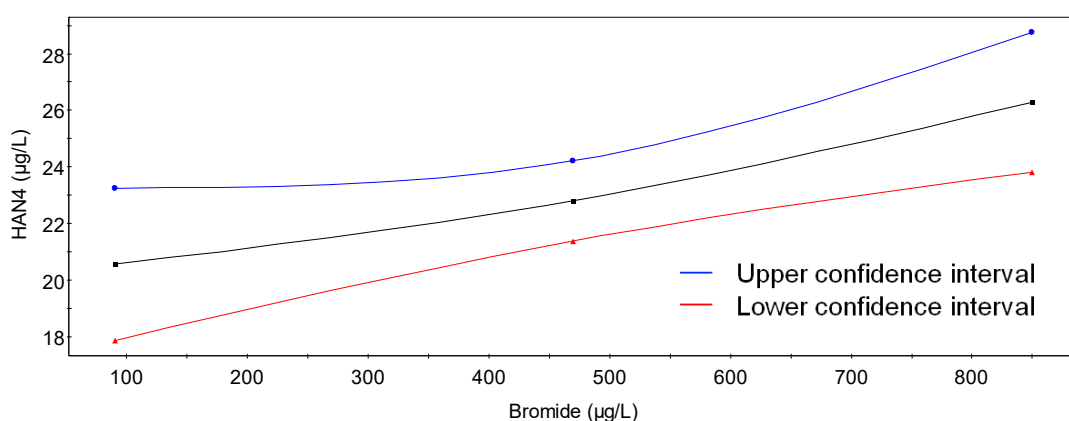


Figure 31: Change in HAN4 with increasing bromide concentration. Confidence level is 0.95, $R^2 = 0.985$.

8.3. NOM Concentration and Bromide:DOC Ratio

NOM concentration (measured as DOC) is well known to be an important factor in DBP formation, due to the high reactivity of organic compounds with disinfectants used in water treatment. Specifically, NOM concentration is positively correlated with the formation of more highly chlorinated DBPs (Figure 32). More importantly, however, it is negatively correlated with the more highly brominated DBPs. That is, lower NOM concentration leads to a higher Br-DBP formation, when bromide is present in the source water (Figure 33). This is important since the brominated DBPs are in general more toxic than the chlorinated forms of the same class of compounds [4], and formation of these can be favoured by traditional water treatment methods such as coagulation/flocculation because they lower NOM concentration without removing bromide. The oxidation of Br^- to form reactive HOBr (which then reacts to form DBPs) occurs more slowly in the presence of NOM than in its absence, due to competition reactions between NOM and Br^- for oxidant [322]. The impact of this is significant in ozonation, since ozone does not retain a residual and therefore competition for oxidant becomes important. In a chlorination system, a residual is typically maintained, and competition reactions for access to oxidant would not be expected to be of great significance because a large excess of disinfectant is present and the complete reaction of Br^- to form HOBr occurs quickly [52]. At low NOM concentrations, the Br:DOC ratio can be high, leading to greater bromide substitution into the organic material available. The Br:DOC ratio is known to be an important predictor for bromine incorporation into several classes of DBP compounds [320]. Overall, THM4 and HAN4 were shown to decrease with decreasing DOC, despite the increases in specific Br-DBPs that occur (Figure 34), so in terms of adhering to guidelines, water treatment practices such as coagulation/flocculation are effective, however, they do not take into account the change in speciation of the THMs present and its toxicological implications.

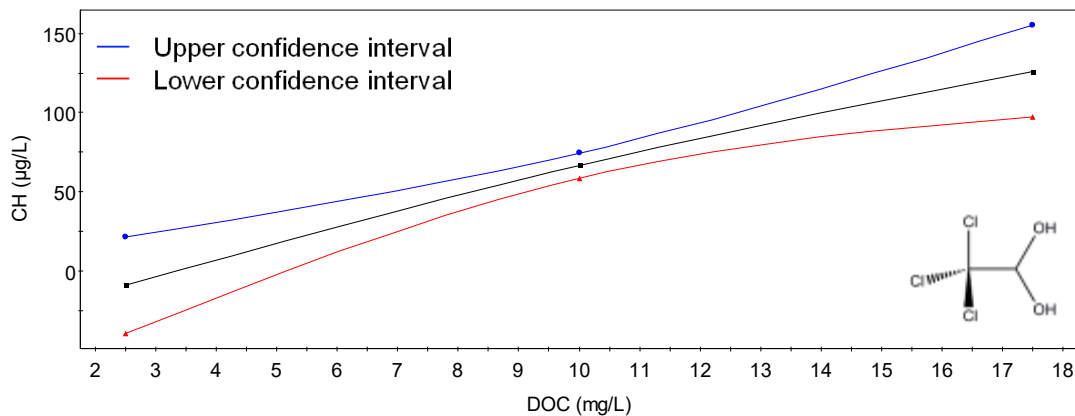


Figure 32: Change in CH with increasing DOC concentration. Confidence level is 0.95, R² = 0.980.

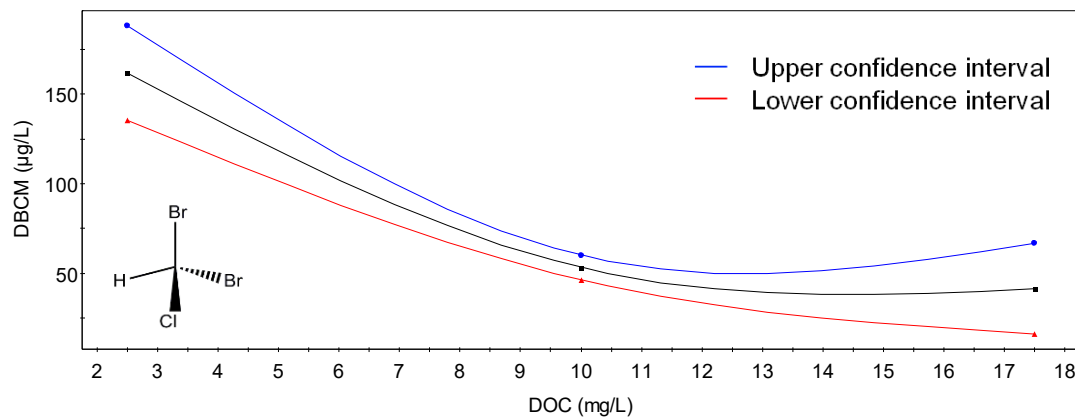


Figure 33: Change in DBCM with increasing DOC concentration. Confidence level is 0.95, R² = 0.997.

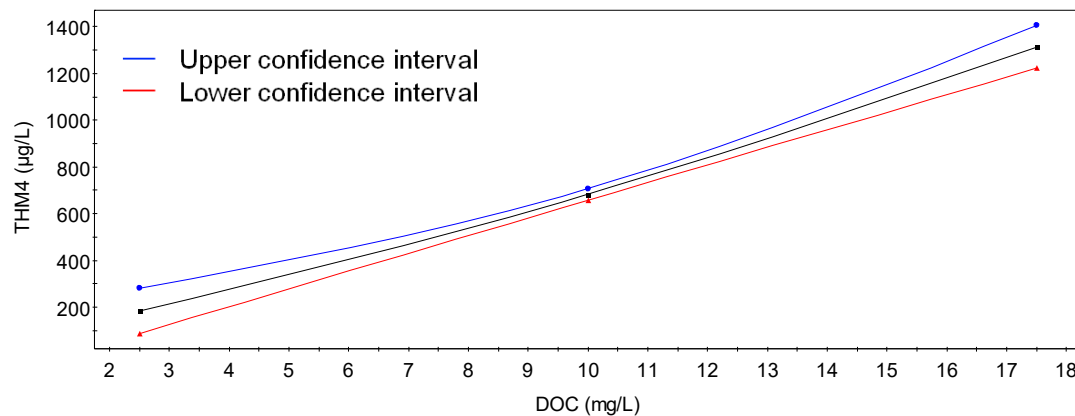


Figure 34: Change in THM4 with increasing DOC concentration. Confidence level is 0.95, R² = 0.997.

This study, based on laboratory-generated samples, shows a strong correlation between NOM concentration and formation of DBPs with no or low bromide incorporation. TCM, BDCM, TCAN, DCAN, BCAN, CH, TCNM, and both 1,1-DCP and 1,1,1-TCP were positively correlated with DOC concentration, while DBCM, TBM and DBAN (the most highly brominated THMs and HAN) were negatively correlated to DOC concentration. This preferential formation of highly brominated DBPs is a reflection of the high Br:DOC ratio of the samples (Figure 35), and is an important consideration in planning suitable NOM removal strategies during water treatment. If NOM removal is applied to a high bromide source water (such as a salinity impacted source water) without bromide removal, the

Br:DOC ratio of the water will favour the formation of these more toxic DBPs upon chlorination or ozonation [323]. The BSF was inversely proportional to DOC concentration for both THM4 and HAN4 ($SC = -0.081$ and -0.097 respectively), reflecting the greater bromination that occurs under high Br:DOC ratio conditions.

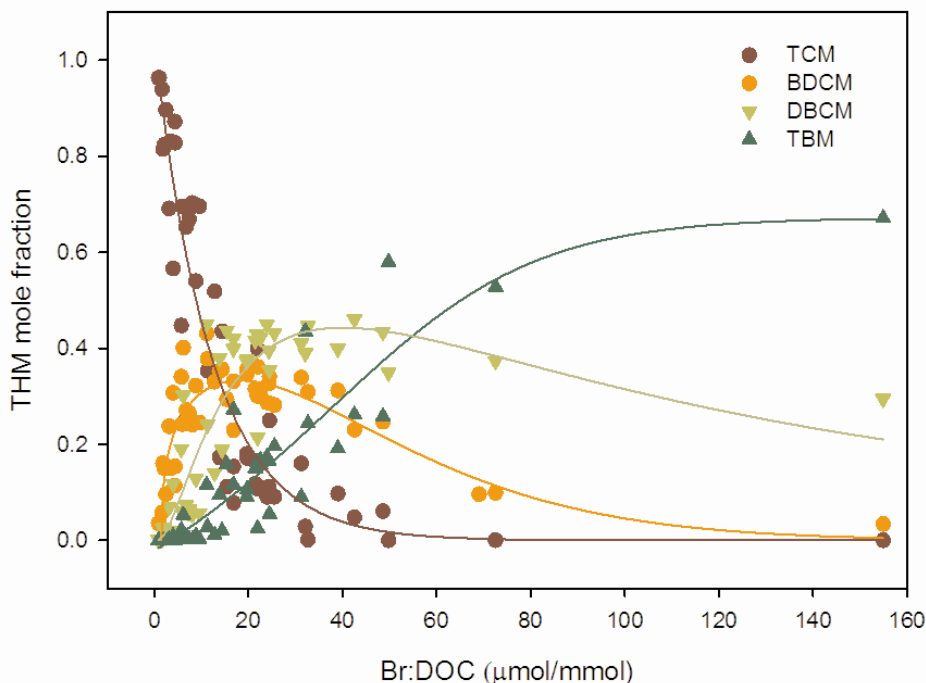


Figure 35: Shift toward more highly brominated THMs species with increasing molar Br:DOC ratio.

The change in individual THMs concentration as a function of DOC and bromide concentration is again outlined in the models in (Figure 36). Progressing from TCM (top left) through each bromine substitution step to ultimately form TBM (bottom left), the changing relationship of each compound with DOC and bromide concentration is apparent. This demonstrates the importance of viewing these compounds as individual chemical species with unique chemical behaviour, rather than as a group of compounds (THM4) to be treated as similar. Similar behaviour as seen in Figure 35 and Figure 36 for THMs was observed for HANs, and could be expected to be held generally across other DBP classes with different possible levels of bromination. Given the toxicological importance of brominated DBPs generally compared to chlorinated DBPs, it could be appropriate to define a Br:DOC ratio suitable for source water disinfection, rather than simply monitoring THM4 with no understanding of the speciation of the compounds present. Importantly, formation of high levels of brominated THMs would be expected to be an indicator for the presence of other brominated DBPs.

8.4. Conclusions

Bromide substitution into both THM4 and HAN4 is most strongly dependent on bromide ion concentration of the water at the time of disinfection, with the inverse relationship with DOC being the second most dominant parameter. Alkalinity was positively correlated with BSF for both THM4 and HAN4, although this influence was less than what was observed for bromide ion and DOC concentrations. Formation of fully chlorinated DBPs was highly dependent on DOC concentration at the point of disinfection, with high DOC levels being correlated to high chlorinated DBP formation. Fully chlorinated DBPs susceptible to bromination by substitution decreased with increasing bromide concentration. However, other fully chlorinated DBPs (such as CH) did not appear to be dependent on bromide concentration. Fully chlorinated DBPs occurred at higher concentrations under low alkalinity conditions. The Br:DOC ratio of each sample was important to determining which DBPs would be formed, and at what concentrations.

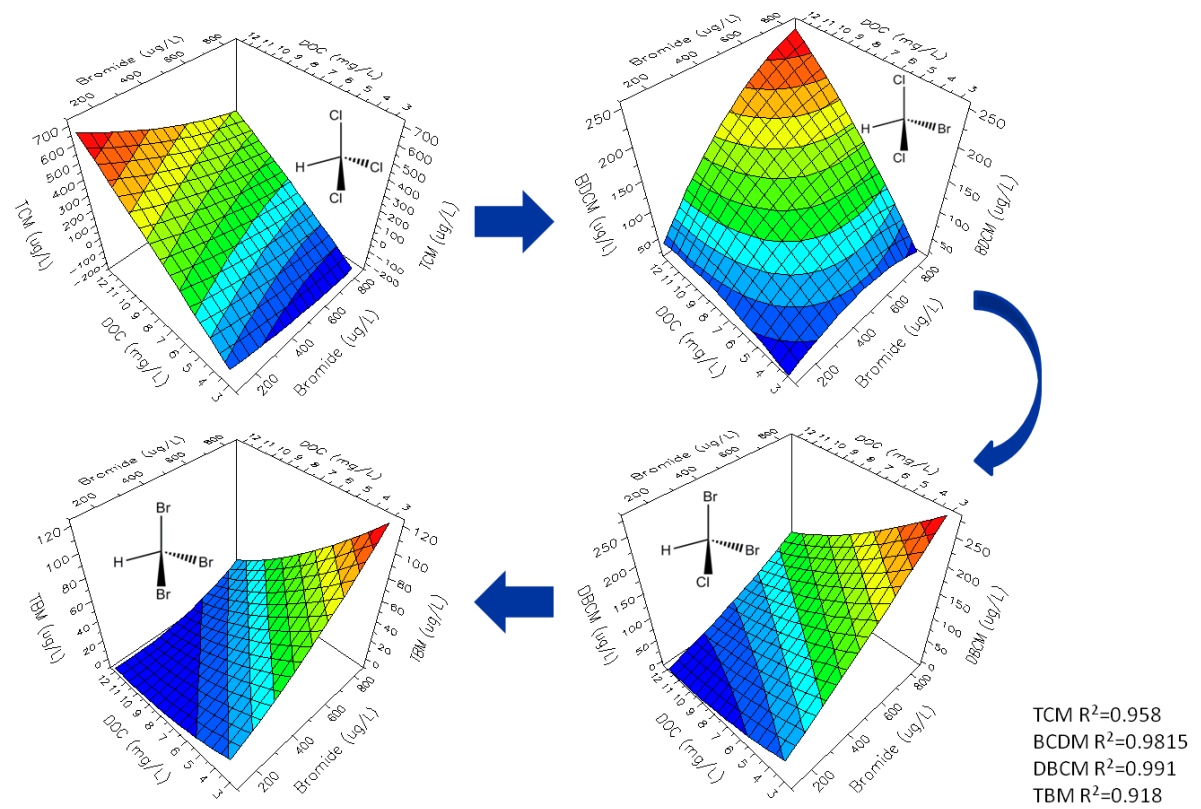


Figure 36: Response surface models showing 3D depiction of individual THM concentrations as they vary with DOC and bromide concentrations. Top left indicates TCM then arrows progress through mono-, di-, and tri-brominated species.

9. NOM REMOVAL

EC is defined in this study as treatment with Alum (aluminium sulfate octadecahydrate hydrate) at a dose optimised for each sample to give a final pH in the range 5-6 and a maximum NOM removal (measured as DOC removal). Trials were undertaken for each sample from the 17 samples in the experimental matrix to determine this optimal alum dose (data not shown). NOM removal by EC was in general quite successful, with between 25 – 73% of DOC being removed from each synthetic water sample (mean 60% removal) depending on the specific water characteristics (Figure 37). In particular, the greatest NOM removal was achieved in waters with high starting NOM concentrations and low starting alkalinity. This observation agrees with previous reports that NOM removal by EC becomes more difficult with decreasing NOM concentration and increasing alkalinity [290]. The direct correlation between DOC removal and starting DOC concentration was strong ($SC = 6.7 \pm 3.4$) while the inverse relationship between DOC removal and alkalinity, although significant, was not as strong ($SC = -5.4 \pm 2.8$). Halide concentration did not impact the DOC removal by EC.

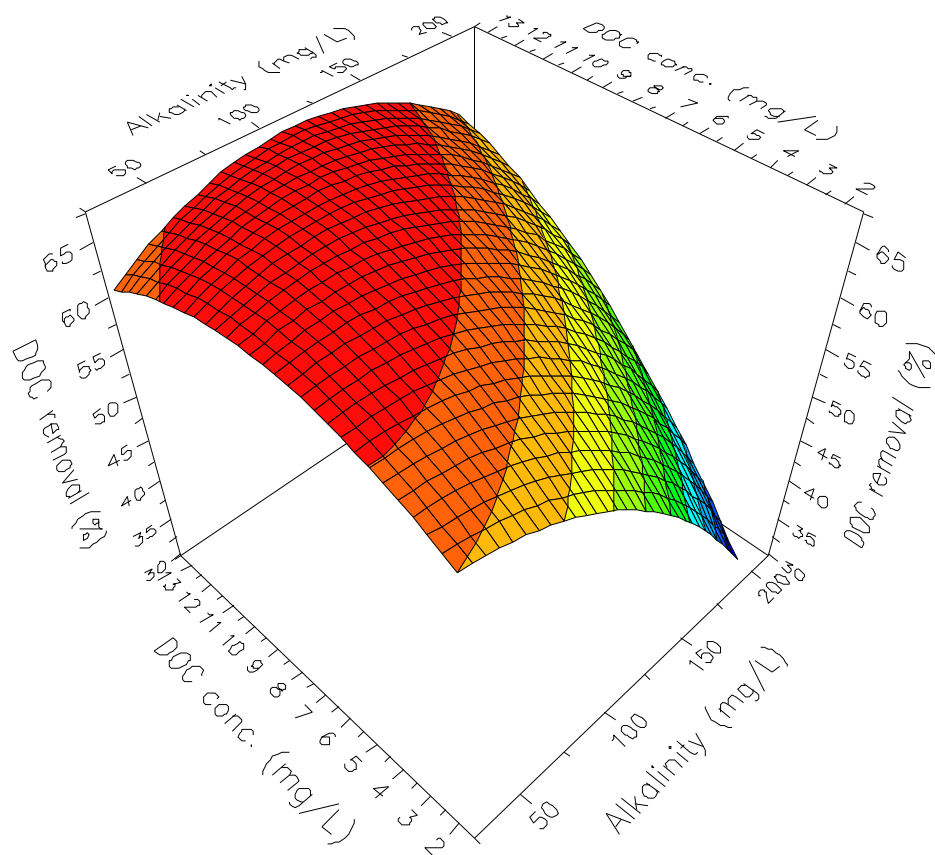


Figure 37: DOC removal by EC as a function of sample DOC concentration and alkalinity. $R^2 = 0.78$.

PAC treatment was able to remove an average of 19 ± 10 % of DOC that was recalcitrant to removal by EC, however, removal was highly variable depending on the water sample. The capacity for PAC to adsorb NOM could not be correlated to alkalinity or DOC concentration of the sample to be treated. The combined treatment of EC/PAC removed a mean of 70 ± 10 % of the total DOC present. Excitation-emission matrix (EEM) spectra show the decrease in fluorescence across the 5 regions for different NOM character after EC treatment, and also demonstrate the great improvement in NOM removal across the humic acid, fulvic acid and aromatic protein II regions after PAC treatment, relative to EC treatment alone, although some fluorescence arising from fulvic acid-like compounds was still visible.

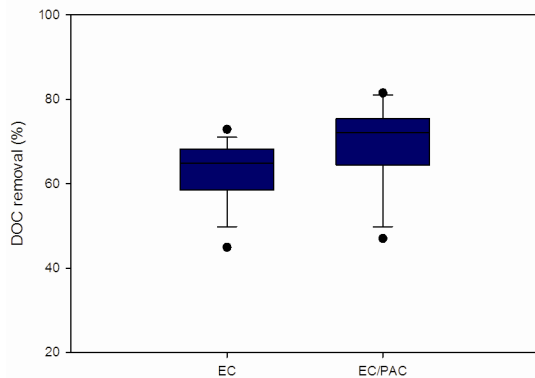


Figure 39: Range of DOC removals across the synthetic water matrix using EC followed by PAC treatment.

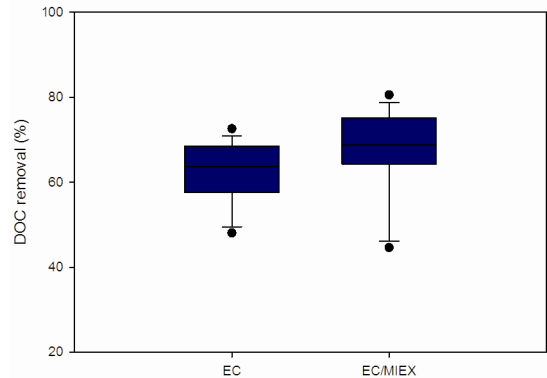


Figure 38: Range of DOC removals across the synthetic water matrix using EC followed by MIEX® treatment.

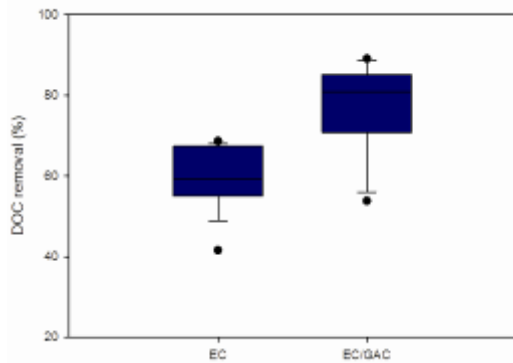


Figure 41: Range of DOC removals across the synthetic water matrix using EC followed by GAC treatment.

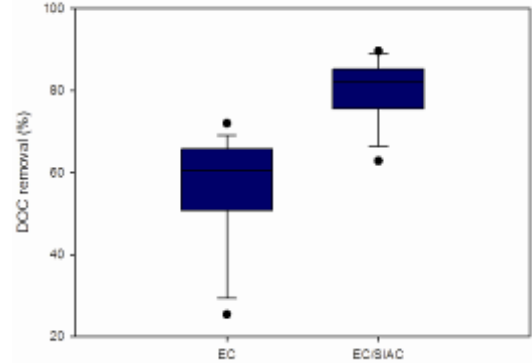


Figure 40: Range of DOC removals across the synthetic water matrix using EC followed by SIAC treatment.

MIEX® resin adsorbed a mean of 14% of the DOC remaining after EC treatment, however DOC adsorption was highly dependent on starting DOC concentration, with DOC removals of approximately 28% from high NOM samples. Low NOM samples were not amenable to MIEX® treatment after EC, with only a mean of 1.5% DOC removal, beyond what could be achieved with EC alone. DOC removal was dependent on sample alkalinity, with increased alkalinity leading to lower DOC adsorption. This reflects competition for binding sites on the MIEX® resin between bicarbonate ions and NOM. The halide concentration of the samples did not impact on DOC removal, over the concentration ranges studied. Previous studies investigating MIEX®’s NOM removal capacity have found greater adsorption capacity than what we report here [47], however in these previously published cases the MIEX® was used to treat raw waters, rather than EC treated waters, suggesting that MIEX® is able to adsorb the high molecular weight, hydrophobic component of NOM that is also removed by EC. The EC treatment also results in a drop in pH of the water to between 5-6, which may not be ideal for MIEX® function since more organics will be charged at higher pH’s and therefore more suitable for removal by anion exchange. Therefore, the use of MIEX® after an EC step may not be optimal without an interim pH adjustment step. EEM spectroscopy illustrated the incomplete removal of primarily fulvic acid-like compounds from solution after EC/MIEX® treatment, although all other regions were removed to a large extent after the combined treatment (Figure 45).

Activated carbon beds (GAC and SIAC) both exhibited excellent additional DOC removal beyond what was achieved by EC alone, with average removals of $57 \pm 16\%$ by GAC and $55 \pm 10\%$ by SIAC. The observed variability in DOC removal was dependent on starting DOC concentration and alkalinity, with greater starting DOC concentration leading to the greatest DOC removals and lower sample alkalinity leading to greater DOC removals for both GAC and SIAC (Figure 43). The two GAC's studied were identical in all ways apart from the presence of 0.1% silver embedded in the SIAC, which enables it to behave as both an adsorbent and an anion-exchanger. Experimental conditions were identical for both sets of experiments, allowing a direct comparison between the two carbons, and therefore allowing a study of the impact of silver impregnation on DBP precursor removal. Average DOC removals were remarkably similar between the two activated carbons, suggesting that 0.1% silver impregnation does not improve organics removal relative to unimpregnated activated carbon. EEM spectra of the centrepoint samples for both EC/SIAC treated synthetic waters and EC/GAC treated synthetic waters demonstrate the excellent removal of NOM from all regions of the spectrum, to beyond the detection capacity of the technique (Figure 46 and Figure 47). By comparison of these data to the EEM spectra shown for the other treatments studied (EC/PAC, EC/MIEX®, EC alone) it is clear that the activated carbon beds were superior in NOM removal capacity under the conditions studied. It is important to note that fresh (unused) activated carbons were used in these experiments, and thus the results will not directly reflect the NOM adsorption capacity of a used, biologically activated carbon. Given the greater cost-effectiveness of GAC compared to SIAC, GAC would be advised for NOM removal in a WTP scenario in preference to SIAC.

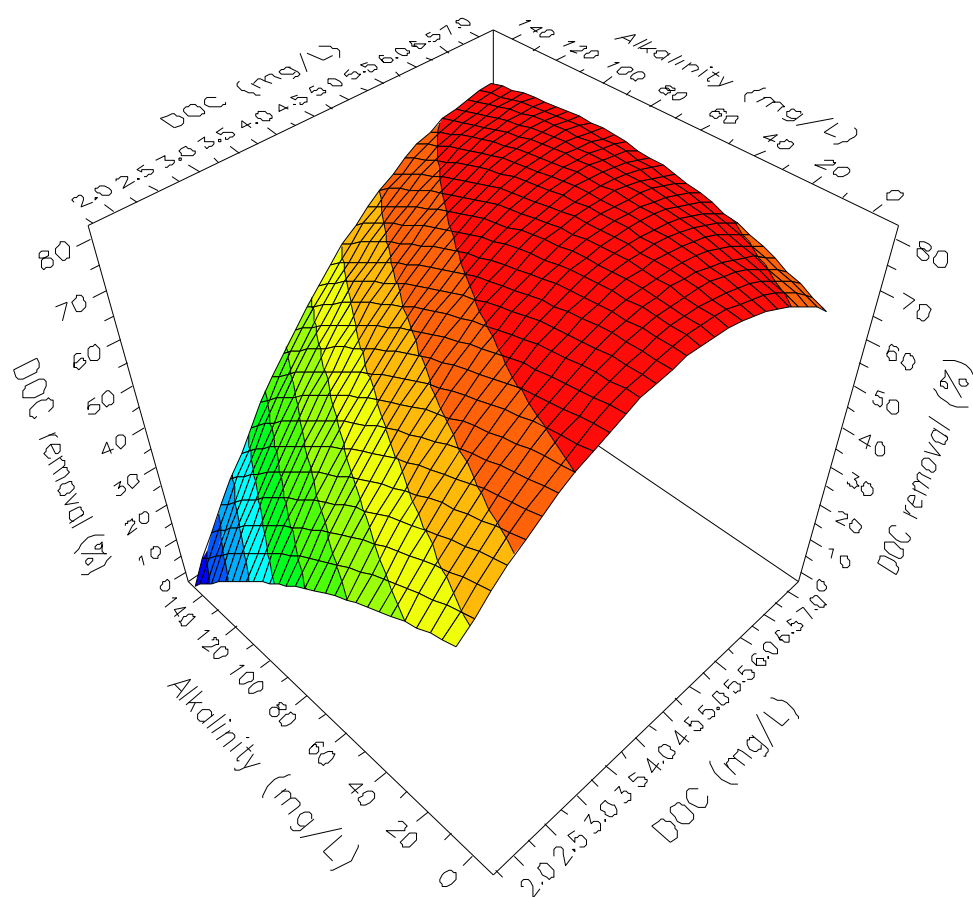


Figure 42: GAC DOC removal as a function of sample DOC concentration and alkalinity. $R^2 = 0.70$.

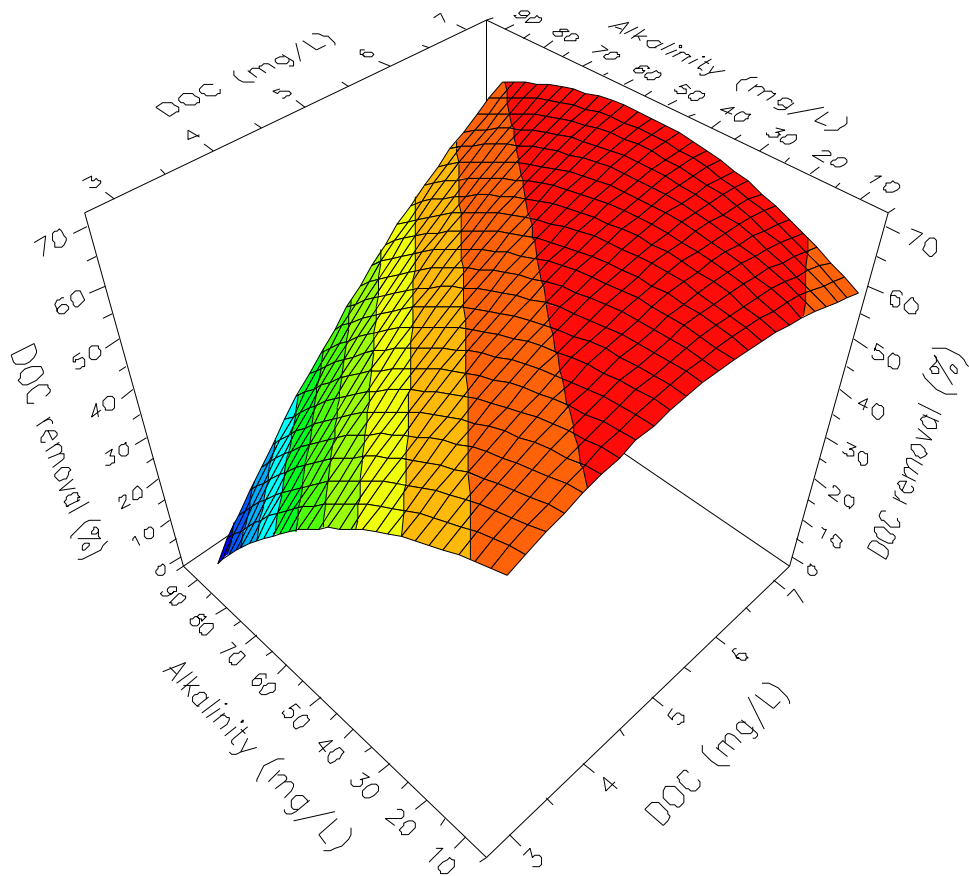


Figure 43: SIAC DOC removal as a function of sample DOC concentration and alkalinity. $R^2 = 0.92$.

9.1. Conclusions

Overall, EC followed by activated carbon beds (either silver impregnated or unimpregnated) were the most effective NOM removal treatments, giving greater DOC removals than EC alone, EC/MIEX®, or EC/PAC. Therefore, for DBP minimisation, if halide removal is not required for the source water of interest, EC/GAC treatment would provide an efficient NOM removal process while being more cost-effective than EC/SIAC.

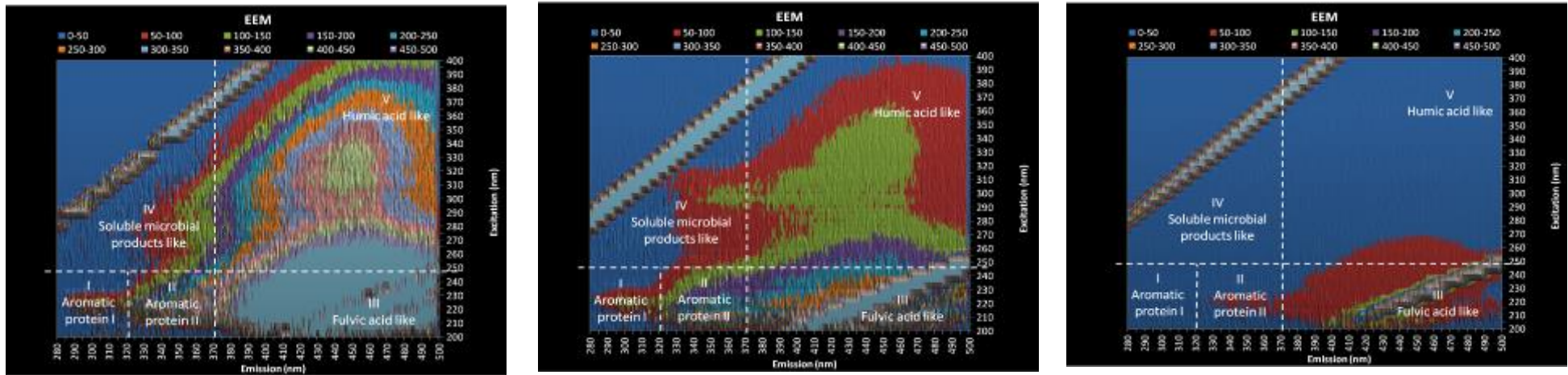


Figure 44: EEM spectra showing the change in synthetic water sample fluorescence after EC (middle), then PAC treatments (right), relative to 'no treatment' samples (left). Starting water quality parameters were: 138 mg/L alkalinity (as CaCO₃), 450 µg/L Br⁻, 18 µg/L I⁻, 12 mg/L DOC.

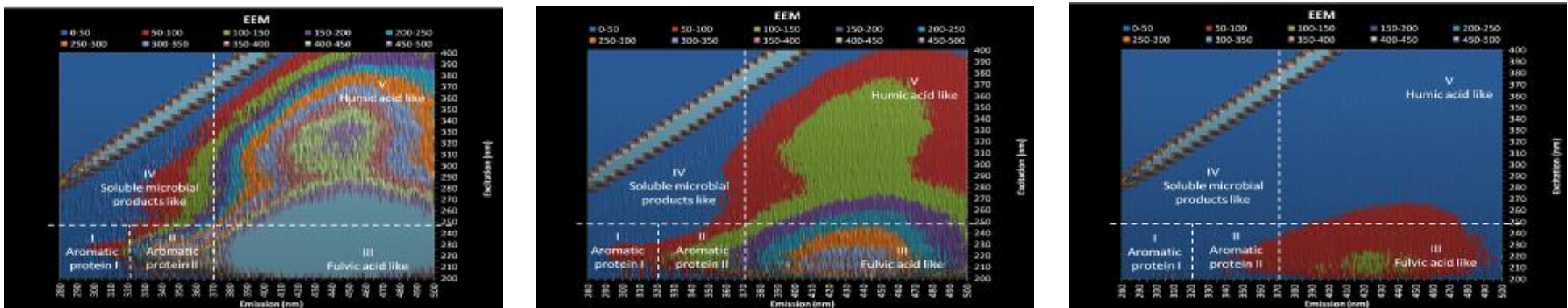


Figure 45: EEM spectra showing the change in synthetic water sample fluorescence after EC (middle), then MIEX® treatments (right), relative to 'no treatment' samples (left). Starting water quality parameters were: 138 mg/L alkalinity (as CaCO₃), 450 µg/L Br⁻, 18 µg/L I⁻, 12 mg/L DOC.

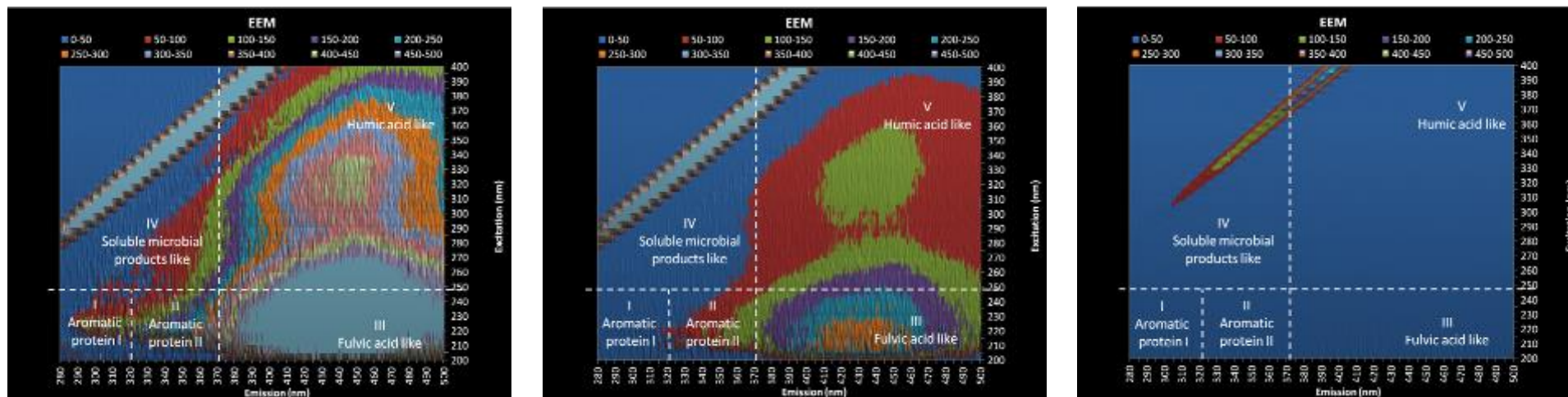


Figure 46: EEM spectra showing the change in synthetic water sample fluorescence after EC (middle), then GAC treatments (right), relative to 'no treatment' samples (left). Starting water quality parameters were: 138 mg/L alkalinity (as CaCO₃), 450 µg/L Br⁻, 18 µg/L I⁻, 12 mg/L DOC.

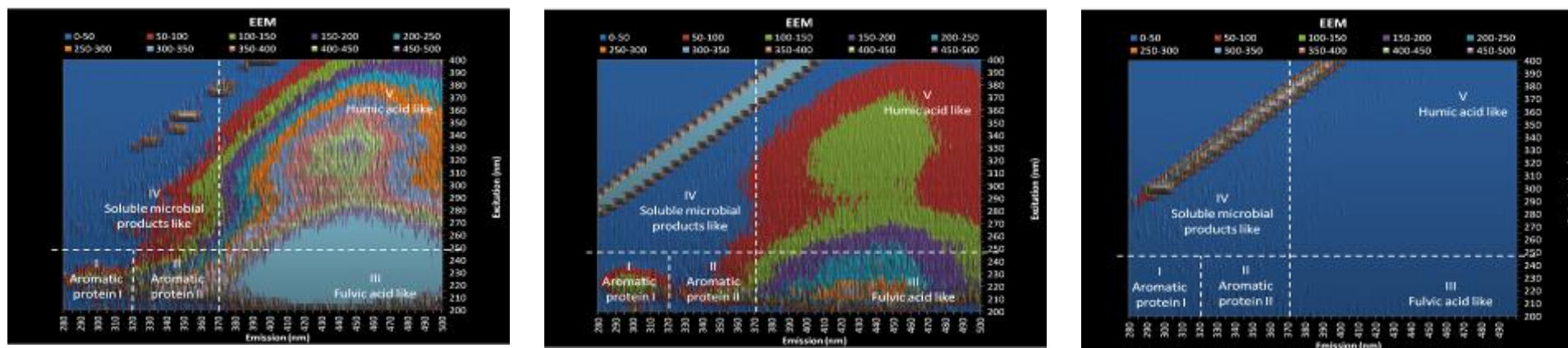


Figure 47: EEM spectra showing the change in synthetic water sample fluorescence after EC (middle), then SIAC treatments (right), relative to 'no treatment' samples (left). Starting water quality parameters were: 138 mg/L alkalinity (as CaCO₃), 450 µg/L Br⁻, 18 µg/L I⁻, 12 mg/L DOC.

10. HALIDE REMOVAL

EC did not change the starting concentration of bromide or iodide in any case, regardless of the initial sample alkalinity, NOM or halide concentration. Previous reports agree that EC does not significantly alter bromide concentration [324]. PAC treatment did not adsorb bromide or iodide from any of the samples of the synthetic water matrix, thus the combined EC/PAC treatment made no change to the starting halide concentrations of the samples, irrespective of starting NOM or halide concentration, or sample alkalinity (Figure 48). This is in agreement with previously published work [324].

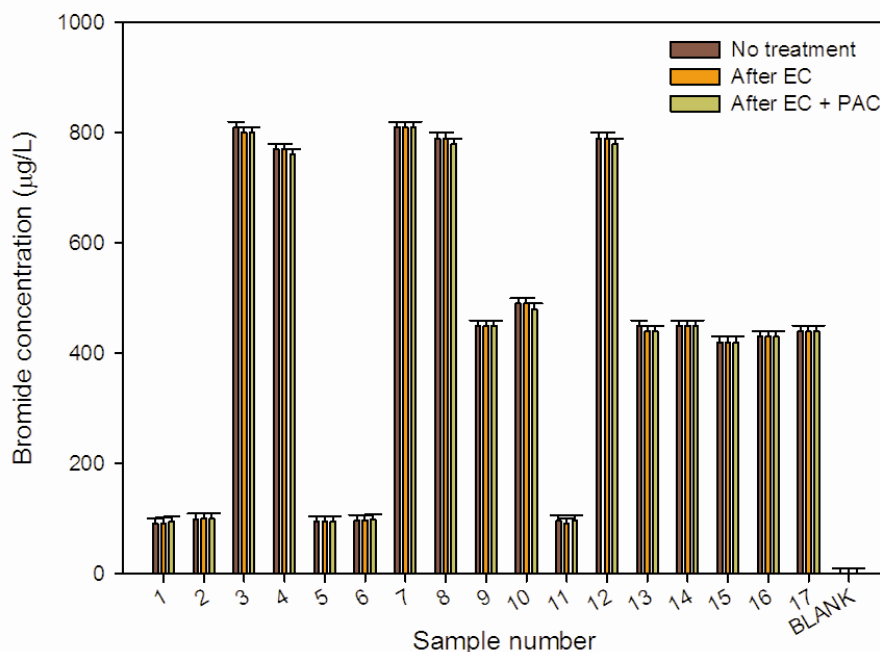


Figure 48: All samples in the synthetic water matrix are listed as samples 1-17 plus blank, and bromide concentration is illustrated both before treatment, after EC, and after combined EC/PAC treatment.

GAC and MIEX® had a moderate affinity for bromide ions. MIEX® was able to achieve $49 \pm 4\%$ bromide removal under conditions of low alkalinity (i.e. 11 ± 5 mg/L as CaCO_3 after EC treatment), but this was reduced to $20 \pm 14\%$ under higher alkalinity conditions (i.e. 95 ± 8 mg/L as CaCO_3 after EC treatment) (Figure 49). This reflects competition for binding sites on the MIEX® anion exchange resin, between bicarbonate and bromide ions. The mean bromide removal achieved by MIEX® overall was $32 \pm 16\%$, depending on sample alkalinity and starting NOM concentration. Lower bromide adsorption was generally observed in higher NOM samples, again, reflecting the competition for binding sites occurring on the anion exchange resin. Importantly, low levels of bromide were introduced into each sample from the MIEX® resin itself ($31 \mu\text{g/L Br}^-$ detected in the blank sample). This phenomena was likely caused by the NaCl used to regenerate the resin. If this problem was able to be mitigated by ensuring bromide-free NaCl was used for MIEX® regeneration, the bromide removals may be somewhat higher than what we report here. Bromide is, however, a common contaminant of commercially available NaCl, and this source of bromide contamination should be taken into account by WTPs when regenerating MIEX® resin.

GAC beds adsorbed $26.5 \pm 3.9\%$ of the bromide present, and this was remarkably consistent throughout the sample matrix, being unaffected by sample alkalinity, NOM concentration or halide concentration, across the concentration ranges studied. This consistency in behaviour across water quality parameters makes GAC beds an attractive alternative for bromide adsorption relative to MIEX® resin, unless specifically dealing with a low alkalinity water, in which case MIEX® is clearly superior. Although the iodide adsorption capacity of GAC has been previously reported [209, 220, 325], the authors were unable to find previous studies on bromide adsorption by GAC.

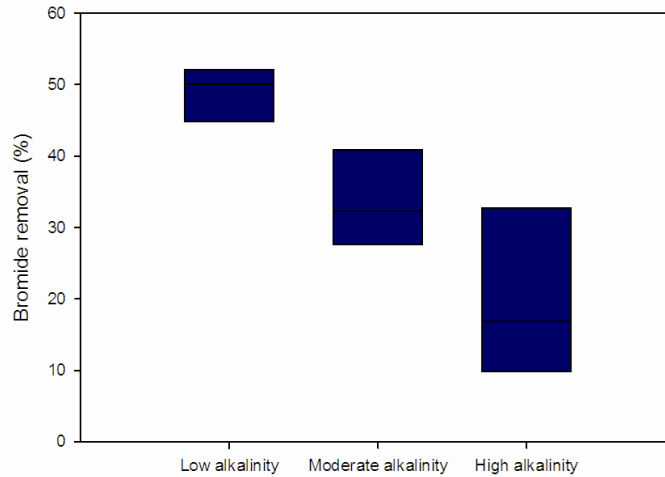


Figure 49: Bromide removal by MIEX® under conditions of varying alkalinity. Alkalinity = 11 ± 5 mg/L, 49 ± 5 mg/L, or 95 ± 8 mg/L as CaCO_3 after EC, for low, medium, high alkalinity samples, respectively.

SIAC exhibited excellent bromide removal capacity irrespective of sample alkalinity or starting NOM and bromide concentration. Waters as high as $800 \mu\text{g/L}$ in bromide had bromide concentration reduced to below detection limit ($<10 \mu\text{g/L}$). It is important to note that the SIAC used here was a virgin activated carbon bed, thus silver sites available for halide adsorption were maximal. This bromide adsorption capacity would be expected to decrease with increasing column volumes passed over the column, as binding sites became unavailable. The GAC and SIAC beds studied here differed only in the 0.1% silver-impregnation present in the SIAC. All other parameters, such as activated carbon mesh size, and sample volume, composition and flow rate, were held constant, to ensure a direct comparison between the silver-impregnated and unimpregnated activated carbons was possible (Figure 50). Activated carbons are generally regenerated after exhausting their capacity to enable re-use and thus improving cost-effectiveness. A comparison of the cost of a non-impregnated activated carbon with a 0.1% silver-impregnated activated carbon shows the non-impregnated GAC to be most economical, being $\$6.62/\text{kg}$ for 1000 kg of the GCN1840 GAC compared to $\$11.58/\text{kg}$ for 1000 kg of 18×40 AG1 SIAC (prices current October 2012). Thus, despite the excellent halide removal achieved by the SIAC, its use may be cost-prohibitive.

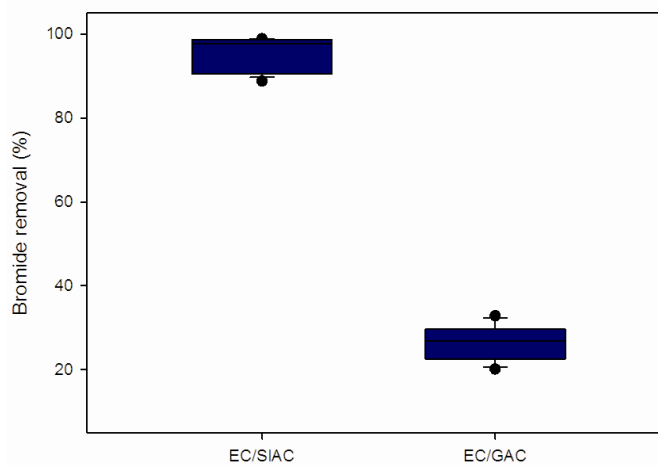


Figure 50: Bromide removal by EC/SIAC treatment compared to EC/GAC treatment, across the experimental sample matrix.

Although iodide was not removed by EC or EC/PAC, MIEX® did have an affinity for iodide. However, it also introduced low levels of both bromide and iodide as contaminants into the blank sample (halide free water treated with MIEX®). Iodide was detected at 3.7 µg/L in the blank sample, however it was <0.5 µg/L in the untreated blank. The authors suggest that the observed halide introduction into the treated water during MIEX® treatment may arise from the salt used to regenerate the MIEX® resin. The introduction of halides into the system through MIEX® treatment is an important observation, since these can then act as DBP precursors upon water disinfection. To the extent of the author's knowledge, iodide removal by MIEX® resin has not been studied previously, although NOM and bromide removal has been assessed [233]. MIEX® was able to adsorb a mean of $58 \pm 21\%$ of the iodide present in solution. The iodide adsorption capacity was not dependent on the DOC concentration or alkalinity of the sample, despite the importance of these factors in bromide adsorption. Lower iodide removals were associated with low starting iodide concentrations.

SIAC (0.1% Ag) beds were able to adsorb iodide to below detection limit (<2 µg/L) across all samples. This is at least an average adsorption of $74 \pm 26\%$ of iodide present. The extent of the iodide removal could not be thoroughly evaluated due to the presence of an interfering peak in the chromatographic analysis obscuring iodide detection below 2 µg/L. As observed with bromide adsorption on SIAC, the presence of competing anions did not appear to hamper iodide adsorption under the conditions studied. Previous reports have suggested that iodide adsorption by SIAC is initially controlled by precipitation of AgI, then by direct adsorption onto the activated carbon once the silver sites are saturation [220]. The study found an increase in iodide adsorption capacity with increasing percentage by weight of silver-impregnation into the GAC, with the 0.5% Ag SIAC having essentially the same iodide adsorption characteristics as the unimpregnated GAC. Although the binding of iodide to silver sites on the SIAC is not a pH dependent phenomenon, the subsequent adsorption of iodide directly onto the activated carbon is, and therefore the use of this treatment after Alum EC would provide a similar advantage to unimpregnated GAC in terms of pH depression improving iodide adsorption.

Similarly to the SIAC treatment, GAC beds were able to remove iodide from all samples to below detection limit (<2 µg/L), regardless of the initial iodide concentration, sample NOM concentration or alkalinity. A similar interfering peak as seen in the GAC samples meant quantification of iodide at a lower detection limit was not possible. From these data we can see that both GAC and SIAC have an improved iodide adsorbing capacity compared to MIEX®, under the conditions studied, however, since both activated carbons remove iodide to below detection limit we cannot determine which, if any, offers superior results. Previous reports have shown that iodide can be adsorbed onto GAC [209, 220], however most of these studies were not conducted in the presence of competing anions. In the present study, we demonstrate high iodide adsorption onto GAC regardless of the presence of competing anions and NOM. Importantly, iodide adsorption onto GAC is known to be a pH dependent phenomenon [209, 220, 325] and has been shown to generally increase with decreasing pH, at least over the pH range 5-10 (data on more extreme pH's not available). This is an advantage of the treatment scenario studied here, since EC using Alum produces a drop in pH to approximately 5-6, enabling high iodide adsorption compared to what could be achieved at higher pH values.

10.1. Conclusions

EC and PAC were not able to adsorb either bromide or iodide at all, therefore these treatments may be expected to lead to the greatest formation of brominated and/or iodinated DBPs upon disinfection, relative to the other treatments studied. MIEX® was able to adsorb some bromide and iodide, however, the extent of bromide adsorption was highly dependent on the concentration of competing anions (such as bicarbonate) present. GAC was able to adsorb significant concentrations of iodide as well as some bromide at the low pH studied, and thus, water treated with combined EC/GAC would be expected to form lower concentrations of iodo- and bromo- DBPs than non-halide removing treatments. Despite the good halide removal achieved with EC/GAC, the EC/SIAC treatment was superior for bromide removal. However, the extent of iodide removal for both GAC and SIAC could not be determined since iodide removal by both GAC and SIAC reduced iodide concentration to below detection limit in all cases.

11. ALKALINITY REMOVAL

Since we have determined that alkalinity is related to Br-DBP formation, the impact of water treatment on alkalinity must also be considered. Since EC using Alum causes a drop in pH, there is an associated decrease in alkalinity, as bicarbonate is reduced to carbon dioxide gas. This decrease in alkalinity would be expected to lead to lower Br-DBP formation than water of higher alkalinity, for a given NOM and bromide concentration. Alkalinity removal from Alum coagulation (measured as dissolved organic carbon (DIC)) ranged from 26 – 66% across all samples, depending on the specific water quality parameters (Figure 51). The greatest alkalinity removals occurred in low alkalinity waters ($SC = -14.5 \pm 3.2$), and the relationship between alkalinity removal and other the parameters investigated (bromide and DOC concentration) were not statistically significant.

Sample alkalinity (as DIC) was unchanged by PAC treatment, SIAC treatment and GAC treatment, therefore no change in Br-DBP formation due to alkalinity would be expected as a consequence of these treatments. MIEX® treatment resulted in some decreases in sample alkalinity ($31 \pm 14 \%$) (Figure 52) however, this could not be strongly correlated to sample alkalinity, halide concentration or DOC concentration. MIEX®, being a strong base anion exchanger, would be expected to have some affinity for bicarbonate, as observed. Halide removal by SIAC is believed to occur by precipitation of the silver salts at the silver binding sites as well as adsorption onto the activated carbon [220]. Bicarbonate does not precipitate on the silver sites of the SIAC since $AgHCO_3$ does not exist as a solid (i.e. it is completely soluble) therefore there is no change in alkalinity from SIAC treatment despite the potential charge interaction between the silver ions of the SIAC and free HCO_3^- in solution. Ag_2CO_3 could potentially precipitate onto the SIAC under high pH conditions (K_{sp} of $Ag_2CO_3 = 8.46 \times 10^{-12}$) however, under the neutral to low pH's studied here, carbonate would not be present in solution. Both $AgBr$ and AgI are highly insoluble ($K_{sp} = 5.35 \times 10^{-13}$ and $K_{sp} = 8.52 \times 10^{-17}$, respectively) allowing the halide ions to precipitate onto the silver binding sites of the SIAC quite effectively.

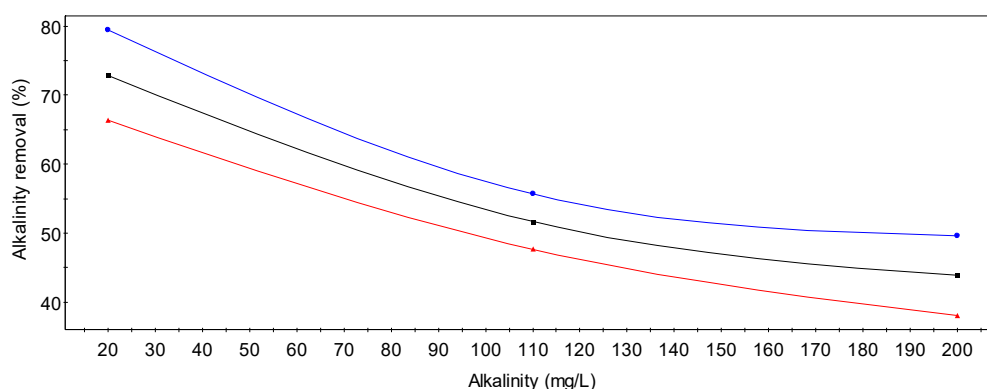


Figure 51: Alkalinity removal by EC as a function of starting sample alkalinity. $R^2 = 0.71$, confidence = 0.95.

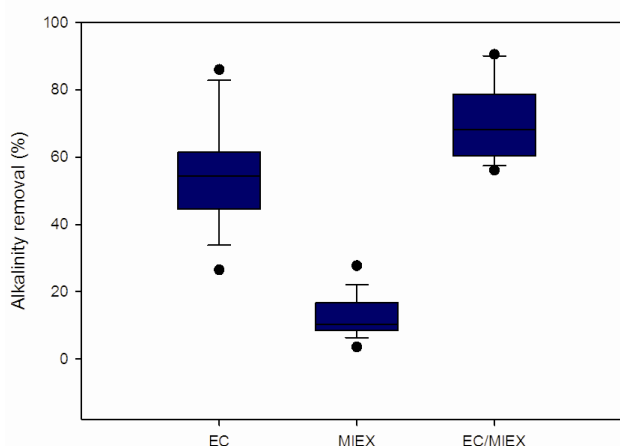


Figure 52: Range of alkalinity removals across all samples from EC, MIEX® (after EC), and total removal by combined EC/MIEX® treatment.

12. IMPACT OF TREATMENTS ON DBP FORMATION

Concentrations of DBPs formed by formation potential test of samples that did not undergo any treatment prior to disinfection were compared to the concentrations after EC treatment (Figure 53 and Figure 54). NOM removal by EC was associated with decreases in the formation of chlorinated DBPs generally, in particular TCM and CH, which decreased in concentrations by an average of $83 \pm 14\%$ and $74 \pm 19\%$, respectively, regardless of sample water quality characteristics. However, this treatment was associated with increases in concentrations of TBM (the most highly brominated THM studied). TBM concentration was increased by up to 28-fold across the matrix of treated synthetic waters compared to 'no treatment' samples, with no examples showing a decrease in TBM concentration. DBAN (the most highly brominated HAN studied) experienced up to an approximately 2-fold increase in concentration after EC (the greatest increases were under high Br:DOC ratio conditions). However, its concentration often remained relatively unchanged before and after the treatment. DBCM was increased by up to 6-fold after EC of low and moderate Br-DBP forming waters, but decreased in high Br-DBP forming waters since in this case THM precursors were preferentially completely brominated (i.e. to TBM). This reflects the general trend that speciation of THMs or HANs (excluding TCAN) changes from decreasing in concentration from least to most brominated in low Br:DOC waters, to increasing in concentration from least to most brominated in high Br:DOC waters, with an intermediate level of bromination occurring under moderate Br:DOC conditions in which BDCM and DBCM occur at higher concentrations than TCM and TBM, and BCAN occurs at higher concentrations than DCAN and DBAN. BDCM and BCAN (both mono-brominated species) were either unchanged by EC treatment or lowered, with the greatest removals (up to 80%) occurring at high Br:DOC ratio in which case more highly brominated species were preferentially formed. Overall, the total concentrations of THMs (tTHMs) and HANs (tHANs) decreased in all samples irrespective of the increases in the concentrations of specific DBPs within these classes, although tTHMs reductions were much greater than HANs reductions (average of $61 \pm 9\%$ and $39 \pm 19\%$, respectively).

The ability of EC/PAC treatment to remove a large percentage of NOM, yet not adsorb bromide, leads to a large increase in Br:DOC ratio as a consequence of treatment. The result of this is a clear preference for formation of highly brominated DBPs, rather than chlorinated DBPs, when bromide is present in the source water. A comparison of the DBP concentrations arising in the synthetic water matrix before and after EC/PAC treatment shows the change in speciation of both the THMs and the HANs from predominantly chlorinated or monobrominated species before treatment, to predominantly di- or tri- brominated species after treatment (Figure 53 and Figure 55). TBM was increased by EC/PAC treatment in 82% of samples, by between 3 – 221 fold. EC/PAC created the largest increases in TBM concentrations of all the treatments studied. DBAN concentration increased by up to approximately 2-fold after EC/PAC treatment, which was similar to what was observed with EC treatment alone. Chlorinated DBPs were again greatly reduced overall due to the excellent NOM removal achieved by this treatment, with averages of $98 \pm 1\%$ and $92 \pm 5\%$ reduction in TCM and CH concentrations, respectively. BDCM was also consistently lowered regardless of sample water quality characteristics ($82 \pm 16\%$). DBCM varied from 60% reduction to 2.5-fold increase and BCAN varied from 70% reduction to 2-fold increase depending on water quality parameters. Total THMs and tHANs were decreased by this treatment to a greater extent than EC alone, with a mean of $86 \pm 7\%$ removal for tTHMs and $46 \pm 27\%$ for tHANs, respectively.

The combined EC/MIEX® treatment resulted in consistent increases in TBM concentration, in 82% of the sample matrix (Figure 56). This varied from a 2-61 fold increase, which was less than observed for the EC/PAC treatment due to the bromide adsorbing capacity of the resin. DBCM and DBAN also saw occasional increases in concentration in some samples (up to 2.5 fold) however these DBPs were often decreased by the treatment (up to 8 fold decreases) particularly in waters with low alkalinity (under which circumstance bromide removal by MIEX® is maximised) and low starting bromide concentration. Fully chlorinated DBPs were consistently reduced (TCM by $87 \pm 10\%$, CH by $80 \pm 16\%$) which improves on what was achieved with EC alone but is less than what was observed with EC/PAC. BDCM was also consistently lowered relative to 'no treatment' samples ($66 \pm 16\%$) as was BCAN ($56 \pm 12\%$). More importantly, BCAN was consistently reduced by EC/MIEX® treatment, unlike EC/PAC treatment, again, due to the bromide adsorbing capacity of the resin. Reduction in

tTHMs was $84 \pm 8\%$ and tHANs was $65 \pm 14\%$, which is improved on EC alone and EC/PAC for tHANs, similar to EC/PAC for tTHMs and improved on EC alone for tTHMs. Samples exposed to MIEX® resin were also monitored for nitrosamine formation after maximum NDMA formation potential test (chloramination). This resulted in increases in NDMA formation potential from below detection limit (5 ng/L) to between 5 - 9 ng/L for all samples. This increase in NDMA formation occurs due to leaching of NDMA precursors from the MIEX® resin. No other nitrosamines were detected. The resin used here was a used, regenerated resin, therefore NDMA precursor leaching would be expected to be less than what would be anticipated for a virgin resin. NDMA precursor leaching from MIEX® would be expected to decrease over the lifetime of the resin. NDMA was not formed upon chlorination of MIEX® resin.

Combined EC/GAC treatment provided excellent NOM removals and some bromide removal. Consequently, DBP formation upon chlorination was often low. Like previously discussed methods, chlorinated DBPs were greatly lowered by this treatment, with TCM and CH being reduced by $95 \pm 5\%$ and $89 \pm 8\%$, respectively (Figure 57). The monobrominated DBPs, BDCM and BCAN were both consistently lowered by this treatment, relative to untreated samples, which improves on the treatments discussed above. Reductions of $79 \pm 13\%$ and $57 \pm 25\%$ were attained for BDCM and BCAN, respectively. In general, the dibrominated species, DBCM and DBAN were reduced in concentration by the combined EC/GAC treatment regardless of sample characteristics, however, there were from 1.4 - 2.3 fold increases observed for both of these DBPs approximately 15% of the time, specifically under conditions suitable for high Br-DBP formation. TBM was again the DBP that experienced the greatest and most consistent increases in concentration due to the treatment, with 82% of samples forming from 1.1 – 55 fold greater TBM concentrations than what was formed in untreated water (average increase of 12-fold). This was less than what was observed in EC/PAC and EC/MIEX treated samples. Total THM and tHAN was consistently reduced in all samples, by $89 \pm 5\%$ and $72 \pm 19\%$, respectively, which is the greatest removal for both groups of compounds of the treatments discussed thus far.

EC/SIAC treatment was the only treatment of those studied in which all DBPs decreased in concentration throughout the synthetic water matrix, regardless of starting water quality parameters (Figure 58). This is attributed to the excellent combined NOM and halide adsorption of the SIAC, however, it is important to note that the SIAC studied was a fresh, unused product, so the silver binding-sites on the activated carbon were unsaturated. Further study would be required to understand the lifetime of the SIAC, potential for regeneration, and longer-term halide adsorption capacity/halide breakthrough. THMs concentrations were dramatically reduced by the treatment: TCM, $94 \pm 6\%$; BDCM, $98 \pm 1\%$; DBCM, $98 \pm 2\%$; TBM, $90 \pm 3\%$. HANs were also greatly reduced: DCAN, $83 \pm 15\%$; BCAN, $97 \pm 3\%$; DBAN, $87 \pm 13\%$. CH concentration was reduced by $75 \pm 24\%$, while tTHMs and tHANs were decreased overall by $96 \pm 4\%$ and $87 \pm 13\%$, respectively. TCNM, TCAN and 1,1-DCP (all fully chlorinated DBPs) were formed at very low levels both in untreated and treated samples, however, 1,1,1-TCP was reduced by $87 \pm 9\%$ by the EC/SIAC treatment relative to untreated samples. Although similar removals were achieved for chlorinated DBPs using other methods (in particular EC/GAC) no other treatment was able to lead to the low levels of brominated DBP formation achieved with this treatment.

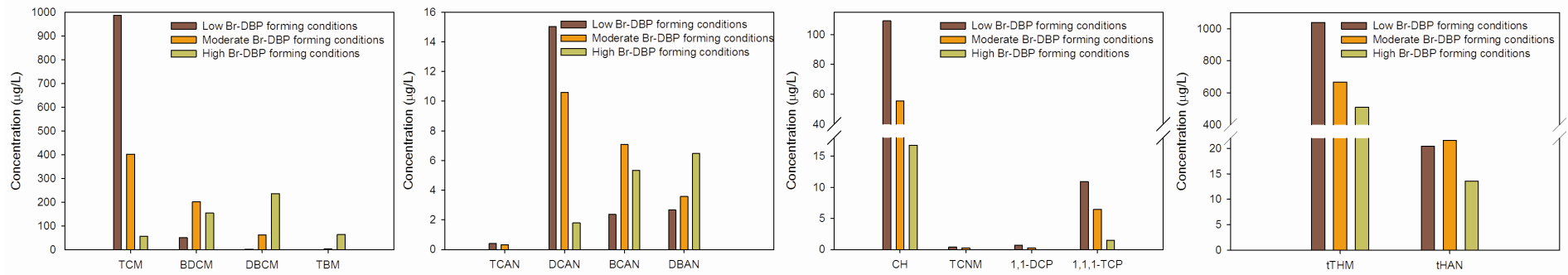


Figure 53: Concentrations of individual DBPs formed in ‘no treatment’ samples (synthetic waters dosed with chlorine to give approximately 2 mg/L chlorine residual) under low Br-DBP forming conditions (starting sample concentrations: 12 mg/L DOC, 100 µg/L Br⁻, 38 mg/L alkalinity (as CaCO₃)), moderate Br-DBP forming conditions (starting sample concentrations: 7.5 mg/L DOC, 450 µg/L Br⁻, 138 mg/L alkalinity (as CaCO₃)) and high Br-DBP forming conditions (starting sample concentrations: 3 mg/L DOC, 800 µg/L Br⁻, 238 mg/L alkalinity (as CaCO₃)) Each sample was measured in duplicate and error was always <10%.

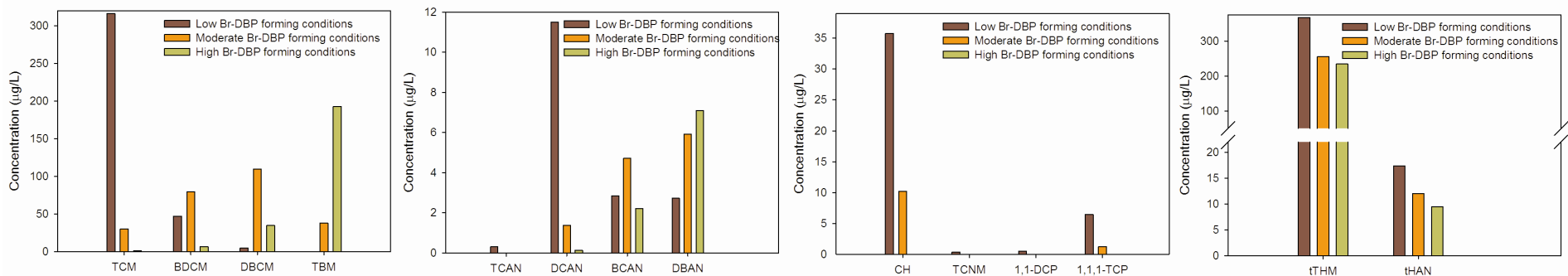


Figure 54: Concentrations of individual DBPs formed in samples subjected to EC treatment (synthetic waters treated with Alum then dosed with chlorine to give approximately 2 mg/L chlorine residual) under low Br-DBP forming conditions (starting sample concentrations: 12 mg/L DOC, 100 µg/L Br⁻, 38 mg/L alkalinity (as CaCO₃)), moderate Br-DBP forming conditions (starting sample concentrations: 7.5 mg/L DOC, 450 µg/L Br⁻, 138 mg/L alkalinity (as CaCO₃)) and high Br-DBP forming conditions (starting sample concentrations: 3 mg/L DOC, 800 µg/L Br⁻, 238 mg/L alkalinity (as CaCO₃)) Each sample was measured in duplicate and error was always <10%.

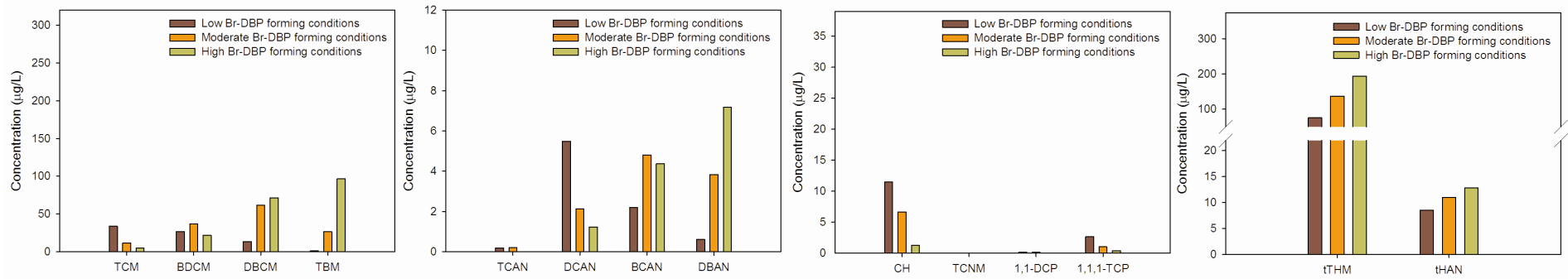


Figure 55: Concentrations of individual DBPs formed in samples subjected to EC/PAC treatment (synthetic waters treated with Alum then PAC, then dosed with chlorine to give approximately 2 mg/L chlorine residual) under low Br-DBP forming conditions (starting sample concentrations: 12 mg/L DOC, 100 µg/L Br⁻, 38 mg/L alkalinity (as CaCO₃)), moderate Br-DBP forming conditions (starting sample concentrations: 7.5 mg/L DOC, 450 µg/L Br⁻, 138 mg/L alkalinity (as CaCO₃)) and high Br-DBP forming conditions (starting sample concentrations: 3 mg/L DOC, 800 µg/L Br⁻, 238 mg/L alkalinity (as CaCO₃)) Each sample was measured in duplicate and error was always <10%.

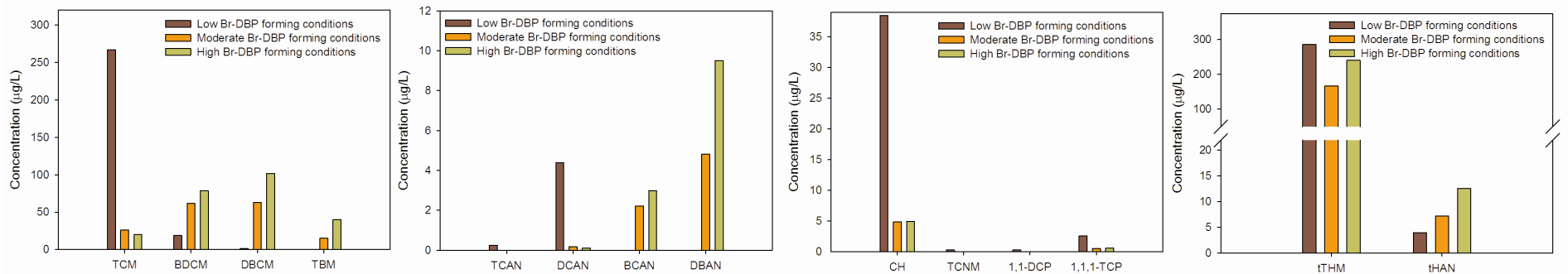


Figure 56: Concentrations of individual DBPs formed in samples subjected to EC/MIEX treatment (synthetic waters treated with Alum then MIEX, then dosed with chlorine to give approximately 2 mg/L chlorine residual) under low Br-DBP forming conditions (starting sample concentrations: 12 mg/L DOC, 100 µg/L Br⁻, 38 mg/L alkalinity (as CaCO₃)), moderate Br-DBP forming conditions (starting sample concentrations: 7.5 mg/L DOC, 450 µg/L Br⁻, 138 mg/L alkalinity (as CaCO₃)) and high Br-DBP forming conditions (starting sample concentrations: 3 mg/L DOC, 800 µg/L Br⁻, 238 mg/L alkalinity (as CaCO₃)) Each sample was measured in duplicate and error was always <10%.

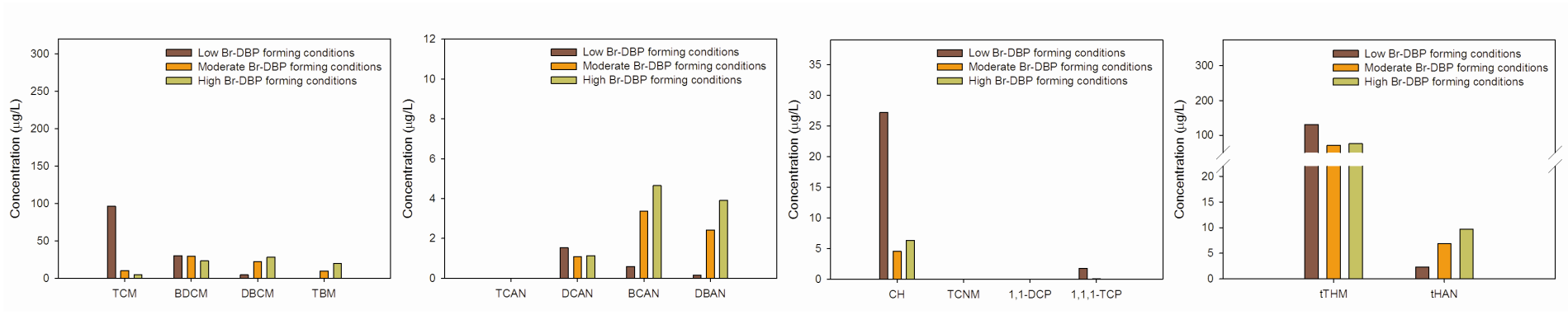


Figure 57: Concentrations of individual DBPs formed in samples subjected to EC/GAC treatment (synthetic waters treated with Alum then GAC beds dosed with chlorine to give approximately 2 mg/L chlorine residual) under low Br-DBP forming conditions (starting sample concentrations: 12 mg/L DOC, 100 µg/L Br⁻, 38 mg/L alkalinity (as CaCO₃)), moderate Br-DBP forming conditions (starting sample concentrations: 7.5 mg/L DOC, 450 µg/L Br⁻, 138 mg/L alkalinity (as CaCO₃)) and high Br-DBP forming conditions (starting sample concentrations: 3 mg/L DOC, 800 µg/L Br⁻, 238 mg/L alkalinity (as CaCO₃)) Each sample was measured in duplicate and error was always <10%.

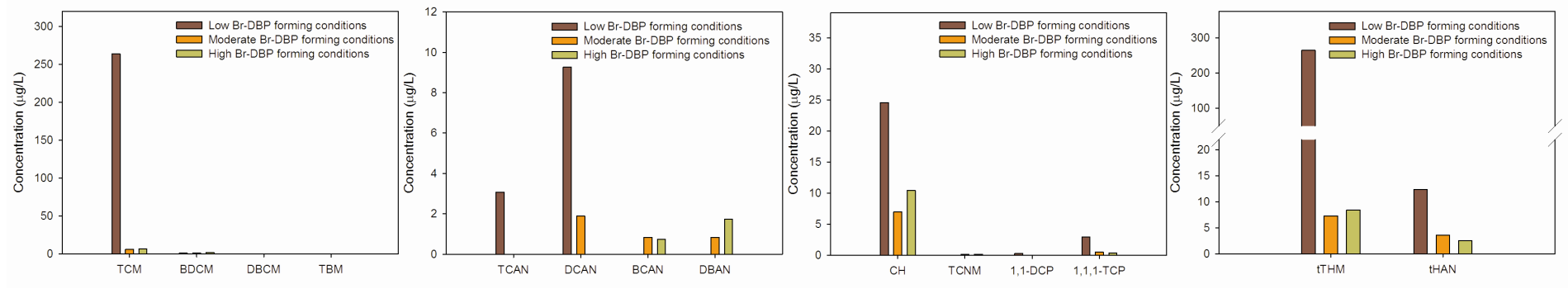


Figure 58: Concentrations of individual DBPs formed in samples subjected to EC/SIAC treatment (synthetic waters treated with Alum then SIAC beds dosed with chlorine to give approximately 2 mg/L chlorine residual) under low Br-DBP forming conditions (starting sample concentrations: 12 mg/L DOC, 100 µg/L Br⁻, 38 mg/L alkalinity (as CaCO₃)), moderate Br-DBP forming conditions (starting sample concentrations: 7.5 mg/L DOC, 450 µg/L Br⁻, 138 mg/L alkalinity (as CaCO₃)) and high Br-DBP forming conditions (starting sample concentrations: 3 mg/L DOC, 800 µg/L Br⁻, 238 mg/L alkalinity (as CaCO₃)) Each sample was measured in duplicate and error was always <10%.

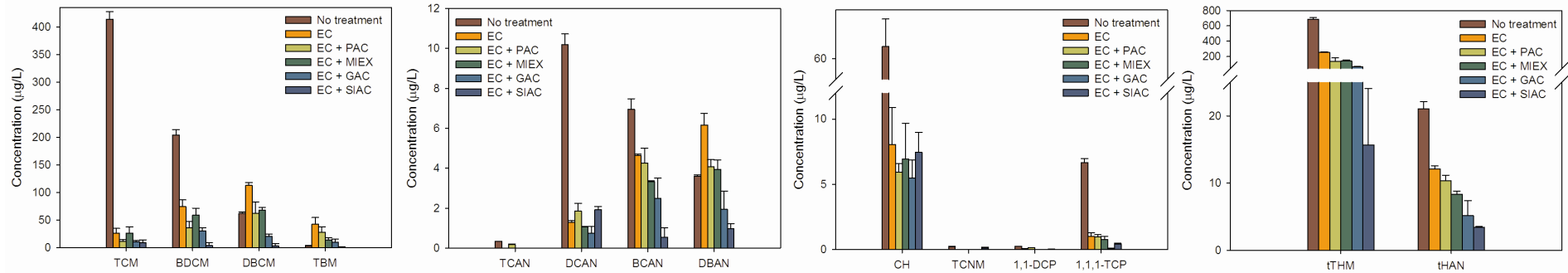


Figure 59: Comparison of average DBP concentrations from chlorination of triplicate centrepont samples (starting DOC concentration = 7.5 mg/L, starting bromide concentration = 450 µg/L, starting sample alkalinity = 138 mg/L as CaCO₃) for each treatment method studied.

12.1. Conclusions

- Overall, the treatment that produced water with the lowest concentrations of all DBPs, regardless of the water quality parameters, was the combined EC/SIAC treatment. This treatment warrants further investigation into its applicability in a full-scale setting.
- Further information is required in regards to the economic feasibility of using this treatment on a large scale, and the lifetime of the activated carbon beds before halide breakthrough is experienced. The EC/GAC treatment was excellent for Cl-DBP removal and caused smaller increases in Br-DBP formation than EC/MIEX® and EC/PAC treatments.
- EC/MIEX® improved on EC/PAC in terms of preferential Br-DBP formation, although significant increases in specific Br-DBPs were still experienced under particular water quality conditions. EC/PAC was the least effective treatment of those studied, causing large increases in Br-DBP formation due to the high NOM removal that can be achieved with the treatment along with an inability to adsorb bromide. Chlorinated DBP concentrations were easily lowered to a large extent by all of these treatments, although GAC and SIAC were the best. EC alone, although it did not lower Cl-DBPs to the extent that could be achieved by the combined treatments, did not cause as large an increase in Br-DBP formation as the combined treatments (apart from SIAC). A comparison of triplicate analyses of the centrepoin samples taken from each of the treatments (including ‘no treatment’) are shown to summarise (Figure 59).

13. APPLYING TREATMENT STRATEGIES TO RAWSEQ DRINKING WATER SOURCES

13.1. DBP Precursor Removal

Raw water samples taken from Capalaba WTP, Molendinar WTP and Mt Crosby WTP and treated at the laboratory scale are compared herein in terms of DBP formation and DBP precursor removal. DOC and IC concentrations remained fairly constant for a particular sampling site over the duplicate sampling events undertaken for each site, while TN showed more variation between sampling events (Table 28). Capalaba had a high organic carbon load compared to the other two sites, however, Mt Crosby had a high salt load (inorganic carbon, bromide and iodide) compared to Molendinar and Capalaba.

Table 28: Water quality data for raw waters sampled from Capalaba WTP, Mt Crosby WTP, and Molendinar WTP.

Sample Site	DOC (mg/L)	TN (mg/L)	Alkalinity (as mg/L CaCO ₃)	Br ⁻ (µg/L)	I ⁻ (µg/L)
Capalaba (17/5/12)	10.2361	0.37158	26	97	1.4
Capalaba (16/6/12)	10.2161	0.59158	25	74	1.4
Mt Crosby (17/5/12)	3.9031	0.37418	188	238	3.7
Mt Crosby (16/6/12)	4.0141	0.71148	208	388	3.3
Molendinar (17/5/12)	3.8761	0.18478	34	43	<0.5
Molendinar (16/6/12)	3.9822	0.28089	36	33	<0.5

Alum coagulation for Molendinar and Capalaba raw waters resulted in a DOC decrease of $21.6 \pm 2.8\%$ (Table 29). Mt Crosby was less amenable to Alum coagulation, due to the relatively high alkalinity and low DOC of the water (Table 28). This led to a DOC reduction of $4.0 \pm 2.8\%$ from Mt Crosby water with Alum treatment. PAC treatment afforded a further $26.5 \pm 4.5\%$ DOC removal when applied after EC treatment, across all sampling sites. MIEX® treatment produced more variable DOC removals, with Capalaba water having a further $49.6 \pm 0.4\%$ DOC removed beyond the removals achieved with EC, Mt Crosby achieving $18.5 \pm 0.2\%$ further DOC removal, and $34.5 \pm 4.8\%$ DOC being removed by the MIEX® treatment of Molendinar water. This variation reflects the high NOM concentration of Capalaba source water, in which MIEX® performs well, and the high alkalinity/low NOM concentration of Mt Crosby source water, under which conditions, MIEX® treatment was found to be less effective (Chapter 8). GAC or SIAC treatments, like PAC treatment, provided fairly consistent DOC removals regardless of the source water treated. GAC removed $41.2 \pm 5.1\%$ of DOC beyond the removal achieved by EC, while SIAC removed $52.9 \pm 7.4\%$ of DOC remaining after EC.

As was observed with the model waters discussed in previous chapters, neither bromide nor iodide were removed by EC or EC/PAC treatments, regardless of sample site (Table 29). GAC treatment adsorbed $27.1 \pm 7.7\%$ bromide, and this was relatively consistent between sample sites. The bromide removal capacity of the activated carbon was improved to $87.0 \pm 5.5\%$ when using the SIAC, and again, this was not dependent on sample site water quality characteristics. MIEX® treatment was more dependent on the source water treated, with the high alkalinity of Mt Crosby water impeding bromide adsorption somewhat to give $50.8 \pm 6.7\%$ bromide removal compared to the $77.0 \pm 11.1\%$ bromide adsorption achieved in Capalaba and Molendinar waters (both of which had similar alkalinity) (Table 28).

All waters treated with EC/GAC or EC/SIAC resulted in iodide concentrations below detection limit ($0.5 \mu\text{g/L}$), regardless of sampling date or sample site (Table 29). Iodide concentrations of raw waters are shown (Table 28) and were quite low in all cases. This is further reflected in the low concentrations of I-THMs formed by chloramination of these source waters, as discussed in Chapter 3. EC/MIEX® treatment exhibited more variable behaviour, with iodide concentrations being reduced to below detection limit in Capalaba ($>65\%$ I⁻ removal) and no significant change in I⁻ concentration after treatment of Mt Crosby water.

Table 29: DOC and halide removals for each treatment of the three source waters studied. Note DOC removals refer to total % removal from combined treatment. N.a. = data not available.

Sample Site	EC			EC/PAC			EC/GAC			EC/SIAC			EC/MIEX®		
	DOC removal (%)	Br ⁻ removal (%)	I ⁻ removal (%)	DOC removal (%)	Br ⁻ removal (%)	I ⁻ removal (%)	DOC removal (%)	Br ⁻ removal (%)	I ⁻ removal (%)	DOC removal (%)	Br ⁻ removal (%)	I ⁻ removal (%)	DOC removal (%)	Br ⁻ removal (%)	I ⁻ removal (%)
Capalaba (17/5/12)	20	0	0	39	0	0	61	34.0	>65	81	87.6	>65	70	74.0	>65
Capalaba (16/6/12)	21	0	0	47	0	0	65	14.9	>65	83	88.5	>65	71	n.a.	>65
Mt Crosby (17/5/12)	2	0	0	31	0	0	n.a.	21.6	>87	49	94.5	>87	20	55.5	0
Mt Crosby (16/6/12)	6	0	0	n.a.	0	0	n.a.	26.5	>87	61	n.a.	>87	25	46.1	0
Molendinar (17/5/12)	20	0	0	49	0	0	54	33.2	n.a.	68	84.9	n.a.	51	67.4	n.a.
Molendinar (16/6/12)	26	0	0	55	0	0	72	32.5	n.a.	70	79.4	n.a.	64	89.2	n.a.

13.2. DBP Formation across All Sites and Treatments

Iodinated THMs were not formed in any case, regardless of starting raw water iodide concentration (Table 28). The remaining DBPs in the suite studied (4THMs, 4HANs, CH, TCNM, 1,1-DCP, 1,1,1-TCP) are discussed herein, for raw water samples taken from Capalaba WTP, Mt Crosby WTP, and Molendinar WTP, and subjected to various treatments before chlorine disinfection.

Raw water samples from each site that were chlorinated in the laboratory without any pre-treatment formed high concentrations of many DBPs. In particular, Mt Crosby raw water led to formation of the greatest concentrations of the more highly brominated DBPs in the suite, such as TBM, DBCM and DBAN, compared to the other two sites, due to the high concentration of bromide and relatively low concentration of organic matter (high Br:DOC ratio) of this source water (Figure 60, blue graph). Conversely, Molendinar raw water did not form detectable TBM or DBAN, despite having a similarly low DOC concentration to Mt Crosby, because of the low bromide ion concentration of the water (Figure 60, red graph). Capalaba raw water has a high organic load, with a DOC concentration of approximately 10.2 mg/L. It is also a fairly low bromide water, leading to formation of very high concentrations of fully chlorinated DBPs such as TCM compared to the other sites (Figure 60, green graph).

All sites formed lower concentrations of fully chlorinated DBPs when Alum coagulation was employed prior to chlorination, compared to chlorination with no pre-treatment (Figure 61). However, this treatment caused a change in the speciation of THMs and HANs in Mt Crosby water, as a consequence of the changing Br:DOC ratio of this water upon organics removal. Specifically, coagulation of Mt Crosby water led to increases in TBM and DBAN concentration upon chlorination. The speciation of THMs and HANs shifted from decreasing in concentration from fully chlorinated to fully brominated forms (with the exception of TCAN which was consistently formed at concentrations below 1 µg/L, for all sites and treatments) to preferentially forming higher concentrations of most brominated THMs and HANs than fully chlorinated THMs and HANs. Alum coagulation of Capalaba raw water, although leading to large decreases in TCM concentration and moderate decreases in formation of many other chlorinated DBPs, still caused increases in concentration of the highly brominated DBPs; BCAN and DBCM. Despite the raw water not having a particularly high bromide concentration, the shift in Br:DOC ratio caused by coagulation still exerted this brominating effect on the DBPs monitored. Molendinar raw water, with its very low starting DOC and bromide concentration, behaved similarly, with decreases in concentration of all chlorinated DBPs, as well as BDCM, and modest increases in DBCM and BCAN concentration, upon Alum coagulation and chlorination. The fully brominated DBPs; TBM and DBAN were not formed in either Molendinar water or Capalaba water with either direct chlorination (no pre-treatment) or Alum coagulation followed by chlorination.

After a combined EC/PAC treatment (Figure 62), Mt Crosby water experienced decreases in concentrations of most DBPs, for both chlorinated and brominated species, relative to coagulation alone. This is despite the increase in Br:DOC ratio that occurs as a result of this treatment, and may imply that once the DOC concentration is taken below a defined threshold concentration, there is insufficient organic material available to react with hypobromous acid present in the water to cause the increase in Br-DBPs often observed as a result of treatments that remove NOM without removing bromide. For Capalaba, small increases in DBCM and BCAN were again noted in EC/PAC treated water relative to Alum treated water, however, all other DBPs saw improved reductions in concentration from the combined treatment relative to coagulation alone. Molendinar water treated with EC/PAC exhibited decreases in all chlorinated DBPs, however, increased concentrations of DBCM were observed, and TBM and DBAN increased from not detected in EC treated or untreated waters to being observed in one of the two replicate sampling events after EC/PAC treatment. BCAN concentration was similar with either 'no treatment', Alum coagulation or combined EC/PAC treatment, although it was only observed on one of the two sampling dates for 'no treatment' samples. EC/PAC treatment, although capable of leading to chlorinated waters with low total DBP

concentrations, has the potential to form higher concentrations of Br-DBPs than other treatment methods (or 'no treatment') because of the inability of this treatment to remove bromide.

Waters treated with combined EC/MIEX® improve on what is achieved with EC/PAC since MIEX® has some bromide adsorbing capacity under appropriate conditions. Comparing EC/PAC treated Mt Crosby water with EC/MIEX® treated Mt Crosby water, we see that THM speciation has shifted back to what we observed with 'no treatment' Mt Crosby water, in that concentration decreases from fully chlorinated to fully brominated species (Figure 63). This speciation profile is preferable since toxicity generally increases with increasing bromination. HANs speciation is still showing increasing concentrations from least to most brominated with EC/MIEX® treatment of Mt Crosby water, as we observed for the previously discussed treatments (excluding 'no treatment') however, HANs concentrations are somewhat lower than observed with 'no treatment' or Alum treatment. Capalaba water treated with EC/MIEX® showed lower DBP concentrations generally than the other 3 treatments discussed thus far, with the exception of DBCM, which was similar or marginally increased in EC/MIEX® treated water compared to 'no treatment' samples. Molendinar water formed lower concentrations of all DBPs after EC/MIEX® treatment compared to 'no treatment', and formed lower concentrations of Br-DBPs than any other treatment of this water discussed so far. Since MIEX® adsorbs both NOM and bromide to different degrees depending on the source water characteristics, the Br:DOC ratio after this treatment (and therefore Br-DBP formation) can increase or decrease relative to the untreated sample. This shows the importance of tailoring treatments to the specific water quality characteristics of the source water to get optimal results.

Combining EC/GAC treatment is similar to EC/MIEX® treatment, in that GAC has both NOM and bromide adsorbing capacity (Table 29). Although the speciation of THMs and HANs became less favourable compared to 'no treatment' by increasing the Br:DOC ratio, the concentrations of the compounds of these two classes were appreciably diminished, with DBAN reaching 'not detected' concentrations (<0.1 µg/L) for the first time of all the treatments discussed thus far (Figure 64). The two 1,1-DCP were also not detected for the first time using this treatment. Capalaba water treated with EC/GAC also saw decreases in all DBPs compared to 'no treatment' samples, with the exception of one occurrence of DBCM at increased concentrations (the other sampling event for this site had <0.1 µg/L DBCM after EC/GAC). The chlorinated DBPs; TCNM and 1,1,1-TCP were not detected after this treatment (<0.1 µg/L). The chloropropanones were also absent from Molendinar water treated with EC/GAC, and all DBPs observed were at low concentrations compared to 'no treatment' samples, and lowered DBP concentrations generally compared to all other treatment methods described above. EC/GAC is demonstrated to be an excellent treatment overall for targeting a range of DBPs.

The final treatment studied was combining EC with SIAC treatment (0.1% Ag impregnation). The results reflect the excellent bromide and NOM adsorption capacity of the SIAC (Figure 65). The only brominated THM formed was the monobrominated BDCM, which occurred at low levels at all sites. DCAN was the only HAN formed, apart from a single sample from Capalaba, which formed a very low concentration of BCAN. TCM and CH were still formed at concentrations similar to or a little higher than the EC/GAC treatment, but these concentrations are still well below guidelines. Comparing Mt Crosby DBP concentrations before and after EC/SIAC treatment demonstrates the impressive ability to reduce Br-DBP formation in this quite high bromide source water. Going from 12 DBPs occurring at concentrations reaching up to approximately 100 µg/L in the untreated water, to only five detectable DBPs, only one of which is brominated, with a maximum DBP concentration of approximately 30 µg/L, demonstrates how DBP precursor removal prior to water disinfection has the potential to be a successful strategy.

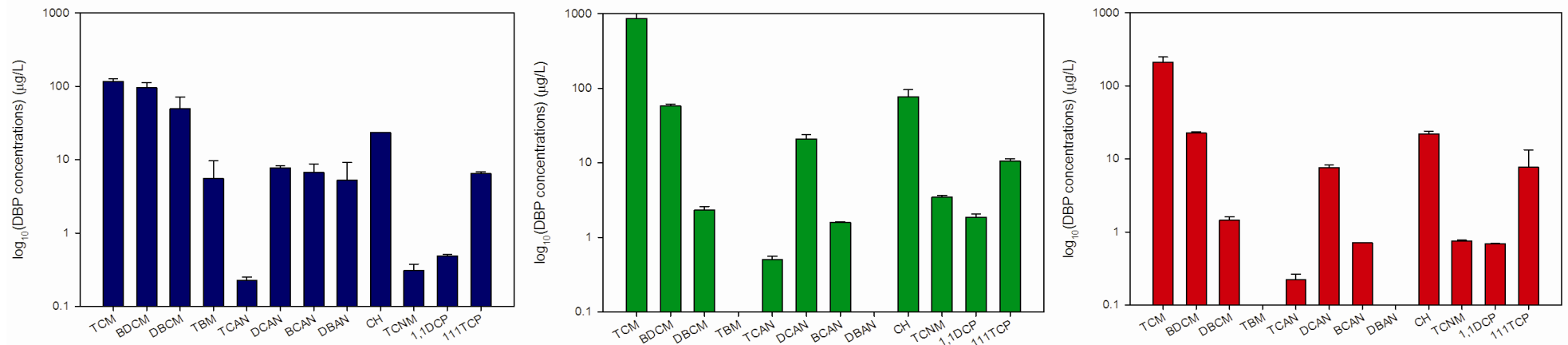


Figure 60: DBP formation from chlorination of raw waters (no DBP precursor removal treatment). Blue = Mt Crosby, Green Capalaba, Red = Molendinar. Error bars show variation between duplicate sampling events. No error bar indicates the DBP was only detected in one of the two sampling events.

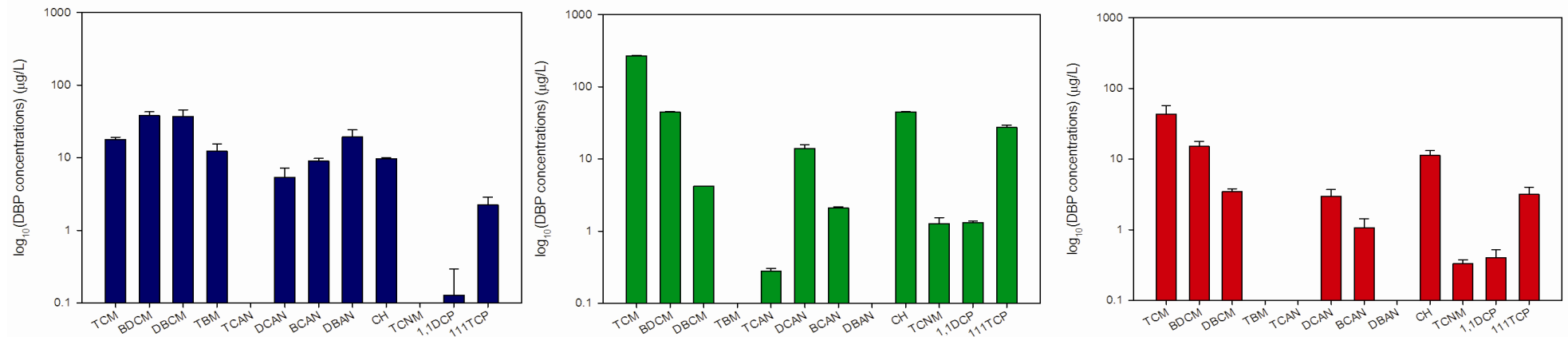


Figure 61: DBP formation from chlorination of raw waters that have undergone Alum coagulation treatment. Blue = Mt Crosby, Green Capalaba, Red = Molendinar. Error bars show variation between duplicate sampling events. No error bar indicates the DBP was only detected in one of the two sampling events.

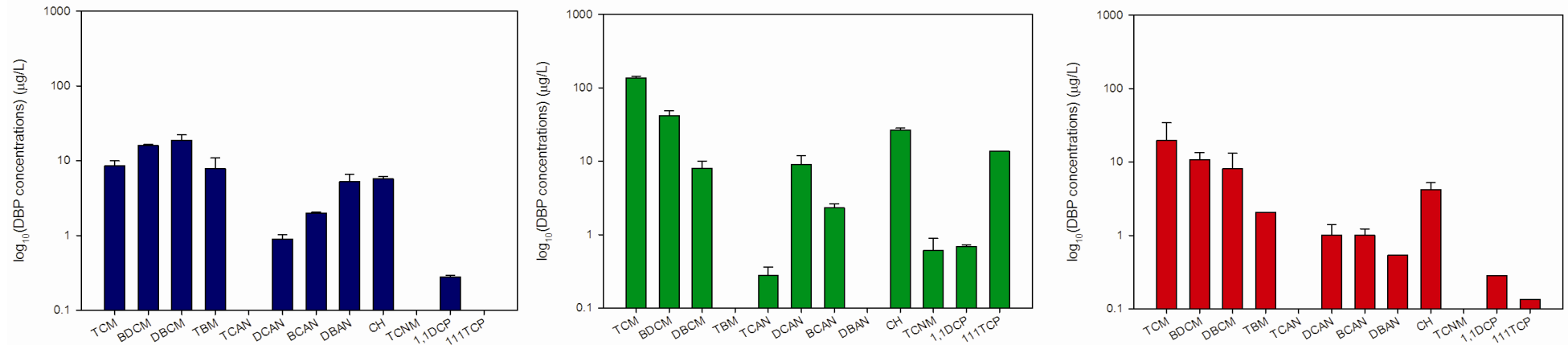


Figure 62: DBP formation from chlorination of raw waters that have undergone Alum coagulation followed by PAC treatment. Blue = Mt Crosby, Green Capalaba, Red = Molendinar. Error bars show variation between duplicate sampling events. No error bar indicates the DBP was only detected in one of the two sampling events.

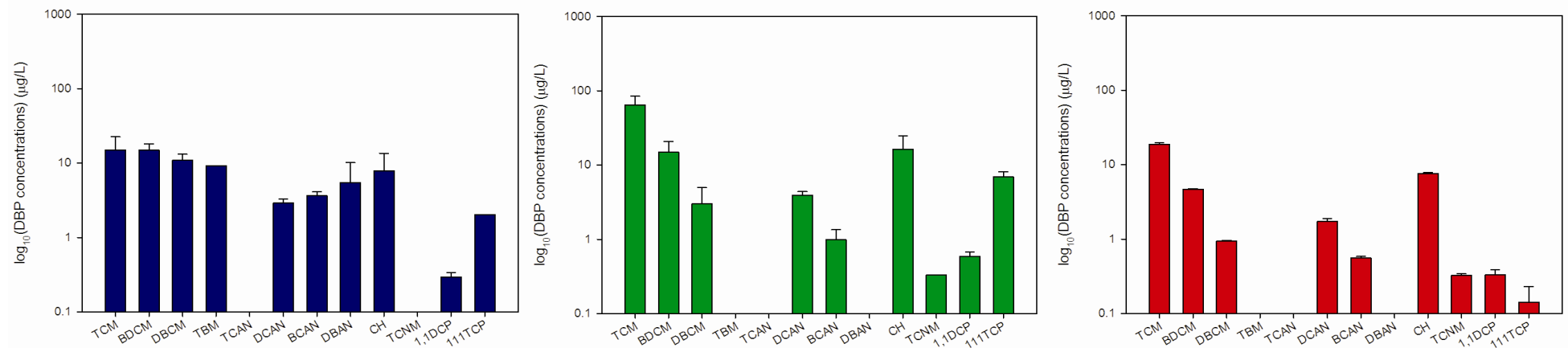


Figure 63: DBP formation from chlorination of raw waters that have undergone Alum coagulation followed by MIEX® treatment. Blue = Mt Crosby, Green Capalaba, Red = Molendinar. Error bars show variation between duplicate sampling events. No error bar indicates the DBP was only detected in one of the two sampling events.

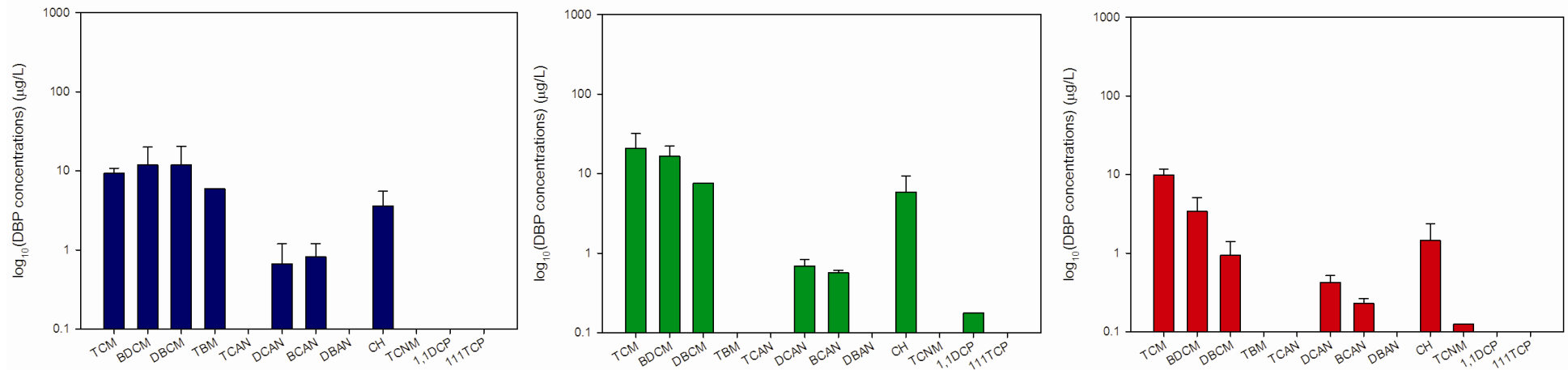


Figure 64: DBP formation from chlorination of raw waters that have undergone Alum coagulation followed by GAC treatment. Blue = Mt Crosby, Green Capalaba, Red = Molendinar. Error bars show variation between duplicate sampling events. No error bar indicates the DBP was only detected in one of the two sampling events.

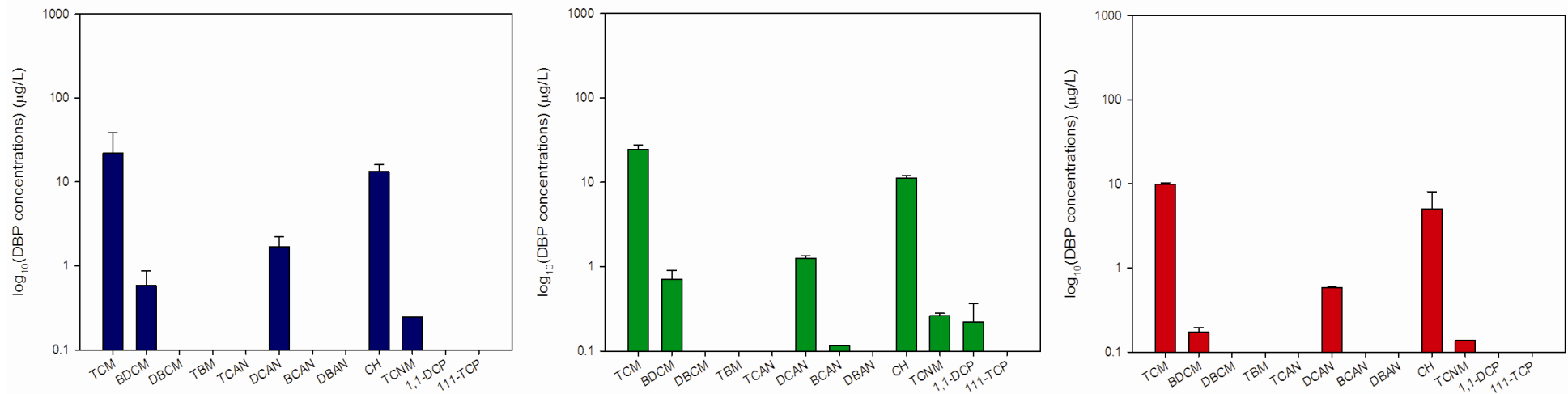


Figure 65: DBP formation from chlorination of raw waters that have undergone Alum coagulation followed by SIAC treatment. Blue = Mt Crosby, Green Capalaba, Red = Molendinar. Error bars show variation between duplicate sampling events. No error bar indicates the DBP was only detected in one of the two sampling events.

13.1. Conclusions

- Halide concentration should be taken into account in determining optimal treatment strategies for SEQ drinking water sources, and halide removal techniques employed prior to water disinfection when concentrations are sufficient to lead to high Br-DBP formation upon chlorination (e.g. Mt Crosby).
- In lower bromide waters (e.g. Molendinar), coagulation followed by GAC treatment enables low DBP formation, however, in higher bromide waters (e.g. Mt Crosby) the decreases in Br-DBP formation achievable by using a SIAC rather than a traditional GAC may be warranted if chlorination is the preferred disinfection method. In practice, Mt Crosby water is chloraminated rather than chlorinated so Br-DBP formation should be minimised in any case.
- PAC treatment is not recommended for treatment of high bromide source waters when chlorination is the disinfection method to be used due to expected increases in Br-DBP formation.
- MIEX® treatment was not optimal for Mt Crosby water compared to the other two sites, however, some DOC and bromide removal was still achieved and led to an improved DBP profile for the finished water compared to EC or EC/PAC.
- Regardless of source water studied, EC/SIAC provided lowest overall concentrations of DBPs in the finished water.

GLOSSARY

1,1-DCP:	1,1-dichloropropanone	IMS:	integrated membrane systems
1,1,1-TCP:	1,1,1-trichloropropanone	Kd:	dissociation constant
ADWG:	Australian drinking water guidelines	LDH:	layered double hydroxides
BAT:	best available technologies	LOD:	limit of detection
BCAN:	bromochloroacetonitrile	LOR:	limit of reporting
BDCM:	bromodichloromethane	MCDI:	membrane capacitative deionisation
BDIM:	bromodiodomethane	MIEX®:	Magnetic Ion Exchange
BSF:	bromide substitution factor	MS:	mass spectrometry
CDI:	captive deionisation	MtBE:	methyl tert-butyl ether
CDIM:	chlorodiodomethane	NDMA:	N-nitrosodimethylamine
CH:	chloral hydrate	NF:	nanofiltration
COD:	chemical oxygen demand	NOM:	natural organic matter
Ct:	contact time	NSI:	North Stradbroke Island WTP
DBAN:	dibromoacetonitrile	PAC:	powdered activated carbon
DBCM:	dibromochloromethane	PCI:	positive chemical ionisation
DBIM:	dibromodiodomethane	REF:	relative enrichment factor
DBP:	disinfection by-product	RO:	reverse osmosis
DC:	direct current	RPD:	relative percentage difference
DCAN:	dichloroacetonitrile	RSM:	response surface modelling
DCIM:	dichlorodiodomethane	SC:	standard coefficient
DMA:	dimethylamine	SEQ:	South East Queensland
DOC:	dissolved organic carbon	SIAC:	silver-impregnated activated carbon
DON:	dissolved organic nitrogen	SPE:	solid phase extraction
DPD:	N,N diethyl-1,4 phenylenediamine sulfate	SUVA:	specific ultra violet absorbance
DSA:	dimensionally stable anodes	SW:	source water
DWTP:	desalination drinking water treatment plant	TAC:	total alkalinity
EBCT:	empty bed contact time	TBM:	tribromomethane
EC:	effective concentration/enhanced coagulation/electrical conductivity	TCAN:	trichloroacetonitrile
ECD:	electron capture detector	TCM:	trichloromethane/chloroform
ED:	electrodialysis	TCNM:	trichloronitromethane
EDR:	electrodialysis reversal	TDS:	total dissolved solids
EEM:	excitation-emission matrix	TEQ:	toxic equivalent concentration
EPA:	Environmental Protection Agency	THMs:	trihalomethanes
FP:	formation potential	tTHM:	total trihalomethanes
GAC:	granular activated carbon	TKN:	total Kjeldahl nitrogen
GC:	gas chromatograph	TOBr:	total organic bromide
HAAs:	haloacetic acids	TOC:	total organic carbon
HAM:	haloacetamides	TOCl:	total organic chloride
HANs/HAN4:	haloacetonitriles	TOI:	total organic iodine
HK:	haloketones	TOX:	total organic halogens
HNMs:	halonitromethanes	UV:	ultraviolet light
HTC:	hydrohalicite-like compounds	WTP:	water treatment plant
		WHO:	World Health Organisation

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